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Graphical Abstract

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

Philippe Poizat<sup>1,2,\*</sup>, Franck Dolhem<sup>3,4</sup>, Joël Gaubicher<sup>1</sup>

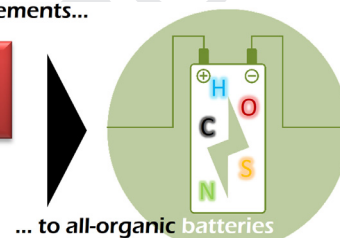
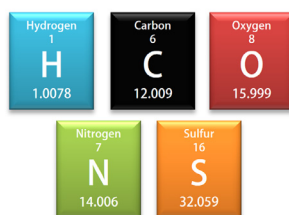
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From abundant chemical elements...





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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<sup>1,2,\*</sup>, Franck Dolhem<sup>3,4</sup> and Joël Gaubicher<sup>1</sup>

Q1

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 partic-  
ular 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-  
lar 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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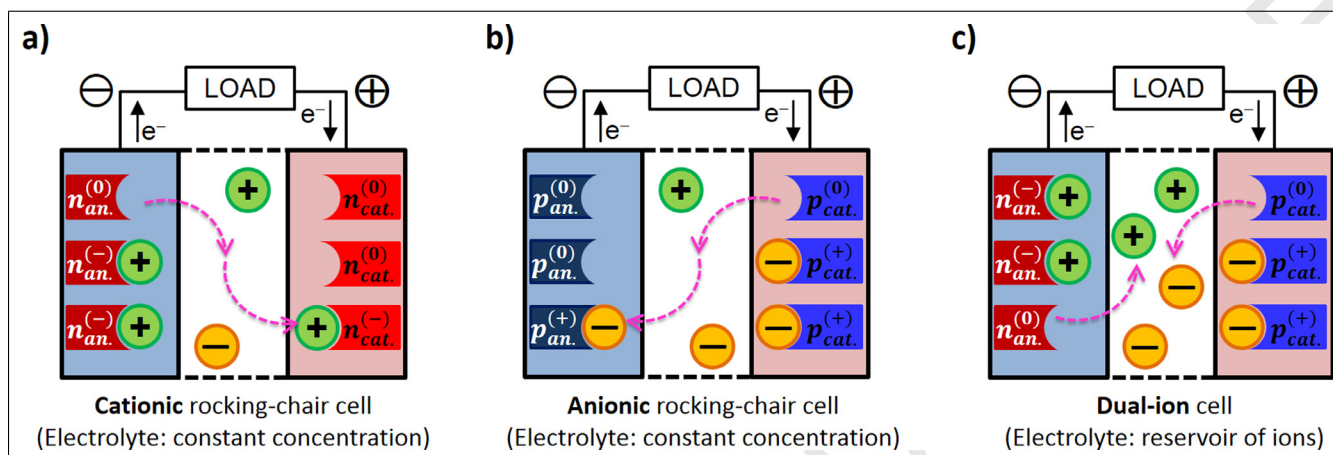
This review comes from a themed issue on **Batteries and Supercapacitors**Edited by **Daniel Belanger**For a complete overview see the [Issue](#) and the [Editorial](#)

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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 materials<sup>1</sup> 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  $\text{LiCoO}_2$  as the cathode material (Table 1, #2). Medabalmi *et al.* [14] made a Na-ion coin-cell prototype operating at  $\sim 3.2$  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-

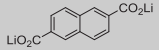
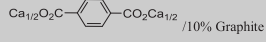
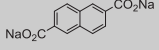
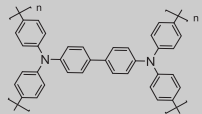
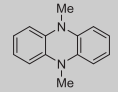

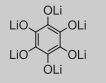
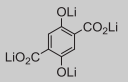
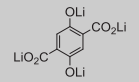
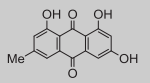
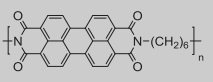
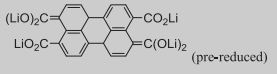
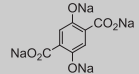
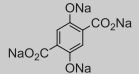
ited stabilities upon cycling were observed (Table 1, #3). Changing for a p-type cathode, Fan *et al.* [15] recently reported a potassium-based dual-ion full battery (PDIBs) based on graphite anode, polytriphenylamine cathode, and KPF<sub>6</sub>-based electrolyte (Table 1, #4) that shows quite good 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  $\sim 1$  V as output voltage (Table 1, #6). Later we tried to go further by investigating dilithium (2,5-dilithium-oxy)-terephthalate ( $\text{Li}_4$ -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  $\sim 1.8$  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

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

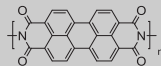
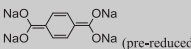
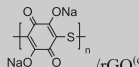
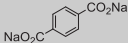


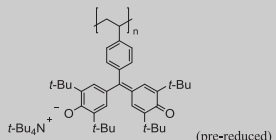
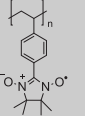
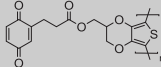
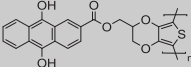




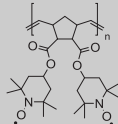
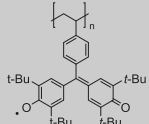
**Table 1**

**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 <sup>2</sup> )	Ref.
<b>n-type inorganic cathode assembled with n-type organic anode</b>								
1	Li-ion	LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub>		1 M LiPF <sub>6</sub> in EC:DMC:EMC 3:4:3 (v/v/v)	3.9	96%, 100, 1 C	77 <sup>(c)</sup> , 300 <sup>(c)</sup> , -, -	[12]
2	Li-ion	LiCoO <sub>2</sub>		1 M LiPF <sub>6</sub> in EC:DMC 1:1 (v/v)	2.75	82%, 50, 1 C	138 <sup>(a)</sup> , -, 92%, -	[13]
3	Na-ion	Na <sub>3</sub> V <sub>2</sub> O <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> /rGO <sup>(d)</sup>		1 M NaClO <sub>4</sub> in PC	3.2	68%, 20, 13 mA/g	150 <sup>(a)</sup> , -, 33% <sup>(b)</sup> , 2	[14]
4	Dual-ion (K <sup>+</sup> /PF <sub>6</sub> <sup>-</sup> )		Graphite	0.8 M KPF <sub>6</sub> in EC:DC 1:1 (v/v)	3.23	75.5%, 500, 50 mA/g	60 <sup>(b)</sup> , 105, -, 1.2	[15]
5	Dual-ion (Li <sup>+</sup> /TFSI <sup>-</sup> )		Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub>	1 M LiTFSI in TEGDME	1.9	-, -, 50 mA/g	163 <sup>(b)</sup> , -, -, -	[16]
<b>n-type organic cathode assembled with n-type organic anode</b>								
6	Li-ion			1 M LiPF <sub>6</sub> in EC:DMC 1:1 (v/v)	1.0	70%, 50, C/20	-, -, -, -	[17]
7	Li-ion			1 M LiPF <sub>6</sub> in EC:DMC 1:1 (v/v)	1.8	91%, 20, 48.2 mA/g	225 <sup>(a)</sup> , 130, 99.7%, 1-1.5	[19]
8	Li-ion		Electrochemically pre-reduced lithium humates	1 M LiPF <sub>6</sub> in EC:DMC 1:1 (v/v)	1.5	50%, 100, 100 mA/g	127 <sup>(b)</sup> , -, 99%, -	[21]
9	Li-ion			1 M LiPF <sub>6</sub> in EC:DMC:EMC 1:1:1 (v/v/v)	1.2	81%, 200, 11.3 mA/g	78 <sup>(b)</sup> , 32, 99.6%, 0.8-2	[22]
10	Na-ion			1 M NaClO <sub>4</sub> in EC:MC 1:1 (v/v)	1.8	76%, 100, 19 mA/g	198 <sup>(a)</sup> , 65, 99%, 1-2	[23]

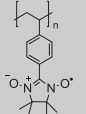
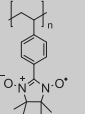
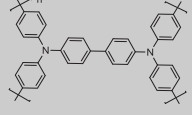


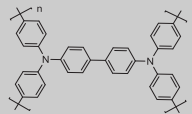
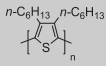


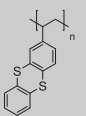
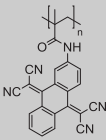
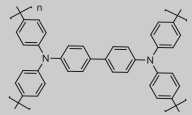
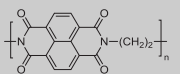
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Table 1 (continued)

#	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 <sup>2</sup> )	Ref.
11	Na-ion			1 M NaPF <sub>6</sub> in PC	1.35	75%, 20, 50 mA/g	73, -, -, 1.4	[24]
12	Na-ion			1 M NaClO <sub>4</sub> in tetraglyme	1.1	62%, 30, 130 mA/g	210, -, 99.2%, 1	[25]
13	K-ion			1.25 M KPF <sub>6</sub> in DME	1.1	-, 10, 25 mA/g	70 <sup>(b)</sup> , 35, -, -	[26]
14	R <sub>4</sub> N-ion			0.1 M <i>n</i> -Bu <sub>4</sub> NClO <sub>4</sub> +0.01 M <i>n</i> -Bu <sub>4</sub> NOH in CH <sub>3</sub> 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 <sup>(a)</sup> , -, 99.9%, -	[28]
<b>p-type organic cathode assembled with n-type organic anode</b>								
16	Dual-ion (ClO <sub>4</sub> <sup>-</sup> / <i>n</i> -Bu <sub>4</sub> N <sup>+</sup> ; BF <sub>4</sub> <sup>-</sup> / <i>n</i> -Bu <sub>4</sub> N <sup>+</sup> )			0.5 M <i>n</i> -Bu <sub>4</sub> NClO <sub>4</sub> in PC; 0.3 M <i>n</i> -Bu <sub>4</sub> NBF <sub>4</sub> in THF	3.7 2.5	-	-	[29]
17	Dual-ion (BF <sub>4</sub> <sup>-</sup> / <i>n</i> -Bu <sub>4</sub> N <sup>+</sup> )			0.2 M <i>n</i> -Bu <sub>4</sub> NBF <sub>4</sub> in CH <sub>3</sub> CN	3.1	-, -, 24 mA/g	-, 93, -, -	[30]
18	Dual-ion (ClO <sub>4</sub> <sup>-</sup> / <i>n</i> -Bu <sub>4</sub> N <sup>+</sup> )			0.5 M <i>n</i> -Bu <sub>4</sub> NClO <sub>4</sub> +0.01 M <i>n</i> -Bu <sub>4</sub> NOH in CH <sub>3</sub> CN	0.66	57%, 250, 10 C	32, 22, -, -	[31]

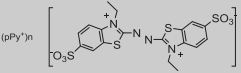
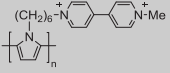

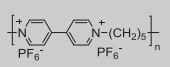
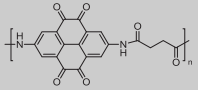
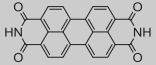
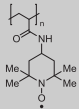
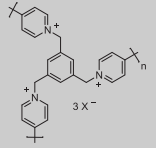
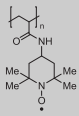
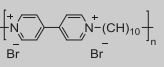
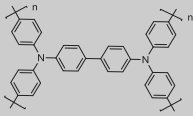
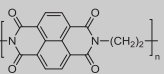
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Table 1 (continued)

#	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 <sup>2</sup> )	Ref.
19	Dual-ion (ClO <sub>4</sub> <sup>-</sup> / <i>n</i> -Bu <sub>4</sub> N <sup>+</sup> )			0.5 M <i>n</i> -Bu <sub>4</sub> NClO <sub>4</sub> + 0.01 M <i>n</i> -Bu <sub>4</sub> NOH in CH <sub>3</sub> CN	1.3	68%, 250, 60 C	44, -, -, -	[27]
20	Dual-ion (PF <sub>6</sub> <sup>-</sup> /Na <sup>+</sup> )			NaPF <sub>6</sub> saturated in DME:DOL 1:1 (v/v)	1.8	85%, 500, 8 C	200 <sup>(a)</sup> , 92, 99, -	[32]
21	Dual-ion (ClO <sub>4</sub> <sup>-</sup> /Na <sup>+</sup> )	P(AN-NA) <sup>(f)</sup>		5% <sub>mol</sub> NaClO <sub>4</sub> in plastic crystal electrolyte	1.7	80%, 50, 50 mA/g	200 <sup>(a)</sup> , -, -, -	[33]
22	Dual-ion (PF <sub>6</sub> <sup>-</sup> /Li <sup>+</sup> )			1 M LiPF <sub>6</sub> in EC:DMC:EMC 1:1:1 (v/v/v)	2.35	-, -, 40 mA/g	250 <sup>(a)</sup> , -, -, -	[34]
23	Dual-ion (PF <sub>6</sub> <sup>-</sup> /Li <sup>+</sup> )			1 M LiPF <sub>6</sub> in EC:DMC:EMC 1:1:1 (v/v/v)	3	63%, 60, 40 mA/g	153 <sup>(a)</sup> , -, -, -	[35]
24	Dual-ion (ClO <sub>4</sub> <sup>-</sup> /Li <sup>+</sup> )			1 M LiClO <sub>4</sub> in EC:DMC 3:7 (v/v)	1.35	67%, 250, 1C	105 <sup>(b)</sup> , -, -, -	[36]
25	Dual-ion (TFSI <sup>-</sup> /Li <sup>+</sup> )			2 M LiTFSI in ethyl acetate (55°C ≤ T ≤ -70°C)	1.2	-, -, -	90 <sup>(a)</sup> , 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 <sup>2</sup> )	Ref.
<b>p-type organic cathode assembled with p-type organic anode</b>								
26	ClO <sub>4</sub> <sup>-</sup> -ion			0.2 M LiClO <sub>4</sub> in CH <sub>3</sub> CN	1	70%, 100, 0.5 mA/cm <sup>2</sup>	16, 15, -, - (thin films)	[39]
27	PF <sub>6</sub> <sup>-</sup> -ion			1 M <i>n</i> -Bu <sub>4</sub> NPF <sub>6</sub> in PC	1.8	65%, 100, 100 mA/g	100 <sup>(b)</sup> , -, -, -	[11]
<b>Organic batteries with aqueous electrolytes</b>								
28	Li-ion	LiMn <sub>2</sub> O <sub>4</sub>		Li <sub>2</sub> SO <sub>4</sub> 2.5 M (pH 7)	1.13	80%, 3000, 280 mA/g	81, 92%, -, 2	[47]
29	NH <sub>4</sub> <sup>+</sup> -ion	(NH <sub>4</sub> ) <sub>1.47</sub> Ni[Fe(CN) <sub>6</sub> ] <sub>0.88</sub>		(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> 1 M (pH 6)	1	67%, 1000, 0.120 mA/g	35 <sup>(c)</sup> , 35 <sup>(c)</sup> , 97.6%, 2-5	[48]
30	Cl <sup>-</sup> -ion			NaCl 0.1 M (pH 7)	1.3	80%, 2000, 10.5 A/g	165 <sup>(d)</sup> , 214 <sup>(d)</sup> , - (100 nm to 1 μm thin films)	[49]
31	BF <sub>4</sub> <sup>-</sup> -ion			NaBF <sub>4</sub> (pH 7)	1.2	75-80%, >2000, 60 C (67 μA/cm <sup>2</sup> )	104 <sup>(b)</sup> , 125 <sup>(b)</sup> , 95 (100 nm thin films)	[50]
32	Dual-ion (TFSI <sup>-</sup> /Li <sup>+</sup> )			LiTFSI 21 M (pH 7)	1	85%, 700, 0.5 A/g	105 <sup>(b)</sup> , 53 <sup>(b)</sup> , ~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  $\sim 1.2$  V and good cyclability over 200 cycles from pre-reduced perylenetetracarboxylate face to a polyimide as the cathode (Table 1, #9). Taking benefit of the successful Li-ion cell based on Li<sub>4</sub>-*p*-DHT, Chen's group [23] investigated the sodiated counterpart material (Na<sub>4</sub>-*p*-DHT) and published the first all-organic sodium-ion battery (SIB), which gives an average operation voltage of  $\sim 1.8$  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-perylenetetracarboxylic polyimide as the cathode with the disodium terephthalate (Na<sub>2</sub>TP) as the anode. Again the lack of inserted Na<sup>+</sup> in the pristine polyimide forced them to electrochemically pre-reduce Na<sub>2</sub>TP before assembling (Table 1, #11). The cell delivered an initial capacity of 73 mA h/g for an average cell voltage of  $\sim 1.35$  V but with a limited cycling stability. Very recently, Li *et al.* [25\*\*] have gone beyond by associating Na<sub>2</sub>TP with sodiated poly(2,5-dihydroxy-*p*-benzoquinoyl sulfide)/rGO composite material (Table 1, #12). In the continuity of our former works on Li<sub>4</sub>C<sub>6</sub>O<sub>6</sub> [17], in 2016 Chen's group constructed the first example of organic K-ion batteries based on K<sub>4</sub>C<sub>6</sub>O<sub>6</sub>/K<sub>2</sub>C<sub>6</sub>O<sub>6</sub> system [26] which displayed an operation voltage of  $\sim 1.1$  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 ( $\sim 0.6$  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  $\sim 90$  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 (PF<sub>6</sub><sup>-</sup>/Na<sup>+</sup>) 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

## 8 Batteries and Supercapacitors

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  $\sim 1.8$  V as output voltage coupled with  
263 capacity of 100 mA h/g<sub>cathode</sub>.

### 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<sub>18650-cell</sub><sup>2</sup>, 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 ( $\sim 2$ –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., LiMn<sub>2</sub>O<sub>4</sub>  
[44], Na<sub>3</sub>Ti<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> [44], Fe and Mn-based Prussian Blue  
derivatives [45] and Na<sub>3</sub>MnTi(PO<sub>4</sub>)<sub>3</sub> [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-  
thetical 18,650 full cell should enable an energy density  
of about 56 W h/kg<sub>18650-cell</sub> based on 15 mA h/cm<sup>2</sup> 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  $\sim 5$  \$/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  $\sim 0.3$  V vs. SCE (2.95 V vs. Li<sup>+</sup>/Li at neutral  
pH) thanks to the carbonyl/enolate redox moiety. How-  
ever, with the aim to fabricate at least 1 V<sub>cell</sub>, 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<sup>+</sup>/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  $\sim 220$  mA h/g (two fold what can be achieved by  
best inorganic materials) at  $\sim -0.3$  V vs. SCE enabling a  
full cell with LiMn<sub>2</sub>O<sub>4</sub> (LMO) as the cathode material  
to sustain  $\sim 90$  W h/kg<sub>materials</sub> for more than 3000 cycles at

<sup>2</sup> 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<sub>materials</sub> with 1 V 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-(tripyrindiniomesitylene)) [49\*\*] which enable an average voltage of  $\sim 1.3$  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<sub>materials</sub> and 32 kW/kg<sub>materials</sub> can be obtained for 1 mg/cm<sup>2</sup> 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  $\text{Na}^+$  and  $\text{Mg}^{2+}$  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  $\sim 100$  mA h/g<sub>PTMA</sub> 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].

## References and recommended reading

- Papers of particular interest, published within the period of review, have been highlighted as:
- Paper of special interest
  - Paper of outstanding interest.
1. Poizot P, Dolhem F: **Clean energy new deal for a sustainable world: from non-CO<sub>2</sub> generating energy sources to greener electrochemical storage devices.** *Energy Environ. Sci* 2011, **4**:2003–2019. <https://doi.org/10.1039/C0EE00731E>.
  2. Ellingsen LA-W, Majeau-Bettez G, Singh B, Srivastava AK, Valøen LO, Strømman AH: **Life cycle assessment of a lithium-ion battery vehicle pack: LCA of a Li-ion battery vehicle pack.** *J. Ind. Ecol.* 2014, **18**:113–124. <https://doi.org/10.1111/jiec.12072>.
  3. Gottis S, Barrès A-L, Dolhem F, Poizot P: **Voltage gain in lithiated enolate-based organic cathode materials by isomeric effect.** *ACS Appl. Mater. Interfaces* 2014, **6**:10870–10876. <https://doi.org/10.1021/am405470p>.
  4. Perticarari S, Sayed-Ahmad-Baraza Y, Ewels C, Moreau P, Guyomard D, Poizot P, Odobel F, Gaubicher J: **Dual anion-cation reversible insertion in a bipyridinium-diamide triad as the negative electrode for aqueous batteries.** *Adv. Energy Mater.*, vol 8 2018 1701988. <https://doi.org/10.1002/aenm.201701988>.
  5. Chagnes A, Swiatowska J (Eds): *Lithium Process Chemistry: Resources, Extraction, Batteries, and Recycling.* Amsterdam, Boston, Heidelberg: Elsevier; 2015.
  6. Häupler B, Wild A, Schubert US: **Carbonyls: powerful organic materials for secondary batteries.** *Adv. Energy Mater.*, vol 5 2015 1402034. <https://doi.org/10.1002/aenm.201402034>.
  7. Oltean V-A, Renault S, Valvo M, Brandell D: **Sustainable materials for sustainable energy storage: organic Na electrodes.** *Materials* 2016, **9**:142. <https://doi.org/10.3390/ma9030142>.

## 10 Batteries and Supercapacitors

- 469 8. Zhao Q, Guo C, Lu Y, Liu L, Liang J, Chen J: **Rechargeable**  
470 **lithium batteries with electrodes of small organic carbonyl**  
471 **salts and advanced electrolytes.** *Ind. Eng. Chem. Res.* 2016,  
472 **55:5795–5804.** <https://doi.org/10.1021/acs.iecr.6b01462>.
- 473 9. Schon TB, McAllister BT, Li P-F, Seferos DS: **The rise of organic**  
474 **electrode materials for energy storage.** *Chem. Soc. Rev.* 2016,  
475 **45:6345–6404.** <https://doi.org/10.1039/C6CS00173D>.
- 476 10. Zhao Q, Lu Y, Chen J: **Advanced organic electrode materials for**  
477 **rechargeable sodium-ion batteries.** *Adv. Energy Mater.*, vol 7  
478 2017 1601792. <https://doi.org/10.1002/aenm.201601792>.
- 479 11. Yao M, Sano H, Ando H, Kiyobayashi T: **Molecular ion battery: a**  
480 **rechargeable system without using any elemental ions as a**  
481 **charge carrier.** *Sci. Rep.* 2015, 5:10962.  
482 <https://doi.org/10.1038/srep10962>.  
483 Using p-type polymers as both cathode and anode materials together  
484 with a molecular ion a charge carrier in the electrolyte, this article  
485 reports the possible fabrication of a molecular ion-based “rocking  
486 chair” battery operating in aprotic electrolyte.
- 487 12. Ogihara N, Yasuda T, Kishida Y, Ohsuna T, Miyamoto K, Ohba N:  
488 **Organic dicarboxylate negative electrode materials with**  
489 **remarkably small strain for high-voltage bipolar batteries.**  
490 *Angew. Chem. Int. Ed.* 2014, **53:11467–11472.**  
491 <https://doi.org/10.1002/anie.201405139>.  
492 Using an organic anode together with a high potential spinel the authors  
493 demonstrated the feasibility of laminated cells of high specific energy  
494 (300 W h/kgcell).
- 495 13. Mou C, Wang L, Deng Q, Huang Z, Li J: **Calcium**  
496 **terephthalate/graphite composites as anode materials for**  
497 **lithium-ion batteries.** *Ionics* 2015, **21:1893–1899.**  
498 <https://doi.org/10.1007/s11581-014-1357-z>.
- 499 14. Medabalmi V, Kuanr N, Ramanujam K: **Sodium naphthalene**  
500 **dicarboxylate anode material for inorganic–organic hybrid**  
501 **rechargeable sodium-ion batteries.** *J. Electrochem. Soc.* 2018,  
502 **165:A175–A180.** <https://doi.org/10.1149/2.0731802jes>.
- 503 15. Fan L, Liu Q, Xu Z, Lu B: **An organic cathode for potassium**  
504 **dual-ion full battery.** *ACS Energy Lett* 2017, **2:1614–1620.**  
505 <https://doi.org/10.1021/acsenenergylett.7b00378>.
- 506 16. Lee M, Hong J, Lee B, Ku K, Lee S, Park CB, Kang K:  
507 **Multi-electron redox phenazine for ready-to-charge organic**  
508 **batteries.** *Green Chem* 2017, **19:2980–2985.**  
509 <https://doi.org/10.1039/C7GC00849J>.
- 510 17. Chen H, Armand M, Courty M, Jiang M, Grey CP, Dolhem F,  
511 Tarascon J-M, Poizat P: **Lithium salt of**  
512 **tetrahydroxybenzoquinone: toward the development of a**  
513 **sustainable Li-ion battery.** *J Am Chem Soc* 2009,  
514 **131:8984–8988.** <https://doi.org/10.1021/ja9024897>.
- 515 18. Renault S, Gottis S, Barrès A-L, Courty M, Chauvet O, Dolhem F,  
516 Poizat P: **A green Li–organic battery working as a fuel cell in**  
517 **case of emergency.** *Energy Environ. Sci.* 2013, **6:2124.**  
518 <https://doi.org/10.1039/c3ee40878g>.
- 519 19. Wang S, Wang L, Zhang K, Zhu Z, Tao Z, Chen J: **Organic**  
520 **Li<sub>4</sub>C<sub>8</sub>H<sub>2</sub>O<sub>6</sub> nanosheets for lithium-ion batteries.** *Nano Lett* 2013,  
521 **13:4404–4409.** <https://doi.org/10.1021/nl402239p1530-6984>.
- 522 20. Zhao Q, Wang J, Chen C, Ma T, Chen J: **Nanostructured organic**  
523 **electrode materials grown on graphene with covalent-bond**  
524 **interaction for high-rate and ultra-long-life lithium-ion**  
525 **batteries.** *Nano Res* 2017, **10:4245–4255.**  
526 <https://doi.org/10.1007/s12274-017-1580-9>.  
527 This paper reports impressive electrochemical results for an all-organic  
528 Li-ion cell based on Li<sub>4</sub>C<sub>8</sub>H<sub>2</sub>O<sub>6</sub> supported on graphene, which exhibits  
529 capacities of 191 mA h/g after 100 cycles at 0.5 C and 121  
530 121 mA h/g after 500 cycles at 2 C.
- 531 21. Hu P, Wang H, Yang Y, Yang J, Lin J, Guo L:  
532 **Renewable-biomolecule-based full lithium-ion batteries.** *Adv.*  
533 *Mater.* 2016, **28:3486–3492.**  
534 <https://doi.org/10.1002/adma.201505917>.
- 535 22. Iordache A, Delhorbe V, Bardet M, Dubois L, Gutel T, Picard L:  
536 **Perylene-based all-organic redox battery with excellent**  
537 **cycling stability.** *ACS Appl. Mater. Interfaces* 2016,  
538 **8:22762–22767.** <https://doi.org/10.1021/acsami.6b07591>.
23. Wang S, Wang L, Zhu Z, Hu Z, Zhao Q, Chen J: **All organic**  
539 **sodium-ion batteries with Na<sub>4</sub>C<sub>8</sub>H<sub>2</sub>O<sub>6</sub>.** *Angew. Chem. Int. Ed.*  
540 2014, **53:5892–5896.** <https://doi.org/10.1002/anie.201400032>. 541
24. Banda H, Damien D, Nagarajan K, Hariharan M, Shaijumon MM: **A**  
542 **polyimide based all-organic sodium ion battery.** *J. Mater. Chem.*  
543 A 2015, **3:10453–10458.** <https://doi.org/10.1039/C5TA02043C>. 544
25. Li A, Feng Z, Sun Y, Shang L, Xu L: **Porous organic**  
545 **polymer/RGO composite as high performance cathode for half**  
546 **and full sodium ion batteries.** *J. Power Sour.* 2017, **343:424–430.**  
547 <https://doi.org/10.1016/j.jpowsour.2017.01.079>. 548  
The authors assemble an all-organic rocking-chair type full cell SIB  
549 using a sodiated polymeric cathode. 550
26. Zhao Q, Wang J, Lu Y, Li Y, Liang G, Chen J: **Oxocarbon salts for**  
551 **fast rechargeable batteries.** *Angew. Chem. Int. Ed.* 2016,  
552 **55:12528–12532.** <https://doi.org/10.1002/anie.201607194>. 553
27. Suga T, Sugita S, Ohshiro H, Oyaizu K, Nishide H: **p- and n-type**  
554 **bipolar redox-active radical polymer: toward totally organic**  
555 **polymer-based rechargeable devices with variable**  
556 **configuration.** *Adv Mater.* 2011, **23:751–754.**  
557 <https://doi.org/10.1002/adma.201003525>. 558
28. Emanuelsson R, Sterby M, Strømme M, Sjödin M: **An all-organic**  
559 **proton battery.** *J. Am. Chem. Soc.* 2017, **139:4828–4834.**  
560 <https://doi.org/10.1021/jacs.7b00159>. 561  
The all-organic battery proposed by the authors works without any  
562 metallic element (except current collectors) and using an innovative  
563 non-aqueous protic electrolyte. The full cell obtained show original  
564 results. 565
29. MacInnes D, Druy MA, Nigrey PJ, Nairns DP, MacDiarmid AG,  
566 Heeger AJ: **Organic batteries: reversible n- and p-type**  
567 **electrochemical doping of polyacetylene, (CH) x.** *J. Chem. Soc.*  
568 *Chem. Commun.* 1981:317. 569  
<https://doi.org/10.1039/c39810000317>. 570
30. Kaneto K, Yoshino K, Inuishi Y: **Characteristics of polythiophene**  
571 **battery.** *Jpn. J. Appl. Phys.* 1983, **22:L567.**  
572 <https://doi.org/10.1143/JJAP.22.L567>. 573
31. Suga T, Ohshiro H, Sugita S, Oyaizu K, Nishide H: **Emerging**  
574 **n-type redox-active radical polymer for a totally organic**  
575 **polymer-based rechargeable battery.** *Adv. Mater.* 2009,  
576 **21:1627–1630.** <https://doi.org/10.1002/adma.200803073>. 577
32. Deng W, Liang X, Wu X, Qian J, Cao Y, Ai X, Feng J, Yang H: **A low**  
578 **cost, all-organic Na-ion battery based on polymeric cathode**  
579 **and anode.** *Sci. Rep.* 2013, **3:2671.**  
580 <https://doi.org/10.1038/srep02671>. 581
33. Zhu X, Zhao R, Deng W, Ai X, Yang H, Cao Y: **An all-solid-state**  
582 **and all-organic sodium-ion battery based on redox-active**  
583 **polymers and plastic crystal electrolyte.** *Electrochim. Acta* 2015,  
584 **178:55–59.** <https://doi.org/10.1016/j.electacta.2015.07.163>. 585
34. Zhu LM, Shi W, Zhao RR, Cao YL, Ai XP, Lei AW, Yang HX:  
586 **n-Dopable polythiophenes as high capacity anode materials**  
587 **for all-organic Li-ion batteries.** *J. Electroanal. Chem.* 2013,  
588 **688:118–122.** <https://doi.org/10.1016/j.jelechem.2012.06.019>. 589
35. Zhu LM, Lei AW, Cao YL, Ai XP, Yang HX: **An all-organic**  
590 **rechargeable battery using bipolar polyparaphenylene as a**  
591 **redox-active cathode and anode.** *Chem. Commun.* 2013,  
592 **49:567–569.** <https://doi.org/10.1039/c2cc36622c>. 593
36. Wild A, Strumpf M, Häupler B, Hager MD, Schubert US:  
594 **All-organic battery composed of thianthrene- and**  
595 **TCAQ-based polymers.** *Adv. Energy Mater.*, vol 7 2017 n/a-n/a.  
596 <https://doi.org/10.1002/aenm.201601415>. 597
37. Dong X, Guo Z, Guo Z, Wang Y, Xia Y: **Organic batteries**  
598 **operated at –70 °C.** *Joule* 2018.  
599 <https://doi.org/10.1016/j.joule.2018.01.017>. 600
38. Lee JY, Ong LH, Chuah GK: **Rechargeable thin film batteries of**  
601 **polypyrrole and polyaniline.** *J. Appl. Electrochem.* 1992,  
602 **22:738–742.** <https://doi.org/10.1007/BF01027503>. 603
39. Sen S, Saraidaridis J, Kim SY, Palmore GTR: **Viologens as charge**  
604 **carriers in a polymer-based battery anode.** *ACS Appl. Mater.*  
605 *Interfaces* 2013, **5:7825–7830.**  
606 <https://doi.org/10.1021/am401590q>. 607

- 608 40. Suo L, Borodin O, Sun W, Fan X, Yang C, Wang F, Gao T, Ma Z,  
609 Schroeder M, von Cresce A, Russell SM, Armand M, Angell A,  
610 Xu K, Wang C: **Advanced high-voltage aqueous lithium-ion**  
611 **battery enabled by “water-in-bisalt” electrolyte.** *Angew. Chem.*  
612 *Int. Ed.* 2016, **55**:7136–7141.  
613 <https://doi.org/10.1002/anie.201602397>.
- 614 41. Wang F, Suo L, Liang Y, Yang C, Han F, Gao T, Sun W, Wang C:  
615 **Spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode for high-energy aqueous**  
616 **lithium-ion batteries.** *Adv. Energy Mater.*, vol 7 2017 n/a-n/a.  
617 <https://doi.org/10.1002/aenm.201600922>.
- 618 42. Yamada Y, Yamada A: **Superconcentrated electrolytes to create**  
619 **new interfacial chemistry in non-aqueous and aqueous**  
620 **rechargeable batteries.** *Chem. Lett.* 2017, **46**:1056–1064.  
621 <https://doi.org/10.1246/cl.170284>.
- 622 43. Suo L, Borodin O, Wang Y, Rong X, Sun W, Fan X, Xu S,  
623 Schroeder MA, Cresce AV, Wang F, Yang C, Hu Y-S, Xu K,  
624 Wang C: **“Water-in-salt” electrolyte makes aqueous sodium-ion**  
625 **battery safe, green, and long-lasting.** *Adv. Energy Mater.*, vol 7  
626 2017 1701189. <https://doi.org/10.1002/aenm.201701189>.
- 627 44. Whitacre JF, Shanbhag S, Mohamed A, Polonsky A, Carlisle K,  
628 Gulakowski J, Wu W, Smith C, Cooney L, Blackwood D,  
629 Dandrea JC, Truchot C: **A polyionic, large-format energy**  
630 **storage device using an aqueous electrolyte and thick-format**  
631 **composite  $\text{NaTi}_2(\text{PO}_4)_3$ /activated carbon negative electrodes.**  
632 *Energy Technol.* 2015, **3**:20–31.  
633 <https://doi.org/10.1002/ente.201402127>.
- 634 45. Lee H-W, Wang RY, Pasta M, Woo Lee S, Liu N, Cui Y: **Manganese**  
635 **hexacyanomanganate open framework as a high-capacity**  
636 **positive electrode material for sodium-ion batteries.** *Nat.*  
637 *Commun.* 2014, **5**:5280. <https://doi.org/10.1038/ncomms6280>.
- 638 46. Gao H, Goodenough JB: **An aqueous symmetric sodium-ion**  
639 **battery with NASICON-structured  $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$ .** *Angew.*  
640 *Chem. Int. Ed.* 2016, **55**:12768–12772.  
641 <https://doi.org/10.1002/anie.201606508>.
- 642 47. Liang Y, Jing Y, S Gheyhani, Lee K-Y, Liu P, Facchetti A, Yao Y:  
643 **•• Universal quinone electrodes for long cycle life aqueous**  
644 **rechargeable batteries.** *Nat. Mater.* 2017, **16**:841–848.  
645 <https://doi.org/10.1038/nmat4919>.  
646 Authors proved the versatility of an organic quinone-based polymer by  
647 assembling highly performant hybrid inorganic/organic full cells  
648 showing long cycle life and high energy density in acidic, neutral and  
649 basic aqueous media.
- 650 48. Wu X, Qi Y, Hong JJ, Li Z, Hernandez AS, Ji X: **Rocking-chair**  
651 **ammonium-ion battery: a highly reversible aqueous energy**  
652 **storage system.** *Angew. Chem. Int. Ed.* 2017, **56**:13026–13030.  
653 <https://doi.org/10.1002/anie.201707473>.
49. Sano N, Tomita W, Hara S, Min C-M, Lee J-S, Oyaizu K, Nishide H: 654  
655 **•• Polyviologen hydrogel with high-rate capability for anodes**  
656 **toward an aqueous electrolyte-type and organic-based**  
657 **rechargeable device.** *ACS Appl. Mater. Interfaces* 2013,  
658 **5**:1355–1361. <https://doi.org/10.1021/am302647w>.  
659 The introduction this new p-type poly(triipyridiniumsilylene) viologen  
660 derivative delivering 165 165 mA h/g paves the way to much improved  
661 energy density for full organic anionic rocking chair batteries.
50. Chikushi N, Yamada H, Oyaizu K, Nishide H: **TEMPO-substituted** 662  
663 **•• polyacrylamide for an aqueous electrolyte-typed and**  
664 **organic-based rechargeable device.** *Sci. China Chem.* 2012,  
665 **55**:822–829. <https://doi.org/10.1007/s11426-012-4556-3>.  
666 Using p type redox active polymers, authors proved for the first time the  
667 high reversibility of anionic rocking chair full cells in neutral aqueous  
668 media.
51. Dong X, Yu H, Ma Y, Bao JL, Truhlar DG, Wang Y, Xia Y: 669  
670 **All-organic rechargeable battery with reversibility supported**  
671 **by “water-in-salt” electrolyte.** *Chem. Eur. J.* 2017, **23**:2560–2565.  
672 <https://doi.org/10.1002/chem.201700063>.
52. Iwasa S, Yasui M, Nishi T, Nakano K: **Development of organic** 673  
674 **radical battery.** *NEC Tech. J.* 2012, **7**:102–106.
53. Iwasa S, Nishi T, Sato H, Nakamura S: **Flexibility and high-rate** 675  
676 **discharge properties of organic radical batteries with gel-state**  
677 **electrodes.** *J. Electrochem. Soc.* 2017, **164**:A884–A888.  
678 <https://doi.org/10.1149/2.1631704jes>.
54. PHEV Battery Cost Assessment | Department of Energy, (n.d.). 679  
680 [https://energy.gov/eere/vehicles/downloads/](https://energy.gov/eere/vehicles/downloads/phev-battery-cost-assessment-2)  
681 [phev-battery-cost-assessment-2](https://energy.gov/eere/vehicles/downloads/phev-battery-cost-assessment-2) (accessed February 24, 2018).
55. Huskinson B, Marshak MP, Suh C, Er S, Gerhardt MR, Galvin CJ, 682  
683 Chen X, Aspuru-Guzik A, Gordon RG, Aziz MJ: **A metal-free**  
684 **organic-inorganic aqueous flow battery.** *Nature* 2014,  
685 **505**:195–198. <https://doi.org/10.1038/nature12909>.
56. Orita A, Verde MG, Sakai M, Meng YS: **A biomimetic redox flow** 686  
687 **battery based on flavin mononucleotide.** *Nat. Commun.* 2016,  
688 **7**:13230. <https://doi.org/10.1038/ncomms13230>.
57. Winsberg J, Hagemann T, Janoschka T, Hager MD, Schubert US: 689  
690 **Redox-flow batteries: from metals to organic redox-active**  
691 **materials.** *Angew. Chem. Int. Ed.* 2017, **56**:686–711.  
692 <https://doi.org/10.1002/anie.201604925>.