

# Poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene): a new organic polymer as positive electrode material for rechargeable lithium batteries

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## Abstract

A new organic polymer as positive electrode material is presented. Poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene) (PDBM) has oxocarbon cycles which are part of the polymer backbone and exhibit redox properties. Composite materials with acetylene black were investigated as positive electrodes for rechargeable lithium batteries. A specific capacity of 150 mAh g<sup>-1</sup> was reached with 40% acetylene black. The composite electrodes showed moderately good cyclability with less than 10% degradation in the first 100 cycles.

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**Keywords:** Positive electrode; Rechargeable lithium battery; Organic polymer; Conducting polymer; ICP

## 1. Introduction

The use of organic conducting polymers as positive electrode materials in rechargeable batteries has attracted extensive studies [1]. However, the more common conjugated polymers such as polyacetylene, polyaniline, polythiophene and polypyrrole do not have specific redox moieties and therefore have specific charges that are too low for high energy batteries. We have therefore embarked on designing novel polymers with large ion-insertion capacities as a result of the quinone–alkoxide redox reaction.

Recently, Armand and co-workers have shown that a group of organic monomers based on polyoxocyclohexanes (e.g. lithium rhodizonate, Li<sub>2</sub>(CO)<sub>6</sub>) exhibit reversible insertion [2,3], but those may be unsuitable for electrode use because of their solubility in organic solvents. In this work, the redox centres are immobilised and intermediate redox states may be stabilised by a conjugated main chain, facilitating the two-electron transfers comprising the quinone reduction. Even without conjugation, electron hopping conduction is favoured by the proximity of the redox centres.

Here, we present the properties of a new polymer based on 2,5-dihydroxy-1,4-benzoquinone monomer units, poly(2,5-

dihydroxy-1,4-benzoquinone-3,6-methylene) (PDBM), with high theoretical capacity (705 mAh g<sup>-1</sup>) (Fig 1a).

## 2. Experimental

### 2.1. Synthesis of PDBM and its Li salt

One gram of 2,5-dihydroxy-1,4-benzoquinone (7.14 mmol) was dissolved in 75 ml of warm glacial acetic acid. A ca. 37% aqueous formaldehyde solution (3 ml) was then added and the resulting mixture was left stirring for 48 h at room temperature. The precipitate was then collected by filtration, thoroughly washed with water and dried under high vacuum to yield the desired polymer (PDBM) as a yellow solid (0.85 g). <sup>13</sup>C solid state NMR, δ (ppm): 10–20 (br, CH<sub>2</sub>), 104.2 (CH), 114.8 (C–CH<sub>2</sub>), 156 (C–OH), 159.3 (C–OH), 184.3 (C=O). FT-IR (golden gate), ν (cm<sup>-1</sup>): 3296, 1645, 1615, 1193, 772. M<sub>n</sub> (determined by GPC): 18,375.

An amount equal to 0.7 g of the PDBM was dissolved in 100 ml propan-2-ol. Lithium isopropoxide (0.7 g, 2.2 eq.) was added and the mixture was stirred for 10 h under argon. The dark brown product was then filtered off, dried under argon and designated PDBM(Li) (Fig. 1b).

### 2.2. Electrode preparation

Composite electrode materials were prepared by mixing the active materials (PDBM and PDBM(Li)) with acetylene black (AB; 100% compressed, Shawinigan) and PTFE

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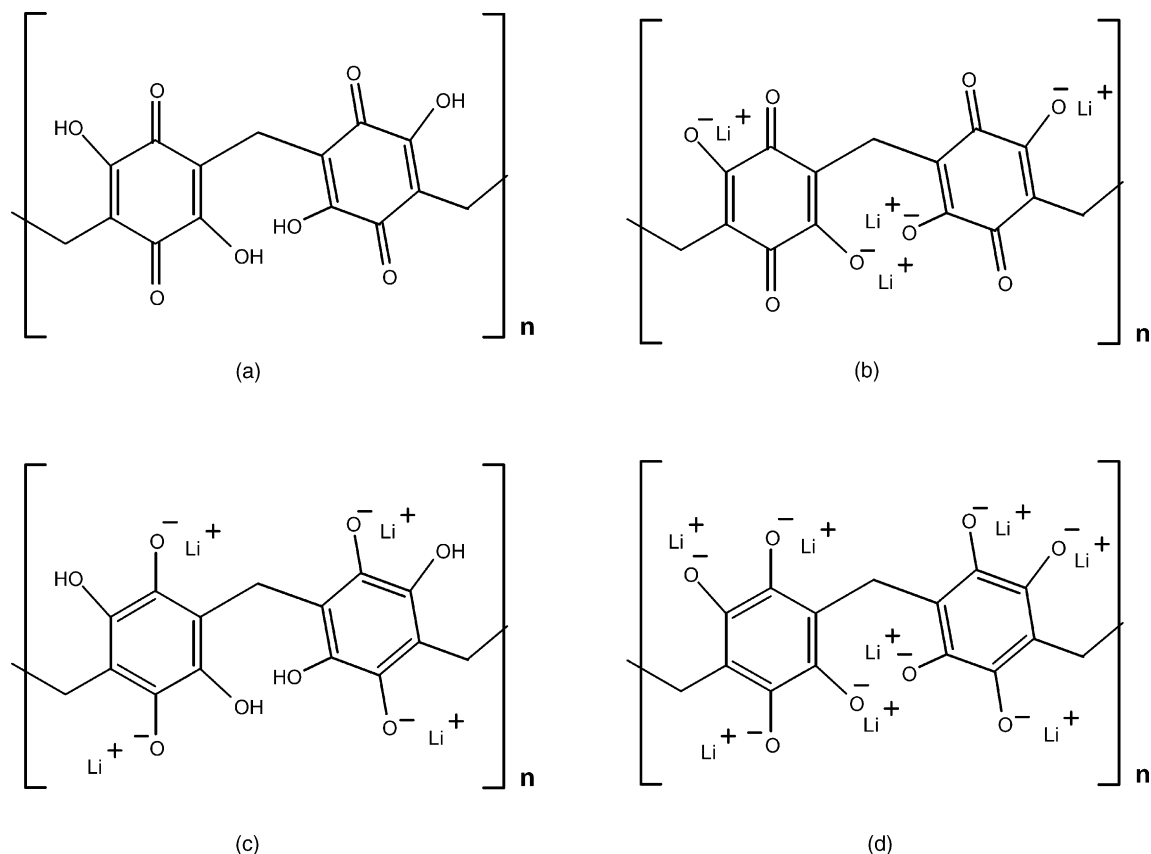


Fig. 1. (a) PDBM; (b) PDBM(Li); (c) reduced PDBM; (d) reduced PDBM(Li).

(Dupont) as a binder. The three materials were thoroughly mixed in an agate mortar with a pestle. Films were obtained by using a rolling machine and pellets of area ca.  $1 \text{ cm}^2$  and thickness of ca.  $120 \text{ nm}$  were prepared, dried for 10 h under

vacuum at  $120 \text{ }^\circ\text{C}$  before cell assembly in anaerobic conditions.

### 2.3. Electrochemical cell

Hermetically sealed two-electrode cells were used as represented in Fig. 2. Typically a pellet of composite material (weight: ca.  $10 \text{ mg}$ ; diameter: ca.  $1 \text{ cm}$ ) was separated from the negative electrode (lithium disc, diameter: ca.  $1 \text{ cm}$ , Aldrich) by a glass microfibre filter (Whatman) imbibed with electrolyte solution ( $1 \text{ M LiPF}_6$  in EC:DMC 1:1 (w/w), Merck). The three layers were pressed between two stainless steel current collectors, one in contact with the active material and the other in contact with the lithium foil.

### 2.4. Electrochemical experiments

Cyclic voltammetry and galvanostatic cycling experiments were performed using a VMP multi-channel potentiostat/galvanostat (Perkin-Elmer). All experiments were carried out at room temperature.

## 3. Results and discussion

No electronic conductivity was detected in a pellet of either of the materials; this is not surprising since there is no

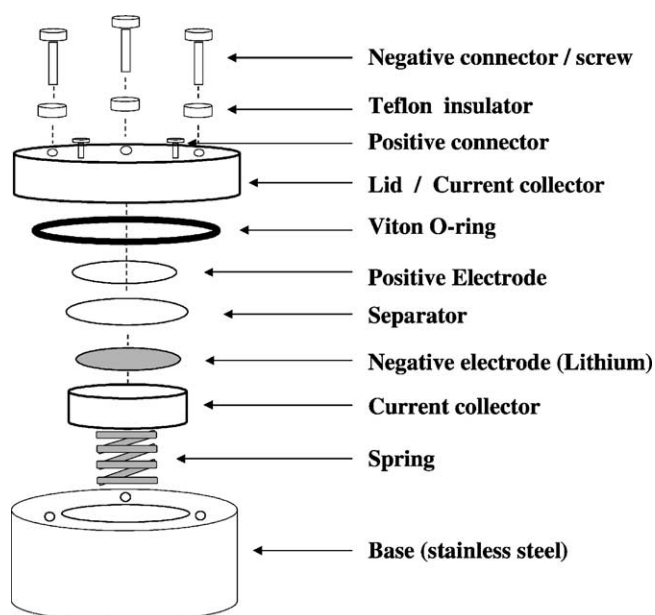


Fig. 2. Schematic representation of a testing electrochemical cell.

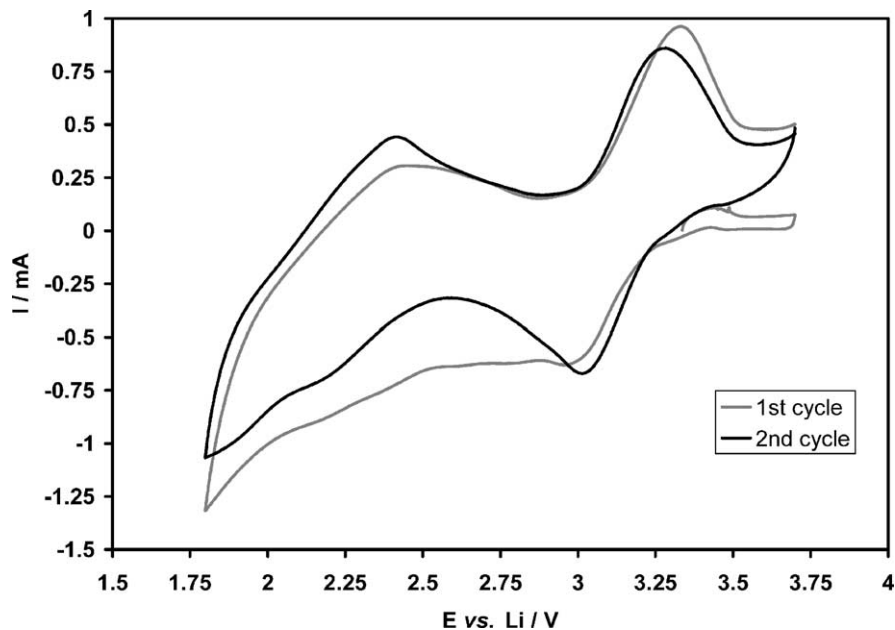


Fig. 3. Cyclic voltammogram of PDBM recorded at  $1 \text{ mV s}^{-1}$ . Conditions: 1 M  $\text{LiPF}_6$  in EC:DMC 1:1 (w/w); 55% PDBM; 40% AB; 5% PTFE.

long range conjugation. Therefore, acetylene black was added to each material along with PTFE as a binder, to form composite electrodes for electrochemical measurements.

A cyclic voltammogram of PDBM electrode at a scan rate of  $1 \text{ mV s}^{-1}$  is presented in Fig. 3. No oxidation is observed on sweeping positive from the open circuit potential of 3.3 V. On the first negative sweep, we observe a clear reduction process at 3.0 V versus Li partially obscured by several other cathodic processes increasing toward the negative potential limit. The first process is assumed to be the reduction of the carbonyl groups to form lithium

alkoxide groups. The causes of the other processes are not identified here. (Reduction of protons to hydrogen would not have been observed because the electrode was not visible during the electrochemical cycling.) Two oxidation processes are shown in the subsequent positive sweeps and these are reflected in the subsequent negative sweeps. A minor peak at 2.3 V is presumed to be the reverse of one of the unidentified reduction during the preceding negative sweep. The well-defined peak at 3.25 V is ascribed to reoxidation of the alkoxide groups. A rise in current near the anodic limit suggests a possible oxidation which requires further investigation. The second cycle shows a much better

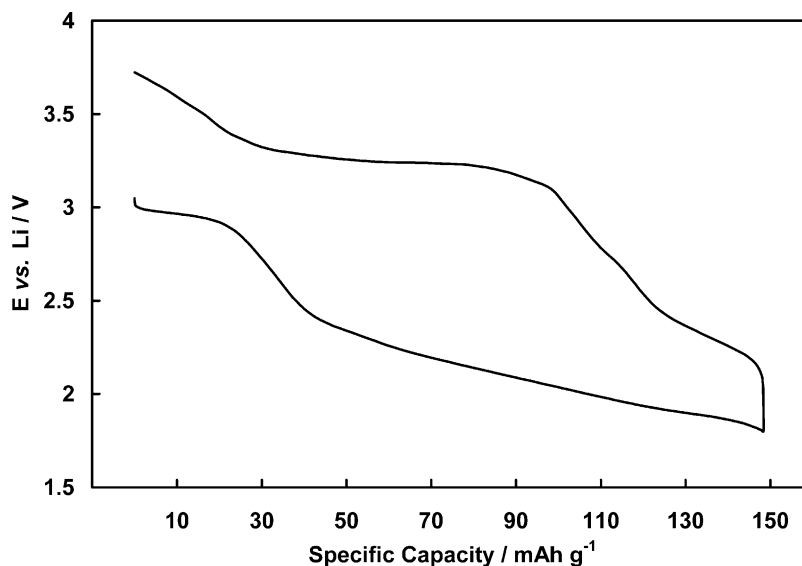


Fig. 4. Potential vs. specific capacity. First charge–discharge cycle for cell with 52% PDBM, 40% AB and 8% PTFE. Cycling at  $100 \mu\text{A cm}^{-2}$ .

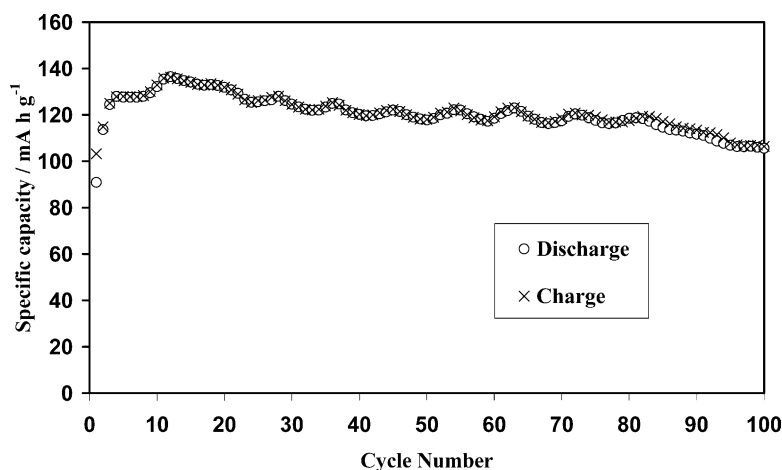


Fig. 5. Galvanostatic cycling of PDBM composite electrode. Conditions: cycling rate,  $C/2$ ; potential limits, 4.2 and 2.0 V; electrolyte, 1 M  $\text{LiPF}_6$  in EC:DMC 1:1 (w/w); 35% PDBM; 60% AB; 5% PTFE.

defined pair of peaks for the quinone–alkoxide transformation, designated (a)–(c) in Fig. 1. Given the possibility of reduction of acidic protons on the hydroxyl groups of PDBM, structure (d) is given in Fig. 1 as another possible product of electrochemical reduction in a non-aqueous lithium salt electrolyte.

The lithiated form, PDBM(Li) was investigated in the same way in the expectation of a simpler voltammogram. Unfortunately this sample not only showed the complex processes below 3 V but also gave no evidence of the prominent redox couple observed in the unlithiated sample. This result is ascribed to a failure of electron transfer to the lithiated form, caused by an extremely low electronic conductivity.

Galvanostatic studies of lithium battery with these composites as cathode material have been performed and the results are shown in Fig. 4. Composites using 40 wt.% AB gave cells with specific capacities of ca.  $150 \text{ mAh g}^{-1}$  between 1.8 and 3.8 V. The larger hysteresis than that obtained on cyclic voltammetry is probably due to the poor electronic conductivity of this material. In general, it was found that the capacity cycling performance were very sensitive to the proportion of carbon and the mode of preparation of the composite.

Fig. 5 shows the cycling performance for a composite electrode containing 60% AB to enhance the electronic conductivity. Charging and discharging was repeated at a cycling rate of  $C/2$ . After 100 cycles, the specific capacity is still ca.  $100 \text{ mAh g}^{-1}$  which illustrates the good cyclability of the composite electrode. It is notable that the capacity increases on the first two cycles; this is interpreted as the formation of electronic conducting pathways connecting electron donor and acceptor sites, similar to the first cycles of lithium insertion in tungsten oxide, for example. The overall capacity of only half that expected from a single quinone group indicates that the electronic network is not adequate to connect to all the redox sites.

The variation of specific capacity of the active material as a function of acetylene black weight fraction was investigated as shown in Fig. 6. It was found that the highest capacity of ca.  $150 \text{ mAh g}^{-1}$  is obtained with 40–50% AB.

Although the measured cycling capacity of PDBM compares well with many inorganic positive electrodes, the results obtained so far leave much room for improvement. This is because the capacity values are less than half of the theoretical value based on a two-electron reduction of the carbonyl groups. Little attempt has been made so far at combining specific redox activity with conjugated backbones, which should greatly enhance electron mobility and electrode kinetics. Further work will proceed with continued

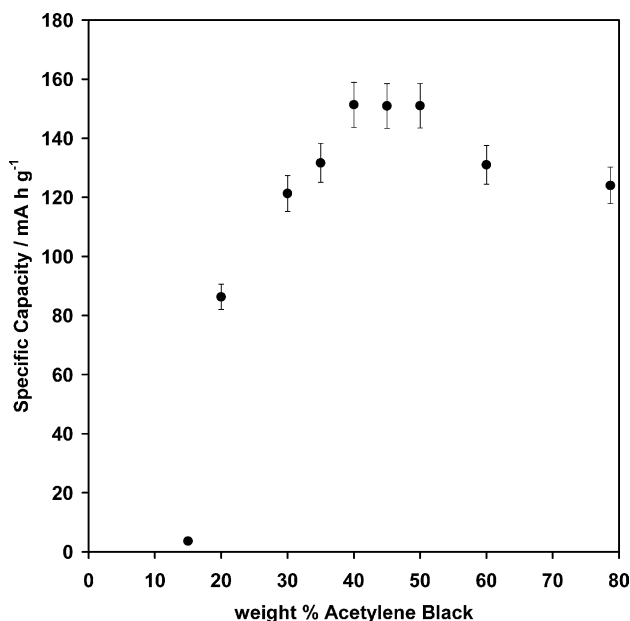


Fig. 6. Specific capacity of PDBM as a function of wt.% AB. The values are the average of the first 10 cycles obtained by galvanostatic cycling at a current density of  $100 \mu\text{A cm}^{-2}$ .

investigation of ion-exchanged forms and the possible oxidation of alkoxide groups to carbonyl at high potentials.

#### 4. Conclusion

A new class of organic polymer with benzoquinone units as part of the polymer backbone have been synthesised. Composite electrodes with acetylene black showed reversible lithium insertion corresponding to partial reduction of the quinone groups, and a capacity of up to  $150 \text{ mAh g}^{-1}$ . Further work is expected to reveal further redox capacity on utilisation of two quinone groups per ring.

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