



Short communication

A rechargeable lithium/quinone battery using a commercial polymer electrolyte

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ABSTRACT

The present study reports superior electrochemical performance with capacity doubled for organic positive electrodes based on a small redox-active molecule when using the Lithium Metal Polymer (LMP) technology. Particularly, the simple use of the regular solid polymer electrolyte currently employed in commercial LMP cells allows obtaining for the first time an efficient two-electron cycling of tetramethoxy-*p*-benzoquinone with high-rate capability at temperatures as high as 100 °C. With no optimization, the restored capacity represents 80% of the theoretical value (190 mAh/g) after 20 cycles operated at a C rate. On the contrary, when cycled in conventional carbonate-based electrolytes, this quinone compound exhibits quite poor electrochemical features such as a very limited depth of discharge (~50% of the theoretical capacity in the first cycle) followed by rapid capacity decay. After cycling, preliminary post-mortem characterizations did not evidence any obvious degradation in the cell. Although the adverse effect of the diffusion of the active material is not fully inhibited, the coulombic efficiency is close to 100% while the Li/electrolyte interface appears stable.

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1. Introduction

Rechargeable Li-batteries are currently essential power sources for numerous valuable applications ranging from microchips to the emerging large-scale applications. Chemically speaking, almost all developed electrode materials are inorganic by nature, which are often costly and not so environmentally benign. In this context, it seems established now that electroactive organic structures can be also considered as promising candidates for promoting new generations of batteries (see for example, Refs. [1–5]). Although significant improvements have been achieved over the past few years, organic electrode materials are not yet used in practice notably due to some recurring limitations in terms of volumetric energy densities, cycle-life performance or power capabilities. Cyclability issues mainly arise from the spontaneous diffusion of the active material out of the electrode especially for small molecular structures [3–5]. However, such low-molecular-weight (neutral) molecules are obviously of particular interest because high specific capacities can be expected. Accordingly new strategies should

be proposed to simultaneously inhibit dissolution and improve the insertion kinetics in neutral organic host structures. Along this line, the introduction of a gelified polyethylene oxide (PEO)-based membrane (concept of quasi-solid state lithium battery) has recently shown interesting performance upon cycling for few small redox-active molecules in Li half cells thanks to a partial inhibition of the dissolution phenomenon [6,7]. However, given the complexity of the proposed electrolyte formulation with its multiphase components (PEO-ionic liquid-silica mixture), the exact role of the gelified membrane is rather difficult to identify. Within this background, it appeared relevant to assess the electrochemical performance of small (multi-electron) molecular structures in a simpler cell assembly and using the dry PEO-based electrolyte membrane currently employed in the Lithium Metal Polymer (LMP) technology. In fact, this mature technology initially proposed and developed by M. Armand [8–10], does not require flammable organic electrolytes and allows the direct use of energy dense Li as the negative electrode by preventing internal short-circuits. Moreover, the implementation of non-lithiated materials as the positive electrode (i.e., charged state) becomes possible, which opens up a larger choice in terms of electroactive organic structures.

The cell assembly used in this study derives from the one presently integrated in LMP batteries developed and placed on the market by the Blue Solutions company since 2011. Operating at high cycling

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temperature (typically 80 °C) such batteries are powering several practical applications including for instance the electric vehicle BlueCar used in several programs like Autolib® in Paris (France) or Blueindy® in Minneapolis (USA). LiFePO₄ is currently used as positive electrode material but alternative compounds are under the scope of development like sulfur [11]. For this preliminary study, we have selected tetramethoxy-*p*-benzoquinone (TMQ) as the prototype organic molecular compound for its thermal stability and an expected two-electron reaction giving rise to a theoretical specific capacity of 235 mAh/g (Fig. 1a), a value never approached up to now due to solubility issues [12–14]. Additionally, this cell was simply constituted by a lithium electrode, the PEO-based solid polymer electrolyte and the organic composite electrode deposited on a carbon-coated aluminum current collector (Fig. 1b); all layers are self-supported and flexible, which is essential for industrial purposes.

2. Experimental

Both synthesis and detailed characterizations of TMQ were previously described [12–14]. The composite electrode was prepared as follows: 50 mg of carbon black (Ketjenblack® EC600JD, AkzoNobel), 40 mg of multiwalled carbon nanotubes (Arkema), 40 mg of LiTFSI (3 M), 120 mg of PEO (Aldrich, *M* ~ 300,000 g/mol) and 250 mg of TMQ powder were ball-milled together with 4 g of water in a silicon

nitride vial with three silicon nitride balls. The slurry was tape-casted onto a carbon-coated aluminum current-collector (Exopack) and dried successively during 12 h at room temperature followed by 20 min at 120 °C in a dry room with controlled moisture (dew point of –55 °C). The electrode loading of TMQ was close to 0.7 mg/cm². Lithium foils as well as PEO/LiTFSI-based electrolyte membranes (O/Li ratio = 25, $\sigma = 0.1$ S/cm at 100 °C) were provided by the Blue Solutions company. The polymer cells were assembled in a dry room by stacking lithium, the solid polymer electrolyte membrane and the cathode onto its current-collector at 80 °C. On the negative side, the current collector was a copper foil hand-welded to lithium. Each current-collector was assembled to copper-connectors by spot welding. Cells were air tight sealed in coffee-bags and vacuumed in order to avoid air pockets (geometrical surface of ~20 cm²). Such cells were cycled in galvanostatic mode using a MPG2 system (Biologic S.A., Claix, France). Reported capacity values refer to the mass of the active material in the positive electrode. Electrochemical measurements obtained at 20 °C were performed by using a Swagelok®-type cell and a composite electrode made of TMQ mixed with 33 wt.% carbon black and soaked with a typical liquid electrolyte (LiPF₆ 1 M in ethylene carbonate/dimethyl carbonate, 50/50 in volume ratio: Merck LP30®). For post-mortem study, the cell was opened in a dry room. A 1 cm²-piece of this cell was cut with a blade, frozen in liquid nitrogen and finally sliced with a microtome to get proper cross-sections. Morphology of the as-prepared samples was

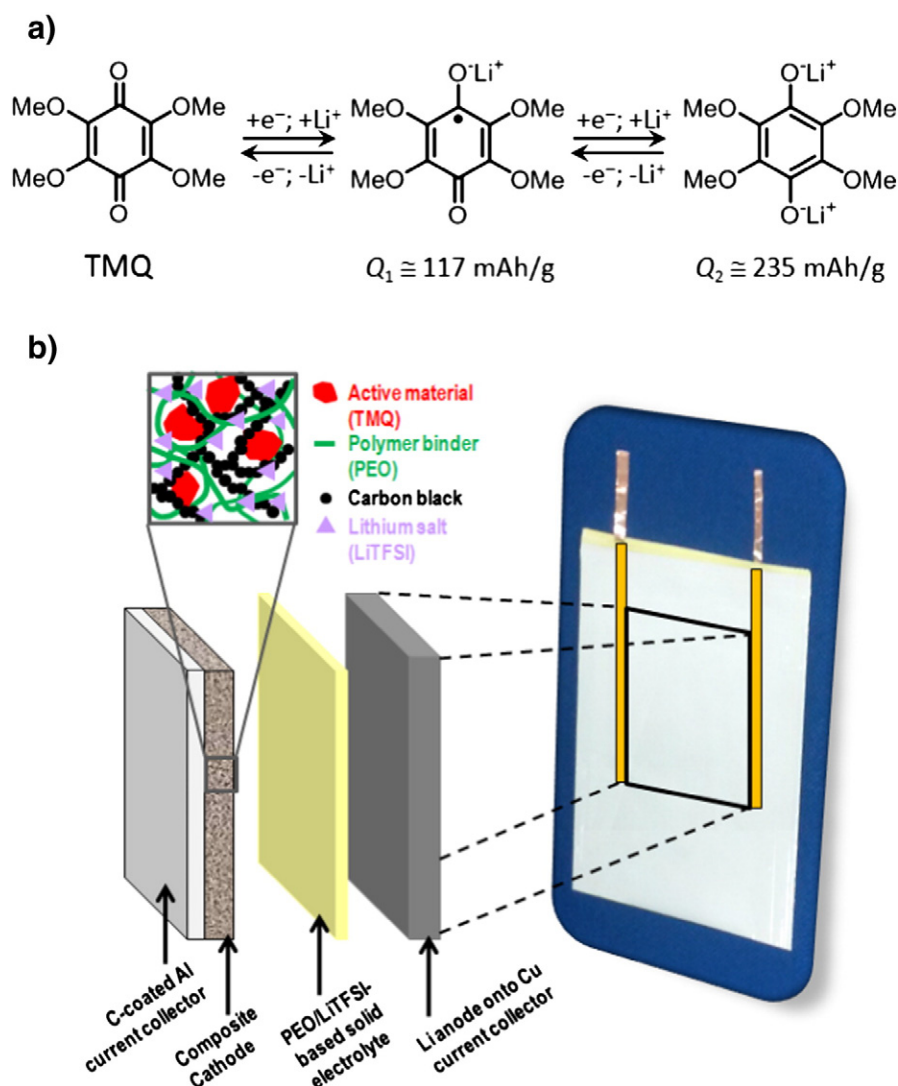


Fig. 1. a) Expected two-electron electrochemical reaction with Li for tetramethoxy-*p*-benzoquinone. b) Schematic representation of the LMP cell operating with TMQ as cathode material.

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