REVIEW



Organic Negative Electrode Materials for Metal-Ion and Molecular-Ion Batteries: Progress and Challenges from a Molecular Engineering Perspective

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In the critical area of sustainable energy storage, organic batteries are gaining momentum as strong candidates thanks to their lower environmental footprint and great structural versatility. A plethora of organic materials have been proposed and evaluated as both positive and negative electrode materials. Whereas positive electrode chemistries have attracted extensive attention in the context of practical research and advances overviews, the negative electrode field remains poorly analyzed from a critical point of view. This review summarizes and provides an assessment of different classes of organic compounds with potential applications as negative electrode materials for metal-ion and molecular-ion batteries. The impact of molecular design on the electrochemical performance and guidelines for remaining challenges are highlighted. years. Thanks to their versatility and flexibility, EOMs have shown broad applicability as bulky solid^[3] or dissolved^[4,5] active material, in aqueous^[6–8] or non-aqueous electrolyte,^[9–11] for portable and stationary batteries, respectively. In practice, OEMs are explored as main active materials in LIBs,^[12] beyond Li systems (e.g., hydrogen,^[13,14] Na-ion,^[15–19] K-ion,^[20–24] and multivalent batteries like magnesium,^[25,26] zinc,^[27] or aluminum^[28,29]) and also redox flow batteries;^[30] or as supporting active materials such as redox mediators for Li-O₂ batteries,^[31] Li-source sacrificial materials for Li-ion capacitor^[32]

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Abstract: In the critical area of sustainable energy storage, organic batteries are gaining momentum as strong candidates thanks to their lower environmental footprint and great structural versatility. A plethora of organic materials have been proposed and evaluated as both positive and negative electrode materials. Whereas positive electrode chemistries have attracted extensive attention from both, practical research and advances overview, negative electrodes field remains marginally analyzed from a critical point of view. This review summarizes and provides an assessment of different classes of organic compounds with potential application as negative electrode materials for Metal-ion and Molecular-ion batteries. The impact of molecular design on the electrochemical performances and guidelines for remaining challenges are particularly highlighted.

1. Introduction

The increasing concerns over the resources availability and environmental manufacture as well as recycling issues are considered as one of the main challenges facing the future of Li-ion batteries (LIBs) given the exponential increase predicted.^[1] In the light of promoting efficient, safe and low-polluting electrochemical energy storage systems.^[2] electroactive organic materials (EOMs) have sparked considerable attention in recent years. Thanks to their versatility and flexibility, EOMs have shown broad applicability as bulky solid^[3] or dissolved^{[4-} ⁵] active material, in aqueous^[6-8] or non-aqueous electrolyte^[9-11], for portable and stationary batteries respectively. In practice, OEMs are explored as main active materials in LIBs,^[12] beyond Li systems (e.g., Hydrogen,^[13-14] Na-ion,^[15-19] K-ion,^[20-24] and multivalent batteries like magnesium,^[25-26] zinc^[27] or aluminum^[28-29]) and also redox flow batteries;^[30] or as supporting active materials such as redox mediators for Li-O₂ batteries,^[31] Li-source sacrificial materials for Li-ion capacitor^[32] and redox electrolytes for high-energy supercapacitors.^[33] In contrast to the state-of-the-art inorganic materials, whose reactivity is based on redox of transition metal center and consequently Li⁺ de/insertion,^[34-35] the redox reaction of EOMs is based on the charge state change of the redox moiety,^[12] for which the charge compensation during redox can be either made by cations, referring to n-type systems, or by anions, belonging then to ptype system, according to the proposed Hünig's classification.^[36-37]

The richness of organic chemistry coupled with molecular modifications have provided thus far a plethora of molecules and architectures operating within a large potential window with high specific capacities, extended cycling stability and high cycling rate. This has enabled building a broad database of electroactive compounds for both positive and negative electrode applications. Organic positive electrode materials (OPEMs) certainly benefit from larger attention since there are more possibilities to explore, e. g., conducting polymers,^[38-39] nitroxides and other stable organic radicals,^[40-43] sulfur compounds,^[11] as well as conjugated amines,^[44-46] conjugated sulfonamides,^[47] nitro-aromatics,^[48] and carbonyls^[49-50]. The latter being certainly the most explored category owing to major advances attained so far but also to opportunities for further improvements to attain simultaneously high energy and power densities combined with good cycling stability.^[12] On the opposite side, the chemical library is less rich for organic negative electrode materials (ONEMs), primarily due to much focus on positive electrode chemistries, for which many issues and strategies are to be addressed and explored, respectively. Today, the ONEMs database counts fewer redox families as OPEMs one, with also less specific chemistries within each class. To cite the some: the most studies conjugated-dicarboxylates,^[51] hückel-stabilized Schiff base,^[52] nitrogen-redox azo compounds^[53] and the most recently reported N-substituted salts of viologen derivatives.^[52] Since 2008 (a year witnessed as the modern area revival of OEMs), dozens of review articles have been published from different perspectives (e.g., molecular design, [20, 22-23, 27, 41-42, 49-50, 54-^{69]} sustainability,^[70-71] opportunity,^[3, 72-74] practicability^[75-78] and technology^[79-82]). It is worth noting that most reviews are focused on OPEMs with less consideration to ONEMs, except two reviews dedicated to ONEMs for Na/K-ion batteries,^[37, 83] yet presenting only a summary of advances and no critical discussion or suggested solutions for remaining challenges.

In this review, we focus exclusively on ONEMs from a molecular engineering perspective, and we emphasize on the molecular structure impact on the electrochemical and charge storage performances from an overview of literature and data reported on metal-ion (Li⁺, Na⁺ and K⁺) as well as anion storage. The material classes are selected based on their redox potential that is considered as suitable for negative electrode application. The limit is set at 1.5 V vs. Li⁺/Li (except for p-type negative electrode class), alike for inorganic Li₄Ti₅O₁₂ displaying the highest redox potential amongst the negative electrode inorganic materials.^[84] Each identified redox class is first discussed separately and an executive summary is presented at the end. Guidelines for future developments within each class, as well as in general for ONEMs are proposed.

2. Conjugated dicarboxylates

Owing to their lowest reversible redox potential attained in an organic material thus far $(1.1 > E > 0.65 V vs. Li^+/Li)$, conjugated dicarboxylates are considered as the most promising candidates for the negative electrode in organic M-ion batteries. In 2009, Armand *et al.*^[51] were the first to report the redox activity of dicarboxylates by proposing aromatic dilithium benzenedicarboxylate (Li₂C₈H₄O₄ or Li₂-TA and hereafter referred to as Li₂-BDC for the purpose of simplicity, all other dicarboxylate derivatives in this article will be denoted based on this notation) and conjugated acyclic dilithium *trans-trans*-muconate (Li₂C₆H₄O₄ and denoted here as Li₂-*ttM*) (**Figure 1-a**).

Similar to most of the organic redox functions (except nitroxide systems, and some nonconjugated carboxylic acid derivatives which will be discussed at the end of this section), an aromatic core unit is required for reversible functioning of conjugated dicarboxylates. Specific capacities of 300 mAh.g⁻¹ (considered as of 2Li⁺/e⁻) can be reached at a redox potential of 0.8 V vs. Li⁺/Li for Li₂-BDC. In contrast, only one Li⁺ was possible to exchange, corresponding to a specific capacity of 170 mAh.g⁻¹, and at higher redox potential (1.4 V vs. Li⁺/Li) for Li₂-*ttM*. This difference in redox reactivity was attributed to the conjugated system linking the two carboxylate moieties. The same electrochemical behavior was also observed for other conjugated acyclic dicarboxylates, even with extending conjugation,^[85] with the additional curiosity that reversible activity towards Li⁺ requires carboxylate functions in *trans*configuration which leads to the formation of a free radical mesomeric form after the complete reduction.

The galvanostatic cycling curves of Li₂-BDC (**Figure 1-a**), the molecule of reference for conjugated dicarboxylates class, display a polarization of 100-200 mV along with an important

irreversible capacity (~30%) during the first cycle, leading to an Initial Coulombic Efficiency (ICE) of 79%, ascribed to the formation of the well-known Solid Electrolyte Interphase (SEI).^[86] Generally, SEI formation is essentially linked to electrolyte decomposition and use of large amount of conductive carbon.^[87] However, the SEI models have been developed for inorganic phases, and for the case of molecular crystals this aspect still requires further understanding. For instance, in the carboxylate-based active materials, the carboxylate/carbonyl might also decompose through reductive decarboxylation (alike Barton groups decarboxylation) or via radical attack processes.^[88-93] The radical species formed during the electrolyte decomposition might further react (or react differently) with the organic material and an SEI different as on inorganic surface may be obtained. Oltean et al., [94] have attempted to clarify this interface chemistry through hard X-ray photoelectron spectroscopy (HAXPES), but more in-depth characterizations remain to be done for better understanding. In addition, Li2-BDC showed limited power performance, requiring large amount of carbon additive (>30 wt.%) for an appropriate use, and suffered from continuous capacity fade upon cycling (20 % of capacity loss after 50 cycles). Among the common reasons for such fading, the structural or morphological material changes on cycling along with ion/electrolyte diffusivity have been proposed, yet the possibility of an unstable, and continuously reactive SEI has to be more considered.



Figure 1. a) First reported conjugated-dicarboxylates as anode material for LIBs and potentialcomposition profile of Li₂-BDC during galvanostatic cycling (reproduced with permission from ^[51]. Copyright 2009 Nature Publishing group). b) Proposed redox mechanism for M₂-BDC, general redox system according to Hünig's classification^[37] and M-ion insertion ability in M₂-BDC. c) Voltage profile of K₂-BDC measured vs. K (reproduced with permission from ^[95]. Copyright 2017 The royal Society of Chemistry). d) Radar plot comparing fundamental properties (qualitative analysis) of conjugated dicarboxylates and state-of-the-art inorganic Lihost anode materials.

For this class of materials, the charge storage mechanism belongs to n-type system, alike enolate/quinone redox class (**Figure 1-b**). During the discharge, the dicarboxylate groups undergo a two-electron reduction and two monovalent metal cations are inserted for charge compensation, forming the reduced dicarboxylate form. During the charge, the reverse oxidation process takes place resulting in the initial dicarboxylate form. Many studies have confirmed, by means of *ex-situ* FTIR and Raman measurements,^[51, 96-97] that the redox reaction in conjugated dicarboxylates arises from carboxylate functional groups (-COO⁻). According to

Hünig's classification,^[37] the redox process of organic compounds comes into consideration as mere electron and charge compensating element (metal cation in this case) transfers which involves i) a conjugated system known as "Wurster type" (aromatic ring) and ii) end groups that have free electron pairs (N, O, S, P or π -system; e.g., carboxylate –COO⁻) (Figure 1-b). In the light of this, it appears unreasonable to consider carboxylate groups separately from the conjugated system. Therefore, both conjugated system and carboxylate groups have to be involved in the redox mechanism, and the carboxylate should be responsible for the low redox potential, as this latter varies according to the chemical nature of the end group (e.g., Li₂-HQ^[98] and TCNQ^[99-102], Figure 1-b). This comes in parallel with the findings by Ogihara and colleagues,^[103-104] through *ex-situ* HAXPES and XRD measurements, in that the inserted Li⁺ are present near electron-rich aromatic-ring carbon atoms through an interaction with π electrons rather than with oxygen atoms of carboxylate units (e.g., formation of O-Li bond as always illustrated in conjugated dicarboxylates). Additionally, the structural packing (e.g., crystal structure) of dicarboxylate salts must also be involved in the redox mechanism, as the electrochemical formation of the reduced form Li₂Na₂-BDC is possible by Li⁺ insertion in Na₂-BDC; whereas was not possible through Na⁺ insertion in Li₂-BDC (Figure 1-b).^[105] Clearly, more fundamental studies should be carried out in order to elucidate the real redox mechanism and clarifying the electron and cation transfers' phenomena.

As it turns out, metal benzenedicarboxylate have been considered as a suitable solution for alternative devices beyond Li-ion, namely the cheaper Na-ion^[106] and K-ion batteries^[107]. In this context, Zhao *et al.*^[108] and Lei *et al.*^[95] have explored the sodium (Na₂-BDC) and potassium (K₂-BDC) salts in Na and K half-cells, respectively. Na₂-BDC was able to deliver its theoretical capacity (250 mAh.g⁻¹, considered as of $2Na^+/e^-$) at a low potential of ~0.29 V vs. Na⁺/Na. The delivered capacity was maintained over 50 cycles at a cycling rate of $1Na^+/5h$. Note that cycling rate for organic materials is often described as current density (mA.g⁻¹) or C/n,

where C and n correspond to theoretical capacity and number of hour respectively; but here, for clarification purposes, we deliberately described it as number of M⁺ exchanged in hour (where M = Li, Na, K). The good electrochemical performances for Na₂-BDC have encouraged Abouimrane and co-workers to build a full-sodium cell coupling Na₂-BDC with high voltage cathode Na_{0.75}Mn_{0.7}Ni_{0.23}O₂.^[105] The as-assembled full-cell exhibited an output voltage of 3.6 V and delivered a reversible specific capacity of 257 mAh.g⁻¹ (based on Na₂-BDC mass), with a capacity retention of 92% after 50 cycles. Similarly, excellent electrochemical performances have been demonstrated with K₂-BDC (**Figure 1-c**).^{[95, 109-110][} Specific capacities of 229 mAh.g⁻¹ (equivalent to two K⁺ exchanged) were reached at a potential of ~0.6 V vs. K⁺/K and at a current density of 200 mA.g⁻¹ (close to 2K⁺/1h).^[95] A high capacity retention of 96% was reached at also a high current density (1000 mA.g⁻¹, 10K⁺/1h) and maintained over 500 cycles. The high-rate capability was ascribed to the reduced particle size (nanometric) as well as the weaker Lewis acidity and higher mobility of K⁺,^[111-112] which ensures larger transfer number and thus faster kinetics; whereas the great cycling stability was attributed to the formation of stable SEI in 1,2-dimethoxy-ethane (DME) based electrolyte.

According to these, conjugated dicarboxylates are positioning themselves as promising candidates among M-host inorganic-based anode materials (**Figure 1-d**). First, they are capable of closing the gap between the commercialized 0.1-0.3 V vs. Li⁺/Li graphite-based electrodes and 1.55 V vs. Li⁺/Li Li₄Ti₅O₁₂ electrodes, which manifest huge energy density penalty for the latter and considerable risk of decomposition/safety associated with Li metal deposition^[113] and heat generation^[114] for the former, in addition its energy-intensive production and low natural abundancy.^[115] Second, conjugated dicarboxylates display a lower volume expansion on alkali metal cation insertion (< 10%), unlike the high capacity (10 times higher than graphite) metal-based, alloy and metal oxide materials that suffer from huge volume expansion (100-400%),^[116-117] which induces SEI instabilities and associated rapid capacity fade with cycling. Other

advantages of these materials include sustainability and the ability to use aluminum current collector, with a weight gain and cost cutting over copper, as well as enhanced thermal stability that should result in safer LIBs.

Following these pioneering advances, researchers have subsequently focused on molecular engineering approaches as a powerful tool to further improve the electrochemical performances. **Scheme 1** summarizes all adopted strategies for molecular modification studied thus far, together with the expected as well as attained impact on the electrochemical properties. These are individually compared and discussed in the following.



Scheme 1. Schematic illustration of Metal benzenedicarboxylate showing the adopted strategies for molecular modification and expected as well as attained impact on the electrochemical properties.

2.1. Effect of the spectator cation

Generally, conjugated dicarboxylates tend to form stable layered crystalline metal-organic structures, *via* metal cation-carboxylate groups ionic interactions (2D-hybrid coordination polymer).^[118] In the case of Li₂-BDC, the terephthalate anions (BDC²⁻) are bridging the LiO₄ polymer layer (anti-fluorite phase).^[118-119] These can be treated as spectator cations as they do not directly participate in the charge storage reaction, but act as structuring element affecting

strongly the crystal structure along with the physicochemical properties, and therefore, the electrochemistry. Accordingly, other alkaline and alkaline earth metal cations have been used with the idea to improve the electrochemical performances of the terephthalate redox center. Data in **Figure 2** summarizes and discusses the spectroscopic, crystallographic and electrochemical data obtained for all reported thus far metal benzenedicarboxylate salts used for charge storage ($M_{2/n}^{n+}$ -BDC, $M^{n+} = Li^+$, Na⁺, K⁺, Ca²⁺, Ba²⁺ and Sr²⁺).^[51, 105, 120-123]

The impact of cation substitution can be first seen on the stretching vibrations of the carboxylate group (**Figure 2-b**). FTIR responses of the reported $M_{2/n}^{n+}$ -BDC show that asymmetric vibration $v_{as}(COO^-)$ is randomly shifted for the monovalent cations (Li⁺, Na⁺ and K⁺), while it increases with the ionic radius for the bivalent cations (Ca²⁺ < Sr²⁺ < Ba²⁺) (**Figure 2-d**). This is kept reasonable as the position of the $v_{as}(COO^-)$ band is known to be sensitive to the electron density on the carboxylate group^[124] and to the coordination number with the metal.^[125] However, the symmetric vibration $v_s(COO^-)$ remains unaffected (~1395 cm⁻¹). Furthermore, the ionic radius seems to impact the deformation vibration δ_{O-M} as this later is shifted accordingly, which indicates that that Mⁿ⁺ could strengthen/weaken the electrostatic interaction between the metal to neighbor oxygen atoms, and thus probably the ionic nature of terephthalate anion.

From crystal structure point of view, alkali and alkali-earth metal terephthalate salts crystallize in different unit cells (monoclinic or orthorhombic) and therefore are not isostructural (**Figure 2-c**). In fact, these form typical lamellar structured materials with alternating M-O inorganic and π -stacking organic terephthalate layers,^[118] but with different atom packing mode for each analogous. For instance, the Li atoms in Li₂-BDC are tetrahedrally coordinated with four neighbor oxygen atoms (LiO₄), while Ba atoms in Ba-BDC form decahedrons with eight neighbor oxygen atoms (BaO₈). The coordination number is linked to the ionic radius and electropositivity of the metal cation. The higher ionic radius and electropositivity are, the higher coordination number will be.^[126-127] As previously observed with IR data, their crystallographic counterparts also present striking coherencies and similarities. The length of C-O bond in the carboxylate function seems to correlate to the metal cation electronegativity, whereas the length of O-M bond tend to vary according to the ionic radius (ionic potential).^[128] Furthermore, all metal terephthalates possess relatively equal C-O bond lengths, except for Na and Ca analogs. Wang *et al.*^[121] have assigned this difference in bond length to the fact that the coordination of Ca²⁺ towards –COO⁻ function yields more likely to ionic-nature bond rather than covalent-like bond for the other metal cations (**Figure 2-a**).^[129] Finally, one can conclude that the ionic radius has some influence on the O-M bond, and thus on the crystal structure orientation, whereas the electronegativity has an effect on the C=O bond, and thus on the electron density and probably the ionic nature of the O-M bond.

In terms of electrochemical properties, all metal terephthalates analogs revealed quasi-similar electrochemical responses as compared to Li₂-BDC. Contrary to expectations, cation substitution shows insignificant impact on the redox potential, as this latter was found to remain close to 0.8 V vs. Li⁺/Li for all $M_{2/n}^{n+}$ -BDC analogs. The current understanding is that the redox potential of OEMs is influenced either by the electron density of the aromatic bearing the redox center,^[102, 130-132] or by electrostatic interaction with the redox center itself^[36, 98] or by a nearby heteroatom.^[133-134]

a)		b) _*						
	444	M ⊕	$\overset{M}{\stackrel{\bullet}{=}} \delta_1 \neq \delta_2$	Molecule	v _{as} (COO ⁻) (cm ⁻¹)	v _s (COO⁻) (cm⁻¹)	δ(O-M) (cm ⁻¹)	
	a axis	$O \bigoplus_{\delta} O \\ \delta$ Ionic Bonding	$\delta_1 = \delta_2$ Covalent-like Bonding	Li ₂ -BDC	<mark>ر</mark> 1575	1394	528	
				Na ₂ -BDC	<mark>ک</mark> 1560	1395	510	
				K ₂ -BDC	⁵ 1575	1395	509	
		Electrostatic	Li	Ca-BDC	1608	1397	530	
	0 — 0 M	I: Li ⁺ Ca ²⁺	^{///} ∕o′ M : Li ⁺	Sr-BDC	1552	1393	507	
	ၜႜၴၟႍႝႜႍၟႍၟႍႜၟၟၜ		\bigcirc Ca ²⁺	Ba-BDC	[↓] 1532	1397	506	
	BDC ²⁻	K* Ba ²⁺	کر ان کر کر ان کر					
2)		Μ	1 ⁿ⁺ _{2/n} (Li ₂)- <i>p</i> -DHT					

c) #

	Molecule		Bond I of C-0	enght O (Å)	Bond lenght o M-O (Å)	f	Coordinati cation	ion of meta 1 (MO _x)	al Space (group	Cell	
	Li ₂ -BDC	c.	1.272 –	- 1.263	1.96		Te	etra	P2 ₁	/c	Monoclinc	
	Na ₂ -BDC	ξ	1.291 –	- 1.239	2.43		Prisme Trigonal Prisme trigonal		Pbc	2 ₁	Orthorhombic	
	K ₂ -BDC	<	1.261 –	1.260	2.79				P2 ₁	/c	Monoclinic	
	Ca-BDC		1.380 -	- 1.190	2.35		Octa		C2/	c	Monoclinic	
	Sr-BDC		1.270 –	1.260	2.53		Octa		P2 ₁	/c	Monoclinic	
	Ba-BDC	•	1.260 –	1.260	⁺ 2.78		Deca		Pbc	2 ₁	Orthorhombic	
d)						e)	*					
	M(ⁿ⁺) - O Coordination bond	Ionic radius (Å) ^φ	χAR (M)	ΔχΑR (O-M)	Ionic potential (n / ionic radius)	-	Molecule	E _{red} (V vs. Li ⁺ /Li)	Capacity at 2 nd cycle (mAh.g ⁻¹)	Capacity at 50 th cycle (mAh.g ⁻¹)	t Capacity retention after 50 cycles (%)	
	Li ⁽⁺⁾ - O	0.76	0.97 ر	2.53	1.315		Li ₂ -BDC	0.8	300	234	78	
	<mark>Na⁽⁺⁾ -</mark> O	1.02	§ 1.01	2.49	0.980		Na ₂ -BDC	0.8	200	~200	99	
	K ⁽⁺⁾ - O	1.38	0 .91	2.69	• 0.724		K ₂ -BDC	0.85	150	130	86	
	Ca ⁽²⁺⁾ - O	1.06	1.04	2.46	1.886		Ca-BDC	0.8	170 ^b	155	91	
	<mark>Sr⁽²⁺⁾ -</mark> O	1.18	0.99	2.53	1.694		Sr-BDC	0.85	125 ^b	91	72	
	Ba ⁽²⁺⁾ - O	[†] 1.35	• 0.97	2.53	1.481		Ba-BDC	0.85	150 ^b	135	86	

Figure 2. Overview of alkali and alkali-earth metal benzenedicarboxylate ($M_{2/n}^{n+}$ -BDC, where $M^{n+} = Li^+$, Na⁺, K⁺, Ca²⁺, Ba²⁺ and Sr²⁺). a) Crystal structure illustration of Li₂-BDC along with the molecular structure of $M_{2/n}^{n+}$ -BDC and $M_{2/n}^{n+}$ (Li₂)-*p*-DHT along with schematic representation of the possible bonding types between M and COO⁻.^[129] b) Values of both antisymmetric and symmetric vibrational modes of carboxylate functions, v_{as}(COO⁻) and v_s(COO⁻), along with deformation vibration mode of O-M, δ O-M, for the corresponding $M_{2/n}^{n+}$ -BDC. * Data retrieved from different reported articles.^[51, 95, 105, 108, 121, 135] c) Crystallographic data of the corresponding $M_{2/n}^{n+}$ -BDC. # Data retrieved from crystal structures resolved by Mazaj, Scholz, Lo and Kaduk groups.^[118, 136-138] d) Physical data related to M(ⁿ⁺)-O coordination bond. Φ Values retrieved from Ahrens's article,^[128] χ AR(M) represents the Allred-

Rochow electronegativity value for M; $\Delta \chi AR$ represents the electronegativity variation related to the M-O bond using $\chi AR(O) = 3.5$. e) Energy metrics of the corresponding $M_{2/n}^{n+}$ -BDC retrieved from various reported papers.

In fact, a similar behavior was also observed on metal - 2,5-dilithium-oxy-terephthalate derivatives (e.g., $M_{2/n}^{n+}(\text{Li}_2)$ -*p*-DHT, $M^{n+} = \text{Li}^+$, Ca^{2+} , Ba^{2+} and Mg^{2+} **Figure 2-a**,^[139] a molecule with amphoteric redox property enabling a use as both positive and negative electrodes thanks to their conjugated dicarboxylates and enolate redox units respectively^{[97, 140][}). When operated at low potential (through conjugated di-carboxylate), the redox potential remains unchanged close to 0.8 V vs. Li⁺/Li, in contrast, when operated through enolate (at higher voltage), a significant potential shift was noticed amidst the analogous (e.g., +800 mV voltage gain for Mg(Li₂)-*p*-DHT in comparison with Li₂(Li₂)-*p*-DHT).^[139] The origin of such potential shift might be related to some specific electrostatic interaction between (carboxylate)Mg-O-Li(enolate) (**Figure 2-a**), which might have similar effect on the carboxylate if the composition is inversed (carboxylate)Li-O-Mg(enolate), yet further information on the composition and crystal structure are required to support this assumption.

Considering that all the terephthalate phases have been evaluated in Li half-cells, which means that all the reduced phases are lithium containing (Li₂-M-terephthalate), those might have similar reactivity as Li₄-terephthalate (reduced phase) which can lead to similar potential values, and this would be further accentuated with plausible cation exchange during cycling. Additionally, this effect should be also considered in other metal half-cells, as the metal cation of this later participates in the redox reaction contrary to the one initially present in the molecule. For instance, Li₂-BDC (vs. Li) and K₂-BDC (vs. K) showed 500 and 300 mV higher than Na₂-BDC (vs. Na) respectively, whereas redox couples of Li⁺/Li (-3.04 V vs. NHE) and K⁺/K (-2.93

V vs. NHE) present only 300 and 200 mV potential shift as compared to Na⁺/Na (-2.71 V vs. NHE).

It is important to note that all reported $M_{2/n}^{n+}$ -BDC electrodes have been prepared and tested in similar conditions to ensure consistency and direct comparison. The electrodes were formulated as hand mixed 60wt.% of active material, 30wt.% of conductive carbon and 10wt.% of binder. The electrochemical evaluation was performed in galvanostatic mode at a cycling rate of 1Li⁺/10h in Li half-cells using 1M LiPF₆ in a mixture of ethylene carbonate/dimethyl carbonate 50/50 (v/v) as electrolyte. Under these experimental conditions, the metal terephthalate analogs attained reversible specific capacities ranging from 125 to 300 mAh.g⁻¹ (**Figure 2-e**) at the second cycle, corresponding to almost two electron redox reaction per molecule. The rate capability was not considerably enhanced and large irreversible capacities was also observed for all $M_{2/n}^{n+}$ -BDC analogs alike the reference Li₂-BDC.

2.2. Effect of the conjugated core unit linking the carboxylates

As discussed at the beginning of this section, the conjugation in the dicarboxylates, plays an important role in the electrochemical performances (e.g., Li₂-BDC vs. Li₂-*ttM*, **Figure 1-a**). In this context, several studies have then focused on other conjugated systems in order to evaluate the impact and effectiveness on the electrochemical performances. Three molecular modification strategies have been applied so far: aromatic extension, incorporation of double/triple bond to extend the conjugation and utilization of heterocyclic dicarboxylates.

2.2.1. Aromatic extension

As a result of their first experimental finding, Fédèle *et al.*^[141] have extensively investigated the aromatic extension with the purpose of enhancing the rate capability of conjugated dicarboxylates (**Figure 3**). Naphthalene, biphenyl, perylene and anthracene have been

employed as core units, within dilithium 2,6-naphthalenedicarboxylate (denoted Li₂-NDC),^{[103-} 104, 141-142] dilithium 4,4'-biphenyldicarboxylate (denoted Li₂-BPDC),^[143] tetralithium Li₄-PTC)^{[87,} 144-147] perylenetetracarboxylate (denoted as and dilithium 2.6anthracenedicarboxylate (denoted Li₂-ADC),^[148]respectively. All the carboxylate derivatives have been electrochemically evaluated in Li half-cells using rigorously the same conditions, namely hand mixing of 60% of active material with 40% of conductive carbon (super P) and mass loading of about 10 mg. In this part, we will discuss each compound separately and compare it to the reference Li₂-BDC (with the same surface area). Along the same discussion, we will review the corresponding carboxylates derivatives explored in Na- and K-ion batteries.

The first reported extended conjugated carboxylate example was the Li₂-NDC (**Figure 3-a**). This compound was found to crystallize in the same unit cell as Li₂-BDC, namely monoclinic lattice with a space group of P2₁/c.^[149] As expected, the distance between the two end carboxylate groups is higher (8.3 Å as compared to 5.7 Å for Li₂-BDC) given the larger size of the naphthyl core. In terms of electrochemistry, Li₂-NDC was found to react reversibly at an average redox potential of 0.88 V vs. Li⁺/Li and exhibited a specific capacity of 200 mAh.g⁻¹ (85% of the theoretical capacity, considered as of $2Li^+/e^-$) at a cycling rate of $1Li^+/10h$.^[104, 141-142] However, a rapid capacity fade with cycling at low rate was also observed. This experimental result remains not fully understood to date, as possible dissolution of one of the reduced intermediates (Li₃-NDC or Li₄-NDC)^[25] or material structural degradation was discarded. Nevertheless, a plausible electrode exfoliation (contact loss between the active material particles and conductive carbon ones)^[150] or bad SEI formation might be behind the capacity loss, which could be solved with electrode engineering (e.g., addition of efficient binder) and electrolyte formulation respectively, and this was not investigated in the author's work.

Interestingly, Li₂-NDC was able to retain 75% of its theoretical capacity at a high cycling rate of 2Li⁺/h with a moderate polarization of about 350 mV. This clearly points out the benefit of naphthalene core with respect to rate capability, as the compound of reference Li₂-BDC was able to achieve only 90 mAh.g⁻¹ (30% of the theoretical capacity) and disclosed higher polarization of 900 mV when cycled at a similar rate (and under similar cell assembly and cycling conditions). The origin of such rate capability enhancement could rely on improved electrical conductivity and/or faster ion diffusion related to lower electrostatic interactions between the intercalated Li⁺ in between layers due to higher distance.



Figure 3. a) Molecular structure, theoretical capacity and measured values of the 1st reduction potential for different extended conjugated-dicarboxylates employing aromatic extension. b) Proposed redox mechanism and corresponding voltage profile of Li₄-PTC (reproduced with permission from ^[87]. Copyright 2017 John Wiley and Sons). c) Molecular structure and structural packing for Na₂-BPDC (reproduced with permission from ^[151]. Copyright 2014 The Royal Society of Chemistry). d) Potential-composition profile of Li₂-ADC recorded at a cycling rate of 20Li⁺/h (reproduced with permission from ^[148]. Copyright 2020 John Wiley and Sons).

The sodium (Na₂-NDC) and potassium (K₂-NDC) versions of NDC²⁻ ligand have been studied by Cabañero *et al.*^[152] and Li *et al.*^[153] respectively. Likewise, Na₂-NDC also crystallizes in the same space group (P2₁/c) as its analogous Li₂-NDC with Na⁺ however being penta-coordinated, as compared to tetrahedral O-coordination in the case of Li^{+,[152]} Both Na₂-NDC and K₂-NDC showed promising electrochemical performances. For instance, Na₂-NDC was found to react reversibly with Na at an average potential of 0.4 V vs. Na⁺/Na, giving a specific capacity of 200 mAh.g⁻¹ (almost the theoretical capacity, considered as of $2Na^+/c^-$) at a cycling rate of $1Na^+/20h$. As regards K₂-NDC, specific capacity of 171 mAh.g⁻¹ (almost the theoretical capacity, considered as of $2K^+/c^-$) was reached at an average potential of 0.55 V vs. K⁺/K and at a current density of 50 mA.g⁻¹ (equivalent to $1K^+/5h$). Interestingly, a potential shift of ~100 mV is obtained for Na₂-NDC (vs. Na) and K₂-NDC (vs. K) by conversion to Li⁺/Li scale, emphasizing once again the effect of the intercalated cation's chemical nature on the redox potential of conjugated dicarboxylates.

Contrary to K₂-NDC, but alike Li₂-NDC, the Na₂-NDC also displayed low stability upon cycling. But in this case, the authors overcome this by playing with binders in the electrode composition, achieving thereby a good stability over 200 cycles. The enhanced rate capability was also maintained in Na half-cells, as Na₂-NDC was able to attain 76% of its capacity at a cycling rate of 4Na⁺/h, contrary to Na₂-BDC which delivered only 30% of its capacity at the same cycling rate.^[108] Meanwhile, 76% of the capacity was also reached for K₂-NDC at a current density of 100 mA.g⁻¹ (equivalent to 1K⁺/h).

Whereas fundamental aspects of Li/Na/K-storage in NDC framework remain to be understood, the practical performances attained has motivated Toyota laboratories to build full-cell prototypes^[104]. Indeed, a quasi-solid-state (gel polymer is used as electrolyte) Li-ion full-cell was assembled using Li₂-NDC coupled with the high voltage spinel LiNi_{0.5}Mn_{1.5}O₄ as positive

electrode. The compact full-cell delivered an output voltage of 3.9 V with 96% capacity retention after 100 cycles at a cycling rate of $2Li^+/5h$. Such a good cycling stability emphasizes on the difference of reactivity of Li₂-NDC in liquid and quasi-solid-state cells. Although with a large Li reservoir, a rapid capacity decay was observed in liquid cell, which likely stems from the electrolyte decomposition generating reactive/radical species that could further react with the active material, and thus lead to continuous degradation of the molecule. In contrast, these might be impeded by using a solid electrolyte with a good active material electrolyte interface. Medabalmi *et al.*^[154] have also reported a Na-ion full-cell using Na₂-NDC coupled with Na₃V₂O₂(PO₄)₂/rGO (rGO standing for reduced graphene oxide). The full-cell was able to deliver a specific capacity of 150 mAh.g⁻¹ (based on Na₂-NDC mass) at an output voltage of ~3.2 V, yet with limited stability over cycling. Considering the good stability of Na₂-NDC in half cell, the capacity decay might be attributed to cell imbalance at the full cell level.

Similarly to Li₂-BDC and Li₂-NDC, Li₂-BPDC also crystallizes within the space group P2₁/c, but with a longer interlayer distance (carboxylate-carboxylate) of 9.84 Å (**Figure 3-a**).^[155] The molecular structure of the compound was found to be planar. The centrosymmetric structure was however preserved by an inversion centre. Note that the centrosymmetry is seemingly required to ensure good reversibility for conjugated dicarboxylate.^[156] At a cycling rate of 1Li⁺/20h, Li₂-BPDC has delivered its theoretical specific capacity (211 mAh.g⁻¹, considered as of 2Li⁺/e⁻) at an average potential of 0.7 V vs. Li⁺/Li, accompanied with relatively stable capacities upon 25 cycles. At high rate (2Li⁺/h), Li₂-BPDC was able to attain 86% of its capacity and displayed a polarization of 50 mV, which remains considerably lower than the one observed for Li₂-NDC (350 mV). In a recent work by Ogihara and co-workers,^[103] it was demonstrated that this rate capability enhancement stems from the pure solid-solution-type mechanism and larger Li⁺ diffusivity for Li₂-BPDC, in contrast to Li₂-NDC, whose redox reactivity follows a

mix of two-phase transition and solid-solution mechanisms and presents relatively low Li⁺ diffusivity.

Prior to this work, Choi *et al.*^[151] have already investigated the sodium version of BPDC²⁻ (Na₂-BPDC) in Na half-cells. Specific capacities of 200 mAh.g⁻¹ (considered as of 2Na⁺/e⁻) was reached at ~0.5 V vs. Na⁺/Na and at a cycling rate of 1Na⁺/10h, accompanied with excellent cycling stability over 150 cycles. Interestingly, Na₂-BPDC was able to attain the full capacity at 4Na⁺/h and half of it at 40Na⁺/h, emphasizing thus the rate capability enhancement observed with its analogous Li₂-BPDC. Moreover, thanks to single crystals, the authors have succeeded to solve the crystal structure of the monohydrate version (e.g., Na₂-BPDC.H₂O), which is also crystallized within the same space group alike the pervious carboxylate derivatives. In this crystal structure (**Figure 3-b**), the BPDC²⁻ ligand was found to be in a planar configuration, with a dihedral angle close to 0° between the two phenyl rings, and water molecules being trapped within structure. The planarity of BPDC²⁻ ligand might be induced by the coordination of water molecules with Na⁺, contributing thus to the formation of inorganic layers (Na-O) along with carboxylate functions. At this stage, however, it is hard to attribute the enhanced rate capability of Na₂-BPDC to the planarity of BPDC²⁻ ligand, since the crystal structure of the desolvated Na₂-BPDC to solved.

The potassium version of BPDC²⁻ ligand (denoted K₂-BPDC) was reported by Li *et al.*,^[157] and for which satisfactory specific capacities and rate capabilities were obtained in K half-cells. In fact, a reversible two electron redox reaction was demonstrated with K₂-BPDC, leading to a specific capacity of 165 mAh.g⁻¹ at ~0.3 V vs. K⁺/K and at current density of 100 mA.g⁻¹ (equivalent to 1K⁺/h). Good cyclability was also observed by maintaining 73% of the capacity after 100 cycles. In terms of rate capability, K₂-BPDC could realize stable capacities of 87%/81%/60% under high current densities of 200/500/1000 mA.g⁻¹ corresponding to 2, 5 and $10K^+/h$ respectively.

Alike M₂-BDC and M₂-NDC (M = Li, Na, K), the conversion of M₂-BPDC (vs. M) to Li⁺/Li scale revealed an impact of the intercalated metal cation on the redox potential of BPDC²⁻ ligand. For instance, K₂-BPDC (vs. K) shows 200 mV higher whereas Na₂-BPDC (vs. Na) displays 100 mV lower than Li₂-BPDC (vs. Li). This negative potential shift was not perceived with Na₂-BDC and Na₂-NDC in Na half-cells, which indicates that the conjugated system (core unit) might interact with the intercalated cation, thus emphasizing the participation of the former in the redox mechanism of conjugated dicarboxylates.

More interestingly, the use of a hyper conjugated perylene core unit in Li₄-PTC (**Figure 3-a**) has led to further improved rate capability. In theory, assuming that all four carboxylate functions are active, the Li₄-PTC should be able to store 4Li⁺/e⁻ per formula unit giving a theoretical capacity of 237 mAh.g⁻¹ (capacity remains comparable to those for Li₂-NDC and Li₂-BPDC). Experimentally, Li₄-PTC was found to deliver only half of its capacity (e.g., 108 mAh.g⁻¹ corresponding to nearly two Li⁺/e⁻ exchanged) at a cycling rate of 1Li⁺/10h (**Figure 3-**c). In fact, the reversible redox reaction of the perylene-tetracarboxylate (PTC⁻) is limited to only two electrons (reduction of two carboxylate redox moieties), and the extra capacity observed beyond this range can be attributed to the utilization of large amounts of conductive carbon.^[87] This two-electron limited redox reaction is also observed with many other aromatic-tetracarboxylic acid dianhydride or diimide, to cite perylen-tetracarboxylic acid dianhydride (PTCDA),^[158] naphthalene-tetracarboxylic acid diimide (NDI),^[47, 159] and pyromellic diimide (PDI).^[160] In contrast, the reduction of the last two carboxylate proceeds through irreversible processes occurring at much lower potential (usually in the 0.5-0.1 V potential range), triggering thereby a peculiar phenomenon called "Superlithiation"^[161] (refer further to section

1.2.2). This chemistry exhibits a higher potential (i.e., 1.1 V vs. Li⁺/Li) as compared to other dicarboxylate derivatives. The increase of the redox potential is presumably due to the conjugation extension in the core unit that affords $n-\pi^*$ orbital energy stabilization (hypothesis supported by Density Functional Theory (DFT) calculations^[156]).

Fédèle *et al.*^[144] reported that Li₄-PTC could maintain its two-electron capacity at higher cycling rate of 5Li⁺/h with relative stable cyclability over 100 cycles. Further to this work, Iordache *et al.*^[87] have reported excellent electrochemical performances attained with the same molecule. In a genuine electrode formulation, they were able to replace the large amount of Super P (40 wt.%) with only 0.5 wt.% of Multiwall Carbon Nanotubes (MWCNTs) as conductive additive. Owing to a peculiar affinity between Li₄-PTC and MWCNTs (believed to be a columnar phase of Li₄-PTC which is electronically conductive), it was possible to build and test electrodes with a high areal capacity of 1.2 mAh.cm⁻¹ (mass loading of 12 mg.cm⁻¹) accompanied with a high ICE of 87% and good cycling stability (87.4 %) over 70 cycles. Note that the improved ICE is due to the higher redox potential and the low carbon content used in this electrode composition, which, however, seems to remain specific to Li₄-PTC and cannot be generalized to other OEMs.

Similarly, sodium and potassium versions of PTC⁴⁻ ligand were also realized and showed interesting electrochemical performances.^[146, 162-164] For instance, Na₄-PTC/Na cell revealed a reversible electrochemical feature characterized with a redox potential of ~0.75 V vs. Na⁺/Na and low polarization in the order of 5-10 mV. Specific capacity of 175 mAh.g⁻¹ was delivered in the 2nd cycle at a current density of 25 mA.g⁻¹ (equivalent to 5Na⁺/h) accompanied with a moderate cycling stability (71%) over 120 cycles. Note that the theoretical capacity of Na₄-PTC is limited to 104 mAh.g⁻¹ (considered as of 2Na⁺/e⁻), and the observed extra capacity can be assigned to electrochemical charge storage contribution from conductive carbon. Unfortunately, the rate performance was not investigated by the authors so it remains difficult to discuss and

compare this aspect. In contrast, the typical electrochemical feature of K₄-PTC/K cell showed sloping curves without obvious plateaus (exhibiting a large polarization) with an average operating potential estimated at 1 V vs. K⁺/K. Again, similar effect can be noticed for this PTC⁴⁻ ligand by converting the potential values to Li⁺/Li scale but without any tendency.

Very recently, thanks to an important effort on organic synthesis (7 steps synthetic procedure), the most-extended conjugated structure so far, anthracene, was applied as core unit for conjugated dicarboxylates and investigated in Li half-cells.^[148] The simple addition of an aromatic ring (from naphthalene to anthracene) showed a significant impact on the rate capability without any influence on the redox potential, as Li₂-ADC was found to be reduced at a potential of ~0.81 V vs. Li⁺/Li. Rate capability revealed to be enhanced as well, since the compound was able to maintain 84% of its capacity (162 mAh.g⁻¹, considered as of 2Li⁺/e⁻) at a high cycling rate rarely reported for a carboxylate-based material in Li half-cells, namely 20Li⁺/h. Satisfactory specific capacities were obtained also at lower cycling rates, yet with bad cycling stabilities as observed with Li₂-NDC. For this time, the authors have ascribed this capacity fade to a continuous partial dissolution of the fully-reduced form (Li₄-ADC) at low cycling rate (confirmed by blue fluorescence visualization of the separator after extended cycling, attributed to anthracene derivatives dissolution). Such solubility issue is rarely observed with ionic compounds, and discovering its origin could lead us to reconsider the introduction of ionic groups as an efficient strategy to prevent the solubility. Interestingly, as claimed by the authors, this partial solubility could contribute to the excellent power performance by boosting the electron transfer at high rate from the carbon additive particle to the active material through a molecular shuttling effect.

In the light of the above, the rate capability of conjugated decarboxylates seems to be enhanced by the aromatic extension (particularly in the case of M₄-PTC, M = Li, Na, K; and Li₂-ADC). Yet, in-depth analysis such as conductivity measurements, coefficient of diffusion determination along with properly designed electrochemical testing protocols are remained to be done in order to understand this enhancement and help designing more efficient OEMs.

2.2.2. Extending conjugation through incorporation of unsaturated C-C bond (sp2 and sp hybridized carbons)

Another approach to extend the conjugation in aromatic systems is the incorporation of unsaturated C-C bonds within or out of the aromatic system (Figure 4). In this context, Renault and coworkers^[165-168] have explored extended conjugated-dicarboxylates containing C=C and $C \equiv C$ outside the aromatic core unit (Figure 4-a), leading to dilithium benzendiacrylate (denoted Li₂-BDA) and dilithium benzenedipropiolate (denoted Li₂-BDP) respectively. The presence of the adjacent C=C in Li₂-BDA induced a considerable redox potential increase as compared to Li₂-BDC (i.e., 1.2 V vs. Li⁺/Li).^[166-167, 169] The origin of this potential increase was not discussed by the authors, but it might be induced by the extended delocalization which leads to higher stability and thus higher potential, as observed for Li₄-PTC. In terms of electronic effect, the C=C may act as electron-donating or electron-withdrawing depending on the context.^[170-171] Considering that the redox reaction of Li₂-BDA should proceed through radical formation, C=C would likely act as electron-donation for radical stabilization and thus not being responsible for the potential increase. Overall, the compound was able to deliver a reversible capacity of 180 mAh.g⁻¹ (77% of the theoretical capacity, considered as of $2Li^{+}/e^{-}$) at $1Li^{+}/10h$ and ~90 mAh.g⁻¹ at 1Li⁺/1h that was barely maintained upon 100 cycles. In this work, the authors highlighted carbon-coating in the liquid-state as new electrode preparation to enhance the low conductivity of Li₂-BDA. The same group has also reported the sodium version Na₂-BDP,^[166] and demonstrated a specific capacity of 177 mAh.g⁻¹ (corresponding to 86% of the theoretical capacity, considered as of 2Na⁺/e⁻) at an average potential of 0.7 V vs. Na⁺/Na. In contrast to Li₂-BDA, whose ICE was about 79%, Na₂-BDA showed an enhanced ICE (~91%)

that might be explained by the difference of the SEI formation between the two homologues, since different electrolyte formulation has been used. However, Na₂-BDP experienced a rapid capacity fade during cycling that was accounted for dissolution or decomposition reaction of the molecule under battery operation.

Introduction of an ethynyl bond (-C \equiv C-) instead of C=C resulted on drastically different electrochemical features as compared to Li₂-BDA. Within a narrow potential window of 3.5-0.5 V vs. Li⁺/Li, Li₂-BDP exhibited a reversible capacity of 200 mAh.g⁻¹ at a rate of 1Li⁺/5h.^[165] The redox potential was hard to determine in this case due to the large voltage hysteresis characterizing the galvanostatic cycling profile (**Figure 4-b**), but it was estimated to be around 0.5 V vs. Li⁺/Li according to DFT computations. In contrast, when cycled within an extended potential window of 3.5-0 V vs. Li⁺/Li and at a lower cycling rate (of 1Li⁺/50h), Li₂-BDP revealed an unusually high specific capacity of 1363 mAh.g⁻¹ (corresponding to 11Li⁺/e⁻ exchanged) that was assigned to super-lithiation (**Figure 4-b**).

The super-lithiation was firstly established by Taolei *at al.*,^[161] in 2012, where 1,4,5,8naphthalenetetracarboxylic dianhydride (NTCDA), a material with 4 carbonyls, showed an unprecedented specific capacity (1800 mAh.g⁻¹) corresponding to $18Li^+/e^-$ exchanged per molecule. In fact, this peculiar electrochemical process consists in a two-electron reduction of an unsaturated C-C bond with the concomitant uptake of two Li⁺ for charge compensation. In theory, a 1/1 Li/C ratio could be reached, leading to attractive specific capacities could be six times higher than the capacity of graphite (> 1000 mAh.g⁻¹), for which only a 1/6 Li/C₆ ratio could be reached. Many molecular templates were found to be prone to super-lithiation,^[172-180] while others are not for unknown reason so far,^[165] and the process is not restricted to only lithium ion.^[181-183] In contrast, this redox mechanism as proposed involves the formation of highly reactive organolithium species (**Figure 4-b**).^[184] Such compounds are known for their strong nucleophilic-carbanion nature whose reactivity highly depends on the electropositivity of the metal.^[185] For instance, a highly electropositive metal (such as lithium in this configuration) leads to a highly active carbanion, that can subsequently attack the carbonyl carbon of a ketone (e.g., as in carbonate-based electrolyte solvents) to form tertiary alcohols.^[186] Organolithium compounds also require the employment of precautionary conditions such as working at low temperatures (-78°C) and air-free atmosphere due to their flammable and pyrophoric higher stability, and decreased reactivity at lower temperatures.^[187-188] Considering these, it is not surprising that the characterization of some super-lithiation phases revealed structural (molecular and crystalline) degradation upon cycling,^[161, 174] making thus the nature of the respective lithiated phases questionable. Despite many reports highlighting the benefits of super-lithiation, the science of this redox chemistry remains poorly understood and the required cycling conditions (e.g., employment of large potential window and very low current) along with the low energy efficiency makes this approach so far of limited practical use.

Complementary, disodium 4,4'-stilbenedicarboxylate (denoted Na₂-SDC)^[189] and dilithium 4,4'-tolanedicarboxylate (denoted Li₂-TDC)^[190] are some exemplary configurations containing unsaturated C-C bonds within the core unit (e.g., between phenyl groups). With respect to a standard electrode formulation (e.g., using 50:40:10 wt% of active material/Super P/CMC), Na₂-SDC was able to be sodiated/desodiated at high rate (12Na⁺/h) and maintains a specific capacity as high as 160 mAh.g⁻¹ (93% of the theoretical capacity, considered as of 2Na⁺/e⁻).^[189] The authors attributed this high-rate performance to the lamellar packing and the large d-spacing distance of the molecules (deduced from DFT, PXRD and AFM analysis, not from crystal structure), which forms a fast diffusion channel for Na⁺ insertion/extraction into the interspace between the layers (**Figure 4-c**). Furthermore, this chemistry exhibits an operating potential of 0.5 V vs. Na⁺/Na, which represents a slight increase of 160 mV if compared to its homologous Na₂-BPDC, presumably for to the same reasons as for M₂-BDA and M₄-PTC (M

= Li, Na).). In respect of cyclability, Na₂-SDC showed a capacity retention higher than 70% over 200 cycles. Unfortunately, the lithiated version of this compound has not been reported yet making a direct comparison difficult.



Figure 4. a) Molecular structure, theoretical capacity and measured values of the 1st reduction potential for different extended conjugated-dicarboxylates incorporating unsaturated C-C bond. b) Illustration of the "Super-lithiation" redox concept for Li₂-BDP and its corresponding voltage profile (reproduced with permission from ^[165]. Copyright 2016 American Chemical Society). c) Simulated structural packing for Na₂-SDC (reproduced with permission from ^[189]. Copyright 2015 American Chemical Society). d) Potential-composition profile and the corresponding derivative curve (inset) of Li₂-TDC (reproduced with permission from ^[190]. Copyright 2010 The Royal Society of Chemistry).

The potential-composition trace of Li₂-TDC revealed a peculiar electrochemical behaviour characterized with a large irreversible plateau located at \sim 0.9 V vs. Li⁺/Li, followed by a

reversible process taking place at ~0.65 V vs. Li⁺/Li (accounting for almost two Li⁺ exchanged) accompanied with minimal polarization (~15 mV) (**Figure 4-d**).^[190] The irreversible process was attributed to the SEI formation and the large amount of carbon (50%) required to trigger the electrochemical activity of the molecule. The origin of such low potential was not discussed by the authors, however, it could be ascribed to the electron-donating effect of pi-electron rich tolane unit^[156, 191] since the reversible redox activity of alkyne (-C=C-) might be discarded.^[192]

Polymorphism was another interesting feature observed for Li₂-TDC. In fact, depending on the solvent used during the preparation, Li₂-TDC was found to crystallize in different ways. The changes in structural packing dramatically affected the electrochemical performances of the obtained polymorphs, especially in terms of specific capacity, with nevertheless negligible impact on the redox potential. Despite the authors' attempts to elucidate the redox mechanism of Li₂-TDC, this latter remained elusive as the chemical nature of the reduced form (Li₄-TDC) remained still to be confirmed. Finally, even if Li₂-TDC is the molecule with the lowest reversible redox potential (flat plateau) among all reported ONEMs, its application as negative electrode material is hampered by the large amount of conductive additive required and efficient active material utilization only at low cycling rates ($1Li^+/20h$).

2.2.3. Influence of heteroatoms in the core unit

One way to affect the electronic density of the aromatic core unit is by making use of heterocyclic chemistry, a well-known concept in organic chemistry. The electrochemistry of conjugated dicarboxylates with heterocyclic core units make no exception here and indeed show significant differences in redox potential. So far, only thiophene, pyridine and pyrazine heterocyclic dicarboxylate derivatives have been reported (**Figure 5-a**).^[174, 193-195] The electrochemistry of dilithium thiophenedicarboxylate (denoted here as Li₂-ThDC) revealed a large reduction plateau at 1.0 V vs. Li⁺/Li (**Figure 5-b**), about 200 mV higher than of Li₂-

BDC.^[174] In fact, it is not obvious a priori why this compound shows a higher reduction potential in view of (i) S has electronegativity values similar to those of C ($\chi AR(S) = 2.44$; $\chi AR(C) = 2.50$), and (ii) the redox potential should not be that much affected when replacing 6-atom aromatic core unit by 5-atom aromatic ring one.^[131] The reason of such potential increase might be inherited from the electron density of the core unit as observed with some sulfur fused quinone derivatives,^[133, 196] but other reasons should not be excluded such as aromaticity^[197] (thiophene is less aromatic then benzene) and position of the dicarboxylates in the aromatic ring^[36, 198] (e.g., 1,3 dicarboxylate for Li₂-ThDC and 1,4 dicarboxylate for Li₂-BDC). Note that the theoretical capacity of Li₂-ThDC is limited to 291 mAh.g⁻¹ (considered as of 2Li⁺/e⁻). However, Li₂-ThDC shows the ability of an excessive lithiation by achieving a reversible specific capacity of 850 mAh.g⁻¹ (corresponding to 5.8 Li⁺/e⁻ exchanged) within large potential window (3-0 V vs. Li+/Li). In fact, Li2-ThDC was studied in the context of investigating the origin of super-lithiation, and to conclude about the accurate electrochemical performances (notably the operation potential), an electrochemical assessment within a narrower potential window (e.g., typically in the OCV-0.5 V potential range) might be more appropriate.

The pyridine core in disodium pyridine-dicarboxylate (denoted Na₂-PDC) leads to an important potential increase of almost 300 mV in comparison with Na₂-BDC,^[193] as would be expected from the higher electronegativity of N as compared to C (χ AR(N) = 3.04; χ AR(C) = 2.50). This rationale has been already explored on some quinone derivatives and showed similar effect.^[133-134, 199] The compound was able to attain a specific capacity of 192 mAh.g⁻¹ (76% of the theoretical capacity, considered as of 2Li⁺/e⁻), which was maintained for the subsequent 20 cycles.



Figure 5. a) Molecular structures, theoretical capacities and measured values of the 1st reduction potential for different conjugated-dicarboxylates containing heterocycles. b) Voltage profile for Li₂-ThDC cycled vs. Li⁺/Li (reproduced with permission from ^[174]. Copyright 2014 American Chemical Society). c) Voltage profile for Na₂-PDC cycled vs. Na⁺/Na (reproduced with permission from ^[194]. Copyright 2014 Elsevier Ltd). d) Proposed redox mechanisms governing the redox reaction of Na₂-PDC and Na₂-PZDC.

The Na⁺ insertion ability of the same compound was studied by Padhy *et al.*,^[194] and for which a reversible capacity of 236 mAh.g⁻¹ (corresponding to the theoretical capacity, considered as of $2Na^+/e^-$) was achieved at a cycling rate of $1Na^+/10h$. To note, the reduction process of Na₂-PDC reveled two distinct plateaus at 0.57 and 0.41 V vs. Na⁺/Na (marked as region II and III in **Figure 5-c**), higher than the potential of the single plateau observed for Na₂-BDC (e.g., ~0.29 V vs. Na⁺/Na), maintaining thus the potential increase observed in Li half-cells. Two hypotheses might explain this potential increase for Na₂-PDC. The first one is the lower LUMO energy of the core unit caused by the N atom,^[133] whereas the second one consists on a possible chelation between the inserted Na⁺ and N thanks to the lone electron pair (**Figure 5-d**).^[134] Padhy and coworkers adopted the second assumption. Based on DFT calculations on the reduced Na₂-PDC phase, they found that the first sodiation (region II, **Figure 5-c**) proceeds through bond formation between N atom of pyridine and the inserted Na atom, while the second sodiation (region III, **Figure 5-c**) proceeds through normal sodiation alike Na₂-BDC. This remains to some extent coherent with the claim of Ogihara and co-workers regarding the redox mechanism of conjugated dicarboxylates (refer to the beginning of this section).^[103-104]

Similarly, the aforementioned assumptions might rationalize the electrochemical behavior of disodium pyrazinedicarboxylate (denoted Na₂-PzDC, **Figure 5-d**).^[193] In Li half-cells, the lithiation of Na₂-PzDC occurs through two distinct plateaus located at 1.5 and 1.2 V vs. Li⁺/Li, representing an average potential increase of 600 mV in comparison to Na₂-BDC/Li cell. However, considering such higher potential as never observed for a conjugated dicarboxylate, in this case the lithiation could also proceed through redox at N centers rather than carboxylate functions (**Figure 5-d**), as the pyrazine unit is also redox active in the same redox potential range.^[200-201]

2.3. Impact of substituent groups on the redox potential

The energy density ($E_{cell} = Capacity \times V_{cell}$) of a Li-ion cell is directly proportional to the output voltage ($V_{cell} = V_{cathode} - V_{anode}$), in that, for a given specific capacity, the higher is the output voltage the higher will be the energy density.^[50, 76] One way to enhance the output voltage is to reduce the redox potential of the anode material. To do so, electron-donating groups have been proposed as substituents to decrease the redox potential of dicarboxylates. Lakraychi *et al.*^[202] have designed and evaluated an ortho-disubstituted terephthalate, namely dilithium 2,5-dimethylterephthalate (denoted as Li₂-DMT, and here as Li₂-DMBDC) (**Figure 6-a**). Thanks to the pure inductive effect (+I) of methyl groups, Li₂-DMBDC displayed a reduction potential

of 0.65 V vs. Li⁺/Li (i.e., 110 mV lower when comparison with Li₂-BDC, **Figure 6-b**). The compound was also able to deliver a maximum capacity of 160 mAh.g⁻¹ (61% of the theoretical capacity, considered as of $2\text{Li}^+/\text{e}^-$) after electrode optimization using only 20% of conductive carbon. This relatively low capacity was related to an irreversible process during the first cycle (ICE = 61%), which was ascribed to the non-planarity of the molecule caused by the substitution.

In terms of cycling stability, Li₂-DMBDC was able to display an excellent capacity retention by maintaining its capacity stable over 50 cycles accompanied with coulombic efficiency values of ~99.9%. Such encouraging result was obtained with a binder-free electrode composition. Moreover, the authors have established an energy density-oriented comparison between Li₂-DMBDC and Li₄Ti₅O₁₂ which revealed advantageous in favor of Li₂-DMBDC.

In the same vein, the effect of other functional groups, such as -OCH₃, -OLi, -NH₂ and -Br, on the electrochemistry of parent Li₂-BDC structure was studied (**Figure 6-a**).^[97, 203-204] In contrast to –CH₃ group, these substituents can act both as an electro-donating group (due to π donor mesomeric effect), and as electron-withdrawing group (due to electronegativity - inductive effect) which may result in a competition between the two effects. Although the mesomeric effect is more dominant than the inductive effect, all the terephthalate derivatives have displayed equivalent or higher redox potentials as compared to the compound of reference Li₂-BDC. Similar as for Na₂-PDC (**Figure 5**), this could be explained by overriding the mesomeric effect due to stronger electrostatic interaction between the heteroatom of the substituent and the inserted lithium (**Figure 6-c**),^[134] which, consequently, keeps only the inductive effect and causes a potential increase. Yet, further structural and compositional investigations should be realized to confirm this hypothesis and lift the veil on this behavior.



Figure 6. a) Molecular structure, theoretical capacity and measured value of the 1st reduction potential for different disubstituted-terephthalates highlighting the substituent effect. b) Potential-composition profiles of selected disubstituted-terephthalates cycled in Li half-cells (adapted with permission ^[202]. Copyright 2017 Elsevier Ltd). c) Substituent effect comparison between methyl (-CH₃) and amine (-NH₂) substituents pointing to a possible Li-N chelation after reduction for which the mesomeric effect is discarded. d) First reduction of selected monosubstituted-terephthalate cycled in Na half-cells (reproduced with permission from ^[205]. Copyright 2012 John Wiley and Sons).

Alike Li₂-DMBDC, and except Li₄-DHBDC (also denoted Li₄DHTPA) that was able to deliver its full capacity in the condition of being synthesized in the form of nanosheets,^[97] all the disubstituted terephthalates systematically indicated a reversible redox process restricted to one Li⁺/e⁻ exchanged per formula unit leading to only half of the expected specific capacities.^{[203-^{204]} This comes together with low ICE values (< 50%) which might indicate (i) thick SEI formation and thus render the accommodation of more Li⁺ difficult or (ii) possible Li⁺ trapping inside the solid after the first discharge that prevents its re-extraction. However, in-depth} characterization such as resolution of the crystal structure at different states of charge and particle imaging after the first discharge are compulsory to confirm these hypotheses.

Renault and colleagues^[206] reported a monosubstituted Li₂-BDC with primary amine (-NH₂) as a substituent. The compound revealed an average operating potential equivalent to Li₂-BDC (e.g., 0.85 V vs. Li⁺/Li) and a specific capacity of 180 mAh.g⁻¹ (65% of the theoretical capacity, considered as of 2Li⁺/e⁻) after electrode optimization by freeze drying. In addition to –NH₂, our group has also explored secondary (-NHCH₃) and tertiary (-N(CH₃)₂) amines for monosubstituted Li₂-BDC.^[207] It was found that the redox potential decreases with the addition of methyl groups on the amine, leading to a reduction potential of 0.71 V vs. Li⁺/Li for -N(CH₃)₂ monosubstituted Li₂-BDC (i.e., -50 mV and +60 mV in comparison with Li₂-BDC and Li₂-DMBDC respectively, **Figure 6-b**). This could be explained by (i) strengthening the electrondonating effect of the amine with the addition of methyl groups or (ii) steric hindrance that might prevent the electrostatic interaction between nitrogen and inserted Li⁺. However, low ICE and only half of the capacity were recorded for these monosubstituted terephthalates.

Interestingly, despite the molecular asymmetry, Park *et al.*^[205] have reported good electrochemical performances in Na half-cells for monosubstituted terephthalates using –NH₂, -Br and –NO₂ as substituents. All the terephthalates showed specific capacities close to the theoretical values (considered as of 2Na⁺/e⁻) and exhibited different reduction potentials depending on the substituent. For instance, Br-Na₂-TP reacted at a higher potential while NH₂-Br-Na₂-TP reacted at a lower potential when compared to parent Na₂-BDC (**Figure 6-d**). Contrary to Li-terephthalates, these Na-terephthalate revealed expected electrochemical features, two-electron redox reaction and potential tuning coherent with the electronic effect of the substituents, pointing out the difference in reactivity between Na and Li.

2.4. Other molecular modifications

To attain high specific capacity, both number of redox centres and the molecular weight are important. From this perspective, organic battery researchers have studied many quinone derivatives as OPEMs with multiple redox centres.[112, 199, 208-210] Dilithium rhodizonate $(Li_2C_6O_6)$ is the most illustrative example,^[208] as it is able to deliver a reversible specific capacity as high as 580 mAh.g⁻¹ in Li half-cells, given the reactivity of its four carbonyl redox groups. Similar approach was adopted for conjugated dicarboxylates (Figure 7-a).^[211-215] Maiti and co-workers^[211] reported on trilithium 1,2,4-benzenetricarboxylate (denoted here as Li₃-B3C) with a theoretical capacity of 352 mAh.g⁻¹, if the reactivity of all carboxylates is being considered (exchange of 3Li⁺/e⁻). Experimentally, Li₃-B3C delivered less than half of the expected capacity (152 mAh.g⁻¹, considered as of less than 2Li⁺/e⁻), pointing towards low utilization of the carboxylate redox functions. The redox potential remains similar to Li₂-BDC, as Li₃-B3C revealed an average potential ~1.0 V vs. Li⁺/Li with well-defined discharge/charge profile and low ICE (~56%) (Figure 7-a). The sodium version of Na₃-B3C was explored by Tripathi et al.,^[216] and showed a voltage profile as compared to the lithiated form (e.g., two separate plateaus at approximately 0.4 and 0.5 V vs. Na⁺/Na) accompanied with a reversible exchange of 1.8 Na⁺.

Within the same trend, Cahyadi *et al.*,^[212] studied the tetra-carboxylate version of Li₂-BDC, by first of all, shedding light on the preparation method of Li₄-B4C via two synthesis procedures: room-temperature and solvothermal (**Figure 7-a**). Thanks to the well-ordered nanosheet morphology of the solvothermally prepared Li₄-B4C_S, much better cycling stability and rate capability was observed in comparison with the room-temperature synthesis material (Li₄-B4C_R, powder in the form of irregularly shaped particles). Surprisingly, both versions of Li₄-B4C were found to deliver much higher capacity than expected for 2Li⁺/e⁻ exchanged (234 mAh.g⁻¹) or even four Li⁺/e⁻ exchanged (385 mAh.g⁻¹). For instance, Li₄-B4C_S exhibited an

increase in the reversible specific capacity to 1016 mAh.g⁻¹ upon the initial 25 cycles, before stabilizing at ca. 600 mAh.g⁻¹ after 100 cycles (**Figure 7-a**). This extra capacity was assigned to the super-lithiation phenomenon, as both materials were cycled in a large voltage range of 3.0 - 0 V vs. Li⁺/Li, leaving however questions about the reversible reactivity of the carboxylate groups. Nevertheless, long term cycling was attained for Li₄-B4C_S by maintaining 400 mAh.g⁻¹ after 1000 cycles at a cycling rate of 2C (with respect to the capacity of $2Li^+/e^-$ exchanged).

Relying on DFT calculations, Wang *et al.*,^[213] have designed a new anode material by bridging carbonyl group between two sodium phthalic moieties, giving sodium 5,5'- carbonylbis(isobenzofuran-1,3-dione (denoted as SCID) (**Figure 7-b**). The motivation of this work was to activate the redox of ortho-dicarboxylate in sodium phthalic moiety in order to attain higher capacities, as this later delivers only half of its capacity when cycled versus sodium metal (e.g., 120 mAh.g⁻¹, considered as of 1Na⁺/e⁻). Theoretically, DFT analysis revealed that SCID tends to have the first electron redox event on the bridging carbonyl followed by the second on the distal *para*-carboxylate, leaving room for the activation of the adjacent *ortho*-carboxylate for more Na⁺ uptake (**Figure 7-b**). Subsequently, two additional redox events have been predicted to the reduction of carboxylate groups on different benzene rings of the phthalate moieties.


Figure 7. a) Molecular structures and theoretical capacity values for conjugated-dicarboxyltes with multicarboxylate moieties, and voltages profile of Li₃-BT_{ri}C (reproduced with permission from ^[211]. Copyright 2017 Elsevier Ltd) and Li₄-BT_{etra}C (reproduced with permission from ^[212]. Copyright 2018 American Chemical Society). b) Proposed redox mechanism for sodium 5,5'- carbonylbis(isobenzofuran-1,3-dione) (SCID) and its corresponding voltage profile in Na half-cell (reproduced with permission from ^[213]. Copyright 2020 The Royal Society of Chemistry). Molecular structure of sodium diphenylmethane-3,3',4,4'-tetracarboxylates (SDTC) is shown for comparison. c) Molecular structure of Na₂-BDC and various thiocarboxylates, schematic illustration showing the benefits of sulfur doping and the voltage profile of Na₂-TTC cycled in Na half-cell (reproduced with permission from ^[217]. Copyright 2012 John Wiley and Sons).

Experimentally, SCID delivered 70% of its theoretical capacity (e.g., 168 mAh.g⁻¹, as considered of 4 Na⁺/e⁻) with a featureless voltage profile (absence of plateau) in the voltage range of 3.0 - 0.01 V vs. Na⁺/Na (**Figure 7-b**). Meanwhile, solid-phase cyclic voltammetry

(CV) revealed cathodic events at 0.8 and 0.3 V along with anodic events at 1.4 and 1.7 V vs. Na⁺/Na. The SEI formation as well as the activation of SCID have led to a low ICE (~49%). After incorporating SCID in MWCNTs, the compound was able to attain its capacity (240 mAh.g⁻¹) upon the first five cycles and maintained a capacity retention of 75% after 100 cycles. A control experiment using methyl bridged phthalates, giving sodium diphenylmethane-3,3',4,4'-tetracarboxylates (denoted SDTC, **Figure 7-b**), delivered a lower capacity (130 mAh.g⁻¹) indicating the crucial role of carbonyl group in reaching higher capacity for the phthalate redox moieties.

Zhao *et al.*,^[217] reported another molecular modification dwelling on substitution of oxygens in dicarboxylate scaffolds with sulfur atoms to form thiocarboxylate compounds as an alternative anode materials for sodium batteries (**Figure 7-c**).^[217-219] The authors proposed three different chemistries: sodium dithioterephthalate, (denoted as Na₂-DTT), sodium tetrathioterephthalate (denoted as Na₂-TTT) and sodium 4,4'-biphenyltetrathiodicarboxylate (denoted Na₂-BTTC). Contrary to conjugated dicarboxylates derivatives, which have a typical aspect of white powders (empirically attributed to poor electronic conductivity), the thiocarboxylate samples present darker colouring, an indication of intrinsic electrical conductivity. For instance, conductivity measurements (by four-probe testing method) of Na₂-BDC and Na₂-TTT revealed 4.0 μ S.cm⁻¹ for the latter and 0.01 μ S.cm⁻¹ for the former (e.g., two order of magnitudes higher in thiocarboxylates).

In terms of electrochemical properties, Na₂-TTT exhibited a sloping discharge/charge profile within the potential range of 3.0 - 0 V vs. Na⁺/Na (average potential estimated to be 1.5 V vs. Na⁺/Na). The authors ascribed this electrochemical feature to the low crystallinity of the compound. Na₂-TTT was also found to undergo super-sodiation as it delivered a specific capacity exceeding the two-electron exchange (e.g., 567 mAh.g⁻¹, corresponding to $6Na^{+}/e^{-1}$).

exchanged) (**Figure 7-c**). Good cycling stability with 60% capacity retention was attained after 250 cycles at a cycling rate of 2Na⁺/h. To be noted that 30% of carbon additive was used for electrode composite preparation, despite the material has an improved intrinsic electrical conductivity.

Recently, Ma *et al.*,^[180] have reported on the usage of non-conjugated system to link the dicarboxylate redox centers. Cyclohexanedicarboxilic acid (denoted as CHDA) is a good example to cite since it showed slightly higher capacity as compared to Na₂-BDC. In the first cycle, CHDA delivered an excessive capacity of 1195 mAh.g⁻¹ accompanied with well-defined discharge plateau at 1.2 V vs. Na⁺/Na. Note that this flat plateau corresponds to the electrochemical reduction of carboxylic acid protons, and Fédèle *et al.*,^[220] have recently reported on the efficiency of this *in-situ* preparation of conjugated-dicarboxylates, without any chemical lithiation step, and its benefits on the texture of the particles. Next, the charge/discharge curves of CHDA were characterized with a downslope character in the voltage region of 0.01 - 3.0 V vs. Na⁺/Na giving a reversible specific capacity of 284 mAh.g⁻¹. This slightly increased capacity would make us to consider the non-conjugated design (CHDA) in favor of the conjugated design (Na₂-BDC, 258 mAh.g⁻¹), yet the energy efficiency is also an important parameter to take into account for the assembled full cell, and for which CHDA is much inferior than Na₂-BDC (nice flat plateau at an average potential of 0.29 V vs. Na⁺/Na).

Whereas most of the reported carboxylate precursors are commercially available and can be obtained through facile acid-base reaction, harsh synthetic procedures (e.g., multi-step synthesis involving environmentally non-benign solvents) might be required for additional designs as already reported for new carboxylate structures.^[148, 202-203, 221] Of course organic chemical composition would win on sustainability criteria against its inorganic counterpart; but source of precursor, synthesis process and recyclability are also important parameters to be

considered if we want to promote the true sustainability. In this connection, possible options to be explored could include eco-friendly synthetic processes, *via* for example chemical CO₂ sequestration (retro-Kolbe Schmitt)^[36, 198] and recyclability of Li through combustion at moderate temperatures.^[222] Additionally, electrode-processing is also an important parameter to be seriously considered for the implementation of conjugated dicarboxylates as negative electrode material. In this context, Maurel *et al.*,^[223] have showed some encouraging result involving solvent-free electrode processing using 3D printing techniques.

3. Hückel-stabilized Schiff bases

Castillo-Martinez *et al.*^[224] were the first to explore Schiff bases (R¹HC=NR²) moieties as ONEMs for sodium batteries, as these can operate at potentials below, or close to 1.2 V vs. Na⁺/Na. The redox process proceeds akin to imine-based compounds, for which the nitrogen in azomethine group (C=N) reacts according to an n-type redox mechanism (**Figure 8**).^{[52, 67, 224-^{228]} For process reversibility, the Schiff bases must be integrated within a 10- π electron unit (-N=CH- Φ -CH=N-) in order to abide by the Hückel's rule of aromaticity.^[37] By way of comparison, the C=N functional groups are easier to reduce than the homologous C=O ones,^[229] and their redox potential could be tuned through intramolecular hydrogen bonds or lengthening the conjugation chain.^[230]}

Pure schiff base redox activity

Mixte schiff base/carboxylate redox activity

$$\underbrace{\overset{O}{\underset{H}{\longrightarrow}}}_{MO} \underbrace{\overset{C=N-\frac{1}{2}}{\underset{H}{\longrightarrow}}} \underbrace{\overset{+2M^{+},+2e^{-}}{\underset{-2M^{+},-2e^{-}}{\longrightarrow}}} \underbrace{\overset{MO}{\underset{MO}{\longrightarrow}}}_{MO} \underbrace{\overset{MO}{\underset{H}{\longrightarrow}}} \underbrace{\overset{MO}{\underset{H}{\longrightarrow}}}_{H} \underbrace{\overset{MO}{\underset{H}{\longrightarrow}}_{H} \underbrace{\overset{MO}{\underset{H}{\longrightarrow}}}_{H} \underbrace{\overset{MO}{\underset{H}{\longrightarrow}}_{H} \underbrace{\overset{MO}{\underset{H}{\longrightarrow}}}_{H} \underbrace{\overset{MO}{\underset{H}{\longrightarrow}}_{H} \underbrace{\overset{MO}{\underset{H}{\longrightarrow}}_{H} \underbrace{\overset{MO}{\underset{H}{\longrightarrow}}_{H} \underbrace{\overset{MO}{\underset{H}{\longrightarrow}}_{H} \underbrace{\overset{MO}{\underset{H}{\longrightarrow}}_{H} \underbrace{\overset{MO}{\underset{H}{\longrightarrow}}_{H} \underbrace{\overset{MO}{\underset{H}{\overset{MO}{\underset{H}{\longrightarrow}}}_{H} \underbrace{\overset{MO}{\underset{H}{\longrightarrow}}_{H} \underbrace{\overset{MO}{\underset{H}{\overset{MO}{\underset{H}{\longrightarrow}}}_{H} \underbrace{\overset{MO}{\underset{H}{\overset{MO}{\underset{H}{\longrightarrow}}}_{H} \underbrace{\overset{MO}{\underset{H}$$

Figure 8. Proposed redox mechanisms highlighting pure Schiff base and mixed Schiff base/carboxylate redox activities.

Several crystalline polymeric Schiff bases have been explored in Na half-cells (**Figure 9**).^[224] Polymers with aliphatic or aromatic conjugation have been evaluated and compared. Operating potentials below 1 V vs. Na⁺/Na were recorded and specific capacities ranging from 150 to 350 mAh.g⁻¹, at a cycling rate of 1Na⁺/5h per repeating unit, were attained for both aliphatic and aromatic polymers. However, large polarization and rapid capacity decay have been observed for the polymers with aliphatic/non-aromatic conjugation, whereas low hysteresis and stable electrochemical activity were recorded for the polymers with aromatic conjugation, which might be explained by improved electrical conductivity given the conjugation in these structures. Appending donor groups (-CH₃, -OCH₃) on the aromatic unit was found to impact the redox potential and the process reversibility of the polymers. Similar to disubstituted terephthalates, polymers substituted with –CH₃ have shown lower redox potential as compared to those witch –OCH₃, despite the stronger electron-donating effect of the latter. This unexpected feature could be attributed to some coulombic interaction between the inserted Li⁺ and the oxygen from – OCH₃,^{[204][}



Figure 9. a) Polymerization strategy for producing polymeric Schiff bases and corresponding molecular structures. b) First galvanostatic oxidation in Na half-cell of selected aromatic polymeric Schiff bases (reproduced with permission from ^[224]. Copyright 2014 John Wiley and Sons). c) Voltage profile curves of mixed Schiff case/carbonyl aromatic polymer cycled in Li half-cells (reproduced with permission from ^[228]. Copyright 2021 Elsevier Ltd).

Additionally, other groups have explored polymeric structures of Schiff base units with redoxactive fragments and reported high reversible capacities with extended cycling stabilities (**Figure 9**).^[226-228, 231] For instance, a Schiff base polymer containing naphthalene diimide units maintained a reversible capacity of 627.5 mAh.g⁻¹ (as considered of more than 4Li⁺/e⁻ per repeat unit) over 200 cycles, whereas other enclosing antraquinone units led to reversible capacity of 1130 mAh.g⁻¹ (as considered of much more than 4Li⁺/e⁻ per repeat unit) with a capacity retention of 96.5% after 100 cycles. Undoubtedly, such high capacities are inherent to superlithiation of the polymeric structures at low potentials, as it is indicated by sloppy voltage profiles within the voltage range of 0.01-3.5 V vs. Li⁺/Li (**Figure 9**). In general, the idea of hybridizing different redox functionalities across the same polymer could lead to high-capacity materials, and some interesting examples start emerging in this direction.^[232-235] In contrast, in order to be more efficient, such hybridization should take into consideration the redox potential of both redox-active units that have to be close to each other.

Further functionalization with carboxylate end groups, giving various oligomers (see the molecular structures O1, O2, O3, O4 and O5 in **Figure 10**), were explored and showed improved electrochemical performances.^[52] The charge/discharge profile for all the oligomers was characterized with large irreversible capacities at the first cycle (ICE = 33%), which was accounted for electrolyte decomposition and SEI formation. A large dependence of the capacity and the redox potential on the molecular structure was found. For instance, O2 and O5 displayed higher reversible capacities (~250 mAh.g⁻¹, considered as of 4Li⁺/e⁻ for O2 and 6Li⁺/e⁻ for O5) at low working potentials (~ 0.6 V vs. Na⁺/Na), whereas O3 and O4 delivered lower reversible capacities (~120 mAh.g⁻¹, considered as of 2Li⁺/e⁻ for O3 and 3Li⁺/e⁻ for O4) at relatively higher working potentials (~ 0.9 V vs. Na⁺/Na).

After taking into consideration the stereochemistry of all studied oligomers, it was established by the authors that the electrochemical activity was higher for the oligomers with the azomethine carbons connected to the aromatic core (e.g., -OOC- Φ -C=N- and -N=HC- Φ -CH=N-, O2 and O5 **Figure 10**). Whereas the inverse configuration (e.g., -OOC- Φ -N=C- and -CH=N- Φ -N=CH-, O3 and O4 **Figure 10**) were found to have lower activity. According to DFT calculations^[52] and crystal structures analyses,^[236] this was ascribed to the planarity and the enhanced electronic conjugation of the repeat units: whereas it was found to be planar for O2 and O5 type structures (and thus the pi-conjugation is allowed after the electron transfer); the O3 and O4 structures are non-planar due to strong interactions between the unpaired electrons of N-centers and the π electron cloud of the adjacent aromatic ring (and thus the conjugation is blocked between the redox moiety and the aromatic ring). This is consistent with analyses on disubstituted terephthalates that experimentally deliver only half of the capacity (1Li⁺/e⁻ instead of 2Li⁺/e⁻ per formula unit) and for which the molecule was estimated to be non-planar as well.^[202] Interestingly, the carboxylate end groups were also found to react and contribute to the storage capacity thanks to their redox activity at low potentials (**Figure 10**). This carboxylate-Schiff base combination illustrates a good example proving the feasibility of hybridizing different redox functionalities across the same molecule, and worth to be explored in an adequate molecular structure. Overall, his work unveiled crucial molecular consideration of Schiff-type materials that should be considered for the proper functioning of redox moieties. However, deeper mechanistic studies are required for more clarification.



Figure 10. Molecular structures and theoretical/recorded capacities of reported oligomeric Schiff bases and theirs corresponding voltage profiles in Na half-cell (reproduced with permission from ^[52]. Copyright 2015 The Royal Society of Chemistry). Molecular conformation *vs.* redox activity is highlighted for clarification.

In terms of cycling stability, thanks to the ionic nature and oligomeric structure, all the oligomers (O1, O2, O3, O4, O5, **Figure 10**) demonstrated a capacity retention of 97% after 25 cycles at 1Na⁺/5h and 92% after 25 cycles at Na⁺/2.5h. Furthermore, a rate capability test was performed on the oligomers with higher capacity, O2 and O5, and the reversible capacity seems to be affected by increasing the rate of cycling (decreasing from 97% at 1Na⁺/20h to 36% at 4Na⁺/h). However, at high cycling rate corresponding to 10Na⁺/h, the oligomer with longer chain length, O5, have shown higher capacity than the oligomer with shorter chain length O2. This might be explained by the extended conjugation in O5 structure, which is also ascertained for some conjugated carboxylates structures (see section 2.2.1 and 2.2.2).

Overall, thanks to the easiness of the synthesis which is based on a simple condensation between aromatic primary amine and aldehyde compounds,^[237-238] there still more room left for new designs that could further improve the electrochemical performances. Options to be explored could encompass lengthening of the conjugation chain and introduction of electron-donating groups without excluding polymerization with appropriate redox-active fragments. So far, the reported examples are synthesized through condensation reactions involving organic solvents, in contrast, preparation through aqueous synthesis is highly sought in order to decrease the environmental footprint.

4. Di-azo-based compounds

A new class of OEMs based on the di-azo functional group (-N=N- groups) was proposed recently by Wang and colleagues (**Figure 11**).^[53] This chemistry was found to be electroactive at potentials around 1.5 V vs. Li⁺/Li, and therefore were presented as ONEM for metal batteries. The redox activity of di-azo function proceeds through an n-type redox mechanism, for which the double bond in di-azo function is converted into a single bond upon a two-electron reduction and then converted back to the double bond upon oxidation (**Figure 11-a**).^[53, 239-243] This

process is accompanied by a cation ($M^+ = Li^+/Na^+/K^+$) uptake/extraction on nitrogen atoms for charge compensation. The basic molecular model of this category, the azobenzene (AB), revealed an electrochemical response characterized with low ICE of 55% and two charge/discharge plateaus at ~2.0/1.6 V and ~1.6/2.5 V vs. Li⁺/Li (**Figure 11-a**).^[53, 241] The low ICE and rapid capacity fade were attributed to the high solubility of the oxidized di-azo phase, preventing its utilization as solid-phase electrode in batteries.

To reduce the solubility, the mono and di-carboxylate versions were designed to form the (phenylazo)benzoic acid metal salt (PBAMS) and azobenzene-4,4'-dicarboxylic acid metal salt (ADAMS), respectively (Figure 11-b)^[53, 241, 243]. Both compounds were able to nearly deliver the theoretical capacities of 230 mAh.g⁻¹ and 190 mAh.g⁻¹ (considered as of 2Li⁺/e⁻) for the lithiated forms of PBAMS (denoted as PBALS) and ADAMS (denoted as ADALS) respectively, with an excellent cycling stability over 100 cycles at a rate of 1Li⁺/h. However, highconcentration electrolyte (7M LiTFSI in DOL/DME) was required for PBALS to counteract the solubility, whereas a 1M salt in carbonate electrolyte (LP30) was sufficient for ADALS. This confirms the necessity of at least two ionic groups to limit the dissolution. Usually small molecules that are not soluble in aprotic polar electrolytes they bear two ionic groups (such as -COO⁻,^[36, 44, 139, 198, 244-246] -SO₃⁻,^[132, 246-249] -OLi^[209, 250]), thanks to their increased polarity and formation of coordination network (O--M--O),^[251] whereas others with only one ionic group were found to be soluble due to their lower polarity and probably the absence of coordination network.^[247] Moreover, the incorporation of carboxylate groups has also a positive impact on the redox potential and the reversibility of the process. Indeed, ADALS revealed an average working potential of approximately 1.5 V vs. Li⁺/Li, with low polarization (50 mV) and enhanced ICE (77%). To be noted that ADALS has two potential redox units: di-azo and dicarboxylate groups. As the redox potential of di-azo groups is higher, these will be reduced first, breaking the conjugation, and thus rendering the di-carboxylate redox functionality inactive.



Figure 11. Overview of di-azo-based compounds as ONEMs for metal-ion batteries. a) Proposed redox mechanism of azobenzene (AB) and its corresponding voltage profile in Li half-cell (reproduced with permission from ^[53]. Copyright 2018 John Wiley and Sons). b) Molecular structures, theoretical capacities and measured values of the 1st reduction potential for PBAMS and ADAMS (M: Li, Na, K) along with voltage profile of ADALS (reproduced with permission from ^[243]. Copyright 2018 Proceedings of National Academy of Sciences). c) Proposed electrochemical generation path for Azo formation. d) Schematic illustration a nitrogen-redox rocking-chair full-cell using Li₄-PTtSA and ADALS as positive and negative electrodes respectively, corresponding voltage vs. time curves (reproduced with permission ^[47]. Copyright 2021 Nature Publishing group).

Interestingly, ADALS showed excellent rate-capability performances by retaining 89% of its capacity at a rate of 10Li⁺/h and over 5000 cycles. The cycling features suggest fast reaction kinetics, with possibly also intrinsic electrical conductivity and fast Li⁺ diffusivity. However, none of these parameters was investigated in depth and the use of a 30wt.% high carbon content might have masked these. The high rate capability might be attributed to this molecule in particular and not to the whole diazo class, since the same feature was also observed for extended conjugated dicarboxylates (refer to section 2.2.1 for more details). Important to note is that the di-azo derivatives can be electrochemically synthetized from nitrobenzene derivatives, by in-situ reductive conversion of nitro groups (at ~2.35 V vs. Li⁺/Li) and formation of Li₂O as by-product (**Figure 11-c**). The in-situ formed di-azo materials displayed comparable electrochemical performances to the chemically prepared phases (e.g. a discharge sloped potential from 2.1 to 1.75 V vs. Li⁺/Li and specific capacity of 131 mAh.g⁻¹ attained after 100 cycles at 1Li⁺/h for electrochemically synthesized PBALS).

To highlight the practicality of such di-azo structure, full-cells combining ADALS with LiFePO₄ (LFP) and LiCoO₂ (LCO) positive electrodes were reported.^[239] The full-cells delivered output voltages of 1.7 and 2.5 V with 88% (98 mAh.g⁻¹) and 73% (69 mAh.g⁻¹) capacity retentions after 200 cycles, using LFP and LCO respectively. More importantly, ADALS, the flagship molecule of this di-azo family so far, was combined with tetralithium benzene-1,2,4,5-tetrayltetrakis((methylsulfonyl)amide) (Li₄-PTtSA), the flagship molecule of the conjugated sulfonamide family, to build the first all-organic nitrogen redox based Li-ion battery.^[47] The full-cell delivered an output voltage of 1.2 V with a specific capacity of 81 mAh.g⁻¹ based on the mass of Li₄-PTtSA.

Furthermore, excellent electrochemical properties were also reported for ADAMS in Na and K half-cells.^[53, 240-241] The sodium form of ADAMS (denoted as ADASS) was found to react at

1.2/1.26 V vs. Na⁺/Na during the discharge and deliver 170 mAh.g⁻¹ at 0.4Na⁺/h,^[53, 241] while the potassium form (denoted as ADAPS) was able to attain 131 mAh.g⁻¹ at an operating potential of 1.43/1.24 V vs. K⁺/K.^[53, 241] However, very low ICE (43%) was recorded for ADAPS, attributed to the SEI formation in potassium-based electrolyte, with improved CE on the following cycles. Both compounds demonstrate good cycling stability by maintaining their capacities over 100 cycles, with excellent rate-capability observed for ADASS (e.g., 58% capacity retention at 40Na⁺/h and over 2000 cycles) and high-temperature cycling ability demonstrated for ADAPS (e.g., 81% capacity retention at 60 °C and over 80 cycles).

Despite the broadness of the chemical space of di-azo compounds, only very few examples are reported thus far due to the lack of new di-azo molecules that could be suitably integrated in organic batteries. Whereas molecular engineering constitutes an efficient strategy to enrich the di-azo library, design of targeted molecules with low redox potential and increased capacity remains compulsory for this class in order to compete with the carboxylate and Schiff base classes. Furthermore, the synthetic methods available today might be critically considered from sustainability point of view, since the most used methods are based on azo-coupling, Mills reaction and Wallach reaction;^[252] whose reaction conditions involve explosive intermediates and use of excess amounts of oxidant or reductant reagents.

5. Viologen derivatives

Different to n-type ONEMs discussed in previous sections, N,N' di-quaternized bipyridyl salts, also known as viologens, have emerged recently as promising candidates among ONEMs (**Figure 12**). Viologen derivatives have been extensively used as dissolved active materials mainly explored to date as negolyte in redox flow batteries^[253-256] but also in aqueous organic batteries.^[234-235] Their redox activity can evolve between three reversible redox states according to p-type redox mechanism, starting from the fully oxidized form (V²⁺) to the intermediate

radical cation (V⁺⁺) and lastly the fully reduced neutral form (V), accompanied with reversible anion extraction/uptake (**Figure 12-a**). A particularly appealing property of the viologen backbone is that it exhibits the lowest redox potential among all other p-type systems along with being air-stable in its oxidized state (anion-containing),^[257] which makes it to date, the unique p-type material suitable for negative electrode application in anion rocking-chair batteries with low toxicity.^[258] Consequently, this has opened new avenues towards metal-free batteries, or what is now broadly accepted as "Molecular-ion Batteries".^[259]

The first example in bulky solid phase for non-aqueous batteries was reported by Yao and coworkers,^[259] where poly (1,1'-pentyl-4,4'-bipyridinium dihexafluorophosphate) (denoted [PBPy](PF₆)₂) was prepared and the electrochemical properties evaluated in n-Bu₄N•PF₆/PC electrolyte system (Figure 12-b). The polymer displayed excellent reversible extraction/uptake of PF_6^- at -0.7 and -1.2 V vs. Ag^+/Ag , indicating a two-electron transfer redox reaction. The material provided an initial specific capacity as high as 79 mAh.g⁻¹ (corresponding to 76% of the theoretical capacity, considered as of $2PF_6^{-}/e^{-}$), which, however, decreased to 38 mAh.g⁻¹ after only 20 cycles. The authors ascribed this capacity decay to the solubility of the polymer in the electrolyte, given the low polymerization degree. Additionally, Cadiou et al. [260] reported about cross-linked polymerization as an alternative way to lower the dissolution and shuttle issues, by designing a cross-linked polyviologen ([c-PV](ClO₄)₂) (Figure 12-b). The polymer was found to undergo two redox processes at 2.5 and 2.1 V vs. Li⁺/Li, and deliver its theoretical capacity of 88 mAh.g⁻¹ (considered as of 2ClO₄⁻/e⁻). Despite the cross-linked polymerization, [c-PV](ClO₄)₂ was able to show good cycling stability (capacity of 38 mAh.g⁻¹) only when cycled on the second redox process (activity at 2.1 V), while a capacity loss as high as 40 was observed when the polymer was cycled on the first redox process (activity at 2.5 V). The authors thought that this behavior could be attributed to steric/electronic hindrance in the polymer as

the second anion uptake (reoxidation at 2.5 V vs. Li⁺/Li), since similar behavior was also reported on other cross-linked polyviologen hydrogel in aqueous electrolyte.^[261]



Figure 12. Overview of viologen derivatives as p-type ONEMs for metal-free "molecular-ion" batteries. a) Proposed redox mechanism of viologen. b) Polymerization as an adopted strategy to reduce the solubility and voltage profile of [c-PV](Anion)₂ cycled vs. Li⁺/Li (reproduced with permission ^[260]. Copyright 2020 John Wiley and Sons). c) Ionic groups as an adopted strategy to reduce the solubility, voltage profile of (Li₂)[diacetate-V](ClO₄)₂ cycled vs. Li⁺/Li (reproduced with permission ^[245]. Copyright 2019 John Wiley and Sons), and proposed design showing the difference between negatively and positively charged ionic groups. d) Potential

tuning through aromatic extension and voltage profile of phenylene-inserted extended viologen cycled vs. Li⁺/Li (reproduced with permission ^[262]. Copyright 2020 John Wiley and Sons). e) Schematic illustration of molecular-ion battery (adapted with permission from ^[259]. Copyright 2020 John Wiley and Sons). f) Voltage profile of an anionic rocking-chair full-cell involving Li₂-DAnT and (Li₂)[diacetate-V](ClO₄)₂ as positive and negative electrodes respectively (reproduced with permission from ^[245]. Copyright 2019 John Wiley and Sons). g) Configuration of a solid-state polymer molecular-ion battery; polymer structures employed as positive electrode, electrolyte and negative electrode; charge/discharge curves of the corresponding full-cell (inset photographs of the flexible and form free electrodes) (reproduced with permission from ^[263]. Copyright 2020 John Wiley and Sons).

Taking advantage of the already proven solubility-preventing strategy of "ionic organic salt", Jouhara *et al.*^[245] recently reported on two crystallized zwitterionic forms of viologen, namely dilithium diacetate-4,4'-bipyridinium di-perchlorate (denoted as $(Li)_2$ [diacetate-V](ClO₄)₂) and dilithium (E)-diacetate-1,2-bis(4-pyridyl)ethylene di-perchlorate (denoted as $(Li)_2$ [diacetate-bpe](ClO₄)₂) (**Figure 12-c**). The two crystalline salts were electrochemically evaluated in Li half-cells and showed reversible deintercalation/intercalation of ClO₄⁻ at ~2.4 and ~1.4 V vs. Li⁺/Li, corresponding to specific capacities of 130 and 110 mAh.g⁻¹ (almost the theoretical capacities, as considered of 2ClO₄⁻/e⁻) for (Li)₂[diacetate-V](ClO₄)₂ and (Li)₂[diacetate-bpe](ClO₄)₂ respectively. Despite the presence of the two permanent negative charges, the compounds still displayed dissolution in the electrolyte, leading to progressive capacity loss upon cycling. This might be plausibly explained by some intra-molecular (self-charge) compensation in the zwitterionic form which can lead to a neutral compound after the complete oxidation, and thus render the molecule soluble (**Figure 12-c**). Ideally, the viologen should be substituted with positively charged ionic groups (such as $-NR_3^+$) in order to maintain the ionic

form in both states (oxidized and reduced), alike quinone derivatives that are often substituted with negatively charged ionic groups (such as $-CO_2^-$ and $-SO_3^-$).^[36, 44, 132, 139, 198, 246-247]

In an attempt to lower the redox potential of viologen derivatives, Kato et al.[262] have proposed to extend the π -conjugation of the viologen skeleton following the rationale of increasing the electronic density by the addition of electron-rich aromatic rings (Figure 12-d). This strategy does not seem to disrupt the two-electron transfer reaction (due to a potential conjugation disruption), and the proposed compounds were able to deliver near to full theoretical capacities, ranging from 54 to 70 mAh.g⁻¹ (considered as of 2anion/e⁻). As designed, lower redox potentials were also measured for these chemistries, with average potentials close to 2.0 V vs. Li⁺/Li. Interestingly, the conjugation extension also resulted in lower potential difference (100-200 mV) between the two processes as compared to typically 500 mV for conventional viologens (Figure 12). This could be attributed to charge separation in the molecule that would reduce the interaction between the two pyridinium moieties, and thus make the potential difference in the two-electron redox reaction smaller. In fact, similar behavior was also observed for anthraquinone^[264-266] and other one-ring quinone derivatives,^[267] where two distinct oneelectron processes were recorded for the latter versus one two-electron process for the former. The redox kinetics of these compounds was not investigated in this work and poor cycling stability was recorded for all the compounds due to the high dissolution of reduced species.

In order to confirm the concept of molecular-ion batteries, many prototypes pairing viologenbased ONEMs with p-type OPEMs have been proposed (**Figure 12-e**).^[245, 258-260, 263, 268] Poizot's group has reported one example involving two crystalline small molecules, (Li)₂[diacetate-V](ClO₄)₂ and dilithium 2.5-(dianilino)terephthalate (Li₂-DAnT),^[44] as negative and positive electrode materials respectively while using a Li-containing electrolyte.^[245] The anionic rocking-chair full-cell was found to deliver an average output voltage lower than 0.7 V along with a specific capacity attaining 20 mAh.g⁻¹ (based on the mass of both electrodes) (**Figure 12-f**). This limited capacity is inherent to Li₂-DAnT that has to be limited to cycle over one electron only in order to avoid solubility.^[44] Excellent cycling stability over 400 cycles was obtained and worth being mentioned that the electrodes were made with low conductive carbon additive amount. More interestingly, Oyaizu's group^[263] have reported recently a real device metal-free molecular-ion battery based on aliphatic polyethers containing 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and viologen as positive and negative electrode materials respectively (**Figure 12-g**). The full-cell provide an average output voltage of ~0.9 V and can be charged/discharged at cycling rates as high as 5anion/h. Additionally, thanks to the plasticity and the polymeric nature of the electrodes as well as the electrolyte (solid-state), the authors were able to assemble flexible cells and showed motivating result towards free-form 3D printable batteries (**Figure 12-g**).

Air-stability of dicationic species as well as p-type charge storage at tolerably low potentials are the unique and interesting properties promoting viologens as particular candidates for ONEMs. Today, these electrochemical properties coupled with the versatile choice from the p-type OPEMs have opened doors to unprecedented opportunity towards the development of the "true all-organic" metal-free battery. However, the relatively high potential and the low capacity of viologen scaffold remain a serious challenge to overcome. Note that viologen-based ONEMs are still in their infancy and further improvements could be achieved thanks to molecular design. Carbonaceous electrodes could also be considered as suitable cathode materials to assemble hybrid molecular-ion cells. The high anion-intercalation potential of graphite (~4.0 V vs. Li⁺/Li) would be benefiting to increase the cell voltage.^[269] Fortunately, due to the basicity of the nitrogen atoms, the synthetic route to prepare viologens is relatively easy, typically nucleophilic substitution (SN2) where halide-containing compounds react with bipyridine followed by a simple anion exchange.^[270-272] Options to be considered might include

nitrogen substitution, polymerization as well as conteranions without excluding the development of new light-weight organic supporting salts for the electrolyte.

6. Outlook and perspectives

OEMs have become a hot and intriguing research topic with continuously increasing interest from the energy storage community. In this context, concise and timely follow-ups on different classes and battery chemistries are continuously required. Whereas much focus has been oriented on positive electrode chemistries, a focused overview of recent advances on ONEMs is required. In this review, by retrieving and analyzing data from experiments performed in metal batteries, we discuss the molecular structure-electrochemical property relationship of all ONEM classes (excluding conducting polymers). As of today, only four redox families appear to be suitable for ONEM application, either in metal-ion or molecular-ion batteries: conjugated-dicarboxylates, hückel-stabilized schiff bases, di-azo and viologen compounds. Each of these classes comes with advantages and drawbacks and in **Figure 13** we critically analyze and compare the fundamental properties of these four ONEM classes.



Figure 13. Radar plot comparing fundamental properties of the four reported classes of ONEMs.

Conjugated-dicarboxylates stand out as the most promising candidates in terms of energy density given their lowest operating potential (0.6 - 1.1 V vs. Li⁺/Li), high capacities (160 -300 mAh.g⁻¹) and good cycling stability. Starting from the pioneering report on Li₂-BDC, different molecular modifications have been proposed and evaluated, leading to redox potential tuning and rate capability enhancement as a result of substituents incorporation or aromatic extension, respectively. Extending the π -conjugation in dicarboxylates led to significant redox potential changes, yet the rationale behind requires further in-depth analysis. Replacement of the spectator Li-cation in the model structure, M-BDC by various s-block metals (e.g. Li, Na, K, Ca, Ba, Sr), allowed electrochemical evaluation of different isostructural terephthalates with also differences in terms of cycling stability. However, the impact of the spectator cations on the redox mechanism remains a challenge to overcome. Whereas many reported carboxylate structures are commercially available or, could be also accessed through relatively complex synthetic protocols, eco-friendly synthetic processes are highly sought in order to decrease the environmental footprint of this class of materials. Although many designs have been proposed, there is plenty room for additional designs to further improve the electrochemical performances given to the molecular flexibility of this class combined with the richness of the organic chemistry.

Hückel-Schiff bases have been proposed recently as interesting alternatives to conjugated dicarboxylates as ONEMs. Particularly appealing is their high specific capacity (ranging from 150 to 300 mAh.g⁻¹), and operating potentials ranging between 0.5-1.1 V vs. Na⁺/Na (e.g., 0.7-1.3 V vs. Li⁺/Li), comparable thus to conjugated dicarboxylates in terms of a given energy density (**Figure 11**). So far, the exploration of this class remains limited, with only few research groups active in this direction, leaving thus plenty of room for further molecular design to

advantageously tune the electrochemical properties. For example, further lower the redox potential while concomitantly increase the capacity could render these chemistries better appealing than conjugated dicarboxylates. Important to note is that the few developments so far point the fact that electrochemical reversibility in Schiff bases is attained only in planar molecular configuration, obeying the Hückel rules of aromaticity and thus further developments should consider this aspect. Additional advantage of this still unexplored class of ONEMs is that the synthetic procedure generally consists of condensation process of aldehydes and amines. However, one aspect that remains to be solved is the seemingly lower power capabilities of this class of materials.

Undoubtedly, thanks to their fast redox kinetics, di-azo compounds is the only one chemistry so far that could offer opportunities for developing high-rate and long-life metal-ion storage technologies. However, the high redox potential of di-azo group (1.5 V vs. Li⁺/Li) constitutes the main bottleneck for this class as this will inevitably result in low output voltage and low energy density of a given full-cell. Specific capacities for the reported di-azo structures are also not yet appealing and further work is required to design molecules with lower molecular weight. However, considering the infant stage of this class of ONEMs, with only three compounds explored thus far, more can be expected upon further molecular modification. The criterion that seems to be excelling for this class is the fast reaction kinetics resulting in high charge/discharge rates reported so far. One should note that this high rate is only reported for one particular molecular structure, ADAMS, which might be accounted for the crystal packing of this specific molecule and not for the whole class. Overall, more examples should be studied and further indepth characterization must be carried out in order to draw a conclusion. Additional investigations should also focus on deeper characterization of the redox mechanism, as well as structural and chemical reversibility. The so far reported examples are all commercially available and their synthesis might rely on azo-coupling reactions involving explosive intermediates and excess amounts of oxidant/reductant reagents.

Finally, the viologen-derivatives class remains the unique ONEMs candidate for p-type anion storage, which promises the "true" all-organic metal-free batteries. The so far reported viologen-derivatives operate at relatively high potentials (> 2.0 V vs. Li⁺/Li) and remain soluble in the electrolyte. Additional challenges come from the fact that the high molecular weight combined with the heavy anions required for charge compensation, resulting thus to unsatisfying specific capacities, at least when compared to conventional n-type metal-ion storing ONEMs. The experience on the molecular modification-electrochemical performance relationship accumulated for conjugated-dicarboxylates may be readily extrapolated to viologen-derivatives in order to improve the energy metrics. Some options to be explored would focus on the nature of substituents on the ternary nitrogen redox center, employing smaller and with lower molecular weight counter anions, others could consist on introducing electron-donating to lower advantageously the redox potential. To this end, thanks to the ease of synthesis, many molecules can be prepared from various synthetic strategies and scalable procedures.

When looking back at the history of battery developments, OEMs have been proposed and showed great promises already at early stages. The rise of Li-ion battery technology has nevertheless eclipsed the developments of organic batteries since organic Li-ion cathodes has become a reality only recently. The advent of these later chemistries (organic Li-ion reservoir cathodes) makes now possible to also built all-organic Li-ion cells, so ONEMs should be now considered from a different perspective. It will not be an easy task to recover the decades of advances with inorganic batteries, and it should be also clear that it is not the purpose of organic batteries to replace the inorganic equivalents from their current use. Organic batteries may become interesting for specific applications, that will have lower constrains on gravimetric and volumetric energy metrics, and will more consider the environmental factors. Despite the considerable retard over the inorganic battery materials, past decade has seen the renaissance of organic battery materials with also breakthrough advances provided. The developments with ONEMs thus far show that all organic batteries are possible, with prototype cells already built and tested. Reviewing ONEM developments now becomes critical given that organic Li-ion reservoir and p-type OPEMs are now available so that organic Li-ion or molecular-ion cell assembly can become a reality. And with this work we provide a timely overview of the materials and classes developed thus far, advantages and drawbacks, as well as alternative developments for further performance improvements. Other than further molecular re-design of individual molecules within each of the disclosed ONEM classes, intramolecular hybridization of various redox centers could provide additional avenues for augmenting the ONEM energy metrics. For instance, molecular designs of hybrid dicarboxylate-di-azo with higher capacity can be envisioned with certainly the richness and versatility of organic chemistry as a powerful strategy to design the ONEM of tomorrow.

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