Through-Space Charge Modulation Overriding Substituent Effect: Rise of the Redox Potential at 3.35 V in a Lithium-Phenolate Stereoelectronic Isomer

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Through-Space Charge Modulation Overriding Substituent Effect: Rise of the Redox Potential at 3.35 V in a Lithium-Phenolate Stereoelectronic Isomer

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ABSTRACT: Raising the operating potential of the organic positive electrode materials is a crucial challenge if they are to compare with lithium-ion inorganic counterparts. Although many efforts have been directed on tuning through substituent electronic effect, the chemistries that can operate above 3 V vs Li^+/Li^0 , and thus be air stable in the Li-reservoir form (alike the conventional inorganic Li-ion positive electrode materials) remain finger-counted. Herein, we report on a new *n*-type organic Li-ion positive electrode material—the tetralithium 2,5-dihydroxy-1,4-benzenediacetate—with a remarkably high redox potential of 3.35 V vs Li^+/Li attained notably in the solid phase. The origin of the high-energy content in this quinone derivative is found in a stereoelectronic chameleonic effect with an intramolecular conformation change and charge modulation leading to a redox potential increase of 650 mV in the solid state as compared to the same chemistry tested in solution (2.70 V vs Li^+/Li). The conformational dependent electroactivity rationale is supported by electrochemical and crystallography analysis, comparative infrared spectroscopy, and DFT calculation. We identify and make a linear correlation between the enolate vibrational modes and the redox potential, with general applicability for possibly other phenolate redox chemistries. Owing to these effects, this lithiated quinone is stable in ambient air and can be processed and handled alike the conventional inorganic Li-ion positive electrode materials. Whereas intrinsic to high voltage operation stability issues remain to be solved for practical implementation, our fundamental in nature and proof-of-concept study highlights the strong amplitude of through-space charge modulation effects in designing new organic Li-ion positive electrode chemistries with practical operating potential.

A dance of bonds and atoms

INTRODUCTION

One of the primary assets of current Li-ion battery technology is the availability of positive electrode chemistries that are stable to ambient air in the lithium containing, electrochemically reduced form.¹ Whereas there are many opportunities for the transition metal-based chemistries to fulfill these criteria, the organic-based compounds with alike properties remain finger-counted.² Organic batteries emerge as one of the attracting alternative technologies for the forthcoming massive adoption of electrochemical energy storage (EES) systems. Indeed, these would allow to cope with raw material supply shortages, lead to a reduced environmental production and recycling footprint, and potentially result in an enhanced manufacturing scalability, globally improving the sustainability of EES devices.^{3–7} Whereas the gravimetric and volumetric energy metrics of organic batteries may not currently compete with their inorganic counterparts, the natural abundance of their constituent elements (e.g., C, H, N, O), and the expected mitigation of the battery life-cycle's environmental burden constitute arguments of choice to counterbalance and eventually overthrow this already receding disadvantage.²

For all these reasons, the organic battery field has experienced flourishing developments over the past decade. Many classes of redox chemistries have been explored, and the number of these investigations is continuously increasing as a result of the high versatility of organic chemistry.^{2,5–12} Moreover, capacity and energy performance metrics are steadily increasing with values that verge on competitiveness.^{2,13–16} However, despite all the progress achieved up to date, this emerging field still misses flagship chemistries that would once and for all put it on the map of EES systems by fulfilling the paramount criteria of conventional Li-ion battery technology: Li-ion positive electrode materials prepared in their lithiated (reduced) state stable to ambient air, so that

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Scheme 1. Modulation of the Redox Potential in Quinone Derivatives^a

^aConventional through-bond electronic effects result in either electron-deficient quinones with increased redox potential, or electron-rich systems with lower redox potential. Through-space electrostatic charge and redox potential modulation can override the through-bond effects, and results in considerably higher redox potential as expected.

59 these can be handled and processed in the same way as
60 conventional Li-ion positive electrode materials.

61 In this work, we discuss a hitherto unexplored organic
62 battery material, the tetralithium salt of 2,5-dihydroxy-1,4-
63 benzenediacetic acid ($\text{Li}_4\text{-p-DOBDA}$). Although closely similar
64 to the extensively explored tetralithium salt of 2,5-dihydrox-
65 yterephthalic acid ($\text{Li}_4\text{-p-DHT}$),^{17,18} $\text{Li}_4\text{-p-DOBDA}$ displays
66 valuable electrochemical performances since it can undergo a
67 reversible two-electron electrochemical reaction at a higher by
68 800 mV redox potential ($\langle E \rangle \approx 3.35$ V vs Li^+/Li^0) with a
69 theoretical capacity of 215 mAh/g of $\text{Li}_4\text{C}_{10}\text{H}_6\text{O}_6$. Other than
70 the high-energy content, this lithiated organic chemistry is also
71 found to be stable in ambient air, with no signs of oxidation or
72 hydrolysis even for long periods of exposure. The origin of the
73 air-stability and high energy content in $\text{Li}_4\text{-p-DOBDA}$ is the
74 result of an exotic intramolecular charge modulation that leads
75 to a redox potential increase of about 650 mV in the solid state
76 as compared to the same chemistry in solution. This rationale
77 is supported by electrochemical and crystallography analyses,
78 comparative infrared spectroscopy, and DFT calculations.
79 These electrochemical properties, combined with the fact that
80 $\text{Li}_4\text{-p-DOBDA}$ is stable to ambient air, making this one of the
81 highest energy containing organic Li-ion positive electrode
82 materials reported to date. Whereas further optimization of
83 electrode formulation, cell design, and cycling stability are
84 required, this organic battery chemistry is the first one to
85 challenge the archetypal inorganic Li-ion positive electrode
86 chemistries, LiFePO_4 and LiCoO_2 , in terms of gravimetric
87 energy density.

88 ■ EXPERIMENTAL SECTION

89 **Reagents and Chemicals.** 2,5-Dihydroxy-1,4-benzenediacetic
90 acid ($\text{H}_4\text{ p DOBDA}$, 97%), lithium methoxide (LiOCH_3 , 98%),
91 and lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$, 98%) were
92 purchased from Sigma-Aldrich. Hydroquinone (H_2Q , 98%), tetrahy-
93 drofuran (THF), and anhydrous methanol were purchased from Alfa
94 Aesar. The deuterated dimethyl sulfoxide ($d_6\text{-DMSO}$) and deuterium
95 oxide (D_2O) were purchased from Euriso-top.

96 **Synthesis of the Tetralithium Salt ($\text{Li}_4\text{-p-DOBDA}$).** Lithium
97 salts of p-DOBDA were prepared under inert atmosphere (argon-
98 filled glovebox). To a solution of 2.262 g (10 mmol) of $\text{H}_4\text{-p-DOBDA}$

in 100 mL of anhydrous methanol, 4 equiv of LiOCH_3 (40 mmol;
1.519 g) were added. The mixture was stirred overnight at room
temperature and led to the precipitation of the corresponding
tetralithium salt as a beige powder ($\text{Li}_4\text{-p-DOBDA}$ yield: 88%). The
solid was retrieved by filtration in the glovebox and washed with dry
methanol. The powder was finally dried under vacuum at 120 °C for 3
h.

Instrumentation. ^1H NMR spectra were acquired on a 300 MHz
Bruker Advance II. ^{13}C NMR spectra were acquired on a 500 MHz
Bruker Advance III. Samples were prepared by dissolution of 5–10
mg of the product in 600–700 μL of deuterated solvent (D_2O or $d_6\text{-}$
DMSO-Sigma-Aldrich). FTIR spectroscopy was carried out on
pristine powders using a Bruker Alpha P or an Agilent Technologies
Cary 630 spectrometer with a Single reflection ATR module.
Thermogravimetry (TG) and differential scanning calorimetry
(DSC) experiments were carried out under argon with a SENSYSeco
instrument from Setaram using a heating rate of 5 °C min^{-1} between
25 and 600 °C. Scanning electron microscopy (SEM) images were
collected on using a JEOL JSM-7600F microscope.

Powder X-ray powder diffraction (PXRD) patterns were collected
on a STOE Stadi P diffractometer in transmission geometry equipped
with a Cu anticathode ($K\alpha$ radiation, operating at 50 kV to 40 mA).
For structure resolution, data were acquired at the ESRF synchrotron
(Grenoble, beamline BM01) with a wavelength of $\lambda = 0.69425$ Å.

Electrochemical Assembly and Analysis. The electrochemical
performances of $\text{Li}_4\text{-p-DOBDA}$ in the solid phase (galvanostatic
charge/discharge) were determined using two-electrode coin cells
assembled in an argon-filled glovebox. A typical $\text{Li}_4\text{-p-DOBDA}$
working electrode (cathode) was composed of 5 mg of active material
(60 wt %) manually mixed with 30 wt % of Ketjenblack EC600
(denoted as KB600 carbon) and 10 wt % poly(tetrafluoroethylene)
(PTFE) dry binder. The resulting mixture was pressed on stainless
steel mesh disks with a pressure of 8 tons to form the working
electrode (5 mg/cm^2 of active material typically). A lithium foil disk
was used as counter and reference electrode (anode), two PE/PP
sheets as separator and LiPF_6 1 M in ethylene carbonate/dimethyl
carbonate (EC/DMC) 1:1 (v/v) as electrolyte (LP30, battery grade,
Solvionic). The galvanostatic measurements were recorded using a
Biologic VMP potentiostat/galvanostat battery cyler. All solutions for
cyclic voltammetry (CV) measurements were 2 mM in active
material, and alkaline aqueous (KCl 0.5 M/NaOH 0.1 M – pH
13.3) conditions were applied. The setup consisted of glassy carbon
working electrode, a Pt wire counter electrode, and an Ag/AgCl
aqueous reference electrode. A scan rate of 5 mV/s was systematically

applied. Potassium ferricyanide (giving the $[\text{Fe}(\text{CN})_6]_{3-}/[\text{Fe}(\text{CN})_6]_{4-}$ redox couple) was used as internal reference for all CV experiments.

In Situ X-ray Measurements. In situ PXRD patterns were collected in the $5.00\text{--}31.13$ 2θ degrees ranges, with a step size of 1.005° and total acquisition time per diffractogram of 80 min. Measurements were performed with a simple holder able to accommodate an in-house in situ coin cell. The working electrode was prepared by mixing $\text{Li}_4\text{-}p\text{-DOBDA}$, KB600, and PTFE with a composition ratio of 60:30:10 wt %. The lithium metal disk was used as negative electrode, 2 sheets of PE/PP (Celgard) as separator, and LP30 as electrolyte. The galvanostatic measurements were collected on a Parstat 3000 potentiostat/galvanostat.

RESULTS AND DISCUSSION

Design Considerations for High Potential Organic Positive Electrode Chemistries. Our current efforts are oriented on finding n -type organic positive electrode materials capable of fulfilling the paramount criteria of a conventional Li-ion cathode. Whereas most results are based on conventional approaches to the electron withdrawing effect to increase the redox potential, recently we reported on a new class of organic materials based on conjugated sulfonamide (CSA) as an efficient organic Li-ion cathode material, given its intrinsic high voltage properties.¹⁹ Various CSA chemistries were explored and found to be operating within a wide range of potential between $2.85\text{--}3.45$ V vs Li^+/Li^0 (with also excellent air stability) with tunable electrochemical performance.

The archetypal carbonyl redox chemistry nevertheless remains the most explored to date, owing to its tangible ability to simultaneously attain high energy and power densities combined with extended cycling stability. For instance, quinone chemistry (Q^0/Q^{2-} , Scheme 1), promises an impressive theoretical energy density of more than 1 kWh/kg [two electron redox, specific capacity of 440 mAh/g (mass of the Li^+ cations considered), for an average electrode potential of 2.7 vs Li^+/Li^0].²⁰ However, benzoquinone presents two key drawbacks: the reduced Q^{2-} form is sensitive to oxidation in air, whereas the oxidized form Q^0 is highly soluble in typical liquid battery electrolytes.

Concerning the latter, many approaches have been developed in the past to counteract the solubility.^{21–26} In addition to the inclusion of permanent negative charges to increase the polarity²⁷ such as in the tetralithium 2,5-dihydroxyterephthalate salt ($\text{Li}_4\text{-}p\text{-DHT}$ also known as Li_4DHTPA),^{17,18} we have explored intermolecular H-bonding in 2,5-diamino-1,4-benzoquinone (DABQ)²⁸ as a new efficient strategy to reduce the solubility of the low-molecular weight quinone-based systems. However, the electron-donor nature of the amine and carboxylate substitution comes along with the reduction of the redox potential (Scheme 1).

One key element to enable ambient air stability of lithiated (reduced state) organic electrode materials, which will also translate into higher energy content, is to increase the redox potential above the limit of 2.91 V vs Li^+/Li^0 ; the redox potential at which oxygen reduction occurs vs Li .^{17,29} Considering that few lithiated reduced organic phases comply to this criterium, it is not surprising that most organic battery chemistries proposed thus far are assembled out of the oxidized phase, requiring a lithium reservoir counter electrode, and thus suitable only for lithium–metal (rechargeable or primary) cells. Since this latter technology is still facing major challenges,^{30,31} organic materials do not yet make the cut for Lithium-ion batteries. All-organic Li-ion cells have nevertheless

been made possible by synthesizing the reduced phases of organic quinone-based compounds.^{6,18,32} However, these phases are reactive toward oxygen and moisture, making them hardly practical, as many are impossible to handle even in dry rooms. It should be mentioned that there exist organic battery chemistries with a formal redox potential above 3 V vs Li^+/Li^0 , however their redox mechanisms is based on the ingress/removal of anions (also known as p -type redox systems).^{6,33,34} Whereas such chemistries are suitable for Li-free batteries^{33,35–42} or better known as molecular-ion batteries,⁴³ these cannot comply with conventional Li-ion design.

In accordance with the inductive or mesomeric effects rationales (Scheme 1), several electron-deficient quinones have been designed, with effectively increased redox potentials.^{44–47} But it is only very recently that practical organic Li-ion cathode chemistries—defined as Li-containing in the reduced form, while also being stable in ambient air—have been proposed. Lakraychi et al. were the first to report on the tetralithium salt of 2,5-dihydroxy-1,4-benzenedisulfonic acid ($\text{Li}_4\text{-}p\text{-DHBDS}$), with a redox potential of ~ 3.25 V vs Li^+/Li^0 , making it processable under dry air conditions (the materials however pointed to be sensitive to moisture).⁴⁸ The same year, Jouhara et al. reported an innovative approach to achieve significant increase of the redox potential in $p\text{-DHT}^{4-}$.⁴⁹ The authors successfully tuned the electronic effects in the redox-active organic skeleton of $\text{M}_{2/n}^{n+}(\text{Li}_2)\text{-}p\text{-DHT}$ by playing on the electronegativity of the spectator cation (M^{n+}). Impressively, substituting lithium for magnesium in $\text{Li}_4\text{-}p\text{-DHT}$, to yield $\text{Mg}(\text{Li}_2)\text{-}p\text{-DHT}$, led to a voltage gain of nearly $+800$ mV, raising the redox potential up to 3.4 V vs Li^+/Li^0 .

Taking a global look at these different investigations,^{2,15,45–49} the possible approaches to tune the redox potential can be broadly resumed to one fundamental rationale (Scheme 1): the through-bond electronic effect, with either increase or decrease in the charge density, resulting in redox potential decrease or increase, respectively. The strength of these effects correlates with the redox potential and effectively explains the redox potential values of many studied materials and those under development.^{3,46,49,50} However, adding substituents always compromises the specific capacity given the increase in the molecular weight.

Alternatively, there are few reports on exotic effects, which have proven effective in increasing the redox potential of organic materials with limited impact on the capacity. For example, Banda et al. have exploited steric hindrance in perylene diimide derivatives and found that molecular distortion can lead to increased redox potential as compared to a planar equivalent.⁵¹ In the same category, the investigation of $\text{Li}_4\text{-}o\text{-}p\text{-DHT}$, where the carbonyls switch from the para to ortho position, also resulted in an increased potential.⁵² Through our explorations of high voltage n -type organic materials, we found that $\text{Li}_4\text{-}p\text{-DOBDA}$ is another example of organic battery material with unusually elevated redox potential due to an exotic effect—namely, the through-space intramolecular electronic charge modulation. Whereas a similar effect could also explain the para to ortho ($\text{Li}_4\text{-}o\text{-DHT}$, as well as in catechol vs quinone) increased redox potential, in $\text{Li}_4\text{-}p\text{-DOBDA}$ this effect is found to be unexpectedly amplified, leading to a 650 mV increase in potential as compared to traditional (through bond) rationalized values.

Figure 1. (A) Typical cyclic voltammetry curves of Q²⁻ and p-DOBDA⁴⁻ measured in aqueous solutions (pH 13.4). The pH of all solutions was adjusted with NaOH 0.1 M, in addition to the 0.5 M KCl electrolyte carrier salt. A glassy carbon working electrode was used, and a scan rate of 5 mV/s was applied. (B) Potential-composition profiles at the first galvanostatic charge–discharge cycle of Li₄-p-DHT, Li₂Q and Li₄-p-DOBDA measured in a lithium half-cell with a nonaqueous electrolyte [cycling rate: 1 electron (1 Li⁺) per equivalent exchanged in 5 h].

Figure 2. (A) Overlaid FTIR spectra of selected quinone derivatives in their respective reduced state. The IR spectra are displayed from bottom to top in the order of increased redox potential. The _aq and _cr subscripts for Li₄-p-DOBDA are used to indicate the dissolved and solid crystalline forms used for measurement, respectively. Insert to the right: close up on the enolate vibration band ν(C-O⁻Li⁺). The ν(C-O⁻) vibration band is identified by comparison of the lithiated and protonated form for each compound. The evolution of the enolate (C-O⁻) vibration band is highlighted by the red dotted line and the band shift between Li₄-p-DOBDA_cr and Li₄-p-DOBDA_aq is highlighted by the blue arrow. (B) Modeling of the correlation through linear regression.

The Curious Case of Li₄-p-DOBDA Electrochemical Response.

The striking point that triggered our interest for extensive analysis of Li₄-p-DOBDA was the major discrepancy between the electrochemical responses in aqueous solution as compared to the solid phase (Figure 1). The measured half-wave redox potential of p-DOBDA⁴⁻ obtained by cyclic voltammetry (aqueous solution, pH 13.4) was found to be approximately 120 mV lower than that of hydroquinone (Q²⁻) measured in similar conditions: -0.365 V and -0.485 V vs [Fe(CN)₆]³⁻/ [Fe(CN)₆]⁴⁻ for Q²⁻ and p-DOBDA⁴⁻, respectively (Figure 1A). This observation corroborates the rationale presented in Scheme 1 and is in accordance with the through bond electronic effects at play. The acetate groups (-CH₂-COO⁻) in p-DOBDA⁴⁻ have an inductive donor nature and would thus enrich the electronic density of the quinone/enolate redox center, resulting in a lower (than for Q²⁻) redox potential. A similar dependence is also known for other substituted p-benzoquinones.⁴⁶ When an electron withdrawing group (e.g., -CF₃, giving 2.5-bis-(trifluoromethyl)-1,4-benzoquinone - CF₃-BQ) was used, the redox process occurred at -0.41 V vs Ag⁺/Ag⁰, while it dropped to -1.08 V vs Ag⁺/Ag⁰ when an electron donating

group (e.g., -CH₃ in 2.5-dimethyl-1,4-benzoquinone - CH₃-BQ) was used.⁴⁶

Counterintuitively, when tested as solid in a lithium half-cell, the reversible electrochemical activity of Li₄-p-DOBDA occurred at an impressively higher, but also practical potential around 3.35 V vs Li⁺/Li⁰ (Figure 1B), about 700 mV higher than what could be predicted from comparative experimental study and through-bond electronic effect (Scheme 1 and Figure 1B). The chemical nature and similarity of Li₄-p-DOBDA to Li₄-p-DHT did not allow prediction of this peculiarly high potential value, and the large discrepancy between the redox activity in the dissolved phase as compared to the solid-state further adds to the exotics of this system.

In Li₄-p-DHT, the electron donating nature of the carboxylates effectively lowers the redox potential to 2.55 V vs Li⁺/Li⁰ as compared to 2.8 V vs Li⁺/Li⁰ for Li₂Q (Figure 1B). While the methylene group increases the distance between the quinone center and the negatively charged carboxylate and should effectively reduce the inductive donor effect, -CH₂- is not an electron-withdrawing group and thus cannot, in terms of electronic effects, explain the potential gain. Moreover, the disubstituted p-benzoquinones studied by

Yokoji⁴⁶ seemed to keep the same trend in solid and in solution. Indeed, CF₃-BQ revealed an average redox potential of 3.0 V vs Li⁺/Li⁰, while CH₃-BQ operated at 2.7 V vs Li⁺/Li⁰, indicating that the potential is tuned in accordance with the conventional through-bond electronic effects, independently of whether the measurement was performed in solid phase or through molecule electrochemistry analysis. Following the same rationale, the redox potential of Li₄-*p*-DOBDA should be at best somewhere between the redox potentials of Li₄-*p*-DHT (2.55 V vs Li⁺/Li⁰) and of Li₂Q (2.8 V vs Li⁺/Li⁰). Whereas this is the case for molecular electrochemistry analysis (cyclic voltammetry in solution, Figure 1A), it is no longer valid for the solid phase behavior (half-cell, Figure 1B).

Correlating the Redox Potential Gain with the Bond Vibration Energy. The high redox potential of Li₄-*p*-DOBDA in the solid state is nearly on par with the recently investigated Mg(Li₂)-*p*-DHT⁴⁹ and is among the highest observed yet for a lithiated *n*-type organic positive electrode material. This previous investigation suggested a theory that correlated the influence of spectator cation (Mⁿ⁺ = Li⁺, Mg²⁺, Ca²⁺, Ba²⁺) in the M_{2/n}ⁿ⁺(Li₂)-*p*-DHT system by tuning of the π -electron density distribution in the aromatic unit depending on the electronegativity value of M. It was put forward that the blueshift of the $\nu_{\text{as}}(\text{COO}^-)$ band as well that of the aromatic band—when varying the counteranion in the following order: Mⁿ⁺ = Ba²⁺, Li⁺, Ca²⁺, and Mg²⁺—demonstrate the nature of M–O bonds can affect the electronic distribution along the aromatic system. This interaction resulted notably in a mitigation of the inductive donor (+I) effect of the carboxylate groups with a resulting electronic density decrease. This model perfectly explained the 800 mV potential gain in Mg(Li₂)-*p*-DHT via the through-bond electronic effect (Scheme 1). However, the respective rationale, relying on the effect of the electro-attracting spectator metal cations, cannot be applied to the Li₄-*p*-DOBDA chemistry presented in this work.

To explore the link between redox potential and FTIR spectrum, we have analyzed a series of quinone derivatives (all selected to be in the reduced, lithium-containing form) with well-established redox properties and available FTIR data. The results of this analysis are shown in Figure 2, and the chemistries included are the following: Li₂-DABQ,²⁸ Li₂Q, and Li₄-*p*-DHBDS,⁴⁸ as well as the four M_{2/n}ⁿ⁺(Li₂)-*p*-DHT (Mⁿ⁺ = Ba²⁺, Li⁺, Ca²⁺, Mg²⁺) derivatives studied in Jouhara's work.⁴⁹ For Li₄-*p*-DOBDA, data include the partially deprotonated products of H₄-*p*-DOBDA (Figure S16 of the Supporting Information, SI) as well as the IR data acquired in the solid and dissolved states. Whereas the former set of data helped to better identify the specific vibration feature in Li₄-*p*-DOBDA, the latter was motivated by the discrepancy observed between molecular and solid phase electrochemistry results (Figure 1).⁴⁸

The position of the $\nu_{\text{as}}(\text{COO}^-)$ band in solid Li₄-*p*-DOBDA is almost identical to that of Li₄-*p*-DHT—1576 and 1573 cm⁻¹—whereas the formal redox potentials are 3.35 and 2.55 V vs Li⁺/Li⁰, respectively. Both compounds share the same spectator cation in the solid phase, and the electron density of the carboxylate remains thus relatively unaffected. Further, the –COO⁻ vibration frequency for dissolved Li₄-*p*-DOBDA is located at a lower frequency (1560 cm⁻¹, Figure 2A). Indeed, in aqueous solution, Li₄-*p*-DOBDA is fully dissociated, with minimal ion-pairing interaction (as confirmed with a slight shift of Li⁺ at –0.11 ppm with respect to LiOH·H₂O and

lithium benzoate, Figure S17). Clearly, there is no correlation between the vibration frequency of $\nu_{\text{as}}(\text{COO}^-)$ band and the redox potential when including the solid and dissolved Li₄-*p*-DOBDA phases in this correlation analysis. The IR band shift of the aromatic stretch $\nu(\text{C}=\text{C}_{\text{aromatics}})$ tends to correlate to a certain extent with the redox potential (Figure 2A). However, given the complexity in unambiguously assigning the specific bands in this region of the spectrum, we decided to concentrate our investigation on an additional key vibration band—the enolate vibration $\nu(\text{C}-\text{O}^-)$.

The wavenumber of the enolate $\nu(\text{C}-\text{O}^-)$ vibration band (Figure 2A, inset to the right) was found to scale linearly ($R^2 = 0.91$) with the redox potential (Figure 2B) for all analyzed compounds in the solid phase, confirming the existence of a correlation between both parameters. A higher vibration energy of the enolate bond is thus at the origin of the higher redox potential of solid Li₄-*p*-DOBDA. This additionally corroborates with the seminal work of Josien et al., where the redox potential of quinones was linearly correlated to the carbonyl $\nu(\text{C}=\text{O})$ stretching frequency.⁵³ Importantly, this correlation could be used as guideline for future developments of quinone-based redox chemistries to estimate the redox potential from simply measuring or estimating the vibration frequency of the respective band.

It is further interesting to point out the noticeable red shift of the $\nu(\text{C}-\text{O}^-)$ and $\nu_{\text{as}}(\text{COO}^-)$ for dissolved Li₄-*p*-DOBDA as compared to the solid Li₄-*p*-DOBDA. According to the rationales presented above, this should correspond to a lower redox potential, which is actually the case. However, correlating the potential with only $\nu_{\text{as}}(\text{COO}^-)$ would imply a much lower potential than was actually measured, additionally supporting the idea that the carboxylate group has a different impact on the redox of Li₄-*p*-DOBDA as compared to Jouhara's work.⁴⁹ Furthermore, the vibration frequency of the enolate bond in dissolved Li₄-*p*-DOBDA has a value of 1208 cm⁻¹, which would correspond to a redox potential of approximately 2.7 V vs Li⁺/Li⁰, following the linear regression presented in Figure 2B. Measuring the redox potential of dissolved Li₄-*p*-DOBDA vs Li⁺/Li⁰ is experimentally complicated and may be prone to additional errors and redox potential shift due to differences in ionic strengths and ion solvation structures between aqueous and aprotic solution required.⁵⁴ However, it is possible to estimate its value from the data shown in Figure 1. Since a redox potential difference of approximately 100 mV exists between the standard quinone (Q²⁻) and *p*-DOBDA⁴⁻ in aqueous solution, and Q²⁻ has a potential of 2.8 V vs Li⁺/Li⁰, the redox of dissolved Li₄-*p*-DOBDA should indeed evolve around 2.7 V vs Li⁺/Li⁰. This further supports the validity of the linear correlation analysis (Figure 2B) and that the strength of the enolate bond is a more generalized approach to understand and predict the redox potential in quinone derivative battery materials.

Crystal Structure, Molecular Conformation, and Correlation with the Redox Potential. In terms of donor inductive effects (+I), the acetate groups in Li₄-*p*-DOBDA should have an influence on the electronic density of the aromatic cycle similar to that of the carboxylate groups in Li₄-*p*-DHT (Scheme 1). If these were to be considered as dominantly affecting the redox potentials of both chemistries, then it would be reasonable to expect comparable values. This approximation is however significantly distant from the reality of our experimental observations (Figure 1B), which led us to investigate another possible influence factor: the through-space

electrostatic modulation of charge distribution in Li_4 -*p*-DOBDA (Scheme 1). A similar effect could be accounted to explain the difference in electrochemical reactivity of the Li_4 -*o*-DHT and Li_4 -*p*-DHT regioisomers, investigated by Poizot and co-workers⁵² in the solid phase; but also known to occur in solution from the molecular electrochemistry analyses of catechol (*o*-) and quinone (*p*-) systems.^{55,56} The work by Poizot et al. in fact confirmed that the effect is qualitatively preserved in the solid state. While the electrostatic interaction between the enolate groups has not been specifically mentioned in these studies, it is reasonable to assume an electrostatic interaction between the adjacent (*ortho*-) enolate groups to result in the voltage gain. However, in the situation of Li_4 -*p*-DOBDA, the enolate groups are in the *para*-position, just like those in Li_4 -*p*-DHT. This means the suspected electrostatic effect would not occur between the two enolates, but rather between adjacent enolate ($-\text{CO}^-\text{Li}^+$) and carboxylate ($-\text{CH}_2\text{COO}^-\text{Li}^+$) groups.

This hypothesis was confirmed through powder X-ray diffraction (PXRD) analysis and DFT calculation. Rietveld refinement results displayed in Figure 3A (refer to SI Section

between the $-\text{CH}_2-\text{COO}^-$ bond and the plane formed by the benzene ring (blue double arrow).

The significant +650 mV redox potential difference detected in the solid phase as compared to measurements in solution can thus be understood by major molecular conformation differences, translated into electronic charge perturbation between the carboxylate and phenolate groups in the solid and dissolved phases. To verify this hypothesis, additional DFT calculations were carried out to predict the conformation as well as atom charge distribution in *p*-DOBDA⁴⁻ in both solid and dissolved phases. On the basis of DFT calculations, *p*-DOBDA⁴⁻ adopts on average a different configuration in vacuum, or in aqueous solvated phase, than in the solid state (Figure 3B, and SI Section S3). The larger dihedral angle (111.3°) formed in average by CH_2-COO^- with the benzene ring can be related to steric and electrostatic repulsions between enolate and carboxylate groups, allowed by free rotation in the solvated or gas phase.

An additional interesting feature is the asymmetry of C–O bonds in the carboxylate functional groups. While in the solid state a clear distinction between the two oxygen occurs (i.e., a difference about 0.05 Å between the bonds), in vacuum or in solution the effect is completely removed, the two C–O bonds being of same length (refer to SI Section S3.4 for more details). It is also interesting to note that a similar conformation (with a low dihedral angle) is also observed for the parent protonated version, H_4 -*p*-DOBDA, with the H-bonding being at the origin of the peculiar molecular conformation (SI Section S4).

In the solid phase, the lower dihedral angle—and thus the proximity between the *ortho*-phenolate and carboxylate groups—is the consequence of the local tetrahedral oxygen coordination environment (LiO_4) of the lithium cations (Figure 3, and SI Section S2). Metal induced conformational change in ligands is a known process, especially significant in biological systems. For small ligand molecules, along with the effect of metal on electronic configuration, conformation changes are also possible, unless for ligand molecules that are so rigid that coordination cannot promote a conformational change. The acetate groups in DOBDA⁴⁻ allow for structural flexibility so that the system displays stereoelectronic chameleonic behavior dependent on the counteraction.

The redox potentials of the solid and dissolved *p*-DOBDA⁴⁻ (averaged) molecular conformations were also computed using the SIESTA and GAMESS software for solid state and solvent model calculations, respectively.^{57,58} The solvent effects were taken into account using the density polarized continuum model.⁵⁹ Total energies for each of the oxidation states in the solvent were computed for the relaxed structures using the Minnesota M11 exchange-correlation functional⁶⁰ and the 6-31G** Pople basis set. For the solid state calculations, the vdW-DF-cx exchange-correlation functional of Berland and Hyldgaard⁶¹ and a double- ζ polarization basis set was used. The results are presented in Table 1 and the full calculation details and methods are presented in SI Section S3. Computed and experimental redox potential values for solid *p*-DOBDA⁴⁻ are in good accordance, whereas larger differences are observed for computed redox potentials in solution (i.e., around 0.35 V). These are assigned to errors arising from the solvation energy as well as solvent reorganization effects, since a relatively important change in the geometric structure occurs between the *p*-DOBDA⁴⁻ and *p*-DOBDA²⁻. Indeed, the dihedral angle α formed by the $-\text{CH}_2-\text{COO}^-$ bond with the benzene ring

Figure 3. (A) Rietveld refinement of the PXRD pattern of Li_4 -*p*-DOBDA. The red circles correspond to the experimental data, whereas black, blue, and gray lines respectively correspond to the simulated, difference, and background patterns. Inset: crystal structure view along *b*-axis with a representation of the tetrahedral oxygen environment of the lithium cations. (B) Molecular conformation of *p*-DOBDA in the solid phase (as determined from PXRD data) and aqueous solution (as determined from DFT calculations). Views along the $\text{CH}_2-\text{C}_{\text{AR}}$ and perpendicular to the AR-ring.

S2 for details) allowed us to determine the structure of solid Li_4 -*p*-DOBDA in the $P2_1/n$ space group. The unit cell has a volume of 501.3 Å³ with the following lattice parameters: $a = 12.581$ Å, $b = 5.0934$ Å, $c = 9.5012$ Å, $\beta = 124.511^\circ$. Taking a closer look at the molecular conformation of solid Li_4 -*p*-DOBDA (Figure 3), it is interesting to note that the carboxylate groups are oriented toward the *ortho*-situated phenolate groups, with a rather low dihedral angle of 54.4°

Table 1. Computed Equilibrium Redox Potentials of Quinone and *p*-DOBDA⁴⁻ Redox Couples in the Solid State and Water Solvated Phases^a

redox couple	redox potential (V vs Li ⁺ /Li ⁰)	
	dissolved	solid
Q ⁰ /Q ²⁻	2.69	^a
<i>p</i> -DOBDA ²⁻ / <i>p</i> -DOBDA ⁴⁻	2.33	3.45

^aFor the Q⁰/Q²⁻ couple, the redox potential was not possible to compute in solid phase since the crystal structure of Li₂Q is not available.

varies from 111.3° in *p*-DOBDA⁴⁻ to 61.6° in *p*-DOBDA²⁻ (see the SI). That stated, the trend observed experimentally is respected (Figures 1A and 1B), confirming the validity of the models.

To grasp further insight into the structure–property correlation of solid and solvated phases of *p*-DOBDA⁴⁻, Bader charge analysis⁶² was carried out (Table 2, SI Section

Table 2. Bader Charges Analysis, N₀–N, with N₀ being the Number of Electrons in the Isolated Atom, N is the Bader Population of the Atom in Molecule^a

	solution (_aq)	solid (_cr)
O1	-1.34	-1.78
O2/O3	-1.34/-1.34	-1.79/-1.82
C1	0.7	1.22
C2	-0.13	-0.03
C3	-0.05	0.03
C4	0.0	0.04
C5	1.66	2.80
C1–O1 DC	2.04	3.00
C5–O2/3DC	3.00	4.60

^aDC is the dipole charge. Top scheme, atom labeling.

S3.5). While the charge distribution is minimally affected for the aromatic C2, C3, and aliphatic C4 atoms (see the notations for carbons in the graphic associated with Table 2), the charge differences between oxygen and carbon atoms in the carboxylate (O2, O3, C5) and enol (O1, C1) groups are significantly higher in solid phase as compared to aqueous solution. The dipole charges (C1–O1, C5–O2/3 DC) are estimated to be larger in the respective carboxylate and enol groups in the solid *p*-DOBDA⁴⁻, leading to stronger bonding and thus higher vibration energy. This closely correlates with the FTIR analysis presented in Figure 2 (higher vibration frequency-wavenumbers for the respective bonds for solid when compared to dissolved *p*-DOBDA⁴⁻) and confirms the

higher redox potential displayed by Li₄-*p*-DOBDA in its solid crystalline form.

Combining these analyses, we can ascribe the increase of the redox potential in the solid phase to a pronounced through-space charge modulation arising between the carboxylate (COO⁻) and enol (CO⁻) groups. In solution, the molecule adopts a relaxed conformation in which the carboxylate groups are far afeld from the adjacent enolate groups, resulting in a reduced interaction and higher charge density. In this case, the redox potential can solely be rationalized by the through-bond electronic effects (Scheme 1) with the measured and computed formal redox potential values being indeed lower than those of the parent quinone system (Figure 1A). The constrained molecular conformation in the solid state leads to a hitherto undocumented type of intramolecular charge perturbation and redox potential gain of +650 mV, when switching from liquid to solid phase.

Air-Stability of Li₄-*p*-DOBDA. Air-stability of the positive electrode materials is a key requirement in battery materials handling, storage and cell manufacture.^{63,64} Therefore, beyond the Li-reservoir characteristic, air-stability is an additional important parameter to be considered for Li-ion positive electrode materials. The fact that Li₄-*p*-DOBDA undergoes redox in the solid phase at a potential above 2.91 V vs Li⁺/Li⁰ already indicates that this chemistry should be resistant to oxidation in air, but not necessarily to moisture, as previously observed with Li₄-*p*-DHBDS⁴⁸ (i.e., air exposure of Li₄-*p*-DHBDS lead to poor electrochemical performances). In order to investigate the air-stability, Li₄-*p*-DOBDA powders were exposed to ambient air for a week, and a comparative FTIR and PXRD analysis was carried out. Remarkably, as displayed in Figure 4, both analyses yielded identical features as compared to the pristine material.

Figure 4. FTIR (A) and PXRD (B) survey of the as synthesized Li₄-*p*-DOBDA and after being exposed to ambient air for 1 week. No changes can be detected.

From the FTIR spectra, it can be concluded that no oxidation occurs upon exposure to air, since no additional carbonyl band (corresponding to the quinone) is observed (Figure 4A). There is also no hydrolysis of the phenolate or acetate groups. The band at 1220 cm⁻¹ is preserved and no phenolic O–H vibration band (3400 cm⁻¹) or characteristic

Figure 5. (A) Overlaid potential–composition profiles for Li₄-p-DOBDA and LiFePO₄ (binder-free) electrodes galvanostatically cycled in lithium half-cell configuration, with LP30 electrolyte, at a Li⁺ insertion/extraction rate of 1 Li⁺/5 h (C/10). (B) Cycling stability of Li₄-p-DOBDA electrodes with LP30 electrolyte and at a Li⁺ insertion/extraction rate of 1 Li⁺/4 h (C/8). (C) In situ PXRD data collected during the first two cycles. LP30 used as electrolyte, at a Li⁺ insertion/extraction rate of 1 Li⁺/15 h (C/30).

broad carboxylic O–H vibration band (3100–2400 cm⁻¹) can be observed. The carboxylate carbonyl C=O stretching band (1575 cm⁻¹) also remains unchanged. Additionally, no free H₂O or CO₂ bands can be observed, implying that Li₄-p-DOBDA is not hygroscopic and thus no extensive drying processes are needed for electrode preparation. The PXRD survey further supported the ambient air stability: all the peak positions as well as intensities remained unchanged, confirming that the molecular conformation along with the crystal structure is maintained (Figure 4B). Considering the excellent oxidation and hydrolysis stability, Li₄-p-DOBDA was also successfully obtained in ambient air through reaction of H₄-p-DOBDA with lithium hydroxide monohydrate (LiOH·H₂O) in methanol (refer to the SI for the Experimental Details). FTIR, PXRD, and electrochemical analysis confirmed the feasibility of this protocol (Figure S18).

Considering all the above, it can be concluded that Li₄-p-DOBDA fulfills all the key prerequisites of a practical Li-ion positive electrode material—a chemistry stable to ambient air (including moisture) in the reduced, lithium-containing form, and thus processable in the same way as conventional Li-ion positive electrode materials.

Electrochemical Reversibility and Cycling Performance in Solid State. With the origins of the high energy content and the air stability confirmed, we next discuss the electrochemical performances of Li₄-p-DOBDA. Figure 5A displays typical galvanostatic potential–capacity plots measured within the 2.8–4.2 V (vs Li⁺/Li⁰) window, at a cycling rate of 2 Li⁺ equivalents exchanged in 10 h (i.e., 1Li⁺/5 h or a C-rate of C/10). Upon charging, Li₄-p-DOBDA undergoes a two-electron process at an average oxidation potential of 3.7 V vs Li⁺/Li⁰, yielding its full two-electron capacity (215 mAh/g). This is superior to carboxyphenolate derivatives (e.g., Li₄-p-DHT, Li₄-o-DHT, and Mg(Li₂)-p-DHT) which consistently yield to only one-electron reversible activity without special nanostructuration of the electrode.^{17,49,52} At the first discharge, approximately 75% of the capacity is recovered at an average potential of 3.2 V vs Li⁺/Li⁰ (the quasi-equilibrium redox potential of Li₄-p-DOBDA was estimated at 3.35 V vs Li⁺/Li⁰ from GITT measurements, Figure S19). The first cycle polarization and irreversible capacity loss are considerably

reduced over the subsequent cycles with good capacity retention (Figure 5B).

The dynamic molecular conformation of the p-DOBDA⁴⁻ skeleton (Figure 3) prompted us further to investigate the structural reversibility of the redox process in the solid phase. Figure 5C displays the in situ PXRD data for the first two cycles (rate of 1Li⁺ exchanged in 15 h). Upon Li extraction the XRD pattern of the Li₄-p-DOBDA electrode is strongly modified, with the progressive disappearance of the intense Bragg peaks near 2θ (Cu Kα) = 19.5°, 21.5°, and 24.6°, accompanying the appearance of new intense peaks at 2θ = 18.5° and 24.0°. The Li₄-p-DOBDA undergoes a biphasic two-electron process with no intermediate semiquinone phase being detected (possibly because the respective radicals are short-lived), corroborating the direct two-electron mechanism as also observed in the galvanostatic charge–discharge profile (only one plateau). To should be noted that this process is unusual for quinone derivatives, most of which display sequential charge transfer (one-by-one electron) in the solid state or in aprotic environment.^{17,28,45,47,65,66} Upon discharge, the phase transition proved to be perfectly reversible, proceeding again through a direct two-electron, biphasic process. The collection of XRD patterns during the second cycle show the occurrence of the same phases and transitions, which indicate that the molecular conformation along with the crystal structure are preserved with cycling. In other words, the electrochemical pathway observed during the first cycle is completely reversible and maintained during the second cycle even though the oxidation profile is being slightly modified.

The tetrahedral LiO₄ coordination is imposing significant strain on p-DOBDA⁴⁻ skeleton in solid, resulting in unexpected molecular conformation (Figure 3B). Upon oxidation, with two lithium atoms (as well as the two negative charges from the phenolate groups) removed, it is reasonable to assume that Li₂-p-DOBDA will adopt a different conformation, also with modified crystal packing. The quality of the in situ XRD patterns did not allow us to unambiguously refine the structure of the oxidized phase. However, the DFT calculations confirm drastic conformational changes upon oxidation in solution and in vacuum (refer to SI Section S3.4 for details) and alike process can be also considered to take place in the solid phase. This would imply possible subtle

gliding or rotation of the phenyl/acetate groups, resulting in turn in possible particle shape and volume changes, grinding and ultimately electrode degradation. This conformation changes in the solid phase could also explain the slow kinetics (or experimentally observed high polarization) of the solid-phase $\text{Li}_4\text{-}p\text{-DOBDA}$ electrodes.

In terms of specific gravimetric capacity and energy metrics, $\text{Li}_4\text{-}p\text{-DOBDA}$ is already on par with LiFePO_4 and LiCoO_2 and is expected to outperform these once the energy efficiency and degradation issues are fixed. The slow kinetics and polarization can be assigned to various parameters, typical of organic battery materials, and including charge and mass transport, molecular orbital, as well as conformation reorganization. The estimated electrical conductivity of $\text{Li}_4\text{-}p\text{-DOBDA}$ is of the order of 10^{-12} to 10^{-13} S/cm. No significant ionic conductivity was measured in macroscale pellet-form samples even at 70 °C. Combining these with the significant structural and conformational changes, the rather elevated electrode polarization and slow kinetics of the $\text{Li}_4\text{-}p\text{-DOBDA}$ electrodes are not surprising.

Further improvements required to render this chemistry practically appealing could thus focus on electrode and active material morphology optimization to achieve better reversibility and cycling stability. Nanostructuration with conductive carbon allotropes¹⁸ or other 2D materials could be viable solutions to explore. In terms of chemical stability, further investigation of the intrinsic stability of the oxidized phase ($\text{Li}_2\text{-}p\text{-DOBDA}$) is needed, and oxidative decarboxylation at the high operation voltage required for this chemistry is an additional factor not to be excluded.⁶⁷ High voltage organic redox chemistries, close to and above 4 V, remain hitherto unexplored, and high energy advantages arise with yet to be investigated intrinsic stability toward decarboxylation, as well as the nature and reactivity toward products of electrolyte anodic decomposition.

CONCLUSIONS

With this work we disclose a new member in the very young, yet highly promising family of quinone-based organic Li-ion positive electrode materials. The high capacity—from the reversible two electron exchange, combined with the high redox potential of $\text{Li}_4\text{-}p\text{-DOBDA}$ —is the result of an exotic intramolecular charge modulation, providing in an impressive theoretical gravimetric energy density in the 700 Wh/kg range, placing this new organic chemistry above all other lithiated organic LIB positive electrode materials. Moreover, $\text{Li}_4\text{-}p\text{-DOBDA}$ can be synthesized and handled in ambient air without impact on either its molecular and structural nature or on its electrochemical behavior, meaning this robust material can be processed in conditions similar to conventional inorganic LIB compounds. Further developments should focus on cycling stability and energy efficiency optimization to allow this chemistry to practically compete with typical inorganic materials such as LiCoO_2 (LCO, 600 Wh/kg) or LiFePO_4 (LFP, 550 Wh/kg).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.0c02989>.

Materials and methods; crystal structured determination from XRD; computational methods; and additional data and figures (PDF)

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Notes

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