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Graphical Abstract

Current Opinion in Electrochemistry xxx (2018) xxx–xxx

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Philippe Poizat^{1,2,*}, Franck Dolhem^{3,4}, Joël Gaubicher¹

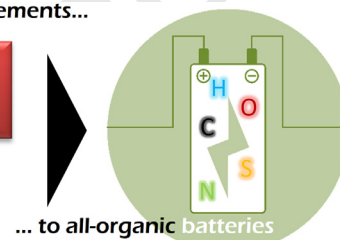
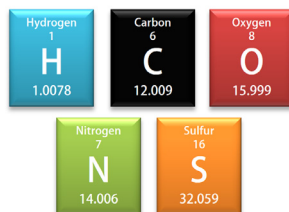
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From abundant chemical elements...





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Review Article

Progress in all-organic rechargeable batteries using cationic and anionic configurations: Toward low-cost and greener storage solutions?

Philippe Poizot^{1,2,*}, Franck Dolhem^{3,4} and Joël Gaubicher¹

1 Our entry into the Fourth industrial revolution since the turn of
2 the century is set to revolutionize our daily life notably with the
3 blooming of digital technologies such as communications,
4 artificial intelligence, technologies related to the Internet of
5 Things, 3-D printing or nano/biotechnologies. It is however
6 hoped this new paradigm shift will integrate sustainable
7 development goals and actions to address the critical damage
8 caused by the previous industrial revolutions especially the
9 threat of global warming. We have to be particularly aware
10 there remains the urgent need for cleaner energy technologies
11 which calls for a radical change in the energy mix to favor
12 renewable energy and environmentally responsible energy
13 storage solutions. Organic materials should provide
14 opportunities to further improve existing energy storage
15 technologies while offering sustainable, versatile and
16 potentially low-cost energy storage devices. This review seeks
17 to provide an update on all-organic battery assemblies
18 reported to date as well as some perspectives we can expect
19 in the future notably for stationary applications.

Addresses

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Introduction

A few years ago, we outlined a personal view about the
tricky questions of energy supply, its storage and conver-
sion in the early 21st century and underlined the impor-
tance of developing efficient, safe but also low-polluting
electrochemical storage solutions [1]. To date, commercial
batteries exclusively include inorganic electrode materi-
als notably 3d transition metals which are scarce, expen-
sive and energy greedy [2]. In contrast, organic materials
enable access to low cost and possibly greener compounds
because composed of naturally abundant elements (i.e.,
C, H, O, N or S) moreover they are easier to recycle. In
addition, they offer high structural designability through
the well-established principles of organic chemistry and
notably access to both n- and p-type electrochemical stor-
age mechanisms [3] making various cell or electrode con-
figurations possible (Figure 1).

In 10 years, tremendous progress has been made to pro-
mote organic compounds in various rechargeable storage
devices giving rise to nearly 15 published review articles
especially for applications in non-aqueous (metallic) Li or
Na-based batteries; for very recent examples, the reader
could refer to refs. [5–10]. Notwithstanding this abundant
literature, there appeared to be a lack of a comprehen-
sive summary dedicated to all-organic cells that are also
increasing in number thanks to this rapid progress on or-
ganic electrode materials. Herein, we have attempted to
fill the gap by thoroughly reporting prototype examples of
all-organic batteries investigated until now including the
pioneering examples studied in the mid-80s. One particu-
lar exciting option is the true possibility of storing elec-
tricity through cell reactions devoid of metals making the
concept of molecular-ion batteries possible as pointed out
by Yao's group in a recent visionary article [11**]. In fact,
the shuttling ion can be either protons or ammonium-type
cations but also anions. In the latter case, a large choice of
chemical structures is accessible from atomic to molecular
anions. Moreover, anions tend to show higher limiting mol-
ar conductivity values in ordinary organic solvents due to
lower solvation effects. In aqueous electrolytes, promising
organic assemblies based on the use of low-cost chemical
compounds could also pave the way for innovative local
stationary electrochemical storage devices.

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This review comes from a themed issue on **Batteries and Supercapacitors**

Edited by **Daniel Belanger**

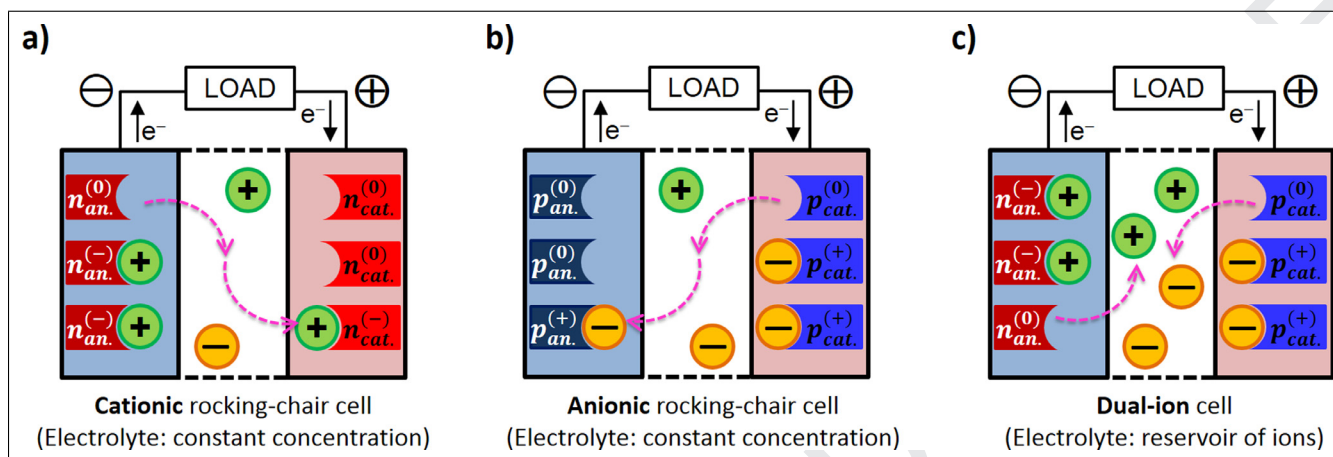
For a complete overview see the [Issue](#) and the [Editorial](#)

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Figure 1



Schematic of fundamental cell configurations obtained by playing with both n- and p-type organic electroactive materials shown during the discharge process. (a) All-organic cell incorporating n-type electrode materials only (cationic rocking-chair). (b) Symmetric situation with p-type electrode materials (anionic rocking-chair). (c) Mixing both n- and p-type electrode materials (dual-ion configuration). Note that the use at the electrode level of mixed n/p-type moieties can be envisaged too [4]. In addition, a given organic skeleton bearing a redox-active p-type moiety exhibits as a rule a formal potential higher than that of the corresponding n-type counterpart.

Advances in non-aqueous all-organic batteries

All-organic batteries are naturally characterized by very different assemblies depending on the selected active material (p- and/or n-type) as well as the chemical nature of the charge carriers (cationic or anionic charge balance). Therefore, we opted for a summary table for the sake of comparison and to make the discussion easier. Hence, Table 1 lists the possible organic cell configurations, the chemical nature of the used electrode materials¹ and electrolyte as well as some performance metrics. First of all, it seemed to us relevant to start our overview with battery examples coupling inorganic and organic electrodes. In this area, since aromatic carboxylates proved to be interesting candidates as negative material [7], Toyota Laboratories reported in 2014 [12*] very good electrochemical performance by coupling the high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with dilithium 2,6-naphthalene dicarboxylate leading to 3.9 V Li-ion cells and demonstrated the possible construction of 8 V-bipolar laminated Li-ion batteries (LIBs) delivering high specific power and energy values (Table 1, #1). Preliminary data were also published by Mou *et al.* [13] using a composite anode made of calcium terephthalate ball-milled with graphite face to LiCoO_2 as the cathode material (Table 1, #2). Medabalmi *et al.* [14] made a Na-ion coin-cell prototype operating at ~ 3.2 V by using the sodiated form of 2,6-naphthalene dicarboxylate and $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2/\text{rGO}$ (rGO standing for reduced graphene oxide) for the cathode side but lim-

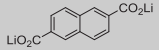
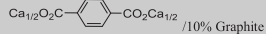
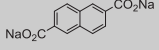
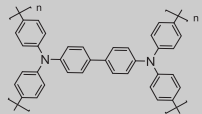
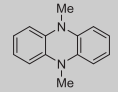


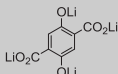
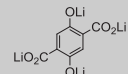
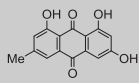

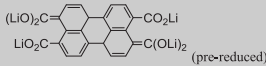
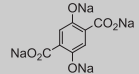
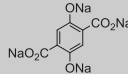
ited stabilities upon cycling were observed (Table 1, #3). Changing for a p-type cathode, Fan *et al.* [15] recently reported a potassium-based dual-ion full battery (PDIBs) based on graphite anode, polytriphenylamine cathode, and KPF₆-based electrolyte (Table 1, #4) that shows quite good cycling stability over 500 cycles. Kang and co-workers [16] examined in a parallel research the performance of a lithium-based dual-ion full batteries (LDIBs) with the *N,N*-substituted phenazine/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ assembly but the cyclability was not discussed at all (Table 1, #5).

The second section of Table 1 concerns all-organic batteries incorporating n-type materials only (cationic configuration). Our group [17] was the first to report an all-organic Li-ion cell based on renewable raw materials thanks to the amphoteric redox property of $\text{Li}_4\text{C}_6\text{O}_6$ which makes the design of a cell exhibiting ~ 1 V as output voltage (Table 1, #6). Later we tried to go further by investigating dilithium (2,5-dilithium-oxy)-terephthalate (Li_4 -p-DHT) as another dual-function electrode material deriving from biomass [18]. However, Chen's group reported the best performance with this material (Table 1, #7) at the condition to be prepared as nanosheets [19]. This second prototype of organic LIBs exhibits an average operation voltage of ~ 1.8 V and an energy density of about 130 W h/kg together with long cycling life (1000 cycles) when supported on graphene [20**]. A biomolecule-based full LIB was even proposed by Hu *et al.* [21] using a naturally occurring quinone (emodin) as the cathode and lithium humates as the anode. Nevertheless, a fast capacity fading was observed probably due to the poor stability of the electrode materials (emodin bears three OH groups whereas lithium humates cannot be well

¹ Note that the following terms "cathode" and "anode" refer to positive and negative electrodes, respectively.

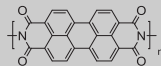
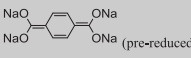
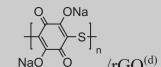
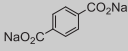


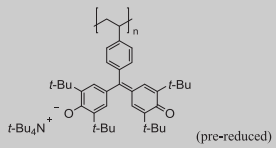
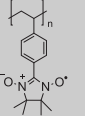
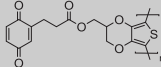
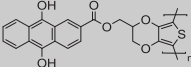




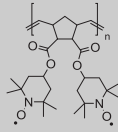
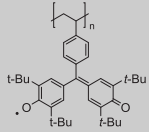
Table 1

Organic batteries.

#	Cell configuration (ionic carriers)	Positive material or "cathode"	Negative material or "anode"	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh/g), Specific energy (Wh/kg), Final coulombic efficiency, Loading (mg/cm ²)	Ref.
n-type inorganic cathode assembled with n-type organic anode								
1	Li-ion	LiNi _{0.5} Mn _{1.5} O ₄		1 M LiPF ₆ in EC:DMC:EMC 3:4:3 (v/v/v)	3.9	96%, 100, 1 C	77 ^(c) , 300 ^(c) , -, -	[12]
2	Li-ion	LiCoO ₂	 /10% Graphite	1 M LiPF ₆ in EC:DMC 1:1 (v/v)	2.75	82%, 50, 1 C	138 ^(a) , -, 92%, -	[13]
3	Na-ion	Na ₃ V ₂ O ₂ (PO ₄) ₂ /rGO ^(d)		1 M NaClO ₄ in PC	3.2	68%, 20, 13 mA/g	150 ^(a) , -, 33% ^(b) , 2	[14]
4	Dual-ion (K ⁺ /PF ₆ ⁻)		Graphite	0.8 M KPF ₆ in EC:DC 1:1 (v/v)	3.23	75.5%, 500, 50 mA/g	60 ^(b) , 105, -, 1.2	[15]
5	Dual-ion (Li ⁺ /TFSI ⁻)		Li ₄ Ti ₅ O ₁₂	1 M LiTFSI in TEGDME	1.9	-, -, 50 mA/g	163 ^(b) , -, -, -	[16]
n-type organic cathode assembled with n-type organic anode								
6	Li-ion			1 M LiPF ₆ in EC:DMC 1:1 (v/v)	1.0	70%, 50, C/20	-, -, -, -	[17]
7	Li-ion			1 M LiPF ₆ in EC:DMC 1:1 (v/v)	1.8	91%, 20, 48.2 mA/g	225 ^(a) , 130, 99.7%, 1-1.5	[19]
8	Li-ion		Electrochemically pre-reduced lithium humates	1 M LiPF ₆ in EC:DMC 1:1 (v/v)	1.5	50%, 100, 100 mA/g	127 ^(b) , -, 99%, -	[21]
9	Li-ion		 (pre-reduced)	1 M LiPF ₆ in EC:DMC:EMC 1:1:1 (v/v/v)	1.2	81%, 200, 11.3 mA/g	78 ^(b) , 32, 99.6%, 0.8-2	[22]
10	Na-ion			1 M NaClO ₄ in EC:MC 1:1 (v/v)	1.8	76%, 100, 19 mA/g	198 ^(a) , 65, 99%, 1-2	[23]

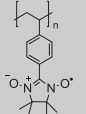
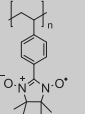
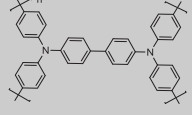


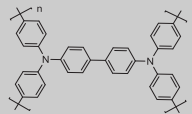
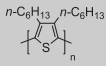


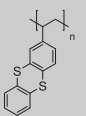
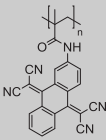
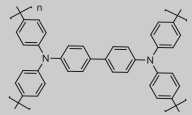
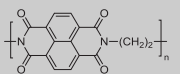
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Table 1 (continued)

#	Cell configuration (ionic carriers)	Positive material or “cathode”	Negative material or “anode”	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh/g), Specific energy (Wh/kg), Final coulombic efficiency, Loading (mg/cm ²)	Ref.
11	Na-ion		 (pre-reduced)	1 M NaPF ₆ in PC	1.35	75%, 20, 50 mA/g	73, -, -, 1.4	[24]
12	Na-ion	 /rGO ^(d)		1 M NaClO ₄ in tetraglyme	1.1	62%, 30, 130 mA/g	210,-, 99.2%, 1	[25]
13	K-ion			1.25 M KPF ₆ in DME	1.1	-, 10, 25 mA/g	70 ^(b) , 35, -, -	[26]
14	R ₄ N-ion	 (pre-reduced)		0.1 M <i>n</i> -Bu ₄ NClO ₄ +0.01 M <i>n</i> -Bu ₄ NOH in CH ₃ CN	0.6	91%, 250, 150 C	29, -, -, -	[27]
15	H-ion			2-fluoropyridinium triflate: 2-fluoropyridine 1:1	0.5	66%, 100, 400 mA/g	103 ^(a) , -, 99.9%, -	[28]
p-type organic cathode assembled with n-type organic anode								
16	Dual-ion (ClO ₄ ⁻ / <i>n</i> -Bu ₄ N ⁺ ; BF ₄ ⁻ / <i>n</i> -Bu ₄ N ⁺)			0.5 M <i>n</i> -Bu ₄ NClO ₄ in PC; 0.3 M <i>n</i> -Bu ₄ NBF ₄ in THF	3.7 2.5	- - -	- - - -	[29]
17	Dual-ion (BF ₄ ⁻ / <i>n</i> -Bu ₄ N ⁺)			0.2 M <i>n</i> -Bu ₄ NBF ₄ in CH ₃ CN	3.1	-, -, 24 mA/g	-, 93, -, -	[30]
18	Dual-ion (ClO ₄ ⁻ / <i>n</i> -Bu ₄ N ⁺)			0.5 M <i>n</i> -Bu ₄ NClO ₄ +0.01 M <i>n</i> -Bu ₄ NOH in CH ₃ CN	0.66	57%, 250, 10 C	32, 22, -, -	[31]

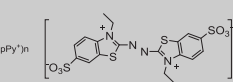
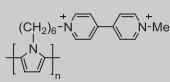

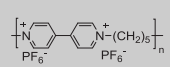
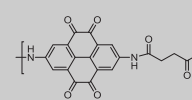
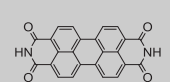
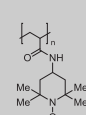
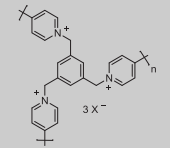
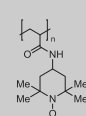
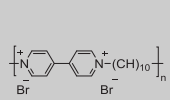
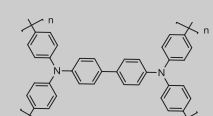
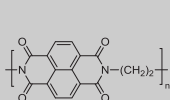
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Table 1 (continued)

#	Cell configuration (ionic carriers)	Positive material or "cathode"	Negative material or "anode"	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh/g), Specific energy (Wh/kg), Final coulombic efficiency, Loading (mg/cm ²)	Ref.
19	Dual-ion (ClO ₄ ⁻ / <i>n</i> -Bu ₄ N ⁺)			0.5 M <i>n</i> -Bu ₄ NClO ₄ + 0.01 M <i>n</i> -Bu ₄ NOH in CH ₃ CN	1.3	68%, 250, 60 C	44, -, -, -	[27]
20	Dual-ion (PF ₆ ⁻ /Na ⁺)			NaPF ₆ saturated in DME:DOL 1:1 (v/v)	1.8	85%, 500, 8 C	200 ^(a) , 92, 99, -	[32]
21	Dual-ion (ClO ₄ ⁻ /Na ⁺)	P(AN-NA) ^(d)		5% _{mol} NaClO ₄ in plastic crystal electrolyte	1.7	80%, 50, 50 mA/g	200 ^(a) , -, -, -	[33]
22	Dual-ion (PF ₆ ⁻ /Li ⁺)			1 M LiPF ₆ in EC:DMC:EMC 1:1:1 (v/v/v)	2.35	-, -, 40 mA/g	250 ^(a) , -, -, -	[34]
23	Dual-ion (PF ₆ ⁻ /Li ⁺)			1 M LiPF ₆ in EC:DMC:EMC 1:1:1 (v/v/v)	3	63%, 60, 40 mA/g	153 ^(a) , -, -, -	[35]
24	Dual-ion (ClO ₄ ⁻ /Li ⁺)			1 M LiClO ₄ in EC:DMC 3:7 (v/v)	1.35	67%, 250, 1C	105 ^(b) , -, -, -	[36]
25	Dual-ion (TFSI ⁻ /Li ⁺)			2 M LiTFSI in ethyl acetate (55°C ≤ T ≤ -70°C)	1.2	-, -, -	90 ^(a) , 33, -, 1	[37]

(continued on next page)

Table 1 (continued)

#	Cell configuration (ionic carriers)	Positive material or “cathode”	Negative material or “anode”	Electrolyte	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Specific capacity (mAh/g), Specific energy (Wh/kg), Final coulombic efficiency, Loading (mg/cm ²)	Ref.
p-type organic cathode assembled with p-type organic anode								
26	ClO ₄ ⁻ -ion			0.2 M LiClO ₄ in CH ₃ CN	1	70%, 100, 0.5 mA/cm ²	16, 15, -, - (thin films)	[39]
27	PF ₆ ⁻ -ion			1 M <i>n</i> -Bu ₄ NPF ₆ in PC	1.8	65%, 100, 100 mA/g	100 ^(b) , -, -, -	[11]
Organic batteries with aqueous electrolytes								
28	Li-ion	LiMn ₂ O ₄		Li ₂ SO ₄ 2.5 M (pH 7)	1.13	80%, 3000, 280 mA/g	81, 92%, -, 2	[47]
29	NH ₄ ⁺ -ion	(NH ₄) _{1.47} Ni[Fe(CN) ₆] _{0.88}		(NH ₄) ₂ SO ₄ 1 M (pH 6)	1	67%, 1000, 0.120 mA/g	35 ^(c) , 35 ^(c) , 97.6%, 2-5	[48]
30	Cl ⁻ -ion			NaCl 0.1 M (pH 7)	1.3	80%, 2000, 10.5 A/g	165 ^(d) , 214 ^(d) , - (100 nm to 1 μm thin films)	[49]
31	BF ₄ ⁻ -ion			NaBF ₄ (pH 7)	1.2	75-80%, >2000, 60 C (67 μA/cm ²)	104 ^(b) , 125 ^(b) , 95 (100 nm thin films)	[50]
32	Dual-ion (TFSI ⁻ /Li ⁺)			LiTFSI 21 M (pH 7)	1	85%, 700, 0.5 A/g	105 ^(b) , 53 ^(b) , ~100, 1	[51]

(a) Based on anode material weight. (b) Based on cathode material weight. (c) Based on the total battery weight or (c') on anode and cathode materials. (d) rGO stands for reduced graphene oxide (e) PANi stands for polyaniline emeraldine base. (f) P(AN-NA) stands for poly(aniline/*o*-nitroaniline). (g) Initial coulombic efficiency.

characterized). Note that a pre-discharge step of the anode was necessary prior to final assembly since emodin (quinone form) is a non-lithiated compound (Table 1, #8). Similarly, Gutel and co-workers [22] assembled a LIB able to show an average cell voltage of ~ 1.2 V and good cyclability over 200 cycles from pre-reduced perylene-tetracarboxylate face to a polyimide as the cathode (Table 1, #9). Taking benefit of the successful Li-ion cell based on Li₄-*p*-DHT, Chen's group [23] investigated the sodiated counterpart material (Na₄-*p*-DHT) and published the first all-organic sodium-ion battery (SIB), which gives an average operation voltage of ~ 1.8 V for a specific energy of about 65 W h/kg (Table 1, #10). Shaijumon and co-workers [24] proposed as SIB the coupling between *N,N*-diamino-3,4,9,10-perylene-tetracarboxylic polyimide as the cathode with the disodium terephthalate (Na₂TP) as the anode. Again the lack of inserted Na⁺ in the pristine polyimide forced them to electrochemically pre-reduce Na₂TP before assembling (Table 1, #11). The cell delivered an initial capacity of 73 mA h/g for an average cell voltage of ~ 1.35 V but with a limited cycling stability. Very recently, Li *et al.* [25**] have gone beyond by associating Na₂TP with sodiated poly(2,5-dihydroxy-*p*-benzoquinoyl sulfide)/rGO composite material (Table 1, #12). In the continuity of our former works on Li₄C₆O₆ [17], in 2016 Chen's group constructed the first example of organic K-ion batteries based on K₄C₆O₆/K₂C₆O₆ system [26] which displayed an operation voltage of ~ 1.1 V and an energy density of 35 W h/kg (Table 1, #13). Other cations than alkali ones were also tested as ionic carriers. Interestingly, when using pre-reduced poly(galvinoxylstyrene) with the tetrabutylammonium ion as the cathode together with poly[4(nitronylnitroxyl)styrene] as the anode, Nishide and co-workers [27] constructed the first n-type full polymer battery free of metal. The test cell certainly exhibited a limited output voltage (~ 0.6 V) but achieved impressive rate performances with 90% of the original capacity maintained at 150 C rate (Table 1, #14). More recently Sjödin and co-workers [28] reported a proof-of-principle study on an all-organic proton battery also devoid of metals using poly(3,4-ethylenedioxythiophene) (PEDOT) functionalized either with *p*-benzoquinone (cathode) or dihydroxyanthraquinone (anode) and working thanks to an original protonated pyridinium triflate-based non-aqueous electrolyte (Table 1, #15).

The third section of Table 1 concerns the dual-ion cell configuration employing naturally (for potential reason) a p-type electrode material for the cathode side (Figure 1); in this cell configuration the electrolyte is the reservoir of ions for the charge compensation within electrode materials. There are more examples reported in the literature for this type of assembly, the first one dating back to the 80s following the discovery of conducting polymers. The first completely organic rechargeable storage battery of this kind were described by MacDiarmid and co-workers in 1981 by taking benefit of

the reversible n- and p-type electrochemical doping of polyacetylene [29]. However, neither cycling curves nor electrochemical performance data were mentioned in the article (Table 1, #16). Then, polythiophene-based full cells were proposed by Inuishi and co-workers exhibiting an energy density of ~ 90 W h/kg [30] (Table 1, #17). Fifteen years ago, a new class of polymers emerged consisting of a polymeric chain with stable radical pendant groups leading to the development of the so-called organic radical batteries (ORBs). Such systems possess the right properties to allow the construction of organic dual-ion cells as well. Nishide and co-workers [31] proposed the poly(galvinoxylstyrene) as an n-type redox active polymer and used the poly(TEMPO-substituted norbornene) as the p-type one (Table 1, #18). The totally organic polymer-based radical battery thus obtained (also devoid of metals) gave an interesting power rate capability since it retained 60% of its initial capacity after 250 cycles at a 10C rate. Later, the same group [27] using poly[4(nitronylnitroxyl)styrene] assembled a symmetric (poleless) cell exhibiting good cycle life (more than 250 cycles) at a 60C rate (Table 1, #19). Deng *et al.* [32] assembled a low-cost all-organic dual ion battery (PF₆⁻/Na⁺) with poly(triphenylamine) as the p-type material and poly(anthraquinonyl sulfide) as the n-type one (Table 1, #20). The same anode was also used by Cao and co-workers [33] together with a poly(aniline/*o*-nitroaniline) and a plastic crystal electrolyte (Table 1, #21). Subsequently, Yang's group proposed to assemble poly(triphenylamine) with poly(3,4-dihexylthiophene) [34] (Table 1, #22). In another study, this group [35] exploited the gap in potential between the p- and n-doping processes occurring in poly(paraphenylene) (Table 1, #23). However, compared to ORBs, such dual-ion cells exhibit featureless cycling curves which resemble more supercapacitor electrochemical profiles. Another dual-ion all-organic battery consisting in poly(2-vinylthianthrene) as the positive material and poly(2-methacrylamide-tetracyanoanthraquinodimethane) as the negative was also investigated by Schubert's group [36]. Although the output voltage was only 1.35 V, the cell was able to sustain almost 70% of its initial capacity after 250 cycles (Table 1, #24). Very recently, Dong *et al.* [37] were able to cycle at very low temperature (up to -70 °C) a dual-ion cell based on poly(triphenylamine) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA)-derived polyimide thanks to an ethyl acetate-based electrolyte (2 M LiTFSI) which exhibits sufficiently high ionic conductivity at low temperature (Table 1, #25).

Lastly, the fourth section of Table 1 recaps the few examples of cell combining two p-type electrode materials. In fact, such cells are scarcer because p-type compounds are naturally characterized by high formal redox potentials except the single family of viologen-related materials. Note that Lee *et al.* studied in the 90s polypyrrole/polyaniline (PAni) then PAni/PAni

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248 full cells but reported data were poor [38]. Pal-
 249 more and co-workers [39] have prepared a polypyrrole
 250 with covalently bonded viologen (4,4'-bipyridine) moi-
 251 eties as the anode and polypyrrole doped with 2,2'-
 252 azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) for the
 253 cathode side, both releasing or accepting a perchloro-
 254 rate anion during the redox processes. Experimentally
 255 this battery exhibited a very low capacity (Table 1,
 256 #26). Yao's group proposed also such a molecular ion-
 257 based "rocking-chair" type battery [11**] with poly(*N*-
 258 vinylcarbazole) as the cathode and also a viologen poly-
 259 mer as the anode (poly(1,1'-pentyl-4,4'-bipyridinium di-
 260 hexafluorophosphate)) (Table 1, #27). The performance
 261 of the battery was much better with this last configura-
 262 tion giving rise to ~ 1.8 V as output voltage coupled with
 263 capacity of 100 mA h/g_{cathode}.

264 Promise and challenges of aqueous organic 265 batteries

266 Organics can also operate in aqueous electrolytes. Al-
 267 though at the expense of energy density, aqueous rocking-
 268 chair batteries constitute a novel and promising technol-
 269 ogy as they are inherently safe, minimize cost and envi-
 270 ronmental impact by comparison to other battery tech-
 271 nologies [5,40–42], which is particularly relevant for pro-
 272 moting low-cost energy storage solutions. This approach
 273 is still affiliated however, with relatively low energy den-
 274 sity, below 50 W h/kg_{18650-cell}², which puts even more pres-
 275 sure on material costs and durability in order to ensure
 276 economic viability. It has been recently shown that the
 277 electrochemical window of superconcentrated aqueous
 278 electrolytes can be expanded to 3 V thanks to the for-
 279 mation of electrolyte-electrode interphase and unusual
 280 water molecule coordination environment [40,43]. How-
 281 ever, it should be stressed as far as energy cost (\$/kW h)
 282 is concerned this voltage gain is counterbalanced by the
 283 mass (~ 2 –5 times that of a 1 M electrolyte) and the price
 284 of these additional salts. Indeed, a bulk energy storage
 285 unit will only be implemented if the cost per unit of en-
 286 ergy falls below 0.03 \$/kW h, a value lower than the cost
 287 of electricity from conventional power sources. This im-
 288 plies that the device must be able to deliver many thou-
 289 sands of charge-discharge cycles over many years (which
 290 for the time being rules out zinc-based systems) to in-
 291 sure storage cost remains in the vicinity of 100 \$/kW h.
 292 Moreover, aqueous batteries are intended for both do-
 293 mestic and large-scale applications and therefore the enor-
 294 mous scale of the required energy transition places limits
 295 on poorly abundant, non-uniformly distributed as well as
 296 monopolized metal resources. To sum up, the relatively
 297 narrow electrochemical window available in aqueous me-
 298 dia together with costs and abundance issues makes even
 299 more challenging the development of appropriate host

materials with optimal potential as well as high chemical
 and electrochemical stability.

One of the emerging approaches followed by several
 groups consists also in considering organic active materi-
 als to substitute inorganic ones with the promise of abun-
 dancy in elements, lower costs and high structural desig-
 nability. Note that only five inorganic materials were
 identified to design aqueous batteries (i.e., LiMn₂O₄
 [44], Na₃Ti₂(PO₄)₃ [44], Fe and Mn-based Prussian Blue
 derivatives [45] and Na₃MnTi(PO₄)₃ [46]). Another de-
 cisive advantage is related to the potential access to su-
 perior specific capacities as organics benefit from multi-
 electron redox reactions. Lastly, the low volumetric den-
 sity of organic compounds is obviously not as detrimen-
 tal for stationary application as it is for mobile ones.
 Despite these benefits, several key issues remain and re-
 cent literature proves the design of economically viable
 full aqueous batteries based on organic materials is still
 a challenging and exciting prospect. First, as mentioned
 earlier for stationary storage the most important criterion
 remains the overall cost of the storage device. Consider-
 ing a plausible voltage of 1.2 V and capacity of 150 mA h/g
 for both the positive and the negative materials, a hypo-
 theoretical 18,650 full cell should enable an energy density
 of about 56 W h/kg_{18650-cell} based on 15 mA h/cm² elec-
 trodes containing 80% of active material. In these con-
 ditions, costs of goods should stay in the vicinity of 5–
 10 \$/kg and therefore any organic chemistry involved for
 material design cannot exceed one or two steps (as a rule
 of thumb, one step corresponds to ~ 5 \$/kg in the pig-
 ment industry). This also serves to reiterate that neutral
 pH and molar range salt concentration of the electrolyte
 should be preferred to minimize production costs and cor-
 rosion issues. The second bottleneck arises from the cor-
 relation between the potential range of the organic mate-
 rials depending on the p- or n-type character. For aque-
 ous batteries plethora of n-type organic materials can be
 designed as anode materials allowing the access to poten-
 tials below ~ 0.3 V vs. SCE (2.95 V vs. Li⁺/Li at neutral
 pH) thanks to the carbonyl/enolate redox moiety. How-
 ever, with the aim to fabricate at least 1 V_{cell}, it is quite
 challenging to reach sufficiently high working potentials
 with n-type materials for the cathode side (>0.4 V vs.
 SCE or 3.65 V vs. Li⁺/Li at neutral pH). Inversely, ex-
 cept for the viologen group for which redox potentials can
 fit the negative side, organic p-type redox centers match
 better the positive side. Consequently, *cationic rocking-
 chair aqueous batteries* only exploit hybrid cells with inor-
 ganic(cathode)/organic(anode) combination. Yao's group
 [47**] (Table 1, #28) nicely illustrate the advantages of
 organic active materials in this field. Indeed, their study
 demonstrated polypyrene-4,5,9,10-tetraone (PPTO) can
 store ~ 220 mA h/g (two fold what can be achieved by
 best inorganic materials) at ~ -0.3 V vs. SCE enabling a
 full cell with LiMn₂O₄ (LMO) as the cathode material
 to sustain ~ 90 W h/kg_{materials} for more than 3000 cycles at

² The 18650 (18 mm by 65 mm) battery is a size classification of lithium-ion batteries.

0.23 A/g (1C \leftrightarrow 3500 h cycling) with near to 100% coulombic efficiency. As a comparison, similarly loaded cells exploiting LMO and $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) lead to similar energy density and cyclability but with somewhat higher estimated cost since PPTO would be $\sim 10\text{--}15$ $\$/\text{kg}$ and LTP higher than 20 $\$/\text{kg}$ [47]. Another interesting hybrid cationic full cell from Ji's group [48] consisted in using an ammonium inserted Ni-based Prussian white as the cathode against a 3,4,9,10-perylenetetracarboxylic diimide in a 1 M $(\text{NH}_4)_2\text{SO}_4$ (Table 1, #29). This is the first aqueous cell exchanging a non-metal cationic charge carrier. Although the capacity retention is moderate (67% upon 1000 cycles at 3C rates) it enables up to 43 W h/kg_{materials} with 1V of voltage at 1.5C based on a two-fold excess of positive electrode. The sole full organic aqueous cells to date incorporate n-type materials only (anionic configuration). To our knowledge only two systems have been reported since 2012: Nishida and co-workers considered thin film batteries (up to 1 mm thick) fabricated using a TEMPO derivative, the poly(2,2,6,6-tetramethylpiperidin-4-yl) acrylamide (PTMA) as the cathode coupled to two different polyviologen derivatives, either highly cross-linked polyviologen hydrogel (poly-(tripyridiniummesitylene)) [49**] which enable an average voltage of ~ 1.3 V over 2000 cycles (Table 1, #30), or to the poly(*N*-4,4'-bipyridinium-*N*-decamethylene dibromide) (Table 1, #31) which sustains more than 2000 cycles with 1.2 V average voltage [50]. Recently, Dong *et al.* [51] proposed a full organic dual-ion cell based on p-type polytriphenylamine and n-type polynaphthalene diimide polymers at the positive and negative electrode, respectively (Table 1, #32). Despite the cell requires the use of a 21 m LiTFSI water-in-salt electrolyte to prevent water oxidation, the authors showed near to 53 W h/kg_{materials} and 32 kW/kg_{materials} can be obtained for 1 mg/cm² electrodes. Another direction has been recently proposed by our group by coupling p-type bipyridinium and n-type naphthalene diimide redox moieties into one of a new family of non-soluble oligomer for negative electrodes. The latter was shown to exchange both cations and anions simultaneously on cycling, therefore paving the way to the design of a new type of dual cation-anion where the salt concentration does not vary on cycling. The synergistic coupling of the two redox units enables to reach competitive capacities ranging from 60 to 90 mA h/g in both neutral Na^+ and Mg^{2+} electrolytes of molar range concentration [4].

Conclusions and outlook

The peculiar field of organic batteries has seen significant progress these last few years with promising research directions attracting positively more and more interest from the energy storage community. The unique features of organics including flexibility, processability, structure diversity as well as the true possibility of being prepared from renewable resources and eco-friendly processes are today substantive arguments even if practical energy den-

sity values remain low. Let us recall that NEC group announced ORBs close to reaching the market in 2012 [52]. However, improvements are still needed to push forward organic batteries especially to get a better stability upon cycling. In fact, several organic materials are notably prone to solubility issues, including some polymers. Thus NEC have recently reported that the use of cross-linked PTMA gels enable very good electrochemical performance compared to linear PTMA with ~ 100 mA h/g_{PTMA} for more than 500 cycles [53]. This short review was also the occasion to underline that the richness of the redox organic chemistry enables the development of both various innovative electrode materials and cell configurations. Aqueous organic batteries appear notably as promising devices for stationary electricity storage at the condition to have low production costs and long cycling stabilities. In this regard, the high ionic conductivity of aqueous electrolytes that allows in principle to use ultra-thick electrodes should enable to pull the price per unit of energy even lower [54]. This aspect could be all the more important that the price of actual organic active materials remains too high ($> 5\text{--}10$ $\$/\text{kg}$). Although it was beyond the scope of this article, it is worth noting that very promising results have also been reported in regard to the use of organic redox materials for the redox flow technology [55–57].

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