



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

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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>

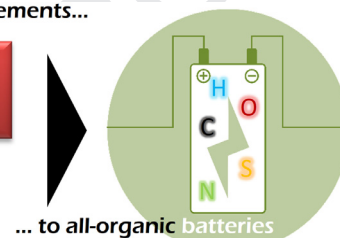
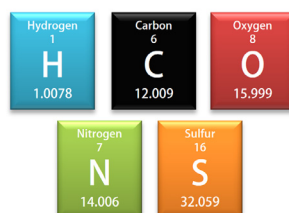
<sup>1</sup> Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, UMR CNRS 6502, 2 rue de la Houssinière, B.P. 32229, 44322 Nantes Cedex 3, France

<sup>2</sup> Institut Universitaire de France (IUF), 1 rue Descartes, 75231 Paris Cedex 05, France

<sup>3</sup> Laboratoire de Glycochimie, des Antimicrobiens et des Agroressources (LG2A), UMR CNRS 7378, Université de Picardie Jules Verne, 33 rue Saint-Leu, 80039 Amiens Cedex, France

<sup>4</sup> Réseau sur le Stockage Electrochimique de l'Énergie (RS2E), FR CNRS 3459, Amiens Cedex, France

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>

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

## Addresses

<sup>1</sup> Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, UMR CNRS 6502, 2 rue de la Houssinière, B.P. 32229, 44322 Nantes Cedex 3, France

<sup>2</sup> Institut Universitaire de France (IUF), 1 rue Descartes, 75231 Paris Cedex 05, France

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<sup>4</sup> Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, Amiens Cedex, France

\*Corresponding author.: Poizot, Philippe ([philippe.poizot@cnrs-imn.fr](mailto:philippe.poizot@cnrs-imn.fr))

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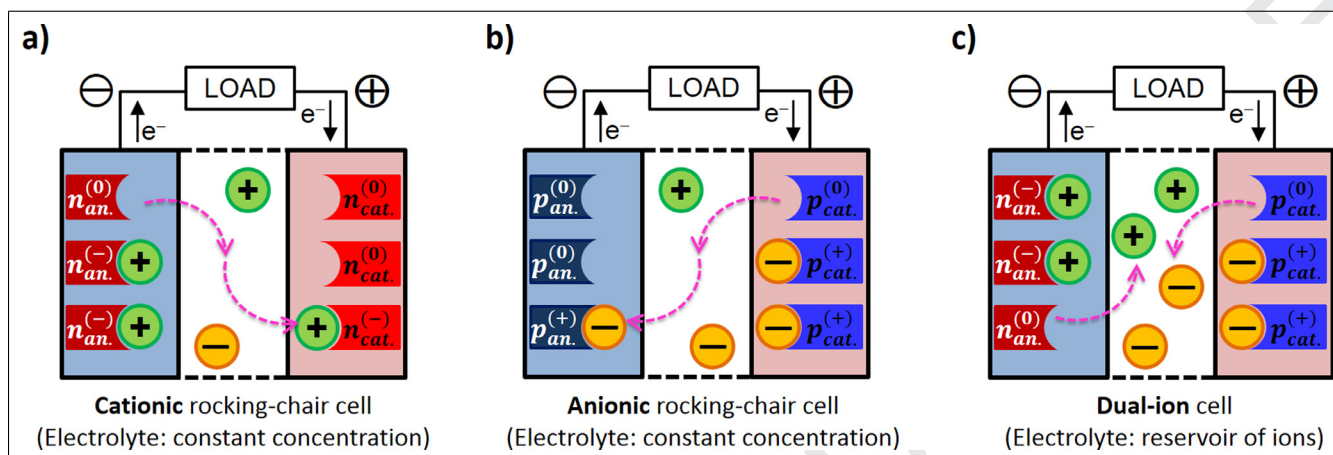
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## Introduction

A few years ago, we outlined a personal view about the tricky questions of energy supply, its storage and conversion in the early 21st century and underlined the importance of developing efficient, safe but also low-polluting electrochemical storage solutions [1]. To date, commercial batteries exclusively include inorganic electrode materials notably 3d transition metals which are scarce, expensive 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 storage mechanisms [3] making various cell or electrode configurations possible (Figure 1).

In 10 years, tremendous progress has been made to promote 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 comprehensive summary dedicated to all-organic cells that are also increasing in number thanks to this rapid progress on organic 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 particular exciting option is the true possibility of storing electricity 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 molar 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.

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<sup>•</sup>] 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 ~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 limited

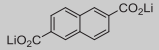
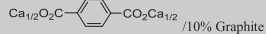
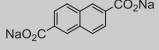
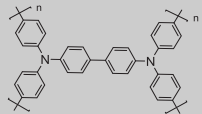
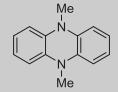


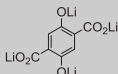
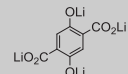
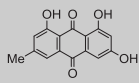

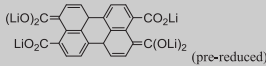
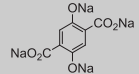
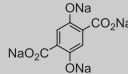
stabilities upon cycling were observed (Table 1, #3). Changing for a p-type cathode, Fan *et al.* [15] recently reported a potassium-based dual-ion full battery (PDIBs) based on graphite anode, polytriphenylamine cathode, and KPF<sub>6</sub>-based electrolyte (Table 1, #4) that shows quite good cycling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

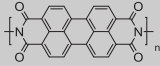
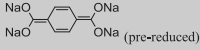
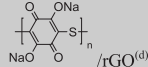
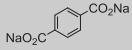


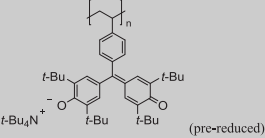
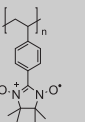
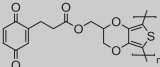
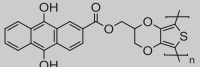




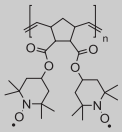
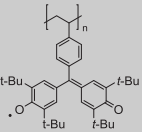
Table 1

## 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>	 /10% Graphite	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		 (pre-reduced)	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]

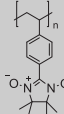
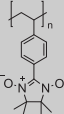
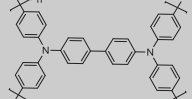
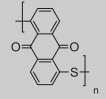
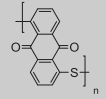
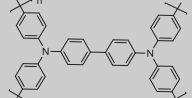
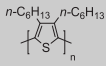


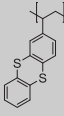
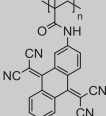
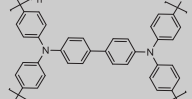
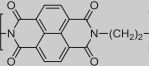
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Table 1 (continued)

#	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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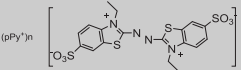
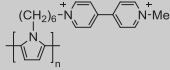

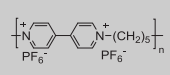
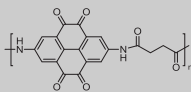
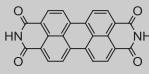
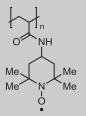
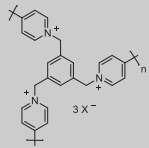
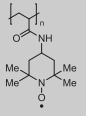
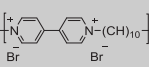
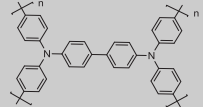
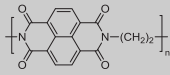
Table 1 (continued)

#	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>(d)</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 perylene-tetracarboxylate 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-perylene-tetracarboxylic 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 10 C 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 60 C 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

full cells but reported data were poor [38]. Palmore and co-workers [39] have prepared a polypyrrole with covalently bonded viologen (4,4'-bipyridine) moieties as the anode and polypyrrole doped with 2,2'-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) for the cathode side, both releasing or accepting a perchlorate anion during the redox processes. Experimentally this battery exhibited a very low capacity (Table 1, #26). Yao's group proposed also such a molecular ion-based "rocking-chair" type battery [11\*\*] with poly(*N*-vinylcarbazole) as the cathode and also a viologen polymer as the anode (poly(1,1'-pentyl-4,4'-bipyridinium dihexafluorophosphate)) (Table 1, #27). The performance of the battery was much better with this last configuration giving rise to  $\sim 1.8$  V as output voltage coupled with capacity of 100 mA h/g<sub>cathode</sub>.

### Promise and challenges of aqueous organic batteries

Organics can also operate in aqueous electrolytes. Although at the expense of energy density, aqueous rocking-chair batteries constitute a novel and promising technology as they are inherently safe, minimize cost and environmental impact by comparison to other battery technologies [5,40–42], which is particularly relevant for promoting low-cost energy storage solutions. This approach is still affiliated however, with relatively low energy density, below 50 W h/kg<sub>18650-cell</sub><sup>2</sup>, which puts even more pressure on material costs and durability in order to ensure economic viability. It has been recently shown that the electrochemical window of superconcentrated aqueous electrolytes can be expanded to 3 V thanks to the formation of electrolyte-electrode interphase and unusual water molecule coordination environment [40,43]. However, it should be stressed as far as energy cost (\$/kW h) is concerned this voltage gain is counterbalanced by the mass ( $\sim 2$ –5 times that of a 1 M electrolyte) and the price of these additional salts. Indeed, a bulk energy storage unit will only be implemented if the cost per unit of energy falls below 0.03 \$/kW h, a value lower than the cost of electricity from conventional power sources. This implies that the device must be able to deliver many thousands of charge-discharge cycles over many years (which for the time being rules out zinc-based systems) to insure storage cost remains in the vicinity of 100 \$/kW h. Moreover, aqueous batteries are intended for both domestic and large-scale applications and therefore the enormous scale of the required energy transition places limits on poorly abundant, non-uniformly distributed as well as monopolized metal resources. To sum up, the relatively narrow electrochemical window available in aqueous media together with costs and abundance issues makes even 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 materials to substitute inorganic ones with the promise of abundance in elements, lower costs and high structural designability. 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 decisive advantage is related to the potential access to superior specific capacities as organics benefit from multi-electron redox reactions. Lastly, the low volumetric density of organic compounds is obviously not as detrimental for stationary application as it is for mobile ones. Despite these benefits, several key issues remain and recent 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. Considering a plausible voltage of 1.2 V and capacity of 150 mA h/g for both the positive and the negative materials, a hypothetical 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> electrodes containing 80% of active material. In these conditions, 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 pigment 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 corrosion issues. The second bottleneck arises from the correlation between the potential range of the organic materials depending on the p- or n-type character. For aqueous batteries plethora of n-type organic materials can be designed as anode materials allowing the access to potentials below  $-0.3$  V vs. SCE (2.95 V vs. Li<sup>+</sup>/Li at neutral pH) thanks to the carbonyl/enolate redox moiety. However, 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, except 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 inorganic(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 polypyrrole-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  $\sim 10\text{--}15$  \$/kg and LTP higher than 20 \$/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-(tripyridiniummesitylene)) [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 ( $> 5\text{--}10$  \$/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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- Papers of particular interest, published within the period of review, have been highlighted as:
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