

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

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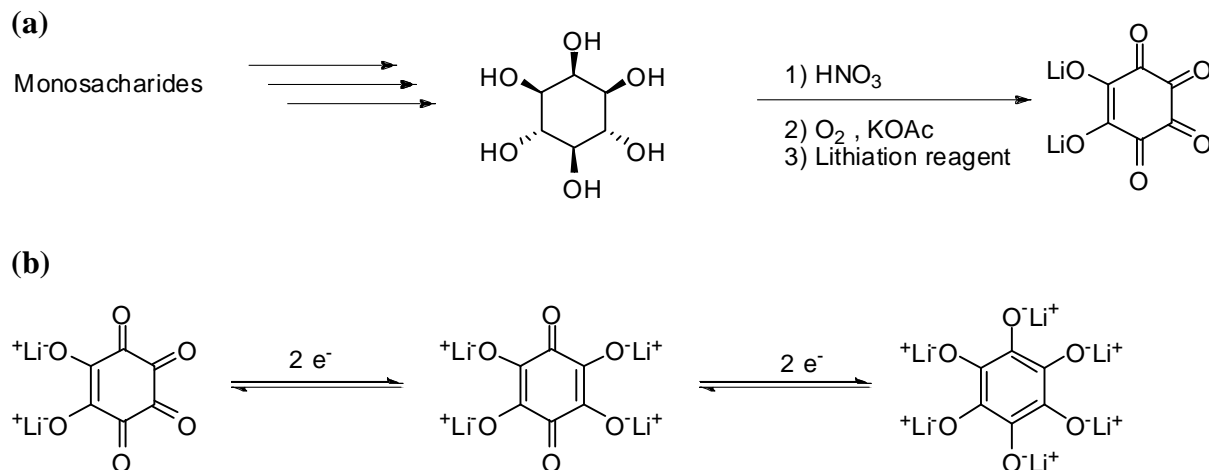
## Abstract

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 GCEP and entitled Advanced Li-ion Batteries, is based on the use of renewable ORGANIC electrodes termed “ALIBORG” aimed towards the design of better batteries by introducing the concepts of sustainability and renewability. The project started on September 1<sup>st</sup>, 2008, and the present document reports our progress over the last six months. Following our work on oxocarbonyl derivatives, emphasis has been placed on the synthesis of tetraketopiperazine-based molecules and their electrochemical performances. We have been quite successful in our new synthesis endeavours, therefore the electrochemical performances of our prepared molecules are lagging behind as they show limited initial capacities and poor cyclability owing to dissolution problems. Directions to eschew such difficulties within the next coming months are presented.

## 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<sub>2</sub> footprint criteria, owing to the use of active inorganic materials obtained from limited mineral resources while 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. The objectives of the ALIBORG project involve two main aspects: 1) the creation of a new bank of scientific knowledge in synthesizing/designing organic molecules/polymers electrochemically active towards Li and 2) the practical integration of these materials into laboratory test cells for performance evaluation while favouring some “Green Chemistry” concepts. During these last 6 months, we have focused our attention on organic molecules containing C=O functionalities (polyquinone-type structure). Actually, we have previously shown that dilithium rhodizonate salt Li<sub>2</sub>C<sub>6</sub>O<sub>6</sub> displays quite an interesting electrochemical behaviour vs. Li<sup>1</sup> whereas

deriving from *myo*-inositol,<sup>2</sup> a natural compound widely distributed in plant as phytic acid (scheme 1).<sup>3</sup>



**Scheme 1:** a) Chemical synthesis of dilithium rhodizonate from natural resources, (b) typical electrochemical reactivity of  $\text{Li}_2\text{C}_6\text{O}_6$  vs. Li.

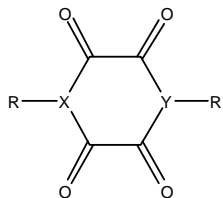
Having identified the positive attribute of the six-membered oxocarbon  $\text{Li}_2\text{C}_6\text{O}_6$ , a wide variety of single/multiple ring molecules containing chemically active  $\text{C}=\text{O}$  functions with various heteroatom can be considered; the presence of heteroatom having a possible effect on the redox potential of the considered molecule. Multiple atomic organizations can be considered, the challenge being to grasp an efficient redox-active system.

## Background

The demand for electric energy does increase even faster than the world's population due to improving well-being in the Developing World. 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 for finite fossil-fuel supplies coupled with 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.;  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiC}_6$ ), 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). Interestingly, to the best of our knowledge, this concept has never been proposed in the literature.

## Results

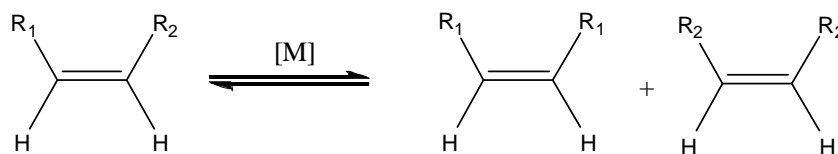
With the GCEP support starting from September 2008, we have investigated the chemical synthesis and probed the electrochemical signature of a series of tetraketo derivatives having the general formula:



The preliminary tests have shown an interesting electrochemical activity characterized by a flat plateau and a low polarization value ( $\sim 100$  mV) for a specific capacity around 200-250 mAh/g after the first discharge (depending on the nature of X and Y atoms). However, the nature of both R and R' appeared obviously quite important for two main reasons. First, these substituents introduce generally an inert mass explaining why small groups are typically used. Second, the possibility of having a delocalization effect between the heterocycle and R/R' also plays an important role.

Some attempts to produce polymers of such tetraketo derivatives have been performed to decrease the solubility of such compounds. Along that line, we then decided to use an ADMET (Acyclic Diene Metathesis) polymerization approach, never reported using such monomers to date, taking into account the specificity of this reaction (i.e.; diene groups, compared to a radical polymerization that could affect carbonyl groups). Furthermore this approach enables the incorporation of a short spacer between the active redox ring units without possible delocalization.

Metathesis reaction is a catalyzed reaction by transition metal complexes (M being W, Ru or Mo) to redistribute olefin's substituents (Scheme 1).



**Scheme 1:** General equilibrium for Metathesis reaction.

ADMET is an application of the metathesis reaction basically used to polymerize terminal olefins. The involved equilibrium is linked to the product side with ethylene evolution.

## Future plans and conclusions

We have shown that tetraketo derivatives can be considered as electrochemically active vs. Li. However, we have pinpointed both the ability for small molecules to be dissolved in currently used electrolytes for Li-ion batteries and a possible beneficial effect of substituents making a delocalization possible. Consequently, we plan to synthesize a tetraketo derivative characterized by a spacer stabilizing electrons such as a phenyl, bi-phenyl or naphthalenic group. On the other hand, the operating potential being a bit low for a positive electrode application, the study of other types of redox-active entities is presently considered.

## References

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