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Organic Batteries – the route towards sustainable electrical energy storage technologies

Abstract

Transition metal compounds have been long dominating the field of rechargeable batteries. The recent times however led to an explosion of portable electric powered applications requiring portability of the energy sources. Portable electronics, Internet-of-Things, Electric vehicles are only few of the major domains to be cited here. But this aggressive demand has also led to a sustainability dilemma: green energy management should proceed through green processes as well. It has therefore become crucial the consideration of the material abundance, efficiency of synthesis and recycling processes, life-cycle analysis and scalability. Within this context, all-organic batteries are emerging as probably one of the most promising approaches to render the electrochemical energy storage (EES) technology green and sustainable. But there are also many fundamental challenges to overcome in this direction before claiming technological relevance. In this article we discuss the feasibility, the challenges and the potential technological impact of the all-organic batteries.

Keywords
electrochemistry; organic battery; alkali metal battery; solid-state chemistry

1. Introduction

Global warming, fossil fuel availability and energy management have become popular yet highly debated topics of our modern society [1]. Whereas the sustainable energy production has already a significant role to play in the energy production landscape, storage technologies lag behind. This is particularly true for the electrical energy production and storage. Wind and hydropower turbines, photovoltaic panels, biomass conversion and geothermal power plants continuously increase their share in the (direct) electrical energy production [2]. Further exponential trend is to be expected here as the impact of fossil fuel consumption is being largely recognized as the main cause for climate change. Yet, competitive electrical energy storage solutions are scarce; and while Tesla's "Power Plant" initiative demonstrates that this can become our reality, worldwide implementation remains difficult given several bottlenecks to overcome, in particular when it comes to versatile and multi-scale electrical energy storage solutions.

Electrochemical energy storage systems (EESS) (e.g. batteries and supercapacitors being the most representative here, with the Lithium-ion technology monopolizing by far this field) have thus become essential elements towards a sustainable energy management economy. The ever-increasing demand for transportation and

consumer electronics mobility further adds to the strategic importance of EESS. The lithium-ion battery (LIB) rush is about to entirely re-shape our economy!

The main challenges to overcome for EESS to really enable this revolution can be resumed to three words - Cost, Abundance and Reliability (CAR) [3]. Making a battery at lowest costs, based on abundant elements and resources and with a long cycle life has become the challenging dream of any battery scientist and engineer. Low costs should be associated to any aspect related to battery life cycle - raw materials, production, assembly, use and end-of-life disposable (here, ideally, through efficient recycling). Closely related to raw materials costs, abundance is also an important element. Since the stored energy (or the stored charge) scales linearly with the mass of the active battery materials, massive production of batteries will inevitably require enormous amounts of raw materials (e.g. lithium, cobalt, nickel following current technology) so that developing chemistries based on scarce elements is not justified. Finally, a long and safe cycle life (ideally, more than 25 years of unfaulty operation or equivalent of 10.000 re-charges) is highly sought.

The currently used battery technologies seem to be out of the energy storage strategic intent. The oldest rechargeable battery is still used nowadays: the lead-acid (Pb-acid) battery invented in 1859 by G. Planté, offering an energy density of 25-40 $W.h.kg^{-1}$ with an output voltage of 2.0 V and a life of 200-300 re-charge cycles [4]. Higher energy densities and longer cycle life were attained with Ni-Cd or NiMH (Nickel-Metal Hydride) rechargeable batteries (40-80 $W.h.kg^{-1}$ at a nominal voltage of 1.2 V and up to 1500 re-charges), a technology that entered the market in 1989 [5]. The so used LIB, commercialized for the first time by Sony Corp in 1991, combines the low lithium intercalation potential of the negative graphite electrodes with the high potential $LiCoO_2$ positive electrode, delivering a voltage above 4.2 V along with high energy density ranging from 100 to 150 $W.h.kg^{-1}$ and longer cycle life of 500-2500 re-charges [6].

With these numbers, it is not surprising that LIB has become the dominating EES technology. But why do we need better batteries? The answer here lies in comparison with other energy storage and delivery technologies. For instance, gasoline can deliver 10 times more energy per unit mass than the currently most performing LIB. Costs are also largely different and set some limitations with, for example, Pb-acid batteries still being cheaper to use for most of the vehicle currently (along with factors like the temperature of operation).

Still, independently of the technology to be used, current LIB electrode materials still largely rely on (transition) metal chemistries. These not only require extensive mining, energy consuming metallurgical and ceramic processes but also pose problems at the end of life - if not properly recycled (that may be again based on energy consuming processes) may pose environmental problems. Ultimately, this could also led to partial or total depletion of these elements. A new shift may soon be needed, and this time, directed towards greened and more sustainable EES!

2. Towards a Sustainable Electrochemical Energy Storage

When looking at the composition of current LIBs, a clear mismatch exists between the elements that can be naturally recycled (in other words, are part of biomass) and the main contained in LIBs. Referring the use of *3d* metals in LIBs, *Co, Ni, Cu, Cr or V* might not be the best and long term choice and switching to *Mn* and *Fe* might be more sustainable (being constituents of biomass and thus naturally recycled). *Li* has been also pointed as an element with limited natural abundance and switching to *Na, Mg* or *Ca*-based chemistries should eliminate this issue. However, inorganic materials synthetic and recycling approaches still remain energy consuming due to high processing temperatures required so that alternatives may be needed soon.

Thus, to truly promote low emission electrochemical energy storage systems, a possible alternative would be in partially
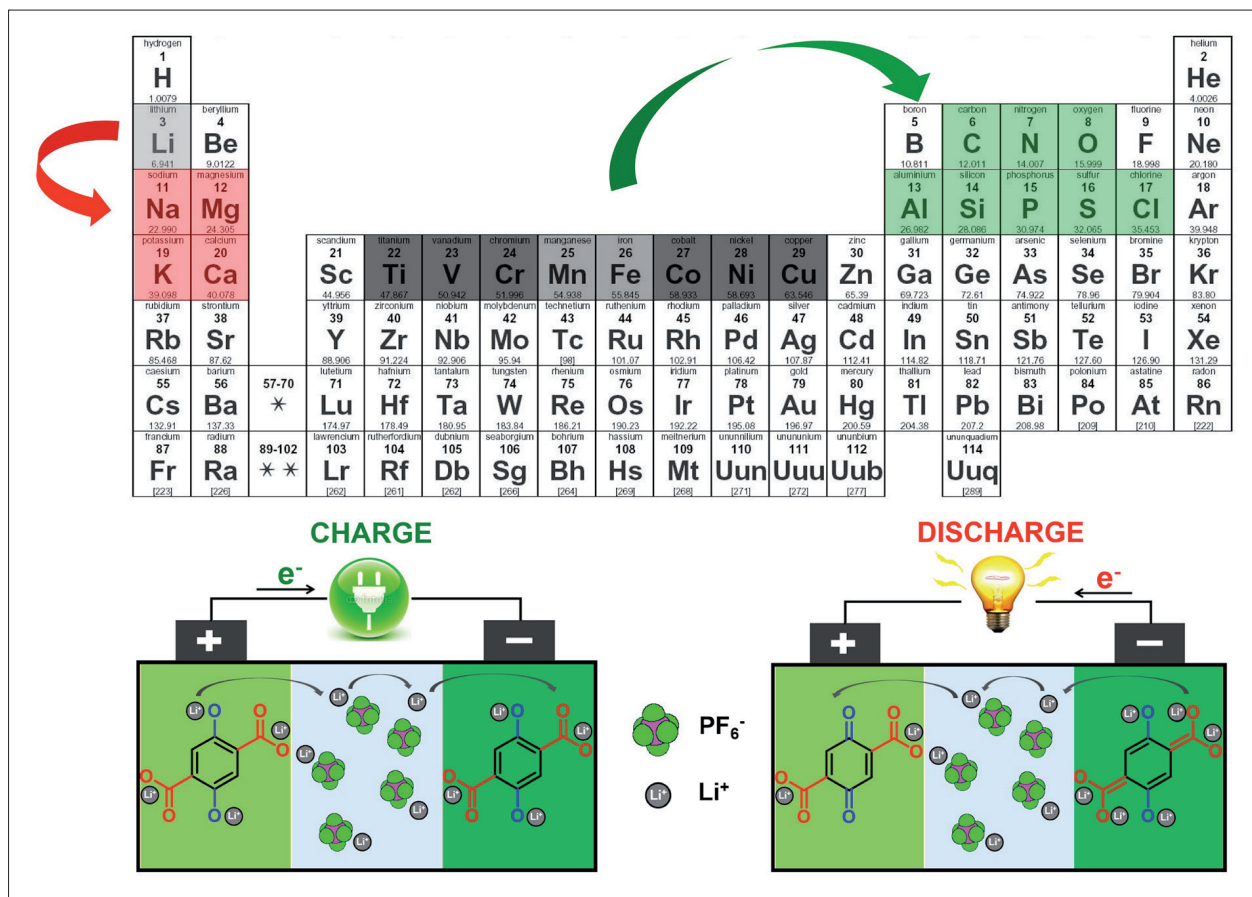
Figure 1. Moving away from traditional battery chemistries. Adapted from reference 3

moving away from inorganic-based to all-organic-based electroactive electrode materials. Indeed, organic materials are based on naturally abundant elements (e.g. *C, H, O, N, S*) coupled with the real possibility of being generated from renewable resources (biomass) [7]. In addition, organic materials are typical fuels that can be easily burned by simple thermal combustion at medium temperatures making readily possible the recyclability of constituent elements *via* CO_2 valorisation [8]. All of these advantages offer new possibilities for low cost, greener and sustainable energy storage devices (Figure 1).

Unlike most of the inorganic materials, organic electrode materials are also much easily compatible with chemistries beyond lithium including sodium, potassium, magnesium, aluminum and zinc [3]. Additionally, the application of organics can be in dissolved (redox flow batteries) or solid-state, in aqueous or non-aqueous electrolytes, which makes them more versatile for a broad type of electrochemical storage devices. More importantly, the richness of organic chemistry provides great opportunities for elaborating innovative electrode materials based on material design and molecular engineering, this allowing to get tailored structures for : i) tuning the redox potential (cathode or anode), ii) tuning the theoretical capacity (reversible multi-electrons reaction) and iii) being used as bulk (small molecules) or flexible electrodes (polymers) [9].

3. Batteries from Biomass ?

Environmentally speaking, the richness of organic chemistry allows us to design green battery materials from renewable starting compounds through low environmental footprint processes. Figure 2 highlights some examples of potential organic battery materials that can be generated from bio-sources *via*
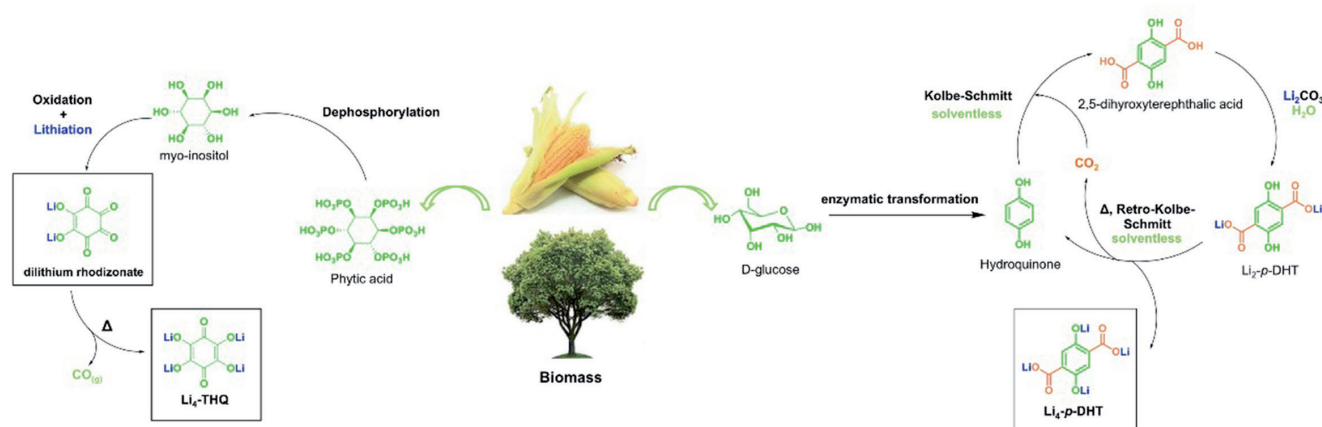
Figure 2. Examples of bio-sourced synthesis of organic battery materials

eco-friendly synthetic processes. The dilithium rhodizonate may be obtained from the natural compound myo-inositol that can be found in the majority of plants in the form of phytic acid. Note that dilithium rhodizonate is a competitive electrode material that can provides high specific and volumetric energy densities, of 1100 W.h.kg^{-1} and 2400 W.h.L^{-1} respectively [10]. Furthermore, the tetralithium salt of tetrahydroxybenzoquinone (denoted Li$_4$-THQ) may be derived from dilithium rhodizonate through thermal disproportionation in solvent free conditions and absence of any strong base, which can improve the E-factor of the process (relation between the amount of waste and product for a given process) [11].

The tetralithium salt of dihydroxyterephthalate (Li$_4$-p-DHT), another potential organic battery material, can be also obtained from natural products through synthetic process free of harmful solvents and in agreement with some principles of green chemistry. Typically D-glucose may be transformed to hydroquinone via enzymatic transformation followed with Kolbe-Schmit reaction implying chemical sequestration of CO_2 [12]. Note that Li$_4$-p-DHT can be used as Li-reservoir cathode material necessary for LIBs.

Inspired by cellular energy respiration and storage, several redox active biomolecules derived from biomass could be used as electrode materials for energy storage. Emodin (6-methyl-1,3,8-trihydroxyanthraquinone), extracted from polygonum cuspidatum, and humic acid, produced by biodegradation of dead plants, are examples for this category [13]. Overall, these examples show that bio-sourcing for organic battery materials is feasible and upon further optimization could become of practical importance.

4. Basic Principles of Organic Batteries

It should be pointed at this stage that organic batteries is not a new concept, and the origin can be traced back to 1969 when the first application of dichloroisocyanuric acid as electroactive material was proposed by William *et al.* [14]. Whereas the field remained dormant for a longer time, the recent decade has shown revived interest in this technology, with a plethora of organic electrode materials and architectures been reported so far. Here, we will focus and highlight only few efficient examples amongst (in Figures 3 and 4).

The choice of an electrode material for a rechargeable battery, whether for cathode or anode, is principally based on the reversibility of the electrochemical (redox) reaction of the active material. For organic molecules, the redox chemistry is based on the change of the state of charge of the molecule, which offers access to three different redox mechanisms according to

the proposed classification of Hünig (Figure 3) [15]. Firstly, *n*-type systems are characteristic of the organic molecules evolving from a neutral state to a negatively charged one accompanied by cation uptake. Quinones are the most studied examples of this type.

Oppositely, *p*-type systems is considered if the molecule is evolving from a neutral to a positively charged state, accompanied by anion uptake. Conjugated amines and conducting polymers are typical examples here. Finally, bipolar-type systems combine both types of mechanisms. The same organic molecule or eventually, the same redox center, can evolve from neutral state to a positively one and acts as *p*-type system or to a negative one and acts as *n*-type system. Nitroxide radicals are the most typical here but they are usually used as *p*-type system owing to their high redox potential (> 3.5 V vs. Li^+/Li) and better stability than the *n*-type redox.

Similarly to the inorganic counterparts, there is much more focus and work on organic positive electrode materials rather than on negative materials. We found materials derived from the three types of redox mechanisms presented above. Typically, the *p*-type materials exhibit high redox potentials (> 3.0 V vs. Li^+/Li) but with low capacities due to the high molecular weight of both electroactive molecule and

inserted anion. As an example, dilithium salt of 2,5-(dianilino)terephthalate (denoted Li_2-DAnT) has been recently reported by Poizot *et al.* as p-type cathode material displaying a redox potential of 3.1 V vs. Li^+/Li with an excellent reversibility for many anion chemistries, but with specific capacities not exceeding 80 mA.h.g^{-1} [16]. Poly (2,2,6,6-tetramethylpiperdinyloxy-4-yl methacrylate) (PTMA) as bipolar-type cathode material presents an excellent cycling stability (1000 re-charged) with a specific capacity of 111 mA.h.g^{-1} and a redox potential of 3.5 V vs. Li^+/Li [17]. This molecule led to a new concept proposed by Neshide, named " Organic Radical Batteries" [17] which has been commercialized by NEC on 2005 [18].

The most studied organic cathode materials are however *n*-type systems, with the carbonyl-based chemistries being by far the most focused due to their potential to achieve simultaneously high energy and high power densities and as well as extended cycling stability [19].

Carbonyls or quinones can be also prepared and used in batteries either in the oxidized or in the reduced state. The latter one, being lithium containing, is of high relevance for LIBs as it can allow the use of non-lithiated anode, an aspect that is practical and low cost to implement (Figure 1). Yet, the developments in this direction are scarce. For example, the di-lithium (2,3-dilithium-
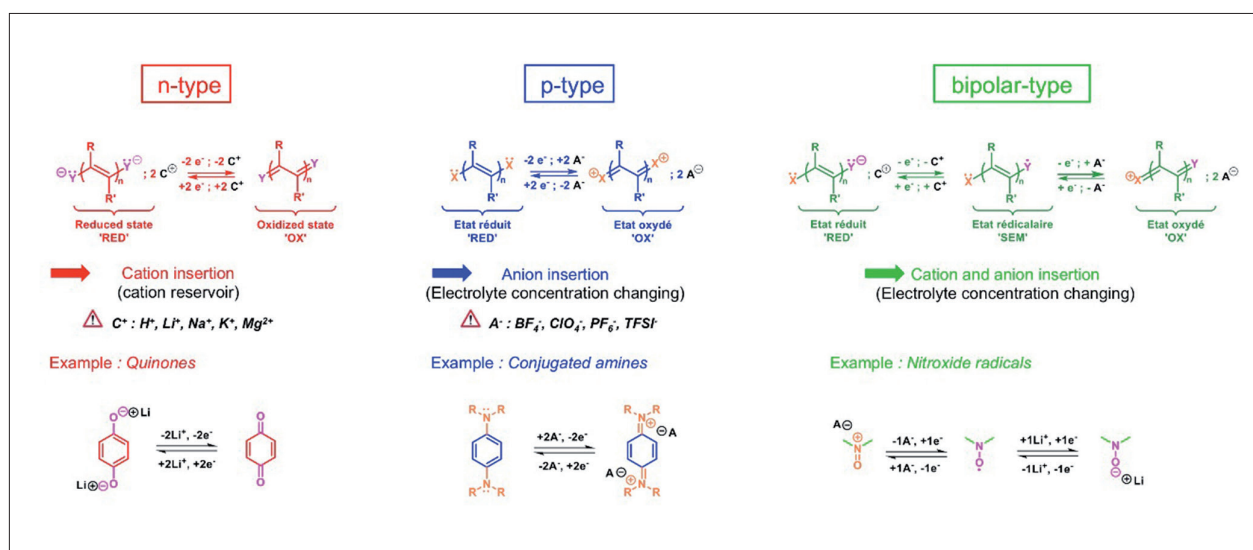

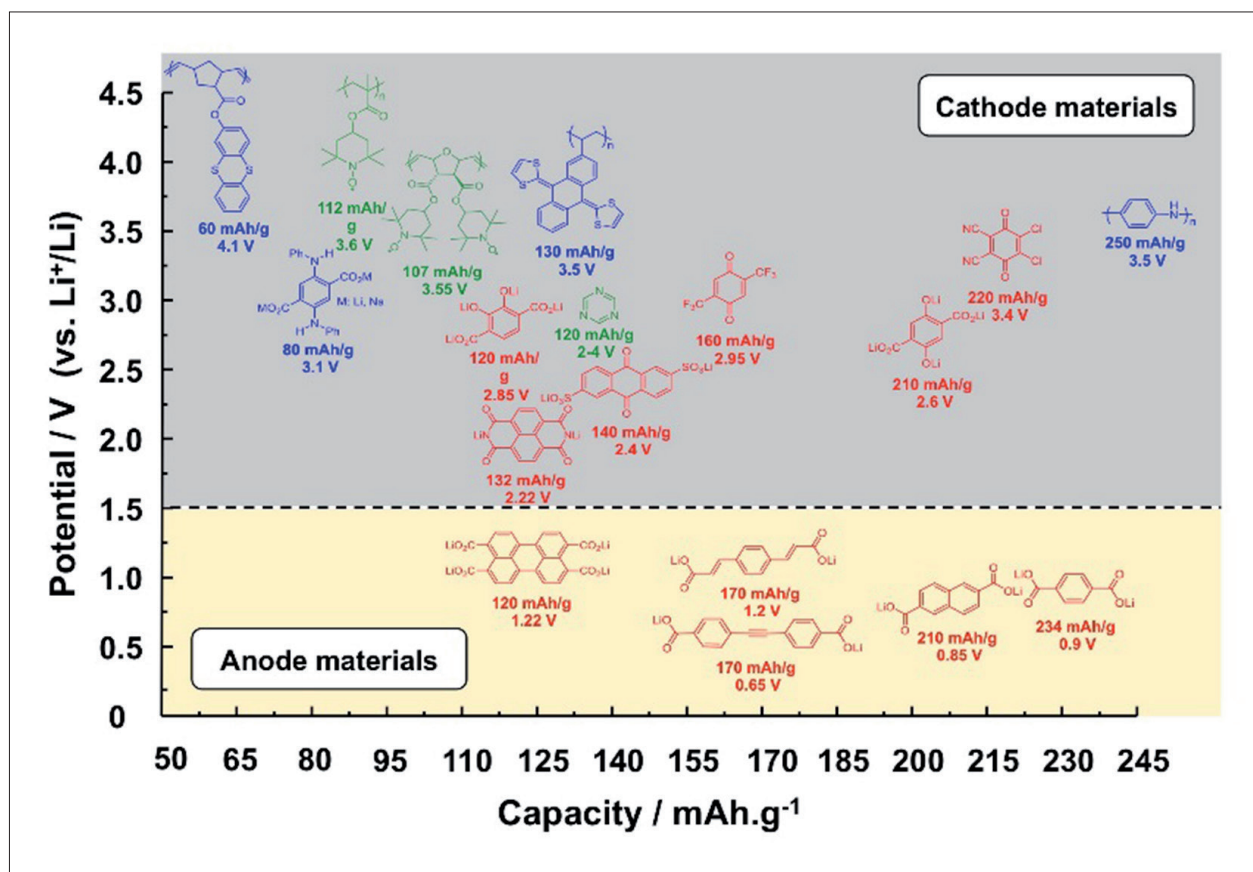Figure 3. The possible redox mechanisms for organic battery materials. Adapted from reference 13

Figure 4. Classification of most studied organic battery materials by their redox potential and gravimetric capacity

oxy)-terephthalate (denoted Li$_4$-o-DHT) has been proposed as a good candidate, delivering a specific capacity of 120 mA.h.g^{-1} at a redox potential of 2.85 V vs. Li$^+$/Li [15]. Nevertheless, its potential is still low to compete with inorganic materials but most importantly, the lithiated compound is not stable in ambient atmosphere, that would require costly manipulation in a protected environment.

Developing lithium containing, air-stable, organic redox material has become a major challenge in the field.

Contrary to rather numerous examples of positive electrode materials, there are only conjugated dicarboxylate-based systems that display a low enough redox potential to be used as anode materials. M. Armand *et al.* have presented for the first time the dilithium terephthalate as anode material for lithium batteries [20]. This molecule exhibits a theoretical capacity equal to the one of graphite carbon (300 mA.h.g^{-1}) at a

however higher redox potential of 0.9 V vs. Li$^+$/Li (whereas it is 0.1 V for graphite). Following this pioneering work, other carboxylate derivatives have been reported with different molecular designs allowing the tuning of the potential [21] and the enhancement of lithium conduction inside the crystal structure [22]. Yet, the operational redox potential of these is still above 0.5 V, an aspect that will penalize the full cell voltage for an all-organic battery.

5. Next Generation Organic (Hybrid) Batteries

So what should we expect next? Despite the exciting opportunities and promises, the current organic battery materials and technologies are still far from being ready to challenge the inorganic based LIBs. At best, an all-organic LIB will deliver a voltage of 2 V whereas inorganic systems operate already above 4 V. Gravimetric capacities may be comparable yet the volumetric energy metrics remain poorly competitive. And

as already mentioned, the air stability of lithium containing organic compounds remains a major challenge, with only little examples known to date [23].

Yet the potential of organic batteries is still to be uncovered and there is great scientific and technological potential behind. Organic chemistry is versatile and can offer access to different chemical functionalities so that the capacity, voltage, solubility and the reaction kinetics could be tuned at will. Recycling routes may be also more efficient, since the organic materials could be derived from biomass and combusted at medium temperatures. Finally, organic battery materials are less sensitive to the cation metal chemistry so that it can easily allow switching form *Li*-ion technology towards *Na*, *Mg* and *Ca* based batteries.

Several classes of organic battery materials are worth to be further studied, each of these bringing advantages but also having limitations (Figure 5). We have identified most promising and we discuss them shortly in the following.

Molecular crystals - probably the most straightforward concept consisting in using small organic molecules. Low costs and simplicity are clear advantages here. Low molar mass is beneficial as the charge storage capacity scales inversely with the mass so that smaller is the molecule, more gravimetric capacity it can store[a]. Dilithium rhodizonate is one typical example, with a capacity of 589 mA.h.g^{-1} being possible to attain for a full 4-electrons / 4-lithium redox. Unfortunately, these excellent performances come along with also major challenges. Molecular solids typically have weak intermolecular interactions, these leading to elevated solubility in organic battery electrolytes or crystal structure instability during redox and lithium (or other cation) (de)

insertion. The solubility can be tackled by the introduction of ionic groups that increase the polarity of the molecule yet, at the detriment of the capacity. Going at nano-scale could enhance solid crystal stability yet the high surface area can give rise to enhanced parasitic reactions.

Polymers and macromolecules is an approach broadly used in the organic battery community and is based on the polymerization of small organic redox units (soluble molecules) or grafting them on a polymeric backbone [24]. This strategy allows the improvement of the cycling stability by drastically curbing the solubility (to be mentioned however that many so made polymers still remain soluble). Yet, probably the main advantage brought here is that it can allow for intrinsic electrical conductivity if a conjugated (or electron conducting) backbone is used [25]. Polymer based batteries allow also to go a step further by paving the way towards flexible batteries. Nevertheless, the polymerization increases the synthesis complexity as well as the molecular weight leading thus to lower specific capacities.

Supramolecular assemblies is a relatively new concept proposed with few examples studied so far. Stoddart *et al.* were amongst the first to build a redox active supramolecular architecture [26]. The proposed system is original and attractive in that it allows the enhancement of both electronic and ionic conductivities through electron-sharing and nanoporosity respectively. The solubility as well as the synthetic complexity may still be of concern here.

Covalent / Metal Organic Frameworks (COFs and MOFs) are considered very attractive and promising directions to be explored. The ionic conductivity (cation, anion, solvent molecules diffusion) is supported by the large open

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a   The energy stored (**E** - W.h.kg^{-1}) in a battery is proportional to **E = V x C**, where V = voltage (V); C = charge storage capacity (mA.h.g^{-1}); the capacity could be calculated according to the following formula:

$$C \text{ (mA.h.g}^{-1}) = \frac{n \times F \text{ (C.mol}^{-1})}{M \text{ (g.mol}^{-1})} = \frac{n \times 96\,485 \text{ (A.s)}}{M \text{ (g)}} = \frac{n \times 26\,801}{M} \text{ (mA.h.g}^{-1})$$

Where **n** - N° of exchanged electrons; **F** - Faraday constant (96 485 A.s.mol^{-1}); **M** - molar mass (g.mol^{-1}).

channels available in these materials. Solubility and thus the cycling stability are enhanced given the "polymer"-like nature [27]. The synthesis of COF materials requires at least two different conformers, and so far with only one of these conformers was selected with electroactive properties, leading to low specific capacities. This can be improved by using only electroactive conformers [28] or introducing transition metals (e.g. MOFs) to enable multi-electron redox [29]. Furthermore, the concepts of surface and bulk loose significance in C/MOFs. So does the meaning of battery-like (bulk, faradaic) and capacitive (surface, coulombic) charge storage.

Exploring both concepts within one single material & technology is bound to provide a major advance in the field with some advances already achieved with electron conducting MOFs [30].

The organic battery field is still in its early stages and there is large room for improvements in terms of gravimetric capacity, redox potential, cycling as well as air stability. And if the perfect chemistry is found here, the synthesis method should then be optimized to achieve this in only a few steps (less than 3 ideally to limit the costs) and proceed through sustainable processes (solvent free, abundant catalysts and co-reactants). Fundamental processes underlying the electrochemical processes in solid phase in organic battery compounds are also poorly explored and will require further work. Solvent co-intercalation, surface passivation, side-reactions as well as possible inter- or intra-molecular reactions will need to be carefully considered for future developments. The obstacles seem to be multiple, but not surmountable, and only by solving them the organic batteries will be able to claim supremacy. All in all, the future of electrochemical energy storage looks organic!
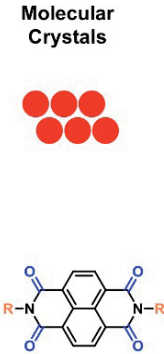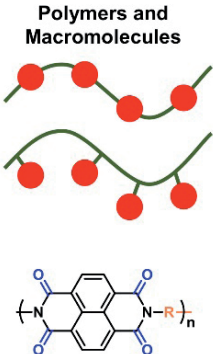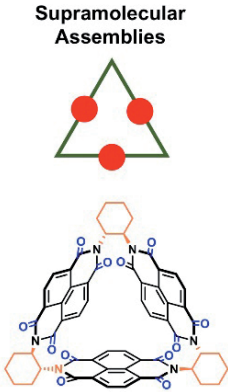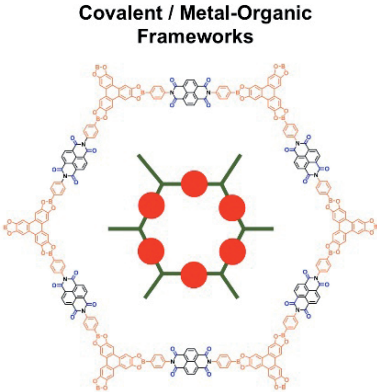

Figure 5. Classification of organic battery materials by topology. One single organic redox unit can be assembled into different molecular assemblies so that the electrochemical and battery performances are affected. This is exemplified here through the use of naphthalenetetracarboxylic diimide redox unit

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