J|A|C|S
ARTICLES

Lithium Salt of Tetrahydroxybenzoquinone: Toward the Development of a Sustainable Li-Ion Battery

Haiyan Chen,[†] Michel Armand,[†] Matthieu Courty,[†] Meng Jiang,[‡] Clare P. Grey,[‡]
Franck Dolhem,[§] Jean-Marie Tarascon,[†] and Philippe Poizot*,[†]

Laboratoire de Réactivité et Chimie des Solides-UMR CNRS 6007, Université de Picardie Jules Verne, 33 rue Saint-Leu, 80039 Amiens, France, Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400, and Laboratoire des Glucides-UMR CNRS 6219, Université de Picardie Jules Verne, 10 rue Beaudelocque, 80039 Amiens, France

Received March 30, 2009; E-mail: philippe.poizot@u-picardie.fr

Abstract: The use of lithiated redox organic molecules containing electrochemically active C=O functionalities, such as lithiated oxocarbon salts, is proposed. These represent alternative electrode materials to those used in current Li-ion battery technology that can be synthesized from renewable starting materials. The key material is the tetralithium salt of tetrahydroxybenzoquinone ($Li_4C_6O_6$), which can be both reduced to $Li_2C_6O_6$ and oxidized to $Li_6C_6O_6$. In addition to being directly synthesized from tetrahydroxybenzoquinone by neutralization at room temperature, we demonstrate that this salt can readily be formed by the thermal disproportionation of $Li_2C_6O_6$ (dilithium rhodizonate phase) under an inert atmosphere. The $Li_4C_6O_6$ compound shows good electrochemical performance vs Li with a sustained reversibility of ~200 mAh g^{-1} at an average potential of 1.8 V, allowing a Li-ion battery that cycles between $Li_2C_6O_6$ and $Li_6C_6O_6$ to be constructed.

1. Introduction

A major goal in the production of clean energy is to identify sustainable energy supplies, which can be stored and utilized (or converted) in a way that necessarily protects the environment and helps to reduce carbon dioxide emissions.[1−4] One of the major technological challenges in this field relies on designing advanced batteries to store more electrical energy while being environment-friendly. Although current Li-ion battery technology represents a promising power source for advanced electric vehicles and portable electronic devices, it still falls short of both the sustainability and CO_2 footprint criteria, owing to the use of active inorganic materials (e.g., $LiCoO_2$, $LiFePO_4$, ...) obtained from limited mineral resources and their synthesis by high temperature reactions. Towards this goal, our group[5,6] has recently suggested a possible alternative consisting in moving from inorganic to organic matter-based electrodes, which could be prepared (i) from renewable resources (biomass) and (ii) via eco-efficient processes (green chemistry principles)[7] making the concept of "greener and sustainable" Li-ion batteries possible. Ironically, the first commercial Li-ion batteries used a conducting polymer as a positive electrode,[8] but research on organic systems has been limited because of poor performances, energy density-wise, coupled with the lower emphasis on producing lower-cost devices with smaller CO_2 footprints at that time. Our first interest in the field of organics was mainly focused on carbonyl-based molecules,[5,9,10] which display a reversible electrochemical reactivity vs Li for nonoptimized half cells. For instance, in the case of the dilithium rhodizonate salt ($Li_2C_6O_6$) an outstanding cyclability was noted vs Li in the formal composition range "$Li_4C_6O_6$"−"$Li_6C_6O_6$" (i.e., involving two different lithiated states). Thus, inspired by the possibility of designing an organic-based Li-ion battery and taking into account the poor solubilities of highly charged anion-based salts in aprotic solvents (which will help to prevent dissolution of the electrode materials in the electrolyte, which can be a major cause of capacity loss), we have focused our attention on $Li_4C_6O_6$ and probed its electrochemical behavior vs Li both in oxidation and in reduction.

"$Li_4C_6O_6$" constitutes the two-electron reduced form of dilithium rhodizonate, which formally corresponds to the tetralithium salt of tetrahydroxybenzoquinone (THQ, 2,3,5,6-tetrahydroxy-1,4-benzoquinone).[11] The electrochemical proper-

---

[†] Laboratoire de Réactivité et Chimie des Solides, Université de Picardie Jules Verne.

[‡] State University of New York at Stony Brook.

[§] Laboratoire des Glucides, Université de Picardie Jules Verne.

(1) Mann, M. E.; Bradley, R. S.; Hughes, M. K. *Nature* **1998**, *392*, 779.

(2) Mann, M. E.; Zhang, Z.; Hughes, M. K.; Bradley, R. S.; Miller, S. K.; Rutherford, S.; Ni, F. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 13252.

(3) Armaroli, N.; Balzani, V. *Angew. Chem.* **2007**, *119*, 52; *Angew. Chem., Int. Ed.* **2007**, *46*, 52.

(4) Metzger, J. O.; Eissen, M. C. R. *Chimie* **2004**, *7*, 569.

(5) Chen, H.; Armand, M.; Demailly, G.; Dolhem, F.; Poizot, P.; Tarascon, J.-M. *ChemSusChem* **2008**, *4*, 348.

(6) Armand, M.; Tarascon, J.-M. *Nature* **2008**, *451*, 652.

(7) Anatas, P. T.; Warner, J. C. *Green Chemistry Theory and Practice*; Oxford University Press, Oxford 1998.

(8) Novák, P.; Müller, K.; Santhanam, S. V.; Hass, O. *Chem. Rev.* **1997**, *97*, 207, and references therein.

(9) Chen, H.; Basir, N. I.; Dolhem, F.; Mentré, O.; Poizot, P.; Tarascon, J.-M. *Electrochem. Solid-State Lett.* **2009**, *12*, A102.

(10) Armand, M.; Grugeon, S.; Vezin, H.; Laruelle, S.; Ribière, P.; Poizot, P.; Tarascon, J.-M. *Nat. Mater.* **2009**, *8*, 120.

(11) West, R.; Niu, J. *The Chemistry of the Carbonyl Group, Vol. 2*; Interscience: London, 1970; Chapter *4*, pp 241−276.

10.1021/ja9024897 CCC: $40.75

ties of THQ in aqueous media are well documented,[12−16] exhibiting two-electron reversible behavior on reduction to form hexahydroxybenzene (HHB). This is indicative of an efficient charge transfer process, motivating again our interest in the $C_6O_6^{4-}$ anion. Most promising, however, is that THQ can readily be produced in aqueous solution in high yield from *myo*-inositol,[17−19] a natural compound widely present in plants as phytic acid[20] (i.e., it is a renewable raw material source). Little data on the synthesis and characterization of tetraalkali metal salts of THQ have been reported. A short description of the $K_4C_6O_6$ solid was reported in 1962 by West and Niu,[21] whereas the lithiated salt $Li_4C_6O_6$ was mentioned by M. Armand in a more recent patent.[22] However, its electrochemical behavior was barely commented on and was studied upon oxidation only.

In this paper we first show that $Li_4C_6O_6$ can be produced either directly from tetrahydroxybenzoquinone or via a novel thermal disproportionation reaction of $Li_2C_6O_6$. The disproportionation reaction appears general to other alkali metal salts. We characterize the products and decomposition reaction via IR and NMR spectroscopies and thermogravimetric analysis. We show that the $Li_4C_6O_6$ salt can be both cycled reversibly in a lithium ion battery and use this material to produce the first all-organic lithium-ion battery.

2. Experimental Methods

2.1. Synthesis of $Li_4C_6O_6$ from Tetrahydroxybenzoquinone (THQ). The reaction was carried out in an argon-filled glovebox to avoid oxidation of the $C_6O_6^{4-}$ anion. At room temperature, 20 mL of a MeOLi-based solution (Aldrich, 1 M in MeOH) was slowly injected into a 20 mL solution prepared by dissolving 60 mg of THQ (Fluka) in oxygen-free dry MeOH. A dark-violet precipitate occurs immediately. After 134 h, the mother liquor was removed by centrifugation and the as-obtained solid was washed successively by methanol, THF, and ether. Finally, the solid was dried in vacuum overnight (reaction yield: 80%).

Decomposition point: >200 °C; IR (KBr disk-pellet): 1390, 1086, 517, 476 cm^{-1}; Elemental analysis: calcd for $Li_4C_6O_6$: C, 36.80%; Li, 14.18%. Found: C, 36.52%; Li, 13.89%.

2.2. Preparation of $Li_4C_6O_6$ by Thermal Disproportionation of $Li_2C_6O_6$. $Li_4C_6O_6$ was also obtained by annealing of dilithium rhodizonate at 400 °C for 1 h under Ar.

2.3. Extended Characterization. The morphology of the powders was observed by scanning electron microscopy (SEM) using QUANTA 200 F (FEI). X-ray diffraction patterns were collected on a Bruker D8 diffractometer ($CuK_{\alpha_{1-2}} = 1.54018$ Å) equipped with a Vantec detector. Each pattern was recorded for 12 h with a step of 0.034°. Temperature-controlled XRD under N_2 was performed on a Bruker D8 diffractometer equipped with an Anton Parr Chamber HTK. Each pattern (every 50 °C) was recorded with a step of 0.032° and an acquisition time of 1.5 s. Infrared spectra were collected in transmission mode using a Nicolet Avatar 370 DTGS spectrometer between 4000 and 400 cm^{-1}. Thermal analyses coupled with a mass spectrometer were performed with a Netzsch STA 449C Jupiter instrument using alumina crucibles and a heating rate of 5°C min^{-1} (gas flow 50 mL min^{-1}). ^{13}C MAS NMR spectroscopy was performed with a 5 mm probe on a Varian InfinityPlus-500 spectrometer using a magnetic field strength of 11.7 T. Spinning frequencies of 8 or 10 kHz and one pulse sequence were used to acquire the spectra. The spectra were collected at an operating frequency of 125.69 MHz, with $\pi/2$ pulses of 3.5 μs and a delay time of 150 s. All spectra were referenced to the lower frequency peak of adamantane at 38.6 ppm. Rotors with Teflon spacers were used to acquire the spectrum of $Li_4C_6O_6$, the other ($Li_2C_6O_6$) spectra being collected with the low carbon background probe, which used boron nitride spacers.

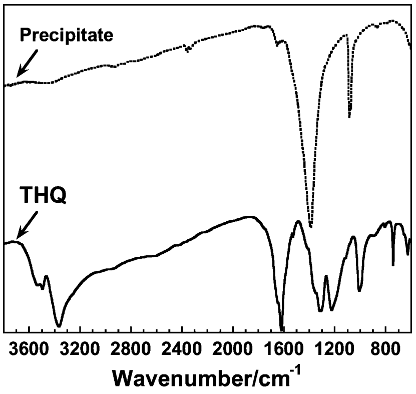


Figure 1. Infrared spectra recorded in transmission mode of both the as-prepared precipitate (dashed line) and THQ (solid line) powder.

2.4. Electrochemical Behavior with Lithium. Unless otherwise noted, the electrochemical performances were tested vs Lithium in Swagelok-type cells using a Li metal disc as a negative electrode and a fiberglass separator soaked with a molar $LiPF_6$ solution (in ethylene carbonate dimethyl carbonate/1:1 in volume ratio) as the electrolyte. The positive electrode was prepared without binder by ball-milling $Li_4C_6O_6$ powder with 20% carbon Ketjen Black (in total mass) for 5 min. Mechanical mixing was carried out on a Retsch PM100 mixer mill under an Ar atmosphere. The powder and three stainless steel balls (diameter 10 mm) were stowed in a stainless steel milling container (capacity 25 mL). Cells were cycled in a galvanostatic mode using a Macpile or a VMP system (Biologic S.A., Claix, France) at a rate of one lithium ion exchanged in 10 h (denoted 1 Li$^+$/10 h).

3. Results and Discussion

$Li_4C_6O_6$ was synthesized by using West's method, replacing the potassium precursor with MeOLi. An excess of lithium methoxide dissolved in methanol was reacted with THQ neutralizing all its enediolic functions, the reaction being carried out in an inert atmosphere to avoid oxidation of the tetraanion.[21] A dark-violet precipitate, which can easily be separated by centrifugation, occured as the reaction proceeds. After washing and drying, the as-produced compound, which was isolated in a 80% yield, was characterized using several techniques. The recovered powder was found to be air-sensitive due to its reducing properties, as reported by West and Niu for the potassium form.[21] The solid composition was confirmed by chemical analyses, and the corresponding IR spectrum (Figure 1) contains two main vibrations only at similar energies to those for $K_4C_6O_6$, (e.g., 1450 and 1050 cm^{-1}) but is clearly quite different from that of THQ.

---

[12] Souchay, P.; Tatibouet, F. *J. Chim. Phys.* **1952**, *49*, C108.
[13] Fleury, M. B.; Molle, G. *Electrochim. Acta* **1975**, *20*, 951.
[14] Moiroux, J.; Escourrou, D.; Fleury, M. B. *Electrochim. Acta* **1980**, *25*, 785.
[15] Moiroux, J.; Escourrou, D.; Fleury, M. B. *Bioelectrochem. Bioener.* **1980**, *7*, 333.
[16] Kokkinidis, G.; Sazou, D.; Moumtzis, I. *J. Electroanal. Chem.* **1986**, *213*, 135.
[17] Gelormini, O.; Artz, N. E. *J. Am. Chem. Soc.* **1930**, *52*, 2483.
[18] Holgan, F. A.; Bartow, E. *J. Am. Chem. Soc.* **1940**, *62*, 2397.
[19] Preisler, P. W.; Berger, L. *J. Am. Chem. Soc.* **1942**, *64*, 67.
[20] Sands, S. H.; Biskobing, R. J.; Olson, R. M. *Phytic Acid, Chemistry and Applications*; Pillatus Press: Minneapolis, MN, 1986.
[21] West, R.; Niu, H. Y. *J. Am. Chem. Soc.* **1962**, *84*, 1324.
[22] Armand, M.; Michot, C.; Ravet, N. Patent WO 9928984 A1, 1999.

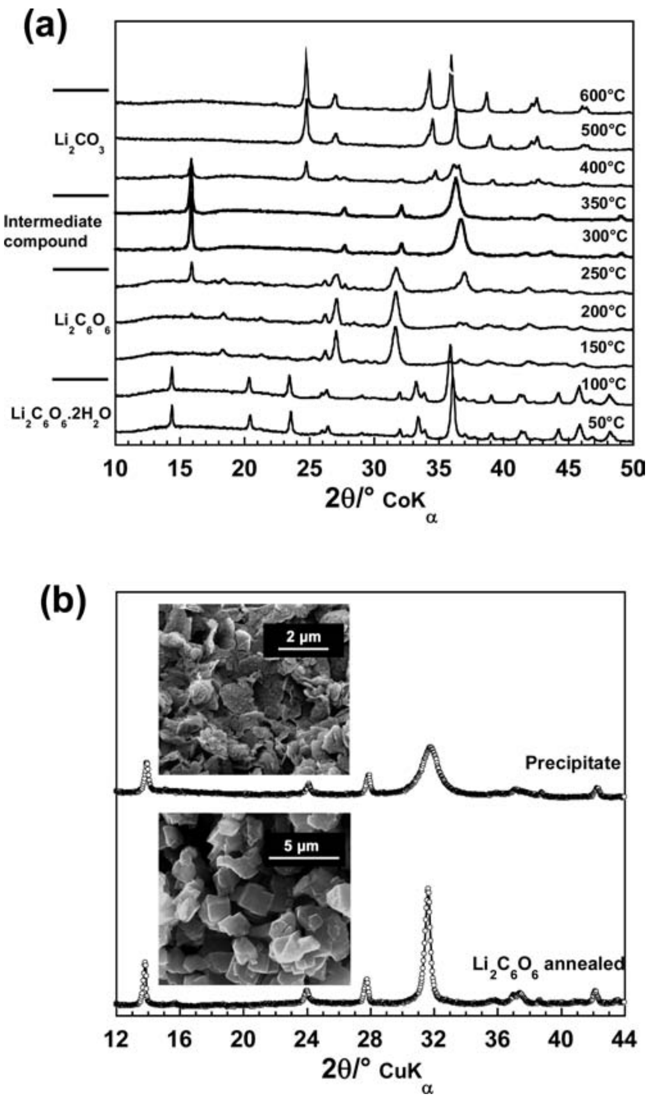


Figure 2. (a) Temperature-controlled XRD patterns under N_2 of $Li_2C_6O_6 \cdot 2H_2O$. The transformation into a new phase occurs within the 300−400 °C range prior to Li_2CO_3 formation. (b) XRD patterns and corresponding scanning electron micrograph for both the directly synthesized $Li_4C_6O_6$ and the compound obtained after $Li_2C_6O_6$ annealing under argon at 400 °C, indicating the presence of the same crystalline phase.

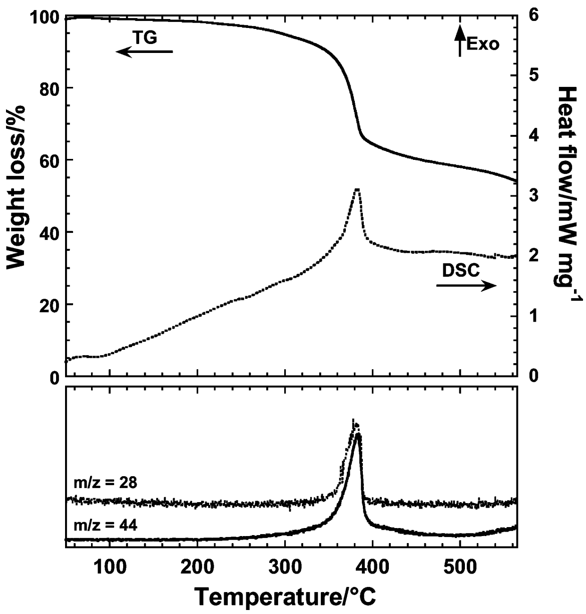


Figure 3. Coupled thermal analysis and mass spectrometry measurements of anhydrous dilithium rhodizonate at a heating rate of 5 °C min^{-1} under argon flow. The counting time for MS is of 20 ms per *m*/*z* values with a resting time of 1 s. Both CO and CO_2 gases are released at ∼380 °C, corresponding to a 35% weight loss.

The powder was also characterized by powder X-ray diffraction in the absence of air, using a specially designed cell,[23] but the poor crystallinity made the indexation of the peaks difficult. Interestingly, to address the constant concern in the use of organics in many solid state applications, be they electronics or photonics, i.e., their thermal stability, we had previously studied the thermal behavior of $Li_2C_6O_6 \cdot 2H_2O$ under both air and neutral atmosphere.

To our surprise, the typical XRD pattern of the dark-violet precipitate was similar to patterns obtained during the course of the thermal treatment of $Li_2C_6O_6 \cdot 2H_2O$ (Figure 2a), under N_2, at intermediate temperatures, between the dehydration process and the exothermic decomposition leading to Li_2CO_3 (i.e., 250°C < T < 450°C). Figure 2b shows the XRD pattern of as-synthesized $Li_4C_6O_6$ and together with a typical pattern for a $Li_2C_6O_6$ powder after annealing under argon at 400 °C. The same crystalline phases are clearly present. To obtain further insight into this unexpected temperature-driven evolution of $Li_2C_6O_6$, thermogravimetric analyses (TGA) coupled with mass spectrometry (MS) measurements were undertaken (Figure 3). The first significant weight loss of 35% is observed near 380 °C, which is associated with an exothermic phenomenon that corresponds to a CO_2/CO evolution, as deduced from mass spectroscopy. However, the amount of each released gas could not be deduced, because these MS measurements are not quantitative. In light of these observations, the thermal decomposition of $Li_2C_6O_6$ under an inert atmosphere occurs via a disproportionation mechanism producing both lithiated THQ and the unstable anhydrous triquinoyl molecule, the latter being rapidly converted to carbon monoxide (Scheme 1). The pure C_6O_6 entity has never been isolated because triquinoyl is stabilized in its octahydrate form $C_6(OH)_{12} \cdot 2\ H_2O$ only, the latter decomposing at 99 °C.[11]

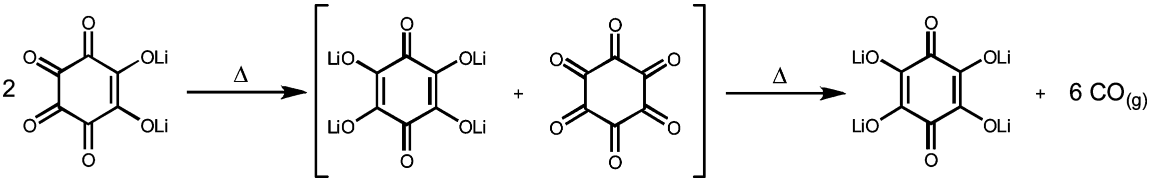
A conventional ^{13}C NMR liquid-phase spectrum of this material could not be obtained due to its very low solubility in all common organic solvents. The ^{13}C MAS NMR spectrum of the solid $Li_4C_6O_6$ phase (Figure 4a) is dominated by a broad resonance at 156 ppm, which is quite distinct from the ^{13}C NMR spectra of both the THQ and $Li_2C_6O_6$ phases: THQ contains two distinct resonances at 180 and 134 ppm, with an intensity ratio of 1:2, due to the carbonyl and alcohol groups, respectively,[24] while $Li_2C_6O_6$ gives rise to resonances at 175 and 180 ppm (Figure 4b, 180°C spectrum), which are ascribed to a resonance structure involving the carbonyl and $C{-}O^-$ groups of this anion (175 ppm) and carbonyl groups (180 ppm). The resonance at 169 ppm in this spectrum is tentatively ascribed to Li_2CO_3, on the basis of its chemical shift and the fact that the intensity of this resonance varies slightly from sample to sample. The resonance at 111 ppm is due to the Teflon in the MAS rotor. The shift of the ^{13}C resonances from $Li_2C_6O_6$ to

---

(23) Morcrette, M.; Chabre, Y.; Vaughan, G.; Amatucci, G.; Leriche, J.-B.; Patoux, S.; Masquelier, C.; Tarascon, J.-M. *Electrochim. Acta* **2002**, *47*, 3137.

(24) Philipsborn, W. *Pure Appl. Chem.* **1974**, *40*, 159.

Scheme 1. Solid-State Disproportionation Reaction of Dilithium Rhodizonate under Argon Flow Producing the Tetralithium Salt of the Tetrahydroxybenzoquinone



$Li_4C_6O_6$ is consistent with the reduction of the carbon atoms, and the reduction in the double bond character of the C−O bonds, the carbon atom in the fully reduced material, HHB, resonating at 128 ppm.[25] However, the shift of $Li_4C_6O_6$ is slightly higher than the average chemical shift of the ^{13}C atoms in THQ (149 ppm), which is ascribed to the increased aromatic character of the $C_6O_6^{4-}$ anion in the lithiated material. The simplicity of the NMR spectrum of $Li_4C_6O_6$ (namely the observation of one, major albeit broad, resonance), in comparison to that of THQ (which contains resonances separated by more than 40 ppm), shows that all six carbons are chemically similar (i.e., the C−O bond lengths and bond orders are similar). This indicates that a resonance form, involving delocalization of the charge over all six-carbon atoms, is present, consistent with the IR spectrum of this material (which also suggests that the symmetry of the $C_6O_6^{4-}$ ion is higher than that found in THQ). However, the breadth of the resonance suggests that there is more than one crystallographically distinct carbon atom (i.e., the environments are not identical, and not surprisingly, that symmetry of this ion in the solid state is lower than C_6). Again, this is consistent with the IR spectrum of this compound, as discussed previously for $K_4C_6O_6$.[21] This symmetry lowering will originate from both the nature of the packing of the $C_6O_6^{4-}$ ions and the bonding arrangements of the Li^+ ions surrounding the $C_6O_6^{4-}$ ions, leading to very slight variations in the C−O bond lengths.

There are only a few examples of solid-state disproportionation of organic substances in the literature,[26] constituting an interesting result in itself. Scheme 1 would imply a weight loss of ∼46%, larger than the experimental value (35%, Figure 3). This discrepancy is ascribed to the thermodynamic instability of carbon monoxide for $T < 980$ K under $p = 1$ bar (i.e., 2 $CO_{(g)} \rightleftharpoons C_{(s)} + CO_{2(g)}$, Boudouard's equilibrium). Under constant argon flow, this equilibrium is shifted to the right side producing carbon and CO_2 and an expected weight loss restricted to 36%, which is very close to the value obtained in the TG measurement. The thermal decomposition of $Li_2C_2O_6 \cdot 2H_2O$ was also followed by ^{13}C MAS NMR (Figure 4b). As expected, the spectrum of the sample heated to 180 °C corresponds to that of $Li_2C_6O_6$.[5] On further heating, decomposition occurs, and no well-resolved resonances can be observed above the very broad baseline, for the 300 °C sample. By 350 °C a distinct resonance becomes visible at ∼160 ppm, at a similar shift position to that found for directly synthesized $Li_4C_6O_6$ phase. On further heating to 400 °C, the resonance sharpens, and a smaller shoulder is observed to higher frequency. A very broad resonance at ∼125 ppm is seen, which can be ascribed to coke formation, consistent with CO disproportionation. To determine whether similar thermal disproportionation mechanisms occur in the other dialkali metal salts of rhodizonate, the experiments were repeated with $Na_2C_6O_6$ and $K_2C_6O_6$ under inert atmospheres. The same transformation sequence as that for $Li_2C_6O_6$ was observed, suggesting that the disproportion mechanism appears to hold for the thermal evolution of the oxocarbons regardless of the nature of the alkali metal. One driving force for this reaction is the increased aromaticity of the $C_6O_6^{n-}$ ring.

The electrochemical performances of both synthesized $Li_4C_6O_6$ and annealed $Li_2C_6O_6$ were tested vs Li in Swagelok-type cells. As expected, the electrochemical features for the two samples are quite similar, exhibiting two reversible plateaus at 1.9 and 1.75 V vs Li in reduction, respectively (Figure 5a,b). The specific capacity reaches ∼200 mAh g^{-1} involving a two-electron mechanism per formula unit. Thus this electrochemical reactivity appears quite similar to the one of THQ reported in aqueous solution[12−16] leading here to the fully lithiated salt of HHB. It is worth noting that excellent capacity retention is observed, particularly for the thermal treated sample, where there is a capacity decay of only 10% after 50 cycles for an average potential of 1.8 V. Note also a fairly low irreversible part close to 10% after the first cycle associated with a low polarization value. As a general trend, the electrochemical performances are better for the material obtained from annealed $Li_2C_6O_6$ probably due to the extra carbon generated during the disproportionation reaction. In a rate capability study,[5] this sample maintains 90% of its initial capacity at a 1C rate (Figure 5c). Finally, it should be stressed that the shape of the potential−capacity curve is very similar to the one obtained at low potential (below 1.8 V) for a $Li_2C_6O_6$/Li cell.[5] Furthermore, the ^{13}C NMR spectrum of electrode material extracted from a $Li_2C_6O_6$ cell discharged to 2.2 V contains a broad resonance at 157 ppm, consistent with the presence of $Li_4C_6O_6$. However, additional resonances at ∼174 and 144 ppm are also observed in this spectrum, due to

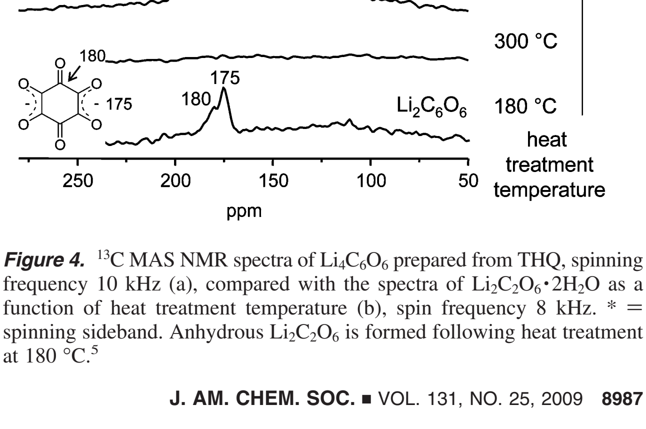


Figure 4. ^{13}C MAS NMR spectra of $Li_4C_6O_6$ prepared from THQ, spinning frequency 10 kHz (a), compared with the spectra of $Li_2C_2O_6 \cdot 2H_2O$ as a function of heat treatment temperature (b), spin frequency 8 kHz. * = spinning sideband. Anhydrous $Li_2C_2O_6$ is formed following heat treatment at 180 °C.[5]

---

[25] Teng, J.; Zubarev, E. R. *J. Am. Chem. Soc.* **2003**, *125*, 11840.

[26] Stevenson, G. R.; Zigler, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 2513.

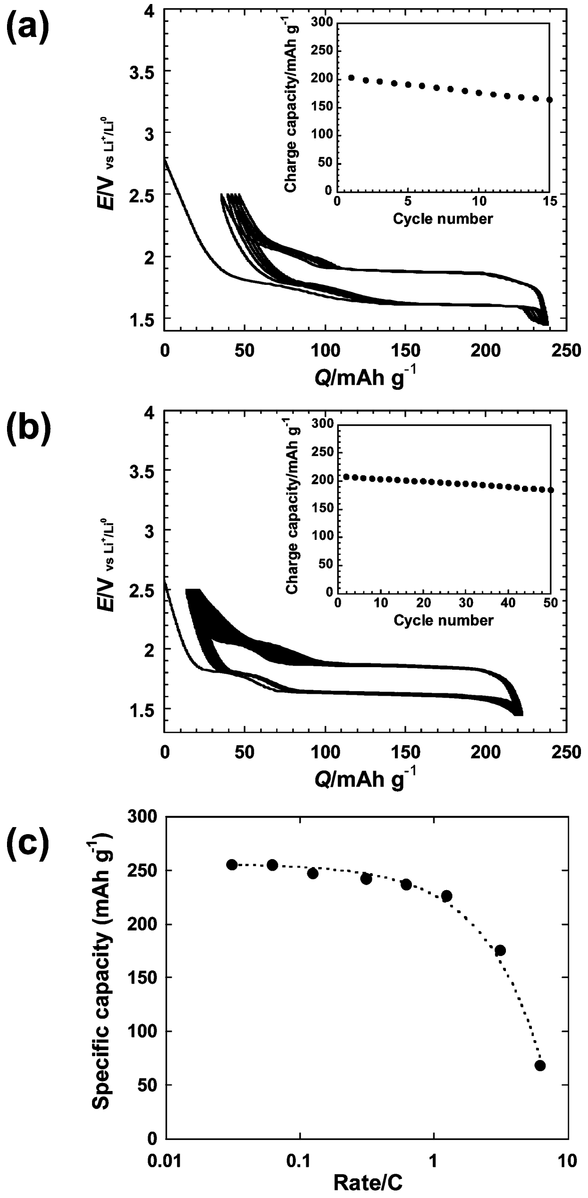


Figure 5. Room temperature potential-capacity curve for a Li half cell using (a) $Li_4C_6O_6$ synthesized in methanol and (b) produced by disproportionation of $Li_2C_6O_6$ at 400 °C. Inset: the corresponding capacity retention curve. (c) Rate capability of $Li_4C_6O_6$ produced by disproportionation of $Li_2C_6O_6$.

less and more reduced C−O groups, respectively, indicating that the reduction process is more complex in the case of $Li_2C_6O_6$, consistent with the different electrochemical processes seen at higher voltages for this material in the electrochemistry experiments.[5] Finally, since the $Li_4C_6O_6$ oxocarbon salt exhibits an intermediate oxidation state between $Li_2C_6O_6$ and the fully reduced $Li_6C_6O_6$ form, it is also possible to design a symmetrical Li-ion cell, as was done previously with $Li_xMo_6Se_6$[27] or $Li_{1+x}Mn_2O_4$.[28] Thus the use of a $Li_4C_6O_6$-based symmetrical cell or the charged version $Li_2C_6O_6$/$Li_6C_6O_6$ constitutes the first example toward a "greener and sustainable" Li-ion battery that is readily recycled and has a low CO_2 footprint. For instance, the electrochemical behavior of a $Li_2C_6O_6$/$Li_6C_6O_6$ cell is shown in Figure 6. However, we are far from reaching acceptable performances for most applications since the output voltage is quite low, but we hope that this first attempt illustrates some of the advantages of utilizing C═O-bearing organic molecules that react with Li through two-step processes, separated by a ΔV. Since each ΔV is based on the respective potential values of each process, these can be tuned by chemical modification (e.g., by altering the nature of the active species, substituting functional groups, or adding heteroatoms), so as to either separate or merge the two redox processes.

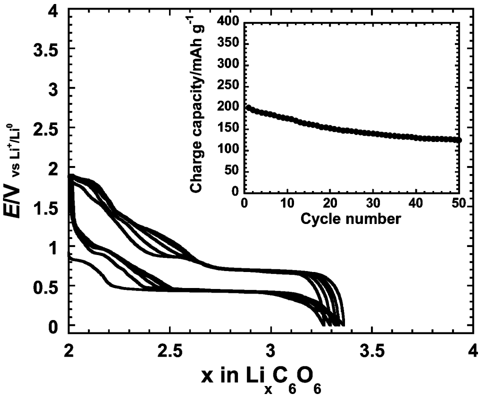


Figure 6. Voltage−composition profile for galvanostatically cycled $Li_2C_6O_6$/$Li_6C_6O_6$ cell (nonoptimized) at a rate of 1 Li^+/10 h. Inset: corresponding capacity retention curve.

4. Conclusions

In summary, through the simple $Li_4C_6O_6$ salt, we have demonstrated the feasibility of designing advanced Li-ion batteries that display a more efficient life cycle assessment (LCA), compared to present technology based on inorganic electrode materials, thanks to the incorporation of redox-active organic materials. Because such compounds can be synthesized from renewable resources in water, "sustainable" materials characterized by low CO_2 footprints can be envisioned as next generation electrode materials. Moreover, an unusual solid-state disproportionation reaction of $Li_2C_6O_6$ leading to $Li_4C_6O_6$ was observed. We show that an all-organic battery using this material can be designed. Although the operating voltage of this battery is low, it should be possible to tune the potential values of the oxidation and reduction processes via chemical substitutions, providing multiple opportunities in the future. Our current efforts are now focused on multifunctional molecules in which the Li salt can be oxidized while remaining air stable.

Acknowledgment. This work was supported by the Région Picardie. The authors thank Mathieu Morcrette for fruitful discussions. C.P.G. and M.J. thanks the Office of FreedomCAR and Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, via subcontract No. 6517749 with the Lawrence Berkeley National Laboratory, for support, and H. Huo and N. Leifer for help with the NMR data collection and analysis.

JA9024897

---

(27) Tarascon, J.-M. *J. Electrochem. Soc.* **1985**, *132*, 2089.

(28) Tarascon, J.-M.; Guyomard, D. *J. Electrochem. Soc.* **1991**, *138*, 2864.