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Air-stable lithiated cathode material based on 1,4-benzenedisulfonate backbone for organic Li-ion batteries

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Abstract

To meet the current market demands as well as the emerging environmental concerns there is a need to develop low polluting battery technologies. Organic electrode materials could offer the possibility of preparing electrode materials from naturally more abundant elements and eco-friendly processes coupled with a simplified recycling management. However, the potential use of organic electrode materials for energy storage is still challenging and a lot of developments remain to be achieved. For instance, promoting high-energy Li-ion organic batteries inevitably require the development of lithiated organic electrode materials able to be charged (delithiated) at high enough potential (> 3 V vs. Li^+/Li^0); a challenging point rarely discussed in the literature. Here, we evaluate tetralithium 2,5-dihydroxy-1,4benzenedisulfonate as air-stable lithiated cathode material for the first time and its reversible Li^+ electrochemical extraction. Quite interestingly, in comparison with the dicarboxylate counterpart, it was observed that the theoretical two-electron reaction is readily reached with this organic structure and at an overage operation potential of 300 mV higher.

Introduction

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Rechargeable (or secondary) batteries are nowadays considered as essential energy storage technologies able to power a diverse and always increasing range of applications (electronic devices, electric vehicles, integration of renewable electricity on and off the grid, ...). This accelerating worldwide demand for powerful, safer and greener batteries urges researchers to explore new battery chemistries and cell technologies.¹⁻⁴ To this respect, the last decade has notably seen a renewed interest in investigating and promoting redox-active organic compounds since they can bring real added value to the existing rechargeable systems as demonstrated by the series of recent reviews on the topic.^{5–16} In fact, organic electroactive materials could pave the way towards all-organic batteries notably for some low-cost applications (e.g., from disposable devices or grid energy storage) as recently reviewed.¹⁷ One particularly attractive point is that the redox chemistry of organic materials offers access to two different electrochemical storage mechanisms: (i) n-type systems where the organic structure evolves from a neutral state to a negatively charged one with a cation uptake (and release), and conversely (ii) p-type systems where the structure evolves from a neutral state to a positively charged one with anion uptake (and release).^{18,19} Note that ptype organic structures have already offered to the positive organic electrode family some successful materials in the late 1980s with all the examples of 'doped' conducting polymers and finally the first commercialized Li-organic cells based on polyaniline (PANI) and BF₄⁻ as counter ion.²⁰⁻²² More recently great achievements have also been realized with so-called Organic Radical Batteries (ORBs),²³ especially thanks to R&D efforts from NEC and Nishide's group,^{24–29} even if this technology is still in development stages and not commercial yet.³⁰ In this case, the formal p-type redox center of the positive electrode in ORBs deals with the nitroxide radical/oxoammonium cation reversible system. Nonetheless, the development of metal-ion organic batteries requires, in principle, the use of n-type system for both electrodes (except when an ionic self-compensation mechanism is involved at the molecular level)^{31,32}. Hence the assembly of an all-organic Li-ion battery in its discharged state obviously needs a negative electrode material able to accommodate Li⁺ at low potentials (such as conjugated dicarboxylates) $^{33-41}$ together with a lithiated positive electrode material.

For the latter, examples are scarce in the literature and the large majority of reported positive organic materials consist in oxidized compounds (charged state) electrochemically tested in Li-half cell,^{7,8,16} as a result, very few examples of all-organic Li-ion cells have been reported.¹⁷ Having rapidly recognized this bottleneck, our group have designed and elaborated several lithiated host materials over the past few years. First, we reported on the tetralithium salt of tetrahydroxyguinone ($Li_4C_6O_6$) which can be reversibly oxidized to $Li_2C_6O_6$ but at relatively low potential (1.8 V vs. Li⁺/Li⁰).^{42,43} Substitution with methoxy groups at the 2 and 5 positions giving the dilithium salt of 3,6-dihydroxy-2,5-dimethoxy-p-benzoguinone (Li₂DHDMQ), increased the average potential at 3 V vs. Li⁺/Li, however this compound is hampered by an important polarization phenomenon.⁴⁴ More recently, we demonstrated that dilithium (2,5-dilithium-oxy)-terephthalate (Li₄-p-DHT) lead to a robust lithiated material exhibiting quite good electrochemical behavior upon cycling with good reversibility and low polarization for an average operating potential at 2.55 V vs. Li⁺/Li^{0.45} Note that such performances were confirmed not long after by Chen's group while demonstrating the full capacity of this material can be achieved when using nanosheet particles (~220 mAh/g for the theoretical 2-electron electrode reaction).⁴⁶ Finally, a voltage gain was attained by switching from a para to an ortho-dihydroxyterephthaloyle system giving dilithium (2,3dilithium-oxy)-terephthalate (Li₄-o-DHT) for which the reversible Li deinsertion/insertion reaction occurs at 2.85 V vs. Li⁺/Li⁰).¹⁹ Nevertheless, most of these materials were found unstable under air (autoxidation) due to a working potential below 3 V vs. Li⁺/Li⁰ complicating their processing.

To overcome this issue while keeping in mind the efficiency of the *para*-benzoquinoid system, we were interested to switch from the carboxylate functional groups present in Li₄-p-DHT⁴⁵ to the sulfonate substituent comforted by a recent study from Zhou et *al*.⁴⁷ which demonstrated the benefic effect of the sulfonate group on the reversible reduction of the anthraquinone backbone vs. Li. Therefore, we were interested in studying tetralithium 2,5-dihydroxy-1,4-benzenedisulfonate (namely Li₄-p-DHBDS) as the sulfonated analogue compound of Li₄-p-DHT. Herein, we report the synthesis and the characterization of this organic Li-salt as well as its electrochemical behavior evaluated in Li half-cell. Interestingly, the lithium extraction occurs at high operating potential (<*E*> ~3.25 V vs. Li⁺/Li⁰) making it the first organic and lithiated positive material processable under dried air (*i.e.*, discharged of state the material).

Experimental

Chemicals

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Acetonitrile, methanol, acetone, dimethyl carbonate (DMC) and anhydrous diethyl ether solvents were purchased from Sigma Aldrich, anhydrous *N*,*N*-dimethylformamide (DMF) was purchased from Alfa Aesar. Oleum (23% in SO₃), lithium hydride, lithium methoxide, hydrogen peroxide solution (30% v/v in H₂O) were purchased from Sigma Aldrich, hydroquinone from Alfa Aesar and 1,4-benzenedithiol from TCI Europe. All solvents and reactants were used as received.

Analytical and characterization techniques

Infrared spectra were recorded in transmission mode on a FTIR spectrometer at room temperature (Nicolet AVATAR 370 DTGS). Air-free pellets were prepared in an argon-filled glovebox by mixing the sample with spectroscopic-grade potassium bromide at 1 wt.%. Spectra were measured over range of 4000 to 400 cm⁻¹ with a resolution of 2 cm⁻¹. ¹H and ¹³C NMR spectra were recorded on a BRUKER 400 MHz Advance III HD spectrometer (at 400 and 100 MHz, respectively) at 298 K. Chemical shifts (δ) are given in ppm relative to TMS. Deuterated dimethyl sulfoxide and deuterium oxide were purchased from Sigma Aldrich (higher than 99.5% purity). Thermal analyses were performed on a Netzsch thermal analyzer STA 449C Jupiter equipped with a differential analysis microbalance coupled with a mass spectrometer QMS 403 Aëolos (heating rate: 5°C min⁻¹ under argon flow). Lithium stoichiometry was determined by atomic absorption spectroscopy using a Perkin-Elmer AAnalyst 300 (hollow-cathode lamp: Li, wavelength: 670.8 nm, oxidant/fuel: air/acetylene. The morphology of the powders was observed by scanning electron microscopy (SEM) using QUANTA 200 F (FEI). Temperature-resolved X-ray powder diffraction (TRXRPD) patterns were recorded with a Bruker D8 Advance diffractometer equipped with an Anton Parr XRK900 high-temperature chamber (purged under N₂) using a heating rate of 0.1° C s⁻¹. Data were collected in the Bragg-Brentano geometry with a Cu-anode X-ray source operating at 40 kV and 40 mA. The Cu K_{β} radiation was filtered by means of Ni foil. The experiments were systematically performed in the 5-45° 2θ range with a step of 0.016° and an acquisition time of 1.2 s per step.

Synthetic procedures

Preparation of 2,5-dihydroxy-1,4-benzenedisulfonic acid (H₄-*p***-DHBDS). The synthesis was adapted from a procedure by Wan et** *al.***⁴⁸ 8 g of 1,4-dihydroxybenzene were added by portions to 28 mL of oleum (23%) under stirring. The green solution was heated to 120°C for 8 h and then cooled to room temperature (rt). The green obtained paste was filtered off to give a white precipitate which was washed three times with acetonitrile (3 × 50 mL). The white solid was then dried under vacuum overnight at 120°C giving pure 2,5-dihydroxy-1,4-benzenedisulfonic acid (8 g, 60% yield). ¹H NMR (400 MHz, D₂O) δ (ppm) 7.14 (s, 2H, H_{arom.}). ¹³C NMR (100 MHz, D₂O) δ (ppm) 145.53 (C-OH), 131.17 (C-SO₃H), 115.93 (CH). IR (KBr pellet) v_{max}/cm^{-1}: 3430-3195 (υ O-H, υ C-H), 1421 (υ C=C), 1213, 1108 (υ SO₃H), 1226, 1030 (υ C-O), 882, 813 (δ O-H), 660, 539, 473.**

Preparation of tetralithium 2,5-dihydroxy-1,4-benzenedisulfonate as solvate (Li₄-*p***-DHBDS-2DMF).** The lithiation of 2,5-dihydroxy-1,4-benzenedisulfonic acid (3 g, 11.1 mmol) was performed in anhydrous *N*,*N*-dimethylformamide (50 mL) with a stoichiometric amount of lithium hydride (0.35 g, 44.4 mmol). The solution was stirred at room temperature over 3 days inside an argon-filled glovebox containing less than 1 ppm of oxygen and water. After filtration of the precipitate, washing with diethyl ether and drying step at 60°C under vacuum overnight, a pale yellow powder was recovered (3.52 g, 80% yield). The complete chemical formula of the compound was Li_{3.988±0.005}-*p*-DHBDS·2DMF (solvate) as deduced by AAS for the Li content and thermogravimetric measurement (TG) for the solvation degree. Li₄-*p*-DHBDS·2DMF: ¹H NMR (400 MHz, D₂O) δ (ppm) 7.87 (s, H, DMF), 6.92 (s, 2H, H_{arom}.), 2.95, 2.80 (s, 2CH₃, DMF). ¹³C NMR (100 MHz, D₂O) δ (ppm) 164.94 (C=O, DMF.) 150.72 (C-OH), 132.74 (C-SO₃H), 118.24 (CH), 36.91, 31.39 (2CH₃, DMF). IR (KBr pellet) υ_{max}/cm⁻¹: 1669 (υ C=O, DMF), 1452 (υ C=C), 1300 (DMF) 1230, 1095 (υ SO₃H), 1208, 1043 (υ C-O), 900 (DMF) 847 (δ O-H), 673, 512, 456.

Desolvation of Li₄-*p***-DHBDS·2DMF.** 100 mg of previously grounded powder of Li₄-*p*-DHBDS·2DMF were heated in a Büchi glass oven (B-585 Kugelrohr) installed inside an argon-filled glovebox at a temperature of 300°C over 20 h. The final Li₄-*p*-DHBDS compound was

obtained (70 mg scale, quantitative yield). The efficacy of the desolvation process was monitored by thermal analysis, and the absence of DMF traces was confirmed by NMR and IR spectra. Li₄-*p*-DHBDS: grey powder; IR (KBr pellet) υ_{max} /cm⁻¹: 1452 (υ C=C), 1230, 1095 (υ SO₃H), 1208, 1043 (υ C-O), 847 (δ O-H), 673, 512, 456.

Preparation of 1,4-benzenedisulfonic acid (H₂-*p***-BDS).** 0.65 g of 1,4-benzenedithiol was dissolved in 9 mL of methanol at 40°C, followed with addition of 7.5 mL of H₂O₂ (30% v/v in H₂O).⁴⁹ The suspension was stirred at room temperature (20°C) for 16 h and dried under vacuum overnight at 70°C giving H₂-*p*-BDS as a white solid (0.9 g, 84% yield). ¹H NMR (400 MHz, D₂O) δ (ppm) 7.72 (s, 4H, H_{arom}). ¹³C NMR (100 MHz, D₂O) δ (ppm) 143.83 (C-SO₃H), 126.15 (CH). IR (KBr pellet): υ_{max} /cm⁻¹ 1452 (υ C=C), 1243, 1130 (υ SO₃H), 673, 512, 456 cm⁻¹.

Preparation of dilithium 1,4-benzenedisulfonate (Li₂-*p***-BDS). The lithiation reaction of 1,4benzenedisulfonic acid (H₂-***p***-BDS) (0.3 g, 1.1 mmol) was performed in methanol (10 mL) with lithium methoxide (0.175 g, 2.5 mmol). After refluxing at 90°C for 20 h, the precipitated compound was washed 3 times with acetone and dried under vacuum for 6 h at 60°C. The final product (Li₂-***p***-BDS) was obtained as white powder (0.29 g, 93% yield). ¹H NMR (400 MHz, D₂O) \delta (ppm) 7.88 (s, 4H, H_{arom.}). ¹³C NMR (100 MHz, D₂O) \delta (ppm) 144.83 (C-SO₃H), 126.20 (CH). IR (KBr pellet): \upsilon_{max}/cm⁻¹ 1434 (\upsilon C=C), 1234, 1056 (\upsilon SO₃H), 686, 585, 496 cm⁻¹. The Li content was measured by AAS giving rise to the following chemical formula: Li_{1.992±0.005}-***p***-BDS.**

Electrochemical study

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The electrochemical performance of the materials was tested vs. lithium in Swagelok[®]-type cells using a Li metal disc as the negative electrode and fiberglass separators (Whatman[®]) with a 1 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in vol.) electrolyte. The positive electrodes were prepared in an argon-filled glovebox by grinding powder of organic active materials with 30 wt.% of carbon black (Ketjenblack EC-600JD, AkzoNobel) and 5 wt.% of polytetrafluoroethylene (PTFE) with a pestle in a mortar. The typical loading of the cells was 5-7 mg of active material. The cells were cycled in

galvanostatic mode using a MacPile automatic/data recording system (Bio-Logic SAS, Claix, France) in the potential range of 2.5-4.0 V vs. Li^+/Li at a typical rate of one lithium ion exchanged per ring in 10 h (*i.e.*, 1 Li⁺/10 h = C/20 cycling rate).

Investigation of the electrochemical mechanisms

Operando X-ray diffraction (XRD) powder patterns were recorded, during battery operation, with a Bruker D8 Advance AXS diffractometer operating in Bragg-Brentano geometry with the Cu K_{α} radiation using special stainless steel electrochemical cell equipped with a Be window described elsewhere.⁵⁰ The positive electrode was prepared by directly depositing \sim 40 mg of the composite electrode (carbon additive: 30 wt.% and active material: 70 wt.%) onto the Be window in an argon-filled glovebox. Li metal was used as the negative electrode pasted and a Whatman glass fiber sheet separator was soaked with a 1 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in vol.) electrolyte. The cell was cycled in the 2.5-4.0 V potential range in galvanostatic mode at a cycling rate of 1 $\text{Li}^+/20 \text{ h}$. Complementary ex situ characterizations were also performed by both FTIR and ¹³C liquid NMR spectroscopies. Composite positive electrodes were recovered by disassembling cells at different states of charge and rinsed several times with dimethyl carbonate (DMC) in order to eliminate residual traces of electrolyte and then dried at 100°C for 4 hours under vacuum in an argon-filled glovebox. The as-obtained samples were either mixed with potassium bromide at 1 wt.% for FTIR measurement or solubilized in D₂O then filtered through a 2 μ m syringe filter to remove carbon for ¹³C NMR characterization.

Results and discussion

An up-scalable two-step procedure was applied for the synthesis of desired material. (Scheme 1). The first step was adapted from a procedure by Wan et *al.* in which the preparation of the dihydroxybenzenedisulfonic acid was described.⁴⁸ The acid was synthesized from the hydroquinone in a straightforward double electrophilic aromatic sulfonation. The dihydroxybenzenedisulfonic acid was characterized by FTIR, liquid ¹H, and ¹³C NMR (Fig. S1). Afterward, the tetralithium salt was prepared by a neutralization reaction with a stoichiometric amount of lithium hydride conducted in anhydrous *N*,*N*-dimethylformamide under an inert atmosphere since Wan et al. have already reported the

failure in using water as the solvent.⁴⁸ Our non-aqueous synthetic procedure produced a yellow powder which was characterized with different analytical techniques.



Scheme 1. Two-step synthetic procedure for the preparation of the target lithiated organic salt

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First, the deprotonation of the sulfonic functional groups was readily confirmed by ¹H NMR (Fig. S1) with a noticeable chemical shift of the aromatic proton peak from 7.14 ppm (s, H_{arom.} acid) to 6.92 ppm (s, H_{arom.} salt) due to the modification of the electronic environment of the molecule. In addition, the presence of characteristic peaks located at 7.87 ppm (s, H), 2.95, 2.80 ppm (s, $2CH_3$) indicated the presence of DMF molecules present, which was also corroborated by FTIR measurements (Fig. S2). SEM imaging of the sample revealed an acicular and layered morphology a few micrometers in length and hundreds of nanometers in width (Fig. S3a). The thermal stability of the compound was first probed by thermal analysis under inert atmosphere. The typical TG curve (Fig. 1a, dark blue curves) shows a first weight loss of about 30% starting at 150°C associated with an endothermic phenomenon on the DSC trace which is attributed to the loss of two DMF molecules per ring; the same content being deduced by the ¹H NMR spectroscopy proton integration methodology. After the desolvation step, a good thermal stability of the sample is observed up to 400°C (stable TG trace). The desolvation process was then further monitored by TRXRPD under nitrogen (Fig. 1b). Basically, the pristine compound appeared well-crystallized with the presence of a particular intense diffraction peak located at low angle $(2\theta = 9^\circ)$, which supports the growth of a lamellar-type phase. Nevertheless, the series of typical Bragg peaks related to Li_4 -p-DHBDS-2DMF vanish upon heating for producing a poorly-crystalized phase as the desolvation proceeds. An isotherm step maintained at 300°C during several dozens of hours does not bring any change.



Figure 1. (a) Thermal analysis measurements of Li_4 -*p*-DHBDS·2DMF (dark blue) together with the TG curve related to desolvated Li_4 -*p*-DHBDS (black) obtained under argon flow at a heating rate of 10°C min⁻¹. (b) TRXRPD patterns recorded from rt to 300°C under N₂ flow. The series of XRD patterns in dark blue are representative of Li_4 -*p*-DHBDS·2DMF phase (* corresponds to the diffraction peak of the sample holder made of Al₂O₃).

The stability of Li₄-*p*-DHBDS·2DMF under ambient air was also checked by FTIR spectroscopy (Fig. 2). Experimentally, a series of FTIR spectra was recorded coupled with sequential photography at different exposure times (Fig. 2). Both the starting spectrum and picture were unchanged after 24 hours indicating a good chemical stability against oxygen unlike Li₄-*p*-DHT or Li₄-*o*-DHT that exhibit rapid autoxidation in the presence of oxygen.^{19,45}



Figure 2. FTIR spectra of Li₄-*p*-DHBDS·2DMF for different times of exposure to air. Note that no color change is observed after 24 hours.

Before the electrochemical investigation of Li₄-p-DHBDS, the dilithium 1,4benzenedisulfonate salt was synthesized and electrochemically evaluated vs. Li within 4.0 -2.5 V voltage range in order to probe the stability of the sulfonate groups at high potential. The compound showed no electrochemical response meaning that the sulfonate groups do not present any electrochemical activity in our experimental conditions (Fig. S4). The electrochemical performance of Li₄-p-DHBDS·2DMF was evaluated vs. Li metal in Swagelok®type cell. Interestingly, the starting open circuit potential displayed a value of about 3 V (against 2.5 V for Li_{4} -p-DHT⁴⁵), which supports well the as-observed stability of the compound in air reported above. Fig. 3a shows the as-obtained potential-composition trace upon cycling within 4.0-2.5 V vs. Li⁺/Li⁰ potential window at a cycling rate of 1 electron per molecule exchanged in 10 h (C/20). The first oxidation (charge) is mainly characterized by a first plateau located at 3.3 V followed by another one ~100 mV higher corresponding to an overall extraction of two Li^+ per ring as expected ($Q_{\text{theo.}} = 122 \text{ mAh g}^{-1}$) unlike the carboxylate-based analogous compound (namely Li₄-p-DHT) that exhibit only half of the expected specific capacity^{19,45} except when using nanosheet particles as reported by Chen's group. 51,52



Figure 3. (a) First two cycles of a Li half-cell using Li₄-*p*-DHBDS-2DMF as the positive electrode material (carbon additive: 30 wt.% and PTFE: 5 wt.%) and galvanostatically cycled in EC-DMC/LiPF₆ 1 M at a rate of 1 Li⁺/10 h (C/20, $I = 6.08 \text{ mA.g}^{-1}$). (b) Corresponding capacity retention curve, together with the coulombic efficiency. (c) Specific capacity vs. cycle number for current rate changes ranging from C/20 to C per series of five cycles.

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However, only 1.4 Li ions is inserted upon the subsequent discharge leading to a reversible capacity stabilized at 86 mAh g^{-1} (*i.e.*, 70% of the theoretical one) whereas the electrochemical profile is modified into a more complex feature with a sloppy region in the second part of the reduction process. This new electrochemical profile is then maintained upon cycling. Quite interestingly, this active electrode material presents a gain in terms of operating potential by approaching 3.2 V vs. Li⁺/Li⁰ compared to the carboxylate-based analogous compound (2.55 V vs. Li^+/Li^0 for Li_4 -*p*-DHT⁴⁵), which represents roughly a voltage gain of +650 mV. The capacity retention curve obtained a rate of 1 Li⁺/10 h shows a slight increase in capacity during the ten first cycles up to $\sim 100 \text{ mAh g}^{-1}$ before stabilizing at 90 mAh g^{-1} through the 40 subsequent cycles (Fig. 3b). The recovered capacity was also assessed at different cycling rates (Fig. 3c). The slight increase of the restored specific capacity value during the beginning of the cycling was also observed during this electrochemical experiment. A reversible capacity of \sim 40 mAh.g⁻¹ was only measured at Crate, however, the stabilized capacity value at 90 mAh. g^{-1} was restored when decreasing the cycling rate at C/10. To grasp further insight regarding the electrochemical reactivity of this organic electrode material, we first performed an electrochemical operando XRD experiment. Figure 4a shows the series of XRD powder patterns collected for every change in Δx of 0.2 during the 1st charge/discharge of a typical Li₄-p-DHBDS·2DMF/Li half-cell galvanostatically cycled at a rate of 1 $\text{Li}^{+}/10$ h. As expected, the two plateaus observed during the 1st charge correspond to phase transitions as demonstrated by the progressive disappearance of all diffraction peaks of the pristine material at 3.3 V giving rise to a poorly crystallized compound (Fig. 4a, light green XRD pattern). Then, new Bragg peaks clearly emerge during the second electrochemical step at 3.4 V for producing a new crystallized phase with a better crystallinity compared to the starting material (Fig. 4a, red XRD pattern). During the 1st discharge, all the diffraction peaks of the latter progressively vanish in a continuous manner without changes in the Bragg positions which seems indicate that an amorphous compound is formed as the reduction proceeds (lithium insertion). Interestingly, the collection of XRD patterns related to the full second cycle (Fig. 4b, red XRD pattern) show the occurrence of a single reversible phase transition between the electrochemically generated crystallized phase and an amorphous state. In other words, the electrochemical pathway observed during the 1st charge is irreversible.



Figure 4. Operando XRD investigations during both the first (a) and the second (b) cycle of Li_{4} -p-DHBDS·2DMF as the positive electrode material (carbon additive: 30 wt.%) galvanostatically cycled vs. Li in EC-DMC/LiPF₆ 1 M at a rate of 1 Li⁺/10 h. The XRD powder patterns were collected for every change in Δx of 0.2.

Complementary *ex situ* characterizations were also performed by both FTIR and ¹³C liquid NMR spectroscopies especially to better understand the origin of this irreversible transformation and further explore the electrochemical reaction mechanism. Liquid ¹³C NMR (Fig. 5a) and FTIR (Fig. 5b) analysis were realized by recovery of the organic electrode material at various states of charge and discharge. A simple observation of ¹³C NMR spectra indicates that the DMF initially present in the pristine material (i.e., carbonyl carbon peak: 164 ppm, methyl carbon peaks: 36 and 31 ppm) is not there anymore at the end of the first charge (Fig. 5a, black spectrum). However, characteristics peaks related to DMC (i.e., carbonyl carbon peak: 157 ppm, methoxy carbon peak: 55 ppm) can be unambiguously identified after the 1st charge as well as the subsequent discharge (one cycle). Note that a

blank experiment was performed to make sure that the DMF removal was not related to the washing step conducted prior NMR analysis. Experimentally, powder of Li₄-*p*-DHBDS-2DMF (5 mg) in contact with 2 mL of pure DMC has been sonicated during 1 hour and finally stirred for 24 hours under inert atmosphere. The recovered powder was dried and then dissolved in DMSO- d_6 for liquid ¹³C NMR measurements showing no changes. At the end of the first charge, the corresponding spectrum show also, as expected, a chemical shift in oxidation (Fig. 5a, red spectrum) of aromatic carbon peaks from 132 and 118 ppm to 145 and 135 ppm, respectively, due to the switch from aromatic structure to a quinone one which is confirmed by the appearance of the carbonyl peak at 184 ppm and the disappearance of the peak at 151 ppm peak from the oxygen-bonded carbon. After the 1st cycle, NMR data confirm well the recovery of the dihydroxybenzenoate electroactive core (Fig. 5a, dark green spectrum) but also the presence of DMC.



Figure 5. (a) *Ex situ* ¹³C NMR spectrum of the electrode material at different state of charge: pristine material, after first charging and subsequent discharging at 4.0 and 2.5 V vs. Li^+/Li^0 , respectively (*denote typical peaks either for DMF or DMC molecule). (b) Corresponding FTIR response focused within the 1300-1800 cm⁻¹ region including the typical spectrum obtained during the first charge when using 3.3 V vs. Li^+/Li^0 as cut-off potential.

The FTIR investigation has readily confirmed the ¹³C NMR analysis with the disappearance of all absorption bands relative to DMF at 1669, 1300 and 900 cm⁻¹ (Fig. 5b). In addition, one observes the appearance of new band at 1552 cm⁻¹, attributed to the formation of the quinonoid carbonyl groups, which becomes more intense at the end of the charge (Fig. 5b, red spectrum). After the 1st cycle (Fig. 4c, dark green spectrum), the quinonoid carbonyl vibration band has partially vanished and all other bands remaining unchanged, pointing out

the reversibility of the process at the molecular level. To sum up, the solvent exchange reaction occurring as the first discharge proceeds induces an irreversible phase transition of the pristine organic electrode material giving rise thereafter to a different electrochemical profile upon cycling. Note that the peculiar amorphisation step observed during the beginning of the first charge (Fig. 4, green XRD) could be related to the concomitant DMF release as the lithium extraction proceeds giving rise to a turbostratic stacking of the pristine layered structure.

To complete our study and with the aim at improving the intrinsic theoretical specific capacity value of this compound, Li_4 -p-DHBDS-2DMF was desolvated and then electrochemically assessed vs Li. Basically, Li₄-p-DHBDS was readily prepared at the gramscale by thermal annealing of the solvate at 300°C for 20 hours under Ar. The corresponding TG/DSC traces related to the annealed compound confirm the complete removal of DMF molecules present in the material (Fig. 1a, black curves). Figure S3b shows a selected SEM image of the sample after this thermal annealing that exhibits alteration of the morphology of the pristine particles. The particles length and size remained the same but the lamellar stacking is clearly revealed since a beginning of exfoliation is visible due to the extraction of the DMF molecules. Consequently, the as-obtained material appeared not enough crystallized (Fig. S5) to perform again an Operando XRD investigation. The electrochemical investigation of Li_4 -p-DHBDS (Fig. 6) was then performed according to a similar procedure compared to Li₄-p-DHBDS·2DMF (Fig. 3) for the sake of comparison. When the non-solvated phase Li_a-p-DHBDS was oxidized up to 4 V, it was also possible to extract two Li⁺ at an oxidation potential of about 3.35 V vs. Li⁺/Li⁰, corresponding to a theoretical capacity of 180 mAh.g⁻¹ (Fig. 6a). Basically, the recorded electrochemical cycling curve is quite similar whatever the considered active material (i.e., Li_4 -*p*-DHBDS or Li_4 -*p*-DHBDS·2DMF) as shown in Figure S6. However, to our surprise and on the contrary of our previous studies reporting the electrochemical performance of several desolvated electroactive organic lithiated phases,^{42,43,53} Li₄-p-DHBDS presented a poorer retention capability (Fig. 6b) compared to the pristine solvated phase (Fig. 3). Basically, the typical retention curves exhibit a quasi-linear capacity fading upon cycling. In the present case, the exfoliation process of the pristine particles due to the thermal desolvation seems very detrimental for getting long stable cycling; this situation has never been encountered with other of our tested n-type organic

electrode materials. A better electrochemical stability upon cycling being anticipated by an appropriated formulation of the composite electrode, a dedicated study to address this issue is currently in progress.



Figure 6. (a) First two cycles of a Li half-cell using Li₄-*p*-DHBDS as the positive electrode material (carbon additive: 30 wt.% and PTFE: 5 wt.%) and galvanostatically cycled in EC-DMC/LiPF₆ 1 M at a rate of 1 Li⁺/10 h (C/20, $I = 9.11 \text{ mA.g}^{-1}$). (b) Corresponding capacity retention curve, together with the coulombic efficiency. (c) Specific capacity vs. cycle number for current rate changes ranging from C/20 to C per series of five cycles

Conclusions

Continuing our effort to promote high-energy organic LIBs, the disulfonate analog of tetralithium 2,5-dihydroxy-1,4-benzenedicarboxylate was synthesized and electrochemically assessed in Li half-cell as a novel lithiated insertion organic material for positive electrode. In its solvated form (Li_4 -*p*-DHBDS·2DMF), this redox-active organic structure exhibits a stable cycling profile at 100 mAh.g⁻¹ but also an average operating potential of ~3.25 V vs. Li⁺/Li⁰ making this lithiated positive material processable under dried air. Based on several characterization techniques it was demonstrated that DMF molecules incorporated in the crystal structure of the pristine disulfonate were irreversibly exchanged with DMC of the electrolyte during the first charge. Regarding the desolvated phase (Li_4 -*p*-DHBDS), the electrochemical performance upon cycling was amazingly inferior in comparison probably due to the damage caused by the desolvation reaction; the latter exfoliating a lot the pristine lamellar particles.

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References

- 1 M. Armand and J.-M. Tarascon, Nature, 2008, 451, 652–657.
- 2Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon and J. Liu, *Chem. Rev.*, 2011, **111**, 3577–3613.
- 3 Slater Michael D., Kim Donghan, Lee Eungje and Johnson Christopher S., *Advanced Functional Materials*, 2012, 23, 947–958.
- 4J. B. Goodenough, *Energy Environ. Sci.*, 2013, 7, 14–18.
- 5P. Poizot and F. Dolhem, Energy Environ. Sci., 2011, 4, 2003–2019.
- 6Y. Liang, Z. Tao and J. Chen, Adv. Energy Mater., 2012, 2, 742-769.
- 7Z. Song and H. Zhou, Energy & Environmental Science, 2013, 6, 2280–2301.
- 8B. Häupler, A. Wild and U. S. Schubert, Advanced Energy Materials.
- 9A. Chagnes and J. Swiatowska, Eds., *Lithium process chemistry: resources, extraction, batteries, and recycling*, Elsevier, Amsterdam Boston Heidelberg, 2015.
- 10V.-A. Oltean, S. Renault, M. Valvo and D. Brandell, Materials, 2016, 9, 142.
- 11M. Miroshnikov, K. P. Divya, G. Babu, A. Meiyazhagan, L. M. R. Arava, P. M. Ajayan and G. John, *J. Mater. Chem. A*, 2016, 4, 12370–12386.
- 12T. B. Schon, B. T. McAllister, P.-F. Li and D. S. Seferos, *Chem. Soc. Rev.*, 2016, **45**, 6345–6404.
- 13Q. Zhao, C. Guo, Y. Lu, L. Liu, J. Liang and J. Chen, Ind. Eng. Chem. Res., 2016, 55, 5795–5804.
- 14Y. Wu, R. Zeng, J. Nan, D. Shu, Y. Qiu and S.-L. Chou, *Adv. Energy Mater.*, 2017, 7, n/a-n/a.
- 15Y. Zhang, J. Wang and S. N. Riduan, J. Mater. Chem. A, 2016, 4, 14902–14914.
- 16Q. Zhao, Z. Zhu and J. Chen, Adv. Mater., 2017, 29, n/a-n/a.
- 17P. Poizot, F. Dolhem and J. Gaubicher, *Current Opinion in Electrochemistry*, 2018, **9**,70–80.
- 18K. Deuchert and S. Hünig, *Angewandte Chemie International Edition in English*, 1978, **17**, 875–886.
- 19S. Gottis, A.-L. Barrès, F. Dolhem and P. Poizot, ACS Appl. Mater. Interfaces, 2014, 6, 10870–10876.
- 20Miller Joel S., Advanced Materials, 2004, 5, 671–676.
- 21P. Novák, K. Müller, K. S. V. Santhanam and O. Haas, Chem. Rev., 1997, 97, 207–282.
- 22D. Naegele and R. Bittihn, Solid State Ionics, 1988, 28–30, 983–989.
- 23S. Muench, A. Wild, C. Friebe, B. Häupler, T. Janoschka and U. S. Schubert, *Chem. Rev.*, 2016, **116**, 9438–9484.
- 24H. Nishide, S. Iwasa, Y.-J. Pu, T. Suga, K. Nakahara and M. Satoh, *Electrochim. Acta*, 2004, **50**, 827–831.
- 25K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro, M. Satoh and E. J. Cairns, J. Power Sources.

- 26H. Nishide and K. Oyaizu, Science, 2008, 319, 737-738.
- 27T. Suga, S. Sugita, H. Ohshiro, K. Oyaizu and H. Nishide, Adv. Mater., 2011, 23, 751-754.
- 28N. Sano, W. Tomita, S. Hara, C.-M. Min, J.-S. Lee, K. Oyaizu and H. Nishide, ACS Appl. Mater. Interfaces, 2013, 5, 1355–1361.
- 29T. Sukegawa, A. Kai, K. Oyaizu and H. Nishide, Macromolecules, 2013, 46, 1361-1367.
- 30S. Iwasa, M. Yasui, T. Nishi and K. Nakano, NEC Technical Journal, 7, 103–106.
- 31I. S. Chae, M. Koyano, K. Oyaizu and H. Nishide, J. Mater. Chem. A, 2013, 1, 1326–1333.
- 32H. Tokue, T. Murata, H. Agatsuma, H. Nishide and K. Oyaizu, *Macromolecules*, 2017, **50**, 1950–1958.
- 33M. Armand, S. Grugeon, H. Vezin, S. Laruelle, P. Ribière, P. Poizot and J.-M. Tarascon, *Nature Materials*, 2009, **8**, 120–125.
- 34L. Fédèle, F. Sauvage and M. Bécuwe, *Journal of Materials Chemistry A*, 2014, **2**, 18225–18228.
- 35L. Fédèle, F. Sauvage, J. Bois, J.-M. Tarascon and M. Bécuwe, J. Electrochem. Soc., 2014, 161, A46–A52.
- 36V. A. Mihali, S. Renault, L. Nyholm and D. Brandell, *RSC Advances*, 2014, 4, 38004–38011.
- 37N. Ogihara, T. Yasuda, Y. Kishida, T. Ohsuna, K. Miyamoto and N. Ohba, *Angew. Chem. Int. Ed.*, 2014, **53**, 11467–11472.
- 38A. Iordache, V. Delhorbe, M. Bardet, L. Dubois, T. Gutel and L. Picard, ACS Appl. Mater. Interfaces, 2016, 8, 22762–22767.
- 39A. Iordache, D. Bresser, S. Solan, M. Retegan, M. Bardet, J. Skrzypski, L. Picard, L. Dubois and T. Gutel, *Adv. Sustainable Syst.*, 2017, 1, n/a-n/a.
- 40L. Fédèle, F. Sauvage, S. Gottis, C. Davoisne, E. Salager, J.-N. Chotard and M. Becuwe, *Chem. Mater.*, 2017, **29**, 546–554.
- 41A. E. Lakraychi, F. Dolhem, F. Djedaïni-Pilard, A. Thiam, C. Frayret and M. Becuwe, *Journal of Power Sources*, 2017, **359**, 198–204.
- 42H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot and J.-M. Tarascon, *ChemSusChem*, 2007, 1, 348–355.
- 43H. Chen, M. Armand, M. Courty, M. Jiang, C. P. Grey, F. Dolhem, J.-M. Tarascon and P. Poizot, *J. Am. Chem. Soc.*, 2009, **131**, 8984–8988.
- 44A.-L. Barrès, J. Geng, G. Bonnard, S. Renault, S. Gottis, O. Mentré, C. Frayret, F. Dolhem and P. Poizot, *Chem. Eur. J.*, 2012, **18**, 8800–8812.
- 45S. Renault, S. Gottis, A.-L. Barrès, M. Courty, O. Chauvet, F. Dolhem and P. Poizot, *Energy & Environmental Science*, 2013, 6, 2124.
- 46S. Wang, L. Wang, K. Zhang, Z. Zhu, Z. Tao and J. Chen, *Nano Letters*, 2013, **13**, 4404–4409.
- 47W. Wan, H. Lee, X. Yu, C. Wang, K.-W. Nam, X.-Q. Yang and H. Zhou, *RSC Advances*, 2014, **4**, 19878–19882.
- 48W. Wan, Z.-B. Zhu, L.-H. Huo, Z.-P. Deng, H. Zhao and S. Gao, *CrystEngComm*, 2012, 14, 5274–5284.
- 49Mietrach Andrea, Muesmann Thomas W. T., Christoffers Jens and Wickleder Mathias S., *European Journal of Inorganic Chemistry*, 2009, **2009**, 5328–5334.
- 50M. Morcrette, Y. Chabre, G. Vaughan, G. Amatucci, J.-B. Leriche, S. Patoux, C. Masquelier and J.-M. Tarascon, *Electrochimica Acta*, 2002, **47**, 3137–3149.
- 51S. Wang, L. Wang, K. Zhang, Z. Zhu, Z. Tao and J. Chen, *Nano Letters*, 2013, **13**, 4404–4409.
- 52Q. Zhao, J. Wang, C. Chen, T. Ma and J. Chen, Nano Res., 2017, 10, 4245-4255.
- 53S. Renault, J. Geng, F. Dolhem and P. Poizot, Chem. Commun., 2011, 47, 2414-2416.

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