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Opportunities and Challenges for Organic Electrodes in Electrochemical Energy Storage

Philippe Poizot, Joël Gaubicher, Stéven Renault, Lionel Dubois, Yanliang Liang, Yan Yao

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1 Opportunities and Challenges for Organic Electrodes in 2 Electrochemical Energy Storage

3 Philippe Poizot,* Joël Gaubicher, Stéven Renault, Lionel Dubois, Yanliang Liang, and Yan Yao



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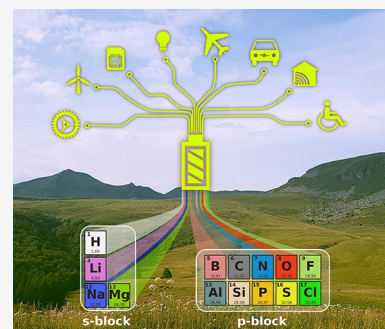


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Supporting Information

4 **ABSTRACT:** As the world moves toward electromobility and a concomitant decarbon-
5 ization of its electrical supply, modern society is also entering a so-called fourth industrial
6 revolution marked by a boom of electronic devices and digital technologies. Consequently,
7 battery demand has exploded along with the need for ores and metals to fabricate them.
8 Starting from such a critical analysis and integrating robust structural data, this review aims
9 at pointing out there is room to promote organic-based electrochemical energy storage.
10 Combined with recycling solutions, redox-active organic species could decrease the pressure
11 on inorganic compounds and offer valid options in terms of environmental footprint and
12 possible disruptive chemistries to meet the energy storage needs of both today and tomorrow.
13 We review state-of-the-art developments in organic batteries, current challenges, and prospects,
14 and we discuss the fundamental principles that govern the reversible chemistry of organic
15 structures. We provide a comprehensive overview of all reported cell configurations that involve
16 electroactive organic compounds working either in the solid state or in solution for aqueous or nonaqueous electrolytes. These
17 configurations include alkali (Li/Na/K) and multivalent (Mg, Zn)-based electrolytes for conventional “sealed” batteries and redox-flow
18 systems. We also highlight the most promising systems based on such various chemistries relying on appropriate metrics such as
19 operation voltage, specific capacity, specific energy, or cycle life to assess the performances of electrodes.



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1. INTRODUCTION

1.1. Current Status in Electrochemical Energy Storage in Short

The need to build innovative electrochemical energy storage (EES) technologies and conversion solutions is now recognized to be particularly critical not only by specialists in the field but also by ordinary consumers eager to use different

nomadic electronic devices which make their life easier, safer, and more enjoyable. Representative devices of EES are rechargeable (or secondary) batteries and (super)capacitors. Chemists, electrochemists, and materials science researchers helped by theoreticians (see for example the Materials Genome Project launched by G. Ceder¹) have already thoroughly screened the periodic table of the elements in the quest to find the best electrode associations essentially focused on increased gravimetric and volumetric energy densities while improving the safety, power, lifetime, and cost. Thus, decades of intensive and innovative research have enabled us to develop and to place on the market different kinds of primary and secondary batteries able to power an increasingly diverse kind of applications from microchips to the emerging large-scale application markets.² Without describing them one by one, it must be underlined that the pioneered lead-acid (PbA) battery devised by G. Planté in 1859 is still in growing demand because it is unrivalled for microhybrid and internal combustion vehicles or large-scale power storage units (load-leveling applications, uninterrupted power supply (UPS) for entire cities) at this time; this technology is also robust, safe, and affordable associated with efficient recycling and disposal management programs notably to prevent lead emission.³ Regarding Li-ion batteries (LIBs)—the current flagship technology to get high energy densities—thanks to substantial improvements and notably the discovery of new insertion positive electrode materials (e.g., LiFePO₄, LFP; Li(Ni_{1/2-x}Mn_{1/2-x}Co_{2x})O₂, NMC; Li-rich layered oxides Li(Li_xM_{1-x})O₂), they have become essential to power the vast world of electronic equipment, robots, ongoing electric transportation technologies, and some stationary applications too. Consequently, nickel/metal hydride (Ni/MH) rechargeable batteries, which have fully replaced nickel/cadmium (Ni/Cd) cells, are struggling to compete with LIBs in the light of recent achieved progress including at the price level. For the moment, Ni-MH batteries still power more than 10 million hybrid electric vehicles, and companies like BASF-Ovonic maintain their R&D activities.⁴ Redox flow batteries (RFBs) represent another promising choice for stationary energy storage because this particular cell configuration operating basically with redox-active solutions is more durable and scalable than conventional “sealed” battery systems working with solid state electrode materials. The major plants ever built to date are essentially based on the vanadium/vanadium redox flow battery technology (VRFB)⁵ first patented and developed by Skyllas-Kazacos in Australia in the mid 80s.^{6–8} This rapid survey shows that all commercially available electrochemical storage solutions deal with redox-active inorganic systems, which poses now more than ever certain problems in terms of metal resource constraints, production cost, and environmental footprint in view of the ever growing demand.

1.2. Rise of Organics for Electrochemical Energy Storage

For several reasons, which will be thoroughly explained later, it is now recognized that searching for organic matter-based electrodes could bring new chemical opportunities to further improve existing EES technologies while opening new playgrounds to create innovative cell configurations. Thus, over the last ten years, tremendous progress has been made to promote electroactive organic systems attracting much interest from the broad electrochemical storage community. This occurs to such an extent that today we are witnessing a considerable increase in the literature on the subject, ranging from

188 nonaqueous/aqueous RFBs to nonaqueous/aqueous “sealed”
189 batteries including both organic polymers and crystallized
190 organic compounds as will be developed in this article. In only
191 ten years, more than 45 review papers have been published for
192 which the scope was initially broad but in view of the booming
193 of primary research papers due to the versatility of the organic
194 synthesis and molecular engineering. The most recent reviews
195 are now focused on thematic research areas although it should
196 be recognized that some of them overlap. In the following list
197 sorted by year, the reader can find the series of review papers
198 on organic-based EES published since 2012 including notably
199 several remarkable contributions of both Chen’s group at Nankai
200 University and Schubert’s group at Friedrich Schiller University:
201 2012,^{9,10} 2013,^{11,12} 2015,^{13–15} 2016,^{16–27} 2017,^{28–35} 2018,^{36–46}
202 2019.^{47–58}

203 Basically, before 2011 the literature on the topic was clearly
204 limited. The reference review article dealing with organic
205 electrodes in this period was published by Novák et al. in
206 1997⁵⁹ on the basis of the existing literature focused at that
207 time only on conducting polymers following the discovery
208 of polyacetylene (PAC) by Shirakawa in 1974⁶⁰ and its
209 subsequent chemical “p- or n-doping” (see section 4.3) to give
210 a series of semiconductors and ultimately “organic metals”
211 thanks to overlap of adjacent π -orbitals.^{61–64} A few years later,
212 the possible use of PAC as electrode material to store electricity
213 was readily demonstrated by MacDiarmid taking advantage of
214 both p- or n-doping.^{65,66} Channels were opened to develop
215 other conjugated polymers such as polyaniline (PANI), polypyrrole
216 (PPy), or polythiophene (PT), which were particularly
217 explored in the 80s as positive electrode materials in “dual-
218 ion cell configurations” (see section 4.3) using metals or alloys
219 as the negative electrode (e.g., lithium (Li), sodium (Na), or
220 the stoichiometric lithium–aluminum alloy (LiAl)), which led
221 to the first practical polymer batteries with the commercializa-
222 tion of two types of metal–organic dual-ion cells by Varta
223 Corp. (with PPy) and Bridgestone Corp. (with PANI).^{67–69}
224 Note that for the discovery and the development of conductive
225 polymers, Alan G. MacDiarmid, Alan J. Heeger, and Hideki
226 Shirakawa were awarded the 2000 Nobel Prize in Chemistry.
227 However, shorter cycle life (~500 cycles), higher self-discharge
228 values, and limited volumetric energy densities compared to the
229 newcomer LIB commercialized by Sony Corp. in 1991 were
230 some of the reasons for the abandonment at the end of the 20th
231 century of efforts to make organic batteries from conjugated
232 polymers. Note that in the 1990s organosulfur polymers were
233 also investigated in Li batteries but as “n-type” electrode
234 materials for which reversible Li^+ uptake/release reactions take
235 place. Indeed, among the myriad of possible molecular organic
236 arrangements, sulfur atoms can also be linked onto a carbon
237 backbone ($-\text{C}-\text{S}-\text{S}-\text{C}-$) allowing the use of the redox-
238 active disulfide bond; the charge transfer reaction involves 2
239 electrons together with the cleavage of the S–S bond. Pioneering
240 research was performed by Visco and co-workers^{70–72} with a
241 survey of diverse groups of organodisulfide as positive electrode
242 materials essentially main-chain type organosulfur polymers.
243 For example, 2,5-dimercapto-1,3,4-thiadiazole (DMcT) with a
244 theoretical specific capacity as high as 362 mAh g^{-1} is one
245 of the best well-known organosulfur compounds. However,
246 such electrode materials are generally impeded by sluggish
247 kinetics along with a large polarization as well as solubility
248 issues stemming from the repeated scission/reconstruction of
249 disulfide bonds. Better results were obtained with side-chain
250 type organodisulfide polymer such as poly(2,2'-dithiodianiline)

(PDTDA) and other related derivatives, but long-lasting cyclings
were never attempted.⁷³ Note that in the quest to develop
lithium–sulfur (Li–S) batteries while limiting the polysulfide
shuttle, high sulfur content organic materials have been recently
investigated such as a new cross-linked disulfide material
 $\text{C}_6(\text{SLi})_6$ developed by Wudl’s group but the restored specific
capacity is still limited with 1/4 of the theoretical value.⁷⁴

A new class of polymers (nonconjugated) able to store
electric energy and consisting of a stable organic polymeric
chain bearing stabilized nitroxyl radicals such as 2,2,6,6-
tetramethylpiperidiny-N-oxy (TEMPO) radicals emerged in
the early 2000s thanks to joint efforts of NEC Corp. and
Nishide’s group in Japan.^{75–77} These studies have led to the
development of the so-called organic radical batteries (ORBs)
which are characterized by excellent rate performance, a
flexible design, but moderate energy density values due to the
adding of high amounts of conductive carbon in electrodes.
The achievement of robust 0.3 mm-thick ORB prototypes
compatible with functional smart card and wearable devices
was, however, announced by NEC Corp. as early as 2012.⁷⁸
This innovative chemistry coupled with the emergence of
promising high-capacity organic compounds characterized by
multiple electroactive carbonyl ($\text{C}=\text{O}$) functional groups^{79–83}
(a redox-active moiety encountered in the chemistry of life and
numerous natural substances) enabled the publication of a
broader review in 2011 focused this time on the perspectives of
organic batteries in addressing some eco-development issues
through the possibility of integrating the concept of “renew-
ability” in electrode material design and the prospect of
realizing greener and sustainable batteries.⁸⁴ The use of
organics emerges also in RFBs with a first organic/inorganic
flow battery reported in 2009 by Xu et al.⁸⁵ based on the Cd–
chloranil system operating in sulfuric acid aqueous medium.
Two years later, an all-organic redox flow battery (ORFB)
working in nonaqueous medium ($\text{NaClO}_4/\text{acetonitrile}$) was
reported by Li et al.⁸⁶ employing 2,2,6,6-tetramethyl-
1-piperidinyloxy as the polysolite and N-methylphthalimide as
the negolyte, respectively. Many other examples were then
reported in the literature as developed later (section 9). The
interest taken over time by organics in the field of electro-
chemical storage can simply be assessed thanks to common
data analysis tools like Scopus with suitable query string
(Figure S1). The histogram shows that the number of
publications (including articles, conference papers, reviews,
book chapters, conference reviews) focused on organic-based
electrochemical storage devices and published by year from
1972 onward follows a clear increase over the past 10 years.
One can also observe two successive bumps ranging from 1980
to 2000 due to the investigations of conducting polymers then
organodisulfide positive electrode materials followed by a
larger increase thanks to the impetus given by ORBs.

Although beyond the scope herein, it seems instructive to
briefly recall in this Introduction that the addition of elec-
troactive molecules has also been shown to benefit carbon-
based electrostatic double-layer capacitors (EDLCs) as well as
the merging field of Li-ion capacitors.^{87–102} As early as 1983,
Saga Sanyo was the first company to integrate highly conducting
organic material (tetracyanoquinodimethane, TCNQ) in
electrolytic capacitors.⁶⁹ Electroactive molecules are used to
significantly improve storage performance by adding a reversible
faradaic contribution (pseudocapacitance) to the double-layer
capacitance at the carbon electrode surface; these devices,
referred to as supercapacitors or ultracapacitors, can work both

314 in aqueous and nonaqueous electrolyte media. Different
315 chemistries such as the functionalization of the carbon surface
316 by self-assembly or grafting of the redox-active organic
317 molecule can be used.^{87–97} Although covalent anchoring of
318 the carbon substrate via the diazonium chemistry⁹⁴ appears as
319 the main approach, some authors have also reported the direct
320 incorporation of the redox-active organic molecules into the
321 electrolyte formulation referred to as “redox electrolyte” to
322 improve the specific capacitance of carbon-based electro-
323 chemical capacitors.^{93,95,96} A relevant example of “organic”
324 electrochemical pseudocapacitor consisting of activated carbon
325 powder electrodes modified with naphthalimide and 2,2,6,6-
326 tetramethylpiperidine-*N*-oxyl (TEMPO) was reported by
327 Lebègue et al.⁹⁷ It shows an increase in specific capacitance
328 up to 51%, an extended operating voltage of 2.9 V in propylene
329 carbonate, compared to 1.9 V for the unmodified system, and a
330 power 2.5 times higher. Alternatively, redox-active polymer
331 electrodes can be employed including, for instance, PPy, PANi,
332 and PT derivatives which offer advantages for making light-
333 weight and flexible (micro)supercapacitors while being com-
334 patible with aqueous electrolytes.^{98–100} Note that electroactive
335 organic molecules have also recently been introduced as key
336 materials to improve the sought-after “prelithiation” step of
337 Li-ion capacitors as well as the sustainability while reducing the
338 cost and complexity.^{101,102}

339 It should be underlined that the boundary between faradaic
340 organic-adding for supercapacitors and capacitive carbon-adding
341 for organic batteries is sometimes not so clear. For instance,
342 Wang's group¹⁰³ have reported a home-made hierarchical
343 porous carbon nanotubes (HPCNTs) decorated with anthra-
344 quinone (AQ) molecules exhibiting ultrahigh specific capacitance
345 of 710 F g⁻¹ (measured at 1 A g⁻¹) when tested in 1 M H₂SO₄
346 aqueous solution with the optimized mass ratio 7:5 indicating a
347 larger specific organic loading. Otherwise, recent years have
348 seen the emergence of so-called carbon-supported organic
349 electrode materials for LIBs/SIBs, that actually mirrors a
350 strategy to counteract common physical limitations of most
351 low-weight (neutral) organic molecules: their high solubility in
352 organic electrolytes and poor electrical conductivity. By mixing
353 these small organic molecules with large amounts of carbon
354 (generally by impregnation), a better stability can be expected
355 on cycling especially at high rate thanks to the establishment of
356 π - π stacking bonds with the surface of carbon particles (typical
357 carbon loading: >55 wt %); this phenomenon being reinforced
358 with extended aromatic cores. Note that biomolecules such as
359 flavine¹⁰⁴ or dopamine¹⁰⁵ were reported. Chen and co-workers
360 have reviewed this peculiar topic in 2015¹³ by questioning
361 some relevant points for practical applications such as the
362 uniformity/reproducibility at large scale production of carbon-
363 supported organic electrodes or the poor as-obtained energy
364 density values (especially in volumetric metrics).

1.3. Goal, Scope, and Organization of This Review

365 Following these introductory elements, it is obvious that a
366 consequent and growing amount of literature is now easily
367 available on organic batteries after years of silence. However, it
368 must be noted that because a certain disciplinary boundary
369 naturally exists between inorganic and organic compounds and
370 because the redox chemistry of organics is sometimes subtle
371 (involving often reactive delocalized charges), reading research
372 articles dealing with organic batteries (whatever the considered
373 technology) could be somewhat challenging for nonspecialist
374 readers. Therefore, the authors have thought it would be timely

to bridge the gap by providing a kind of “tutorial”-oriented
review for a broader audience to take smoothly in hands the
most relevant points and achievements dealing with this
peculiar field without being redundant with the multiple review
articles already published today. Based on the latest selected
and reliable input data from both general and specialized
scientific literature (typically reported after 2015), this contri-
bution aims also at providing the readers with a better critical
view of the current evolution trends in our technology-oriented
modern societies and the consecutive global demand for elec-
trical energy sources, materials, and batteries before reviewing
the main achievements obtained with organic-based electrode
materials.

In practice, the layout of the article is structured in such a
way as the reader will be able to select the parts that interest
him most. From a chemical point of view, the following
approach will be stepwise addressed in this review:

- *basic working principles and fundamental properties of key redox-active organic moieties and comparison with the formalism commonly used for inorganic materials together with corresponding cell configurations (section 4),*
- *a selection (with description) of original/promising organic-based batteries to date working either in the solid state (“sealed” batteries) or in solubilized state (ORFBs) for designing better realistic organic batteries in the future (sections 5–9). Note that the reader can find specific reviews on polymer-based organic batteries including radical polymers in refs 10 and 18.*

But as a preliminary step of this overview, it is thought particularly relevant for some readers to provide a snapshot of the global context that justifies there is room for reversible electroactive organic systems in the future electrochemical storage landscape in view of the particular conjunction of several critical factors facing mankind at the turn of the 21st century. Such a tricky exercise, which is seldom considered in other review articles, will constitute the background of sections 2 and 3 of this paper.

2. FOURTH INDUSTRIAL REVOLUTION: BATTERIES AT THE CROSSROADS

2.1. Background

Since the appearance on the market of LIBs 30 years ago the world has drastically changed. We have now entered the so-called Fourth Industrial Revolution!¹⁰⁶ In short, the First Industrial Revolution used water and steam power to mechanize production, the Second used electric power to create mass production, and the Third, emerging in the 60s with the birth of computers, used electronics and information technologies to automate production. Starting at the end of the 20th century, the Fourth Industrial Revolution is built on the Third and is characterized by (i) a fusion of technologies that is blurring the lines between the physical, digital, and biological spheres, (ii) an exponential rather than a linear pace, and (iii) probably no control over either technology or the disruption that will come. Basically, the driving forces of this revolution are nestled in the digital and information technologies with more active roles for the artificial intelligence (AI) that enables innovations in “physical assets” such as autonomous vehicles, Internet of things (IoT), robotics, electric unmanned aerial vehicles (UAVs) or drones, 3-D printing, ... as well as “digital” innovations (e.g., blockchain¹⁰⁷). It is worth noting that a rapid analysis of these innovative steps relies on a common

denominator which is the finer and finer control of the electron.

If we ignore herein that such innovations are also raising major ethical and spiritual questions,¹⁰⁶ the corollary of all this technology-oriented and more recently “connected” society is the ever-growing demand for energy especially for electrical power sources and related storage devices ranging from mWh to MWh: an era sometimes named “the Power Revolution”. Unambiguously, it is well established that access to electricity improves life in a tangible way.¹⁰⁸ However, as previously pointed out in a former Perspective article a few years ago,⁸⁴ two related crucial threats cannot be ignored:

1. “Global warming” with its numerous and dangerous induced impacts (e.g., extreme and destructive climate events, rise in sea level with its aftermath, relocating industrial and farming areas, biodiversity alteration, new distribution of populations with conflicts over water and food, and so on). This major threat which seems to correlate to anthropogenic greenhouse gas (GHG) emissions represents not only ecological but also socio-ecological and economic issues. At the COP21/CMP11 (Conference of the Parties) meeting in Paris in 2015, 195 countries signed a legally binding agreement to keep global warming “well below 2°C above pre-industrial levels, and to pursue efforts to limit the temperature increase even further to 1.5°C” within this century. In practice, this means an 81% reduction of GHG intensity by 2050, which is equivalent to 4.4% annual improvement.¹⁰⁹ In 2018 almost all countries in the world have committed themselves to reduce their GHG emissions in their pledges to the *Paris Agreement*. Note that global warming is likely to reach 1.5 °C between 2030 and 2052 if it continues to increase at the current rate as reported by the Intergovernmental Panel on Climate Change (IPCC) special report on January 2019.¹¹⁰
2. The constant increase in the world population which results in more and more energy consumers and therefore more GHG emissions as nicely shown in Figure 1.

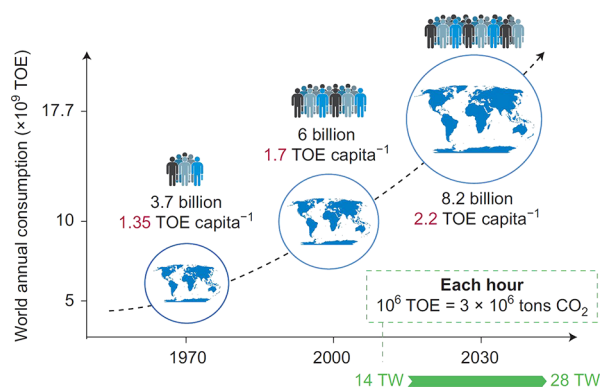


Figure 1. Forecast of the world’s energy needs up to 2050. With the changing lifestyles of an increasing number of inhabitants, our energy rate demand will double from 14 TW (2010) to 28 TW (2050). TOE = ton of oil equivalent. Reproduced with permission from ref 112. Copyright 2015 Nature Publishing Group.

Predictions estimate around 9–10 billion the human load by the year 2050 (2.5 billion in Africa against 1.3 billion today) 66% of which will reside in urban areas in developing economies.¹¹¹ For comparison, the

population was 700 million at the beginning of the first Industrial Revolution.

Although not yet fully accepted all over the world, such a mankind development still falls short in terms of sustainability and calls for a rapid and radical change in our current energy engineering together with a responsible behavior in our consuming fashion (pro-environmental behavior, “Nudge” theory, ...^{113,114}). It is interesting for example to read the study of Dong et al.¹¹⁵ on the nexus among carbon dioxide emissions, economic and population growth, and renewable energy across regions. Their data allow us to underline that economic growth is highly emission intensive, and economic growth often means rising energy consumption and increasing CO₂ emissions with a proportional effect of the population size. Hence our entering this Fourth Industrial Revolution can be perceived as a threat but also as an opportunity to rethink the development of mankind as a whole. Positive initiatives are now under way, and some policy makers and important energy stakeholders are making things happen probably also pushed by the ostensibly large number of recent extreme weather events¹¹⁶ such as Category 5 Katerina hurricane in 2005. Basically, new political goals and innovative/disruptive economy models (like the “green growth” models, the circular economy governed by 3Rs, namely Reduce, Reuse, and Recycle) must also be formulated, notably in reference with CO₂ emission limits, in the quest for a long-term sustainability conjugating Ecology/Economy/Society. [The reader who would be interested in this exciting field could find relevant and very informative economic analyses in the specialized literature.^{109,117–119}]

For a more technological point of view, *generation of decarbonized electricity* and *low-carbon transportation solutions* are the two main levers (in association with better energy efficiency and conservation and the *carbon capture utilization and storage*¹²⁰) put traditionally forward to move toward a deep decarbonization of the energy system.¹²¹ To better forecast the future in this regard, we recap below the main observed trends with supporting figures highlighting that rechargeable batteries are expected at the crossroads of several paths in the global demand pattern for electrical functionalities of today and tomorrow, some applications being to mitigate GHG emissions while others are probably less virtuous.

2.2. Decarbonizing the Power Supply and Its Related Storage Challenges

Regarding the future of electric grids, thanks to the efforts of worldwide researchers, engineers, and policy makers, remarkable progress has been made to connect renewable energy sources (RESs) for electricity generation.¹²² For instance, the European Directive 2009/28/EC¹²³ aims at promoting the use of RESs in the European Union (EU) with a targeted value of 20% by 2020 with specific values regarding each member state. The most exploited RESs are hydroelectric, photovoltaic (PV), and wind. Other emerging renewable technologies include wave and tidal energy conversion and biomass energy conversion. Therefore, some predictions seem to indicate that GHG emissions in the power sector could be drastically reduced thus becoming a major contributor to decarbonization (Figure 2). Although the total electricity production is expected to more than double between 2010 and 2050 giving rise to the incredible value of more than 40 000 TWh of generated energy per year (notably to power the electromobility, see below), total emissions for the power sector could be divided by more than four according the Deep

a) Power generation mix at the worldwide scale

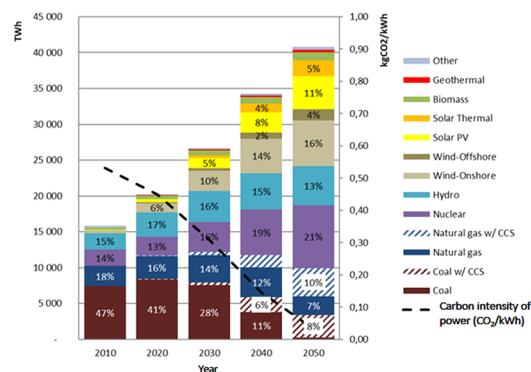
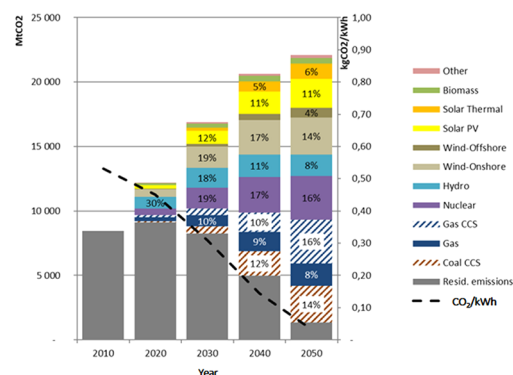
b) Power CO₂ emissions at the worldwide scale

Figure 2. (a, b) Decarbonization Wedges in the power sector extracted from the ANCRE's report¹²⁴ (with permission) elaborated in the DDPP and by considering the most ambitious scenario in each country; "worldwide scale" refers to only the 16 most emitting countries. These histograms show the emission trajectories for the electricity sector in the absence of any technological evolution and (in gray) the evolutions of the emissions within the framework of decarbonization scenarios; the difference between the two corresponds to reductions that allow different technologies (e.g., solar in yellow and orange, hydro in blue); CCS meaning carbon capture and sequestration. Further descriptions of the "Decarbonization Wedges" methodology can be found in ref 126.

Decarbonization Pathway Project (DDPP)^{124,125} by considering the most ambitious scenario in the 16 largest GHG-emitting countries representing 75% of current GHG emissions. According to these scenarios, the electricity mix could be completely modified with almost 90% of power generation from non-CO₂ emitting technologies, among which 54% is from renewable sources (together with 21% from nuclear power plants); coal is today responsible for 42% of CO₂ emissions worldwide. The electricity sector could be widely decarbonized by 2050 with a reduction from the current 530 gCO₂ kWh⁻¹ to about 33 gCO₂ kWh⁻¹ [the complete description of the "Decarbonization Wedges" methodology as well as additional subscenarios have been recently published by Mathy et al.¹²⁶].

However, huge infrastructure investments will obviously be needed to satisfy such perspectives in electricity generation. For instance, some of these newly developed technologies (e.g., PV, wind power) cannot serve as stable energy sources alone because of their natural sensitivity to weather, landform, or other environmental conditions (i.e., variability and high ramping characteristics) requiring sophisticated planning and operation scheduling to ensure the necessary and subtle

balance between electricity production and consumption. New technologies are currently being developed to upgrade existing electricity grid infrastructures that will enable so-called "smart grids", which are characterized by improved grid reliability and utilization, the synergies between the power electronics, control, and communication fields as well as the change from radial networks to mesh networks with the possibility to reconfigure and self-heal.^{127,128} Thus, the role of IoT will be eminent with a significant reduction of costs associated with sensors, bandwidth, processing, and memory/storage.¹²⁹

Consequently, energy storage is increasingly seen as a valuable asset for electricity grids and one of the important tools of mitigation not only as a technical solution for network management, ensuring real-time load leveling, but it is also a means of better utilizing RESs by avoiding load shedding in times of overproduction. For the moment, the worldwide stationary electrical storage remains by far dominated by pumped storage hydropower (98% of the installed power) but the use of rechargeable batteries is emerging fast as underlined in 2011 by Dunn et al.¹³⁰ in a visionary paper; the wide use of batteries is now clearly included in the roadmap storage technologies.^{131,132} Already widely used for load-leveling applications and UPS for entire cities (especially the PbA technology), the reduction of costs in the electrochemical storage technologies is attracting considerable interest for short-term storage (for a period of seconds to a few days) using "sealed" batteries and redox-flow batteries (RFBs) as shown in Figure 3. Thus, LIBs in various chemistries are even

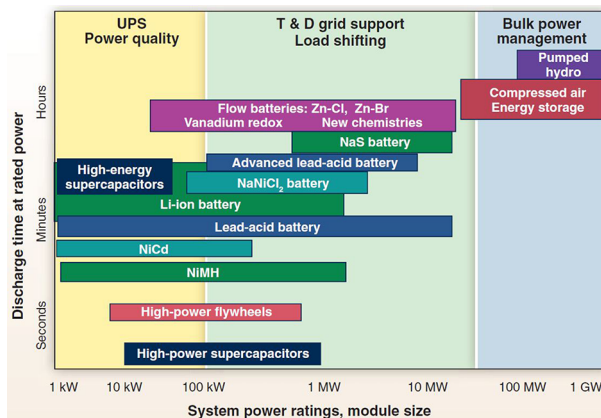


Figure 3. Comparison of discharge time and power rating for various electrical energy storage technologies highlighting the broad contribution of batteries with various chemistries; the latter being only based on inorganic electroactive materials, essentially metals. Reproduced with permission from ref 130. Copyright 2011 Science Publishing Group.

more seriously envisaged¹³² because the cost of battery storage has declined fast in a few years with a drop of 73% between 2010 to 2016 to reach \$273 kWh⁻¹ as market value while a value of \$73 kWh⁻¹ is forecast in 2030.¹³³ Competing with gas-fired peaking plants is made possible. For example, more than 18 000 LIB packs (400-MW peak hour battery) would replace a gas-fired power in California.¹³⁴ Interestingly, the analysis of 3 years of real usage of LIBs (1 MW/250 kWh using 384 modules connected in series) installed and in operation in Hawaii has been recently reported by Dubarry et al.¹³⁵

For such stationary applications, the capital invested and operational costs (maintenance, energy lost during cycling,

aging) are very important factors to consider for the entire life of the system. The reader could find compared cost factors in the literature including PbA, RFBs, LIBs, and so on.^{5,130,136} The cost of storage can be calculated through the so-called leveled cost of stored energy (LCOE) defined as the total lifetime cost of the investment divided by the cumulated generated energy by this investment. The LCOE values at 25 years for an installed storage power of 1 MW are estimated at 0.338 and €1.978/kWh for RFBs and LIBs, respectively (against 3.072 for the PbA technology).¹³⁷

2.3. Decarbonizing the Transportation Sector Through the Electrification Scheme

Beyond the electric grid, the pressure on batteries is also particularly intensive due to the deployment of decarbonized transportation systems through the massive use of electric motors (the so-called “electromobility” or “e-mobility”) although the use of biofuels, oil-based fuels, and liquefied natural gas (LNG) has recently gained more attention.^{121,138} [LNG consists mostly of CH₄ and has the potential to reduce SO₂-emissions over 90%, NO_x-emissions with 80%, and CO₂-emissions 20%, which seems a competitive alternative in this sector provided there is less than 2% leakage.] Indeed, the transport sector’s dependence on fossil fuels is another big part of the necessary transition toward a climate-neutral and sustainable society. Transport is a major source of total GHG emissions (22%), with road transport being the biggest contributor and responsible for about 72% of CO₂ emissions worldwide according to IPCC analyses.¹³⁹ Note that over 1.2 billion vehicles were in service in 2015 according to the International Organization of Motor Vehicle Manufacturers (OICA).¹⁴⁰ Moreover commercial air transportation still represents about 11% of global fuel consumption across all sectors, 2% of global CO₂ emissions, and 13% of emissions in the transport sector alone.¹⁴¹ Beyond the dangerous GHG emissions when using Internal combustion engines (ICEs), the electric motor intrinsically possesses several advantages that have always been known such as better energy efficiencies (>90% because not subject to the Carnot cycle limitations of heat engines). They are also quieter, easy to miniaturize, and more importantly simpler in their design making the direct motor and wheel coupling possible. Conversely, a conventional ICE powered car typically has 10 000 moving parts (essentially within the drive train) against only 150 in battery electric vehicles (BEVs) today and only one of which is in the drive train as underlined by Parker.¹⁴² The gains in maintenance as well as in energy efficiency are obvious.

Historically, the invention of ICE occurred in the middle of the 19th century just like that of the electric motor but at a time when oil and its derivatives were becoming cheap and widely available whereas high energy batteries did not exist yet. Gaston Planté had just invented the first rechargeable battery with its PbA technology (then improved by Camille Faure in 1881), which enabled however the first automobile speed record in 1899 (100 km h⁻¹ but only on 2 km range) thanks to the first BEV named “*La jamais contente*” powered by 750 kg of Fulmen PbA batteries. In the early 1900s, 38% of the US automobile market was captured by electric vehicles. Even after this feat, ICEs would increasingly supplant the electric car for the next century especially thanks to Ford’s innovations with the consequences that we are now witnessing. Now vehicle emission regulations have been forcing the automotive industry worldwide to reduce its carbon footprint especially in the EU,

China, and India while governments around the world (like the Electric Vehicles Initiative (EVI))¹⁴³ are providing incentives to the citizens for buying electrified vehicles (EVs). The French government is to take the initiative to propose an ambitious Euro 7 emission standard at European level and set the goal of ending the sale of cars emitting greenhouse gases in 2040! The Swedish automaker Volvo has announced that from 2019 all its new models would be either hybrid or 100% electric. Note that EVs include battery electric vehicles (BEVs), plug-in hybrid electric vehicles (PHEVs), and fuel-cell electric vehicles (FCEVs). As a reminder, the key difference between BEVs and PHEVs is that FCEVs use a primary electrochemical cell (*i.e.*, fuel cell) to power the electric motor; the recharging step of FCEVs needing hydrogen as a fuel instead of electricity.

Based on the current roadmap reported by the International Energy Agency (IEA) in the BLUE Map scenario¹⁴⁴ (Figure 4a), rechargeable batteries are likely to remain the better choice to power light duty vehicles (LDV) in the next 2 decades whereas FCEVs are considered as the future vision for the global automotive industry beyond 2040–2050 because this technology and related hydrogen supply infrastructures are still not at the desirable level,^{121,145} with the production of low-carbon H₂ being required too. For the present time progress made in recent years to improve battery performance and reduce costs¹³³ has already enabled the use of LIBs in numerous e-mobility applications such as two-wheelers, buses, taxis, shared cars, ride-hailing services, and the upcoming self-driving (or driverless) cars.

Thus, sales of new electric cars worldwide surpassed 1 million units in 2017 (for 3 million EVs in circulation), a record volume which represents a growth in new electric car sales of 54% compared with 2016 (more than half of global sales of electric cars were in the People’s Republic of China) whereas the EV30@30 scenario makes as projection 228 million EVs (excluding two- and three-wheelers) on the road by 2030 as shown in Figure 4b;¹⁴³ the EV30@30 campaign redefining the EVI ambition originally set at 20 million EVs on the road by 2020. More recently, Hache et al.¹⁴⁶ have reported a bottom-up analysis using the Times Integrated Assessment Model (TIAM-IPFN version) to forecast the diffusion of electrified road transportation modes by integrating two climate scenarios (4 and 2 °C) and two shapes of mobility (high/low mobility). The electric vehicles fleet could reach up to 1/3 of global fleet by 2050 in the 4 °C scenarios, while it could be up to 3/4 in the 2 °C scenarios both with high mobility, mostly located in Asian countries (China, India, and other developing countries in Asia) due to the large presence of 2- and 3-wheelers (Figure S2). Consequently, electric transportation is integrated into the smart grid/smart cities master plans¹⁴⁷ first because the electricity needs will boom but also as a means of flexibility since integrating BEVs/PHEVs into the electric utility grid facilitates both vehicle-to-grid (V2G) and grid-to-vehicle applications owing to the bidirectional nature of the power flows between the BEVs/PHEVs and the grid.

Last but not least, developing electric/hybrid aircraft is in progress too because electric propulsion has the potential to revolutionize aviation opening real opportunities for cleaner, quieter travel to completely new types of transportation models. In November 2017 Airbus announced the launching of E-Fan X with its partners Siemens and Rolls-Royce which is an ambitious technology demonstrator project: a hybrid civil aircraft, another emerging sector calling for high-performance batteries. Other equivalent projects exist such as the ZUNUM

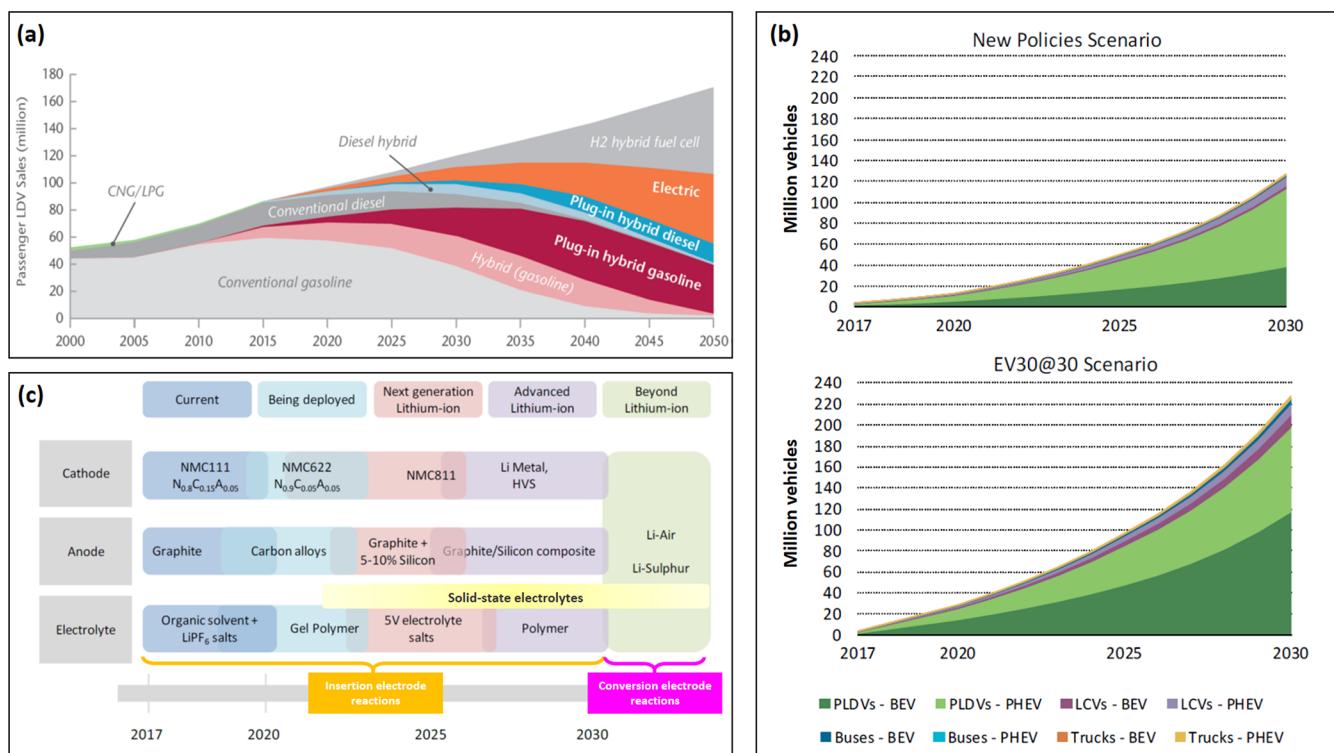


Figure 4. (a) Annual light-duty vehicle (LDV) sales according to the BLUE Map scenario,¹⁴⁴ 2000–2050 reported by IEA; combined EV/PHEV sales should share at least 50% of LDV sales worldwide by 2050. (b) Global EV stock for 2017–2030 excluding two- and three-wheelers by considering both New Policies Scenario and the EV30@30 Scenario reported by IEA¹⁴³ (PLDVs = passenger light duty vehicles; LCVs = light commercial vehicles; BEVs = battery electric vehicles; PHEV = plug-in hybrid electric vehicles). (c) Battery technology roadmap adapted from IEA¹⁴³ (HVS = high voltage spinel). Adapted with permission, copyrights of IEA.

722 Aero airliner project supported by Boeing. Interesting inno-
723 vations can therefore be expected in the next decade even if
724 there is a long way to go for large-scale practical applications.

725 2.4. Digitalization and Growing Consumption of Electronic 726 Devices

726 The boom in electronic devices and digital technologies has
727 been going on for almost 30 years, and batteries are generally
728 needed to power them. The worldwide development of mobile
729 phones is probably the most vivid example. As underlined by
730 Galetovic et al.¹⁴⁸ in a very interesting world mobile phone
731 industry study, the number of mobile phones sold rose 62-fold
732 between 1994 and 2013 whereas in June 2015 there were
733 around 7.5 billion subscriber connections, one for every person
734 on the planet. But all this has an energy cost but also an
735 environmental one. As an example, the entire mobile phone
736 system in a small country like Italy consumes approximately
737 2200 GWh per year (0.7% of the national electricity consump-
738 tion) while producing potential e-waste from end-of-life
739 devices totaling over 11 thousand tons for the period from
740 2007 to 2012.

741 Today, consumer electronics (CE) mainly encompasses the
742 whole range of home electronic equipment, from audio systems,
743 home automation, home computing, and low-power electronics
744 to multimedia systems. In addition, IoT has nowadays gained
745 an incredible attraction^{149,150} imparting networked connectiv-
746 ity to everyday objects in the physical world with numerous
747 implications in logistics, manufacturing, retailing, environ-
748 mental monitoring, healthcare monitoring, industrial monitor-
749 ing, traffic monitoring, ... (as well as important monitoring in
750 the smart grid and EVs to relate to the previous paragraph).

In 2015, IBM predicted that 1 trillion devices would be connected
to the Internet and the IoT. In 2017, a Cisco-revised forecast
called for 50 billion devices to be connected by 2020 and, most
recently, the GSMA Association predicted 25 billion IoT devices
by 2025! Interesting data are reported by “The Shift Project” in
several reports.¹⁵¹ For example, the energy consumption of
Information and Communication Technologies (ICT) is
increasing by 9% every year while the share of ICT in GHG
emissions has increased by half since 2013, rising from 2.5% to
3.7% in a few years.

Remarkable progress has also been made in many aspects of
robotics for which 10 grand challenges have recently been
pointed out in a Perspective article published in *Science*
*Robotics*¹⁵² including one related to power and energy sources
to make the deployment of mobile robotics possible. In particu-
lar, “service robots” which smartly mix IoT and AI to assist
human beings—typically by performing a job that is dirty, dull,
distant, dangerous or repetitive, including household chores—
are on the verge of equipping our homes and some public
places. Impressive statistics and forecast have been announced
by The International Federation of Robotics in the Executive
Summary World Robotics 2018 Service Robots reports.¹⁵³ For
instance, it was estimated in 2017 that nearly 6.1 million robots
for domestic tasks, including vacuum cleaning, lawn-mowing,
window cleaning and other types, were sold which corresponds
to a 31% increase compared to 2016. The market for elderly
and handicap assistance is also expected to increase substan-
tially within the next 20 years.

In the same vein of recent developments, benefiting of
electric propulsion R&D, the market of drones (UAVs) is also
expected to rise at unprecedented rates due to growing interest

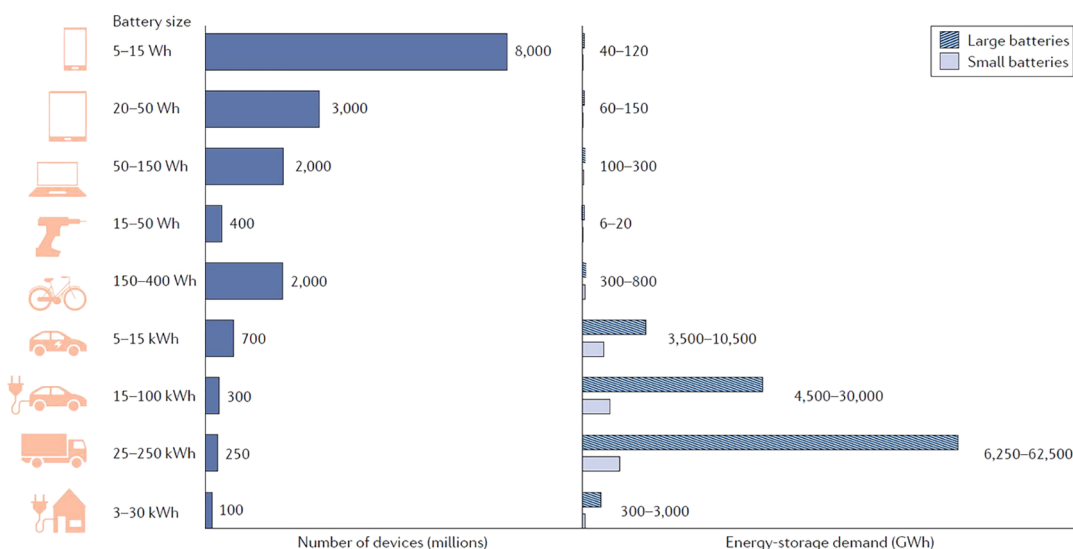


Figure 5. Estimated number of devices and related energy demand for 2016–2050. Note that all possible needs are not considered like the electric grid. Reproduced with permission from ref 154. Copyright 2019 Nature Publishing Group.

782 in monitoring applications by the military, researchers, farmers,
783 hobbyists, and investors in e-business since drones offer
784 superior abilities over their ground alternatives. It should be
785 pointed out that using drones for commercial deliveries was
786 something improbable ten years ago. Interestingly, Vaalma
787 et al.¹⁵⁴ have very recently established a scenario-based supply
788 and demand analysis concerning LIBs for 2016–2050 con-
789 sidering some selected applications including portable elec-
790 tronic devices and tools as well as several electrified road trans-
791 portation modes and small stationary energy-storage devices
792 (Figure 5). Clearly, if portable electronics dominates in terms
793 of number of devices, they account for much less in terms of
794 the total energy-storage demand if electric vehicles and
795 residential energy-storage devices reach the high production
796 numbers estimated in their scenarios.¹⁵⁴ However, several key
797 applications such as the powering of domestic robots, drones,
798 or IoT are not included in the scenario.

2.5. Summary

799 To sum up this overview, we are unambiguously facing a
800 tremendous need for EES for a double reason, first as a key
801 ingredient of the future energy engineering to fight global
802 warming and, second, as a central hub for the emergence of
803 disruptive technologies consecutive to the continuous moderni-
804 zation and development of mankind. The scale-up of industrial
805 facilities for the production of rechargeable batteries, especially
806 LIBs due to their high energy density values, is consequently
807 an opened and sensitive question. The production is currently
808 dominated by East-Asian competitors; with Panasonic (Japan)
809 and LG Chem (South Korea), these leading manufacturers on
810 the automotive market are closely followed by Samsung SDI
811 (South Korea), CATL (China), and SK Innovation (South
812 Korea). With its Gigafactory built in Nevada, Tesla (with
813 Panasonic as a partner) is now on the road too on US soil
814 whereas in the EU, things are moving forward to reduce its
815 dependence on the Asia and US suppliers. Sweden's Northvolt
816 has raised in June 2019 \$1 billion in equity capital to complete
817 funding for its future Gigafactory while France and Germany
818 launched an Airbus-style €6 billion foray into the battery-
819 building business. Considering a typical battery capacity range
820 of 20–75 kWh, these factory capacities translate into a yearly

production volume ranging between 6 000 to 400 000 packs.¹⁴³ 821
To better visualize the world LIB manufacturing capacity and 822
related international trade flows, Figures S3–4 report the 823
thorough mapping analysis performed by Mayyas et al.¹⁵⁵ 824
based on reliable collected data in 2016; the total LIB manu- 825
facturing capacity for this year was 189 762 MWh including 826
114 484 MWh for automobile LIBs. Finally, Bloomberg NEF 827
announced in November 2018 a need for 1800 GWh by 2030 828
of LIBs including annual passenger EVs and E-buses, consumer 829
electronics, and stationary storage; roughly eight out of every 830
10 batteries sold annually will find their way into a passenger 831
electric vehicle;¹⁵⁶ however, details regarding the modeling and 832
technical assumptions are not available. Anyway, the bottom 833
line is battery production will have to be strongly scaled up in 834
any scenario because a significant difference between supply 835
and demand could occur. 836

But departing from these capability considerations, it is 837
particularly important to avoid any pitfalls in this frenetic 838
endeavor and make sure that proposed technical solutions are 839
themselves sufficiently eco-friendly and sustainable. In other 840
words, such large-scale perspectives force us to consider the 841
environmental impact of rechargeable batteries (notably LIBs) 842
as well as dependencies on raw materials. This critical point 843
will be specifically discussed in the next section on the base of a 844
selection of relevant data again ranging from chemical element 845
abundance to potential environmental concerns related to their 846
production and disposal. 847

3. MATERIAL SUPPLY FOR ELECTROCHEMICAL STORAGE: RESOURCE CONSTRAINTS ISSUES, ENVIRONMENTAL BURDEN, AND OPPORTUNITIES PROVIDED BY ORGANIC ELECTRODE MATERIALS

Even if some currents of thought advocate a negative or zero 851
growth as a solution, it is believed that technology and its 852
progressive developments should constitute the most important 853
pillars of energy saving and GHG reducing. Nevertheless, it 854
seems also established that with all decarbonization innovations 855
notably in the broad field of energy, new environmental and 856
resource issues are introduced with the growing need for ores 857
and refined metals;^{126,157} which partly offset the gains of 858

859 innovative solutions; a phenomenon known in the economic
860 field as the “Jevons’ paradox” or the Rebound effect.^{158,159} In a
861 very interesting paper published in 2011, Graedel wrote:¹⁶⁰
862 *Assessors of technology no longer tend to ask, “What is being used?”*
863 *but rather, “What is not being used?” The answer to the last*
864 *question is, increasingly, “Almost nothing.”* In the last 20 years
865 (1994–2014), world mining production of indium, rare earth
866 elements (REEs), lithium, and cobalt increased from 149 to
867 819 tons, 64.5 to 133 ktons, 6.0 to 36.0 ktons, and 18.5 to
868 112.0 ktons, respectively, together with e-waste which is at the
869 world scale unfortunately poorly collected and recycled.¹⁶¹

870 Hence the large quantities of waste electrical and electronic
871 equipment (WEEE) generated have raised a serious alarm on
872 their potential adverse health and environmental consequences
873 when incorrectly disposed of.

874 In 2012, Vesborg and Jaramillo¹⁶² very nicely studied the
875 tricky question about the scalability in the supply of chemical
876 elements (and the related cost in energy) to promote tech-
877 nologies for energy harvesting, conversion or storage at the
878 required TW-level for a sustainable future. Numerous relevant
879 data are provided in this article such as correlations between
880 crustal abundance and production of dozens of chemical elements
881 while underlining the significant energy costs associated with
882 providing the current flow of raw materials for energy tech-
883 nologies. Today’s turbine blade alloys and coatings for wind
884 energy converter make use of as many as a dozen metals while
885 Electrical and Electronic Equipment (EEEs) incorporate some
886 60 metals most of which are classified as “critical metals”
887 (CMs).^{160,163,164} In short, CM refers roughly to imbalances
888 between metal supply and demand (real or anticipated) at
889 national, regional, or very local level, which induces variable
890 appreciations, several definitions, and assessment method-
891 ologies. An extension to “critical raw materials” (CRMs) and
892 the “criticality” term have appeared in the literature too.^{146,164}

893 For instance, through the Raw Materials Initiative (RMI)
894 adopted in 2008,^{146,165} the European Commission¹⁶⁶ has
895 defined CRM when it faces high supply risks (e.g., geological,
896 geopolitical, or production risk) or high environmental risks
897 and is of high economic importance; 14 CRMs were identified
898 in 2011, 20 in 2014, and 27 in 2017 as shown in Figure S5.
899 Interestingly, Li is not considered as CM for the European
900 Commission while the US has included it in its own list as
901 reported by the Department Of the Interior in 2018.¹⁶⁷

902 Respective to the scope of this article, the relevant question
903 is therefore to establish if the current available and future
904 battery technologies depend on high material resource constraints
905 and at what cost in terms of environmental burden. A few
906 elements of an answer will be provided below.

3.1. Resource Constraints Forecast in Conventional Material Supply

908 Based on the present state-of-the-art and whatever the con-
909 sidered technologies, electrode reactions involve redox-active
910 inorganic compounds especially metal-based electroactive com-
911 ponents, which is an historic heritage of the pioneered redox
912 chemistry (the voltaic pile followed by the PbA secondary cell)
913 as well as the material engineering that resulted (Figure 3). For
914 instance, if we consider the battery technology roadmap for
915 electrified vehicles (Figure 4c) it is expected that at least until
916 2030 matured and advanced insertion inorganic positive
917 electrode materials will be essentially based on the 3d-metal
918 redox chemistry. However, it is also widely acknowledged that
919 traditional Li-ion batteries are starting to approach their limits

especially for long-range EVs. Beyond 2030 other battery
chemistries are envisaged namely post-LIB systems. First, it is
commonly forecast that conversion-based cathode reactions
could be used (with O₂ and S) in Li-metal battery configuration
(Figure 4c), which supposes however the achievement of
consequent improvements.¹⁶⁸ Recent R&D trends also indicate
an expected switch from liquid (organic) electrolytes to ceramic
electrolytes (or solid state electrolytes, SEEs) notably following
the recent discovery of lithium superionic conductors at room
temperature by Kanno and co-workers ($\sigma_{\text{Li}^+} = 25 \text{ mS cm}^{-1}$ for
Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}).^{169,170} All-solid-state batteries operating
at moderate temperatures offer an attractive option for non-
flammable batteries while achieving both high power and high
energy densities because it is also a relevant option to reopen
the safe use of pure alkali metals especially Li as anode material
when paired with high-potential insertion materials (5 V spinel
materials, Figure 4c) or with conversion S/O₂-based cathodes.¹⁷¹
Nevertheless, this ceramic electrolyte option could require again
the consumption of more inorganic materials such as metal-based
sulfides, oxides, or phosphates.^{169,172} It is worth noting that the
emerging field of Na and Na-ion batteries which are also
considered in the post-LIB field logically follows the same
trajectory in terms of materials choice and design as a sister
material chemistry of Li-based batteries.^{173,174} In addition, it
should be remembered that major built RFBs also draw their
chemical power from 3d-metals as well as already underlined
above.

While the number of publications and other reports has
greatly increased in recent years on the potential bottlenecks in
material supplies due to the ramping up of LIBs,^{146,155,154,175–177}
the resource issue questionings in the field of energy storage
are not new especially for EV fleets since interesting estimates
were already reported by Andersson and Råde¹⁷⁸ as early as
2001 by taking into account almost all cell chemistries at that
time: Li-metal polymer (LMP), LIBs, sodium nickel chloride
(NaNiCl or ZEBRA batteries), Ni-metal hydrides (Ni-MH),
and PbA. Generally speaking, batteries that contain two or
more scarce metals may suffer from being limited by the
availability of any of them. With the pressure on LIBs and
future Li-based technologies, the main current concern is
about the potential risks surrounding the supply (and related
price volatility) of lithium and 3d-metals with battery-grade
quality (Co and Ni, essentially), which also raises the tricky
question of the mining interdependencies of elements;¹⁵⁵ note
that natural graphite is commonly reported as CRM. Indeed,
the supply of cobalt is complicated by the fact that this element
is not typically the primary product of mining operations;
it is a coproduct of nickel (50%) mining.¹⁷⁹ Figure S6 shows a
mapping and quantified data regarding the world mining
industry production for materials used in LIBs.¹⁵⁵ Taking 2016
as the year of reference, the battery industry’s demand for
lithium and cobalt is 46% and 50% of the world production,
respectively.¹⁵⁴ It should also be underlined that 54% of the
mining production of Co comes from the Democratic Republic
of Congo, a country characterized by socio-political instability,
a persistent economic stagnation, and no environmental policies;
the country could lose 40% of its forests by 2050 notably due to
mining activities.¹⁸⁰

To ensure continuous flows of raw materials, new agreements
are set up between critical material suppliers and different
customers; for example, Apple Inc. seems interested in buying
long-term supplies of cobalt directly from miners.¹⁸¹ As previ-
ously stated by Andersson and Råde,¹⁷⁸ closed loop recycling

solutions and a high level of collection of spent batteries are required to ensure that the stock of available metals for batteries is not drained. The case of PbA batteries constitutes a textbook example with a collection of spent batteries above 99.9% thanks to environmental rules due to the lead toxicity together with existing efficient recycling processes of this simpler battery chemistry based essentially on Pb(Bi). In 2016, almost all end-of-life LIB were batteries from consumer electronics and 95% of spent LIB were unfortunately landfilled.¹⁸² Unlike recycling of PbA batteries, recycling of LIBs seems for the moment not economically profitable albeit recycling LIBs could save up to 51.3% of the natural resource required to produce virgin materials (concept of Urban Mines).¹⁸² Today, most recyclers focus on recovering expensive materials mainly from positive electrode powders, but lithium is rarely recovered (less than 1% of lithium is recycled). Stronger political incentives seem required to promote recycling. In the EU, the 2006/66/EC European directive¹⁸³ imposes a minimum recycling efficiency of Li-batteries at 50% by average weight into materials for their original purpose or for other purposes and second, encourages technological developments that improve the environmental performance of batteries throughout their entire life. The reader can get precise and recent data regarding recycling end-of-life batteries, processing, and collections reported in refs 146, 155, 182, and 184–187. Another hot point is that predictions underlined that all the material demand just for EV batteries will have to be supplied by resource extraction at least up to 2030 whatever the collection and recycling of spent battery electrode materials due to the eight-to-ten-year lifetime of EV batteries.¹⁴³ Note that reuse of EV batteries can offset the production burden of new batteries by extending battery service life.

3.2. Sustainability and Environmental Aspects

Beyond battery resource considerations which are getting all the attention today, let us also remember that mining operations are destructive for the environment and energy-greedy and fall short of both the sustainability and CO₂ footprint criteria.^{84,112} Moreover, the scarcity of most of these elements in the earth crust (Figure 6) could make their excavation more and more energy intensive and costly depending on the nature of the deposit because it must be kept in mind that elemental availability cannot be judged by crustal abundance alone (see ref 162 for more details). Moreover, after the extraction of ores, several refining steps are necessary to obtain the final reagents which will be engaged thereafter in high temperature synthesis reactions ($T \approx 600$ °C) to produce the desired electrode material.

At this stage, relevant data to evaluate potential environment concerns as well as the related energy cost for the production of batteries can be found in life cycle assessment (LCA) studies. Although LCA can be considered as a standardized methodology, it depends on the inventory database used and system boundaries. Consequently, LCA results in the literature differ significantly due to these uncertainties. Peters et al.¹⁹² have reported in 2017 an interesting review of LCA studies on LIBs. After a thorough review of 113 available publications on the topic, a total of 36 LCA studies were identified as very reliable because they provide detailed results for LIB production and sufficient information to recalculate the reported results. The conclusion is, on average, a cumulative energy demand (denoted “embodied energy”) of 328 kWh is needed

across all chemistries to produce 1 kWh of stored electrochemical energy producing GHG emissions of 110 gCO₂eq.

Beyond LIBs, other similar values concerning PbA, Ni-MH, or VRFBs can be found in the literature too.^{193,194} Note that the majority of existing studies are focused on GHG emissions or energy demand; however, other Eco indicators such as human toxicity (HTP) might be even more important.^{192,195} More importantly, such LCA studies are restricted at the manufacturing outlet (“cradle-to-gate analyses” and not “cradle-to-grave analyses”), so they do not take into account both collection and recycling steps. Yet the results obtained show that battery manufacturing is energy-intensive because of the involvement of quite high flows of exergy mainly due to the chemical nature of the commonly used materials (inorganic compounds).^{112,162}

As a result, one common recommendation of current LCA analyses is the deployment of batteries with higher round-trip efficiency to extend the cycle life in operation but also the need for low-carbon innovations in future technologies while favoring the use of naturally abundant chemical elements of low toxicity. Within this background, one current trend in the post-LIB field is to reinvestigate Na-ion batteries as candidates for medium and large-scale stationary energy storage in light of possible concerns in terms of cost and abundance of lithium.^{174,196,197}

3.3. Positioning Redox-Active Organic Species in the Battery Landscape

Within this background, which is particularly tense in many ways, the idea of taking advantage of organic chemistry for the electrochemical storage of energy can make sense. As stated in the Introduction, the idea to use organic electrode materials (OEMs) for rechargeable batteries is not new and goes back to the discovery of reversible redox-activity of conducting polymers in the late 70s following the discovery of PAc by Shirakawa^{61–64} and its subsequent electrochemical activity (doping) both in oxidation and in reduction.^{65,66} These findings led to the development of various conducting polymers as well as a first attempt to emerge in the marketplace before the boom of high-energy LIBs.^{59,69} Today the motivations are different and authors agree that organics can be notably seen as a pathway to stabilize the pressure on the CRM for energy storage while seeking to improve the environmental footprint as well as finding innovative storage solutions.^{42,84} Of course, OEMs have limitations especially when talking about volumetric energy density that can be achieved due to their intrinsic low volumetric mass densities (<2 g cm⁻³). Excluding ORFBs, this issue can be exacerbated by the need for large carbon addition when preparing composite electrodes. Moreover, their greater propensity to solubilize in liquids compared to inorganic compounds is an issue for solid electrodes but an asset for ORFBs. The development of organic batteries is clearly in its early stages compared to 150 years of intensive research and innovations dedicated to conventional inorganic-based electrochemical storage devices explaining why some room is expected to be given to redox-active organic species in the battery landscape. To be convinced, Figure 7 reports an interesting assessment for the electrochemical storage of OEMs classified by families.³¹ In fact, organics exhibit several interesting assets as recapped below.

First, organics make potential access to low cost and greener chemistry possible because they are mainly composed of C, H, O, N, and S, which are naturally abundant elements as well as the main constituents of biomass (Figure 6).¹⁹¹ This situation

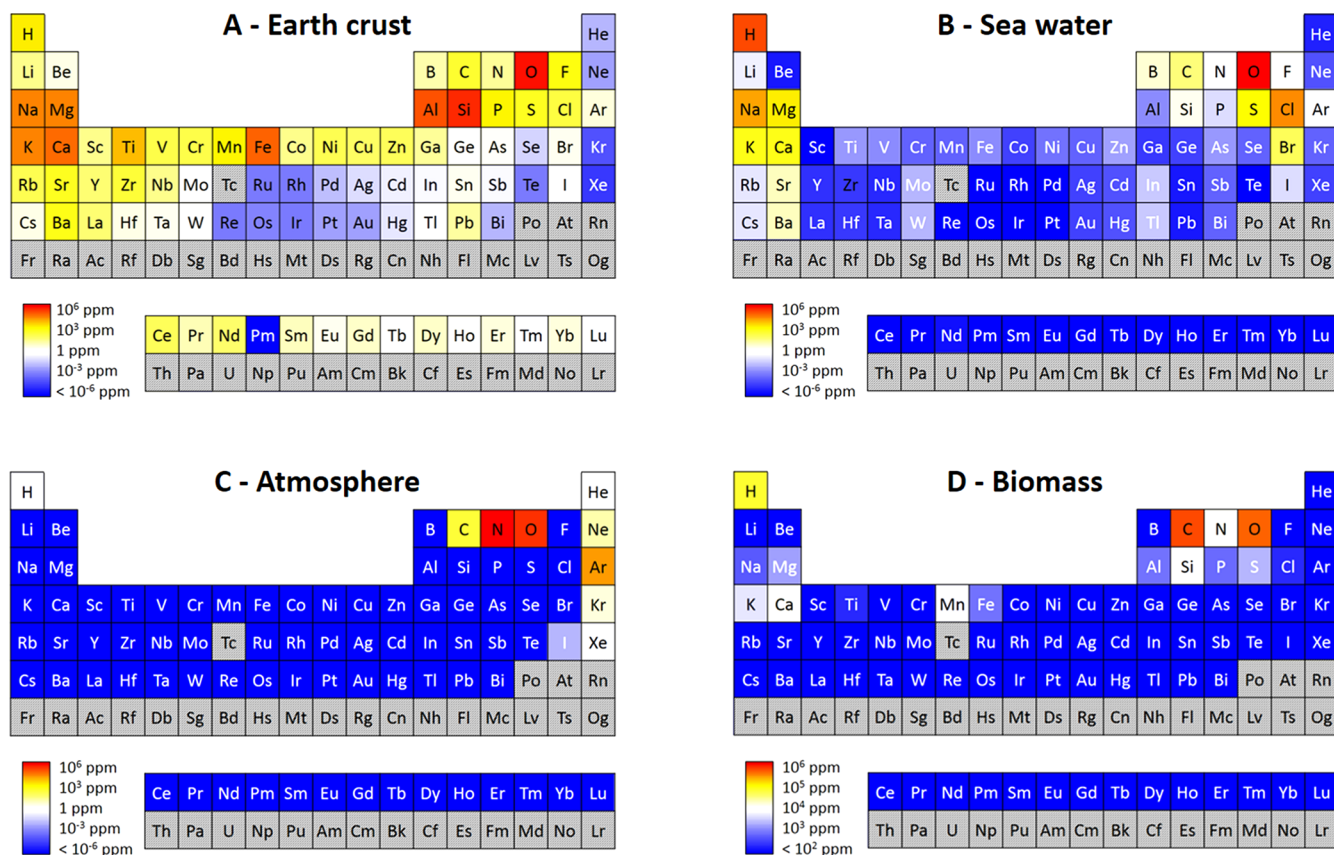


Figure 6. Periodic tables showing the abundance of elements in the Earth's crust (A), in the seawater (B), in the atmosphere (C), and in biomass (D); elements in gray indicate natural and/or radioactive elements. Courtesy of L. Simonin, CEA-Liten, adapted from ref 188 taking into account data from refs 189–191. This analysis highlights that among the naturally occurring elements only a few of them are abundant in each of these four compartments, which demonstrates the importance of developing recycling solutions too.

offers opportunities to prepare electrodes (and other components in a cell like binders)¹⁹⁸ from renewable resources benefiting from ongoing progress in the vast field of biorefineries too.^{199–201} Hydrolysis lignin features were even assessed in primary Li-cell²⁰² or more interestingly in combination with PPy in an interpenetrating lignosulfonate/PPy thin-film composite electrode tested in 0.1 M aqueous HClO₄ as electrolyte, with the catechol moiety in lignin being used for reversible electron and proton storage/uptake.²⁰³ Several naturally occurring polyphenols (e.g., ellagic acid,²⁰⁴ purpurin,²⁰⁵ lawsone²⁰⁶) were electrochemically assessed in Li/Na half cells; however, the proof of concept of making a “renewable” all-organic Li-ion battery was first demonstrated with oxocarbon derivatives as active electrode materials ten years ago.^{82–84} Esquivel and co-workers²⁰⁷ have also demonstrated opportunities for portable and disposable single-use applications to power small devices with the concept of PowerPAD (Power: Portable And Disposable), a fully organic and completely biodegradable battery designed to operate for relatively short periods of time (from minutes to 1–2 h). The promising field of ORFBs (see section 9) has also demonstrated interest in the use of redox-active naturally occurring polyphenols/quinones for abundance and cost reasons.^{20,34} At this stage, it must be underlined that common routes to synthesize OEMs in this emerging field deal with petrochemicals. However, even if large scale production were used for high-performance OEMs in the future, petrochemicals are higher-value products than petroleum products for combustion (only a small fraction ($\approx 4\%$) of oil worldwide is

used to make chemicals⁴²). In terms of cost, it is difficult to make predictions for petrochemical reagents notably if in the future the demand for petroleum products used for combustion decreases; the access to new markets and applications can change the game. However, it is generally accepted that fluorinated derivatives are among the most expensive compounds.

Second, simplified recycling managements of organic spent batteries (Figure S7) can be expected notably with solid electrodes since organic structures are typical fuels that can be consumed by combustion at medium temperatures producing heat (energy recovery). Interestingly, if spent organic batteries were inadvertently not collected (spread out in the wild), the loss of scarce and costly metallic chemical is notably reduced compared to the current battery technologies. Moreover, the use of biodegradable materials can be envisaged too.

Last but not least, organic chemistry offers high structural designability providing great opportunities to find novel and innovative electrode materials with specific properties including the elaboration of multimodal systems such as electrochemical/chemical or electrochemical/photochemical rechargeability.^{208–210} More importantly, physicochemical properties can be rationally tuned using well-established principles of organic chemistry and molecular engineering giving access to redox-active species able to work:

- from dissolved to solid state (including polymers) in aqueous or nonaqueous electrolytes making them versatile in terms of electrochemical storage devices including access to flexible devices;

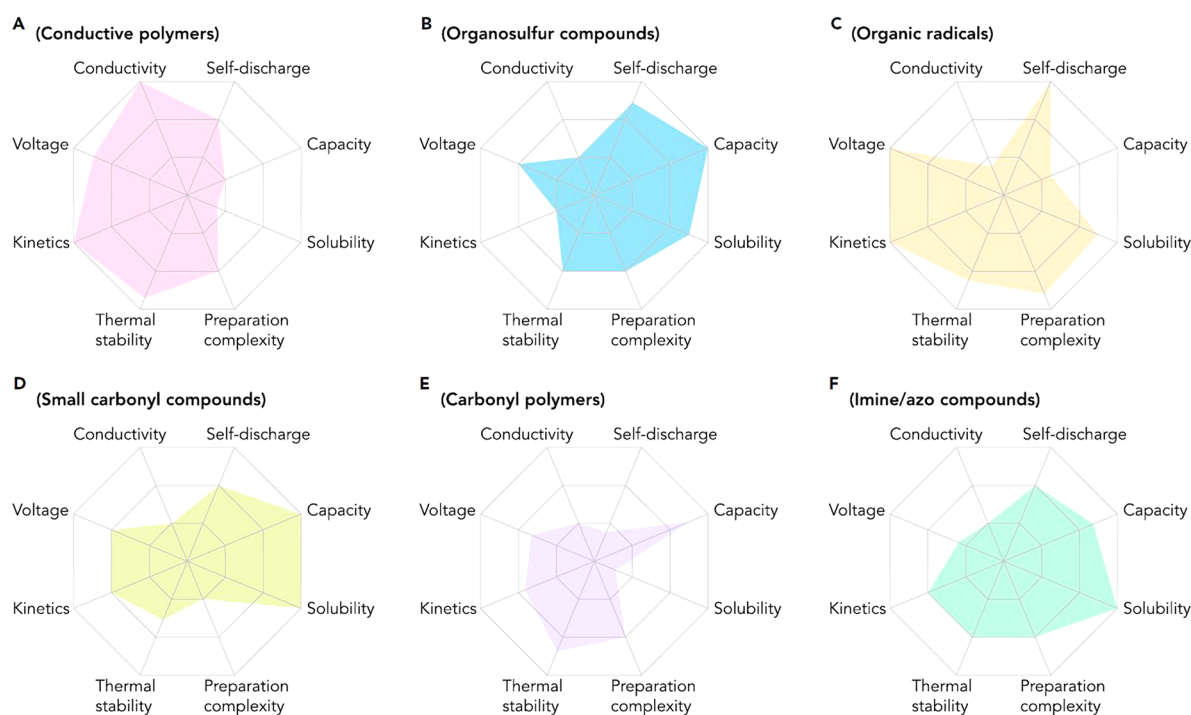


Figure 7. Overview of fundamental properties of different types of organic electrode materials. Reproduced with permission from ref 38. Copyright 2018 Elsevier Ltd.

- through two electrochemical storage mechanisms (n- or p-type electrode reaction with cation or anion charge compensation) making various electrode configurations possible (see the next section);
- at adjusted redox potential because the electron density at the molecular level can be easily tuned by mesomerism in conjugated systems and more importantly by inductive effects using either electron-withdrawing ($-I$) groups or electron-donating ($+I$) groups. For example, computational modeling concerning the one-electron reduction potential of various substituted quinones shows a possible potential tuning (ΔE°) of about 1.5 V;²¹¹
- with potentially reversible multielectron reactions which could counterbalance a slightly too important molecular weight;
- with multivalent cation and bulky ions (e.g., Mg^{2+} , K^+ , PF_6^-) because organics (polymers and crystallized host structures) can better accommodate structural changes thanks to weak-bond networking;
- potentially without any metal following the concept of “molecular organic-ion battery”.^{212–214}

Whether organic chemistry offers high structural designability through this multiplicity of chemical combinations at the molecular level, it could be somewhat challenging to grasp the electrochemical working principle of the reported OEMs in the literature for researchers more familiar with inorganic electrode materials. In the next section we will try to make understandable all the redox functioning of organic molecular assemblies with the basics of electrochemical cells as a starting point.

4. FUNDAMENTALS OF ORGANIC ELECTRODE COMPOUNDS FOR ELECTROCHEMICAL STORAGE

4.1. Basics of Electrochemical Cells

As reported in all undergraduate chemistry books, primary and secondary (rechargeable) cells (or batteries) produce discharge

DC current for an output voltage of a few volts by direct conversion of chemical energy by virtue of two opposite oxidation–reduction processes occurring at two separated electrodes (current collectors) maintained in ionic contact through an electrolytic medium (Figure 8).⁸⁴ In such a situation, the two half redox reactions taking place at electrodes are called “electrochemical reactions”. During discharge (spontaneous cell reaction or galvanic cell reaction), the electrochemical reduction reaction occurs at the positive electrode whereas the electrochemical oxidation reaction occurs at the negative electrode. For rechargeable cells, the terminology should be obviously reversed during charge (electrolysis cell reaction). Therefore, to avoid confusions, the terms “positive” electrode or “negative” electrode are preferred whatever the considered cell reaction (i.e., charging or discharging), with the positive electrode always displaying the highest potential value. Note that a cell is the basic electrochemical unit. A battery is composed, strictly speaking, of two or more such cells connected in series or parallel. However, the term battery has evolved, especially in the language of the end user; therefore, the term “battery” will be used herein without this distinction for the sake of simplicity.

The use of two antagonist redox couples is then required with (e.g., Ox_1/Red_1 and Ox_2/Red_2 characterized by standard potentials $E^\circ(Ox_1/Red_1) > E^\circ(Ox_2/Red_2)$) to reach high electromotive force ($emf = E_{I=0}$, in V) at the cell level under zero current since emf depends on the difference $E^\circ(Ox_1/Red_1) - E^\circ(Ox_2/Red_2) > 0$ or more generally on the difference $E(+)-E(-) > 0$. In short, it depends on the thermodynamics of the chosen electrode chemistries because $E_{I=0}$ is related to the Gibbs free energy change of the galvanic cell reaction, $\Delta_r G$, as follows: $\Delta_r G = -n \cdot E_{I=0} \cdot F$ (n being the number of electrons involved in the cell reaction and F is the Faraday constant, equal to $96,485 \text{ C mol}^{-1}$). Under discharge current (I , in mA), for example, the operating voltage, $E_{I \neq 0}$, is lower than the $E_{I=0}$

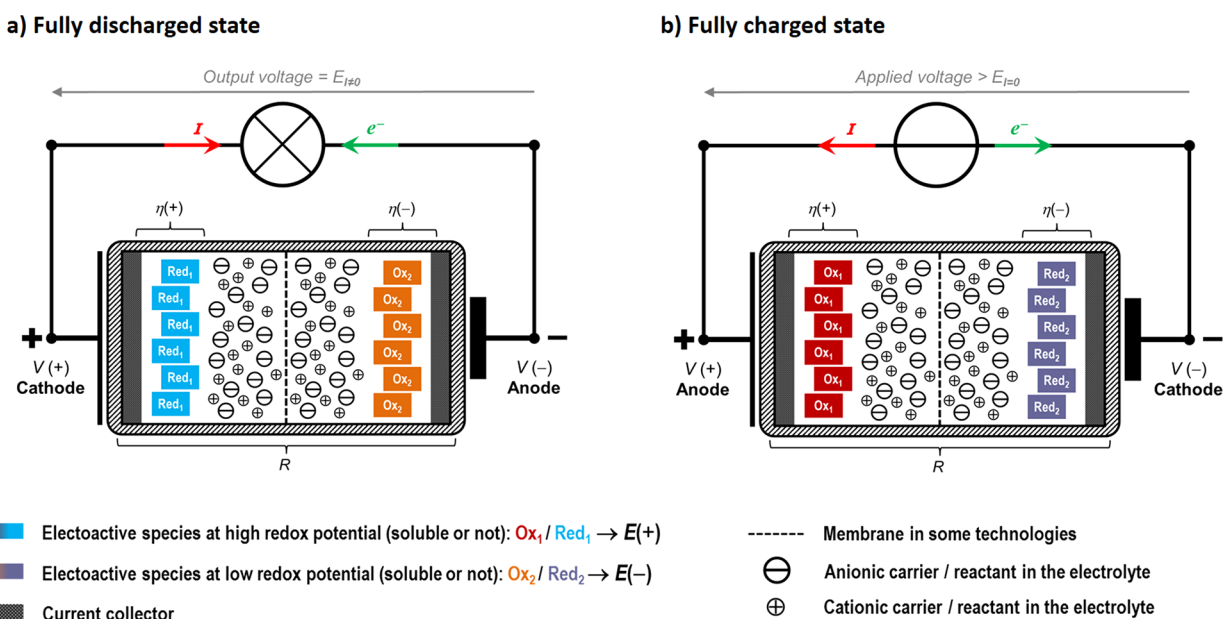


Figure 8. General architecture of an electrochemical cell for energy storage whatever the considered technology is. Note that additional electrolyte can be stored externally and then pumped through the cell in the particular case of a flow battery (see Section 9). (a) Cell under discharge (namely galvanic cell) at 100% depth-of-discharge (DOD). (b) Cell under charge (namely electrolysis cell) at 100% state-of-charge (SOC); the electromotive force value ($emf = E_{I=0}$) is, in principle, at the maximum value. The measured capacity, Q (in mAh), is experimentally obtained by integrating the operating time with current: $Q = \int_0^t I(t) \cdot dt = I \cdot \Delta t$ which gives rise to $Q = I \cdot \Delta t$ whereas the energy, ε (in mWh), is obtained by multiplying Q with the voltage $E_{I \neq 0}$.

1227 value because of (i) kinetic limitations at the electrodes
1228 (overpotentials or polarization losses, η) and (ii) ohmic drop
1229 (“ $R \cdot I$ ” term) due to the overall ohmic resistance (R , in Ω) of
1230 electrodes and electrolytes as shown below:

$$E_{I \neq 0} = [E(+)-E(-)] - [\eta(+)+\eta(-)] - [R \cdot I]$$

1231 Obviously, high $E_{I=0}$ values with minimum losses in
1232 operation are sought after together with high capacity values,
1233 Q , in C (or Ah a unit more generally used in the field of
1234 electrochemical generators). By virtue of Faraday’s law, the
1235 theoretical expected Q value of a cell is proportional to n and
1236 the amounts of the redox (electroactive) chemical species.
1237 Normalizations of Q are often reported to make performance
1238 comparison easier giving rise for example to specific capacity
1239 (Q_m) per gram of electroactive compound and volumetric
1240 capacity (Q_v) per cm^3 of electroactive compound (M being the
1241 molar mass and ρ the specific density of the electroactive
1242 species, respectively):

$$Q_m \text{ (C g}^{-1}\text{)} = n \cdot F / M \text{ or } Q_m \text{ (mAh g}^{-1}\text{)} = n \cdot 26805 / M$$

$$Q_v \text{ (C cm}^{-3}\text{)} = n \cdot F \cdot \rho / M \text{ or } Q_v \text{ (mAh cm}^{-3}\text{)} = n \cdot 26805 \cdot \rho / M$$

1243 Multiplying Q with $E_{I \neq 0}$ at any time during the discharge makes
1244 the calculation of the as-obtained energy, ε (in mWh). Of course,
1245 high reversibility of the cell reaction (good cyclability), high
1246 Coulombic efficiency, and low self-discharge are notably required
1247 for long-lasting cycling of rechargeable batteries. More details can
1248 be found in specialized books (see for example, ref 2).

1249 4.2. Bridging the Gap between Inorganic and Organic Redox Chemistry

1250 As previously recapped, oxidation–reduction reactions make elec-
1251 tricity production possible when properly used in a two-electrode
1252 cell design. Hence, redox-active chemical systems (especially

reversible ones) constitute the workhorse of the electrochemist 1253
in the design of electrochemical generators. Beyond exploiting 1254
the potential values of redox couples (thermodynamics) to 1255
decide if the interest for a given system is related to positive or 1256
negative electrode application, the electrochemist follows with 1257
a great deal of interest variations of oxidation states (OS; or 1258
oxidation number, ON) of chemical elements constituting 1259
the considered redox couples because it allows us to readily 1260
understand and rationalize the formal involved redox center as 1261
well as subsequently determine the number of electrons involved 1262
in the half-reaction. Latimer appears to be the first to introduce 1263
this concept within the context of redox half-reactions.²¹⁵ 1264

According to the IUPAC definition,²¹⁶ the OS of an atom is 1265
the charge of that atom after an ionic approximation of its 1266
heteroatomic bonds. The bonds between atoms of the same 1267
element are not replaced by ionic bonds; they are divided 1268
equally. In other words, to determine the OS of a given atom, it 1269
is therefore considered that all heteroatomic bonds in which it 1270
participates are 100% ionic and the electrons of each of these 1271
bonds are assigned to the most electronegative atom (Allen’s scale). 1272
Moreover, IUPAC recommends two closely related general algo- 1273
rithms for OS calculation in molecules, ions, and extended solids:²¹⁶ 1274

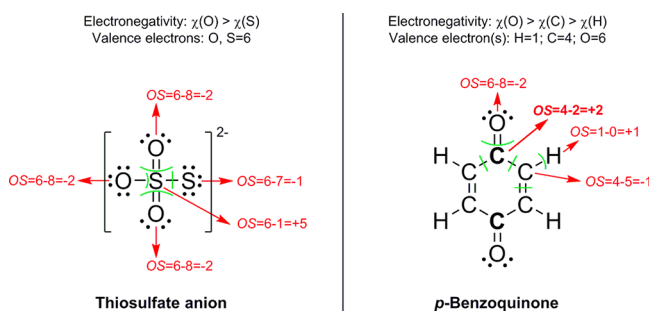
- **Algorithm of assigning bonds.** This algorithm works on 1275
structural Lewis formulas of molecules and ions which 1276
show all valence electrons. 1277
- **Algorithm of summing bond orders.** This algorithm 1278
works on structural Lewis formulas and bond graphs for 1279
an extended solid, especially ionic-covalent structures. 1280

However, as thoroughly explained above, because the used 1281
redox chemistry in battery applications is related to the OS 1282
change of the 3d-metallic redox centers (e.g., Ti, V, Mn, Fe, 1283
Co, Ni) or elemental/diatomic substances (e.g., Li, Na, Mg, C, 1284
 O_2 , Si, P, S, Sn),¹¹ a set of more general rules for determining 1285
OS is more readily used (e.g., “the sum of OS for all atoms in the 1286

1287 species is zero to ensure electroneutrality", "Fluorine: - 1",
 1288 "Oxygen: - 2 unless combined with fluorine", and so on) as
 1289 nicely recalled by Walsh et al.²¹⁷ Although not recommended
 1290 by IUPAC, this simplest method is quite sufficient to assign OS
 1291 of most (inorganic) ions and extended solids. Complications
 1292 occur when two identical atoms have different OS in the same
 1293 compound like observed with several inorganic compounds
 1294 based on chemical elements prone to catenation (e.g., C, N, S,
 1295 Si, I). This is precisely the situation encountered with organic
 1296 compounds, which justifies the use of the algorithm of assigning
 1297 bonds recommended by IUPAC based on Lewis formulas of
 1298 molecules and ions to determine OS or organics. In practice, after
 1299 assignment of electrons of each bond to the most electronegative
 1300 element, the OS of element "i" is calculated as follows:

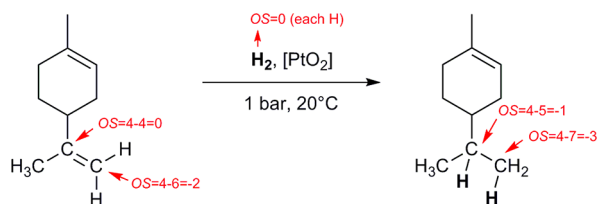
$$\text{OS}(i) = \text{valence electrons of the element "i"} \\ - \sum \text{assigned electrons}$$

1301 Two selected examples are shown below including the case of
 1302 the inorganic thiosulfate anion ($\text{S}_2\text{O}_3^{2-}$) considering that the
 1303 sulfur-sulfur bond is practically a single bond together with
 1304 *p*-benzoquinone as representative redox-active organic molecule.
 1305 Note that only half of OS are reported due to the molecule
 1306 symmetry whereas the green lines indicate the electrons
 1307 assigned per atom. To briefly comment on the redox activity of
 1308 *p*-benzoquinone, each carbon atom bearing the oxygen (in
 1309 bold) exhibits an OS value of +2 that is decreased at +1 after
 1310 the two-electron reduction to produce *p*-hydroquinone.



4.3. Reversible Organic Redox Chemistry and Cell Configurations

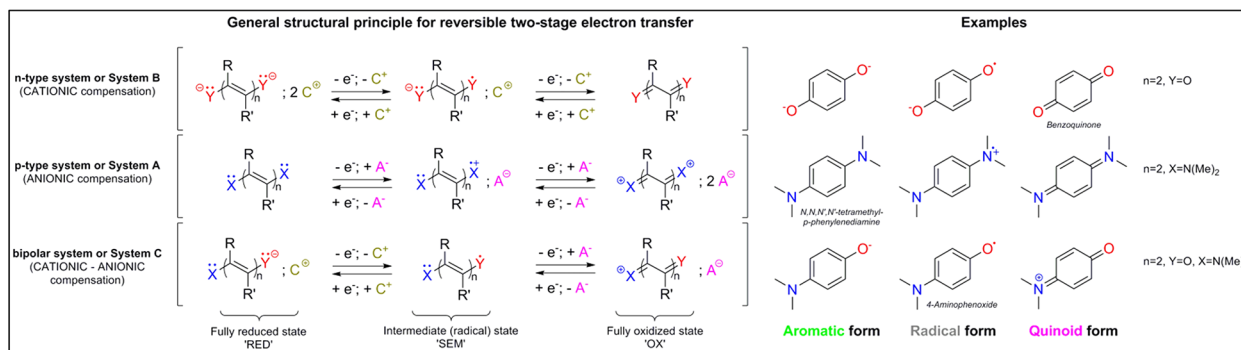
1311 Oxidation-reduction processes in organic chemistry, which
 1312 commonly involve both *s* and *p* orbitals, can be classified in
 1313 two different groups. In the first group, the electronic process
 1314 is accompanied by atom transfer reaction (e.g., gain of oxygen
 1315 for oxidation or hydrogen for reduction) including possible
 1316 fragmentation or condensation subsequent reactions.²¹⁸ However,
 1317 such organic redox reactions are basically used for organic
 1318 synthesis purpose as shown below in the case of the hydro-
 1319 genation reaction of the most accessible double bond of
 1320 limonene (reduction process of the $\text{C}=\text{C}$ double bond with
 1321 decreasing of the OS of the two carbon atoms whereas the two
 1322 incorporated H atoms exhibiting an OS of +1).



More interestingly for us are the redox processes for which
 no formation or rupture of electron-pair single bonds occurs
 after simple charge transfer reaction. In this latter case,
 stepwise transfer of single electrons must in principle be taken
 into account²¹⁹ giving potentially access to reversible organic
 redox couples like conventional third-kind electrode reactions
 (e.g., $\text{Ce}^{4+} + e^- \rightleftharpoons \text{Ce}^{3+}$). However, caution should be
 exercised because one-electron oxidation or reduction of a
 neutral or ionic organic scaffold produces generally reactive ion
 radicals or radicals with possible subsequent reaction such as
 radical coupling. Consequently, some chemical tricks have to
 be used to ensure the production of stable (persistent) radical
 structures after charge transfer.^{220,221} Thus, simple π -extension
 and substituents of resonance electron donating or with-
 drawing groups (mesomerism) make delocalization of spin and
 charge density possible which deeply reduces the reactivity of
 the odd electron (e.g., galvinoxyl or tris(pentachlorophenyl)-
 methyl radicals). Aromatization after electron transfer and
 appropriate steric protection play also important role to protect
 a reactive radical center. Robust functional groups bearing an
 unpaired electron also exist such as nitroxide radicals ($>\text{N}-\text{O}^\bullet$).
 In this family, 2,2,6,6-tetramethylpiperidinyl-*N*-oxy (TEMPO)
 constitutes the most representative example. Beyond the realiza-
 tion of magnetic organic materials,²²¹ the nitroxide redox
 chemistry is at the origin of the rise of ORBs,^{10,75-77} a field
 particularly studied by Nishide, Oyaizu, and co-workers as
 previously underlined in the Introduction. Finally, the general
 structure principles that lead to multistage organic redox
 systems (expected reversible from a redox point of view) are
 owed to Deuchert and Hünig²¹⁹ reported in a comprehensive
 article published in 1978.

Figure 9a recalls the three general key organic structures and
 their related charge transfer steps deriving from Hünig's
 classification together with representative examples of chemical
 compounds. Basically, two electrochemical storage mecha-
 nisms are accessible with organics characterized either by anion
 charge compensation (*p*-type system or System A) or by cation
 charge compensation (*n*-type system or System B); System C
 being a mixed assembly also named "bipolar" system. At other-
 wise constant conditions it is worth noting that redox-active
p-type moiety exhibits as a rule higher formal potential values
 compared to *n*-type systems.²¹⁹ Figure 9b shows the corre-
 sponding cell configurations. For instance, developing Li-ion
 organic batteries requires two *n*-type compounds (Figure 9b-1).
 The *p*-type redox reactivity is rarely encountered with inorganic
 electrode materials. Except carbonaceous materials which
 intercalate ions at relatively high potential (use as positive
 electrode),²²²⁻²²⁵ only a few conversion-type electrode
 materials have been reported to date (for F-ion batteries)
 exhibiting however poor electrochemical performances.²²⁶ On
 the other hand, *p*-type organic compounds enable, in principle,
 the development of anionic rocking-chair cells^{227,228} and
 potentially full "molecular" organic-ion batteries if the shuttling
 anion is metal free (Figure 9b-2). Nevertheless, the cell
 assembly most often encountered in the literature remains the
 dual-ion battery (Figure 9b-3) as recently review by Zhou
 et al.²²⁹ The use at the electrode level of advanced mixed
p/n-type organic scaffolds that exchange simultaneously
 cations and anions can also be envisaged as recently shown
 in aqueous batteries with naphthalene diimide repeating units
 coupled to bipyridinium.²³⁰⁻²³² The molecular engineering
 can even allow cation shuttling in the electrolyte while using
p-type electrodes as reported by Nishide, Oyaizu, and co-workers

a) Electrochemical storage mechanisms using redox-active organic centers



b) Related cell assemblies

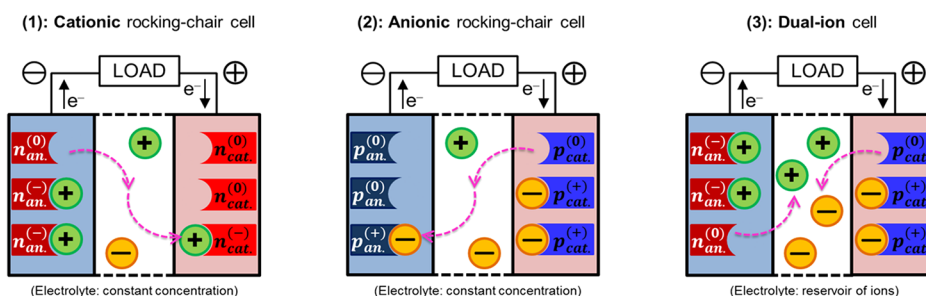


Figure 9. (a) Key reversible redox-active organic systems at the molecular level and their related charge transfer steps (adapted from refs 219 and 234) together with representative examples exhibiting the redox rocking from aromatic to quinoid form. X/Y could be N, O, S, P, π -systems but also carboxylate, anhydride, or amide functional groups; R, R' being potentiality integrated within the same cyclic structure. Note that p- and n-type structures correspond to system A and B, respectively, according to Hünig's classification.²¹⁹ (b) Corresponding cell configurations obtained by playing with both n- and p-type systems shown during the discharge process. Again, additional electrolyte can be stored externally and then pumped through the cell in the particular case of a flow battery (see Section 9). Adapted with permission from ref 36. Copyright 2018 Elsevier Ltd.

with copolymer compositions of TEMPO–sulfonate anionic group.²³³

Finally, before reporting our selection (with description) of the best organic-based batteries to date, a summary of the organic families of interest for electrochemical storage is shown in Table 1 demonstrating the richness in terms of formal redox center as well as the relevance of conjugated structures in general.

5. PERFORMANCES OF NONAQUEOUS LITHIUM–ORGANIC BATTERIES

This section constitutes the first in a series of five (from section 5 to 9) in which a personal selection of organic-based rechargeable cells will be described and commented on. Nonaqueous Li–organic batteries have by far the longest history among all branches of battery OEMs applications. The results from these pieces of research have also directly fueled or inspired the design of OEMs for other emerging organic batteries. Several comprehensive review articles have covered virtually every category of OEMs used in Li–organic batteries;^{9,39,43,47} hence, another comprehensive write-up on the topic is not intended herein. Instead, we will focus on the best performance ever achieved by OEMs in these batteries as well as the design rationale behind these successes. In particular, three key performance parameters will be reviewed: operating potential, specific capacity, and cycling stability. The properties and cell performance of these materials are summarized for comprehensive comparison (Table 2).

5.1. Positioning the Operation Voltage

A large variety of redox active functional groups have been explored for designing OEMs for Li-based batteries, and the

voltages of cells based on these OEMs vary by a wide extent as a result. Depending on their operating potentials, OEMs may be used either as positive electrode (>2.2 V vs Li⁺/Li) or negative electrode (<1.5 V vs Li⁺/Li) active materials. Again, OEMs intrinsically showing the highest potentials, e.g. >3.5 V vs Li⁺/Li, are p-type compounds which, upon charge, lose electrons and accept anions from the electrolytes (Figure 9). As previously mentioned, conductive polymers, which had been intensively studied as positive electrode materials to enable Li batteries (dual-ion cell configuration, Figure 9b-3), fall into this category too. Prime examples include the PAC²⁹² (Table 2, entry 1), PAni, PPy, PT, and poly(*p*-phenylene) families.⁵⁹ Their operating potentials vary according to the type of polymer backbones and can approach 4 V vs Li⁺/Li due to the p-type redox activity. The charge storage mechanism of conductive polymers is based on multiple π -conjugated repeating units stabilizing one positive charge via charge delocalization. Unfortunately, as more charges are stored, fewer repeating units are available to stabilize the charges, and the polymers become less stable.

More recent designs of high-potential p-type OEMs relied on dedicated redox centers for positive charge stabilization. These redox centers usually involve either carbon, oxygen, or nitrogen centers stabilized by aromatic structures and electron-donating functional groups. The polycyclic aromatic hydrocarbon coronene mimics mini graphene sheets and reversibly gives out 0.68 electrons per molecule upon charging (Table 2, entry 2).²³⁵ It delivers one of the highest average discharge potentials of 4.0 V vs Li⁺/Li among OEMs. 2,3,6,7,10,11-Hexamethoxytriphenylene (HMTP) undergoes a full one-electron redox reaction despite the smaller polycyclic aromatic

Table 1. A Few Electrochemical Storage Mechanisms in Redox-Active Organics Together with Examples^a

Reversible redox-active moiety	Classification	General redox mechanism	Example of electrode reaction
Conjugated carbonyl	n-type		
Organodisulfide	n-type		
Conjugated azo group	n-type		
Conjugated nitrile	n-type		
Conjugated amine	p-type		
Conjugated etheroxide	p-type		
Conjugated thioether	p-type		
Nitroxide radical	n/p-type (bipolar)		

^aPBQS: poly(benzoquinonyl sulfide); PDTTA: poly(2,5-dihydro-1H,4H-2,3,6,7-tetrathia-anthracene); ADALS: azobenzene-4,4'-dicarboxylic acid lithium salt; TCNQ: tetracyanoquinodimethane; PPy: polypyrrole; DBMMB: 2,5-di-*tert*-butyl-1-methoxy-4-[2'-methoxyethoxy]benzene; PT: polythiophene; PTMA: poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate). Note the redox-active nitroxide radical is bipolar, in practice, good kinetics are only attempted with the p-type activity.

1445 hydrocarbon core than that found in coronene (Table 2, 1446 entry 3).²³⁶ The auxiliary electron-donating methoxy groups 1447 seem to have contributed to the higher p-doping level albeit 1448 with a lower discharge potential of 3.5 V vs Li⁺/Li. 1449 Tetrathiafulvalene (TTF) is a π -conjugated molecule famous 1450 for its distinctive electronic properties in the highly stabilized 1451 oxidized form. OEMs incorporating the TTF structure, such as 1452 2,2'-bis[5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentanyli- 1453 dene] (TTPY, Table 2, entry 4) and pentakis-fused TTF 1454 (Table 2, entry 5), show almost full utilization of two electrons 1455 per TTF unit in the molecules thanks to the strong stabilizing 1456 power of the sulfur atoms.²³⁷ Pentakis-fused TTF shows a 1457 higher voltage than that of TTPY (3.56 against 3.4 V vs Li⁺/Li) 1458 due to the higher number of electrons involved in the reaction 1459 (Figure 10A).²³⁸

1460 Beyond conjugated hydrocarbon and thioether families, the 1461 one-electron oxidation reaction of nitroxide radical^{10,75–77} has 1462 spawned a large body of literature on radical polymer electrodes 1463 (Table 1). The poster-child building block of radical polymers 1464 is 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), where the 1465 nitroxide radical is sterically stabilized by the neighboring 1466 methyl groups. Polymers incorporating the TEMPO block, 1467 most notably poly(2,2,6,6-tetramethyl-1-piperidinyloxy-4-yl 1468 methacrylate) (PTMA) (Table 2, entry 6), deliver discharge 1469 potential of ~3.55 V vs Li⁺/Li (Figure 10B).^{75,239} The 1470 potential can be tuned by using different nitroxide-containing 1471 cores. For example, poly(2,2,5,5-tetramethyl-3-oxiranyl-3-pyrro- 1472 lin-1-oxyl ethylene oxide) (PTEO, Table 2, entry 7), which 1473 contains the 2,2,5,5-tetramethyl-1-pyrrolidinoxy (PROXYL) 1474 core, shows a higher potential of 3.7 V vs Li⁺/Li.²⁴⁰ Recently, 1475 a nonradical oxygen center was reported in the form of dibenzo- 1476 1,4-dioxin (DD) (Figure 10C, Table 2, entry 8).²⁴¹ A remark- 1477 ably high discharge potential of 4.1 V vs Li⁺/Li was observed,

1478 though only one out of the two oxygen atoms in the molecule 1479 contributed to charge storage. Nitrogen centers in aromatic 1480 amines may be easier to incorporate into a molecule from the 1481 organic synthesis point of view. Triphenylamine (TPA) is 1482 among the most studied building blocks in organic electronics. 1483 TPA-based OEMs, such as triphenylamine-based polymers 1484 (PTPA, Table 2, entry 9) show competitive discharge 1485 potentials of ~3.6 V vs Li⁺/Li.²⁴² Many other aromatic amines 1486 have been studied as OEMs as well including small mole- 1487 cules^{243,244} and organic salt forms such as dilithium 2,5- 1488 (dianilino)terephthalate (Li₂DAnT), which are quite less soluble 1489 than non-salt molecules as further explained below (Table 2, 1490 entry 10).²⁴⁵

1491 Compared with p-type OEMs, the n-type counterparts have 1492 attracted greater research interest because of giving access 1493 to the reversible storage of Li⁺ and potentially to cationic 1494 “rocking-chair”-type batteries when n-type electrode materials 1495 are properly designed (Figure 9). *p*-Benzoquinone (*p*-BQ) is 1496 one of the most studied n-type building blocks for OEMs 1497 (Table 1). The basic *p*-BQ molecule shows two discharge 1498 plateaus at 2.9 and 2.5 V vs Li⁺/Li with equal capacities, 1499 averaging to a discharge potential of 2.7 V vs Li⁺/Li (Figure 10D, 1500 Table 2, entry 12).²⁴⁶ OEMs resembling the *p*-BQ structure show 1501 similar potentials as *p*-BQ. BBQ, a dimer of *p*-BQ, and 1,4,5,8- 1502 phenanthrenequinone (PADQ), a three-ring molecule incorpo- 1503 rating two *p*-BQ units show discharge potentials at 2.9 and 2.77 V 1504 vs Li⁺/Li, respectively (Table 2, entry 18, 19).^{247,248} The slightly 1505 higher potential than that of *p*-BQ may be related to the limited 1506 specific capacity (i.e., relatively small depth of discharge) rather 1507 than performance improvement by design, however. Polymers 1508 that incorporate the *p*-BQ structure without much modifica- 1509 tion to the building block preserve the discharge potential. 1510 PBQS and poly(2,5-dihydro-*p*-benzoquinonyl sulfide) (PDBS) 1511

Table 2. Performances of Selected Nonaqueous Li–Organic Batteries



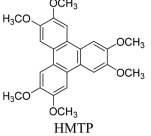
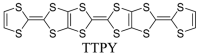
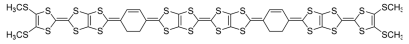
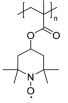



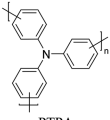
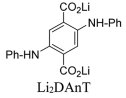
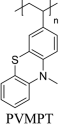
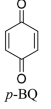
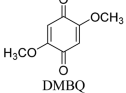
#	Cell configuration (ionic carriers)	Positive electrode (or “cathode”) active material	Negative electrode (or “anode”)	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh g ⁻¹) and Specific energy (Wh kg ⁻¹) ^a per mass of active material, Final coulombic efficiency, Loading (mg cm ⁻²)	Ref.
1	ClO ₄ ⁻	 Polyacetylene	Li	1 M LiClO ₄ in PC	4.0	N/A	200, 471	[292]
2	PF ₆ ⁻	 Coronene	Li	1 M LiPF ₆ in EC/DEC	4.0	92%, 960, 20 mA g ⁻¹	40, 140	[233]
3	PF ₆ ⁻	 HMTP	Li	1 M LiPF ₆ in EC/DEC	3.5	92%, 80, 1 C	67, 190	[236]
4	BF ₄ ⁻	 TTPY	Li	1 M LiBF ₄ in EC/DEC	3.3	84%, 100, 0.2 C	168, 349	[237]
5	PF ₆ ⁻	 Pentakis-fused TTF	Li	1 M LiPF ₆ in EC/DEC	3.56	72%, 30, 0.2 C	196, 414	[238]
6	PF ₆ ⁻	 PTMA	Li	1 M LiPF ₆ in EC/DEC	3.55	95%, 200, 2 C	103, 269	[239]
	Li ⁺ , PF ₆ ⁻	 PTMA	Li	1 M LiPF ₆ in EC/DMC/DEC (w/w/w 1:1:1)	3.0	55%, 20 000, 100 mA g ⁻¹	100, 269	[239]
7	PF ₆ ⁻	 PTEO	Li	1 M LiPF ₆ in EC/DEC	3.7	80%, 1 000, 10 C	85, 242	[240]
8	ClO ₄ ⁻	 DD	Li	5 M LiClO ₄ in EC/DMC	4.1	N/A	80, 256	[241]
9	PF ₆ ⁻	 PTPA	Li	1 M LiPF ₆ in EC/DMC (v/v 1:1)	3.6	95%, 500, 2 000 mA g ⁻¹	98, 263	[242]
10	ClO ₄ ⁻	 Li ₂ DAnT	Li	1 M LiClO ₄ in PC	3.2	87%, 100, 3.7 mA g ⁻¹ (carbon free)	180, 376	[245]
11	PF ₆ ⁻	 PVMPPT	Li	1 M LiPF ₆ in EC:DMC (1:1 v/v)	3.5	93%, 10000, 10 C	50, 149	[280]
12	Li ⁺	 p-BQ	Li	1 M LiTFSI in DOL/DME	2.7	32%, 20, 50 mA g ⁻¹	429, 1004	[246]
13	Li ⁺	 DMBQ	Li	1 M LiClO ₄ in γ -butyl lactone	2.7	82%, 10, 20 mA g ⁻¹	320, 798	[270]

Table 2. continued

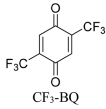
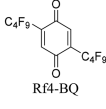
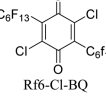
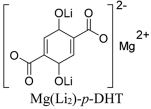
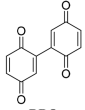
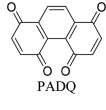
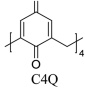
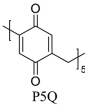
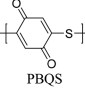
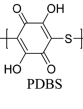
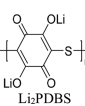

#	Cell configuration (ionic carriers)	Positive electrode (or "cathode") active material	Negative electrode (or "anode")	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh g ⁻¹) and Specific energy (Wh kg ⁻¹) ^a per mass of active material, Final coulombic efficiency, Loading (mg cm ⁻²)	Ref.
14	Li ⁺	 CF ₃ -BQ	Li	1 M LiPF ₆ in EC/DEC (v/v 3:7)	3.0	37%, 20, 0.1 mA	162, 466 [250]	
15	Li ⁺	 Rf ₄ -BQ	Li	1 M LiPF ₆ in EC/DEC (v/v 3:7)	3.0	50%, 20, 0.1 mA	115, 335 [250]	
16	Li ⁺	 Rf ₆ -Cl-BQ	Li	1 M LiPF ₆ in EC/DEC (v/v 3:7)	3.1	55%, 20, 0.1 mA	177, 525 [250]	
17	Li ⁺	 Mg(Li)- <i>p</i> -DHT	Li	1 M LiPF ₆ in EC/DMC (w/w 1:1)	3.4	92%, 80, 23 mA g ⁻¹	100, 340 [252]	
18	Li ⁺	 BBQ	Li	2.75 M LiTFSI in G4	2.8	67%, 20, 40 mA g ⁻¹	358, 917 [247]	
19	Li ⁺	 PADQ	Li	1 M LiPF ₆ in DMC/EMC/EC (v/v/v 1:1:1)	2.77	N/A	370, 935 [248]	
20	Li ⁺	 C4Q	Li	PMA/PEG-based gel polymer electrolyte with LiClO ₄ /DMSO loading	2.6	90%, 100, 0.2 C	422, 989 [272]	
21	Li ⁺	 P5Q	Li	PMA/PEG-LiClO ₄ -SiO ₂ composite	2.6	89%, 50, 0.2 C	409, 964 [273]	
22	Li ⁺	 PBQS	Li	1 M LiTFSI in DOL/DME (v/v 1:1)	2.7	86%, 1 000, 5000 mA g ⁻¹	275, 691 [246]	
23	Li ⁺	 PDBS	Li	1 M LiPF ₆ /EC/DMC (v/v 1/1)	2.0	53%, 100, 15 mA g ⁻¹	250, 470 [274]	
24	Li ⁺	 PDBS	Li	1 M LiTFSI in DOL/DME (v/v 1:1)	2.5	50%, 20, 50 mA g ⁻¹	200, 475 [249]	
25	Li ⁺	 Li ₂ PDBS	Li	1 M LiTFSI in DOL/DME (v/v 1:1)	2.0	87%, 1 500, 500 mA g ⁻¹	247, 464 [249]	

Table 2. continued

#	Cell configuration (ionic carriers)	Positive electrode (or "cathode") active material	Negative electrode (or "anode")	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh g ⁻¹) and Specific energy (Wh kg ⁻¹) per mass of active material, Final coulombic efficiency, Loading (mg cm ⁻²)	Ref.
26	Li ⁺	TPB	Li	1 M LiTFSI in DME:DOL (v/v 1:2)	2.5	91%, 100, 0.2 C	223, 527	[287]
27	Li ⁺	Lawsone-Li	Li	1 M LiTFSI in DME:DOL (v/v 1:2)	2.4	98%, 1 000, 0.5 C	280, 627	[271]
28	Li ⁺	PID	Li	1 M LiPF ₆ in EC/DMC (w/w 1:1)	2.71	80%, 20, 0.1 C	207, 532	[258]
29	Li ⁺	P14AQ	Li	1 M LiTFSI in DOL + DME (v/v 2:1)	2.1	98%, 100, 0.2 C	263, 517	[275]
30	Li ⁺	Poly-LiDHAQS	Li	1 M LiTFSI in DOL/DME (v:v 2:1)	2.5	60%, 1 200, 2 C	330, 760	[276]
31	Li ⁺	DAAQ-TFP	Li	1 M LiTFSI in TEGDME	2.4	98%, 1 800, 500 mA g ⁻¹	107, 250	[283]
32	Li ⁺	PBDTD	Li	1 M LiClO ₄ in DOL/DME (v/v 1:1)	2.5	96%, 250, 0.1 C	200, 475	[288]
33	Li ⁺	TCNQ	Li	1 M Li[TfN] in [EMIm][TfN] and 1 M LiClO ₄ EC/DEC	2.8	78%, 100, 0.2 C	260, 682	[254]
34	Li ⁺	F-TCNQ	Li	1 M LiPF ₆ in EC/DEC	3.1	N/A	183, 542	[255]
35	Li ⁺	F2-TCNQ	Li	1 M LiPF ₆ in EC/DEC	3.15	N/A	110, 342	[255]
36	Li ⁺	1,8-PhenQ	Li	1 M LiPF ₆ EC/EMC (v/v 1:3)	2.94	NA	230, 638	[256]

Table 2. continued


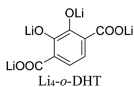
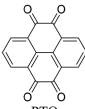
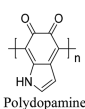
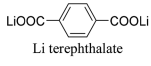
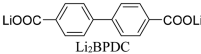
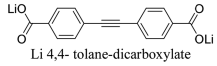
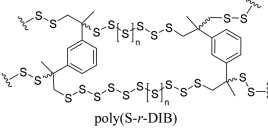
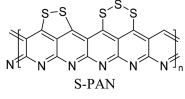


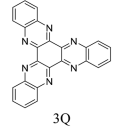
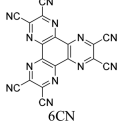
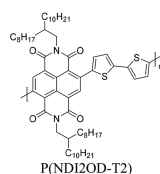
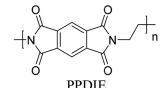
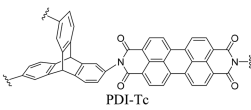
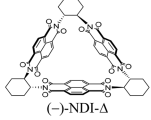

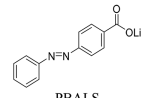
#	Cell configuration (ionic carriers)	Positive electrode (or "cathode") active material	Negative electrode (or "anode")	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh g ⁻¹) and Specific energy (Wh kg ⁻¹) ^a per mass of active material, Final coulombic efficiency, Loading (mg cm ⁻²)	Ref.
37	Li ⁺	 4,5-PhenQ	Li	1 M LiPF ₆ in EC/DMC (w/w 1:1)	2.74	N/A	231, 597	[257]
38	Li ⁺	 Li-o-DHT	Li	1 M LiPF ₆ in EC/DMC (v/v 1:1)	2.85	95%, 30, 0.2–5 C	105, 299	[254]
39	Li ⁺	 PTO	Li	1 M LiPF ₆ in EC-DMC	2.59	27%, 50, N/A	360, 853	[257]
40	Li ⁺	 Polydopamine	Li	1 M LiPF ₆ in EC/DMC (v/v 3:7)	2.5	106%, 10 000, 0.1 A g ⁻¹	108, 263	[105]
41	Li ⁺	 Li terephthalate	Li	1 M LiPF ₆ in EC/DMC (w/w 1:1)	0.8	78%, 50, 0.1 C	300, N/A	[261]
42	Li ⁺	 Li ₂ BPDC	Li	1 M LiPF ₆ in EC/DMC (v/v 1:1)	0.7	60%, 25, 1 C	250, N/A	[264]
43	Li ⁺	 Li 4,4'-tolane-dicarboxylate	Li	1 M LiPF ₆ in EC/DMC (v/v 1:1)	0.65	90%, 50, 0.025 C	130, N/A	[265]
44	Li ⁺	 poly(S-r-DIB)	Li	0.38 M LiTFSI, 0.31 M LiNO ₃ in DOL/DME	2.1	82%, 100, 167 mA g ⁻¹ , 0.1 C	1000, 1668	[266]
45	Li ⁺	 S-PAN	Li	1 M LiPF ₆ in EC/DEC	1.8	73%, 1 000, 0.4 C	1200, 1648	[268]
46	Li ⁺	 Li ₂ C ₆ O ₆	Li	1 M LiPF ₆ in EC/DEC	2.1	N/A	580, 1059	[82]
47	Li ⁺	 C ₆ O ₆	Li	0.3 M LiTFSI-[PY13][TFSI] at 70°C	1.7	82%, 100, 50 mA g ⁻¹	902, 1243	[269]
48	Li ⁺	 3Q	Li	1.0 M LiTFSI in DOL/DME	2.0	70%, 10 000, 20 C	395, 717	[277]
49	Li ⁺	 6CN	Li	1 M LiClO ₄ in EC/DEC (v/v 1:1)	2.4	83%, 30, 0.2 C	300, 668	[278]

Table 2. continued

#	Cell configuration (ionic carriers)	Positive electrode (or "cathode") active material	Negative electrode (or "anode")	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh g ⁻¹) and Specific energy (Wh kg ⁻¹) ^a per mass of active material, Final coulombic efficiency, Loading (mg cm ⁻²)	Ref.
50	Li ⁺	 P(NDI2OD-T2)	Li	1 M LiClO ₄ in DOL/DME (v/v 1:1)	2.4	96%, 3 000, 10 C	54, 128 [281]	
51	Li ⁺	 PPDIE	Li	4 M LiFSI-DME	2.0	82%, 10 000, 10 C	180, 344 [282]	
52	Li ⁺	 PDI-Tc	Li	1 M LiPF ₆ in EC/DME (v/v 1:1)	2.4	80%, 500, 2 C	76, 179 [284]	
53	Li ⁺	 (-)-NDI-Δ	Li	1 M LiTFSI and 0.2 M LiNO ₃ in DOL/DME (v/v 1:1)	2.5	60%, 300, 10 C	146, 352 [285]	
54	Li ⁺	 Benzoic-PDI	Li	1 M LiPF ₆ in EC/DEC (v/v 1:1)	2.4	88%, 200, 5 C	90, 211 [286]	
55	Li ⁺	 PBALS	Li	7 M LiTFSI in DME:DOL (v/v 1:1)	1.4	85%, 500, 10 C	95, N/A [289]	

^aSpecific energy considers the weight of both the cathode and anode materials. For p-type OEMs, LiBF₄ is considered as the Li salt due to its relatively light weight.

show some of the highest discharge potentials for n-type polymer OEMs (Figure 10D, Table 2, entry 22, 23).^{246,249}

Since the discharge potentials of *p*-BQ-containing OEMs are noticeably lower than those of *p*-type OEMs as well as common intercalation compounds (>3.5 V vs Li⁺/Li), efforts have been made to obtain higher potentials. Installation of perfluoroalkyl groups and chlorine atoms at the carbon ring of *p*-BQ gives rise to CF₃-BQ (Table 2, entry 14), Rf₄-BQ (Table 2, entry 15), and Rf₆-Cl-BQ (Table 2, entry 16), which show increased potentials of 3.0–3.1 V vs Li⁺/Li.²⁵⁰ The introduction of these auxiliary groups, however, inevitably decreases the specific capacity and could be counterproductive when high specific energy is the goal. Dilithium (2,5-dilithium-oxy)-terephthalate (Li₂(Li₂)-*p*-DHT or Li₄-*p*-DHT) may be seen as a carboxylate-substituted *p*-BQ (crystallized "host" electrode material) synthesized at its discharged (lithiated) state;^{208,251} with its polyanionic structure making this material highly insoluble.⁸⁴ Since its life as an OEM starts from charging, like commercial positive electrode materials in LIBs do, it is one of the few n-type OEMs that can be paired with a Li-free anode, a great benefit for industrial cell production. However, this very interesting organic was hampered by a relatively low operating potential (2.55 V vs Li⁺/Li). Replacing the Li⁺ in the carboxylate groups with high-electronegativity cations such as Mg²⁺ and Ca²⁺ amazingly increases the redox potential several hundreds of millivolts (Figure 10E).²⁵² Thus the resulting magnesium

(2,5-dilithium-oxy)-terephthalate (Mg(Li₂)-*p*-DHT) shows the highest working potential (3.45 V vs Li⁺/Li) among n-type OEMs approaching the well-known LiFePO₄ electrode material (Table 2, entry 17). Note that an attempt to switch from the carboxylate functional groups present in Li₄-*p*-DHT to the sulfonate substituent giving rise to the tetralithium salt of 2,5-dihydroxy-1,4-benzenedisulfonate (Li₄-*p*-DHBDS)²⁵³ enables also a voltage gain (+650 mV) but with inferior electrochemical performance upon cycling.

A closely related structure to *p*-BQ is tetracyanoquinodimethane (TCNQ), where the oxygen atoms in *p*-BQ are replaced by the even more electron-withdrawing dicyanomethylene groups (Table 2, entry 33). TCNQ itself is known as an electron acceptor for preparation of charge transfer salts, such as TTF-TCNQ. In a Li-battery, TCNQ discharges at 2.9 V vs Li⁺/Li, a noticeable improvement over *p*-BQ.²⁵⁴ Further increase in potential was achieved by installing electron-withdrawing groups to the carbon ring. As the number of fluorine atoms installed to TCNQ increased from two (F-TCNQ) to four (F₂-TCNQ), the average discharge potential increased from 3.1 to 3.15 V vs Li⁺/Li (Figure 10F, Table 2, entry 34, 35).²⁵⁵

The *ortho*-regioisomer of *p*-BQ gives rise to higher discharge potentials in general. The simplest molecule, *ortho*-benzoquinone (*o*-BQ), has not been directly studied probably due to chemical stability issues, but *o*-BQ as a building block for OEMs is well documented. The pyridine rings-fused 1,8-diaza-

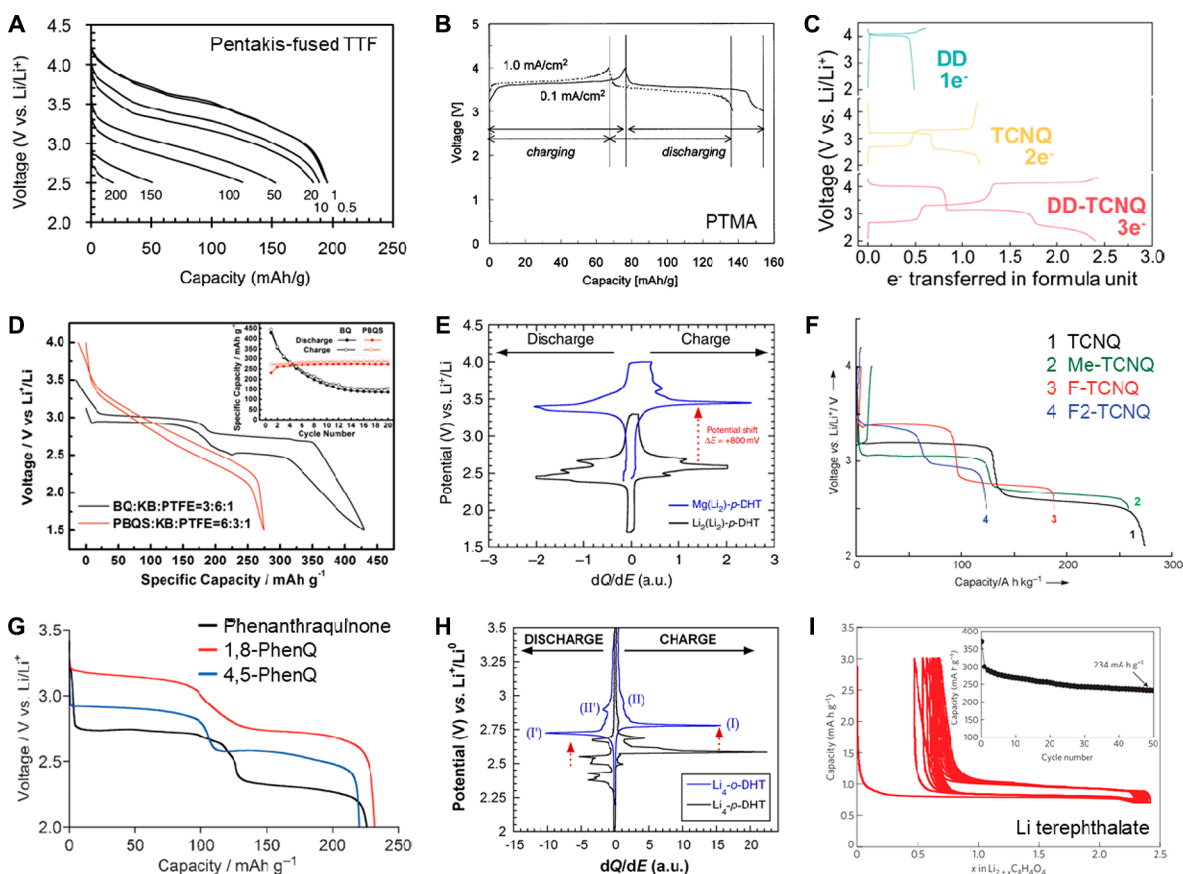


Figure 10. Voltage profiles of selected high-potential positive OEMs and low-potential negative OEMs measured vs Li including (A) pentakis-fused TTF (reproduced with permission from ref 238. Copyright 2014 The Royal Society of Chemistry), (B) PTMA (reproduced with permission from ref 75. Copyright 2002 Elsevier Ltd.), (C) DD (reproduced with permission from ref 241. Copyright 2019 Elsevier Ltd.), (D) BQ and PBQS (reproduced with permission from ref 246. Copyright 2015 John Wiley & Sons, Inc.), (E) $\text{Li}_2(\text{Li}_2)$ -*p*-DHT and $\text{Mg}(\text{Li}_2)$ -*p*-DHT (reproduced from ref 252), (F) TCNQ, F-TCNQ, and F2-TCNQ (reproduced with permission from ref 255. Copyright 2013 John Wiley & Sons, Inc.), (G) 1,8-PhenQ and 4,5-PhenQ (reproduced with permission from ref 257. Copyright 2013 The Royal Society of Chemistry), (H) Li_4 -*o*-DHT (reproduced with permission from ref 234. Copyright 2014 American Chemical Society), and (I) Li terephthalate (reproduced with permission from ref 261. Copyright 2009 Nature Publishing group).

1563 9,10-phenanthrenequinone (1,8-PhenQ, Table 2, entry 36)
 1564 and 4,5-diaza-9,10-phenanthrenequinone (4,5-PhenQ, Table 2,
 1565 entry 37) discharge at 2.94 and 2.74 V vs Li^+/Li (Figure 10G),
 1566 respectively, both higher than the 2.71 V for their *p*-BQ-
 1567 containing isomer pyrido[3,4-*g*]isoquinoline-5,10-dione
 1568 (PID).^{256–258} Interestingly, the position of nitrogen atoms in
 1569 the fusing pyridine rings has a considerable impact on discharge
 1570 potential: the pyridine nitrogen and the carbonyl oxygen being
 1571 adjacent (as in the case of 1,8-PhenQ) promote favorable
 1572 coordination of Li^+ , which leads to extra gain in potential. This
 1573 explains the noticeably higher potential of 1,8-PhenQ than that
 1574 of 4,5-PhenQ (+200 mV as gain). As previously attempted with
 1575 *p*-DHT redox-active ligand, attaching carboxylate functional
 1576 groups to the carbon ring of the reduced form of *o*-BQ gives rise
 1577 to another highly insoluble and lithiated electrode material
 1578 namely (2,3-dilithium-oxy)-terephthalate (Li_4 -*o*-DHT, Table 2,
 1579 entry 38), which can be prepared from biomass too.²³⁴ Alike
 1580 Li_4 -*p*-DHT, this regioisomer is able to release/uptake Li ions
 1581 over dozens of cycles but at higher operating potential (2.85 V
 1582 vs Li^+/Li) due to specific electronic effects²¹¹ occurring in
 1583 orthoquinones (Figure 10H). Since only one out of the two
 1584 lithoxy groups in the carbon ring appears redox active, it may
 1585 be reasonable to assume that upon possible full utilization, an
 1586 even higher average potential could be achieved.

N-type OEMs with sufficiently low operating potential 1587
 can be used as negative electrode materials as well. Many 1588
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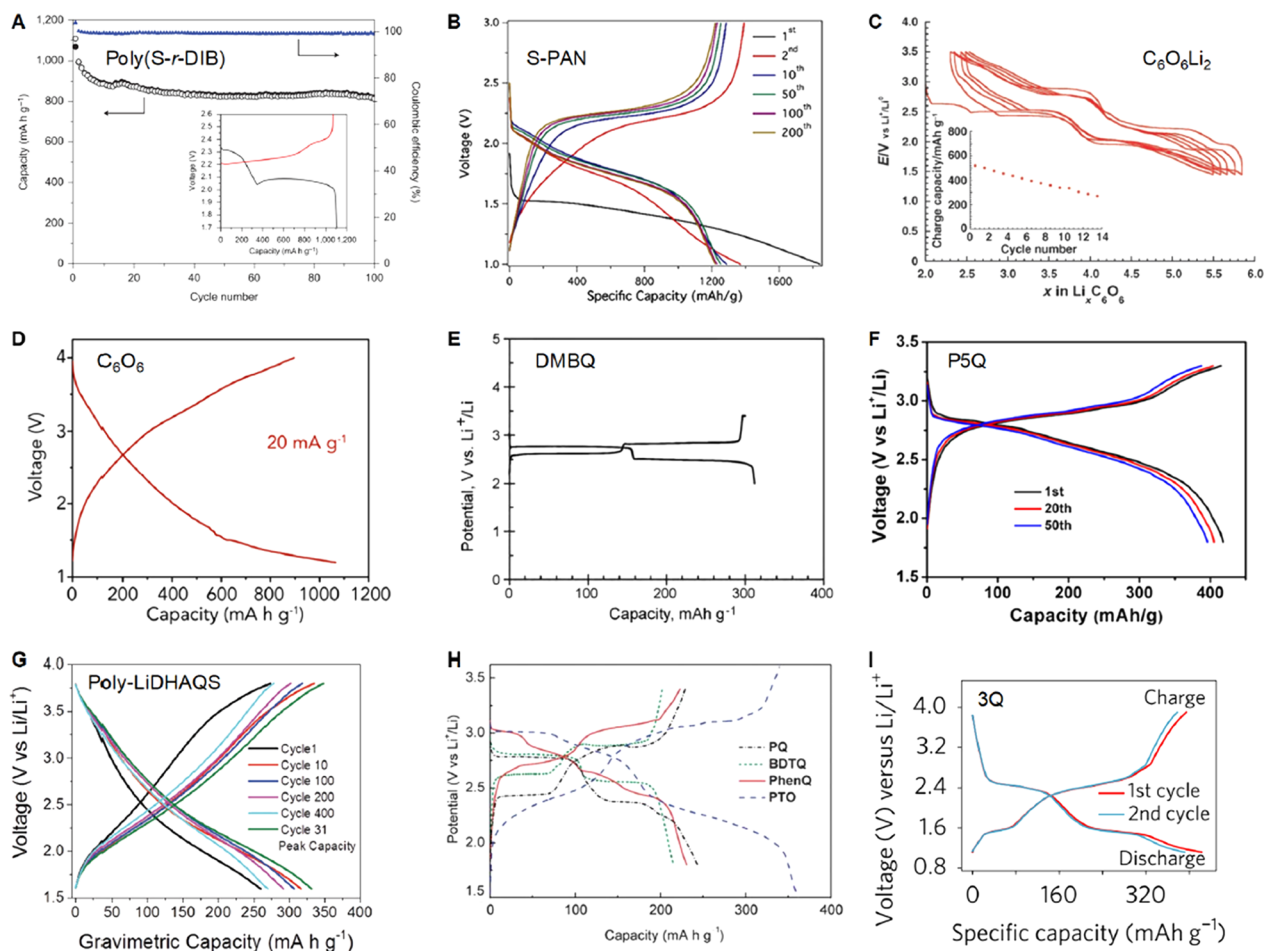


Figure 11. Voltage profiles of selected high-capacity OEMs measured vs Li including (A) poly(S-r-DIB) (reproduced with permission from ref 266. Copyright 2013 Nature Publishing group), (B) S-PAN (reproduced with permission from ref 268. Copyright 2015 American Chemical Society), (C) $\text{Li}_2\text{C}_6\text{O}_6$ (reproduced with permission from ref 82. Copyright 2008 John Wiley & Sons, Inc.), (D) C_6O_6 (reproduced with permission from ref 269. Copyright 2019 John Wiley & Sons, Inc.), (E) DMBQ (reproduced with permission from ref 270. Copyright 2010 Elsevier Ltd.), (F) P5Q (reproduced with permission from ref 273. Copyright 2014 American Chemical Society), (G) poly-LiDHAQS (reproduced with permission from ref 276. Copyright 2017 John Wiley & Sons, Inc.), (H) PTO (reproduced from ref 257. Copyright 2013 The Royal Society of Chemistry), and (I) 3Q (reproduced with permission from ref 277. Copyright 2013 Nature Publishing group).

1611 results in dilithium 4,4'-tolane-dicarboxylate, which discharges
1612 at an even lower potential of 0.65 V vs Li^+/Li (Table 2, entry
1613 43).²⁶⁵ OEMs that undergo the peculiar “superlithiation”
1614 process (see section 7.3) exhibit sloping discharge profiles that
1615 start from >1.5 V and eventually approach 0 V vs Li^+/Li and
1616 then charge at ≥ 1 V vs Li^+/Li on average. Due to the unique-
1617 ness of the reaction, these OEMs are to be separately covered
1618 in section 7.

1619 5.2. Organic Electrode Materials with High Specific Capacity

1620 To gain high specific capacity, both formula weight and
1621 number of transferrable electrons are key considerations.
1622 Among the major classes of organic electrodes, organosulfur
1623 compounds offer the largest capacities. In particular, organo-
1624 sulfur polymers bearing polysulfide bonds not only exhibit high
1625 capacities but also stable cycling. Poly(sulfur-random-1,3-
1626 diisopropenylbenzene) (poly(S-r-DIB)) is one such example,
1627 which was copolymerized between molten S_8 and 1,3-diisopro-
1628 penylbenzene (DIB) through inverse vulcanization.²⁶⁶ The
1629 DIB feed ratios can be varied between 10–50 wt % during the
1630 synthesis. Galvanostatic voltage profiles of poly(S-r-DIB) with
1631 10 wt % DIB show distinct discharge plateaus at 2.3 and 2.1 V

vs Li^+/Li (Figure 11A, Table 2, entry 44). The initial discharge
1632 capacity is 1100 mAh g^{-1} . Sulfur-polyacrylonitrile (S-PAN) is
1633 another organosulfur polymer attracting significant attention
1634 due to the ease of synthesis and high performance.²⁶⁷ S-PAN
1635 was formed by mixing and heating sulfur and polyacrylonitrile
1636 (PAN). It is interesting to note that S-PAN exhibits good
1637 capacity retention in a carbonate-based electrolyte, a behavior
1638 in sharp contrast with sulfur, which works well only in etheral
1639 electrolytes.²⁶⁸ S-PAN shows a single plateau at 2.1 V with a
1640 high specific capacity of 1200 mAh g^{-1} (Figure 11B, Table 2,
1641 entry 45).
1642

1643 Carbonyl group undergoes reversible one-electron reduction
1644 to form a radical anion. When multiple carbonyls are con-
1645 jugatedly connected as in quinones, the uncoupled electrons
1646 generated during reduction could combine intramolecularly to
1647 form multivalent anions. The theoretical capacity of carbonyl-
1648 based electrodes is typically lower than that of organosulfur
1649 polymers. Dilithium rhodizonate ($\text{Li}_2\text{C}_6\text{O}_6$) undergoes rever-
1650 sible four-electron reaction per C_6O_6 ring (Table 2, entry 46).
1651 The observed initial discharge capacity of 580 mAh g^{-1} set the
1652 record capacity among carbonyl-based OEMs since its
1653 discovery in 2008 (Figure 11C).⁸² The fact that $\text{Li}_2\text{C}_6\text{O}_6$ can
1654 be prepared from a renewable natural precursor opens up new
1655

1655 pathways toward sustainable batteries for future clean energy
1656 economy. Recently, cyclohexanehexone (C_6O_6) was claimed to
1657 be successively synthesized and surpass $Li_2C_6O_6$ in terms of
1658 specific capacity (Table 2, entry 47).²⁶⁹ C_6O_6 , a cyclic ketone
1659 composed of carbonyls without redundant mass, exhibits a
1660 higher capacity of 902 mAh g^{-1} (i.e., six-electron reaction per
1661 formula) (Figure 11D). Note that such an ultrahigh capacity
1662 was observed in an ionic liquid-based electrolyte measured at
1663 70 °C. The compound exhibits sloping and polarized cycling
1664 curves, in contrast to the multiple plateaus observed for
1665 $Li_2C_6O_6$.⁸²

1666 After the C_6O_6 motif, *p*-BQ offers the highest theoretical
1667 specific capacity among common n-type OEM building blocks.
1668 *p*-BQ itself can deliver a specific capacity of 429 mAh g^{-1}
1669 during the initial discharge, but the capacity retention was only
1670 32% after 20 cycles due to its high solubility in organic
1671 solvents.²⁴⁶ Due to the ready dissolution of *p*-BQ into non-
1672 aqueous electrolyte solutions, many OEMs containing the
1673 *p*-BQ unit have been developed to reduce dissolution while
1674 maintaining high capacity. They may be categorized into three
1675 types according to their molecular sizes. The first type includes
1676 molecules with one single *p*-BQ core modified with electron
1677 donating or withdrawing groups. Installation of methoxy
1678 functional groups on *p*-BQ results as DMBQ, which improves
1679 the stability compared to *p*-BQ albeit the discharge capacity is
1680 reduced to 320 mAh g^{-1} (Figure 11E, Table 2, entry 13).²⁷⁰
1681 Lawsone-Li is another example showing modification of
1682 naphthoquinone (NQ) with lithoxy results in lawsone-Li salt.
1683 Lawsone (2-hydroxy-1,4-naphthoquinone) is a nature-derived
1684 red-orange dye. Lithium cells based on lawsone-Li as positive
1685 electrode material displayed a capacity of 280 mAh g^{-1} and a
1686 cycle life of 1000 cycles (Table 2, entry 27).²⁷¹

1687 The second type includes molecules with multiple *p*-BQ
1688 units. 2,2'-Bis-*p*-benzoquinone (BBQ), calix[4]quinone (C4Q),
1689 and pillar[5]quinone (P5Q) contain two, four, and five *p*-BQ
1690 units, respectively (Table 2, entries 18, 20, and 21). It seems
1691 that dissolution of oligomers could still be observed in liquid
1692 electrolytes; therefore, polymer electrolytes containing poly-
1693 (methacrylate) (PMA) and poly(ethylene glycol) (PEG)
1694 were used to increase capacity retention. Compared to BBQ
1695 (358 mAh g^{-1}), P5Q and C4Q show higher specific capacity of
1696 409 and 422 mAh g^{-1} (Figure 11F).^{247,272,273}

1697 The third type includes polymers with (modified) *p*-BQ
1698 units. PBQS, PDBS, and Li_2 PDBS present three examples of
1699 *p*-BQ-based polymers when using sulfur as the linker (Table 2,
1700 entry 22–25).^{246,249,274} Among the three polymers, PBQS
1701 shows the highest specific capacity of 275 mAh g^{-1} for 1000
1702 cycles. Due to the addition of lithoxy and hydroxy groups on
1703 PBQS, Li_2 PDHBQS and PDBS exhibit slightly lower specific
1704 capacity of ~250 mAh g^{-1} . Anthraquinone (AQ) can be
1705 considered as *p*-BQ with extended conjugation, which also has
1706 the solubility issue. Polymerization approach has been equally
1707 successful for AQ. P14AQ and poly-LiDHAQS are two
1708 polymers based on AQ. The specific capacities are 263 and
1709 330 mAh g^{-1} , respectively (Figure 11G, Table 2, entries 29
1710 and 30).^{275,276}

1711 A closely related structure to *p*-BQ is pyrene-4,5,9,10-
1712 tetraone (PTO) where two *o*-BQ units are connected with
1713 extended π -conjugated structure (Table 2, entry 39). PTO
1714 undergoes a four-electron reduction with a specific capacity of
1715 360 mAh g^{-1} in EC/DMC and an average discharge voltage
1716 of 2.59 V vs Li^+/Li (Figure 11H).²⁵⁷ TCNQ can also be
1717 formed by replacing the oxygen atoms in *p*-BQ with more

1718 electron-withdrawing dicyanomethylene groups (Table 2,
1719 entry 33). The discharge capacity of TCNQ is lowered to
260 mAh g^{-1} albeit voltage is increased to 3.2 V.²⁵⁴

1720 π -Conjugated heteroaromatic molecules represent another
1721 class of OEMs with high specific capacity. Fused quinoxaline
1722 building blocks afford multiple redox-active sites centered on
1723 N atoms. Hexaazatrinaphthylene (3Q) enables six-electron
1724 reduction with a specific capacity of 395 mAh g^{-1} (Figure 11I,
1725 Table 2, entry 48).²⁷⁷ When hybridized with graphene, 3Q
1726 shows 70% capacity retention after 10 000 cycles. Hexaaza-
1727 triphenylenehexacarbonitrile (6CN, Table 2, entry 49) shows
1728 higher redox voltage at 2.4 V vs Li^+/Li by replacing the
1729 benzene groups in 3Q with electron-withdrawing cyanide
1730 groups.²⁷⁸ When the discharge potential cutoff is set at 1.5 V vs
1731 Li^+/Li , 6CN shows a specific capacity of 300 mAh g^{-1} .
1732

5.3. Organic Electrode Materials with Long Cycle Life

1733 Researchers have almost always attributed the capacity
1734 decay of OEMs to either chemical degradation or dissolution.
1735 In typical nonaqueous Li electrolytes, chemical degradation of
1736 OEMs is rarely observed; hence, material dissolution from the
1737 solid electrode into the electrolyte is the main degradation
1738 mechanism. For the most part, increasing the cycling stability
1739 of OEMs in nonaqueous Li batteries equals minimizing the
1740 solubility of OEMs in electrolytes. As long as material disso-
1741 lution is effectively suppressed, apparently most OEMs can
1742 deliver stable cycling performance. Even small-molecule OEMs
1743 that readily decay due to dissolution can be made stable when
1744 a sufficiently large amount of high-surface-area carbon adsorb-
1745 ent is included in the positive composite electrode as previ-
1746 ously underlined in section 1.2.¹³ Due to practical consid-
1747 erations, cycling performances enabled by intricate adsorbents
1748 are not a priority for this review.

1749 The most stable OEMs for nonaqueous Li batteries have
1750 been polymers. Polymer OEMs containing varying types of redox
1751 centers, from p-type to n-type, from nitroxides (e.g., PTMA)²⁷⁹ to
1752 aromatic amines (e.g., poly(3-vinyl-*N*-methylphenothiazine) or
1753 PVMPT)²⁸⁰ to quinones (e.g., polydopamine)¹⁰⁵ to imides (e.g.,
1754 poly{[*N,N'*-bis(2-octyldecyl)-1,4,5,8-naphthalenedicarboxy-
1755 mide-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)} or P(NDI2OD-T2),
1756 Table 2, entry 50 and poly(ethylene-pyromellitic diimide) or
1757 PPDIE, Table 2, entry 51),^{281,282} have all been reported to
1758 cycle for thousands to tens of thousands of cycles. It may be
1759 reasonable to extrapolate that, with proper polymerization,
1760 OEMs of all types can be made stable, even though synthetic
1761 difficulty may vary from type to type. With judicious selection
1762 of polymerization strategies, two- and three-dimensional
1763 polymer OEMs have been synthesized based on aromatic
1764 amines (e.g., polytriphenylamine or PTPA),²⁴² quinones (e.g.,
1765 2,6-diaminoanthraquinone-1,3,5-triformylphluroglucinol or
1766 DAAQ-TFP),²⁸³ and imides (e.g., perylene diimide-
1767 triptycene or PDI-Tc, Table 2, entry 52).²⁸⁴ These additional
1768 architectures are proposed to further improve cycling stability.

1769 The advantage of polymer OEMs in cyclability does not
1770 preclude molecular OEMs from being important. Molecular
1771 materials can still be preferred for their well-defined structures,
1772 high specific capacity, flexibility in processing, and so on.
1773 Therefore, approaches to improve the cyclability of small
1774 molecules are still being developed. Considering the success of
1775 polymer OEMs, a widely practiced strategy is to increase the
1776 molecular weight of molecules or simply oligomerization. Both
1777 3Q and coronene are big planar molecules which benefit from
1778 relatively strong van de Waals interaction and effective π - π

stacking.^{235,277} Even when the active cores are not as big, it is still convenient to connect multiple building blocks together to artificially increase the molecular weight. Some examples include a triangle molecule (–)-NDI- Δ ²⁸⁵ (Table 2, entry 53) which incorporates three naphthalenediimide (NDI) units plus linkers, benzoic-PDI²⁸⁶ (Table 2, entry 54) which attaches more aryls to the already large molecule perylenediimide (PDI), and 2,3,5,6-tetraphthalimido-1,4-benzoquinone (TPB)²⁸⁷ which incorporates two seemingly unrelated redox centers (tetraphthalimide and *p*-BQ) into one molecule. These molecules exhibit cycling stabilities that clearly set them apart from simple molecules without sacrificing most advantages of molecular OEMs. The large size of these molecules is blurring the boundary between molecules and polymers. In fact, some “polymer” OEMs such as poly(benzo[1,2-*b*:4,5-*b'*]-dithiophene-4,8-dione-2,6-diyl) (PBDTD)²⁸⁸ contain few repeating units (e.g., ≤ 5) per polymer chain. They may as well be considered as molecular OEMs.

Other strategies for stabilizing molecular OEMs include salt formation and grafting as previously mentioned.⁸⁴ Salt formation has long been an established strategy to stabilize molecular OEMs: ionic groups introduced to OEMs increase their intermolecular interactions and decrease the similarity in polarity with nonaqueous electrolytes, thus decreasing solubility.⁸² Some recent excellent examples include Mg(Li₂)-*p*-DHT,²⁵² lawsone-Li,²⁷¹ and 4-(phenylazo) benzoic acid lithium salt (PBALS, Table 2, entry 55)²⁸⁹; all show barely any capacity decay after hundreds of cycles. Grafting is also a known, if still exotic, method for enabling small-molecule OEMs. The key to successful grafting is rational functionalization of high-capacity OEM building blocks for covalent linking to high-surface-area substrates. Grafted naphthoquinone (n-type) and pyrene (p-type) derivatives can show no obvious capacity decay over a long cycling period.^{290–292}

We would like to note that although the cycle numbers for the examples discussed above vary from hundreds to tens of thousands, these numbers, in a lot of cases, seem to be limited by how fast the researchers felt comfortable to cycle their cells instead of the actual stability of the OEMs. Figure 12

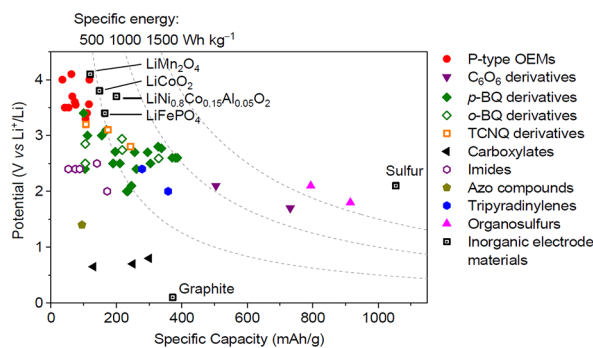


Figure 12. Comparison of the discharge potentials and specific capacities of state-of-the-art OEMs and inorganic electrode materials for Li batteries. Specific capacity calculation considers the weight of the lithiated form of positive electrode materials and delithiated form of negative electrode materials (e.g., azo compounds, carboxylates, and graphite). The highest observed reversible capacities are used instead of theoretical values.

summarizes the discharge potentials and active material-level specific capacities of Li–organic batteries discussed in this section and compares them with those of state-of-the-art

inorganic electrode materials. Note that the specific capacities of batteries with p-type OEMs are impacted by the weight of the Li salt in the electrolyte (dual-ion cell configuration, Figure 9b-3).

For comparison convenience, the calculation of all batteries with p-type OEMs considers LiBF₄ as the Li salt. Although p-type OEMs have comparable discharge potentials and specific capacities as those of inorganic electrode materials, batteries based on them fall short in specific energy where the weight of the electrolyte is included. Therefore, p-type OEMs are not yet contenders as high-energy battery cathode materials but may find applications in, for example, fast charging devices and wearables. Many quinone-based OEMs have surpassed inorganic electrode materials in terms of specific energy at the active material level (i.e., only the weight of active materials is included in calculation). In practice, however, most high-energy OEMs still require too much conductive agents in their electrode composites for decent performance, which decreases specific energies at the cell level. Another challenge for OEMs is to simultaneously achieve high specific energy and high cycling stability. Future development of OEMs for nonaqueous Li batteries demands deeper understandings of their electron and ion conduction mechanics as well as performance degradation mechanisms and strategies to address them.

6. PERFORMANCES OF NONAQUEOUS SODIUM–ORGANIC BATTERIES

For decades, nonaqueous organic sodium-ion batteries have been overshadowed by other electrochemical energy systems (such as inorganic lithium-ion batteries, inorganic sodium-ion batteries, and later organic lithium-ion batteries) and have only been sporadically investigated.²⁹³ However, in 2012, three different groups published their works on disodium terephthalate within a time frame of four months, marking then the beginning of the recent boom in this field.^{294–296} Since then, disodium terephthalate has been regularly investigated as a model compound for composite electrode formulation.^{297–301} In parallel, many other new materials were reported in the literature as already exhaustively covered in recent reviews.^{16,40,41,302} Considering that strategies known to affect the potential with inductive effects (electron-withdrawing/donating groups) or appropriate aromatic ring design will have similar effects in organic LIBs and SIBs, the only distinctions to keep in mind are the differences in electrochemical potential for the reference metal (–3.04 V vs SHE for the Li⁺/Li redox couple against –2.71 V vs SHE for the Na⁺/Na redox couple) and atomic differences. For instance, a sodium carboxylate is expected to insert a sodium ion at an average potential slightly lower than the potential of lithium ion insertion for the corresponding lithium carboxylate with the same aromatic system –0.33 V (e.g., 0.9 V vs Li⁺/Li average redox potential for dilithium terephthalate and 0.4 V vs Na⁺/Na for disodium terephthalate: 0.5 V difference instead of 0.33 V). Similarly, the strategies for improving the specific capacity or reducing the dissolution phenomenon of active species within the electrolyte system such as polymerization work usually as well for organic SIBs as they do for organic LIBs and hence will not be repeated in this section. As a reminder, the use of sodium instead of lithium is also motivated by higher abundance and lower cost of the resource, with Na being widely distributed in the earth’s crust and oceans (Figure 6) and nontoxic.

As previously stated, only the materials delivering the best performances in specific capacity, operating potential, and

Table 3. Performances of Selected Nonaqueous Na–Organic Batteries

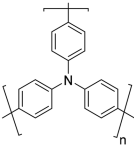
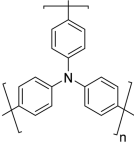
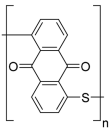
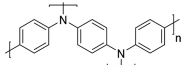
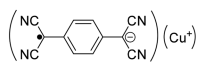
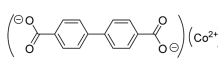
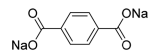
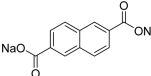
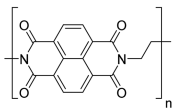
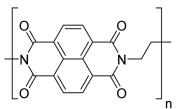
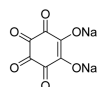
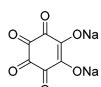
#	Positive electrode (or "cathode") active material	Negative electrode (or "anode") active material	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh g ⁻¹) and Specific energy (Wh kg ⁻¹) per mass of positive active material if not specified otherwise, Final coulombic efficiency, Loading (mg cm ⁻²)	Ref.
Organic electrode materials with high/low voltage							
1		Na	Saturated NaPF ₆ in DOL/DME (v/v 1:1)	3.6	82%, 200, 5 C (500 mA g ⁻¹)	95, 342, 99, n.d.	[307]
2			Saturated NaPF ₆ in DOL/DME (v/v 1:1)	~1.8	85%, 500, 8 C	180-155, ^a 324, ^a 99, n.d.	[307]
3		Na	0.5 M NaPF ₆ in EC/PC (v/v 1:1)	3.38	68%, 1 000, 1 C	94-64, 318, n.d., 1.0-2.0	[308]
4		Na	1 M NaClO ₄ in EC/PC (v/v 1:1)	~3.6	78%, 1 200, 1 C (300 mA g ⁻¹)	98, 353, ~100, n.d.	[309]
5		Na	1 M NaClO ₄ in PC	~0.5	79%, ^b 1 000, (100 mA g ⁻¹)	209, 105, ~100, n.d.	[317]
Na-ion organic batteries							
6	Na _{0.75} Mn _{0.70} Ni _{0.23} O ₂		1 M NaPF ₆ in EC/EMC (v/v 3:7)	~3.6	93%, ^b 50, C/13 (20 mA g ⁻¹)	111, ^c 400, ^c 99, 1.3-2.5	[286]
7	Na ₃ V ₂ O ₇ (PO ₄) ₂ F		1 M NaClO ₄ in PC	3.3	50%, 20, C/10 (13 mA g ⁻¹)	270-135, ^a 891, ^a 73, 2	[324]
8	Na ₄ Fe(CN) ₆		1 M NaClO ₄ in EC/DEC (v/v 1:1)	1.2	73%, 100, 1 C (140 mA g ⁻¹)	158-102, ^d 190, ^d 95, n.d.	[325]
9	Na ₃ V(PO ₄) ₃		1 M NaClO ₄ in EC/DEC (v/v 1:1)	1.2	70%, 100, 1 C (140 mA g ⁻¹)	150, ^d 180, ^d 95, n.d.	[325]
10		Na-predoped hard carbon	1 M NaClO ₄ in PC	~2.2	85%, ^b 40, C/10 (18 mA g ⁻¹)	178-152, ^c 356, ^c n.d., 3.1	[326]
11		Na	0.6 NaPF ₆ in DEG/DME	1.5	91%, 50, 500 mA g ⁻¹	390, 585, ~100, 3-20	[327]
		P@C		1.3	83%, 50, 500 mA g ⁻¹	264, ^a 281, ^a ~100, 3-20	[327]
		Disodium terephthalate		1.25	85%, 30, 50 mA g ⁻¹	137, ^a 141, ^a ~100, 3-20	[327]

Table 3. continued


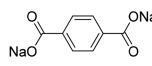
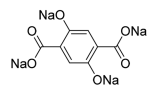
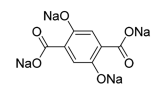
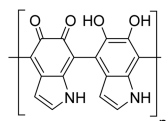
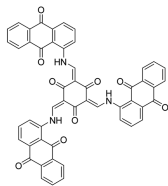
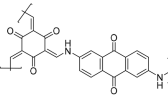
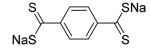
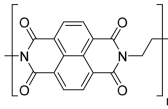
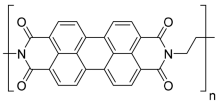
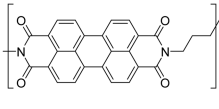
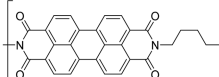
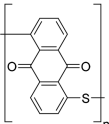
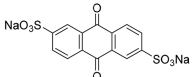
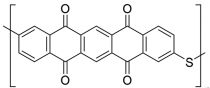
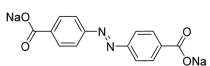
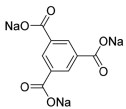
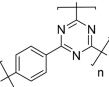
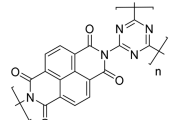
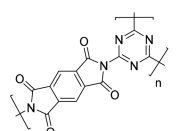
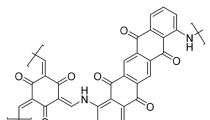
#	Positive electrode (or "cathode") active material	Negative electrode (or "anode") active material	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh g ⁻¹) and Specific energy (Wh kg ⁻¹) per mass of positive active material if not specified otherwise, Final coulombic efficiency, Loading (mg cm ⁻²)	Ref.
12			1 M NaPF ₆ in PC	~1.6	70%, 20, 50 mA g ⁻¹	73-51, ^d 117, ^d n.d., 1.4	[328]
13			1 M NaClO ₄ in EC/DMC (v/v 1:1)	~2.0	76%, 100, C/10 (19 mA g ⁻¹)	204-155, ^e 65, ^e 99, 1.0-1.8	[329]
Organic electrode materials with high specific capacity							
14		Na	1 M NaPF ₆ in EC/PC (v/v 1:1)	1.0	100%, ^b 1024, 50 mA g ⁻¹	500, 500, ~100, 1.0	[330]
15		Na	1 M NaClO ₄ in EC/DMC (v/v 1:1)	~1	95%, 500, 100 mA g ⁻¹ 97%, 2600, 1 A g ⁻¹	320, 320, ~100, 0.7 218-258, 250, ~100, 0.7	[331]
16		Na	1 M NaClO ₄ in EC/DMC (v/v 1:1)	~0.9	82%, 100, 100 mA g ⁻¹ 99%, 10 000, 5 A g ⁻¹	420, 378, ~100, n.d. 198, 178, ~100, n.d.	[332]
17		Na	1 M NaClO ₄ in EC/DMC/FEC	1.3	66%, 250, 500 mA g ⁻¹	567, 737, ~100, 1.0	[333]
Organic electrode materials with high stability							
18		Na	1 M NaClO ₄ in EC/PC/FEC	2.1	90%, 1 000, 10 C	90-80, 189, ~100, 0.7	[338]
19		Na	1 M NaPF ₆ in EC/DMC (v/v 1:1) 1 M NaPF ₆ in EC/DMC (v/v 1:1)	~2.2	87.5%, 5 000, 0.8 C (200 mA g ⁻¹) 100%, 1000, 1 A g ⁻¹	111, 285, ~100, n.d. 100, 220, ~100, 0.8	[339] [340]
20		Na	1 M NaPF ₆ in EC/DMC (v/v 1:1)	~2.1	97%, 1 000, 1 A g ⁻¹	95, 200, ~100, 0.8	[340]
21		Na	1 M NaPF ₆ in EC/DMC (v/v 1:1)	~2.1	93%, 1 000, 1 A g ⁻¹	82, 172, ~100, 0.8	[340]

Table 3. continued

#	Positive electrode (or "cathode") active material	Negative electrode (or "anode") active material	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh g ⁻¹) and Specific energy (Wh kg ⁻¹) per mass of positive active material if not specified otherwise, Final coulombic efficiency, Loading (mg cm ⁻²)	Ref.
22		Na	0.1 M NaPF ₆ in DME/DOL (v/v 1:1)	1.6	84%, 1 000, 0.5 C	157-132, 251, ~100, 2.0	[341]
23		Na	1 M NaPF ₆ in DME	1.8	90%, 1 000, 1 A g ⁻¹	104-94, 187, ~100, 1.8-2	[342]
24		Na	1 M NaPF ₆ in DME	1.6	88%, 10 000, 514 C (50 A g ⁻¹)	110, 176, ~100, 1.0	[334]
25		Na	1 M NaPF ₆ in DEG/DME	1.25	81%, 1 000, 10 C 85%, 2 000, 20 C	140-113, 175, ~100, 1.5 115-98, 144, ~100, 1.5	[335]
26		Na	1 M NaBF ₄ in TEG/DME	-0.5	75%, 1 500, 10 C	100, 50, ~100, 2.0-2.5	[336]
27		Na	1 M NaClO ₄ in PC	-2.6	80%, 7 000, 1 A g ⁻¹	~90, 234, ~100, ~1.5	[337]
28		Na	1 M NaClO ₄ in EC/DEC (v/v 1:1)	~1.25	~100%, ^f 1 000, 5 A g ⁻¹	107, 134, ~100, n.d.	[343]
29		Na	1 M NaClO ₄ in EC/DEC (v/v 1:1)	~1	83%, ^b 1 000, 5 A g ⁻¹	89, 89, ~100, n.d.	[343]
30		Na	1 M NaPF ₆ in DME	1.65	86%, ^f 1 000, 0.56 C (100 mA g ⁻¹) 95%, ^f 1 400, 5.6 C (1 A g ⁻¹)	177-145, 292, ~100, n.d. 128-121, 211, ~100, n.d.	[344]

^aBased on cathode material weight. ^bThe first cycle is not taken into account. ^cBased on anode material weight. ^dBased on cathode and anode.

1881 cycling stability will be presented in the subsequent section
1882 (Table 3).

1883 6.1. High/Low Voltage Organic Electrode Materials and Hybrid/All-Organic High Output Voltage Na-Ion Batteries

1884 The design of high and low voltage OEMs for SIBs has clearly
1885 taken inspiration from the lithium equivalents. "p-type"
1886 materials (*i.e.*, anion insertion materials) are hence the most
1887 common compounds able to react at potential >3.0 V vs Na⁺/
1888 Na, while materials reacting at low potential <1.5 V vs Na⁺/Na
1889 belong to "n-type" (*i.e.*, cation insertion materials). Conductive
1890 polymers are an example of a type of material which could

1891 belong to any or both of these categories. Early research on
1892 conductive polymers for SIBs has been carried out by Yang's
1893 group, who used polyaniline derivatives (p-type),³⁰³ doped
1894 PPY^{304,305} (p-type), or PT³⁰⁶ (n-type) in some of the first
1895 articles in this field. Soon after, they reported the activity of
1896 polytriphenylamine (PTPAN, Table 3, entry 1) as p-type
1897 material with PF₆⁻ ingress.³⁰⁷ Each triphenylamine unit can
1898 lose one electron and intercalate one anion upon oxidation at
1899 an average redox potential of 3.6 V vs Na⁺/Na forming then
1900 quinoneimine units (Figure 13A). PTPAN displays stable
1901 reversible capacity even at high C-rate with 88 mAh g⁻¹ at a

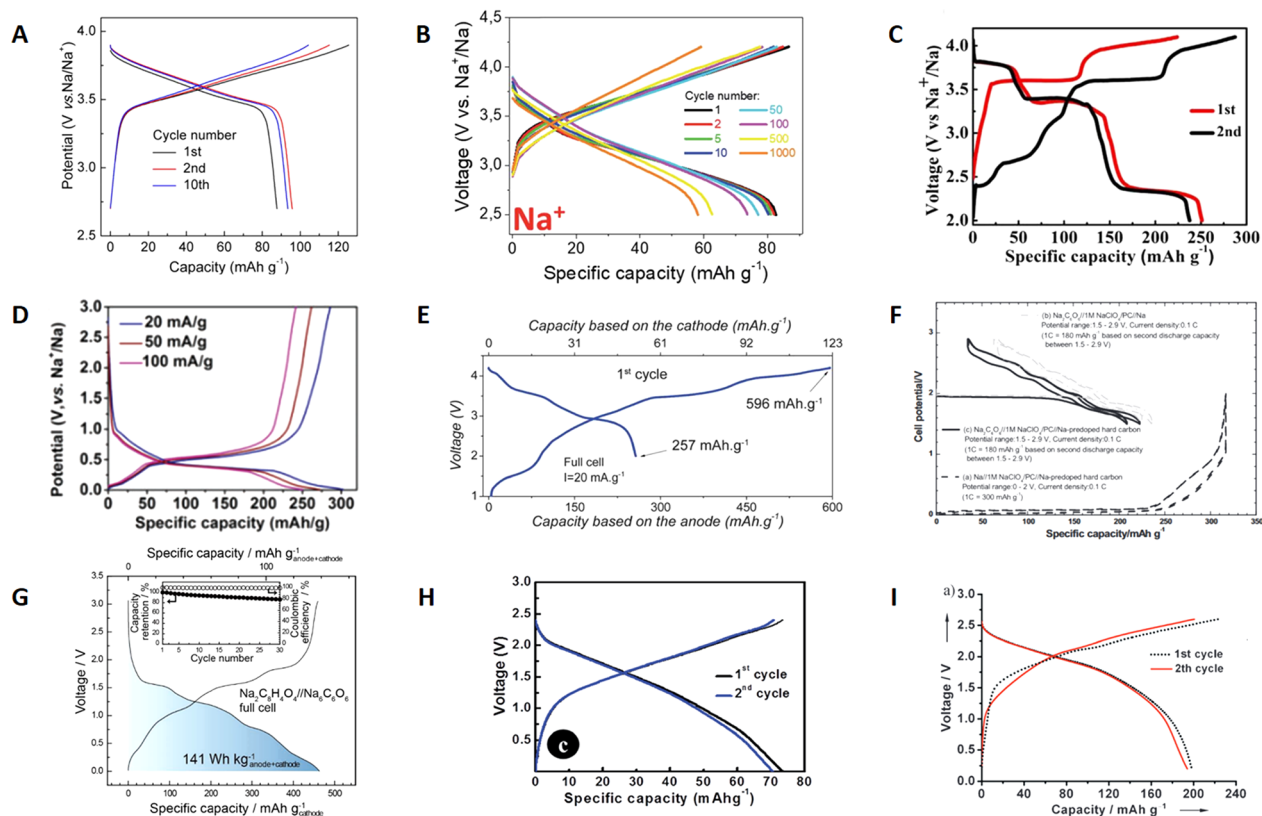


Figure 13. Voltage profiles of selected OEMs measured vs Na and all-organic Na-ion full cells including (A) PTPAn (reproduced from ref 307), (B) PDPPD (reproduced with permission from ref 308. Copyright 2019 The Royal Society of Chemistry), (C) CuTCNQ (reproduced with permission from ref 309. Copyright 2017 John Wiley & Sons, Inc.), (D) Co-bpdc (reproduced with permission from ref 317. Copyright 2018 The Royal Society of Chemistry), (E) $\text{Na}_{0.75}\text{Mn}_{0.70}\text{Ni}_{0.23}\text{O}_2//\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$ (from ref 296. Copyright 2012 Royal Society of Chemistry), (F) $\text{Na}_2\text{C}_6\text{O}_6//\text{Na}$ predoped carbon (reproduced with permission from ref 326. Copyright 2013 Elsevier Ltd.), (G) $\text{Na}_2\text{C}_6\text{O}_6//\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$ (reproduced with permission from ref 327. Copyright 2017 Nature Publishing Group), (H) $\text{PI}//\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$ (reproduced with permission from ref 328. Copyright 2015 The Royal Society of Chemistry), and (I) $\text{Na}_4\text{C}_8\text{H}_2\text{O}_6//\text{Na}_4\text{C}_8\text{H}_2\text{O}_6$ (reproduced with permission from ref 329. Copyright 2014 John Wiley & Sons, Inc.).

1902 current of 20 C and 97% capacity retention over 200 cycles
 1903 when cycled at a current of 5 C. This material has also been
 1904 cycled in dual-ion cell configuration paired with poly-
 1905 (anthraquinoyl sulfide) (PAQS, Table 3, entry 2), an n-type
 1906 material. This cell has an average voltage of 1.8 V and exhibits
 1907 surprisingly high rate capability with 118 mAh g^{-1} reversible
 1908 capacity (anode limitation design) at 32 C rate. At a rate of
 1909 8 C, the cell displays 85% capacity retention over 500 cycles.
 1910 Poly(*N,N'*-diphenyl-*p*-phenylenediamine) (PDPPD, Table 3,
 1911 entry 3) can be seen as another p-type derivative of polyaniline
 1912 and can be used in lithium, sodium, or potassium batteries.³⁰⁸
 1913 At an average redox potential of 3.38 V vs Na^+/Na , its initial
 1914 capacity is 94 mAh g^{-1} and sustains 76% of this value after
 1915 500 cycles at a 1 C rate (Figure 13B). But the most striking
 1916 performance of this polymer is certainly its ability to deliver
 1917 capacity at current as high as 1000 C. At a current rate of 1, 10,
 1918 50, or 100 C, the capacity losses are reasonable after 1000
 1919 cycles.³⁰⁸

1920 Metal organic compounds can also be used as positive
 1921 electrode materials for SIBs. One such example is CuTCNQ
 1922 (Table 3, entry 4).^{309,310} In its original redox state, CuTCNQ
 1923 is a salt formed of cuprous ions (Cu^+) and TNCQ^- anion. Three
 1924 redox stages could be obtained from this material at ca. 2.5, 3.4,
 1925 and 3.9 V vs Na^+/Na , corresponding to $\text{TNCQ}^{2-}/\text{TNCQ}^-$,
 1926 $\text{TNCQ}^-/\text{TNCQ}^0$, and Cu^+/Cu , respectively (Figure 13C).
 1927 When nanostructured as flower-like nanorods anchored on 1-D

1928 carbon nanofibers (CNFs), CuTCNQ/CNFs composite
 1929 displays reversible capacity of 137 mAh g^{-1} with 85% capacity
 1930 retention after 300 cycles at a rate of 300 mA g^{-1} using the
 1931 3 redox couples. If restricted to a cutoff voltage of 2.5–4.1 V vs
 1932 Na^+/Na which corresponds to $\text{TNCQ}^-/\text{TNCQ}^0$ and Cu^+/Cu^0
 1933 redox couples, the cell exhibits a capacity retention of 78%
 1934 after 1200 cycles for an average redox potential of 3.6 V vs
 1935 Na^+/Na . But in this case, the high redox potential is shifted
 1936 up due to the contribution of a metal center, unlike p-type
 1937 OEMs.

1938 For low potential OEMs for SIBs, carboxylates (e.g.,
 1939 disodium terephthalate, disodium naphthalene dicarboxy-
 1940 late,³¹¹ disodium pyridine-2,5-dicarboxylate,³¹² disodium 4,4'-
 1941 biphenyldicarboxylate,³¹³ and so on) or Schiff bases^{314–316}
 1942 have already been covered in recent reviews.^{16,40,41,302} The
 1943 only recent example that will be covered here is the case of a
 1944 metal organic framework (MOF) made of cobalt and 4,4'-
 1945 biphenyldicarboxylate ligands (Co-bpdc, Table 3, entry 5).³¹⁷
 1946 According to the authors, the cobalt ions do not undergo
 1947 reduction during the electrochemical process, leaving the redox
 1948 activity to the sole organic moiety. The reversible sodium
 1949 insertion/deinsertion occurs at an average potential of 0.5 V vs
 1950 Na^+/Na and exhibits stable capacity of ca. 300 mAh g^{-1} with 90%
 1951 capacity retention for 50 cycles at 20 mA g^{-1} or 264 mAh g^{-1}
 1952 and 79% capacity retention for 1000 cycles at 100 mA g^{-1}
 1953 (Figure 13D).

1954 The interest for low potential OEMs for SIBs started to rise
1955 when poor long-term stability or safety issues were reported
1956 with classical inorganic materials or soft/hard carbons, while
1957 positive inorganic electrodes gave promising results.^{173,318–322}
1958 The larger ion diffusion pathways in OEMs are believed to be
1959 appropriate for the large sodium ions (as compared to lithium
1960 ions) while more constrained ion diffusion pathways in inor-
1961 ganic materials might be too restricted for sodium intercalation
1962 at low potentials.³²³ Ideally, a good compromise could be
1963 found with hybrid organic/inorganic sodium-ion batteries
1964 using inorganic materials as the positive electrode and OEMs
1965 as the negative electrode. One early example is the full sodium-
1966 ion cell made of disodium terephthalate as negative elec-
1967 trode and $\text{Na}_{0.75}\text{Mn}_{0.70}\text{Ni}_{0.23}\text{O}_2$ as positive electrode (Table 3,
1968 entry 6).²⁹⁶ With 3.6 V as output voltage, this cell delivers
1969 257 mAh g^{-1} initial capacity (anode limitation design) with
1970 limited capacity loss after 50 cycles (93% capacity retention,
1971 Figure 13E). Interestingly, its stability is better for this full cell
1972 rather than the two half-cells using both electrodes and
1973 metallic sodium as counter electrode. However, this better
1974 stability for a hybrid organic/inorganic sodium-ion full cell is
1975 not systematic. In the case of a $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}/\text{rGO}$ /
1976 disodium naphthalene-2,6-dicarboxylate cell with an average
1977 redox potential of 3.3 V vs Na^+/Na , a severe capacity decay is
1978 noticeable after merely 20 cycles (Table 3, entry 7), while the
1979 half-cells display a better capacity retention.³²⁴ Other examples
1980 with acceptable stability include $\text{Na}_4\text{Fe}(\text{CN})_6$ /poly 1,4,5,8-
1981 naphthalenetetracarboxylic dianhydride (PNTCD) and Na_3V -
1982 $(\text{PO}_4)_3$ /PNTCD.³²⁵ However, like most diimide compounds,
1983 the average redox potential of PNTCD is 2.1 V vs Na^+/Na ,
1984 which considerably restricts the average output voltage of the
1985 full cells to 1.2 V (Table 3, entry 8, 9).
1986 Examples of a hybrid organic/inorganic sodium-ion full cell
1987 using an OEM as the positive electrode are scarcer. One of the
1988 few cases is disodium rhodizonate which was cycled vs Na-
1989 predoped hard carbon with improved cyclability as compared to
1990 cycling vs metallic sodium (Table 3, entry 10 and Figure 13F).³²⁶
1991 Comparably to its lithium counterpart, disodium rhodizonate
1992 is able to reversibly intercalate four sodium ions (Table 3,
1993 entry 11).³²⁷ When nanosized, it delivers up to 484 mAh g^{-1}
1994 with several electrochemical features corresponding to the
1995 different sodium ion insertions. Disodium rhodizonate can also
1996 be cycled in a hybrid organic/inorganic full cell vs phosphorus
1997 encapsulated in a carbon scaffold (P@C) or in an all-organic
1998 configuration vs disodium terephthalate (Figure 13G).
1999 All-organic Na-ion batteries is an attractive concept without
2000 sensitive metals (price, rarity, geopolitics) such as cobalt, nickel,
2001 or lithium. But merely some examples have been reported in the
2002 literature. In addition to previously mentioned cases (Table 3,
2003 entries 2 and 11), a cell using N,N' -diamino-3,4,9,10-
2004 perylenetetracarboxylic polyimide (PI) as the positive elec-
2005 trode and disodium terephthalate as the negative electrode has
2006 been described (Table 3, entry 12, Figure 13H).³²⁸ The
2007 limited output voltage of 1.6 V is here also connected to the
2008 choice of a polyimide whose average redox potential is 2.2 V vs
2009 Na^+/Na .
2010 There is still to date only one example of an all-organic
2011 rocking chair sodium-ion battery published by Chen's group
2012 (Table 3, entry 13 and Figure 13I).³²⁹ The tetrasodium salt of
2013 2,5-dihydroxyterephthalic acid (Na_4DHTPA or $\text{Na}_4\text{-}p\text{-DHT}$) is
2014 used in the same time as both positive and negative electrodes
2015 in a symmetrical cell as previously demonstrated in the case of
2016 the lithium chemistry.²⁵¹ With 2 V as output voltage, this cell is

hampered by the irreversible capacity of the negative electrode
and displays reversible capacity of 198 mAh g^{-1} with 76%
capacity retention after 100 cycles at a rate of C/10.

6.2. Organic Electrode Materials with High Specific Capacity

All materials selected in this section are able to deliver more
than 300 mAh g^{-1} over tens of cycles without conductive
additive contribution. Interestingly, besides the previously
mentioned disodium rhodizonate, many other high-capacity
materials for SIBs involve the intercalation of sodium ions onto
unsaturated carbons, as a sodium equivalent of the mechanism
coined as "superlithiation" (see section 7.3), which will be
thoroughly covered in the section 7.3.^{21,260} Consequently, their
electrochemical features display similarities such as the
requirement for large polarization values, sloping curves, and
poor round trip efficiency. A first example is polydopamine
(PDA, Table 3, entry 14) employed as both electrode and
redox-active binder material, obtained as a mixture of *ortho*-
catechol and *ortho*-quinone.³³⁰ After a first cycle with low
Coulombic efficiency which could be explained by the solid
electrolyte interface (SEI) formation and proton/sodium exchange
in the catechol moieties, it shows an impressive stable capacity of
500 mAh g^{-1} with no obvious capacity loss over 1024 cycles.

The group of Zhouguang Lu has investigated several
derivatives of tri- β -ketoenamine linked compounds, either as a
single molecule or as covalent organic frameworks (COF).^{331,332}
If cycled at low potential vs Na^+/Na , after the expected
reduction of carbonyls from the anthraquinone moieties, the
enolization of carbonyls of the tri- β -ketoenamine generates a
triradical. The storage of three additional sodium ions is
allowed by the reduction of the carbon backbone. Surprisingly,
neither the triradical intermediate nor the organosodium
species display major stability issues. In the case of TSAQ
(Table 3, entry 15), the electrodes show a highly reversible
capacity of 320 mAh g^{-1} with capacity retention higher than
95% after 50 cycles at a current density of 100 mA g^{-1} .³³¹
When cycled at a current 10 times higher, a capacity above
220 mAh g^{-1} is sustained for 2600 cycles (Figure 14A). For
DAAQ-COF (Table 3, entry 16), which can be seen as a
COF derivative of TSAQ, the specific capacities are highly
dependent on the particle size, even if this parameter does not
seem to hamper the stability. The best performances are
obtained with 4–12 nm particles that can sustain specific
capacity above 400 mAh g^{-1} for 100 cycles. More impressively,
when cycled at a current as high as 5 A g^{-1} , ca. 200 mAh g^{-1}
are maintained for 10 000 cycles (Figure 14B).

As an alternative to carboxylates such as disodium terephthalate, their sulfur derivatives thiocarboxylates have been investigated, where either one or two of the oxygen atoms of the carboxylate function are replaced by sulfur atom in this series of analogues.³³³ The best performances are obtained with the compound Table 3, entry 17 with capacity as high as 567 mAh g^{-1} at a current density of 50 mAh g^{-1} and limited capacity loss after 250 cycles. Considering this compound has a larger molecular weight as compared to disodium terephthalate, its theoretical capacity per exchanged electron is lower (97.7 mAh g^{-1} against 127.5 mAh g^{-1}). However, while disodium terephthalate is limited to two electrons exchanged, compound 17 can accommodate up to 6 electrons with partial reversible reduction of its benzene ring through the "supersodiation" process (similar to "superlithiation", see section 7.3).

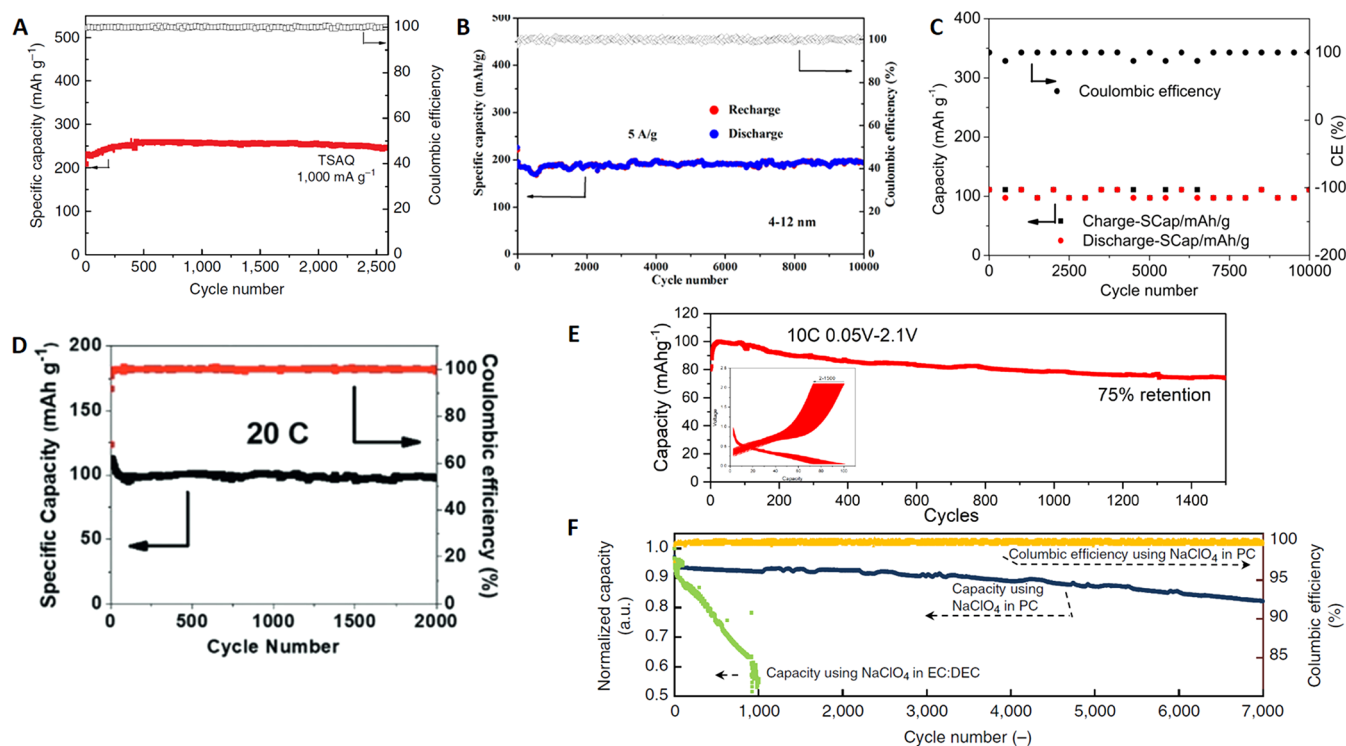


Figure 14. Capacity retention of selected OEMs measured vs Na including (A) TSAQ (reproduced from ref 331), (B) DAAQ-COF (reproduced with permission from ref 332. Copyright 2019 American Chemical Society), (C) PPTS (reproduced with permission from ref 334. Copyright 2018 Elsevier Ltd.), (D) ADASS (reproduced with permission from ref 335. Copyright 2018 John Wiley & Sons, Inc.), (E) Na₃C₉H₃O₆ (reproduced with permission from ref 336. Copyright 2018 John Wiley & Sons, Inc.), and (F) BPOE (reproduced from ref 337).

6.3. Organic Electrode Materials with Long Cycle Life

In general, poorer stabilities are observed for SIBs as compared to LIBs due to SEI layer compounds dissolution in the electrolyte system, to the very unstable metallic sodium for the half-cell configurations (dendrites formation), or to Na_xC formed from sodium intercalation into the conductive additive at low potential. Achieving 1000 cycles or more for SIBs without severe capacity loss is hence a challenge. However, some OEMs are able to sustain high capacities for such long cycling. Some examples were previously commented (Table 3, entries 3, 4, 5, 14, 15, and 16).

As already seen, the average redox potential of polyimides is usually in the 2.1–2.2 V vs Na⁺/Na potential range. Consequently, they suffer less long-term instability due to extreme potential windows. Polyethylenediamine 1,4,5,8-naphthalenetetracarboxylic dianhydride (PEDA-NTCDA, Table 3, entry 18),³³⁸ polyethylenediamine 3,4,9,10-perylene-tetracarboxylic dianhydride (PEDA-PTCDA, Table 3, entry 19),^{339,340} polypropylenediamine 3,4,9,10-perylene-tetracarboxylic dianhydride (PPDA-PTCDA, Table 3, entry 20),³⁴⁰ and polyhexylenediamine 3,4,9,10-perylene-tetracarboxylic dianhydride (PHDA-PTCDA, Table 3, entry 21)³⁴⁰ have all been cycled for at least 1000 cycles with negligible capacity loss. Especially, PEDA-PTCDA retained 87.5% of its initial capacity after 5000 cycles (Figure 14C).³³⁹

Anthraquinones reversibly insert sodium at average redox potential slightly lower as compared to polyimides (*i.e.*, 1.6–1.8 V vs Na⁺/Na), limiting also the risk of side reactions. Anthraquinones as polymers (PAQS, Table 3, entry 22)³⁴¹ or as salts (disodium 9,10-anthraquinone-2,6-disulfonate, Na₂AQ26DS, Table 3, entry 23)³⁴² have been successfully cycled for 1000 cycles. An anthraquinone derivative,

poly(pentacenetetrone sulfide) (PPTS, Table 3, entry 24) exhibits a remarkable stability at a very high rate of 50 A g⁻¹ corresponding to a full charge in 7 s. After 10 000 cycles, it still maintains 97 mAh g⁻¹ (Figure 14C).

Azobenzene-4,4'-dicarboxylic acid sodium salt (ADASS, Table 3, entry 25) is a material that can reversibly insert two sodium ions on its azo (–N=N–) function at an average redox potential of 1.25 V vs Na⁺/Na.³³⁵ It can be cycled at a high current of 10 or 20 C for 1000 and 2000 cycles, respectively, with moderate capacity losses (Figure 14D). The average redox potential of sodium carboxylates is rather low (usually in the 0.3–0.8 V range vs Na⁺/Na) which makes side reaction likely to occur during long time cycling. Still, the group of Palani Balaya succeeded to cycle trisodium-1,3,5-benzene tricarboxylate (Table 3, entry 26) for 1500 cycles at a rate of 10 C with 75% capacity retention with a lower cutoff potential of 50 mV (Figure 14E).³³⁶

Several covalent organic frameworks (COFs) have shown excellent cyclability. An early example from the literature is a p-type material (Table 3, entry 27) that reversibly inserts anion (ClO₄⁻) at an average potential of 2.6 V vs Na⁺/Na and sustains 80% of its capacity after 7000 cycles at a rate of 1 A g⁻¹ (Figure 14F).³³⁷ Other triazine-based COFs have been used as n-type materials with the integration of carbonyl-containing moieties (Table 3, entry 28, 29).³⁴³ After a stabilization period corresponding to 30 cycles, they sustain most of their capacities over 1000 cycles at a high rate of 5 A g⁻¹. In addition to the previously mentioned tri-β-ketoenamine derivatives, which have already shown excellent stability (Table 3, entry 15, 16), the pentacenetetrone derivative 30 is able to maintain 95% of its capacity after 1400 cycles at a rate of 1 A g⁻¹.

Table 4. Performances of Selected Nonaqueous K–Organic Batteries

#	Positive electrode (or “cathode”) active material	Negative electrode (or “anode”) active material	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh g ⁻¹) and Specific energy (Wh kg ⁻¹) per mass of positive active material if not specified otherwise, Final coulombic efficiency, Loading (mg cm ⁻²)	Ref.
1		K	1 M KPF ₆ in DME	0.6	95%, ^a 500, 1 A g ⁻¹	194, 116, ~100, 1.2-1.6	[346]
2		K	1 M KPF ₆ in DME	1.7	74%, 3 000, 24 C (5 A g ⁻¹)	258, 439, 99, 1.0-2.0	[347]
3			1 M KPF ₆ in DME	~1.1	66%, 100, 100 mA g ⁻¹	254, ^b 122, ^b 99, 1.0-2.0	[347]
4			1.25 M KPF ₆ in DME	~1.25	n.d., 10, 25 mA g ⁻¹	~28, ^b 35 ^b n.d., 1.5-2.0	[348]
5		K	1 M KPF ₆ in PC/FEC (v/v 98:2)	4.05	86%, 100, 50 mA g ⁻¹ 55%, 500, 2 A g ⁻¹	125, 487, 88, 2.0 85, 351, 88, 2.0	[349]
6		K	0.5 M KPF ₆ in EC/DEC (v/v 1:1)	3.52	63%, 1 000, 10 C	62-39, 218, n.d., 1.0-2.0	[308]
7		K	PMMA / 0.8 M KPF ₆ in EC/DEC/FEC (v/v/v 45:45:10)	3.15	98%, 100, 50 mA g ⁻¹	125, 394, n.d., 3.0	[350]

^aThe first cycle is not taken into account. ^bBased on cathode material weight.

To sum up, the development of organic SIBs has gained remarkably increased attention since 2012 and is considered an interesting alternative to organic LIBs making the development of cationic rocking-chair batteries made of abundant elements possible. Although great achievements have been made, many challenges still remain to tackle problems such as capacity fading or low energy density. Polymerization, metal/covalent organic frameworks, or insoluble salts are successful strategies to suppress the former, and very long cycling batteries have been reported without structural instability. As compared to their inorganic counterparts, promising results have been obtained for negative electrodes as an alternative to metallic sodium, graphite, or even hard/soft carbons. Improving the energy density is more complex and requires advanced electrode design in order to suppress as much conductive additive as possible. Nevertheless, the combination of renewable organic materials together with the high abundance of sodium raw materials provides an appealing concept, which is enough for encouraging continuous progress, and research in this field should certainly be esteemed.

7. PERFORMANCES OF OTHER NONAQUEOUS ORGANIC BATTERIES

2160

7.1. Performances of Nonaqueous Potassium–Organic Batteries

2161

Surprisingly, despite the natural abundance of potassium, its relative low-cost, and the low electrochemical potential of K⁺/K (−2.94 V vs SHE), K–ion batteries (KIBs) have not been thoroughly investigated until recently,³⁴⁵ with the motivation

being related to its abundance like Na compared to Li. One scientific reason is the large 1.38 Å ionic radius of K⁺ (0.76 Å for Li⁺, 1.02 Å for Na⁺), which makes a challenge the design of inorganic materials able to reversibly insert such large ions into a rigid and constrained framework. Considering their larger interlayer spacing and flexible framework, OEMs for KIBs have then attracted the attention of researchers in parallel with the early development of their inorganic counterparts and not years or decades later unlike LIBs or SIBs. The research on OEMs for KIBs has clearly taken advantage of the years of development of OEMs for LIBs and SIBs and organic templates, which have been proven successful in these devices, have been adapted for KIBs, swapping from lithium or sodium salt to potassium salts when necessary.

One such example is the dipotassium terephthalate (Table 4, entry 1) which intercalates/deintercalates potassium ion at an average potential of 0.6 V vs K⁺/K with a well-defined plateau after the first cycle.³⁴⁶ It exhibits reversible capacity up to 249 mAh g⁻¹, and good capacity retention of 95% over 500 cycles is obtained when cycled at a rate of 1000 mA g⁻¹ (Figure 15A). Quinone derivatives have already displayed their robustness in other EES devices. Poly(pentacenetrone sulfide) (PPTS, Table 4, entry 2) can be cycled for 3000 cycles at a rate of 5 A g⁻¹ with limited capacity decay (Figure 15B).³⁴⁷ Interestingly, at such a high rate, the Coulombic efficiency is much higher as compared to cycling at a rate of 0.1 A/g (~99% against ~90%), which is due to the highly reactive metallic potassium counter electrode and dendrite formation according to the authors.

These two materials have been cycled in an all-organic full cell (thereby without metallic potassium) which delivers 254 mAh g⁻¹

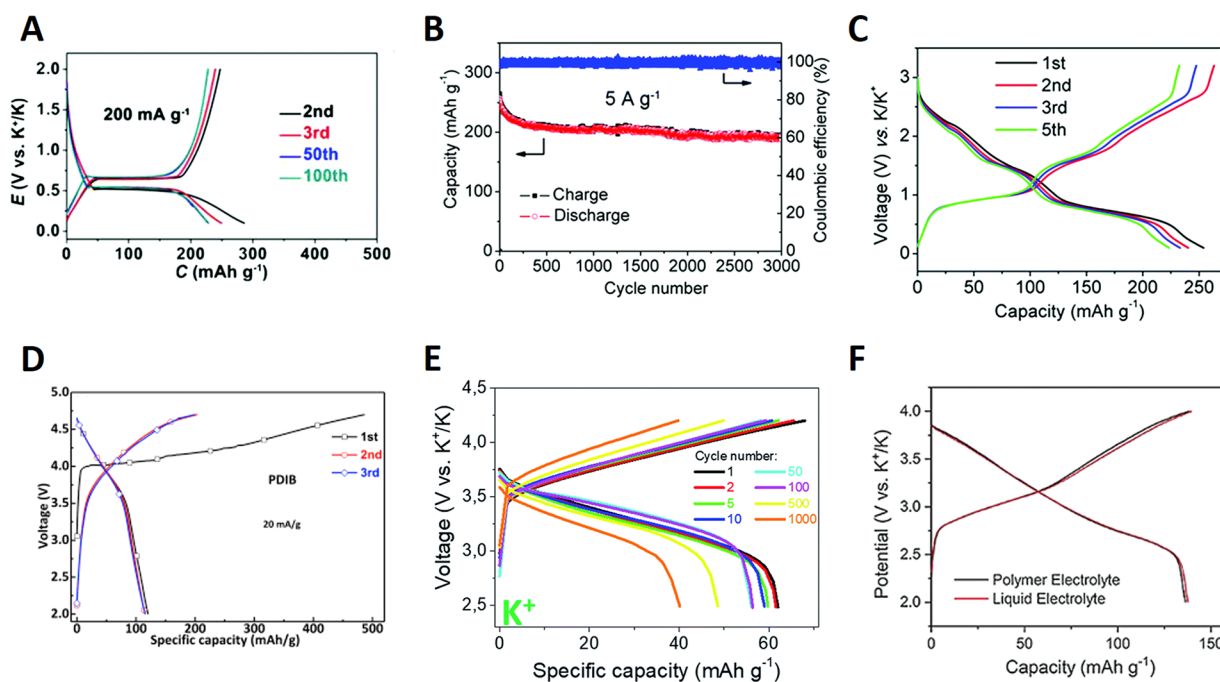


Figure 15. Voltage profiles or capacity retention of selected OEMs measured vs K including (A) $\text{K}_2\text{C}_8\text{H}_4\text{O}_4$ (reproduced with permission from ref 346. Copyright 2017 The Royal Society of Chemistry), (B) PPTS (reproduced with permission from ref 347. Copyright 2019 The Royal Society of Chemistry), (C) PPTS// $\text{K}_2\text{C}_8\text{H}_4\text{O}_4$ (reproduced with permission from ref 347. Copyright 2019 The Royal Society of Chemistry), (D) PVK (reproduced with permission from ref 349. Copyright 2019 Elsevier Ltd.), (E) PDPPD (reproduced with permission from ref 308. Copyright 2019 The Royal Society of Chemistry), and (F) PANi (reproduced with permission from ref 350. Copyright 2018 John Wiley and Sons).

2196 initial capacity and 66% capacity retention after 100 cycles with
 2197 an average Coulombic efficiency of 99% (Table 4, entry 3,
 2198 Figure 15 C). Another example of an all-organic full cell has
 2199 been realized by Chen's group using dipotassium rhodizonate as
 2200 the positive electrode of tetrapotassium salt of tetrahydroxyquinone
 2201 as the negative electrode (Table 4, entry 4).³⁴⁸ Unfortunately,
 2202 this cell displays very limited stability.

2203 Materials with an average redox potential above 3.0 V vs
 2204 K^+/K all belong to the p-type class and hence insert anions instead
 2205 of potassium ions (dual-ion cell configuration, Figure 9b-3).
 2206 The highest redox voltage for an organic KIB to date has been
 2207 obtained using poly(*N*-vinylcabazole) (PVK) which can insert
 2208 PF_6^- at an average redox potential of 4.05 V vs K^+/K but with
 2209 poor Coulombic efficiency (Figure 15D).³⁴⁹ Other remarkable
 2210 performances have been obtained with PDPPD (3.52 V vs
 2211 K^+/K , Figure 15E)³⁰⁸ and polyaniline (PANi, 3.15 V vs K^+/K ,
 2212 Figure 15F).³⁵⁰

2213 In short, the research on KIBs is still in its infancy after starting
 2214 to bloom in 2015 for inorganic electrode materials and 2016 for
 2215 OEMs. One major challenge is the replacement of metallic potas-
 2216 sium with a more stable negative electrode. But this has not pre-
 2217 vented the development of long-term cycling batteries with more
 2218 than 1000 cycles (Table 4, entries 2 and 6; see also refs 351–356).

2219 7.2. Nonaqueous Multivalent Metal–Organic Batteries (Mg, Al, Zn)

2220 Among the investigated post-LIB systems, rechargeable batte-
 2221 ries based on multivalent metal-ion shuttling (including Mg^{2+} ,
 2222 Ca^{2+} , Al^{3+} , Zn^{2+}) are expected to offer significant improvement
 2223 in volumetric energy density simply by using the corresponding
 2224 metal as the negative electrode material (e.g., $\approx 3833 \text{ mAh cm}^{-3}$
 2225 theoretical volumetric energy density for Mg compared to
 2226 $\sim 2046 \text{ mAh cm}^{-3}$ for Li metal). In addition, the abundance of
 2227 such elements is not critical (2.5% of the earth's crust for Mg

2228 against 0.0017% for Li).^{357,358} The current status is that few
 2229 regular host inorganic electrode compounds, based on which
 2230 Li-ion batteries are established, are able to deliver reasonable
 2231 electrode performance for storing multivalent metal-ions. For
 2232 Mg batteries, the flagship multivalent-metal batteries, Chevrel
 2233 phase Mo_6X_8 (X = S, Se), continue to be the only reliable
 2234 positive electrode materials despite the limited specific energy
 2235 of the Mo_6X_8 –Mg systems (up to 140 Wh kg^{-1}).^{359,360} Recent
 2236 discoveries of spinel Ti_2S_4 and sulfur as Mg positive electrode
 2237 materials in conjunction with the continuous development of
 2238 non-nucleophilic chloride-free electrolytes greatly expanded
 2239 the technology, but sluggish kinetics remain and stability issues
 2240 are real.^{361,362} This is where OEMs start to look interesting:
 2241 some OEMs have been reported to show adequate kinetics
 2242 even at room temperature and deliver higher specific energies
 2243 than those achieved by inorganic intercalation compounds at
 2244 elevated temperatures. Due to these early successes, OEMs are
 2245 now regarded by some as a wild card to enable multivalent-
 2246 metal batteries.^{48,358,363} The properties and cell performance of
 2247 these materials are summarized for comprehensive comparison
 2248 (Table 5).

2249 The promises aside, it is necessary to emphasize that
 2250 multivalent chemistries are more complicated than monovalent
 2251 ones, and the ion storage mechanism has not received enough
 2252 scrutiny for many OEMs. For example, Mg^{2+} is noto-
 2253 riously difficult to be dissociated from electrolyte solution
 2254 species such as Cl^- and ethereal solvent molecules.^{364,365}
 2255 While most studies on Mg–organic batteries employed
 2256 Cl^- -containing electrolytes, a very recent study showed that
 2257 probably all n-type OEMs store MgCl^+ instead of the presumed
 2258 Mg^{2+} in these electrolytes.³⁶⁶ This unintended storage mechanism
 2259 would effectively make most Mg–organic batteries hybrid
 2260 batteries, that is, the charge carrier ions at the positive and
 2261 negative electrodes are different, and the electrolyte solution

Table 5. Performances of Selected Nonaqueous Multivalent Metal–Organic^e

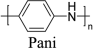
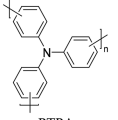
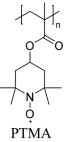
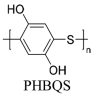
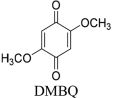
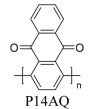
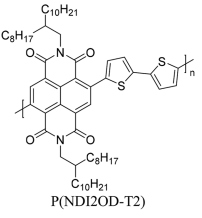
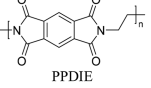

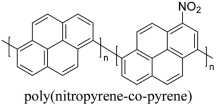
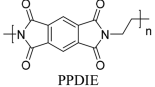
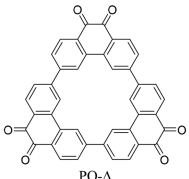
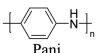
#	Cell configuration (ionic carriers)	Positive electrode (or “cathode”) active material	Negative electrode (or “anode”) active material	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh g ⁻¹) per mass of positive active material if not specified otherwise and Specific energy (Wh kg ⁻¹) per mass of the two active materials plus anions involved in the electrode reactions, Final coulombic efficiency, Loading (mg cm ⁻²)	Ref.
1	N/A ^a	 Pani	(Pt)	0.025 M MgSO ₄ in EMIES	2.09	53%, 60, 667 mA h g ⁻¹	116, N/A	[367]
2	Mg ²⁺ , ClO ₄ ⁻	 PTPA	AC	1 M Mg(ClO ₄) ₂ in AN	3.2	N/A	N/A	[368]
3	Mg ²⁺ , TFSI ⁻	 PTMA	Mg	0.3 M Mg(TFSI) ₂ in G1/G2	~2.3	N/A	38, 62	[369]
4	N/A ^b	carbyne polysulfide	Mg	0.25 M Mg(AlCl ₂ EtBu) ₂ in THF	1.25	71%, 23, 5.4 mA g ⁻¹	328, N/A	[373]
5	N/A ^b	 PHBQS	Mg	0.16 M 3MgCl ₂ –2Mg(TFSI) ₂ in G4/DOL	1.8	^c	158, N/A	[371]
6	N/A ^b	 DMBQ	Mg	0.5 M Mg(ClO ₄) ₂ in GBL 0.5 M Mg(TFSI) ₂ –2 MgCl ₂ in DME	0.95 1.63	85%, 5, 260 mA g ⁻¹ 38%, 30, 0.2C	260, N/A 226, N/A	[374] [370]
7	Mg ²⁺	 P14AQ	Mg	0.2 M Mg(TFSI) ₂ in G2	1.36	72%, 100, 130 mA g ⁻¹	180, 227	[366]
8	Mg ²⁺	 P(NDI2OD-T2)	Mg	0.2 M Mg(TFSI) ₂ in G2	1.45	87%, 2 500, 300 mA g ⁻¹	54, 76	[366]
9	N/A ^b	 PPDIE	Mg	PhMgCl–AlCl ₃ in THF	1.2	89%, 200, 150 mA g ⁻¹	140, N/A	[282]
10	AlCl ₄ ⁻ , Al ³⁺	 polythiophene	Al	2EMImCl–3AlCl ₃	1.35	80%, 100, 16 mA g ⁻¹	88, 76	[375]
11	AlCl ₄ ⁻ , Al ³⁺	 poly(nitropyrene-co-pyrene)	Al	EMImCl–1.3AlCl ₃	1.75	76%, 1 000, 200 mA g ⁻¹	70, 85	[377]

Table 5. continued

#	Cell configuration (ionic carriers)	Positive electrode (or "cathode") active material	Negative electrode (or "anode") active material	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh g ⁻¹) per mass of positive active material if not specified otherwise and Specific energy (Wh kg ⁻¹) per mass of the two active materials plus anions involved in the electrode reactions, Final coulombic efficiency, Loading (mg cm ⁻²)	Ref.
12	N/A ^d	 PPDIE	Al	2EMImCl-3Al Cl ₃	0.5	75%, 100, 150 mA g ⁻¹	140, N/A	[282]
13	AlCl ₂ ⁺ , Al ³⁺	 PQ-Δ	Al	3EMImCl-4Al Cl ₃	1.39	59%, 5 000, 2 A g ⁻¹	94, 97	[380]
14	Zn ²⁺ , TFSI ⁻	 Pani	Zn	0.3 M Zn(TFSI) ₂ in PC	0.8	85%, 2 000, 1 C	154, 44	[376]

^aCould be either SO₄²⁻ or CH₃CH₂SO₃⁻. ^bCould be either Mg²⁺ or MgCl⁺. ^cOnly showed the initial "activation" cycles where capacity was increasing. ^dCould be either Al³⁺ or AlCl₂⁺ or AlCl₂⁺. ^eAbbreviations: EMIES = 1-ethyl-3-methylimidazolium ethyl sulfate; AN = acetonitrile; G1 = monoglyme; G2 = diglyme; G4 = tetraglyme; TFSI = bis(trifluoromethane)sulfonimide; DOL = dioxolane; THF = tetrahydrofuran; GBL = γ -lactone; EMIm = 1-ethyl-3-methylimidazolium; PC = propylene carbonate; DME = dimethoxyethane.

2262 must contain enough of the necessary ions to maintain charge
2263 balance. Cell specific capacity will be heavily limited by the
2264 weight of the electrolyte solution as a result. Since unambig-
2265 uous determination of the stored species in most previously
2266 reported Mg-organic batteries has been overlooked, it would
2267 be difficult to estimate the actual specific capacity of those
2268 systems. In fact, such negligence is not specific to Mg-organic
2269 batteries studies but Mg-ion storing positive electrode material
2270 research in general. In the future, this situation can be reverted
2271 by dedicated characterizations and rational selection of electro-
2272 lyte solutions. This section mainly concerns the apparent spe-
2273 cific capacity of OEMs and only discusses storage mechanism
2274 where sufficient experimental evidence of stored species is
2275 available.

2276 Similar to nonaqueous Li-organic batteries, the highest
2277 discharge potentials for Mg-organic batteries have been
2278 reported for p-type OEMs. Conductive polymer polyaniline
2279 (PAni), nitrogen-centered PTPA, and oxygen radical-centered
2280 PTMA all discharge at >2 V vs Mg²⁺/Mg, with PTPA showing
2281 the highest discharge potential at 3.2 V vs Mg²⁺/Mg.³⁶⁷⁻³⁶⁹
2282 Note that none of these materials were tested in electrolyte
2283 solutions where reversible Mg plating/stripping is possible.
2284 Among n-type OEMs, p-BQ-based molecule DMBQ and
2285 polymer poly(hydrobenzoquinonyl-benzoquinonyl sulfide)
2286 (PHBQS) show the highest discharge potentials of 1.63 and
2287 1.8 V vs Mg²⁺/Mg, respectively (Figure 16B, C).^{370,371} Other
2288 carbonyl compounds based on anthraquinone and imides
2289 discharge at lower potentials, as they also do in Li batteries.³⁷²
2290 As far as specific capacity is concerned, the organosulfur compound
2291 carbyne polysulfide shows the highest 328 mAh g⁻¹ (Figure 16A),
2292 with carbonyl compounds DMBQ (up to 260 mAh g⁻¹) and
2293 P14AQ (180 mAh g⁻¹) following (Figure 16C, D).^{366,373,374} The
2294 change of charge carrier ion from Li⁺ to Mg²⁺ does not seem to
2295 alter the cycling stability generally observed for Li⁺-storing polymer
2296 OEMs. P(NDI2OD-T2) and PPDIE lose 13% and 11% of their
2297 initial capacities after 2500 and 200 deep cycles, respectively, which
2298 stability is rarely seen from inorganic positive electrode materials

(Figure 16E).^{282,366} While these are quite some attractive numbers, 2299
there is no OEM that simultaneously shows high discharge 2300
potential, specific capacity, and cycling stability. There are also few 2301
OEMs that have been confirmed to store Mg²⁺ instead of complex 2302
ions. Therefore, there is a lot of opportunity lying ahead for 2303
developing better OEMs for Mg-organic batteries. 2304

OEMs for other nonaqueous multivalent metal-ions storage 2305
are quite rare. Most OEMs reported for multivalent-metal- 2306
organic batteries have been p-type materials where storage of 2307
anions rather than cations takes place (dual-ion cell configura- 2308
tion). Conductive polymers PT and PAni have been studied 2309
in Al and Zn batteries, respectively, showing decent to great 2310
cycling stability.^{375,376} Poly(nitropyrene-co-pyrene) shows the 2311
highest discharge potential for an Al-organic battery at 1.75 V 2312
with great 75% capacity retention after 1000 cycles.³⁷⁷ Note 2313
that for Al batteries, only graphite, also a p-type material in this 2314
case, shows viable performances despite limited specific 2315
capacity.^{378,379} OEMs are thus welcomed additions to the 2316
technology. More interestingly, very recent studies show that 2317
efficient storage of Al in n-type OEMs is also possible. 2318
Phenanthraquinone triangle PQ-Δ uniquely stores AlCl₂⁺ 2319
instead of AlCl₄⁻ which basically every other decent cathode 2320
stores, hence opening up a brand new design space for Al 2321
positive electrode materials (Figure 16F).³⁸⁰ PPDIE also seems 2322
to store cationic Al species considering it being an n-type 2323
material at the corresponding potential (0.5 V vs Al³⁺/Al), 2324
though more characterization would be needed to reveal the 2325
nature of the stored ions.²⁸² 2326

Overall, OEMs indeed look promising as unique enablers for 2327
the otherwise quite problematic multivalent-metal batteries, 2328
even though detailed studies regarding the ion storage mech- 2329
anism and performance improvement have only just begun. 2330

7.3. Comments on The Peculiar Multiple Cation Insertion Phenomenon in Organics

The electrochemical process coined as "superlithiation" 2332
corresponds to a two-electron reduction of a carbon-carbon 2333

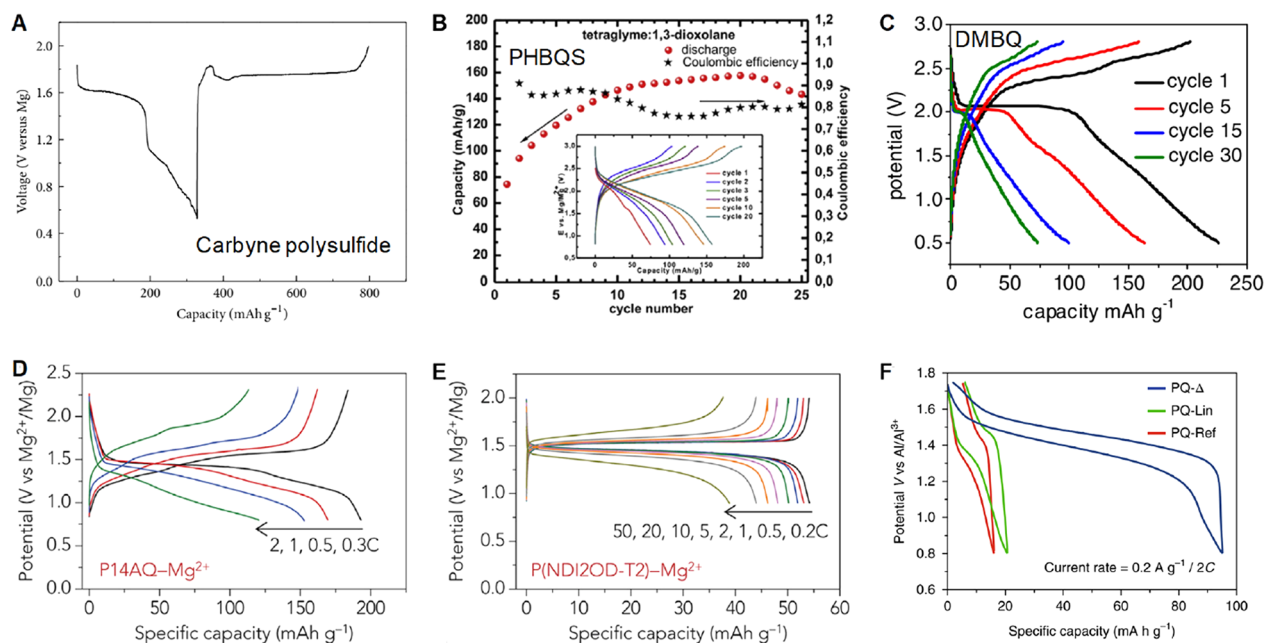


Figure 16. Voltage profiles of selected OEMs studied measured vs Mg (A–E) and Al (F). (A) Carbyne polysulfide (reproduced from ref 373), (B) PHBQS (reproduced with permission from ref 371. Copyright 2016 Elsevier Ltd.), (C) DMBQ (reproduced with permission from ref 370. Copyright 2016 The Electrochemical Society), (D) P14AQ (reproduced with permission from ref 366. Copyright 2018 Elsevier Ltd.), (E) P(NDI2OD-T2) P14AQ (reproduced with permission from ref 366. Copyright 2018 Elsevier Ltd.), and (F) PQ- Δ (reproduced with permission from ref 380. Copyright 2016 Nature Publishing Group).

2334 double bond with a concomitant uptake of two lithium ions for
 2335 charge compensation (Scheme 1A). Consequently, a material
 2336 with solely sp^2 hybridized carbons could in theory reach a 1/1
 2337 Li/C ratio when fully reduced, allowing us to reach extremely
 2338 high specific capacities. It was first established in 2012 in an
 2339 article from Taolei Sun where 1,4,5,8-naphthalenetetracarboxylic
 2340 dianhydride (NTCDA), a material with 4 carbonyls and 14 sp^2
 2341 hybridized carbons, could insert 18 lithium ions.³⁸¹ This work
 2342 was accompanied by an NMR study which displayed particu-
 2343 larly shielded 1H peaks for the “superlithiated” NTCDA,
 2344 matching their proposed mechanism.

2345 Remarkably, some template molecules seem to be subjected
 2346 to diverse multiple alkali metal ions insertions; the process is
 2347 hence not limited to lithium ion uptake. For instance, 3,4,9,10-
 2348 perylene-tetracarboxylicacid-dianhydride (PTCDA) is able
 2349 to uptake up to 28 lithium ions,³⁸¹ 15 sodium ions³⁸² or 11
 2350 potassium ions (Scheme 1B).³⁸³ It is interesting to note that
 2351 the larger the radius of the concerned cation, the fewer could
 2352 be inserted onto PTCDA, possibly due to steric hindrance.
 2353 However, in the case of PTCDA, the mere reduction of the
 2354 first two carbonyls is a reversible process, while the reduction
 2355 of the last two and the “superlithiation/sodation/potation” is
 2356 not. Nonetheless, over the course of the last years, many
 2357 materials have been described reacting according to reversible
 2358 “superlithiation” and are able to deliver specific capacities
 2359 sometimes exceeding 1000 mAh g^{-1} for hundreds of cycles.

2360 The typical electrochemical feature of the “superlithiation”
 2361 process is a sloping curve without obvious plateau requiring a
 2362 large potential window to achieve high Coulombic efficiency
 2363 (typically 0.05–3 V) and exhibiting a large hysteresis
 2364 (polarization) sometimes exceeding 1 V (Figure 17A). Despite
 2365 the attractive specific capacities obtained with these materials
 2366 and the intriguing science (but still poorly understood) behind
 2367 it, these electrochemical features make them of no practical
 2368 use. Nevertheless, while initially believed to be connected with

2369 fused aromatic rings or to be kinetically limited, numerous
 2370 examples have been described with a single²⁶⁰ or no aromatic
 2371 ring³⁸⁴ and with excellent capacity at a high current rate, and
 2372 there is still hope for further developments of this redox
 2373 process. By nature, “superlithiated” materials are typically inves-
 2374 tigated as negative electrode (starting with a cation uptake).
 2375 The only case of a “superlithiated” positive electrode (starting
 2376 with a cation release) is lithium carbide Li_2C_2 , where up to one
 2377 lithium ion can be released from the structure.^{385,386} As previ-
 2378 ously mentioned, this review does not try to be exhaustive, and
 2379 just a few examples will be presented here. The total amount
 2380 of articles on materials which could be related to a “super-
 2381 lithiation” process has exceeded 100. For the sake of
 2382 clarification, OEMs containing a transition metal such as
 2383 metal–organic frameworks, coordination polymers, or organo-
 2384 metallic compounds have been excluded, considering that their
 2385 specific capacity has a contribution from the transition metal in
 2386 addition to the “superlithiation” corresponding to the organic
 2387 moiety.

2388 Polyanthraquinone-triazine (PAT) is a COF using repeating
 2389 units similar to COFs previously mentioned. However, unlike
 2390 the other triazine-based and anthraquinone-based COFs, PAT
 2391 undergoes a 17-electron reduction per repeating unit, corre-
 2392 sponding to the reduction of 2 carbonyls (2 electrons), the
 2393 triazine unit (3 electrons) and the 2 benzene rings of the
 2394 anthraquinone moiety (12 electrons), leading to a maximum
 2395 reversible capacity of 770 mAh g^{-1} (Table 6, entry 1, and
 2396 Figure 17B).³⁸⁷ Interestingly, the capacity decreases in the first
 2397 30 cycles before slowly increasing with time over 400 cycles,
 2398 which has been assigned to a slow activation process. This
 2399 behavior has been observed for several “superlithiated”
 2400 materials, such as F-PDI-3-TC (Table 6, entry 2).³⁸⁸ Its initial
 2401 capacity is merely 95.7 mAh g^{-1} but reaches 783 mAh g^{-1} after
 2402 1000 cycles (Figure 17C). Other examples include poly-
 2403 (benzobisimidazobenzophenanthroline) (BBL) and poly(1,6-

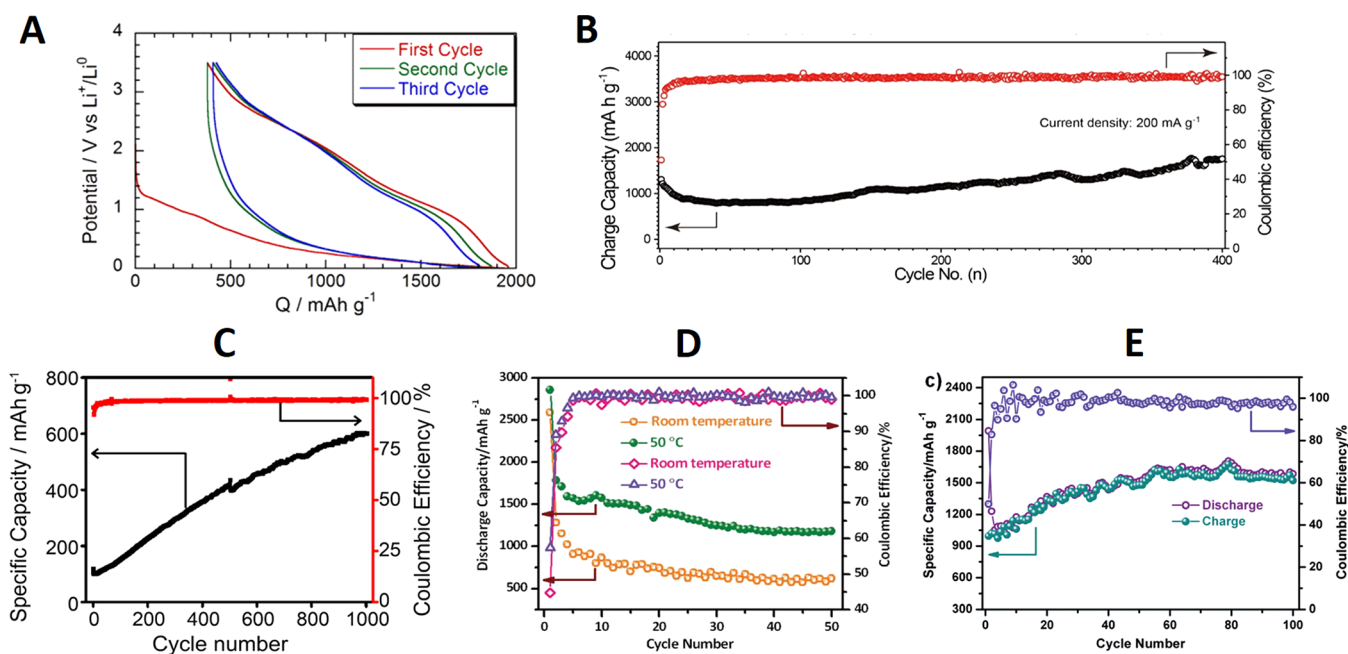


Figure 17. (A) Typical voltage profile of a “superlithiated” material: Li_2BDP (reproduced with permission from ref 260. Copyright 2016 American Chemical Society). (B–E) Capacity retention of selected OEMs: (B) PAT (reproduced with permission from from ref 387. Copyright 2018 American Chemical Society), (C) F-PDI-3-TC (reproduced with permission from ref 388. Copyright 2019 American Chemical Society), (D) BBL (reproduced with permission from ref 389. Copyright 2015 John Wiley and Sons), and (E) PQL (reproduced with permission from ref 390. Copyright 2015 John Wiley and Sons).

Table 6. Performances of Selected OEMs Exhibiting the “Superlithiation” Phenomenon

#	Positive electrode (or “cathode”) active material	Negative electrode (or “anode”)	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh g^{-1}) and Specific energy (Wh kg^{-1}) per mass of positive active material, Final coulombic efficiency, Loading (mg cm^{-2})	Ref.
1		Li	1 M LiPF_6 in EC/DMC	~0.9	n.d., ^a 400, 200 mAh g^{-1}	1 770, 1 593, ~99, 1.1	[387]
2		Li	1 M LiPF_6 in EC/DEC	~0.9	n.d., ^a 1 000, 200 mAh g^{-1}	783, 705, ~99, n.d.	[388]
3		Li	1 M LiPF_6 in EC/DEC	~0.9	48%, 50, 100 mAh g^{-1}	1 285, 1 156, ~99, n.d.	[389]
4		Li	1 M LiPF_6 in EC/DEC	~0.9	n.d., ^a 100, 100 mAh g^{-1}	1 550, 1 395, ~99, n.d.	[390]

^aDue to an activation process, the capacity increases with time.

2454 it is therefore interesting to evaluate the effective chances of
 2455 organics to realize user/market-acceptable aqueous batteries.
 2456 In addition, we believe that such a comparison would not be
 2457 complete if another bottleneck of this technology that is the
 2458 price of active materials is not compared. To address these
 2459 points, the latest literature data associated with the most
 2460 advanced and industry relevant inorganic material for molar
 2461 range aqueous battery (as opposed to water-in-salt type ones
 2462 that will be briefly discussed, *vide infra*) which is the carbon
 2463 coated $\text{Na}(\text{Li})\text{Ti}_2(\text{PO}_4)_3$ (referred to as $\text{C}@\text{NTP}$ or $\text{C}@\text{LTP}$)
 2464 is considered below.

Volumetric Capacity Aspect

2465 On paper, this is not one of the most important factors for
 2466 stationary energy storage although in practice, low energy
 2467 density could also mean more layers in the stack (for a given
 2468 electrode thickness) and therefore a higher price due to a
 2469 larger amount of passive elements. The volumetric capacity of
 2470 the $\text{C}@(\text{Na}(\text{Li})\text{Ti}_2(\text{PO}_4)_3)$ (2.6 g/cm^3) can reach up to 231^{393} –
 2471 $300^{394} \text{ mAh cm}^{-3}$ (93 – 118 mAh g^{-1} , respectively) taking into
 2472 account the carbon coating (2.0 g cm^{-3}). Interestingly, such
 2473 volumetric capacities are actually lower than that obtained for a
 2474

quinone derivative also used on the negative side, the poly pyrene-4,5,9,10-tetraone (PPTO): 1.68 g cm⁻³, 338 mAh cm⁻³, 201 mAh g⁻¹ cycled in Na⁺-based aqueous electrolyte.³⁹⁵ Although the PPTO electrode contained 30 wt.% of carbon additive its electrode volumetric capacity (144 mAh cm⁻³) remains in the vicinity of that derived for the titanium phosphate ones: 121 mAh cm⁻³, ref 393 and 152 mAh cm⁻³, ref 394. It is also important to point out that the previous results were obtained from relatively thin electrodes with areal capacity in the vicinity or below 1 mAh cm⁻².

For thicker ones (close to 2 mAh cm⁻²), Y. M. Chiang's group³⁹⁶ obtained 310 mAh cm⁻³ by volume of C@NTP at 0.6 C, which turns into 161 mAh cm⁻³ by volume of composite electrode. Industrially relevant aqueous batteries were demonstrated by Whitacre with impressive electrode loadings (between 20 and 450 mg·cm⁻²) using NTP derived from very cheap synthesis protocols.³⁹⁷ These good results pair, however, with a lower volumetric capacity of the C@NTP material (182 mAh cm⁻³ in approximately 20 mAh cm⁻² pouch cells and 159 mAh cm⁻³ in approximately 1 mAh cm⁻² coin cells³⁹⁷) which falls down to 83 and 77 mAh cm⁻³ in terms of electrode volume for pouch and coin cells, respectively, using the corresponding electrode chemistry. In comparison, the highest areal capacity demonstrated with organic materials lies in the vicinity of 4.5 mAh cm⁻².^{232,398} Indeed, Peticarari et al.²³² achieved nearly 100 mAh cm⁻³ of material and 66 mAh cm⁻³ of electrode using a diblock oligomer and 25 wt.% of carbon additive for 4.5 mAh cm⁻² while Nishide's group obtained 3 mAh cm⁻² using on a carbon nanotube hybridized poly (2,2,6,6-tetramethylpiperidin-4-yl) acrylamide (PTAm) polymer.³⁹⁸ To sum up, this short literature analysis of both inorganic and organic active materials for aqueous batteries near neutral pH highlights that some of the proposed organic electroactive materials have already surpassed inorganic ones in term of volumetric capacity in the case of thin electrodes and are not too far behind in the case of thick ones.

2511 Cost Aspect

According to Whitacre,³⁹⁷ NTP can be produced with precursor materials cost of \$4 per kg upon two synthesis steps, ball milling and calcination. Taking \$5/kg/step, which is an average in the pigment industry, an estimate of the NTP price should be roughly 14\$/kg. In comparison, competitive organic materials (in terms of volumetric capacity) in neutral molar aqueous media such as PNDI and PPTO are approximately \$4–6/kg and \$10–15/kg, respectively, highlighting similar or even lower prices can indeed be achieved for organics.

Lastly, it is noted that **water-in-salt (WiSE)**³⁹⁹ or **hydrate-melt**⁴⁰⁰ electrolytes have emerged as interesting opportunities to significantly improve the energy density and the Coulombic efficiency and mitigate corrosion issues (materials, current collectors, ...) of these new classes of "water containing" batteries. A comprehensive and critical review of the scientific understanding as well as the electrochemical and physical properties of these new electrolytes has been recently published by Yamada et al.⁴⁰¹ It is noted that the ability of WiSE electrolytes to extend the electrochemical window can be significantly improved by using an immiscible electrolyte additive, the 1,1,2,2-tetrafluoroethyl-2',2',2'-trifluoroethyl ether (HFE). The latter electrochemically decomposes at the surface of the materials and by virtue of its hydrophobicity expels water molecules from the inner-Helmholtz interface of the electrode thereby mitigating hydrogen formation at the

expense of a more efficient SEI.⁴⁰² Because, some articles commented in this review refer to these types of electrolytes, we feel that a few general comments should be recalled regarding this type of battery chemistry. First, such highly concentrated electrolytes have a volumetric density in the range of 1.6–1.9 g cm⁻³, which partially offsets the gain in energy density. For instance the mass of a 700 cm² stack cell such as presented in ref 232 (taking 5 mAh cm⁻² electrodes of 580 μm-thick and 40% porosity) increases by 14% considering a WiSE electrolyte of 1.7 g cm⁻³ compared to a "salt in water" 1 M one. Second, the viscosity of these electrolytes is approximately ten times higher than molar range ones which considerably increases the wetting time of the electrodes and especially thick ones.⁴⁰¹ Last but not least, the price of these electrolytes is obviously the most challenging issue to be overcome before commercialization can be considered. Indeed, recent results point to the fact that expensive imide based anions (as opposed for instance to acetate ones) would have a significant role in the widening of the electrochemical window on the negative electrode side.⁴⁰³

Based on the previous comments, this section aims at providing the reader with a selection of relevant organic materials, that is to say those that allow performances approaching or higher than lead acid battery ones but with much extended cyclability. Accordingly, the lower limits were set to roughly 30 Wh kg⁻¹ per mass of the two materials and a capacity retention >80% after 500 cycles at 1 C rate or equivalent. The intention of the authors is to give a critical view of the selected papers and also to highlight advantages and drawbacks vs those associated with inorganic materials. Key performances are reported in (Table 7) along with materials structures, aqueous electrolyte formulations, cycling conditions and electrode loading. Note that this critical review is focused on neutral pH batteries because they inherently offer reduced production costs and mitigated corrosion issues. Results are subcategorized into hybrid cells, where only one of the electrodes contains an organic electroactive material and all organic cells.

8.2. Hybrid Organic–Inorganic Batteries

8.2.1. Aqueous Lithium-Ion Batteries (ALIBs).

Some of the most attractive organic materials for aqueous battery to date are among the polyimide derivatives. These materials indeed combine both a high capacity (typically 130–160 mAh g⁻¹, 208–256 mAh cm⁻³) and a low price (\$4–6/kg³⁹⁵). To our knowledge such a dual advantage has not been reached by any inorganic materials used in the aqueous battery field. The electrochemical reduction/oxidation of a polyimide core is highly reversible in water at neutral pH. The redox centers have been identified as involving the aromatic-carbonyl system of the imide functional moiety following two redox steps. The first one corresponds to the formation of a radical-anion upon enolization of a carbonyl group by one electron, followed by a second electron reduction into the dianion quinoid form.⁴⁰⁴ Further reduction cannot be reached in molar range electrolyte at neutral pH before water hydrolysis is triggered. The delocalization of excess electron density in the reduced states has been studied by FTIR and UV–vis spectroscopy.⁴⁰⁵ Dong et al.⁴⁰⁶ introduce a mixed liquid/solid cationic rocking chair aqueous battery using a I₃⁻/I⁻ based polysolite and a polyimide derivative negative electrode (poly(1,4,5,8-naphthalenetetracarboxylic)dianhydride-derived polyimide, PNTCDA) separated by a Nafion membrane allowing the Li⁺ (or Na⁺) diffusion. This system delivers roughly 35 000 deep cycles at a high current of

Table 7. Performances of Selected Aqueous Organic Batteries

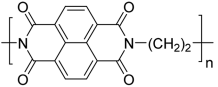
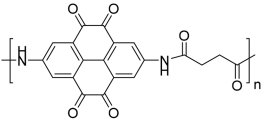
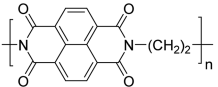
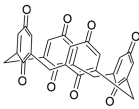
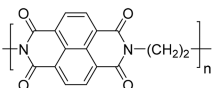
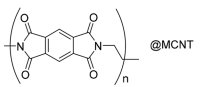
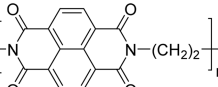

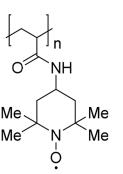
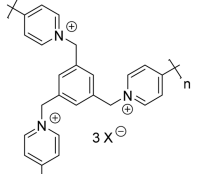
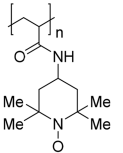
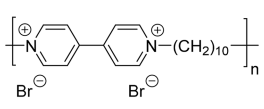
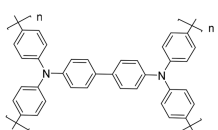
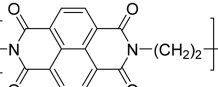
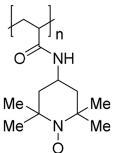
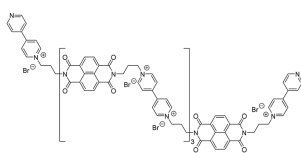
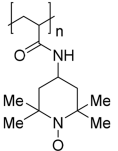
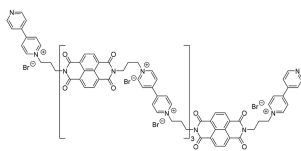
#	Cell configuration (ionic carriers)	Positive electrode (or "cathode") active material	Negative electrode (or "anode") active material	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh g ⁻¹), Specific energy (Wh kg ⁻¹)	Ref.
Hybrid organic/inorganic aqueous systems								
1	Li ⁺ (or Na ⁺)	I ₃ ⁻ /I ⁻		LiNO ₃ 1 M (pH 7)	~0.7-0.8	80%, 35 000, 10 A g ⁻¹ ,	~110, ^a ~88, ^a ~100, 1	[406]
2	Li ⁺ - ion	LiMn ₂ O ₄		Li ₂ SO ₄ 2.5 M (pH 7)	1.13	80%, 3 000 (3 500 h), 280 mA g ⁻¹	81, ^b 92, ^b 92%, -, 2	[395]
3	K ⁺	K _x Fe _y Mn _{1-x-y} [Fe(CN) ₆] _z ·zH ₂ O		KCF ₃ SO ₃ , 22 M	1.27	73%, 2 000, 4 C	63, ^b 80, ^b ~100, 5-6 all these values are at 0.5 C	[411]
4	Zn ²⁺		Zn	Zn(CF ₃ SO ₃) ₂ 3 M	1	87%, 1 000, 500 mA g ⁻¹	197, ^c 80, ^d ~100, 2.5-10	[412]
5	Mg ²⁺	Na _{1.4} Ni _{1.3} Fe(CN) ₆ ·5H ₂ O		MgSO ₄ 1 M	1.3	57, 5 000, 2 A g ⁻¹	35, ^b 45, ^b ~100, 2-3, all these values are at 0.5 A g ⁻¹	[413]
6	Mg ²⁺	Li ₃ V ₂ (PO ₄) ₃ @C		Mg(TFSI) ₂ 4 m	1.9	87%, 1 000, 2 C	52, ^b 62, ^b ~100, 2-3, all these values are at 1C (0.1 A g ⁻¹)	[414]
7	Ca ²⁺	K _{0.02} Cu[Fe(Cu) ₆] _{0.66} ·3.7H ₂ O		Ca(NO ₃) ₂ 2.5 M (pH 5.1)	1.2	88, 1 000, 10 C	45, ^b 54, ^b ~100, 5, all these values are at 1 C	[415]
8	NH ₄ ⁺ - ion	(NH ₄) _{1.47} Ni[Fe(CN) ₆] _{0.88}		(NH ₄) ₂ SO ₄ 1 M (pH 6)	1	67%, 1 000, 0.120 mA g ⁻¹	35, ^b 43, ^b 97.6%, 2-5	[416]
All-organic aqueous systems								
9	Cl ⁻ - ion			NaCl 0.1 M (pH 7)	1.3	80%, 2 000, 10.5 A g ⁻¹	165, ^a 214, ^a - (100 nm to 1 μm thin films)	[418]
10	BF ₄ ⁻ - ion			NaBF ₄ 0.1 M (pH 7)	1.2	75-80%, >2 000, 60 C (67 μA·cm ⁻²)	104, ^c 108, ^c 95 (100 nm thin films)	[419]
11	Dual-ion (TFSI ⁻ /Li ⁺)			LiTFSI 21 m (pH 7)	1	85%, 700, 0.5 A g ⁻¹	105, ^c 53, ^c ~100, 1	[420]

Table 7. continued

#	Cell configuration (ionic carriers)	Positive electrode (or "cathode") active material	Negative electrode (or "anode") active material	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh g ⁻¹), Specific energy (Wh kg ⁻¹)	Ref.
12	Mixed dual and anionic rocking-chair (ClO ₄ ⁻ /Na ⁺)			NaClO ₄ 2.5 M (pH 7)	1.1	70%, 1680 (1100 h), 0.075 to 0.6 A g ⁻¹	33 ^b , 36 ^b , >99.6, all these values are at 0.075 A g ⁻¹ , 10	[231]
13	Mixed dual and anionic rocking-chair (ClO ₄ ⁻ /Na ⁺)			NaClO ₄ 2.5 M (pH 7)	0.8	97%, 500 h, 0.075 A g ⁻¹	35, ^b 28, ^b -100, 85 (4.5 mAh cm ⁻²)	[232]

^aBased on anode material weight. ^bBased on cathode and anode materials weight. ^cBased on cathode material weight. ^dBased on the whole cell weight.

2598 10 A g⁻¹ (55 C nominal, that leads to a nominal ratio (number
2599 of cycles/C-rate) = 636) before reaching 80% of the initial
2600 capacity ($Q_0 = 105 \text{ mAh g}^{-1}$) (Table 7, entry 1).

2601 More recently, another negative electrode organic material
2602 was shown to stand out of the crowd, the quinone derivative
2603 PPTO.³⁹⁵ The latter exhibits storage properties rivaling those
2604 of any inorganic materials from mildly acidic to strongly basic
2605 media. In neutral 2.5 M Li₂SO₄ aqueous electrolyte, this
2606 material enables 92 Wh kg⁻¹ materials (208 Wh L⁻¹) when paired
2607 with LiMn₂O₄ at an average voltage of 1.13 V (Table 7, entry 2).
2608 This performance is in the same range as the competing system
2609 LiTi₂(PO₄)₃-LiMn₂O₄ (90 Wh kg⁻¹ materials (243 Wh L⁻¹, 1.5 V)
2610 thanks to the extremely high capacity of the PPTO electrode
2611 material (229 mAh g⁻¹, 366 mAh cm⁻³ at 1 C rate). In addition,
2612 this PPTO-based cell shows quite a promising capacity retention
2613 of more than 3500 h (3000 cycles) (Figure 18). Among all
2614 aqueous systems that have been reviewed herein, PPTO/
2615 LiMn₂O₄ is by far the most promising one in the authors'
2616 opinion. In addition, as a quinone derivative, the fully reduced
2617 form of PPTO (PPTO-Li₄) can support reversible oxidation by
2618 dissolved oxygen without impacting its charge-discharge
2619 properties.³⁹⁵ This is an important advantage over LiTi₂(PO₄)₃
2620 for instance, which was shown to undergo rapid capacity fading
2621 in nondeaerated electrolyte. Indeed, PPTO based cell can
2622 therefore support the "oxygen cycle" (Figure 18), which is a
2623 built-in safety mechanism for aqueous battery at high charge
2624 states. Importantly, in such events the local pH at the negative
2625 electrode can be fairly alkaline (pH 13). However, thanks to
2626 the combination of the chemical inertness of the quinone core,
2627 as well as the poor solubility, and robust amide linkage of the
2628 PPTO derivative, a capacity retention of 83% was demonstrated
2629 after 1200 h cycling in these pH conditions.³⁹⁵ Accordingly, this
2630 oxygen consumption capability of quinones enables in principle,
2631 to increase the state of charge of the positive electrode material
2632 (such as LiMn₂O₄ for instance) without significantly altering the
2633 mass balancing of the cell therefore paving the way toward the
2634 use of materials working at even higher potentials.

2635 **8.2.2. Aqueous Sodium-Ion Batteries (ASIBs).** As for
2636 Li-ion batteries, Na-based aqueous batteries must be
2637 investigated to counteract possible upcoming issues associated
2638 with geo-localized Li resources. One of the first instances of
2639 hybrid ASIBs bearing an organic electroactive material uses a

polyimide derivative PNDI at the negative electrode and a
NaVPO₄F based positive electrode in a 5 M NaNO₃ aqueous
electrolyte.⁴⁰⁴ This system shows, however, a very poor capacity
retention (-25% in 20 cycles) that was mainly ascribed to
NaVPO₄F (-30% loss of capacity in 20 cycles) compared to
-17% for PNDIE.⁴⁰⁴ Yao's group³⁹⁵ slightly improved these
cyclability results to nearly 80% of capacity retention after
80 cycles (150 h) by substituting Na₃V₂(PO₄)₃ for NaVPO₄F
and PPTO (208 mAh g⁻¹) for PNDIE (160 mAh g⁻¹). To
date, ASIB hybrid aqueous batteries are therefore not compet-
itive with corresponding ALIB as reported above especially in
terms of capacity retention. For this reason, ASIB related research
has mainly focused on the use of inorganic compounds¹⁷³ such as
NaFePO₄⁴⁰⁷ as well as fully inorganic systems based on
Prussian (white)blue,⁴⁰⁸ carbon coated phosphates (NTP³⁹⁷ and
Na₃MnTi(PO₄)₃,⁴⁰⁹) and manganese oxides Na_{0.44}MnO₂³⁹⁶ and
Na_{0.44}[Mn_{1-x}Ti_x]O₂.⁴¹⁰ We note however, that all these materials
enable capacity values in the range of 40 to 60 mAh g⁻¹ and
energy density values in the range of 30-40 Wh kg⁻¹ per mass of
materials in molar range electrolyte which is the average value
generally observed for most organic based aqueous cells.

8.2.3. Aqueous Potassium-Ion Batteries (AKIBs). Full
organic-inorganic hybrid AKIBs have not been reported until
very recently owing to the scarcity of suitable electroactive
materials and electrolytes. Hu's group⁴¹¹ demonstrated an
AKIB cell based on an Fe-substituted Mn-rich Prussian blue
K_xFe_yMn_{1-y}[Fe(CN)₆]_z·zH₂O (KFeMnHCF) as the positive
electrode and the 3,4,9,10-perylene-tetracarboxylic diimide
derivative as the negative one in a 22 M KCF₃SO₃ water-in-
salt electrolyte (Table 7, entry 3). The low water activity of the
latter allowed not only to mitigate dissolution of both electrode
materials but also to charge the positive electrode up to 1.2 V
vs Ag/AgCl electrode, which allowed KFeMnHCF to
reversibly reach 135 mAh g⁻¹ at 0.5 C above 0 V vs SCE. In
addition, thanks to the mitigation of phase transitions by Fe
substitution, KFeMnHCF achieves 70% capacity retention at
100 C over 10 000 cycles. This pioneering AKIB system shows
a high energy density of 80 Wh kg⁻¹ by mass of the two
electrodes at a power density of 41 W kg⁻¹ (0.5 C) and 73%
capacity retention over 2000 cycles at 4 C (Figure 19A-C)
which makes it one of the most attractive systems to date.
Interestingly, authors have evaluated their system in pouch cell

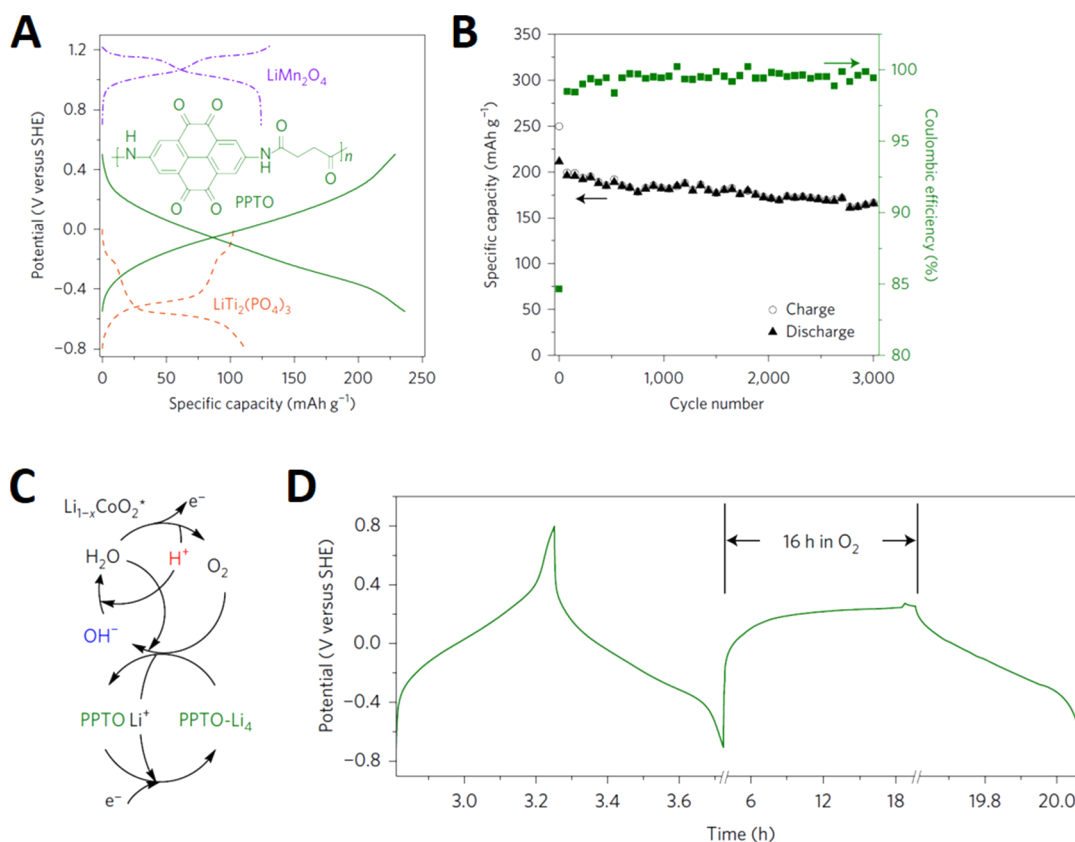


Figure 18. Characteristics of PPTO as an anode material for ALIBs. (A) Galvanostatic charge–discharge profiles for PPTO (280 mA g⁻¹), LiTi₂(PO₄)₃ (120 mA g⁻¹), and LiMn₂O₄ (140 mA g⁻¹) in 2.5 M Li₂SO₄ (pH 7). (B) Capacity retention of a LiMn₂O₄–PPTO cell during galvanostatic cycling at 1 C in 2.5 M Li₂SO₄ (pH 7). (C) Schematic explaining the oxygen cycle in ALIBs: H₂O is oxidized at the catalytic sites (*) on the cathode (for example, LiCoO₂) to generate O₂ and H⁺; the latter is then reduced by the charged anode (for example, PPTO–Li₄) to afford OH⁻. (D) Oxygen consumption by charged PPTO: a PPTO electrode is first electrochemically discharged (oxidized) and charged (reduced) under Ar for one cycle, then left to rest under O₂, and finally put under Ar and charged again. Reproduced from ref 395. Copyright 2017 Nature Publishing Group.

2682 configuration and at several temperatures to better grasp the
2683 prospect of large-scale applications: an 11 mAh pouch cell was
2684 shown to exert superior performance at low rates (i.e., 0.5 C/0.1 C)
2685 and low/high temperatures (i.e., -20 °C/-10 and 25 °C/60 °C)
2686 and was able to operate from -20 to 60 °C (Figure 19 D,E).

2687 **8.2.4. Aqueous Multivalent Metal-Ion Batteries (Mg,
2688 Ca, Zn). Zn²⁺.** Chen's group demonstrated that high energy
2689 values could be obtained at the cell level (pouch cell) by
2690 pairing quinones (calix[4]quinone, referred to as C4Q) to a
2691 zinc negative electrode in a 3 M (ZnCF₃SO₃)₂ aqueous
2692 electrolyte (Table 7, entry 4).⁴¹² This system develops 1 V as
2693 output voltage and up to 337 mAh g⁻¹ by mass of materials at
2694 low current density (5 mA g⁻¹). The pouch cell achieved 220
2695 Wh kg⁻¹ at 500 mA g⁻¹ considering the electroactive mass
2696 fraction of the materials (which are 89% for the C4Q and 49%
2697 for Zn) and 80 Wh g⁻¹ by mass of the whole cell with an
2698 energy efficiency close to 80%. However, due to the dissolution
2699 of the C4Q, a Nafion membrane was required to stabilize the
2700 capacity retention at 87% after 1000 cycles (-0.015%/cycle).
2701 It is instructive to note that although the development of mild
2702 electrolyte based Zn batteries is still in its infancy, this kind of
2703 system clearly brings energy densities in the same order as
2704 those associated with the use of "water-in-salt" electrolytes.
2705 This point should therefore motivate more research in the near
2706 future to enhance the depth of discharge and cyclability and
2707 prevent the use of membranes.

2708 Mg²⁺. Xia et al.⁴¹³ recently developed a 33 Wh kg⁻¹ (1 V as
2709 output voltage) per mass of active materials considering
2710 Na_{1.4}Ni_{1.3}Fe(CN)_{6.5}H₂O paired with poly[N,N'-(ethane-1,2-
2711 diyl)-1,4,5,8-naphthalene tetracarboximide (PNDIE) using 1 M
2712 MgSO₄ aqueous electrolyte (Table 7, entry 4). This assembly
2713 allowed to achieve 1000 cycles at 2 C rate while keeping
2714 approximately 88% of the initial capacity. Interestingly, Wang
2715 et al.⁴¹⁴ obtained nearly two times more energy density
2716 (62.4 Wh kg⁻¹ per mass of materials) using Li₃V₂(PO₄)₃, as
2717 the positive electrode and lighter diimide derivatives (polypyromel-
2718 litic dianhydride), as the negative electrode (Table 7, entry 6).
2719 Compared to the more often used naphthalene derivative,
2720 the smaller delocalization backbone of the polypyromellitic
2721 destabilizes the radical anion and dianions that form on reduc-
2722 tion and push the potential to lower values. The cell shows
2723 indeed a high voltage of 1.9 V which can be realized by using a
2724 relatively concentrated electrolyte (4 M Mg(TFSI)₂).⁴¹⁴ This
2725 resulted in a promising capacity retention of nearly 87% after
2726 1000 cycles at 2 C rate.

2727 Ca²⁺. Ca²⁺ is another interesting abundant ion to play with
2728 in aqueous media. Yao's group⁴¹⁵ recently showed that the
2729 diffusion of Ca²⁺ is higher than that of Mg²⁺ both in the solid
2730 state and in the aqueous electrolyte media. These results were
2731 ascribed to smaller size of the hydrated Ca²⁺ complex and its
2732 more facile dehydration during the charge transfer process.
2733 This group assembled a battery with a copper hexacyanoferrate

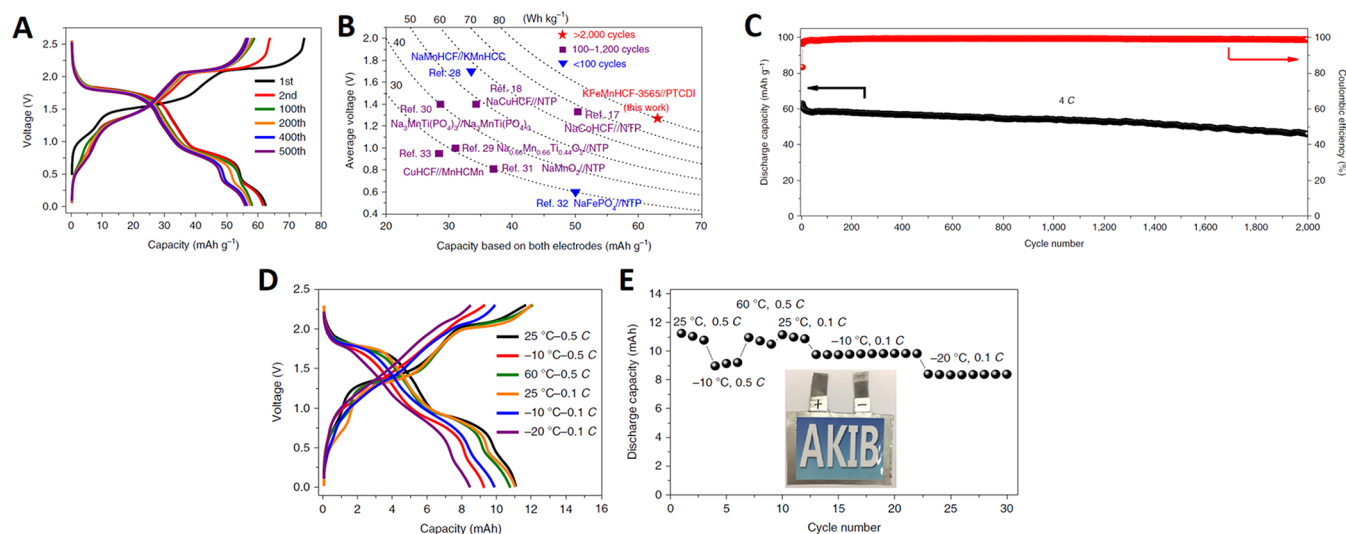


Figure 19. Performance of the $K_{1.85}Fe_{0.33}Mn_{0.67}[Fe(CN)_6]_{0.98} \cdot 0.77H_2O | 22 M KCF_3SO_3 | PTCDI$ full battery. (A) Charge–discharge curves for coin cells at 4 C from 0 to 2.6 V (1 C = 0.13 A g⁻¹). (B) Comparison of average voltage, capacity based on total mass of both electrodes, lifespan, and energy density for the full battery with reported aqueous Na-ion full batteries. (C) Long-term cycling performance of the coin cell at 4 C. (D, E) Corresponding electrochemical performance measured in pouch cell at different rates (0.5/0.1 C) and temperatures (-20/-10/25/60 °C). Reproduced with permission from ref 411. Copyright 2019 Nature Publishing Group.

2734 compound of composition $K_{0.02}Cu[Fe(Cu)_6]_{0.66} \cdot 3.7H_2O$
 2735 (CuHCF) coupled to the PNDIE polyimide derivative in a
 2736 2.5 M $Ca(NO_3)_2$ aqueous electrolyte (Table 7, entry 7).
 2737 CuHCF was found to proceed to insertion/deinsertion of 0.3
 2738 Ca^{2+} ion at a 0.2 C through a single-phase solid solution
 2739 reaction rate at a potential of 0.72 V vs Ag/AgCl electrode.
 2740 This mechanism which is paired with the Fe^{3+}/Fe^{2+} electroactivity
 2741 leads to a specific capacity of 58 mAh g⁻¹ (theoretical capacity
 2742 $Q_{th} = 65 \text{ mAh g}^{-1}$) that retains 88% of its initial capacity after
 2743 2000 cycles at 5 C. On the other hand, PNDIE fully reacts with
 2744 Ca^{2+} at -0.45 V vs Ag/AgCl electrode with a reversible capacity
 2745 of 160 mAh g⁻¹ (theoretical capacity $Q_{th} = 183 \text{ mAh g}^{-1}$).
 2746 At 1 C rate, the full cell delivered 54 Wh kg⁻¹ of active materials
 2747 for an output voltage of 1.2 V. In addition, the battery still
 2748 provides 88% capacity retention after 1000 cycles at 10 C.

2749 **8.2.5. Aqueous Ammonium-Ion Battery.** Little is
 2750 reported with ammonium as shuttling ion. However, it must
 2751 be mentioned that Ji and co-workers⁴¹⁶ reported such an
 2752 aqueous battery using Ni-based Prussian white at the positive
 2753 electrode paired with 3,4,9,10-perylenetetracarboxylic diimide
 2754 using 1 M $(NH_4)_2SO_4$ as electrolyte (pH 6) (Table 7, entry 8).
 2755 This cell enables up to 43 Wh kg⁻¹ per mass of active materials
 2756 with 1 V of voltage at 1.5 C and achieves a capacity retention
 2757 of 67% upon 1000 cycles at 3 C rates (120 mA g⁻¹) with an
 2758 average Coulombic efficiency of 97.6%.

8.3. All-Organic Aqueous Batteries

2759 Due to the lack of high potential n-type organic materials,⁴¹⁷
 2760 cation-rocking chair cells have not been reported yet. Today,
 2761 all-organic aqueous cell electrochemistry is indeed either related
 2762 to counteranions or both counteranion and anions (one at
 2763 each electrode referred to as “dual mode” and the two at one
 2764 electrode referred to as “intermixed mode”). First reports were
 2765 released by Nishide, Oyaizu, and co-workers.⁴¹⁸ They used a
 2766 redox polymer resulting from the attachment of a (2,2,6,6-
 2767 tetramethylpiperidin-1-yl)oxy known as “TEMPO” side groups
 2768 to a polyalkane chain backbone, with poly (2,2,6,6-
 2769 tetramethylpiperidin-4-yl) acrylamide (referred to as PTAM)
 2770 as the positive electrode material. This material was paired to

two different polyviologen derivatives, either the highly cross-
 2771 linked polyviologen hydrogel (poly tripyridiniumstyrene)⁴¹⁸
 2772 which enabled ~1.3 V as output voltage (Table 7, entry 9) or
 2773 the poly(*N*-4,4'-bipyridinium-*N*-decamethylene dibromide)
 2774 (Table 7, entry 10) leading to a cell average voltage of 1.2 V.
 2775 Although both cells demonstrated more than 2000 cycles in 0.1 M
 2776 Na-based aqueous electrolytes, electrodes were thin film deposits
 2777 in the sub- to micron-thick range. Recently however, this group³⁹⁸
 2778 has made decisive advances by demonstrating a thick composite
 2779 electrode made of PTAM with a loading of 3 mAh cm⁻². The
 2780 latter was obtained by hybridizing PTAM with a 3-D self-
 2781 assembled mesh of single-walled carbon nanotubes (SWNT).
 2782 This thick electrode could still reach nearly 80 mAh g⁻¹ of
 2783 material at 10 C rate. Although SWNT represents only 1% of
 2784 the total electrode mass, it is noteworthy that authors demon-
 2785 strated the importance of the contacts with the current
 2786 collectors by showing such a high kinetics also stems from the
 2787 optimization of the current collector/electrode contacts.³⁹⁸
 2788

Dong et al.⁴²⁰ cycled a p-type conjugated tertiary poly
 2789 triphenylamine obtained by oxidative polymerization of the
 2790 triphenylamine (PTPAN). The latter shows a sloppy discharge
 2791 profile resulting from the superimposition of two pairs of broad
 2792 peaks centered at 0.2 and 0.8 V vs SCE associated with the
 2793 *para* and *meta* conformational isomers. Overall the discharge
 2794 of this compound enables approximately 105 mAh g⁻¹ PTPAN at
 2795 0.5 A g⁻¹ (4.6 C-rate). However, the strong oxidative power of
 2796 the N^+ species triggers the hydrolysis of water molecules that
 2797 could be mitigated by the use of a “water-in-salt” electrolyte
 2798 of 21 m LiTFSI. PTPAN was then coupled to 1,4,5,8-
 2799 naphthalenetetracarboxylic dianhydride-derived polyimide
 2800 (PNTCDA) as the negative electroactive material (Table 7,
 2801 entry 11). During charge TFSI⁻ and Li⁺ react with the oxidized
 2802 PTPAN and reduced PNTCDA, respectively (dual mode),
 2803 enabling a maximum of 53 Wh kg⁻¹ per mass of electroactive
 2804 materials and a capacity retention of 85% after 700 cycles at
 2805 0.5 A g⁻¹ (4.6 C-rate).⁴²⁰
 2806

Some of us reported a possible new avenue to design
 2807 aqueous batteries materials based on diblock-oligomers bearing
 2808

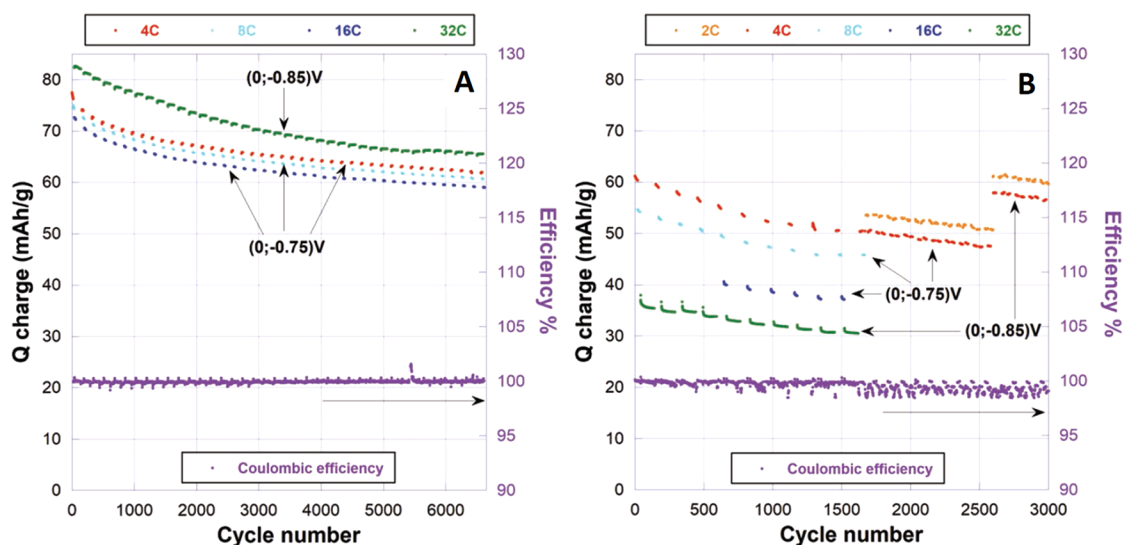


Figure 20. Capacity retention on charge (oxidation of the material) and corresponding Coulombic efficiency curves for diblock-oligomers bearing p-type viologen and n-type naphthalene diimide moieties composite electrodes in (A) 2.5 M NaClO₄ aqueous electrolyte and (B) ocean water. Reproduced with permission from ref 231. Copyright 2019 John Wiley and Sons.

2809 p-type viologen and n-type naphthalene diimide moieties. These
 2810 types of structures enable simultaneous release and uptake of
 2811 anions (ClO₄⁻, Cl⁻) and cations (Na⁺, Mg²⁺) respectively by a
 2812 single electrode (intermixed mode) with the promise of mitigated
 2813 volume variations on cycling.²³⁰ The best performances were
 2814 obtained using an oligomer that can reach up to 105 mAh g⁻¹ per
 2815 mass of material and 80 mAh g⁻¹ per mass of electrode.²³¹ The
 2816 extremely fast kinetics of longer diblock oligomer also allowed to
 2817 reach an unmatched specific capacity of 60 mAh g⁻¹ electrode
 2818 (0.7 mAh cm⁻²) without any conducting additive while the
 2819 optimum amount of carbon black additive was found to be
 2820 10 wt % at C-rate and below. Its capacity retention is remark-
 2821 able for several thousand cycles (6500 cycles, ≈40 days) in
 2822 2.5 M NaClO₄ aqueous electrolyte as well as plain ocean water
 2823 (≈3000 cycles, ≈75 days) (Figure 20).²³¹ A 40 Wh kg⁻¹ materials
 2824 full cell demonstration was shown with more than 1600 cycles
 2825 using the commercial 4-hydroxy TEMPO benzoate as the
 2826 positive material and 0.7 mAh cm⁻² as electrode loading
 2827 (Table 7, entry 12). It is noted that a concentrated (but cheap)
 2828 electrolyte (8 M NaClO₄) was required to prevent dissolution
 2829 of the TEMPO derivative.^{231,232} The same system was also evalu-
 2830 ated using millimeter thick electrodes of 8 mAh cm⁻² (nominal)
 2831 leading to a stable areal capacity of nearly 4.5 mAh cm⁻² for
 2832 500 cycles at 1C rate. To further demonstrate the practicability of
 2833 the system, the same electrodes were evaluated in pouch cells.
 2834 The output voltages were 0.78 V (C-rate) and 1.1 V (C/8-rate)
 2835 leading to 22 Wh kg⁻¹ (C-rate) and 36 Wh kg⁻¹ (C/8-rate)
 2836 per mass of materials with a 97% capacity retention over 500 h
 2837 cycling at both C and C/8 rates (Table 7, entry 13).²³²

8.4. Summary and Outlooks

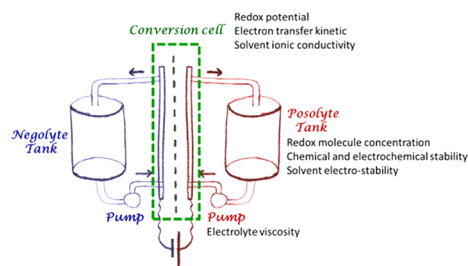
2838 Neutral aqueous batteries based on organic electroactive mate-
 2839 rials have been reviewed and discussed. New results point to
 2840 the fact that some competitive organic materials have now
 2841 surpassed inorganic ones even in terms of volumetric capacity
 2842 while relatively large amounts of electrode carbon additive
 2843 have been proved unnecessary for some derivatives. In addi-
 2844 tion, we feel that this review highlights a decisive advantage of
 2845 organic materials since most of them offer a highly versatile
 2846 ionic compensation chemistry characterized by possible

2847 reactions with many different cations (monovalent and
 2848 divalent), anions, and even both simultaneously. This aspect,
 2849 that is encountered for the Prussian blue family for cations,
 2850 opens up a large panel of possibilities regarding the cell chem-
 2851 istry, with the additional advantage to be coupled to much
 2852 larger storage capacity and, in some instance, with the possibility
 2853 of supporting the oxygen cycle.

2854 Although it still remains far from that achieved with some
 2855 inorganics,³⁹⁷ the technology readiness level (TRL) of organic
 2856 based aqueous batteries has increased in the latest papers by
 2857 the use of either highly loaded electrodes and/or pouch cell
 2858 configurations. However, studies devoted to the impact of electro-
 2859 de formulation are scarce. As an example, the polytetra-
 2860 fluoroethylene (PTFE) binder that is predominantly used so
 2861 far because of its readiness is presumably not the most
 2862 appropriate for the wettability of composite electrodes, for the
 2863 volume variations on cycling, as well as from an industrial
 2864 production point of view.

2865 Among the different cell chemistries that have been reviewed
 2866 herein, three main topics attract research work: all organic
 2867 systems, hybrid ones bearing an inorganic electroactive material,
 2868 and water-in-salt electrolytes. Because of the prohibitive price
 2869 incurred by the water-in-salt type electrolytes and although
 2870 related energy densities can today approach that encountered
 2871 for Li-ion batteries, we believe this strategy will remain
 2872 confined to fundamental studies unless cheap salts are found to
 2873 replace the capability of imide based ones to form stable SEI.
 2874 On the other hand, both all organic and hybrid organic batte-
 2875 ries using molar electrolytes now can show promising capacity
 2876 retention at the cell level. However, this aspect still remains to
 2877 be confirmed in large format batteries, at different temper-
 2878 atures and by including self-discharge tests. Regarding energy
 2879 density and except for a few examples of hybrid cells, most
 2880 results are in the range of 40–60 Wh kg⁻¹ per mass of mate-
 2881 rials. However, as opposed to purely inorganic based aqueous
 2882 batteries, the combination of attractive energy density, 80–
 2883 90 Wh kg⁻¹ per mass of materials, with promising cyclability
 2884 (>3000 h) can be reached thanks to the large capacity of
 2885 organics. In addition, owing to its large voltage and low price,

a) Typical components in RFBs:



b) Various cell designs:

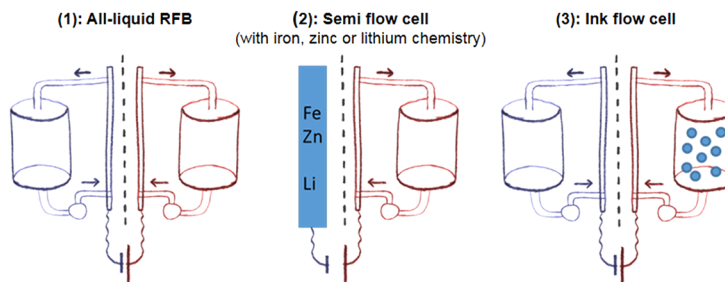


Figure 21. (a) Redox-flow battery schematic with main relevant parameters referred to redox-active compounds. (b) Possible cell configurations.

2886 the Zn system based on mild electrolyte is certainly an option
2887 to be considered more deeply in the future.

2888 Lastly, to close this section it appears interesting to recall
2889 that the ever decreasing price of Li batteries (and the increasing
2890 TRL of their novel high energy chemistries) turns them into a
2891 serious option for (off)in-grid application.⁴²¹ In this context,
2892 the authors believe that the effective chances of organics to
2893 realize user/market-acceptable aqueous batteries (at least for
2894 complementary applications) stem from their low toxicity,
2895 their abundancy, as well as their recyclability which could turn
2896 out to be efficient and profitable.

9. ORGANICS IN REDOX-FLOW BATTERIES

9.1. Specificities of Redox-Flow Batteries

2897 Although we have already described the different cell
2898 assemblies using organics, some complementary details are
2899 required to better grasp the specificities of redox-flow cell for
2900 electrochemical storage (Figures 8,9). Basically, such a cell can
2901 be seen as a fuel cell where the fuel and oxidizer would be
2902 replaced by fluids with redox components in solution. As the
2903 associated electrochemical reactions are reversible, the device
2904 can be easily recharged. RFBs are energy storage devices with
2905 the advantage of dissociating power density (electrode surface
2906 area, number of cells in the conversion cell) and energy (tank
2907 volume). As currently energy densities remain low, these
2908 devices are more dedicated to stationary energy storage. The
2909 duration of storage (hour, day, week) depends mainly on the
2910 type of chemistry used.

2911 Many recent reviews related to ORFBs have been conducted
2912 in the literature.^{15,20,23,24,31,34,35,44,45,422} These reviews focus on
2913 describing the implemented redox molecules and the different
2914 strategies used to integrate them into a redox-flow device. This
2915 section will only focus on systems that are most advanced in
2916 terms of performance and that have been tested in systems as
2917 close to the application as possible and at least in a flow cell.
2918 In terms of concentration, there are many publications where
2919 tests are carried out in a very diluted medium, so we have

2920 decided to retain only studies on the most concentrated
2921 electrolytes. In solvent-based media, generally speaking, the
2922 performance is much weaker than in the case of aqueous
2923 electrolytes, so the selection we made was less drastic.

2924 A RFB consists of three main components: an electro-
2925 chemical conversion cell where electrochemical reactions take
2926 place, tanks to store redox-active fluids, and finally pumps to
2927 allow the circulation through the cell of the two electrolytes
2928 (posolyte/negolyte) containing the redox-actives species
2929 (Figure 21a). Behind this apparent simplicity lies a device
2930 that remains very difficult to optimize. Among the main
2931 parameters or components associated with the chemistry used,
2932 we can mention:

- the nature of the solvent that composes the electrolyte,
on which depends the accessible potential window, as
well as the power density (ionic conduction) of the
conversion cell;
- the redox compounds solubility; it is important that the
different redox states of each couple have the highest
possible solubility. The number of electrons exchanged
during the redox reaction must modulate this solubility;
the important parameter is the quantity of electrons
exchanged by the solution (mole electrons per liter);
- the electron transfer kinetics with the electrode surface;
electron transfers must be fast and perfectly reversible to
avoid losses due to overvoltage problems. In general, for
a redox-flow conversion cell, faradic efficiencies are very
good; main losses come from overvoltage problems at
the electrodes (different potentials between charge and
discharge);
- the chemistry itself which must obviously be stable
enough without bringing corrosion problems that would
shorten the battery life. RFBs must have a very long
lifetime (>20 years) in order to make its components
more cost-effective than in a regular “sealed” battery
(membrane, pumps cost, etc, ...) since stationary storage
applications are targeted as previously underlined;

- the membrane, which allows the two compartments to be chemically and electrically separated, while allowing the diffusion of ions that ensure the system electro-neutrality without crossover.

9.1.1. Short Overview on Inorganic-Based Redox-Flow Batteries. As already mentioned in the Introduction, the most advanced and commercialized flow systems are based on inorganic materials with acidic aqueous electrolyte: vanadium, zinc–bromine, hydrogen–bromine, and so on.^{5,423–425} Each system has its own limitations: cost in the case of vanadium, formation of dendrites for zinc, need to use platinum in the case of H₂, toxicity (Br₂). Energy efficiencies are between 65 to 80% in the case of vanadium RFB for current densities of up to 100 mA cm⁻² and an operating voltage of 1.25 to 1.4 V. Energy densities of 55 Wh L⁻¹ have been achieved. These values should be strongly tempered because at high vanadium concentrations (2 M), electrolytes become very sensitive to temperature, they precipitate easily or become very viscous preventing their circulation, so the concentrations commonly used are rather in the order of 1.6 M. The shutdown system self-discharge would be in the order of 0.1% per week.

From a practical point of view, many problems of matter transfer (solvent, ...) related to electro-osmosis through ion exchange membranes appear during operations. As a result, the volume of electrolytes in each tank changes according to the number of cycles and it is necessary to “redistribute” them by transferring a volume of electrolyte from one compartment to another, this approximately every 200 cycles. With this periodic rebalancing, life times of more than 2000 cycles and 10 years can be achieved. This is independent of corrosion problems that require regular replacement of parts, involving high maintenance costs. In the case of chemistries other than vanadium, electrolyte “rebalancing” is not possible as each compartment has a different chemistry and the management of these solvent transfers becomes problematic. Despite these important limitations, at the moment no “alternative” chemistry can compete with inorganic flow batteries in terms of application.

9.1.2. Possible Cell Configurations for Redox-Flow Batteries. Different types of ORFB have been described in the literature, with the most common being those where both electrolytes are liquid (Figure 21b). In the case where the only purpose is to evaluate a specific molecule, it is possible to use a symmetrical cell (same compounds in each compartment); however, this implies to have access to the two redox states of the molecule. There are also intermediate devices between a flow battery and a solid battery known as semisolid flow battery as proposed by Chiang’s group.⁴²⁶ This latter approach, which generally has the disadvantage of using highly viscous dispersions that require oversized pumps, will not be discussed in this review.

9.1.3. Redox-Active Organic Species and Solvents. Redox-active organic moieties identified in the ORFB literature are the same as those found in solid batteries and also deduced from the general classification reported in Table 1 including the use of pure p- or n-type structures as well as mixed systems. They are however “functionalized” in order to increase solubility in the chosen solvent. These molecules can be combined in an undifferentiated way to form either a rocking chair cation ion or anion ion cell or a dual ion cell (Figure 9). It should be noted that in the latter case, unlike in the case of “sealed” batteries, since the volume of electrolyte is generally very large compared to the mass of active material, the dual-ion cell geometry does not create any problems (significant loss of

conductivity of the electrolyte). The main redox-active moieties are nitroxide, viologen, perylene diimide, ferrocene, quinone, thio, amino, phenol, ... (Figure S8). In a general way, there is a strong lack of redox-active structures able to work at very low potential (as in the case of carboxylates in organic “sealed” batteries working with solid state compounds) in order to obtain higher voltage systems. The main problem to address with redox molecule is stability. Since redox-active compounds are solubilized in the electrolyte, they are more subject to decomposition than solid electrodes. Thus, upon cycling, molecules can react together with solvent or electrolyte giving rise to poor performances. This especially at high concentrations (>0.5 M) which enhance decomposition kinetics.

The main role of the solvent is to dissolve the redox molecule in order to make it transportable between the tanks and the conversion cell. It must also ensure the ionic conductivity necessary to achieve electroneutrality at all points of the solution and avoid polarization phenomena in the conversion cell. For this purpose, the best solvent is water; its high polarity combined with its ability to dissociate electrolytes results from the fact that aqueous solutions have very high ionic conductivities. Moreover, in terms of cost, water is the cheapest solvent and presents the fewest safety problems (nonflammable, nontoxic). However, aqueous electrolytes display low electrochemical stability window (1.23 V from thermodynamics up to 1.5 V for kinetics reason). Organic solvents have the advantage of having larger electrochemical stability windows (>4.5 V in the case of acetonitrile or carbonates), but electrolyte dissociation is less efficient, resulting in an ionic conductivity of about 100 times less than in aqueous solvent.

Organic solvents are chemically unreactive, so they prevent degradation phenomena in solution and increase the lifetime of redox molecules. This also makes possible the stabilization of certain highly reactive redox molecules (e.g., radicals) and makes them relevant for redox-flow applications. The main solvents used are acetonitrile, carbonates, ethers, esters, and, more anecdotally, DMSO. Generally speaking, the solubility of organic molecules is not so different between aqueous and organic electrolytes, for two reasons: in organic media high concentrations of salts are used to increase the conductivity of solutions, with the consequence that the solubility of molecules decreases. An adapted functionalization renders the redox molecules highly soluble in water. The maximum concentrations achievable in a complete electrolyte (salt + solvent) are in the order of 2–3 M. As the conversion cells have not yet been really optimized for organic solvents, at the moment the solvent strongly conditions the type of batteries: high power density (0.1–0.3 W cm⁻²) in aqueous solution (low voltage, high conductivity) and high energy density (>100 Wh L⁻¹) in organic solvent (high voltage, low conductivity). It is of course possible to mix several solvents, even if this makes electrolyte development more complex.⁴²⁷ This approach remains difficult to master because it is difficult to combine the advantages of solvents without also combining the disadvantages.

One way to get around this is to use hydrotropes. A hydrotrope is a concentrated aqueous solution (several molars) of a small organic molecule such as urea, *para*-toluene sulfonic acid, nicotinic acid, and so on. Organic molecules are generally much more soluble in a hydrotrope than in water and the electrochemical properties are preserved or improved. The use of urea, for example, increases the solubility of benzoquinone by a factor of 7.⁴²⁸ Other strategies have been used to make redox

organic molecules “liquid”. The use of ionic liquid was tested by following different paths: as a solvent, with an organic or aqueous cosolvent, and finally by making redox ionic liquids. The use of eutectics based on highly concentrated salts in a solvent has produced interesting results because they produce highly conductive solutions capable of dissolving highly polar redox organic molecules.⁴²⁹ Finally, some redox molecules developed to be highly soluble have been found to be liquid due to their low solid-state cohesion. However, the addition of salt is necessary to make the liquid ionically conductive, resulting in a significant increase in viscosity. While these alternative strategies have proved to be relevant, they have not yet made possible the development of large-scale devices capable of competing with inorganic flow cells in terms of power density, energy density, or stability (cycling and calendar aging). The use of ionized salt is necessary to enhance the solvent ionic conductivity and maintain electroneutrality during the electrochemical process. In aqueous media, acid (H_2SO_4) or base (KOH) could be used if the redox molecule does not react with them. Salts like sodium or lithium associated with nitrate, and chloride or sulfate could be used in neutral pH. In organic medium, salts need to be highly soluble and dissociated, so lithium or tetra-alkylammonium cation associated with noncoordinating anion such as PF_6^- , BF_4^- , or TFSI^- is mainly used, even if these salts are much more expensive than the ones used in aqueous solvents. Independently of the solvent, the choice of the supporting salt is very important on the electrochemical behavior of the redox molecule.

One of the main problems remaining for RFB concerns the fact that the electrolyte in a highly concentrated solution tends to be very viscous (both in inorganic or organic RFB). In organic RFB, the problem is more important in the way that organic molecules possess a higher molecular weight compared to inorganic ones ($M(V) = 50.9 \text{ g mol}^{-1}$). This means, for example, that an organic redox molecule with a molecular weight of 200 g mol^{-1} , typically nonfunctionalized anthraquinonoid derivative, at a concentration of 1 M corresponds to 200 g of molecule in 1 L of solution. In some cases, the solution became as viscous as honey, precluding their use in flowing cells, apart from using a lot of energy to power the pump. A high viscosity also lowers the molecule diffusion in solution, with a direct effect on the apparent electron transfer kinetic and ionic conductivity. As a result, highly concentrated electrolytes suffer from higher cell overvoltage either in charge or in discharge.

9.1.4. Favoring Highly Soluble Redox-Active Species.

In order to make redox organic molecules highly soluble in the desired medium, it is necessary to functionalize them with appropriately selected groups. In aqueous media, ionic functions or functions with a large number of heteroelements (e.g., O or N) will be favored to increase the interactions between the redox compound and water molecules. The main ionic functions used are sulfonates,⁴³⁰ phosphates,⁴³¹ carboxylates,⁴³² ammonium,⁴³³ or hydroxo.⁴³⁴ These ionic functions have also the advantage of increasing the ionic conductivity of the solution, allowing in some cases to eliminate the use of supporting salts. Neutral substituents such as PEGs are also used regularly. However, it is necessary to remain attentive to the positions chosen to graft these solubilizing groups, because the functionalization of redox molecules can completely change the electrochemical response and make it irreversible. The solubility of nonfunctionalized organic molecules is generally better in organic media. However, in most cases, functionalization is necessary to achieve the solubility necessary to

develop an efficient flow battery. In organic media, neutral substituents are preferred, such as alkyl chains or PEGs. Alkyl chains are not necessarily the most efficient because of their low polarity, which is not optimal in polar solvents and which hinders the solubilization and dissociation of salts. PEG chains have the advantage of being more polar and their effect on solubility is more important. By choosing certain chain lengths, it is even possible to obtain liquid redox compounds. Finally, these PEG chains are capable of strongly complexing the alkaline cations contained in the supporting salt, thus improving its dissociation and increasing the conductivity of the solution.

For the redox-flow system, the membrane is an important element; it allows the two compartments to be physically separated to avoid the mixing of species but must permit the passage of ions to ensure the electroneutrality of each of the compartments. In most cases, an ion exchange membrane is used, cationic in the case of a cationic rocking chair battery, anionic in the case of an anionic rocking chair battery, and one or the other in the case of a dual ion configuration. In aqueous environments, the most efficient membranes are mainly made of perfluoro sulfonated polymer. These membranes are very stable and have a high ionic conductivity. They have the disadvantage of not being as stable in organic media or they tend to swell and become porous. Alternative organic membranes have been developed, but unfortunately for the moment they are not as stable as the perfluoro one. To counter this, ceramic membranes have been used, particularly in the case of mixed devices using a lithium electrode. As the cost of such membranes is important, different strategies have been deployed to try to replace them with simpler separators. Size based separators (dialysis membranes) combined with redox molecules in the form of poly/oligomer to block diffusion from one compartment to the other.

9.2. Aqueous Organic Redox-Flow Batteries

9.2.1. Generality. In aqueous media, the most studied organic molecules are undoubtedly quinones and both methylviologen and TEMPO derivatives. Such electrolytes have the advantage of being highly dissociating for the supporting salts, forming solutions of high ionic conductivity allowing high power densities cycling. The highest conductivities are obtained in acidic environments since proton is the cation with the highest mobility (the Grotthuss mechanism). Similarly, the hydroxide ion is the most mobile anion, so many studies in aqueous media are also carried out in basic media. However, these two electrolytes have the disadvantage of being very reactive toward organic molecules: protons are responsible for degradation by acid catalysis (polymerization etc.), and hydroxide ions are good nucleophiles (hydroxylation). For example, it should be remembered that cleaning glassware in organic chemistry is often carried out in potash baths.

In the case of quinones, these reactions are particularly troublesome (e.g., Michael reaction) and very effective in both acidic and basic media, so that after a few cycles, the initial molecule is completely transformed and in general the associated loss of capacity is significant.⁴³⁵ Similarly, quinones tend to dimerize, decreasing the capacity that can be addressed.⁴³⁶ As far as methyl viologen derivatives are concerned, they are stable only in a neutral or acidic medium; in a basic medium an elimination reaction takes place resulting in the loss of redox properties. These compounds also tend to dimerize, resulting in one electron reactions instead of two.⁴³⁷ Similarly, in highly acidic environments, TEMPOs undergo degradation reactions.⁴³⁸

In all cases, it is necessary to develop sometimes complex strategies to avoid these adverse reactions for the battery operation and stability. In terms of solubility, by functionalization it is possible to achieve solubility values in about 2 M. In the case of quinones, the electrochemical and solubility properties are very strongly dependent on the number and substitution positions.⁴³⁰ Thus 9,10-anthraquinone-2,7-disulfonic acid (AQDS) retains a high electrochemical reversibility while being highly soluble, which is not the case for other disulfonates.⁴³⁹ Generally speaking, aqueous ORFBs have many advantages: nontoxic, low solvent and salt costs, highly conductive solution. However, they pose two important and very difficult problems: the small window of potential associated with this solvent and its reactivity with organic molecules.

9.2.2. Main Examples of Aqueous ORFB. Many works have been carried out over the last 5 years in the field of aqueous ORFBs, we have chosen a few didactic examples to show the diversity of approaches and the performances that can be obtained with this technology to date.

Aziz's group (Harvard University) has conducted numerous studies on the use of quinone for ORFBs, or combined organic/inorganic batteries (quinone -Br₂, quinone ferrocyanide).^{434,440} Their studies focus mainly on the use of sulfonated (AQDS acid medium) or hydroxylated (DHAQ basic medium) quinones that can achieve electron concentrations >1 M (Figure 22a). The output cell voltage obtained with the full system 0.5 M DHAQ/0.4 M ferrocyanide is about 1.2 V. The battery was tested for 100 cycles at a current density of 100 mA cm⁻² and showed an energy efficiency greater than 80% and a capacity retention of 90%. The maximum power density is 400 mW·cm⁻². No significant degradation of the electrolyte seems to occur. With ADQS in sulfuric acid medium (1 M) as negative electrolyte, associated with 3.5 M hydrobromic acid and dibromine (0.5 or 2 M) the cell voltage is 0.8 V. Different types of carbon felt and membranes have been tested to optimize battery performances. With a 212 Nafion membrane and 2 M Br₂, 3 M HBr, the battery reaches a power peak at 1 W cm⁻² which is extremely high for a flow battery. It should be noted, however, that this was possible thanks to extremely high electrolyte flows (400 mL min⁻¹) for an electrode surface area of 2 cm², which is very demanding on the consumption of the pumps.

Schubert's group (University of Jena) has developed an approach combining methyl viologen derivatives (low potential) and nitroxide (high potential).^{441,442} These organic compounds are reversible in electrochemistry and have very high electron transfer kinetics. The voltages of the cells reached are 1.4 V (Figure 22b). The TEMPTMA derivative has a solubility of 2.3 M in a solution of NaCl 1.5 M which corresponds to a theoretical capacity of 61 Ah. The flow battery combining MV and TEMPTMA (2 M each) addresses the maximum capacity of the electrolyte up to a current density of about 100 mA cm⁻². The energy efficiency is greater than 70%. At 80 mA cm⁻² the battery is stable over 100 cycles without significant degradation of performance. To avoid using an ion exchange membrane, polymers have been developed from these molecular units. Due to the steric encumbrance of these polymers, a simple porous membrane is sufficient to prevent the two compartments from mixing. Ten Ah L⁻¹ electrolytes are made by dissolving these polymers in 2 M NaCl solution. The battery thus formed is capable of cycling up to current densities of 50 mA cm⁻² without significant loss of capacity. The properties are stable

over 90 cycles with a loss of less than 10% in capacity. The energy density of redox fluids is in the order of 10 W L⁻¹.

Liu's group (Utah State University) has developed several types of chemistry based mainly on viologen derivatives (negative) and either ferrocene derivatives or dibromine in positive compartment (Figure 22c).^{443,444} In particular, they used a sulfonate substituted viologen derivative to make a mixed organic/inorganic (Br₂) RFB. The output voltage of the cell is about 1.4 V. The synthesized molecule has been tested in a neutral medium (NH₄Br) at concentrations up to 1.5 M (3 N). The power densities obtained are as high as 227 mW cm⁻² for a current density of 300 mA cm⁻². The stability in charge and discharge over 50 cycles shows a loss of capacity per cycle of 0.11%; the energy efficiency is 78% at 40 mA cm⁻². The energy density of these ORFBs is 30.3 Wh L⁻¹. Tests have shown that the use of carbon nanotubes on current collectors improves battery performance, significantly reducing overpotential issues. This group has also developed ammonium-substituted ferrocene derivatives to improve solubility in aqueous media (>2 M in 2 M NaCl). The batteries produced have a cell voltage of 1 V and energy efficiencies that are highly dependent on current density (72% at 40 mA cm⁻² and 43% at 100 mA cm⁻²). Aging studies carried out over 700 cycles have shown very high stability (about 0.00014% loss of capacity per cycle).

Narayanan et al.^{445,446} from University of Southern California have developed an ORFB where posolyte and negolyte are quinone based: disulfonated anthraquinone (AQDS) or monosulfonated in negative compartment and disulfonated *ortho*-benzoquinone (BQDS or tiron) as positive electrolyte (Figure 22d). These two compounds have high solubility in acid electrolytes. The cell voltage is 0.8 V at a current density of 80 mA cm⁻². This voltage drops sharply as the current density increases. Several cell geometries and current collectors (carbon felts) have been tested to increase the performance of these batteries. The energy efficiency of a battery composed of BQDS and AQDS 1 M is 70% over 100 cycles. In any case, due to the reactivity of these redox molecules, these batteries have low cycling stability.

Finally, Jin et al.⁴³² from Nanjing University have modified a naphthoquinone by substituting it with a carboxylate group (HCNQ) to increase solubility in a neutral or basic medium (Figure 22e). The battery made with an alkaline electrolyte (KOH 1 M) and 0.5 M HCNQ combined with ferrocyanide exhibits an output voltage of 1 V. Power densities of 250 mW cm⁻² were measured at a current density of about 400 mA cm⁻². The capacity loss measured over 50 cycles is 0.12% per cycle, probably resulting from the reactivity of the reduced form of HCNQ. To increase stability, it would be necessary to modify the structure of these quinones to block hydroxylation reactions.

Concerning ORFBs, the aqueous medium is undoubtedly the one with the best performance in terms of energy efficiency and current density. Contrary to what was anticipated, the solubility of redox molecules in aqueous medium is not much lower than what can be measured in organic medium. The power and energy densities are high and in some cases at the same level as those found in the case of inorganic BFRs (vanadium). Although different conversion cell geometries are being tested in some studies, it would now be useful to conduct systematic studies to try to minimize losses due to ohmic drops, or problems related to cross diffusion through the membrane. In general, many of these systems suffer from

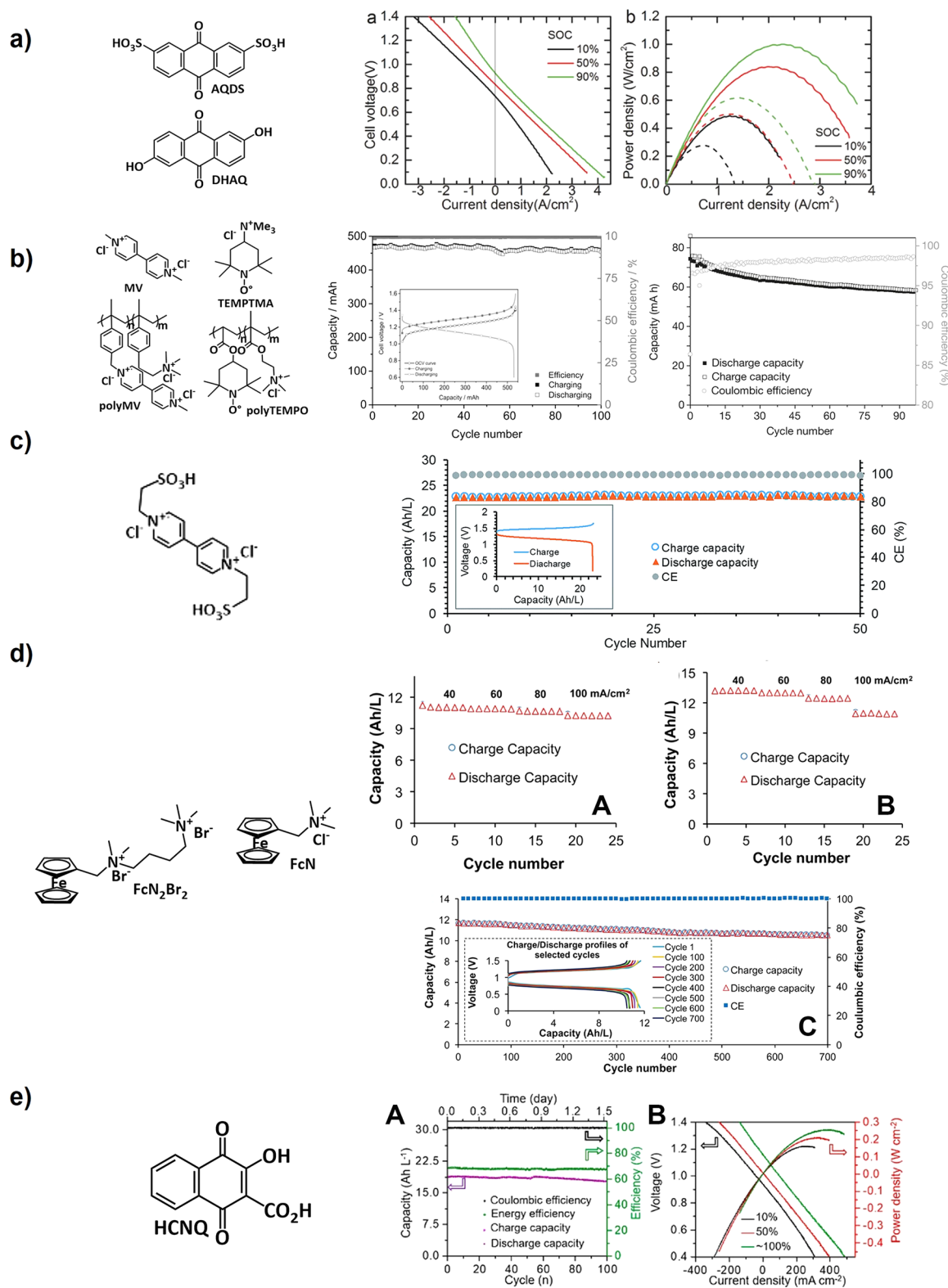


Figure 22. (a) Performance of ORFB composed of AQDS and Br₂ showing both the cell voltage vs current density and the power density vs current density (reproduced with permission from ref 440. Copyright 2016 The Electrochemical Society). (b) Cycling capacity and efficiency of ORFB made of: MV and PEMPMA (center); polymerized MV and TEMPO (left) (reproduced with permission from refs 441 and 442. Copyright 2015 John Wiley and Sons and Nature Publishing Group). (c) Cycling curve and aging behavior of the ORFB developed by Liu et al. Concentration of redox molecule 1 M in NH₄Br (reproduced with permission from ref 443. Copyright 2019 The Royal Society of Chemistry). (d) Capacity vs cycle number at different current densities for (A) FcNCl, (B) FcN₂Br₂ at 0.5 M, and (C) cycling stability of FcNCl/MV battery (0.5 M electrolyte) over 700 cycles (reproduced with permission from ref 444. Copyright 2017 American Chemical Society). (e) Capacity vs cycle number at different current densities for an HCNQ cell (0.5 M) in A. Corresponding voltage and power density vs current density in B (reproduced with permission from ref 432. Copyright 2018 American Chemical Society).

poor cyclability, particularly in concentrated conditions, due to the numerous possible decomposition reactions.

9.3. All-Organic Redox-Flow Batteries

Redox batteries using an organic solvent have been strongly developed in the literature during the years 2000–2010, mainly with compounds from coordination chemistry with several stable redox states; more recently, the use of organic molecules has strongly increased. The main advantage of working with organic solvents is to have larger potential windows and therefore to increase the energy density. The voltages obtained with devices where both fluids circulate are at most in the order of 2.5 V. This is mainly due to the fact that when the molecules are in solution no SEI can be formed. SEI layers are formed on the surface of particles inserting Li at very low potential and protect the solvents from decomposition. Due to main solvent stability window, it is necessary that the redox potential of the compound used in the negative electrolyte should be at the most in the order of 1 V vs Li^+/Li . Therefore, hybrid devices have been developed combining a Li-based negative and an organic positive flow cell. Another difficulty comes from organic electrolytes: low ionic conductivity, about 100 times lower than aqueous electrolytes. This results in important ohmic drop and decreases the voltage efficiency. Thus, a complete optimization of the cell core would be necessary to counter this phenomenon.

Various cells configurations are used to test new compounds by (i) associating two organic redox couples, (ii) carrying test in symmetric cells, or (iii) Li/RFB hybrid cells. The latter, due to the low potential of Li, have very high energy density, up to about 200 Wh L^{-1} but power density remains very low due to current limitation (less than 1 mA cm^{-2}). However, to date, no redox solvent-based electrolyte battery has been able to achieve a true industrial scale demonstrator. Many questions remain to be answered, such as the associated costs, safety, and solubility, electrolyte viscosity, which is generally very high in concentrated organic media, and calendar and cycling stability over very long periods. For example, there are few studies where highly concentrated electrolytes (0.5–1 M) are tested in flux configuration mainly due to the high solutions viscosity. The few systems we have selected to discuss are the most advanced and representative of these devices.

9.3.1. Main Results in Mix Configuration (Li/Organic RFB). The Pacific Northwest National Laboratory (PNNL) has particularly tested several types of strategies and redox molecules in mixed configuration.^{447–449} First, anthraquinone derivatives modified to increase their solubility were used, then TEMPO, and finally ferrocene derivatives. As the latter does not provide better properties than other approaches, it will not be discussed in this review, only the first two strategies are described below.

Wang et al.⁴⁴⁷ proposed to modify anthraquinones with PEG groups (15D3GAQ) to promote the solubility of the molecule as well as the complexing effect toward Li ions. The electrolyte is composed of a solution of LiPF_6 1 M in PC. This solvent forms a stable SEI with respect to Li metal. The static cell is composed of a Li sheet and a simple Celgard separator that confines the redox molecule to the positive compartment; the concentration of 15G3GAQ being 0.25 M. An average voltage of 2.3 V is measured when the battery is cycled to 0.1 mA cm^{-2} (Figure 23a). The battery properties are stable up to a cycling current of 0.5 mA cm^{-2} but collapse beyond that. Two plateaus corresponding to the two consecutive transfers of 1 electron are observed respectively at 2.15 and 2.40 V

(during charging), respectively. An energy efficiency of 82% is measured; the cycling stability evaluated over 40 cycles shows a loss of about 0.8% in capacity per cycle. The measured energy density is about 25 Wh L^{-1} , with the low concentration used to make the electrolyte (0.5 M in electron) being compensated by the output cell voltage (2.3 V).

Xu, Wang, and co-workers found that TEMPO was highly soluble in carbonate solvents.⁴⁴⁸ Thus in an EC/PC/EMC mixture (4:1:5 w/w) 2.3 M LiPF_6 , TEMPO is soluble up to 2 M. However, it should be noted that the solutions obtained are very viscous and difficult to circulate (67.1 cP at 2 M, 4.02 cP at 0.1 M). The flow cell consists of a Li/graphite mixed negative electrode, a porous physical separator, and a carbon felt through which the electrolyte circulates. The energy density was measured with the cell at 2 M TEMPO and 126 Wh L^{-1} , with an energy efficiency of 70%. Stability in concentrated condition does not seem very high, in dilute solution (0.1 M), capacity losses are about 0.2% per cycle. As there is no ceramic membrane, the cycling currents are higher, up to 5 mA cm^{-2} .

Finally, Lu et al.⁴⁵⁰ reported the use of 10-methylphenothiazine (MPT) melted, then mixed with carbon black (Ketjenblack EC-600JD), and finally ground when solidified. The electrolyte consists of a saturated solution of MPT (0.3 M) in an EC/DEC 1 M LiPF_6 mixture to which the ground solid is added. The MPT in solution acts as a redox shuttle to electrochemically address the solid MPT. It should be noted that without carbon, solid MPT is not electroactive. Mixtures of 0%, 20%, and 40% (in vol.) solid and electrolyte were tested. The electrolytes were tested in static and flow cells. The flow cell is composed of a Li sheet, a ceramic separator (LAGP) and of the electrolyte circulating on a carbon paper. On the cycling curves (Figure 23b), the electrolyte alone (0%) has a plateau at 3.55 V vs Li^+/Li and a capacity of 7 Ah L^{-1} , which corresponds to 87% of the theoretical capacity. With 20% mixture, the cycling curves maintain the same behavior, but the capacity is increased to 27 Ah L^{-1} . The 50% mixture allows to reach a capacity of 55 Ah L^{-1} , which corresponds to an electron concentration of 2.23 M. The energy density of the 40% electrolyte is 190 Wh L^{-1} , one of the highest energy densities demonstrated to date. This is mainly due to the high cell voltage (3.55 V) even if the MPT/carbon Ketjenblack mixture significantly increases the capacity of the solution.

The main problem with these mixed Li/organic molecules flow cell approaches comes from the very low current densities (often less than 1 mA cm^{-2}) that can be passed through the device. This is particularly true if the separator between the two compartments is a ceramic membrane. When the separator is porous, it would appear that the SEI formed on the surface of the Li in the carbonates is beneficial. It would act as an ion exchange membrane while blocking electron transfers to the redox molecules. Thus, molecules in solution close to the negative electrode could not be reduced, which would explain the high Coulombic efficiency of these devices. On the other hand, at high concentration in redox molecules, the SEI is modified and/or no longer succeeds in blocking these electron transfers and the Coulombic efficiency falls strongly (Coulombic efficiency 99% at 0.1 M, 91% at 0.8 M, 85% at 1.5 M, and 84% at 2 M).⁴⁴⁸ Finally, these devices do not allow the power and energy density to be separated; they are therefore more limited in terms of application.

9.3.2. Main Results in Liquid All-Organic Cell Configuration. Argonne laboratory and their collaborators have optimized the structure of phenolic ethers used as

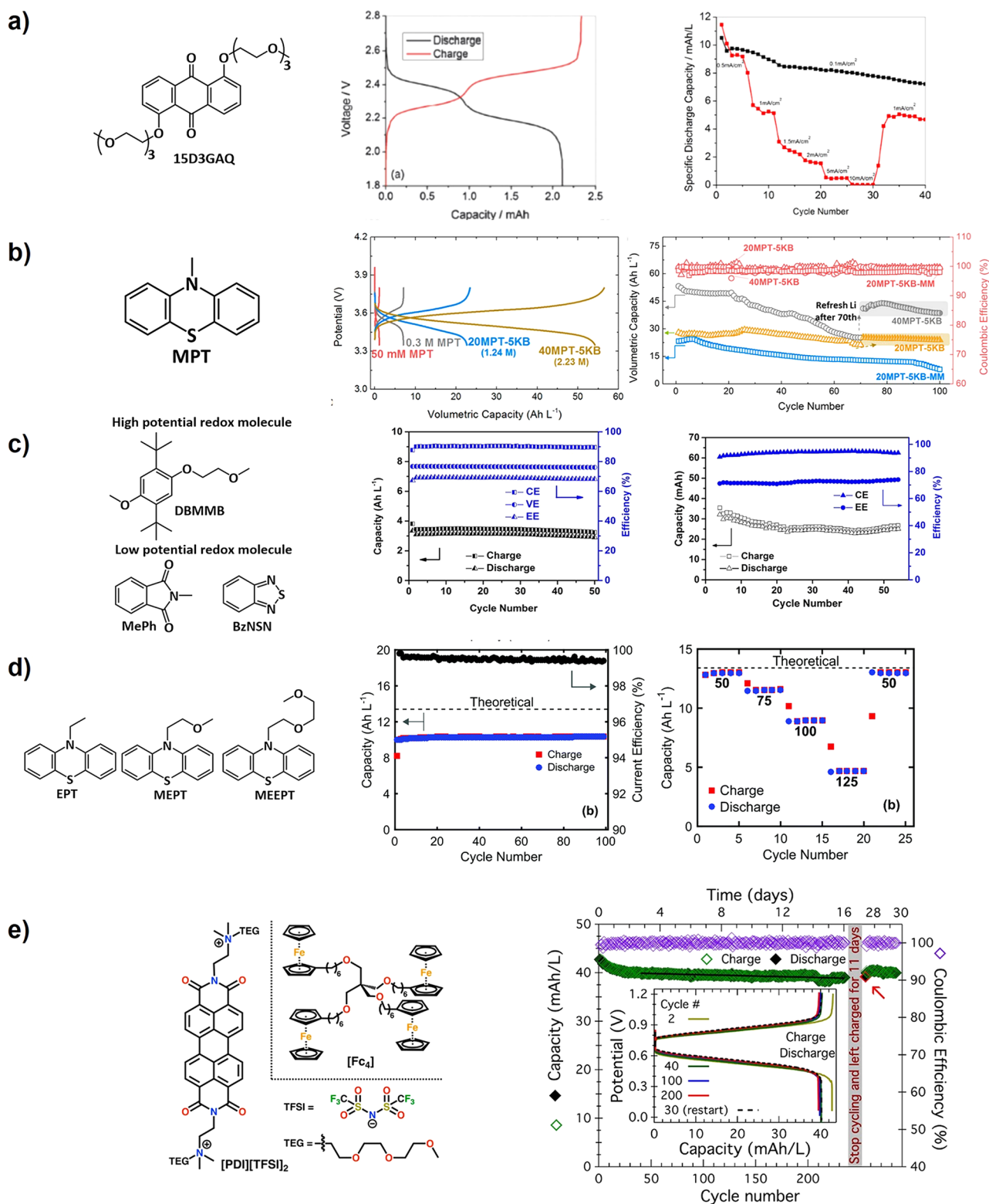


Figure 23. (a) Cycling performance and rate capability reported by Wang and co-workers of the cell with 0.25 M 15D3GAQ as polysolite and lithium foil as anode (reproduced with permission from ref 447. Copyright 2012 The Royal Society of Chemistry). (b) Cycling performance of the Li/MPT flow cell reported by Lu and co-workers (reproduced with permission from ref 450. Copyright 2018 American Chemical Society). (c) Cycling performances of ORFBs based on MePh/DBMMB 0.3 M in DME–M LiTFSI (left) or BzNSN/DBMMB 0.5 M in ACN 1 M LiTFSI (right) reported by Wei and co-workers (reproduced with permission from refs 452 and 453. Copyright 2016 and 2017 American Chemical Society). (d) Symmetric flow cell characterization of MEEPT 0.5 M in ACN 0.5 M TEABF₄ reported by Milshstein and co-workers (reproduced with permission from ref 454. Copyright 2016 The Royal Society of Chemistry). Constant current cycling at 100 mA cm⁻² (left), capacity vs cycle number at different current densities (right). (e) Molecule used by Sisto and co-workers to develop dialysis membrane-based ORFBs (left) together with the cycling performance (right), reproduced from ref 455.

high-potential molecules in order to increase their solubility, and stability.⁴⁵¹ DBMMB offers the best compromise in terms of viscosity, stability and diffusion coefficient. Its redox potential is about 0.78 V vs Ag^+/Ag , so it has been retained and implemented against several low-potential and highly soluble molecules: BzNSN and *N*-methylphthalimide (MePh).^{452,453} MePh has a reduction potential of about -1.79 V vs Ag^+/Ag in 1 M LiTFSI DME electrolyte. A major effort has been made to choose a porous membrane of the Celgard or Daramic-type that is effective in preventing species mixing and does not generate a too high ohmic drop. A Daramic 175 membrane was selected to make a complete redox-flow cell using an equimolar mixture of DBMMB and MePh at 0.3 M in 1 M LiTFSI DME electrolyte. Although tested only over about 50 cycles, the cell capacity is constant at about 3 Ah L^{-1} for an energy density of 9.3 Wh L^{-1} . This cell is able to work at current densities close to those used in aqueous ones: 50 $\text{mA}\cdot\text{cm}^{-2}$ with no significant degradation of its performance. At this current level, the energy efficiency remains above 60%. It is interesting to note that at low current the Coulombic efficiency is not very good due to the cross diffusion of species through the porous membrane while at high current density the voltage efficiency drops due to the ohmic drop. The redox potential of BzNSN is -1.58 V vs Ag^+/Ag in 1 M LiTFSI ACN electrolyte, with its solubility being 2.1 M when considering 2.1 M LiTFSI ACN as the electrolyte.

An electrolyte containing an equimolar mixture of BzNSN and DBMMB (0.5 M) in 1 M LiTFSI ACN as electrolyte was cycled in a redox-flow cell composed of two carbon felt electrodes and a Daramic type separator (800 μm). Due to the viscosity of the solution and the problems of cross diffusion through the membrane, the current density applied is 10 $\text{mA}\cdot\text{cm}^{-2}$. The energy yield is 72%, mainly due to ohmic drops. The energy density is in the order of 6–8 Wh L^{-1} . The stability of the cell is not very good (50 cycles) probably due to the reactivity at high concentration of the species that compose the electrolyte. These studies have shown that DBMMB derivatives are potentially relevant for the design of a fully organic redox-flow battery. They are extremely soluble in organic electrolytes (2–3 M) and the radicals resulting from their oxidation are stable in DME solvents. The two low-potential molecules tested, particularly BzNSN, are soluble up to 5 M, but their solutions are highly viscous precluding their use in flowing cell.

Kentucky University has developed organically soluble phenothiazine derivatives.⁴⁵⁴ MEEPT has been selected as the most efficient compound: it is liquid at room temperature, and its solubility in 0.5 M $n\text{Bu}_4\text{NBF}_4$ ACN is greater than 2 M. It is electrochemically stable, and it is possible to prepare both forms, neutral and oxidized, easily by chemical methods. The core of the conversion cell has been optimized to reduce both ohmic drop and losses related to fluid flowing through the system (channel electrodes). The optimized cell has a resistance of about 3.3 $\Omega\cdot\text{cm}^{-2}$. The assembly was tested in a symmetrical configuration with an electrolyte composed of 0.5 M MEEPT at 50% state of charge with a theoretical capacity of 13.4 Ah L^{-1} . In constant current cycling at 50 and 100 $\text{mA}\cdot\text{cm}^{-2}$, the measured capacity is respectively 97.3% and 60% of the theoretical capacity. Over 100 cycles (80.6 h in total) at 100 $\text{mA}\cdot\text{cm}^{-2}$, the capacity is maintained, and no significant loss is observed.

Columbia University, NY, has developed a flux battery based on perylene diimide derivatives (negative) and ferrocene tetramere (positive), both of which can achieve electron concentrations > 1 M.⁴⁵⁵ The interest of this work is to demonstrate that

cellulose dialysis membranes, combined with redox compounds with a large hydrodynamic radius, are very efficient to avoid mixing the two electrolytes. The authors also carried out studies on aging both in cycling and calendars (even if carried out in diluted solution). They were able to demonstrate that in 11 days in the charged state, no significant loss of capacity was noted. The cell could be cycled 450 times with an average capacity loss of 0.00614% per cycle.

All organic redox-flow cell faces a lot of problems to develop a commercially viable system able to really compete with aqueous inorganic chemistries. This is mainly due to the fact that the molecular parameters are all interdependent. The fact of wanting high cell voltages implies the use of compounds where reduced (materials with very low potential) or oxidized (materials with very high potential) forms are poorly stabilized and therefore very reactive. From a solubility point of view, the use of highly concentrated solutions further increases decomposition phenomena. This often results in poor cycling stability and is in addition to the fact that calendar aging is almost never achieved or under very diluted conditions that are more favorable.⁴⁵⁶ Organic solutions that are highly concentrated generally become highly viscous, causing problems for flowing (pumps power consumption) and voltage efficiencies as these solutions become less conductive. The diffusion coefficients of redox species and ions decrease when viscosity increases with the result of lower apparent electron transfer kinetics. This results in high overvoltage values and low energy yields, often well below 60%. This probably explains why there are no flow cell studies at concentrations above 2 M in the literature, while several molecules have higher solubility values. The main interest of the studies in organic media is that due to the swelling of conventional ion exchange membranes and a high cross over, combined with low electrolyte conduction (high overvoltage), the community has been forced to develop membrane-free approaches, some of which have proven to be relevant.

9.4. Summary

The use of organic molecules to make electrolytes for flow batteries is now well described in the literature. Dozens of different molecules have been tested in various cell configurations. From a properties and behavior point of view, electrolytes based on organic molecules face the same problems as inorganic compounds: solubility, high viscosity of concentrated solutions with the result of a decrease in apparent electron transfer kinetics (overvoltage between charge and discharge), and a high power consumption by the pumps. Since the intrinsic stability of organic molecules in solution is lower than the stability of inorganic compounds, cycling and calendar stability are generally less good.

This stability aspect remains the key point to go further. Many parameters must be taken into account to understand the degradation of ORFB performance: molecules in solutions are much more reactive than in the solid state, in addition they are in contact with different materials (plastic, stainless steel, and so on) which can act as catalysts. Most of these compounds are sensitive at least in one redox state to oxygen traces, which is difficult to prevent in the long term (leakage). Reactions are also possible, for example, with other components of the electrolyte, such as the solvent (substitution reactions, hydrolysis, ...), the supporting salts, or the molecule itself (dimerization or polymerization reaction). In addition, reactivity may change with molecules redox states, a reduced

one will be more sensitive to reactions with an electrophile, while oxidized molecules will be more sensitive to reactions with nucleophiles. Therefore, it is necessary that all other components of the electrolytes be as unreactive as possible. It can be expected thanks to functionalizations to stabilize a molecule by blocking some degradation reactions. For example, the reduced state of dihydroxyanthraquinone tends to degrade through oxidative coupling. To avoid this side reaction, the functionalization of hydroxyl groups by PEG, alkyl carboxylate, or alkyl phosphate chains has been successfully proposed. However, these new molecules become sensitive to hydrolysis reactions and degradation reactions can occur.^{431,457} This observation is general; attempting to stabilize a molecule in a given electrolyte may result in a change of its reactivity or redox property that makes the molecule less or no more relevant for the application.

In most cases, crossover phenomena through the membranes are harmful. To compensate for this, the development of stable molecules in at least three stable redox states, which can serve both as polysolutes and as negolytes (such as vanadium), would greatly improve the stability of ORFBs. This would also allow the reservoirs to be rebalanced when the transfer of solvent by electro-osmosis becomes too high. All these constraints result in rather low overall energy yields (65%) compared to other battery-based storage systems (90%) but much better than the cycle associated with hydrogen: “electrolyzer, storage, fuel cell” whose total efficiency is around 25%. From the grid point of view, the real advantage of RFBs is that they decouple power and energy; they are the only storage systems that allow this.

For the development and credibility of ORFBs, it is now necessary to rationalize the tests and studies carried out in the literature. Indeed, few tests are carried out under the same conditions and these are generally not representative of the final application. For example, it is important that systems should be tested at the highest possible concentrations. Systematic studies of cycling and calendar aging must be carried out. During cycling studies, it is important that the time of each cycle be representative of the RFB application (*i.e.*, 4 to 12 h of energy storage). With regard to the flow rates used to carry out the measurements, very often they are disproportionately high to compensate for the high viscosity of the concentrated solutions. Moreover, depending on the cell geometry used, the flow rate does not have an important meaning. It would be more interesting to indicate the linear velocity of the fluid on the surface of the electrodes and to keep these values as low as possible to avoid that the pumps consume more energy than the energy stored in the battery.

10. CONCLUDING REMARKS

Almost 170 years after the invention of the first operational rechargeable battery by G. Planté thanks to metal-based electrode materials, this tutorial review was intended to highlight several opportunities offered at the turn of the 21st century by the reversible redox chemistry to promote innovative electrochemical devices based on naturally abundant chemical elements (including biomass) while improving the environmental footprint. Indeed, we have shown in this article that the world has drastically changed since Planté's invention through the ongoing modernization of our societies but at the price of continuous consumption of both energy and nonrenewable materials at the expense of the environment.¹¹⁵ Changing the historic roadmap followed by our current energy engineering is

nowadays mandatory in the general interest. In this context, global demand for batteries multiplies to store renewable energy, promote electromobility, and power the continued development of portable electronics and emerging technologies (mobile devices, IoT, AI, robotics, etc.). Seeking to develop innovative, efficient, and less polluting and energy consuming chemistries is therefore important today while jointly developing better recycling solutions (and second use).

Depicted as a parallel and relatively recent research field in the history of rechargeable electrochemical storage systems, we have sequentially summarized the present state-of-the-art and highlighted important works that have contributed to the recent progress in organic-based rechargeable systems by covering all possible technologies and cell configurations to date. The as-obtained performance figures have been described without avoiding limitations. Some of the key performance metrics of organic electrode compounds such as specific energy, working potential, and cycling stability already look promising, and material design strategies specific to these metrics have been preliminarily established. Challenges remain for developing efficient storage solutions that simultaneously excel in all these metrics. It seems probable that the practical use of organics for the electrochemical storage in a near future could be through the development of ORFBs due to their attractive features of high power density and low cost for large-scale energy storage.

In terms of solid electrode materials (for “sealed” batteries), electroactive molecules with simple structures such as simple quinones could offer the best balance between high discharge potential and high specific capacity, but stable cycling requires proper immobilization of these molecules which, until now, cannot be done without impacting potential and capacity. Two directions may directly counter this dilemma. The first is a chemical path revolving no-compromise immobilization. Rational connection of molecular building blocks complemented by suitable synthesis methods has been successful in preserving the full redox characteristics of active cores as seen in OEMs like PAQS and P(NDI2OD-T2). The second is to suit OEMs with solid electrolytes where dissolution is a nonissue. Solid-state batteries are emerging as an alternative to the traditional liquid electrolytes to enable safer and higher-energy batteries. The nondissolving nature of solid electrolytes is an additional perk specifically useful for organic batteries. In addition, p-type materials could offer access to molecular (metal-free) batteries as well as possible assemblies with n-type systems to promote dual-ion cells.

Continued evolution of organic batteries will inevitably involve a better understanding of involved electrochemical mechanisms (especially in the solid state) as well as the development of new OEMs, which is both a strong suit for organic compounds from the fundamental study point of view and a potential uncertainty for practical applications. Organic compounds are known to have good tuning knobs to manipulate the molecular structures and many subsequent properties, but complicated functionalization can drive up synthesis cost. Two currently practiced approaches could lead to a balance between performance and cost. One scours through structures that can be synthesized from cheap raw materials via simple, few-step, and high-yield reactions, the other prioritizes function and performance with no specific focus on minimizing cost. At an early stage of research and development, the former approach rarely affords high-performance candidates due to the limited options, while the latter could end up with prohibitive costs. Overtime, however, the building blocks found by the former and

the design strategies established by the latter will merge the two approaches and strike the balance. Beyond the direct using of redox-active organics as the main active electrode compounds, other functionalities can be used in an electrochemical cell such as the hybridization of the conventional inorganic active materials with organic redox-active polymers giving rise to fast electrode kinetics. Thus let us recall that electrical properties of solid composite electrodes are critical to electrochemical performances, whatever the considered technology. This is especially the case for thick electrodes which are highly sought-after because they enable in principle simultaneous increase in volumetric and specific energy densities and decrease in price. It is estimated that 20 to 80% of power losses in the case of a thick electrode originate from insufficient electronic conduction.⁴⁵⁸ The design of electronic conductivity at different scales is not easy, because it is currently based on the use of carbon-based conductive additives that are difficult to disperse homogeneously on the one hand, and on the other hand, that renders difficult the manufacturing of thick composite electrodes, because of the unstable nature of the electrode inks. In addition, the loss of intercluster and interparticle contacts due to volume variations of active materials is a major cause of the aging of battery electrodes.⁴⁵⁹ It is therefore mandatory to add polymeric binders (insulators), with the downside of a difficult compromise between electronic conductivity and mechanical properties of the composite electrode.⁴⁶⁰ The use of electron conducting binders or even redox binders (“smart binder”) appears therefore quite attractive, since it would enable the design of electrodes with lower amount of carbon and binder additives. This objective was pursued in the particular case of LiMPO_4 ($M = \text{Fe}, \text{Mn}$). As early as 2006, Goodenough and co-workers showed that carbon-coated LiFePO_4 particles can be directly connected to the current collector using a matrix of p-doped PPy or PANi,^{461–463} while Grätzel was actually the first to connect non-carbon-coated LiMPO_4 ($M = \text{Fe}, \text{Mn}$) particles to the current collectors using molecular wires.⁴⁶⁴ In the latter, the Fermi levels of the organic matter and the active material need to be adjusted while the adsorbed wires should be percolated to allow for cross-surface charge. This approach was also recently investigated by Nishide and Oyaizu using nonconjugated radical polymers (radicals are densely introduced as the pendant groups) that were specifically designed for fast charging of LiFePO_4 or LiCoO_2 .⁴⁶⁵ Schougaard and co-workers also showed a poly(3,4-ethylenedioxythiophene) coating at the surface of bare LiFePO_4 particles advantageously replaced the carbon coating.⁴⁶⁶ Targeting the contemporary concerns of industry-relevant electrodes and especially thicker ones, Gaubicher and Blanchard⁴⁶⁷ used a short thiophene-based π -conjugated system as a molecular junction between uncoated LiFePO_4 and multiwall carbon nanotubes within undensified 2 mAh cm^{-2} electrodes. Electrochemical and electrical properties of such electrodes demonstrate the key role of molecular junctions to reach power and cyclability performances comparable to those of carbon-coated LiFePO_4 electrodes. To conclude, although this research activity is still in its infancy and much remains to be done to get attractive performances, redox-active organic compounds can be perceived today more than ever as an alternative chemical choice depending on the targeted application. We hope that this review will be a source of original and fresh ideas for our readers.

ASSOCIATED CONTENT

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Supporting Information

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The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemrev.9b00482>.

Evolution of the global EV stock by vehicle's category; estimated world LIB manufacturing capacity for automotive applications, International trade flows, and LIB cell manufacturing capacities in 2016; critical raw Materials in the EU, 2017; world mining industry production for materials used in LIBs in 2016; the concept of renewable organic battery; selection of redox-active units used in ORFBs. (PDF)

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Notes

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The authors declare no competing financial interest.

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