High-Potential Reversible Li Deintercalation in a Substituted Tetrahydroxy*p*-benzoquinone Dilithium Salt: An Experimental and Theoretical Study

Anne-Lise Barrès,^[a, b] Joaquin Geng,^[a, b] Gaëtan Bonnard,^[a] Stéven Renault,^[a, b] Sébastien Gottis,^[a, b] Olivier Mentré,^[c] Christine Frayret,^[a] Franck Dolhem,^[b] and Philippe Poizot^{*[a]}

a simple three-step method, lithiated

Abstract: Efficient organic Li-ion batteries require air-stable lithiated organic structures that can reversibly deintercalate Li at sufficiently high potentials. To date, most of the cathode materials reported in the literature are typically synthesized in their fully oxidized form, which restricts the operating potential of such materials and requires use of an anode material in its lithiated state. Reduced forms of quinonic structures could represent examples of lithiated organic-based cathodes that can deintercalate Li⁺ at potentials higher than 3 V thanks to substituent effects. Having previously recognized the unique electrochemical properties of the C₆O₆-type ring, we have now designed and then elaborated, through

3,6-dihydroxy-2,5-dimethoxy-p-benzoquinone, a new redox amphoteric system derived from the tetralithium salt of tetrahydroxy-p-benzoquinone. Electrochemical investigations revealed that such an air-stable salt can reversibly deintercalate one Li+ ion on charging with a practical capacity of about 100 mAhg^{-1} at about 3 V, albeit with a polarization effect. Better capacity retention was obtained by simply adding an adsorbing additive. A tetra-

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hydrated form of the studied salt was also characterized by XRD and firstprinciples calculations. Various levels of theory were probed, including DFT with classical functionals (LDA, GGA, PBEsol, revPBE) and models for dispersion corrections to DFT. One of the modified dispersion-corrected DFT schemes, related to a rescaling of both van der Waals radii and s_6 parameter, provides significant improvements to the description of this kind of crystal over other treatments. We then applied this optimized approach to the screening of hypothetical frameworks for the delithiated phases and to search for the anhydrous structure.

Introduction

The global search for electrical energy storage (EES) systems displaying high performance with low environmental

[a] Dr. A.-L. Barrès, Dr. J. Geng, G. Bonnard, Dr. S. Renault, Dr. S. Gottis, Dr. C. Frayret, Dr. P. Poizot Laboratoire de Réactivité et Chimie des Solides - UMR CNRS 7314 Institut de Chimie de Picardie - FR 3085 CNRS Université de Picardie Jules Verne 33, rue Saint-Leu, 80039 Amiens cedex (France) Fax: (+33) 322827590 E-mail: philippe.poizot@u-picardie.fr [b] Dr. A.-L. Barrès, Dr. J. Geng, Dr. S. Renault, Dr. S. Gottis, Dr. F. Dolhem

Laboratoire des Glucides - UMR CNRS 6219 Institut de Chimie de Picardie - FR 3085 CNRS Université de Picardie Jules Verne 33, rue Saint-Leu, 80039 Amiens cedex (France) [c] Dr. O. Mentré

Unité de Catalyse et de Chimie du Solide Équipe de Chimie du Solide - UMR CNRS 8181 ENSC Lille-UST Lille Cité Scientifique - Bât. C7 - BP 80108 59655 Villeneuve d'Ascq cedex (France)

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burden and affordable price is a major technological challenge to promoting a clean energy economy.^[1] Among the various types of EES devices, the rechargeable battery system is a critical energy converter in many respects.^[2] Day and night, in stationary or portable mode, on a large or very small scale, accumulators can directly convert almost reversibly stored chemical energy to direct current. In spite of intensive research and innovation, no universal accumulator or universal chemistry meets all of the possible requirements so far; this means managing existing battery technologies to best meet the required specifications. Basically, the chemistry of electroactive species involved in batteries has not substantially changed since the invention of the first rechargeable battery by G. Planté in 1859, and is dominated by metal-based electroactive components derived from mineral resources. However, to meet the ever-increasing power demand while limiting the environmental footprint, organicbased batteries could be foreseen as an interesting parallel research path for the future, since organic compounds have some advantages such as an abundance of raw materials (e.g., use of biomass) and easy recycling.^[2,3]

In principle, redox-active organic structures could be implemented in a wide variety of existing battery technologies. However, in practice, development of efficient organic elec-

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trodes is clearly in its early stages, and much remains to be done, especially if we expect to transpose existing rockingchair technology to organic electrode materials. Promising results have already been obtained, in particular with polymer-based electrodes^[3] (original concept of organic radical batteries, ORBs) and more recently with small molecules like lithiated quinonic-type structures.^[4] To go further, it seems that one of the remaining problems is to identify stable, insoluble, and efficient organic structures that can accommodate lithium at very different Fermi levels in order to enable a large enough output voltage of the cell. Although several kinds of organic structures can react in reduction (e.g., see the overview in ref. [2]), it appears particularly difficult to find air-stable lithiated organic materials that can reversibly deintercalate lithium on cycling at high enough potentials. For instance, in our previous investigations on dilithium rhodizonate^[5] ($Li_2C_6O_6$) and dilithium chloranilate^[6] $(Li_2C_6O_4Cl_2)$, we observed that these two salts exhibit very poor activity on oxidation whatever the cutoff potential, while Xiang et al.^[7] reported no electrochemical response for parent structure Li₂H₂C₆O₄ (Figure 1a). Dahn and coworkers^[8] recently reported a polymer based on a lithiated naphthazarin unit that reacts at an average potential of 3 V, but this material exhibits limited electrochemical perfor-



Two-electron reduction process (Q_{th.} ~252 mAh g⁻¹): System 2



Figure 1. a) Chemical formulas of lithiated 1,4-benzoquinone derivatives previously studied versus Li. b) Chemical formulas of TMQ, Li_2DHDMQ , and Li_4THQ . c) Schematic of the expected reversible Li-ion insertion/deinsertion in Li_2DHDMQ with oxidation limited to a one-electron process (deeper oxidation is not favored due to the biradical nature of the thus-produced compound).

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mance coupled with an intriguingly high polarization value (i.e., charge/discharge potential difference).

Benefiting from our observations on quinonic-type structures and the efficient and unique electrochemical properties of the Li₄C₆O₆-type unit,^[4] we recently designed two series of organic salts that can reversibly deintercalate lithium. We first focused on lithiated 3,6-dihydroxy-2,5-dimethoxy-p-benzoquinone (Li₂DHDMQ), an intermediate structure between the tetralithium salt of tetrahydroxy-pbenzoquinone (Li₄THQ) and tetramethoxy-p-benzoquinone (TMQ), which has not been reported to date (Figure 1b). Thanks to its redox amphoteric nature, this salt was indeed expected to be electrochemically active in reduction (System 2 in Figure 1 c) but also in oxidation according to a one-electron process (System 1 in Figure 1c). Here we report on the chemical synthesis of Li₂DHDMQ, which is based on a simple three-step method, and discuss its electrochemical performances versus Li in comparison with those of parent structures. A theoretical study at the DFT and dispersion-corrected DFT (DFT-D) levels of theory was also performed. The general objective of this computational study was first to test various methodologies for their abilities to account for powder structural properties. Lattice constants, stacking parameters, intramolecular bond lengths,



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this work, we restricted our scope to phases originating from the lithiated compound, without extending the search to the whole set of crystals, considering all possible structural arrangements. The most stable phase among various hypothetical structural frameworks was selected with a view to providing a computational estimation of the deintercalation potential.

Results and Discussion

Synthesis and characterization of Li₂DHDMQ and related compounds: The chosen synthetic route to prepare Li₂DHDMQ starts with the preparation of TMQ by the protocol described by Verter et al.,^[10] which consists of the reaction of chloranil (2,3,5,6-tetrachlorocyclohexa-2,5-diene-1,4-dione) with a solution of methanolate. Inspired by the work of Eistert et al.,^[11] which described the synthesis of the corresponding potassium salt K2DHDMQ, we prepared the lithium salt by a simple saponification procedure in which TMQ was treated with LiOH·H₂O in water. The final brown product was isolated in 93% yield. Chemical/physical properties of the as-prepared compound were characterized by thermal/elemental analyses and IR/NMR spectroscopy (Figures S1 and S2 in the Supporting Information), which led to the conclusion that a hydrated form was obtained. Clear proof was readily obtained by thermal analysis coupled with mass spectrometry (Figure 2). Indeed, the thermogravimetric (TG) curve shows a first weight loss of about 20% associated with several endothermic phenomena and the release of water molecules (as detected by MS). Then a second weight loss beyond 250°C involves thermal decomposition



Figure 2. Coupled thermal analysis and mass spectrometry of Li₂DHDMQ-3 H₂O at a heating rate of 10 °C min⁻¹ under argon flow. The counting time for MS is 20 ms per m/z value with a resting time of 1 s $(m/z \ 18$ is ascribed to H₂O, 28 to CO, and 44 to CO₂).

of the organic structure. From this first series of characterization it was possible to ascribe Li_2DHDMQ ·3H₂O as chemical formula for the brown compound.

The solid appears to be crystalline according to X-ray powder diffraction (XRPD) measurements (Figure 3). Small purple needles suitable for single-crystal XRD were grown



Figure 3. XRPD pattern of $Li_2DHDMQ-3H_2O$ (top) compared to that of $Li_2DHDMQ-4H_2O$ (bottom).

by slow evaporation of a concentrated aqueous solution of Li₂DHDMQ•3H₂O. Surprisingly, the crystal structure clearly showed a tetrahydrate phase instead of the expected trihydrate. Li₂DHDMQ·4H₂O crystallizes in monoclinic space group $P2_1/n$ with two independent water molecules per quinone half-molecule in the asymmetric unit. One of the two independent water molecules has a disordered hydrogen atom occupying two sites denoted $H_{2b'}$ and $H_{2b''}$ (Figure 4). Molecules are stacked along the *a* axis and linked together through a lithium coordination network in the bc plane forming a layered structure. Lithium is pentacoordinate, with three oxygen atoms from the *p*-benzoquinone derivative (i.e., C=O, CO⁻, and MeO) and two water molecules. One of these water molecules is included in the molecular layer, and the other lies between the layers. The large distance (4.66 Å) between two stacked molecules could be explained by the cumbersome methyl groups pointing out of the layer and especially by the presence of this intercalated water molecule. In the crystal structure of TMQ, this interplanar distance is only 3.51 Å.^[12]

Furthermore, the bulky methyl terminal groups prevent face-to-face stacking of the *p*-benzoquinone and induce slipping of the overlying sheet. Finally, contrary to anhydrous TMQ, which has a weak intermolecular hydrogen-bond network based on C-H···O interactions from methyl groups, this structure exhibits a hydrogen-bond network developed through the hydrogen atoms of the water molecules. They are engaged in five different hydrogen bonds, involving two oxygen atoms from the *p*-benzoquinone and the oxygen atoms of the water molecules (Figure 4b). More precisely, the two oxygen atoms from unsubstituted CO groups interact with two hydrogen atoms from the first water molecule $(O-H···O 1.82(2) \text{ Å}, 176(2)^\circ; O-H···O 1.88(2) \text{ Å}, 168(2)^\circ)$

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Figure 4. a) View along the *b* axis of the layered structure of Li₂DHDMQ-4H₂O. Hydrogen atoms of methyl groups are omitted for clarity. b) View of a layer along the *a* axis showing lithium coordination polyhedra and highlighting the hydrogen-bond network (dashed lines). Nomenclature for water molecules is also detailed, whereby $H_{2b'}$ and $H_{2b''}$ are relative to the disordered hydrogen atom with an occupancy of 0.5.

and with one of the three hydrogen atoms belonging to the second water molecule (O–H···O 2.23(7) Å, 144(6)°). The last two hydrogen bonds are observed between the two remaining hydrogen atoms from the latter water molecule and the oxygen atom from the two other water molecules (O–H···O 2.03(4) Å, 150(4)°; O–H···O 2.15(7) Å, 179(7)°).

To obtain the tetrahydrate in a larger amount and further characterize it, we considered its synthesis from the trihydrate. Interestingly, the latter can be readily converted to the tetrahydrate analogue by further hydration in a watersaturated atmosphere. The brown powder turned purple on further hydration, in agreement with the color of the crystals of Li₂DHDMQ•4H₂O previously obtained. Finally, the obtained tetrahydrate phase was fully confirmed by means of a profile-matching refinement of the XRPD pattern with cell parameters obtained from single-crystal XRD structure resolution (Figure S3 in the Supporting Information). Good agreement between observed and calculated patterns proved the purity of our crude material ($R_p = 7.60, R_{wp} =$ 7.77). However, the corresponding thermal analysis data showed some differences in the dehydration process in comparison with Li₂DHDMQ•3H₂O (Figure 5). While the presence of four water molecules is confirmed by the TG curve,



Figure 5. Coupled thermal analysis and mass spectrometry of Li₂DHDMQ-4 H₂O at a heating rate of 10 °C min⁻¹ under argon flow. The counting time for MS is 20 ms per m/z value with a resting time of 1 s $(m/z \ 18 \text{ is ascribed to H}_2O, 28 \text{ to CO}, \text{ and 44 to CO}_2)$.

water loss now involves two distinct steps but without involving a trihydrated phase as intermediate, although the quite similar appearance of the two TG/DSC traces beyond 250 °C reveals a common decomposition reaction path (Figures 2 and 5). We attempted to produce the anhydrous Li₂DHDMQ phase for testing as electrode material versus Li and to reveal more details of the thermal dehydration process of the two hydrates by performing temperature-controlled powder XRD experiments on the two hydrates from room temperature to 550 °C under N₂ at a heating rate of $0.2^{\circ}Cs^{-1}$, in accordance with the thermal analysis experiments (Figure 6).

Unexpectedly, the tetrahydrate undergoes direct amorphization beyond 60°C, while dehydration of the trihydrate makes formation of crystallized Li₂DHDMQ possible; the latter is obtained in pure form for temperatures ranging from 150 to 230 °C. This fast amorphization step is supported by the DSC measurement showing a first endothermic peak near 70°C (Figure 2), which is not present at all in Figure 5. On heating, a common new phase arises between 300 and 350 °C for the two hydrates, and turned out to be Li₂CO₃, in accordance with the expected thermal decomposition of such compounds. As discussed below, it is better to use anhydrous compounds as electrode materials to avoid side reactions with water in the electrochemical cell. We exploited dehydration of the trihydrate to produce anhydrous Li₂DHDMQ. However, we used the freeze-drying technique (lyophilization) to remove water, since this method, besides being commonly used in organic and biochemistry for fragile compounds like proteins,^[13] can produce very small particles because it leaves microscopic pores.^[14] Residual water was then removed by a short thermal annealing step under





Figure 6. Temperature-controlled XRPD experiment performed under N₂ flow on a) Li₂DHDMQ-4H₂O and b) Li₂DHDMQ-3H₂O. Circles denote peaks of Li₂CO₃ phase, and stars peaks emanating from the sample holder (reported only at T=300 and 550 °C for the sake of conciseness).

vacuum at 180 °C. Finally, Scheme 1 recaps the synthesis routes to get Li_2DHDMQ and the related compounds observed in our investigation.

Electrochemical reactivity of $Li_2DHDMQ \cdot yH_2O$ (y = 4, 3, 0) versus Li: Electrochemical behavior of hydrates 2, 3 and the



Scheme 1. Synthesis of Li₂DHDMQ•y H₂O (y=4, 3, 0).

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During the charging process all curves exhibited a well-defined plateau near 3.4 V related to a capacity of $x_{\text{Li}} \ge 0.8$ (i.e., $\geq 80\%$ of the theoretical value of System 1 in Figure 1 c). In the subsequent discharge process the plateau is mainly recovered for 3 and 4 and completed with a slopingtype profile up to $x_{1,i}=2$ (starting composition), whereas the tetrahydrate exhibits a more complex behavior. Like for the polymer based on a lithiated naphthazarin unit,^[8] this electrochemical deintercalation/intercalation process unfortunately suffers from a large polarization value of about 900 mV, which greatly reduces the energy efficiency of such an electrochemical reaction. Note that the polarization effect is slightly decreased after the first cycle for compounds 3 and 4. Beyond $x_{Li}=2$, the redox amphoteric nature of such compounds makes reduction of the quinonic skeleton possible, too (Figure 1c, System 2). Within this potential-composition domain, the two hydrated phases involve a reversible plateau followed by a sloping-type profile. The lithium uptake is, however, restricted to $x_{Li}=3$, which

corresponding anhydrous compound **4** obtained by freezedrying were first measured versus Li by a similar procedure

to our previous studies.^[4-6] In particular, we used Swagelok-

type electrochemical cells, simple hand-milling of the active

materials with carbon black without binder, and a molar

 $LiPF_6$ solution in ethylene carbonate/dimethyl carbonate as electrolyte. Under such experimental conditions, a preliminary investigation showed that degradation of the compounds

may occur at both too high and too low potentials, and

hence the potential window was restricted to the range 3.5-

1.5 V versus Li⁺/Li⁰. Figure 7 shows the corresponding first

charge/discharge profiles recorded at a typical cycling rate

of one Li⁺ exchanged in 10 h. As expected, reversible elec-

trochemical activity was systematically observed on oxida-

tion, unlike dilithium rhodizonate or dilithium chloranilate.

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Figure 7. Typical potential–composition curve of Li₂DHDMQ-yH₂O/Li cell (y=4, 3 and 0) galvanostatically cycled between 3.5 and 1.5 V versus Li⁺/Li⁰ at a rate of 1Li⁺ exchanged in 10 h with EC–DMC/LiPF₆ 1 m as electrolyte.

seems to indicate a limited reduction process. Interestingly, compound 4 shows quite a different electrochemical feature, as it involves a series of sloppy plateaus dropping step by step, which leads to a larger capacity value. Within this lower potential window (i.e., 1.5-2.5 V), the polarization effect is much more reasonable for the three compounds. In accordance with other studies,^[5-7] it appears that the anhydrous phase exhibits the best electrochemical performance on cycling. Indeed, the presence of water generally induces some side reactions with the electrolyte and a worse electrochemical performance as a consequence. Nevertheless, a noticeable decrease in capacity on cycling is still noticed with Li₂DHDMQ, due to a certain solubility in the liquid carbonate-based electrolyte, like that previously observed with Li₂C₆O₄Cl₂, another parent structure.^[6] Importantly, it was also checked that the electrochemical feature of the potential-composition curve is maintained whatever the adopted cycling direction, that is, by first discharging the cell till 1.5 V before subsequent cycling within the potential range of 3.5–1.5 V versus Li⁺/Li⁰.

Further electrochemical investigations focused on the anhydrous compound. First, to gain insight into the hysteresis effect at high potential, another Li₂DHDMQ/Li cell was cycled by using the galvanostatic intermittent titration technique (GITT) to obtain a charge/discharge curve closer to thermodynamic equilibrium. Experimentally, a constant cur-



Figure 8. Potential–composition curve focusing on the high-potential region for a Li half-cell using Li₂DHDMQ prepared by freeze-drying and cycled in GITT mode at a rate of one Li⁺ exchanged in 10 h for $\Delta x = 0.1$ followed by relaxation period of 20 h ($T=21\pm0.1$ °C). The dashed line correspond to the GITT charge/discharge near-equilibrium potential curve.

rent equivalent to a cycling rate of one Li⁺ exchanged in 10 h was applied during 1 h (i.e., $\Delta x = 0.1$), followed by a relaxation period of 20 h at zero current (Figure 8). As expected, the shape of the GITT curve measured under current is similar to that shown in Figure 7, exhibiting pronounced electrode polarization but restricted to the composition range $1.1 < \Delta x < 2$. Conversely, the charge/discharge nearequilibrium potential curve (Figure 8, dashed line) now shows a polarization value reduced by 75% within this particular composition range, which clearly confirms both the existence of some kinetic limitations for the specific Li⁺ (DHDMQ⁻⁻)/Li₂DHDMQ biphasic system (System 1) and that the corresponding formal potential should be quite close to 3 V versus Li⁺/Li⁰. Several parameters were then adjusted with the aim of decreasing the polarization effect, such as changing the electrolyte composition, Li exchange rate, milling procedure, and nature of the carbon. However, no clear improvement was observed, which seems to confirm that the activation energy is intrinsic to System 1.

Some attempts to improve both the specific capacity and the stability on cycling of Li₂DHDMQ were also investigated. First, we took advantage of the redox amphoteric nature of this compound and the fact that System 2 involves, at the beginning of the process, a flat plateau located at an average value of 2.45 V (Figure 8) to probe the electrochemical performances within a new potential window of 3.6-2.15 V. Secondly, with the aim of simply circumventing the solubility issue at this stage without trying to design efficient composite electrodes, we assessed addition of a load of an adsorbing (inert) material additive during preparation of the composite electrode. In particular, we benefited from recent work that demonstrated the ability of γ -Al₂O₃ nanoparticles to sustain the capacity performance in a lithium/sulfur cell by adsorbing lithium polysulfides and preventing their dissolution in the electrolyte.^[15] We thus prepared another composite electrode by milling Li2DHDMQ/carbon black (SP)/ γ -Al₂O₃ in 56.6/33.3/10 weight ratio. Its electrochemical re-

sponse was then studied under stronger conditions by applying a galvanostatic cycling test at a rate of one Li⁺ exchanged in 2 h. While the charge/discharge profile is interestingly not affected by the presence of this inactive and insulating additive, it appears that capacity retention is clearly improved, with 74% capacity recovered after 20 cycles and a residual capacity of 80 mAhg⁻¹ after 50 cycles (Figure 9).



Figure 9. Capacity retention curves of Li₂DHDMQ/Li cell galvanostatically cycled between 3.6 and 2.15 V versus Li⁺/Li⁰ at a rate of one Li⁺ exchanged in 2 h, with and without a 10 wt% load of γ -Al₂O₃ additive. Inset: corresponding potential–composition curve for composite electrode containing alumina as additive.

This capacity is higher than for an alumina-free electrode even when the total electrode mass is considered, that is, the capacity gain over cycling offsets additional mass due to additive. Such a result demonstrates that better cycling performance is expected by designing elaborate composite electrode architectures, in particular by appropriate use of polymer binders and other additives to prevent residual dissolution phenomenon (e.g., promoting specific interactions towards organic-based electrode materials).^[16] This is an alternative pathway to the use of redox-active polymers or grafting processes to make more insoluble active organic moieties.

Finally, having also prepared TMQ (1) as an intermediate for the synthesis of Li_2DHDMQ (Scheme 1) and knowing the electrochemical reactivity of Li_4THQ ,^[4] we compared in a single layout the typical discharge/charge profile of this series of similar *p*-benzoquinone derivatives under equivalent experimental conditions (Figure 10). As previously mentioned,^[4,5,17] we first confirmed with this series that better stability of the organic electrode material is obtained when the structure is negatively charged (lower solubility). For instance, Li_4THQ reaches its full theoretical capacity (two-electron reduction) after the first discharge due to its higher stability towards the electrolyte. Conversely, the average redox potential is decreased simultaneously due to electron enrichment of the redox-active quinonic structure, that



Figure 10. Comparison of the typical first discharge/charge profiles of TMQ, Li_2DHDMQ , and Li_4THQ cycled galvanostatically versus lithium at a rate of one Li^+ exchanged in 10 h under equivalent experimental conditions.

is, the relationship between substituents and the reduction potentials of quinones^[18] also exists in the solid state.

DFT calculations and methodology

Geometry optimizations: The first step of this theoretical approach was validation of the applied methodology for structural description. In organic crystals, such studies encompass not only identification of the most suitable density functionals, but also inclusion of van der Waals interactions. We first used solvated Li₂DHDMQ•4H₂O as benchmark system to define the most suitable methodology to account for geometry features in our typical phases. We first addressed the relative abilities of various exchange-correlation functionals (LDA,^[19] Perdew-Burke-Ernzerhof (PBE) variant of GGA,^[20] PBEsol,^[21] and revPBE^[22]) to account for both intra- and intermolecular geometries. The experimental single-crystal XRD structure of Li2DHDMQ•4H2O was energy-minimized in full, including unit cell parameters and atomic positions. However, standard DFT methods are known to fail in describing the long range van der Waals interactions. We therefore used a DFT code incorporating dispersion corrections in density functionals, that is, the pseudopotential VASP package (see Computational Details section).^[23]

Three methods adding semi-empirical correction for dispersion were considered (PBE-D, PBE-D*, corr-PBE-D*_0.52) and described hereafter. Using the original van der Waals radii may lead to overestimation of the dispersion forces and hence underestimation of the lattice constants. Results may thus be improved by modification of the semiempirical vdW correction. In addition to DFT-D2 calculations (labeled PBE-D), the original Grimme model was also modified here by rescaling van der Waals radii in the damping function (scaling factors: 1.30 for hydrogen and 1.05 for all other atoms), whereas the value of the global scaling factor s_6 was set to 0.75. This parameters modification was (a) 16

Relative error / %

10

6

proposed by Civalleri et al. (PBE-D*) and normally enables softening of the dispersion interaction.^[24,25] In the method labeled corr-PBE-D*_0.52, an optimized s_6 value (lower than that of 0.75 proposed by Grimme and used for PBE-D/ PBE-D* calculations) was also employed while leaving R_{vdW} fixed at the PBE-D* values (see Computational Details section).^[26]

 $Li_2DHDMQ \cdot 4H_2O$ and related dehydrated or partially hydrated phases: The quality of structural reproduction for the $Li_2DHDMQ \cdot 4H_2O$ crystal can be evaluated by comparing the calculated structures with the available X-ray crystal structure. This allows for a quantitative assessment of the performance for each exchange-correlation functional or DFT-D method for the same set of computational parameters (k-points grid/cutoff energy).

The changes in unit-cell volume V, monoclinic angle β , and lattice dimensions with respect to the experimental Xray data for the full-geometry optimizations are presented in Figure 11. Unit-cell volumes are underestimated by all methods, except PBE and rev-PBE, which lead to overestimation. The absolute discrepancies of calculated V for PBE-D and PBEsol methods with respect to the experiment are



polarization, etc.).

and PBE-D (-5.4%) methods, and an even larger one for LDA (-9.0%). Corr-PBE-D*_0.52 and PBE-D* decrease this discrepancy to about -4%. On the whole, due to the lack of involvement in the dispersion interactions, the *b* lattice parameter is better accounted for by the various tested methodologies, and the most suitable treatment for this parameter is PBE. Only a slight overestimation is introduced within DFT-D (corr-PBE-D*_0.52 and PBE-D*) compared to the PBE. The variation of the calculated interlayer spacing (i.e., interplane distance), *d*, as a function of the level of theory is depicted in Figure 12, which shows that corr-PBE-D*_0.52 still provides the best result among all tested methods, with an underestimation of less than -2%. The calculated *d* values are not satisfactory for pure DFT methods except for PBEsol, which properly represents the interlayer

roughly the same ($\approx 4\%$). The most satisfying results for V

and β are observed for PBE-D* and corr-PBE-D*_0.52,

with deviations from experimental V of -2.8 and -1.1 %, re-

spectively. For β , we find deviations on the order of only 1–

2° with these two DFT-D methods. Rev-PBE gives the worst

result ($\Delta V/V \approx 16\%$) and therefore completely fails to cor-

rectly account for the geometry originating from distinct kinds of interactions in this crystal (electrostatic, dispersion,



Figure 11. Li₂DHDMQ-4H₂O: Relative errors [%] of the DFT or DFT-D calculated values to the experimental ones for a) the unit-cell volume V and monoclinic angle β and b) the optimized lattice parameters, *a*, *b*, and *c*.



distance (slight underestimation by -1.5%). On the other

Figure 12. Li_2DHDMQ ·4 H_2O : Relative errors [%] of the DFT or DFT-D calculated values to the experimental ones for the optimized inter-plane distance *d*.

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hand, PBE-D and PBE-D* do not offer a better description of the stacking parameter than the PBE model, that is, adequate selection of the s_6 value is crucial. From the abovementioned results, we conclude that corr-PBE-D*_0.52 gives the best compromises in the description of crystal structure parameters.

To complete the discussion of the geometry optimization, we also consider the effect of the XC functional or DFT-D method on bond lengths and interatomic distances. Indeed, despite weak influence on the electronic structure, intramolecular geometry directly affects the structure and energy of the systems in the computations, which are meaningful especially for estimation of the intercalation potential. For Li₂DHDMQ•4H₂O, root mean square deviations (RMSDs) for intramolecular bond lengths and intermolecular distances with respect to the experimental data are gathered in Figure 13. The RMSD values for intramolecular bond



Figure 13. Li_2DHDMQ ·4H₂O: RMSD values with respect to experimental data for the intramolecular bond lengths and intermolecular distances without taking into account covalent bonds involving an H atom or Hbonding.

lengths which do not involve any H atoms or H-bonding are fairly uniform across all calculations (except for rev-PBE), and this indicates somewhat consistent reproduction of the covalent molecular structure in full-geometry optimizations regardless of the correction for dispersion forces. As expected, introduction of dispersion does not modify the C–C, C– O, and C=O bond lengths with respect to conventional PBE calculation. The overall RMSD value of about 0.015 Å for these various DFT and DFT-D methods is of similar order of magnitude to typical values found in $\text{Li}_2\text{C}_4\text{O}_4$, which does not have any H atoms in the structure.^[27] The corresponding RMSD value for the rev-PBE functional is almost seven times higher than the best reproduction among all methods, highlighting the bad description of this feature by this functional.

Figure 13 considers solely intermolecular bond lengths that correspond to $Li^+\cdots O^-$ interactions. In this case, the

rev-PBE, PBE, and LDA functionals all fail to describe such interactions, which belong to the electrostatic type, while the best experimental description is observed for the PBEsol method (RMSD as low as 0.03 Å). Addition of the dispersion correction to the PBE functional lowers the RMSD values by more than half, to a more satisfying value of 0.08 Å (i.e., a discrepancy with the experiment of $\approx 4\%$). Modifications of the DFT-D2 parameters also tend in this direction, for instance, with an RMSD value of 0.04 Å for the corr-PBE-D*_0.52 functional (i.e., a discrepancy with the experiment of $\approx 2\%$).

In conclusion, on the whole, geometric features in $Li_2DHDMQ.4H_2O$ crystal are most reliably described by corr-PBE-D*_0.52. Therefore, calculations on the partially delithiated phase LiDHDMQ.4H₂O and those of Li_2DHDMQ or LiDHDMQ.3H₂O crystals have been performed with this methodology, because similar kinds of interactions occur in these compounds, too.

The nature of the crystal phase for Li₂DHDMQ was investigated by removing all water molecules within the relaxed structure of Li2DHDMQ.4H2O and allowing subsequent full-geometry optimization with no constraints on the crystalline symmetry (i.e., P1). The resulting relaxed structure remains in the same space group $(P2_1/n)$. Nevertheless, despite preservation of the symmetry, crystallographic data change significantly. The relaxed lattice dimensions and monoclinic angle for Li₂DHDMO are a=6.068, b=6.408, c = 14.118 Å, and $\beta = 109.85^{\circ}$. Relaxation thus led to reduction of the b lattice parameter, while a and c increase by 12.7 and 10.4% in comparison to Li₂DHDMQ•4H₂O. These variations correspond to a volume diminution of -18.97 % compared with the solvated phase and can be related to the modification of the stacking direction within the lattice, which now involves a and b lattice parameters.

For the partially dehydrated phase Li₂DHDMQ·3H₂O, which was also relaxed without symmetry constraints, the optimized lattice dimensions and angles of the resulting triclinic cell are a = 4.827, b = 9.662, c = 13.156 Å and a = 90.16, $\beta = 109.85$, $\gamma = 87.13^{\circ}$. Since our experimental attempt at of structure determination Li₂DHDMQ and Li₂DHDMQ·3H₂O crystals was not successful, we only compared the experimental XRPD pattern to that generated from our calculated phase (Figure S4 in the Supporting Information). However, due to the mismatch of these two patterns, we consider that our relaxed phase generated by this methodology is not the relevant one.

LiDHDMQ·4*H*₂*O*: We have applied the most suitable methodology identified for the Li₂DHDMQ·4*H*₂O crystal above (corr-PBE-D*_0.52) to relaxation of selected hypothetical crystal structures of the delithiated phases. Three models were screened corresponding to different sites for removal of lithium atoms. The lattice constants, unit-cell volume, and stacking parameters of these relaxed frameworks are listed in Table S1 of the Supporting information. Among all structural hypotheses, the lowest stable phase was 0.2 eV per formula unit (p.f.u.) from the most stable

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Figure 14. Li_2DHDMQ ·4 H_2O : a) Relaxed crystal structure; Li atoms removed from the compound in order to perform optimization of LiDHDMQ·4 H_2O are enclosed within dotted circles; b) Optimized crystal structure showing Li polyhedra.

one. This most stable delithiated structure, LiDHDMQ.4 H₂O, is obtained by removing Li atoms at the following positions: (0.72, 0.14, 0.64) and (0.77, 0.64, 0.85). This phase is denoted 1-4 in reference to Li atom positions (Figure 14a). Other hypothetical frameworks (i.e., 1-2 and 1-3, Figures S5 and S6 in the Supporting Information) correspond to removal at atomic positions (0.77, 0.64, 0.85) and (0.27, 0.86, 0.35); (0.72, 0.14, 0.64) and (0.27, 0.86, 0.35), respectively. Although model 1-4 is slightly more stable (by 0.01 eV) than 1-2, the crystal structures of these two forms emerging from the relaxation are quite similar ($\Delta V/V \approx -7.1$ %; $\Delta d/d \approx -36/$ -37%). Model 1-3 is characterized by less structural change $(\Delta V/V \approx -3.5\%; \Delta d/d \approx +2.4\%)$ and moderately higher energy (by 0.2 eV). Due to the higher stability of the 1-4 form, this phase is the only one considered in the following, including computed estimation of the deintercalation potential. The crystal structure of the Li₂DHDMQ•4H₂O and optimized 1-4 LiDHDMQ·4H2O phases are depicted in Figures 4b and 14b, respectively. The symmetry of the relaxed 1-4 LiDHDMQ•4 H_2O phase is lowered (space group *P*1).

In the non-deintercalated Li₂DHDMQ·4H₂O phase that issued from the corr-PBE-D*_0.52 calculation, Li ions lie in a distorted bipyramidal environment (d_{min} =1.935, d_{max} = 2.338 Å; Figure S7 in the Supporting Information), while in the most stable LiDHDMQ·4H₂O framework, they are located in a distorted tetrahedron (d_{\min} =1.922, d_{\max} =1.988 Å; Figure S8 in the Supporting Information). On lithium extraction from Li₂DHDMQ·4H₂O, a volume decrease of -7.1% is observed in our most stable crystal. The *c* lattice parameter shows a contraction of -15.7%, while the *b* lattice dimension is highly augmented (+12.6%). In comparison, the *a* lattice parameter is much less affected (-2.0%).

Energetics and average potential: Calculated equilibrium potential corresponding to oxidation of $Li_2DHDMQ\cdot4H_2O$ is compared with experimental data obtained from electrochemical measurements. The equilibrium average potential of the deintercalation (oxidation) phenomenon for $Li_2DHDMQ\cdot4H_2O$ experimentally determined through open-circuit voltage is about 3.0 V (Figure 8). The equilibrium potential V(x) relative to lithium metal for lithium insertion into a host material M can be estimated according to Equation (1)

$$V(x) = \frac{G(\mathbf{M}) + xG(\mathbf{Li}) - G(\mathbf{Li}_x\mathbf{M})}{xz}$$
(1)

where G is the Gibbs free energy p.f.u. and z the elementary charge per lithium ion (z=1).

By neglecting small changes in entropy ($T\Delta S$) and volume ($P\Delta V$), which are expected to be relatively small,^[28] the Gibbs free energy (ΔG) can be approximated by the internal energy (ΔE) and the average potential can be expressed as Equation (2)

$$V(x) = \frac{E(\mathbf{M}) + xE(\mathbf{Li}) - E(\mathbf{Li}_x\mathbf{M})}{xz}$$
(2)

where E is the total energy of each system p.f.u and E(Li) the total energy for lithium metal in the bcc structure).

After geometry optimizations of both lithiated $(Li_2DHDMQ\cdot 4H_2O)$ and delithiated $(LiDHDMQ\cdot 4H_2O)$ phases, the average lithium extraction potential can thus be extracted from Equation (2), in which x=1, since one lithium ion p.f.u. is considered to be removed from $Li_2DHDMQ\cdot 4H_2O$. The resulting equation is as follows [Eq. (3)].

$$E = E(\text{LiDHDMQ} \cdot 4 \text{ H}_2\text{O}) + E(\text{Li}) - E(\text{Li}_2\text{DHDMQ} \cdot 4 \text{ H}_2\text{O})$$
(3)

The calculated Li₂DHDMQ-4H₂O deintercalation potential (3.75 V) exhibits quite a noticeable discrepancy of +0.75 V compared to experiment. We note that the selected method of calculation may noticeably impact the total energy of both lithiated and delithiated phases. Thus, other methodologies are currently being tested (including hybrid functionals). In addition, the procedure used in this work does not completely guarantee reaching a global minimum for the delithiated phase in the potential-energy surface of

our system, due to limited probing of the relative arrangement of Li^+ ions and molecules. We should therefore extend our screening of hypothetical structures in a forth-coming work.

Conclusion

Building on our previous investigations on Li₄THQ,^[4] we have designed and synthesized, through a simple three-step method, Li₂DHDMQ, another derivative of the Li₄C₆O₆type unit. As expected, an electrochemical investigation versus Li revealed that Li2DHDMQ can reversibly deintercalate lithium according to a one-electron process at an average potential of 3 V (System 1), while the p-benzoquinone redox center of the structure reacts below 2.5 V (System 2). A noticeable decrease in capacity on cycling was also noticed due to certain solubility in the electrolyte, which can partly be suppressed by simply adding γ -Al₂O₃ nanoparticles to the composite electrode; this suggests that much better performance can be expected by designing efficient composite electrodes. As previously observed by Dahn et al.^[8] for a polymer based on a lithiated naphthazarin unit, the reversible deintercalation process occurring in Li₂DHDMQ (System 1) also suffers from quite large polarization. Efforts to reduce this effect failed, and this suggests a kind of intrinsic limitation phenomenon, as is typically observed for conversion reactions involving metal oxides as active materials.^[29] Further investigations are in progress, including electrochemical impedance spectroscopy measurements to determine the electrode kinetics and to isolate contributions from different physical and kinetic processes.

In addition to electrochemical characterization of hydrated and solvent-free Li₂DHDMQ, the crystal structure of the solvated form of this phase (Li₂DHDMQ·4H₂O) has been determined. Crystallographic data, at room temperature, of this compound were used to test various functionals and dispersion energy corrections within DFT calculations. The original PBE-Grimme method for dispersion corrections (DFT-D2) was tested together with versions of this scheme modified by changing the damping function. The shortcomings of classical functionals (e.g., GGA, LDA, and revPBE) were outlined, whereas a modified DFT-D2 scheme involving changes in particular parameters was identified as the most suitable methodology for description of this particular crystal type. This variant of DFT-D2 was then selected for the relaxation of 1) solvent-free Li₂DHDMQ and partially dehydrated phase Li₂DHDMQ·3H₂O, and 2) selected hypothetical crystal structures after lithium extraction (both unknown experimentally). Due to the used methodology, not all possible frameworks for these two kinds of phases were tested in this work. To complement this first approach, more sophisticated crystal-structure prediction tools will thus be applied in forthcoming work in order to extend our studies to a more complete range of crystal structures.

Experimental Section

General methods: ¹H and ¹³C NMR spectra were recorded on a Bruker DPX-300 at 300 MHz and 75 MHz, respectively; chemical shifts (δ) are given in ppm relative to TMS. For compound 2, the ¹³C NMR spectrum was recorded in D₂O by using a capillary filled with [D₆]DMSO as internal standard. Infrared spectra were recorded with a Thermo Scientific Nicolet iS10 FTIR equipped with an attenuated total reflectance (ATR) probe. ESI-HRMS experiments were performed in positive-ion mode on a Q-TOF Ultima Global instrument (Waters-Micromass, Manchester, UK) equipped with a pneumatically assisted electrospray ion source (Zspray) and an additional sprayer for the reference compound (Lock-Spray). Elemental analyses were performed on a Thermo Finnigan EA 1112 Series Flash elemental analyzer controlled by Eager 300 software. The DSC measurements were carried out with a Netzsch DSC204 calorimeter under argon flow by using sealed aluminum crucibles with cap layers perforated just before analysis to allow gas release. Thermogravimetric (TG) measurements were carried out under argon with a Netzsch STA 449 C coupled with mass spectrometry for gas analysis by using alumina crucibles. TG/DSC analyses were obtained at a heating rate of 10°C min⁻¹.

X-ray diffraction

Powder XRD: Powder XRD was performed on a Bruker D8 Advanced diffractometer with Cu radiation ($\lambda_1 = 1.54056$, $\lambda_2 = 1.54439$ Å) at 40 kV and 40 mA equipped with a Linkseye detector. Temperature-controlled experiments were performed on a Bruker D8 diffractometer with a Co radiation ($\lambda_1 = 1.788970$, $\lambda_2 = 1.792850$ Å) equipped with an Anton Parr Chamber HTK from room temperature to 550 °C. Each pattern was recorded under nitrogen flow with a step of 0.0299° and an acquisition time of 2.7 s per step (heating rate of $0.2^{\circ}Cs^{-1}$). All diffraction profiles and structure refinements were generated by using the FullProf Suite software. This set of programs is developed and constantly updated by Rodríguez-Carvajal and co-workers.^[30]

Single Crystal XRD: XRD data were collected on a Bruker X8 Apex2 CCD4K at room temperature ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). Reflections were collected up to $\theta = 26.14^{\circ}$ to a completeness of 99% by following a strategy based on ϕ and ω scans. Intensities were corrected for absorption effects by a semi-empirical method based on redundancy by using the SADABS program.^[31] The structure was solved by direct methods using SHELXS,^[32] and least-squares refined with the JANA2006 Software package.^[33]

Crystal data for Li₂DHDMQ·4H₂O: $M = 284 \text{ gmol}^{-1}$, monoclinic, space group $P2_1/n$ (no. 14), a = 5.3318(5), b = 9.5162(9), c = 12.7812(13) Å, $\beta = 96.490(10)^\circ$, V = 644.34(11) Å³, Z = 2, $\rho_{calcd} = 1.464 \text{ gcm}^{-3}$, crystal dimensions: $0.3 \times 0.2 \times 0.1$ mm, 26652 reflections collected, 1284 unique, $R_{int} = 4.66\%$, $R_{(obsd)} = 3.16\%$, $wR_{(all)} = 3.21\%$, R indices based on 978 reflections with $I > 3\sigma(I)$ (refinement on F), 120 parameters, max./min. residual electron densities: 0.17/-0.14 eÅ⁻³. Hydrogen positions from methyl groups and from water molecules were located on Fourier difference maps and introduced in the refinement. The hydrogen atoms were refined isotropically and thermal agitation factors were restrained to the same value for hydrogen atoms belonging to the same water molecule (i.e., H_{1a} and H_{1b} for one part and H_{2a}, H_{2b}, and H_{2b}, for the other. CCDC 856689 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemistry: Electrochemical studies were performed in Swageloktype cells with an Li metal disk as negative electrode and a fiberglass separator soaked with a molar LiPF₆ solution in ethylene carbonate/dimethyl carbonate (1/1 v/v) as electrolyte. The positive electrode was prepared without binder by mixing organic compounds with 33% carbon SP (in total mass). Cells were typically cycled in galvanostatic mode by using a Macpile or VMP system (Biologic S.A., Claix, France) at a typical rate of one lithium ion exchanged in 10 h unless otherwise specified.

Synthesis: Methanol was purchased from VWR Prolabo (HPLC grade). LiOH-H₂O was supplied by Fluka (\geq 99%), and tetrachloro-*p*-benzoquinone (99%) by Acros.

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GaA, Weinheim www.chemeurj.org ______ These are not the final page numbers! Tetramethoxy-p-benzoquinone (1): A sodium methanolate solution was prepared in a closed vessel by adding sodium (0.930 g, 40 mmol) by portion to methanol (20 mL) cooled at 0°C. After complete reaction of sodium with methanol, a heterogeneous solution of chloranil (2.46 g, 10 mmol) in methanol (5 mL) was added to the methanolate solution. The mixture, which immediately turned reddish, was then heated at 85°C for 6 h in the closed vessel. The product crystallized on cooling to room temperature. The orange needles were recovered by filtration, washed several times with water and finally dried under vacuum overnight to give the desired compound (1.860 g, 82%). ¹H NMR (300 MHz, CDCl₃): $\delta = 3.98$ ppm (s, 12 H, CH₃); ¹³C NMR (75 MHz, CDCl₃): $\delta = 61.41$ (CH₃), 142.85 (COMe), 180.5 ppm (C=O); IR (ATR): $\tilde{\nu} = 2969-2842$ (C–H), 1666, 1660 (C=O), 1461, 1438 (C=C), 1272 (C-O-C), 1072 (C=C); HRMS (ESI): m/z calcd for $C_{10}H_{12}O_6+Na^+$: 251.0532 [M+Na⁺]; found: 251.0528.

3,6-Dihydroxy-2,5-dimethoxy-p-benzoquinone dilithium salt trihydrate (2): Ground compound 1 (0.250 g, 1.1 mmol) and LiOH-H₂O (0.092 g, 2.2 mmol) were placed in a three-neck round bottomed flask under argon atmosphere. Distilled water (2 mL), previously degassed under a flux of argon, was added to the mixture. After heating at 90 °C for 2 min, the obtained purple solution was placed in the freezer for 2 h. Addition of acetone to the frozen solution led to the formation of a brown precipitate which was immediately filtered off. The compound was finally washed twice with acetone affording pure 2 (0.267 mg, 1.02 mmol, 93% yiel). ¹H NMR (300 MHz, D₂O): δ =3.56 ppm (s, 6H, CH₃); ¹³C NMR (75 MHz, D₂O+[D₆]DMSO): δ =58.84 (CH₃), 134.27 (COMe), 171.73 ppm (C=O); IR (ATR): $\tilde{\nu}$ =3000–3500 (OH), 3070–2750 (C–H), 1623 (C=O), 1500, 1429 (C=O), 1370 (CH₃), 1053, 1033 (C=O), 952, 932 cm⁻¹ (C=C); elemental analysis calcd (%) for Li₂C₈H₁₂O₉: C 36.11, H 4.55; found: C 35.7, H 4.59.

3,6-Dihydroxy-2,5-dimethoxy-p-benzoquinone dilithium salt tetrahydrate (3): Compound 2 (150 mg) was placed in a watch glass installed in a Petri dish containing hot water. The set was then covered and a purple powder was recovered after 12 h. This powder was identified as the pure tetrahydrate phase by comparison of the powder XRD pattern with the pattern simulated from the X-ray crystallographic data of 3. Single crystals of 3 were grown from a concentrated solution of 2 (20 mg) in water (1 mL) by slow evaporation in a partially covered watch glass. ¹H NMR (300 MHz, D₂O): δ =3.56 ppm (s, 6H, CH₃); IR (ATR): $\tilde{\nu}$ =3000–3500 (OH), 3070–2750 (C–H), 1623 (C=O), 1500, 1429 (C=O),1370 (CH₃), 1053, 1033 (C–O), 952, 932 cm⁻¹ (C=C); elemental analysis calcd (%) for Li₂C₈H₁₄O₁₀: C 33.82, H 4.97; found: C 33.58, H 4.93.

3,6-Dihydroxy-2,5-dimethoxy-p-benzoquinone dilithium salt (4): Compound 2 (2.64 g) was dissolved in distilled water (45 mL) and the solution frozen in liquid nitrogen. Lyophilization was carried out for five days before refilling the flask with argon. Residual water was completely removed by subsequent annealing at 180 °C under vacuum for 2 h. The dark green, fluffy compound was stored in a glove box. ¹H NMR (300 MHz, D₂O): δ = 3.56 ppm (s, 6H, CH₃); IR (ATR): $\tilde{\nu}$ = 3000–3500 (OH), 3070–2750 (C–H), 1623 (C=O), 1500, 1429 (C=O), 1370 (CH₃), 1053, 1033 (C–O), 952, 932 cm⁻¹ (C=C).

Computational details: All calculations were performed using the pseudopotential VASP package.^[34] Full geometry optimization was achieved through a conjugate gradient algorithm minimizing the Hellmann-Feynman forces. For the Li2DHDMQ·4H2O phase, calculations were done by taking the experimental structure of the crystal at room temperature. Subsequent calculations on solvent-free Li2DHDMQ or partially dehydrated Li₂DHDMQ•3H₂O along with selected hypothetical crystal structures on lithium extraction (LiDHDMQ-4H2O) were then performed starting from the energy-minimized crystal structure. All minimizations were considered complete when energies converged to better than $1\times$ $10^{-5}\,\mathrm{eV}$ per atom and maximum residual forces were lower than $1\times$ $10^{-3} \text{ eV} \text{\AA}^{-1}$. Projector augmented wave (PAW) potentials were used to describe the electron-ion interaction,[35] while the wave functions were expanded in plane waves with energy below 520 eV. Brillouin zone sampling was performed by using the Monkhorst-Pack scheme,^[36] with a kpoint grid of $4 \times 4 \times 2$.

In the VASP program, the DFT-D2 approach of Grimme is implemented, corresponding to semi-empirical dispersion corrections. They are included by a summation of damped interatomic C_6/R^6 terms (additional atomatom potentials that vanish for covalent bonding distances). The Grimme scheme using such pairwise interaction terms is defined according to Equation (4)

$$E_{\rm disp} = -s_6 \sum_{i=1}^{N-1} \sum_{g=i+1}^{N} \sum_g \frac{C_6^{ij}}{R_{ij,g}^{ij}} f_{\rm dmp}\left(R_{ij,g}\right) \tag{4}$$

where the energy is the summation over all atom pairs and g lattice vectors, N is the number of atoms, s_6 is a functional-dependent global scaling factor, C_6^{ij} are the dispersion coefficients of atom pair ij, and $R_{ij,g}$ is the internuclear separation of the atom pair. The interaction between each pair of atoms is approximated by a damped multipole expansion, often (but not always) truncated after the first term $\frac{C_6^{ij}}{R_{ij,g}}$. To avoid near-singularities for small $R_{ij,g}$ values and double-counting effects of correlation at intermediate distances, a damping function f_{dmp} must be used [Eq. (5)]

$$f_{\rm dmp}(R_{ij,g}) = \frac{1}{1 + e^{-d(R_{i}/R_{i}-1)}}$$
(5)

where $R_{\rm r}$ is the sum of atomic vdW radii $R_{\rm vdW}$.

In the DFT-D2 approach (applied here to the PBE functional), the total energy of the system is thus defined as a sum of the self-consistent Kohn–Sham energy terms as obtained from the chosen XC functional ($E_{\text{KS-DFT}}$) and the semi-empirical correction E_{disp} [Eq. (6)].

$$E_{\rm DFT-D} = E_{\rm KS-DFT} + E_{\rm disp} \tag{6}$$

All calculations were performed by using the default values of C_6^{ij} parameters for each species reported in the original article of Grimme describing this method.^[9] A value of d=20 (dampening parameter) was selected in order to specify the steepness of the dampening function [Eq. (5)]. A cutoff radius of 30 Å for pair interactions was used to truncate the summation over lattice vectors.

To determine an optimal value for the s_6 global scaling factor, a screening of this parameter was tested on the known experimental system Li₂DHDMQ-4H₂O within the range 0.52–0.75, the extreme values of which correspond respectively to the corr-PBE-D*_0.52 (s_6 =0.52) and PBE-D* (s_6 =0.75) methods (Figure S9 in the Supporting Information). According to our results, β rises when s_6 decreases, while the volume of the unit cell undergoes a reverse trend (Figure S9a in the Supporting Information). Due to the moderate absolute value reached for both unit cell volume and monoclinic angle with s_6 =0.52, the corr-PBE-D*_0.52 method was selected to provide an improvement of PBE-D*. In addition, the interplane distance, d, is closer to the experimental one for s_6 =0.52 (Figure S9b in the Supporting Information) and the stacking parameter a is also better described by this value (minor relative error of -3.2% obtained for this s_6).

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Organic Electrode Materials

A.-L. Barrès, J. Geng, G. Bonnard, S. Renault, S. Gottis, O. Mentré, C. Frayret, F. Dolhem, P. Poizot*.....

High-Potential Reversible Li Deintercalation in a Substituted Tetrahydroxy*p*-benzoquinone Dilithium Salt: An Experimental and Theoretical Study



A new redox amphoteric system, derived from the tetralithium salt of tetrahydroxy-*p*-benzoquinone, reversibly deintercalates one Li⁺ on charging and has a practical capacity of about 100 mAh g^{-1} at an average potential of 3 V versus Li⁺/Li⁰ (see figure). A solvated form of the studied salt (Li₂DHDMQ·4H₂O) was also characterized by X-ray diffraction and first-principles calculations.