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Revealing the Solid-State Electrochemistry of Conjugated Oximates: Towards a New Functionality for Organic Batteries

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Abstract: In the rising advent of organic Li-ion cathodes with practical characteristic of being air-stable while in the reduced lithium-reservoir form, we report herein a new class of organic Li-ion positive electrode materials - the conjugated oximate lithium salts. The solid-phase electrochemistry of first five examples of the oximate class, including cyclic (aromatic), acyclic (non-aromatic), aliphatic and tetra-functional stereotypes, uncovers the complex interplay between the molecular structure and the electroactivity in the solid phase, as well as the potential of this rich family as cathode materials for lithium-ion batteries. The conjugation of oximate functions within the molecular core is found to endow excellent air stability of lithiated reduced phases, an important prerequisite for practical use as Li-ion positive electrode materials. Amongst the exotic features characterizing the solid-state electrochemistry of this class of materials, the most appealing one belongs to the reversible solid-state polymerization through intermolecular azodioxy coupling (-ONNO-) and the intramolecular furoxan cyclization of their oxidized forms. In the disclosed series of materials, the best performing candidate delivers high reversible capacity of 357 at an average potential of 3.0 vs. Li^+/Li^0 , attaining over 1 KWh kg^{-1} specific energy content.

Introduction

Organic electrode materials are emerging as potential candidates for electrochemical energy storage applications with most appealing features such as natural abundance, sustainability and lower environmental footprints.¹⁻⁴ The modern battery technologies are heavily dependent on transition metal oxides electrode materials which are procured after extensive mining and expensive synthesis protocols such as energy consuming high temperature processing. Moreover, material cost, handling and recycling encourage the efforts towards development of organic electrode materials. The recent fast advancement of organic electrodes indicates that they are not only emerging as mere alternatives to the traditional transition metal oxide cathodes in conventional rechargeable batteries, but rather have the potential to lead to disruptive technologies.⁵

Conceptually, majority of the organic cathode materials operate either through “*n-type*” or “*p-type*” redox charge storage^{6,7}. While former being studied in their oxidized state (making them suitable only for the still under-developed lithium metal batteries), the latter involve counter anions for application in dual-ion or anionic batteries⁸. Current Li-ion cell assembly relies on a Li-ion source cathode material (“*n-type*”) coupled to a Li-ion host anode material (the rocking chair system^{9,10}). Unlike the large diversity of inorganic cathode materials, the foundation of the state-of-the-art practical Organic Li-Ion Cathodes (OLICs, all developed over the past 4 years as *n-type*) was laid extensively on enolate/carbonyl redox chemistry. It is encouraging to see the advancements in OLICs through electron-withdrawing substituted quinones¹¹, sacrificial metal-mediated charge delocalization^{12,13}, and stereoelectronic chameleonic effect¹⁴, yet they still suffer from low capacity and inefficient redox kinetics. An ideal OLICs must possess ambient stability, reversible multi-electron redox, high theoretical capacity and insolubility in Li-reservoir state, which motivates us to push the limits of organic chemistry in the search and design of new organic Li-ion redox active materials. Recently, this led to the development of the first generation of conjugated sulfonamide redox chemistry with Li-reservoir and excellent ambient air resistance¹⁵. The redox potential of the sulfonamide cathodes is comparable with the best performing enolate-based ones; however, lower capacity (< 200 mAh g⁻¹) leaves ample room to address the inherent challenge of low energy density¹⁶.

In order to bring the existing research achievements with OLICs closer to real application, it is highly demanding to explore new redox centers beyond conjugated enolates and sulfonamides. In this work, we demonstrate the first application of conjugated oximates as positive electrode materials. The

oximate redox functionality not only enriches the family of organic electrode materials (Table S5), but also provides an excellent redox reversibility, low molecular weight (high capacity) and high air-stability of the anionic form, fulfilling the requirement of OLICs as a new candidate for Li-ion batteries. To establish the versatility of the oximate redox chemistry as positive electrode materials for Li-ion batteries, five lithiated oximate molecules with different chemical structures, including cyclic (aromatic), acyclic (non-aromatic), aliphatic and tetra-functional stereotypes, are investigated. The best performing candidate (Li₂-BQDO) displays high reversible capacity of 357 mAh g⁻¹ at high redox potential of 3 V vs. Li⁺/Li⁰, reaching a specific energy density of over 1 kWh Kg⁻¹. Amongst the unique characteristics in conjugated oximates, the most fascinating feature is the in-situ intermolecular polymerization (azodioxy coupling) and intramolecular furoxan ring formation during solid-state electrochemical redox. The excellent chemical and structural reversibility, as well as the promising electrochemical performance of the studied conjugated oximates corroborate the promising potentiality of this class of materials as positive electrode materials for Li-ion batteries.

Design rationale and redox mechanisms of conjugated oximates

The skeleton of oximate redox functionality proposed here exemplifies a fusion of two important families of organic electrochemical storage mechanisms, namely the conjugated carbonyls and nitroxides (Figure 1a). As electrode materials, the conjugated carbonyls being the most investigated, has dominated the organic battery field with more than 100 structural analogues being reported to date¹⁷, whereas the nitroxide redox center is usually grafted on polymer backbones in a variety of battery systems.^{18,19} The reduced form of quinones (enolate) takes advantage of π -conjugation (aromatic system) to achieve stabilization through mesomeric effect.^{11,14,20} The nitroxide radical is an ambipolar redox center with a well-studied reversible *p*-type redox occurring at 3.6 V, with also a less-understood, elusive *n*-type redox evolving at 2.8 - 3.0 V vs. Li⁺/Li.^{7,21,22} Thus, amalgamation of the concept of charge stabilization by conjugation with the nitroxide-based localized redox should result in a nitroxide bearing conjugated π -system *e.g.* pyrazine-N,N'-dioxide that might significantly favor radical stability and redox kinetics, although such a molecular system remains elusive so far (Figure 1a, right-hand panel).

On the other hand, in conjugated poly-carboxylates, the redox potential of the carbonyl group is significantly low (close to 1 V vs. Li⁺/Li) due to the presence of strongly electron donating -OLi group

attached to the C=O carbon, making these suitable only as negative electrode materials (Figure 1a, left panel).¹⁸ We envisioned that the rationale of eschewing electron-donating group (-OLi) for redox potential tuning is a prerequisite which is possible by replacing the tetravalent carbon unit with trivalent nitrogen, leading to the ketoximate group (=N-O-) that attain the essential features of nitroxide and carbonyl redox moieties. The benzoquinone dioximate (BQDO²⁻) represents a hybrid of iminoxy group and quinoneimine center with a reversible two-electron redox process accompanied by a series of exotic processes, depending on the position of redox functionality and conjugation as discussed in the following sections. As the conjugated non-aromatic redox systems have scarcely been studied in organic electrode materials, a series of oximate derivatives (e.g., DMGO, DPGO, PADO and TMTO) draw our attention due to their rich chemistry as well as low molecular weight, translating to high design diversity and theoretical capacity (Figure 1b).

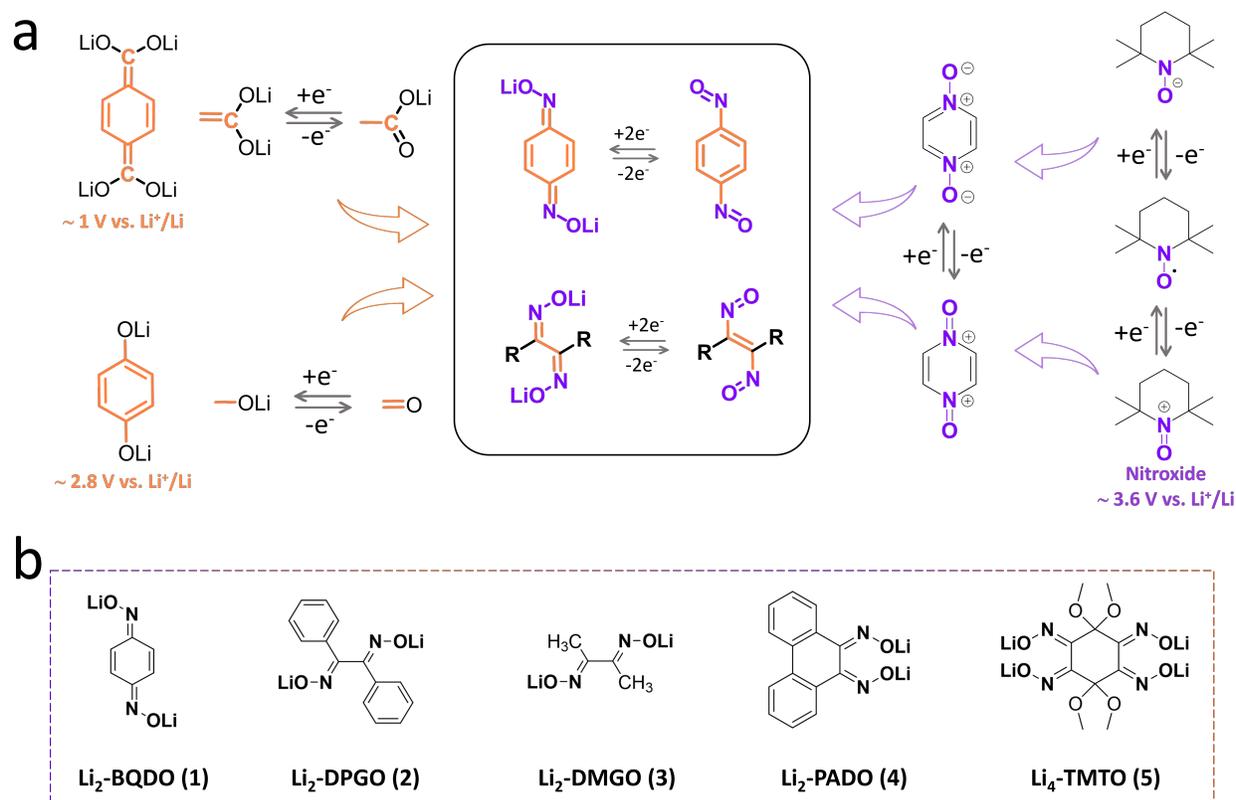


Figure 1. Design rationale and the library of conjugated oximates. a) Left: Conjugated carboxylate and ketoenolate redox. Right: Nitroxide-based redox (oxoammonium cation \leftrightarrow aminoxy anion). Molecular design of conjugated oximates (center) can be regarded as intramolecular hybrid fusion of di-aminoxy (right) and quinoneimine groups (left). b) The first generation of conjugated oximate cathode materials disclosed in this work.

All the lithiated oximates (**1-5**) are prepared by simple acid-base reaction on their protonated versions at room temperature (Refer to SI: materials synthesis). Complete deprotonation is confirmed by the disappearance of the broad OH band in the FTIR spectrum (Figure S1-S2 and S4-S6). Being aware of the fact that air-stability of cathode materials is a crucial parameter for practical applications and only a handful of OLIC materials comply to this requirement thus far^{11,12,14,15}, we focused our initial attention to the reactivity of the lithiated phases in ambient atmosphere. All the studied oximate (**1-5**) materials displayed no noticeable changes in color and Fourier-transform infrared spectroscopy (FTIR) signatures after 2h of air exposure (Figure S3-S6). The excellent air-stability and non-hygroscopic nature make these materials superior to a number of OLICs materials (e.g. quinone-based Li₂-BQ and Li₄-*p,o*-DHT) which are prone to aerial oxidation and hydrolysis.^{6,23,24} The stability of oximates under ambient atmosphere is an inherent property which can be attributed to their unique structural design. For example, the -oxido groups (-O⁻) in Li₂-BQDO are bonded to electronegative imine nitrogens which are in conjugation with the cyclohexa-1,4-dienyl backbone. This arrangement is conducive for delocalization of the negative charge over the cyclohexadienyl-oximate framework through resonance effects as indicated by the broadening of absorption band corresponding to the N-O vibration (1000 cm⁻¹) in FTIR spectrum of Li₂-BQDO (Fig. S1 and S2).

Electrochemically, the disclosed oximates (**1-5**) undergo 1-electron redox per oximate group to form nitroso derivatives followed by significant reversible structural modifications, which is strongly dependent on the conjugation as well as molecular structures (Figure 2). On one hand, para-dioximate compounds (e.g., Li₂-BQDO) are oxidized to the intermediate phase (e.g., *para*-dinitrosobenzene) which undergoes intermolecular polymerization through azodioxy (-ONNO-) linkage²⁵ to poly(1,4-phenyleneazine-N,N-dioxide) (PNND) (Mechanism 1)²⁶. The *in-situ* formation of PNND upon oxidation of Li₂-BQDO is confirmed by Rietveld refinement of the experimental PXRD pattern (Fig. S7 and S8)²⁷. The reversible formation of PNND polymer upon oxidation is an extremely important asset of this specific compound for battery electrode application because the very common dissolution problem of organic electrode materials usually arises from the oxidized/neutral phase (e.g., benzoquinone), whereas PNND is insoluble in commercial electrolytes, making it a promising OLIC material.²⁸ On the other hand, α - or ortho-dioximates (e.g., Li₂-DPGO, Li₂-PADO and Li₄-TMTO) get oxidized to the

intermediate dinitroso states which undergo intramolecular cyclization to produce furoxan derivatives as the final product (Figure 2. Mechanism 2, e.g., 3,4-diphenyl-1,2,5-oxadiazole-2-oxide (DPODO) as the oxidized phase of Li_2 -DPGO).²⁹⁻³¹ The formation of furoxan ring in solid state upon charge-discharge is also a significant feature that influences the redox process and changes the electrochemical performance of the electrode materials, which will be discussed in the next section.

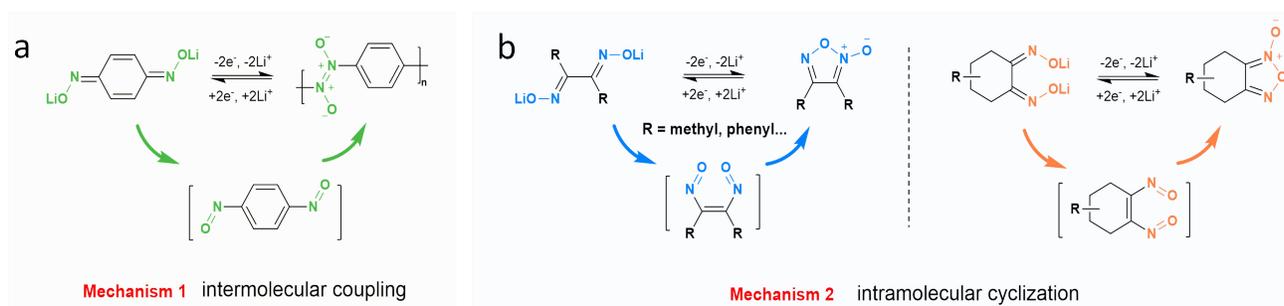


Figure 2. Reversible intra- and inter-molecular conversion during redox in lithium oximates. (a) Redox mechanism of Li_2 -BQDO: upon oxidation, Li_2 -BQDO release two electrons and lithium ions forming the intermediate para-dinitrosobenzene, which undergoes intermolecular interaction to form PNND through azodioxy (-ONNO-) coupling. (b) left panel: Redox mechanism of glyoximates (Li_2 -DPGO and Li_2 -DMGO): after oxidation, the dinitroso intermediate state undergoes a change from “trans to cis” configuration and furoxan ring formation through intramolecular cyclization. Right panel: Redox mechanism of ortho-oximates (α -dioximates): after oxidation the molecules also form furoxan ring through intramolecular cyclization.

Solid-phase electrochemical performances

To establish the versatility of the studied oximates (**1-5**) as positive electrode materials, their solid-state electrochemical performance was evaluated in lithium half-cells (Fig. 3). All the studied molecules show theoretical 1-electron redox per oximate group, with high average redox potential of 2.5-3.1 V vs. Li^+/Li and high achieved capacity of 210-350 mAh/g. Specifically, the Li_2 -BQDO/ Li cell reversibly delivers 97% of the theoretical capacity (357 mAh g^{-1}) at 3.0 V vs. Li^+/Li on the first cycle, corresponding to 1.94 Li^+/e^- equivalents exchange at galvanostatic charge/discharge rate of one Li^+ in 5h (Fig. 3a, green curve). The battery also displays excellent rate capability (Fig. S10), as well as remarkable cycling stability with more than 200 mAh g^{-1} retained after 50 cycles (over 75% of capacity retention) (Fig. S11-S12). To prove the reversibility of the redox process, the oxidized phase of Li_2 -BQDO (PNND²⁶) (Mechanism 1), was

chemically synthesized, characterized and tested as positive electrode material in similar battery configuration (Fig. 3a, black curve). The nearly identical charge-discharge profile starting from PNND polymer (discharge first) validates the polymer formation after electrochemical oxidation of Li₂-BQDO (Fig. 3a and S9). Interestingly, compared to its closest analogue dilithium benzene-1,4-diolate (Li₂-BQ), Li₂-BQDO displays higher redox potential (~300 mV) in both liquid and solid-state electrochemistry¹⁴ (Fig. S13). This can be explained by the introduction of additional nitrogens in the molecule, leading to enhanced electronic delocalization of the negative charge over the cyclohexadienyl-oximate framework through resonance effects. It is also worth noting that Li₂-BQ can barely cycle in liquid electrolytes because of the extremely high solubility of the oxidized phase (1,4-benzoquinone), whereas Li₂-BQDO shows stable cycling benefiting from the polymerized oxidized phase impeding the material dissolution.

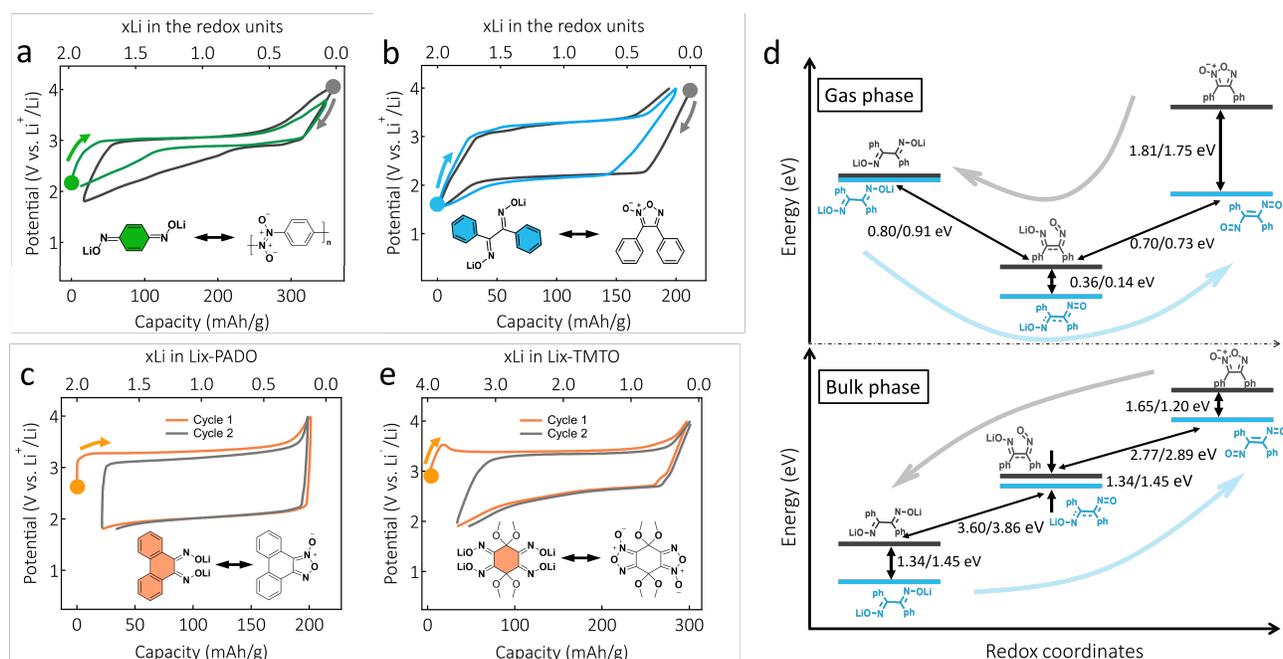


Figure 3. Electrochemical analysis of studied oximate positive electrode materials. Potential-composition charge-discharge profiles of (a) Li₂-BQDO/Li (green curve) and PNND/Li (black curve) cells cycled at galvanostatic current rate of C/10, (b) Li₂-DPGO/Li and DPODO/Li cells, (c) Li₂-PADO/Li cell and (d) Redox coordinates for the conversion of Li₂-DPGO to DPODO (linear/closed structures in both gas and bulk phases); The energy differences for phase transition (eV) are indicated for both experimental/calculated cell parameters. (e) Potential-composition charge-discharge profiles of Li₄-TMTO/Li cell.

As for α - or ortho-dioximates, the oxidized phase of the simplest low molecular weight dioximate $\text{Li}_2\text{-DMGO}$ (dimethylfuroxan) exists as a liquid and thus rendering it not applicable in Li-ion battery system (Figure S14). Therefore, lithiated diphenylglyoxime ($\text{Li}_2\text{-DPGO}$) was chosen as prototype to explore the solid-state electrochemical behavior. Upon charging of $\text{Li}_2\text{-DPGO/Li}$ cell, the potential reached a flat plateau around 3.1 V with efficient extraction of two electrons, reaching close to the theoretical capacity (212 mAh g^{-1}) (Fig. 3b, blue curve). The discharge process was observed to be fully reversible involving a two-electron/lithium reduction with a much lower potential (2.1 V vs. Li^+/Li), giving rise to a high charge-discharge polarization of nearly 1V, an effect which will be explained in the following sections. The oxidized form of $\text{Li}_2\text{-DPGO}$, namely 3,4-diphenyl-1,2,5-oxadiazole-2-oxide (DPODO), was also chemically synthesized and characterized, and the charge-discharge profile of DPODO/Li cell (starts from discharge) displays comparable electrochemical behavior, establishing complete electrochemical reversibility between $\text{Li}_2\text{-DPGO}$ and DPODO (Fig. 3b, black curve).

The 2-electron solid-state electrochemistry between $\text{Li}_2\text{-DPGO}$ and DPODO consistently displayed high polarization ($\sim 1\text{V}$) which is unaffected by cycling rates and remained persistent during subsequent charge-discharge cycles. Galvanostatic Intermittent Titration Technique (GITT) shows that the majority of the polarization ($\sim 80\%$) originates from the delithiation/oxidation process (Figure S15). As mentioned previously, the open chain oximates undergo significant structural modification after oxidation such as rotation around the C=C bond, dilithium 9,10-phenanthrene dioximate ($\text{Li}_2\text{-PADO}$) is expected to bypass the trans-cis transformation hindered by diphenyl rings connection (Fig. S16). However, same polarization value of $\sim 1\text{V}$ was also witnessed in the $\text{Li}_2\text{-PADO/Li}$ cell, indicating that the trans-cis transformation is not the only contributor to the polarization (Fig. 3c). The experimental results are supported by geometry optimization and energy profile of $\text{Li}_2\text{-DPGO}$ and DPODO (linear/closed structures in both gas and bulk phases), which shows an energy barrier around 1 eV between reduced and oxidized process of redox change (Figure 3d, and more DFT details in SI). This significant structural rearrangement requires expense of energy which is reflected in the form of redox hysteresis or polarization. The computational results also indirectly point to the absence of polarization in *para*-oximates (*e.g.*, $\text{Li}_2\text{-BQDO}$) which is due to minimum or no structural changes during the redox process. Moreover, it is logical to comprehend that small energy barrier posed by availability of more than one coordination modes of Li-ions is escaped by the spontaneity of PNND polymer formation. The

polymerization is energetically favorable due to low enthalpy and high negative entropy of activation (-179.7 to -183.0 J K⁻¹ mol⁻¹)²⁷.

The conjugated oximates family is not limited to two-electron redox chemistry, and with proper molecular engineering via incorporating multiple number of oximate units, higher capacity can be achieved. The alicyclic alpha oximates Li₄-TMTO with four oximate units can reach 4-electron redox with a theoretical specific capacity of 311 mAh/g. The Li₄-TMTO/Li cell shows a charge plateau at 3.5 V accompanied by a lower discharge plateau located at around 2.65 V, making a similar large polarization of ~850 mV (Figure 3e). The average redox potential of Li₄-TMTO (~3.0 V) is approximately 400 mV higher than that of Li₂-DPGO (~2.6 V), Li₂-DMGO (~2.6 V), and Li₂-PADO (~2.6 V), which can be explained by the electron-withdrawing mesomeric effect (-M) of the four -OCH₃ groups, thus increasing the redox potential of the molecule.

Structural and chemical reversibility

To gain further in-depth understanding of the conjugated oximate redox, the charge/discharge processes of the cells (Li₂-BQDO and Li₂-DPGO as representative examples) were monitored by *in-operando* XRD and *ex-situ* infrared spectroscopy (Fig. 4, S17 - S19). The pristine Li₂-BQDO exhibits an amorphous phase (Fig. S18). During the charge (delithiation) process of a Li₂-BQDO/Li cell, progressive amplification of a crystalline phase is observed which is characterized by two main diffraction peaks at 15.5° and 25°, corresponding to (020) and (011) reflections plane in the PNND phase, respectively (Fig. 4a and S18). This indicates that the oxidation of Li₂-BQDO proceeds through the formation of intermediate 1,4-dinitrosobenzene followed by polymerization to poly(1,4-phenyleneazine-*N,N*-dioxide) (Fig. 4b). The XRD peaks progressively diminished during the following reduction process (*i.e.* discharge/lithiation) with complete amorphization at the end of this step. This process is also completely reversible in the second cycle (Fig. 4a). Thus *in-situ* PXRD confirms that the inter-conversion of Li₂-BQDO and PNND is a synchronous bi-phasic process with excellent structural reversibility. Though it is rarely observed in organic cathode materials, this type of reversible structural transformation (monomer-polymer) during solid-state electrochemical processing is exclusive and highly efficient in oximate based redox systems. The chemical reversibility and the redox-driven solid-phase polymerization were further confirmed by *ex-situ* FTIR (Fig. 4c), where upon oxidation, the characteristic ν_{N-O} and $\nu_{C=N}$ bands disappear, followed by the appearance of E-azodioxy signature (1264 cm⁻¹), identical with the

chemically synthesized PNND polymer. The FTIR spectrum after the subsequent discharge is similar to that of the pristine $\text{Li}_2\text{-BQDO}$ (Fig. 4c). On similar lines, in-situ XRD and ex-situ FTIR measurements of α - or ortho-dioximates (e.g., $\text{Li}_2\text{-DPGO}$) also revealed the complete chemical and structural reversibility between the reduced (oximates) and oxidized compounds (furoxan). (Fig. S17 and S19)

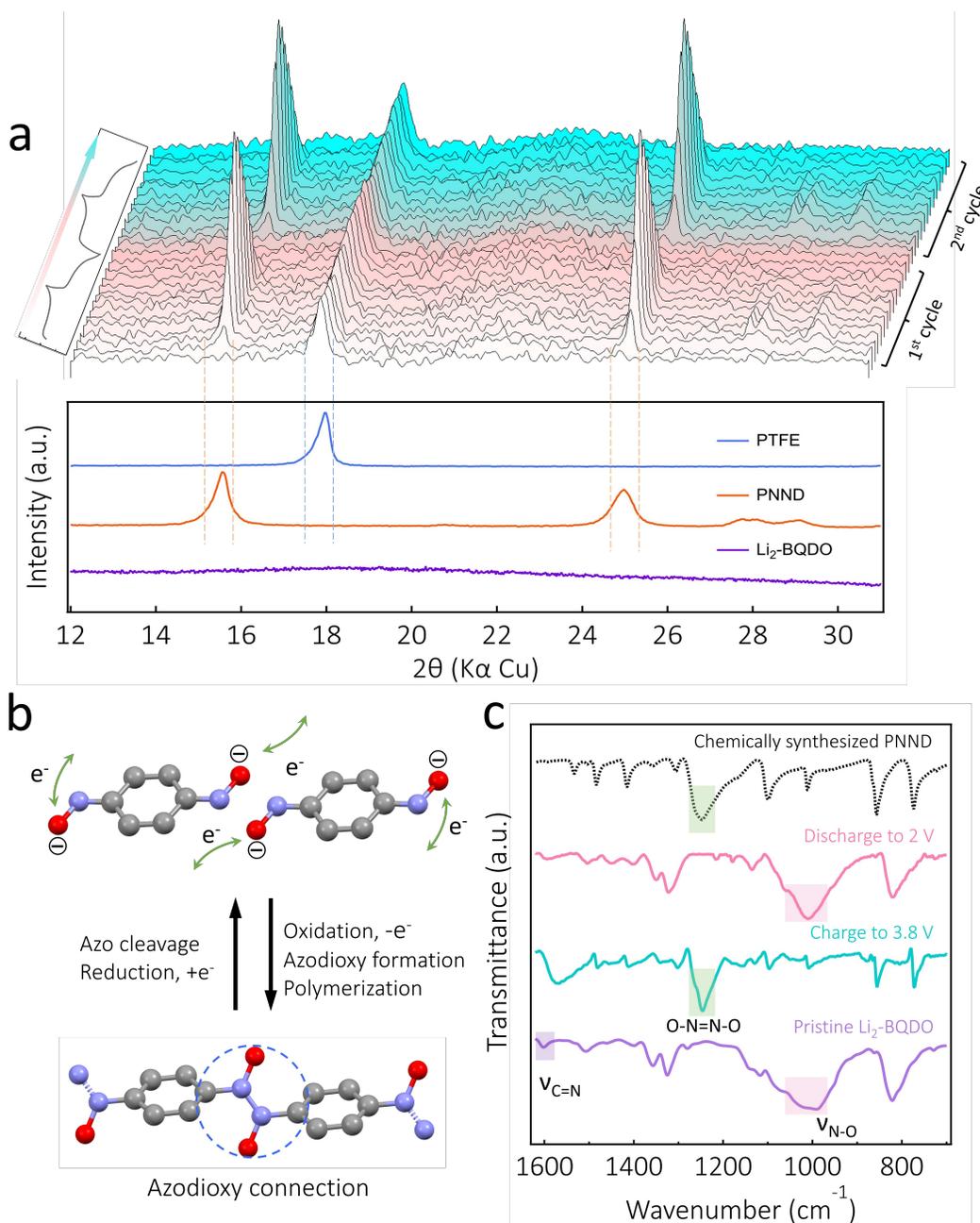


Figure 4. In situ and ex situ analysis of $\text{Li}_2\text{-BQDO}$ cathode. (a) in-situ XRD analysis of $\text{Li}_2\text{-BQDO}/\text{Li}$ cell in complete two cycles; (b) Schematic illustration of the in-situ polymerization upon charging and the cleavage of azodioxy coupling upon discharging; (c) ex-situ FTIR analysis measured at three different charge states, namely pristine, fully charged to 3.8V and fully discharged to 2V.

Energy metrics and future perspectives

Although cycling stability is a concern for majority of organic materials, higher oxidation potential ($\sim 3\text{V}$ vs. Li/Li^+) and outstanding capacity ($\sim 350\text{ mAh g}^{-1}$) achieved with oximate-based cathodes is promising considering the pristine, non-functionalized structure of the redox unit. The disclosed conjugated Li-oximate cathodes show unequivocal redox mechanism, with nitroso compounds formed as intermediate phase followed by interesting molecular rearrangement. The combination of high theoretical capacity and redox potential of this class of new OLICs results in high energy density over 1 kWh kg^{-1} , establishing superiority over previously reported OLICs, such as conjugated Li-enolates and the recent breakthrough of conjugated sulfonamides ($300\text{--}700\text{ Wh kg}^{-1}$) (Fig. 5a). Comparably, the value is also much higher than majority of the inorganic cathode materials ($\text{LiFePO}_4\text{--}550\text{ Wh kg}^{-1}$, $\text{LiCoO}_2\text{--}590\text{ Wh kg}^{-1}$, $\text{LiMn}_2\text{O}_4\text{--}490\text{ Wh kg}^{-1}$, $\text{NMC622--}690\text{ Wh kg}^{-1}$, $\text{LNMO--}570\text{ Wh kg}^{-1}$).

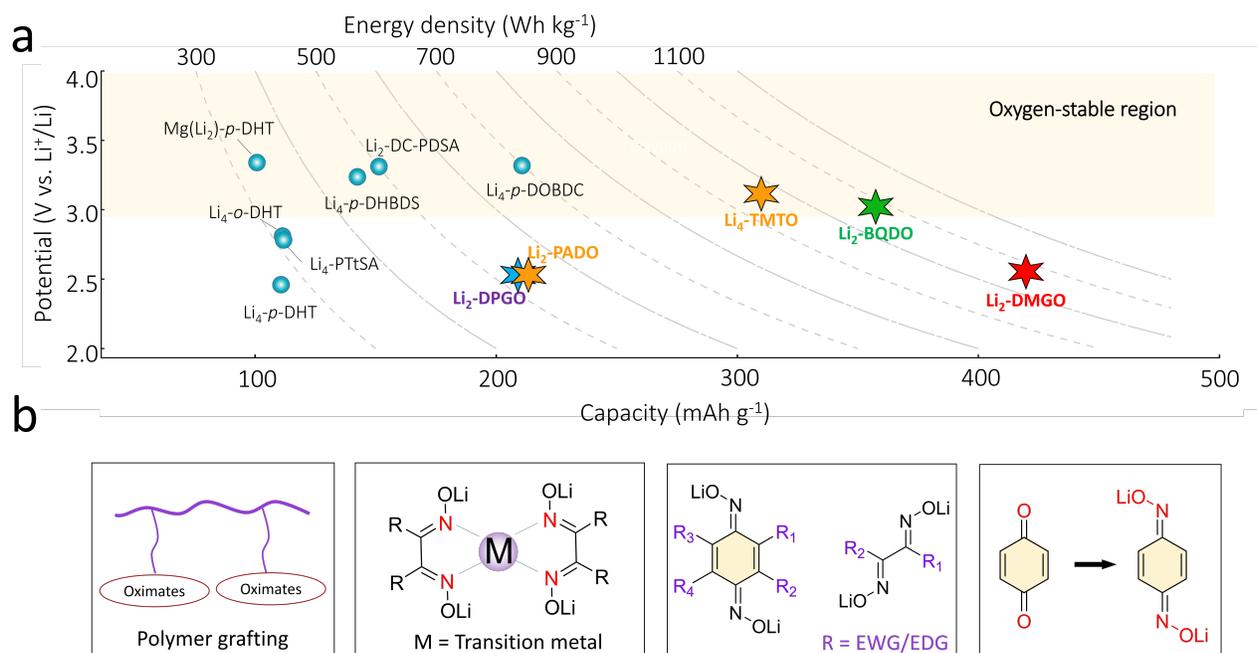


Figure 5. Energy metrics and future perspectives of oximate cathodes. (a) Reversible capacity, average redox potential and corresponding energy density comparison of selective/all organic lithiated positive electrode materials. (b) Methods of improving the oximate cathodes, as well as future directions for further investigation.

The first generation of conjugated oximates as battery electrode materials is still far from

commercialization which demand further improvement of the overall performance. The highly versatile oximate redox can be exploited in the form of a variety of chemical structures (Fig. 5b). For example, multiple oxime functionalities can be incorporated in polymeric or ordered framework backbones where the distinct redox features can still be achieved with improved cycling stability. In addition to this, the α -dioximates can act as chelating groups to metal ions generating coordination complexes and metal-organic frameworks³², which could lead to electronic conductivity, higher redox potential, and superior capacity supported by additional metal redox. The conjugated oximates also offer the possibility of redox property tuning by functionalizing with electron withdrawing/donating groups (e.g., methoxy, carboxylate or sulfonate). These molecular engineering efforts can potentially address the inherent issue of organic cathode material dissolution. The chemical space of conjugated oximate cathodes is by no means limited to the five molecules investigated in this work. Since oximes can be easily accessed by the reaction of hydroxylamine with carbonyl derivatives, it is not excessive to assume that most of the quinone-based cathodes reported so far can be straightforwardly adapted to oximates, thereby leading to a library of new OLICs.³³

Conclusion

A new class of Li-ion redox chemistry based on air-stable conjugated oximates is disclosed. Unlike carbonyl based redox systems, unique molecular design and redox mechanism of the oximate groups offering higher structural versatility, allows the implementation of both cyclic and acyclic derivatives as cathode materials. Upon oxidation, conjugated oximates undergo 1-electron redox per oximate group to form nitroso derivatives followed by significant reversible structural modifications, such as polymerization for cyclic/*para*-dioximates (e.g., BQDO) and cyclization to furoxan derivatives in case of alicyclic α -dioximates. Due to these favorable features, the oximate cathodes display high redox potential (2.5-3.2 V vs. Li⁺/Li) and capacity (210-360 mAh g⁻¹), which translate to energy density as high as 1 KWh Kg⁻¹. The possibility of molecular engineering and structural tunability of oximes (such as straightforward transition from quinone to oxime) provides the opportunity to adjust the redox potential, capacity and cycling stability.

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