Advanced Li-ion Batteries based on the Use of Renewable Organic Electrodes

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Abstract
Developing advanced storage systems for the sustainable use of electric energy with the aim of limiting harmful emissions, energy consumption and waste has become a worldwide imperative. The present project, pursued within GPEC and entitled Advanced Li-ion Batteries, is based on the use of renewable ORGanic electrodes termed "ALIBORG" aimed toward the design of better batteries by introducing the concepts of sustainability and renewability. The project started on September 1st, 2008, and the present document reports our last twelve months advances. Following our investigations on six-atom ring structures (oxocarbon first and then piperazine-type structures), emphasis has been placed on the electrochemical evaluation vs. Li of several series of such structures characterized by specific substituents or the incorporation of nitrogen atoms in the chemical arrangement. Having a substituent linked to the ring turns out to have a stronger impact redox potential than having a carbon substituted by a nitrogen within the ring. Calculations are now under progress to grasp the key factors governing the electrochemical properties of such substituted ring structures.

Introduction

The present project aims at promoting the emergence of alternate means of energy production and energy storage while favouring renewable sources by developing a new generation of Li-ion batteries based on redox organic molecules. Indeed, although the current Li-ion battery technology represents a promising power source for advanced electric vehicles and portable electronic devices, it still falls short of meeting both the sustainability and CO_2 footprint criteria, owing to the use of active inorganic materials obtained from limited mineral resources whereas using conventional thermal reactions as synthesis routes. A possible alternative consists 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 concepts) making the concept of "greener and sustainable" Li-ion batteries possible.

We have previously shown that dilithium rhodizonate salt $Li_2C_6O_6$ displays quite an interesting electrochemical behaviour vs. Li [1] whereas deriving from *myo*-inositol [2] a natural compound widely distributed in plant as phytic acid (Scheme 1) [3].

(a)

(b)
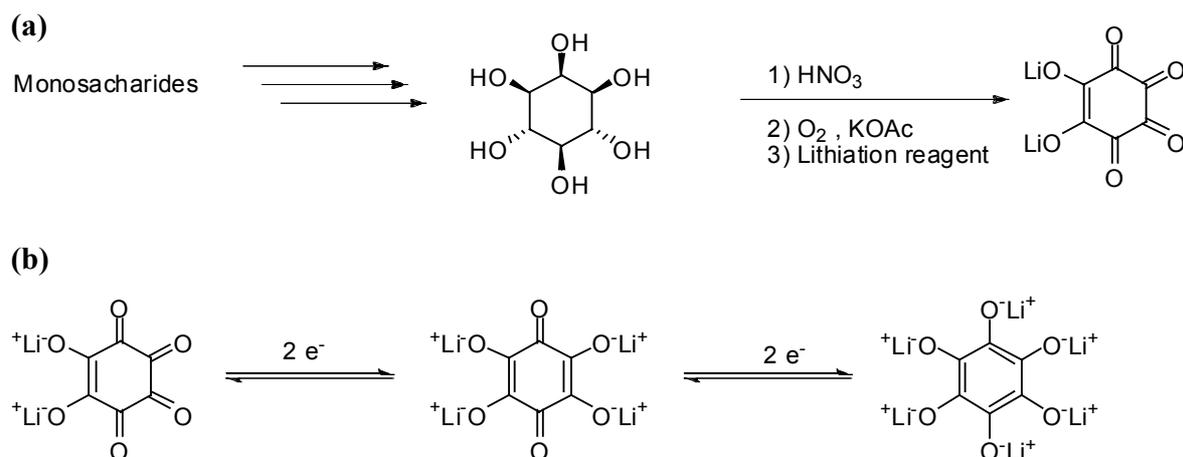
Scheme 1: a) Chemical synthesis of dilithium rhodizonate from natural resources, (b) typical electrochemical reactivity of $Li_2C_6O_6$ vs. Li.

Having identified at that time the positive attribute of the six-membered oxocarbon "C_6O_6", a wide variety of single/multiple ring molecules containing chemically active C=O functions with various heteroatom or substituents had to be considered in connection with a possible effect on the redox potential of the considered molecule. Obviously, multiple atomic organizations can be proposed. However, the challenge is to grasp an efficient redox-active system while chemically stable towards the electrolyte. Thus, one of the main objectives of the ALIBORG project involved the creation of a new bank of scientific knowledge in synthesizing/designing organic molecules/polymers electrochemically active towards Li.

Our first general approach consisted in using a six-atom ring structure, still based on carbonyl units but containing nitrogen, and then probing the potential electrochemical modifications. As reported in the previous progress report, the starting point of our first series of such compounds was the 2,3,5,6-tetraketopiperazine unit (see below), another class of six-membered ring barely studied in the literature compared to oxocarbons.
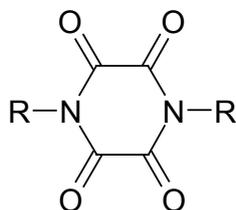
This year, we focussed on the study of such piperazine derivatives and more specifically prepared and evaluated an oligomer version vs. Li more stable towards the electrolyte. Beyond the 2,3,5,6-tetraketopiperazine unit, other N-based cyclic structures as well as compounds deriving from C_6O_6 monocycle have been synthesized and probed vs. Li. Computational methods have also been used to give us new insights into the activity of such organic materials.

Background

The demand for electric energy does increase even faster than the world's population due to the improvement of the Developing World well-being. In this context, the energy storage, such as electricity, constitutes a crucial issue to promote the use of renewable energies in practice. As an example, to *face the finite* fossil-fuel supplies coupled with the global warming effect, the automotive industry turns to Electric vehicles (EVs) and/or Hybrid Electric Vehicles (HEVs); this involves an efficient development of rechargeable batteries and in particular the Li-ion technology. However, Li-ion batteries are presently operating on inorganic insertion compounds (i.e.; $LiCoO_2$, $LiMn_2O_4$, LiC_6), which abundance and materials life-cycle costs can present issues in the long term with foreseeable large-scale applications. A first option enlists the use of not resource-limited elements explaining the interest in silicate/phosphate-based materials as positive electrode and silicon as negative one. However, the chemical production of such compounds as well as their recycling process consumes a large amount of energy mainly due to the inorganic nature of the matter. Thus, in parallel, another alternative can be considered in developing organic-based electrodes synthesized from eco-efficient processes starting from natural/abundant precursors (i.e.; carbon backbone constructed thanks to the photosynthesis).

Results

PART A

With the GCEP support starting from September 2008, we have first investigated the chemical synthesis and probed the electrochemical signature of a series of tetraketopiperazine derivatives, which constituted a logical entry to pursue our previous evaluations of redox active carbonyl functions involved in a six-atom ring structure. Last year, we succeeded in synthesizing several 2,3,5,6-tetraketopiperazine derivatives characterized by quite different R groups (i.e., aromatic, unsaturated and alkyl functions). We first synthesized N,N'-diphenyl-2,3,5,6-tetraketopiperazine (**PHP**) then N,N'-diallyl-2,3,5,6-tetraketopiperazine (**AP**) and N,N'-dipropyl-2,3,5,6-tetraketopiperazine (**PRP**). Table 1 recaps the corresponding molecular structures.

The preliminary electrochemical tests vs. Li showed an interesting electrochemical activity typically characterized by a flat plateau located at an average potential of 2.35 V and a low polarization value about 100 mV (Figure 1, as recap). However, these compounds display a noticeable solubility in the liquid electrolyte, which leads to a rapid capacity fading. Note that the reactivity of both **AP** and **PRP** is restricted to one electron per piperazine ring whereas the **PHP** molecule involves two electrons, which can be explained by the positive effect of the two aromatic groups stabilizing the as-produced bi-radical.

Increasing the molecular mass constitutes a possible pathway to overcome the dissolution phenomenon in the electrolyte. Among the piperazine derivatives, the **AP** molecule obviously appeared as a good starting monomer for polymerization. Along that line, we decided to use an ADMET (Acyclic Diene Metathesis) polymerization approach, never applied to such monomers yet, taking into account the specificity of this reaction (i.e.; diene groups, compared to a radical polymerization that could affect carbonyl groups). Scheme 2 shows the corresponding reaction.

Structure	Name	Acronym
	N,N'-diphenyl-2,3,5,6-tetraketopiperazine	PHP
	N,N'-diallyl-2,3,5,6-tetraketopiperazine	AP
	N,N'-dipropyl-2,3,5,6-tetraketopiperazine	PRP

Table 1: Molecular structures and acronyms of 2,3,5,6-tetraketopiperazine derivatives electrochemically evaluated vs. Li
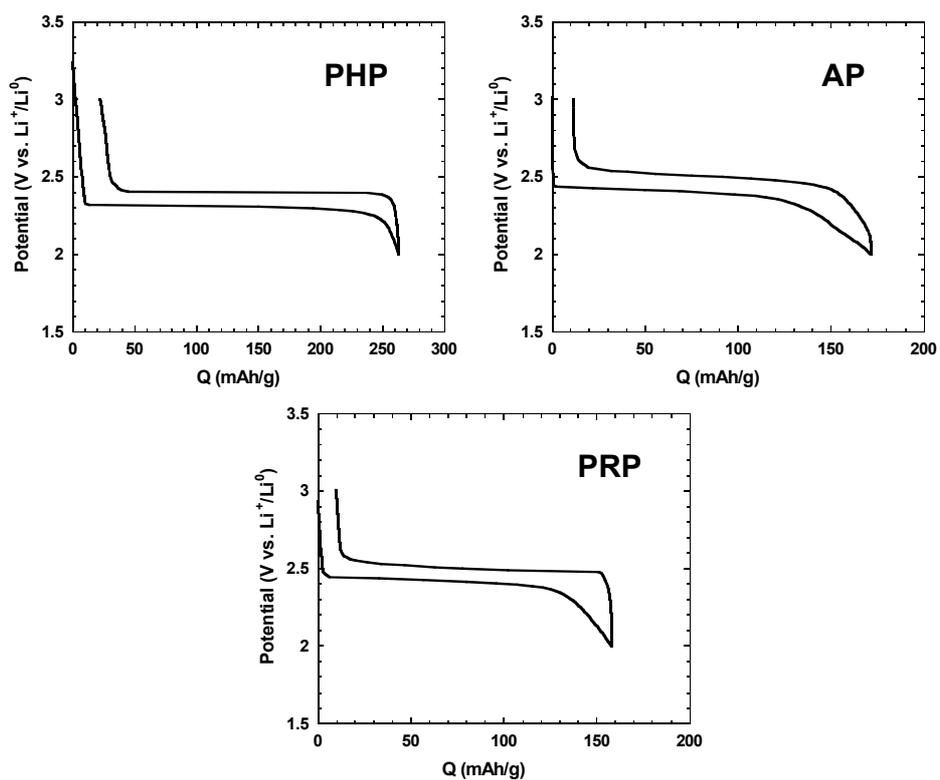
Figure 1: Typical electrochemical feature of **PHP**, **AP** and **PRP** using a Swagelok-type cell [Li metal disc as negative electrode, $LiPF_6$ 1 M in EC/DMC as electrolyte. Active material mixed with 50%(w/w) of carbon. Rate: 1 e^- exchanged in 10 h]
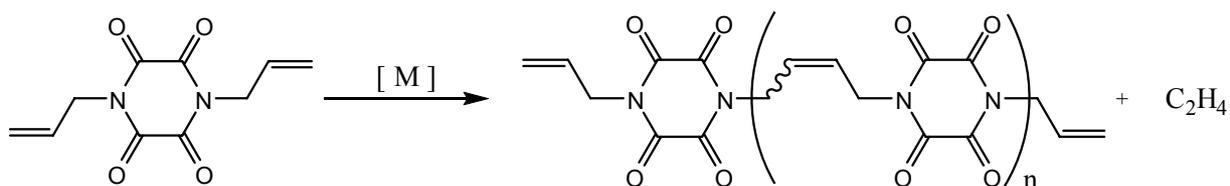
Scheme 2: ADMET polymerization reaction of *N,N'*-diallyl-2,3,5,6-tetraketopiperazine

We tested three kinds of catalysts (Grubbs 1st and 2nd generation, Hoveyda Grubbs 2nd generation, two different solvents (toluene or 1,2-dichloroethane (1,2-DCE)), and two different molar ratios (2% or 5% mol/mol catalyst/substrate). Several reaction temperatures were also checked (temperatures between 60 and 110°C) and the reaction time was 24h. Finally, we have successfully obtained an oligomer for the first time. The optimum set of parameters is the use of Hoveyda-Grubbs 2nd Generation catalyst **5% $^{mol}/_{mol}$** in toluene at 85°C.

Analytical data: ^{1}H NMR (DMSO-*d_6*, 300 MHz) δ 54.37 (m, -CH_2-); 4.57 (d, J=3.94); 5.17 (d, [3]Jcis=16.89 ; q, [2]J=1.53); 5.37 (d, [3]Jcis=16.89 ; q, [2]J=1.53); 5.58 (t, J=3.94); 5.78 (m); ^{13}C NMR (DMSO-*d_6*, 300 MHz) δ) 41.6 (-CH_2-); 42.9 (-CH_2-); 117.8 (=CH_2); 125.9 (-CH=CH-); 130.5 (=CH-); 153.8 (C=O).

The degree of polymerization (DP) for the oligomer was found as being 2.278 thanks to ^{1}H-NMR study [4]. This means that we have a mixture of dimers and trimers.

The obtaining of such a polymer (denoted **p-AP**) enables us to get better electrochemical performances compared to the monomer; the solubility being clearly reduced. Basically, the general feature of the potential-capacity curve appears quite similar to the **AP** one with an average potential of 2.5 V and the uptake of one Li^+ per piperazine ring (Figure 2). However, this polymer derivative is able to sustain the capacity upon cycling. Efforts to stabilize further the capacity retention are under progress.
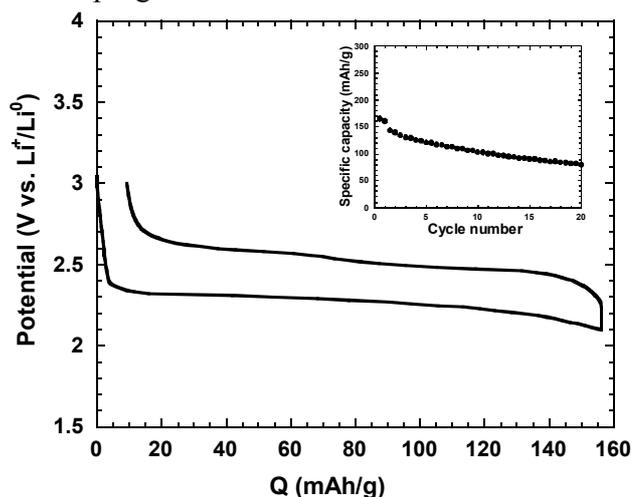
Figure 2: Typical electrochemical feature of **p-AP** using a Swagelok-type cell [Li metal disc as negative electrode, $LiPF_6$ 1 M in EC/DMC as electrolyte. Active material mixed with 50%(w/w) of carbon. Rate: 1 e^- exchanged in 2 h]

PART B

To complete our knowledge on the electrochemical reactivity of nitrogen-containing heterocycles vs. Li, and to set the bases of a structure-electrochemical activity relationship study, we have investigated a second series of molecular structures (Figure 3).

R^1, R^2 : H, Alkyl, Li
R^3 : Aryl
X: C, N
Y : O,S
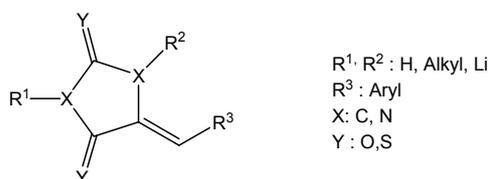
Figure 3: General formula for compounds involved in our study

Preliminary essays showed interesting electrochemical activities for some of the tested compounds, one of them having a non optimized average potential of 1.95 V and a specific capacity about 95 mAh/g (Figure 4). Studies in order to improve these foreseen interesting results are under progress.
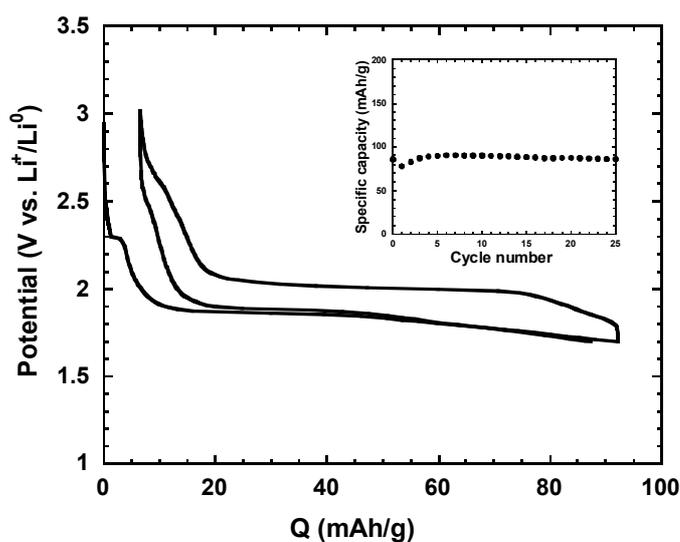

Figure 4: Typical electrochemical feature of the lithium salt [Li metal disc as negative electrode, LiPF$_6$ 1 M in EC/DMC as electrolyte. Active material mixed with 50%(w/w) of carbon. Rate: 1 e^- exchanged in 5 h]

PART C

Beyond our investigations focused on the effect of nitrogen atom on the electrochemical reactivity of heterocycles based on the C=O functions, we have also decided to probe directly the nature of the substituent (i.e., nature of the chemical bond) on the redox active "C$_6$O$_6$"-type oxocarbon. Thus we have centered our attention on a series of tetrahydroxy-p-benzoquinone derivatives (THQ) since previous electrochemical investigations performed on Li$_4$C$_6$O$_6$ (the THQ

tetralithium salt) demonstrated a reversible capacity of near 200 mAh/g for an average potential of 1.8 V [5].

So, we focused on substituting the THQ core for different groups. (Figure 5)

X: substituents having +*I* effect, -*I* effect, +*M* or -*M* effect.
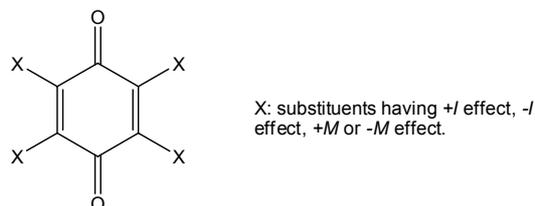
Figure 5: General formula for THQ derivatives

Electrochemical tests and DFT studies (see part D) are under progress.

PART D

To complete our set of experimental data, computational methods have been used to grasp the relevant parameters that tune the redox potential of a defined active centre. At first, solid state (periodic) calculations were performed using the Vienna *ab initio* simulation package VASP, using the crystal structure of one of our p-benzoquinone derivatives, **PBD₁**, issued from the X-ray diffraction refinement. In this package, the exchange correlation functional is expressed in the localized density approximation (LDA) together with the generalized gradient approximation (GGA). Both functionals were used in this work. Due to the periodic nature of the crystal system, the single-electron wave functions may be represented by plane waves. In practice, the infinite number of plane waves required is limited to a finite number with a specified energy cutoff. The energy cutoff controlling the accuracy of the calculation was set to 520 eV, representing a much extended basis set and highly accurate calculations. Projector Augmented Wave (PAW) potentials were used to describe the electron-ion interaction.

In the first set of DFT calculations carried out here, all atomic positions were optimized with respect to minimizing interatomic forces, keeping the cell parameters fixed to the experimentally determined values. Such study has allowed us to probe the ability of the method to account for the intramolecular interactions. Most of the interatomic distances issued from GGA calculations are in closer agreement than those obtained with LDA treatment.

In a second set of calculations, we have carried out DFT calculations involving optimization of the unit cell (full relaxation). Despite the evolutions in lattice parameters after relaxation of the cell, the resulting intramolecular distances are kept in good agreement with the experiment (Figure 6).
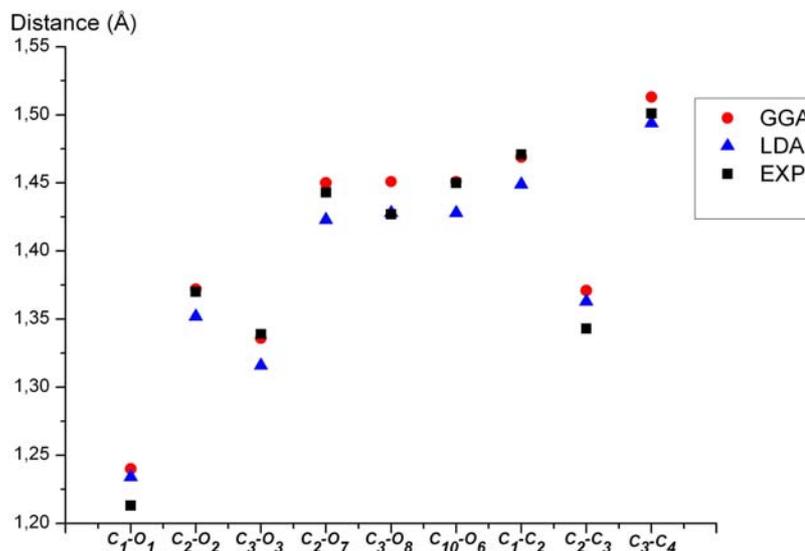
Figure 6: Comparison of intramolecular bond lengths for the **PBD₁** molecule in the crystal between experimental and calculated values allowing full relaxation of the unit cell.

The intercalation process was then probed from the calculation, starting from the crystal structure characterizing the completely delithiated phase. The first step of the calculation was to identify the most suitable sites for the insertion of lithium. Four possible sites, called Left (L), Aligned (A), Right (R) and Intersheet (I) were considered for the position of the lithium within the crystal. All of these configurations were fully optimized in both GGA and LDA treatments of the exchange and correlation effects. After relaxation, the resulting most stable phase originates from the configuration called initially (before relaxation) (L). The coordination number of the lithium evolves during the relaxation from four to six. Features characterizing geometry optimization resulting from the lithium intercalation were analysed. A slight resulting volume contraction is found in GGA while LDA relaxation ends up with a volume expansion of comparative extent.

Beyond structural considerations, the underlying objective of this work was to provide a possible estimation of the average intercalation potential, in order to determine on this particular crystal whether the determined value agrees with the experimental value.

The equilibrium voltage between negative and positive electrodes formally corresponds to the difference of the lithium chemical potential between the two (positive and negative) electrodes:

$\overline{V}(x) = -\dfrac{\mu_{Li}^{positive}(x) - \mu_{Li}^{negative}}{zF}$, in which F is the Faraday constant and z is the charge (in electrons carried by lithium).

The calculation of cell potentials is performed in this study through already developed DFT methods which have proven that a good estimation of the average potential can be obtained

from total energy calculations. If the variation in the Gibbs free energy (ΔG) term is approximated by the internal energy (ΔE) and if small changes in entropy (TΔS) and volume (PΔV) are neglected, the average potential value can be expressed as :

$$\overline{V}(x_1, x_2) = -\frac{\left[E_{tot}\left(Li_{x_2}PBD_1\right) - E_{tot}\left(Li_{x_1}PBD_1\right) - (x_2 - x_1)E_{tot}(Li)\right]}{(x_2 - x_1)} \qquad [1]$$

where x_1 and x_2 are the two limit compositions and E_{tot} refers to the total energy per formula unit (p.f.u.) in eV.

Considering that one lithium ion p.f.u. can be inserted in PBD_1, the first insertion reaction step can be written as :

$$PBD_1 + Li \rightarrow Li\,PBD_1 \qquad [2]$$

$x_1 = 0$ and $x_2 = 1$ are thus taken as composition limits. Therefore, the average lithium insertion potential can be extracted from the following expression:

$$\overline{V} = E_{tot}(PBD_1) - E_{tot}(LiPBD_1) + E_{tot}(Li) \qquad [3]$$

where $E_{tot}(Li)$ is the total energy for metallic lithium in the bcc structure. Within this frame, the determination of an average battery voltage requires thus only three total energy calculations.

The resulting calculated intercalation potentials (Figure 7) lie in between the experimental value, with departure of less than 0.4 V, which shows that we already reach satisfactory values.
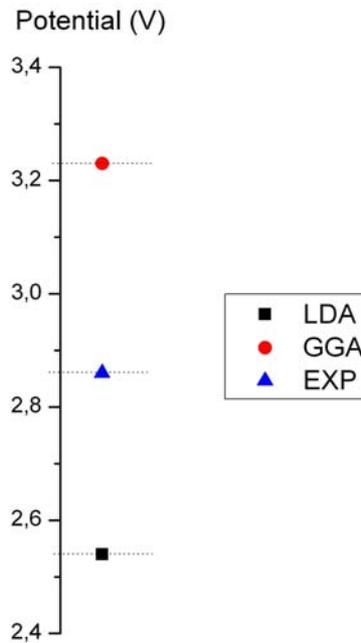
Figure 7: Average intercalation potential in the **PBD₁** phase.

Conclusions

We had previously shown that tetraketopiperazine derivatives could be considered as electrochemically active vs. Li. In order to thwart the solubility issues of such small organic molecules we have succeeded in preparing an oligomeric version (**p-AP**) which is characterized by an average potential of 2.5 V and better capacity retention. However, the operating potential remaining a bit low for a positive electrode application, the study of other types of redox-active entities was considered.

Aiming to set up the bases of a structure-electrochemical activity relationship study around nitrogen-containing heterocycles we prepared and tested vs. Li several lithiated heterocycles derivatives. Quite interestingly one salt is characterized by a stable and reversible electrochemical activity vs. Li at an average potential of 1.95 V with a "proved" specific capacity about 95 mAh/g (potentially improvable to near 180 mAh/g in a near future).

On the other hand we have also focused our efforts on a better understanding of the relationship between the nature of substituents connected to the para-benzoquinone structure and the electrochemical properties of the compound. The study is presently under progress combined with a computational approach to give us some new insights.

Future plans

Our next priority will be to improve the promising results foreseen for nitrogen containing derivatives. The main challenge remains the improvement of the average potential of our organic materials. We will focus on studying the right adequacy between substituents preventing the solubility of a para-benzoquinone molecule and substituents allowing a high potential (3V or more).

Regarding the computational approach, calculations using the same methodology are underway for the study of a further lithium ion inserted in the structure of the considered phase. Experimental work is underway in order to corroborate the geometry issued from theoretical studies and the crystallographic identification provided by XRD. Improvements of the lattice parameters appreciation should be provided by testing other functionals (improved GGA treatment such as PBEsol, hybrid functionals,…) in conjunction with the implementation of Van der Waals interactions. Then, the same methodology should be applied to other classes of organic crystals. Finally, a comparison of the trends in intercalation potential obtained within crystals and redox potentials characterizing the corresponding molecules should be envisaged in order to see if a clear correlation can be identified.

Publications

1. Geng J., Bonnet J.-P., Tarascon J.-M., Dolhem F., Poizot P., submitted

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