Electrochemical characterization of lithium 4,4'-tolane-dicarboxylate for use as a negative electrode in Li-ion batteries[†]‡

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Received 13th October 2010, Accepted 22nd November 2010 DOI: 10.1039/c0jm03458d

Lithium 4,4'-tolane-dicarboxylate has been synthesized and examined for use as a negative electrode material in lithium ion batteries. Cycling studies in Swagelok cells, using lithium as a counter electrode, show a reversible capacity of ~ 200 mAh g⁻¹ at ~ 0.65 V and minimal discharge/charge polarization (~ 15 mV). XRD and SEM analyses reveal that the material crystallizes in two different ways depending on the type of solvent used in the synthesis. The changes in structural packing with methanol or ethanol dramatically affect the capacity of the material leading to electrodes that are able to intercalate almost two vs. one Li per unit formula, respectively.

1. Introduction

As our society moves toward large volume applications for batteries like electric cars and off-grid energy storage, Li-ion technology has become of increasing importance owing to the large energy density and output voltage provided by these batteries. However, in order to meet consumer demands of batteries for large volume applications, Li-ion cells must increase in capacity, power rate, and safety while at the same time decrease cost-wise. In an attempt to address some of these issues, our group has recently begun focusing on either positive or negative organic electrodes and developing batteries with both electrodes being organic.¹⁻⁶ Electrodes based on organic molecules could potentially lower the overall cost of batteries because, if properly designed, they can be generated from biomass which is a renewable resource. This is particularly relevant because, as batteries become more important, large demands will not be placed on mined materials, the cost of which is increasing with scarcity.

Another area in which organic molecules might be useful is the design of overall safer and sustainable batteries. In most Li-ion batteries, graphite is used as the negative electrode because of its low operating potential, excellent cyclability, and high energy density. However, a low operating potential ($\sim 0.2 \text{ V } vs. \text{ Li/Li}^+$) leads to decomposition and safety issues associated with reactions between the electrolyte and the negative electrode. Therefore, in order to make the low potential electrodes safe, solid electrolyte interphase (SEI) additives must be utilized as well as copper current collectors, which add to the overall cost of batteries. By using organic molecules it is possible to tune the

‡ This paper is part of a *Journal of Materials Chemistry* themed issue in celebration of the 70th birthday of Professor Fred Wudl.

redox properties of the electrodes so as to slightly increase the operating potential, thereby decreasing the risk of exothermic reactions with the electrolyte, and enabling the use of cheaper, lighter aluminium as the negative current collector. We recently reported the possibility for Li₂C₈H₄O₄, a conjugated aromatic carboxylate, of electrochemically reacting with Li at 0.7 V vs. Li/Li⁺ in a reversible way. Such a low redox potential was ascribed to the decrease in resonance of the carboxylate molecule. Thus, it was tempting to study how the resonance strength, and hence the redox potential of a carboxylate, would be affected by the presence of a triple bond. This, together with our attempt to rationally design a safer negative electrode material for use in Li-ion batteries, led to the synthesis and fabrication of electrode of lithium 4,4'-tolane-dicarboxylate (Li₂TDC), a material with an operating potential of ~0.65 V vs. Li/Li+, where the presence of " π " orbitals above and below the planes of the molecule may increase the electronic coupling of the stack of discrete moieties.

2. Experimental

General

Chemicals were purchased from Sigma-Aldrich Chemical and Fisher Scientific and used without further purification unless otherwise stated. Solvents, where applicable, were distilled from Na/benzophenone, CaH_2 , or K_2CO_3 . NMR spectra were obtained on a Bruker DMX 500MHz spectrometer utilizing Topspin software.

Synthesis

Lithium 4,4'-tolane-dicarboxylate (2). LiOH (0.1889 g, 7.887 mmol) was added to a stirred solution of the dicarboxylic acid⁷ (1.000 g, 3.756 mmol) in 100 mL of methanol or ethanol (depending on the desired crystal structure), the flask was stoppered, and the reaction allowed to proceed overnight at room temperature. The white suspension was then collected through centrifugation with two rinses of the powder with the reaction solvent, and dried in a vacuum oven at 60 °C (0.9984 g, 95.6%).

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[†] Electronic supplementary information (ESI) available: Further details. See DOI: 10.1039/c0jm03458d

¹H NMR (D₂O): δ 7.98 (4H, dm), 7.74 (4H, dm) ppm. ¹³C NMR (D₂O): 174.91, 136.39, 131.39, 128.92, 124.80, 90.57 ppm.

Powder diffraction

X-Ray powder diffraction patterns were collected on a Bruker D8 diffractometer utilizing Cu-K α or Co-K α (capillary configuration) radiation, equipped with a Gobel mirror and a Braun PSD detector and operating at 40 kV and 30 mA in the 10–100° 2 Θ range with a 2 Θ step size of 0.017°.

SEM studies

The morphology of the powders was observed by scanning electron microscopy (SEM) using a QUANTA 200F (FEI).

EPR studies

The spectra of the compounds were collected at room temperature with an ELEXYS E580E X band spectrometer with a modulation of 0.6 G and a microwave power of 1 mW. 2D-HYSCORE spectra were recorded at room temperature using the sequence $(\pi/2 - \tau - \pi/2 - t1 - \pi - t2 - \pi/2)$ echo, where the echo is measured as a function of t_1 and t_2 . The duration of the $\pi/2$ and π pulse was 16 ns and 24 ns, respectively, for maximum inversion echo. 256 points were recorded in each dimension for a τ value of 300 ns, while the t_1 and t_2 were incremented in steps of 16 ns from their initial value. Eight step phase-cycling procedures were applied in order to remove the unwanted echoes. The background decay in both t_1 and t_2 dimensions was subtracted using a polynomial function followed by zero-filling to 512 points in two dimensions and apodization was performed with a Hamming window; then Fourier transform was carried out in both dimensions and magnitude calculation was done.

Quantum chemistry

Theoretical calculations were performed using Gaussian 03 parallel software with 16 processors Transtec cluster. Geometry optimizations were performed using density functional theory level B3LYP hybrid function with the 6-31+g(2d,2p) basis set. Structures were fully optimized in non-standard ethylene carbonate solvent using IEFPCM with solvent radius computed of 3.53 Å and a dielectric value of 89. The symmetry was turned off for all the calculations and frequencies were computed and achieved for each structure. The free energy differences were provided after ZPE correction.

Electrochemical studies

Swagelok[®] cells were constructed using a disk of Li metal as the negative electrode and a Whatman GF/D borosilicate glass fiber sheet saturated with an electrolyte consisting of 1 M LiPF₆ in a (1 : 1 w/w) mixture of ethylene carbonate : dimethyl carbonate solution. Working electrodes resulted from mixing compound (2) with 50% (by weight) carbon black (SP) in a mortar and pestle. For Swagelok batteries 10–13 mg of the mixture were utilized. The signature curve was obtained using an electrode loaded with 5 mg of active material per cm². All electrode mixing and battery construction was performed in an argon filled glove box.

Galvanostatic charge–discharge experiments were conducted at 20 °C using a VMP system (Biologic S.A., Claix, France) operating in galvanostatic mode. Unless otherwise stated, the cells were cycled between 0.5 and 3 V *versus* Li/Li⁺ at one Li⁺ exchanged per 20 h, and all the capacities are reported in mAh per grams of Li₂TDC only.

3. Results and discussion

3.1 Synthesis

The synthesis of Li₂TDC (2) (Scheme 1) was adapted from a procedure by Mio et al.⁷ in which the dicarboxylic acid is described. The synthesis began with the one pot double Sonogashira palladium-catalyzed cross-coupling reaction⁸ and the corresponding silane deprotection of methyl-4-iodobenzoate and trimethylsilvacetylene resulting in the diester (1). The diester (1) was then hydrolyzed with potassium hydroxide in water and ethanol, followed by acidification resulting in the corresponding dicarboxylic acid. Next, the di-COOH form was purified by precipitation of the lithium salt using LiOH in ethanol, followed isolation of the solid, dissolving in water, acidification, and isolation of the product by centrifugation. Finally, the dilithium salt (2) was synthesized using two separate solvent systems. Half of the dried acid powder was dissolved in methanol (hereafter termed MeOH-2), half in ethanol (hereafter termed EtOH-2) and both precipitated as Li₂TDC with lithium hydroxide. MeOH-2 and EtOH-2 were identical by ¹³C NMR, ¹H NMR, and both showed no mass change up to 300 °C by thermogravimetric analysis.

3.2 XRD and SEM analyses

The XRD powder patterns (Fig. 1) collected for these two samples of Li₂TDC obtained either from MeOH (a) or EtOH (b) are drastically different in terms of intensity of the Bragg peaks and in their 2θ position. This difference in intensity could result from a preferential orientation of the powders. However, after repeating the XRD experiment with the powders in capillary tubes to eliminate orientation differences in the powders, we obtained the same diffraction patterns and verified that indeed the two samples had intrinsically different XRDs, implying different unit cells for the two samples (*e.g.* different stacking sequence of the building block molecules to form the 3D network). Such a result does not come as a total surprise for conjugated organic molecules because of their ability to form " π "-stacks. Indeed, changes in the reaction/recrystallization solvent have previously been shown to affect 3D packing by



Scheme 1 Synthesis of lithium 4,4'-tolane-dicarboxylate (Li₂TDC) (2).

EtOH - 2 (b) MeOH - 2 (a) MeOH - 2 (a) MeOH - 2 (a) MeOH - 2 (b) MeOH - 2 (b) MeOH - 2 (c)

Fig. 1 XRD powder patterns and SEM images (inset) of (a) MeOH-2 and (b) EtOH-2.

modifying the strength of the π - π stacking interactions. This structural change may also be favored in this case by the easy rotation of both the phenyl rings around the triple bond.

Our inability to grow single crystals has prevented us from grasping further insight in the key structural packing difference between the two polymorphs. Besides structural differences, the two samples also show morphological differences as seen from scanning electron microscopy (SEM) studies. The images that result from the powder synthesized from MeOH (Fig. 1a inset) show crystals that are larger and more plate-like than those precipitated out of EtOH (Fig. 1b inset).

3.3 Electrochemical performances

The electrochemical performances of our materials were tested versus Li in a Swagelok®-type cell after grinding with a mortar and pestle along with 50% carbon black (SP®). Fig. 2 shows the voltage-composition trace for Li_{2+x}C₁₆H₈O₄/Li cells cycled at a rate of one Li per 20 h between 3 V and 0.5 V. The potential sharply drops to two separate plateaus located at ~ 0.9 and 0.65 V before tapering off to 0.5 V. For both MeOH-2 and EtOH-2, the first plateau at ~ 0.9 V is ascribed to the reaction between the solvated lithium ions and the carbon SP solid interface (solid electrolyte interphase, SEI). This assignment is justified for two reasons: first, in situ XRD cycling (which will be discussed in greater detail later) shows no change in the powder diffraction pattern of either MeOH-2 or EtOH-2 when the material was discharged past the first plateau and second, the discharge of a blank carbon SP/Li Swagelok cell at a rate of one Li every 20 h (e.g., containing Li as the negative electrode and only carbon SP as the positive electrode), reveals a peak at ~ 0.9 V. In the case of MeOH-2 (Fig. 2a), the second plateau at 0.65 V shows a lithium uptake of \sim 1.7 Li upon discharge. For the subsequent charging cycle, the voltage almost coincides with that of the second discharge plateau (but not the first one) with minimal polarization (~15 mV) (Fig. 3a), demonstrating the reversibility of lithium intercalation into the material but not that

Fig. 2 Voltage *vs.* composition trace with capacity retention curves (inset) for (a) MeOH-2 and (b) EtOH-2.

of the SEI layer. A capacity retention curve of MeOH-2 reveals a loss in capacity by about half after the first cycle due to the irreversibility of the SEI layer (Fig. 2a inset), but only $\sim 10\%$ loss in capacity through 50 subsequent cycles at a rate of one Li per 20 h. This minimal loss of capacity demonstrates that MeOH-2 is reasonably insoluble in the electrolyte solution. Reducing the anodic cut-off during cycling from 3 V to 1.5 V was not found to have any effect on the capacity retention. Additionally, the electrode rate capability was determined via the collection of a charge signature curve (Fig. 3c). To do so, a MeOH-2/Li Swagelok cell was discharged-charged-discharged at a C/20 rate and then charged at decreasing rates (5, 2.5, 1, 0.5, 1/4, 1/10, and 1/20 Li per hour) with a relaxation time of 30 min between each step. Note that the cell can be recharged to 76% of its full capacity at a rate of 5 Li per hour implying good rate capability but bearing in mind that the electrode contains 50% of carbon additive. Attempts to reduce the carbon percentage (<40%) by downsizing the particles size were unsuccessful.

In contrast to cells constructed using MeOH-2, batteries composed of EtOH-2 resulted in voltage–composition traces in which the second plateau at 0.65 V shows a lithium uptake of ~1 Li upon discharge of the cell to 0.5 V (Fig. 2). Once again, as was the case for MeOH-2, the subsequent charging cycle for EtOH-2, which occurs with a minimal polarization (~40 mV) (Fig. 3b), demonstrates the reversibility of lithium intercalation into the material. This difference in charge/discharge polarization is highlighted by plotting the derivative curves (dQ/dV) of both materials (Fig. 3a and 3b inset). Similar to MeOH-2, the capacity retention curve for EtOH-2 shows a loss in capacity by about half after the first cycle due to the irreversibility of the SEI layer, but only ~15% loss in capacity through 50 cycles when cycled at





Fig. 3 Voltage *vs.* zoomed composition trace with derivative curves (inset) for (a) MeOH-2 and (b) EtOH-2. (c) Discharge signature curve for MeOH-2.

a rate of one Li per 20 h (Fig. 2b inset). Signature curves for EtOH-2 were not generated because its lower initial capacity makes it a less interesting compound for use in batteries. Overall, since MeOH-2 and EtOH-2 were chemically identical as determined by ¹H and ¹³C NMR (as well as being synthesized and purified in an analogous way) and the samples used in batteries did not retain any solvent from the synthesis step (as determined by TGA and NMR), the difference in battery cycling behavior is most likely the result of the difference in crystal structure (as highlighted by Fig. 1) resulting from the different solvents used during the lithiation. This is an important point as now, in addition to the proper choice of organic molecule, the ratio of carbon additive and electrode mixing procedure, it is important to control the crystalline habit of the compounds via solvent choice in order to obtain optimum electrode performance for organic materials.

This result does not come as a total surprise in light of what is presently experienced in the field of organic photovoltaics which rely on a conversion layer made of p and n type materials. The efficiency of these devices has been shown to strongly depend on the morphology of the films of these materials, and morphology is affected by a variety of factors including solvent, concentration, processing temperatures, *etc.* which affects the way in which the materials layers are locally stacked together.⁹

3.4 Electrode analyses

In order to gain further insight into the Li insertion-deinsertion mechanism within this organic compound, we followed the progress of the electrode material by in situ XRD and ex situ EPR through one discharge and charge cycle. The electrode material was characterized by in situ XRD while cycling in a specially designed cell.10 The Li_{2+x}C₁₆H₈O₄/Li cell was constructed so that the organic electrode material (either MeOH-2 or EtOH-2 with 50% carbon) was pressed against a beryllium window; next, an initial scan of the material was performed followed by cycling between 0.5 and 3 V at a rate of one Li every 20 h. At specific points (one Li into the first plateau, after the first plateau, one Li into the second plateau (MeOH-2), full discharge and full recharge) the battery cycling was paused, and an XRD pattern was collected (Fig. 4). For reasons of clarity, we only report the evolution of the XRD patterns in the 15-35° 20 (Cu- $K\alpha$) range as it encompasses the relevant action. The initial XRD pattern collected on MeOH-2 (Fig. 4a) resembles the XRD pattern collected on the powder shown in Fig. 1a. Upon cycling, the first plateau at ~ 0.9 V is reached and two XRD patterns were collected, one at one Li intercalated and one after the first plateau. Both patterns were identical to the initial scan, which is consistent with lithium intercalation into the carbon additive and serves to justify our assignment of this plateau. The next two XRD patterns were collected after one lithium ion has been



Fig. 4 In situ cycling XRD powder patterns of (a) MeOH-2 and (b) EtOH-2.

intercalated into the second plateau at ~ 0.65 V and after the second plateau (or fully discharged). The fully discharged pattern shows a structure with roughly the same crystalline nature (i.e. not more amorphous) as the starting material but with major changes in the XRD pattern that are most notable in the following ranges $\sim 2\Theta$ (Cu-K α) = 18°, 19°–21°, 23°–24°, 27°, 29°-31°. Additionally, the XRD pattern collected at the intercalation of one lithium into the second plateau seems to be a mixture of the initial and fully discharged scans. Finally, upon recharge of the cell to 3 V, the resulting XRD pattern nicely superimposes on the initial scan indicating a fully reversible process. The cycling procedure and collected XRD powder patterns of EtOH-2 (Fig. 4b) matched those of MeOH-2 with the exception that after the uptake of solely one Li into the second plateau, the material is fully discharged and therefore a scan at two Li into the second plateau was not performed. As was the case with MeOH-2, cycling of EtOH-2 during the first plateau did not result in a change in the XRD pattern, consistent with the existence of this plateau being rooted in the Li(C + O) electrochemical reactivity. However, unlike MeOH-2, EtOH-2 became more amorphous upon full discharge of the cell, and failed to regain its full crystalline nature upon recharging the cell. Overall, the *in situ* cycling experiment shows that the crystal structure of EtOH-2 degrades upon cycling, and this polymorph is not suitable for reversible insertion/deinsertion.

To gain further insight into the Li reactivity mechanism of this carboxylate, we performed EPR measurements: a powerful tool to look for electronic states with non-zero spin values at 9 GHz. Data were only collected for the MeOH-2 at its initial stage (asmade material), middle of the discharge ($\sim 1Li^+$, 1e⁻ of the 0.65 V plateau) and end of the discharge (stopped at 0.5 V). To get rid of the carbon and eventual Li_xC carbon EPR signal, blanks on a carbon electrode recovered from a Carbon SP/Li cell discharged to 0.5 V were analyzed. The collected spectra for all the above samples, after weight normalization (Fig. 5), display a narrow (2.1 G line width) centered at g = 2.006. As expected, the fully discharged sample shows the largest signal, implying a maximum of radical contents with respect to its pristine or charged state. Additionally, the half discharged sample gives an EPR signal amplitude close to half that of the full discharge. The initial compound, which according to its formula should be diamagnetic (e.g. no EPR signal), contains a weak signal (estimated to be less than 1% by comparing integration of the signal that we ascribed to a small amount of radical anion formed

during synthesis (*e.g.* $Li_{2+x}C_{16}H_8O_4$). Additionally, the lithiated carbon sample, initially paramagnetic, shows an EPR signal whose amplitude is in the order of 10% of the fully discharged sample, and whose origin is due to the formation of some intercalated carbonaceous materials (Li_xC_6). During the subsequent charge, the EPR signal related to $Li_{2+x}C_{16}H_8O_4$ converts back to its initial amplitude further demonstrating the reversibility of the intercalation–deintercalation process, confirming previously reported X-ray data.

To access the nature of the fully lithiated species (Li_4TDC), we have performed pulsed EPR experiments using spin echo techniques. The initial and recharged compounds do not exhibit any echo due to the small amount of radicals while the lithiated carbon displays a homogeneous line (not shown here) having only free induction decay (FID). This FID signal (with no inhomogeneous broadening effect due to surrounding nuclei) can be explained by the presence of solvated electrons. For the discharged compound, we have recorded a HYSCORE spectrum (Fig. 5 inset) that clearly shows the sole resonance of both the lithium isotopes. No proton and carbon resonance frequency was measured indicating a strong localization on the carboxylate function. This is confirmed by the weak coupling with 7Li observed in the HYSCORE spectrum (*i.e.* hyperfine coupling A is less than twice that of 5.8 MHz 7Li nuclear frequency). Moreover the spin density computed by DFT calculation displays a strong localization on the carboxylate moiety with the calculated A_{max} value of 3.2 MHz which is close to the experimental value of 3.8 MHz.

Theoretical calculations, as already done for other carboxylates^{5,6} or a few organic compounds^{11,12} and using similar formalism, have been carried out to predict the number of Li ions that this molecule can accept and to grasp further insight in the insertion mechanism into Li_{2+x}C₁₆H₈O₄. Based on the experimental data and on the capability of the molecule to reversibly uptake almost 2 Li, DFT potential computations based on two electrons + two lithium ions mechanism with dianionic species formation (Fig. 6a) were performed but failed to converge. We attempted to overcome this failure by considering another way of calculation that respectively implies radical anion and radical species for Li insertion (Fig. 6b and 6c). On that basis, our computation involving 2 Li insertion was performed in two steps (Fig. 6b). We found the first step, which leads to the formation of a radical after the insertion of the first Li (1e⁻, 1Li⁺), to have a free energy cost of 61.83 kcal mol⁻¹ corresponding to an E° value of 0.36 V. For the second inserted Li (1e⁻, 1Li⁺), we



Fig. 5 (a) *Ex situ* CW EPR spectra of MeOH-2 recorded at room temperature. (b) 2D HYSCORE spectrum recorded at room temperature for the discharged sample.



Fig. 6 DFT potential computations pathways for Li insertion in $Li_{2+x}C_{16}H_8O_4$ based either on the 2 Li mechanism with (a) dianionic species and (c) radical species formation, or on (b) two-step 2 Li insertion with radical (1st Li) then diradical (2nd Li) formation.

considered both formations of triplet or singlet state molecules. For the triplet, the free energy was 44.85 kcal mol⁻¹ whereas for the singlet state, it was 53.10 kcal mol⁻¹ leading to E° values of 1 V and 0.73 V, respectively. These different E° values (0.36 V then 1 V (triplet) or 0.73 V (singlet)) for both insertion steps do not match the experimental data as the 2 Li are inserted at the same potential. Therefore, a second set of calculations was undertaken considering here the same two steps radical path but with a quasi-simultaneous 2 electron transfer (Fig. 6c), neglecting kinetic limitation. Depending on the spin state of the fully discharged molecule, we obtained E° values of 0.54 and 0.72 V for singlet and triplet states, respectively. These values are closer to what we experimentally found, even though any conclusion could be given about the spin state of the molecule that may be, for instance, pure triplet or a mixture of singlet/triplet. In both calculations, the experimental emf is the average of the two 1 lithium steps.

Conclusion

This study reported a new carboxylate-based molecule capable of reacting reversibly with almost 2 Li⁺ at a potential of ~ 0.65 V which is, like for dilithium terephthalate, attractive as a negative electrode in Li-ion batteries as it enables the use of an Al current collector. Besides, we show that this compound displays high rate capabilities although large amounts of carbon are necessary (>40%) to trigger the electrochemical activity of the molecule even if the Li-driven process enlists radical processes which are kinetically fast. Such an amount of carbon is well above what is needed in inorganic systems with less than 20% whatever the type of particles (1D, 2D or 3D) to reach electronic percolation. The reason for such differences, common to most of the organic molecules so far investigated, most likely results from the fact that we are mainly dealing with weak interactions (e.g. van der Waals bonded molecules) so that the electronic percolation requires larger amounts of carbon as electrons must be brought at the molecular level. The irreversible capacity caused by this carbon fraction is a large handicap in practice. Even though carboxylates turn out to be an attractive family of compounds in the hunt for negative electrodes, especially when the percolation threshold can be reduced possibly by the use of graphene or conjugated polymers instead of carbon, means to increase their capacity still remain to be found; this is the scope of our present research. Here, we have shown that two polymorphs exist, and only one allows fast and reversible intercalation. It underlines a common phenomenon in organic chemistry, when the solvent used for crystallization directs the structure. What is remarkable is the apparently robust interlocking of " π " planes, so that EtOH-2 does not revert to MeOH-2 during intercalation (in contrast with, for instance, the isomerization of *cis*–*cis* (CH)_x into *trans*–*trans* after one Li insertion cycle⁶), but also the very small polarization, similar to the best inorganic electrode materials (LiFePO₄).

Acknowledgements

The authors want to thank M. Courty for running some TGA measurements on the samples, C. Masquelier for helping us in collecting XRD data with capillary, and P. Poizot for discussions.

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