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# Insight in the degradation of polyquinone-based cathode material in lithium-organic battery under cycling

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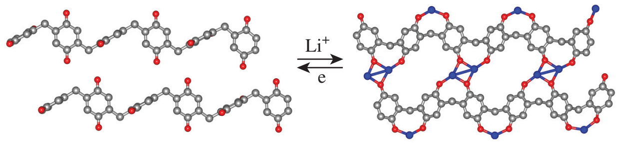
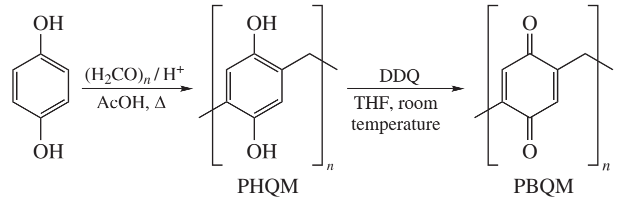
**Electrochemical lithiation of organic polyquinone-based cathode material can occur irreversibly leading thus to a rapid deterioration of the battery performance. Carefully controlled degree of lithium intercalation within the defined charge/discharge potential window provides a stable battery operation within 170 cycles with 100% coulombic efficiency. DFT calculations revealed that deep lithiation results in a strong conformational reorganization of the polymer domains leading to repeatable expansion and shrinkage of the electroactive material and a rapid loss of the cathode integrity.**



Lithium-organic and sodium-organic batteries are of interest due to the fact that organic materials can potentially deliver 200–300% higher specific capacities compared to conventional materials such as lithium iron phosphate and even lithium nickel manganese cobalt oxide.[1,2] Lithium-organic batteries are environmentally friendly since they do not contain heavy metals and, therefore, can be easily recycled as a conventional household waste.[3] There is also a strong promise to design flexible lithium-organic batteries for a new generation of mechanically soft bendable and even stretchable portable electronics.[4] Due to the limited abundance of lithium, sodium battery technology is also in mind for bulk energy storage.[5] However, switching rigid inorganic materials from lithium to sodium intercalation is a very complicated task. On the contrary, such cation replacement is straightforward with soft organic cathode materials. Indeed, organic cathodes can be equally efficient in lithium and sodium batteries.[6,7]

In spite of all aforementioned potential advantages of organic cathode materials, none of them is used industrially by now. Although organic materials are very challenging to handle while forming cathode composites, their durability is not so great at the moment. Therefore, there is an urgent need for a systematic investigation of various organic cathodes, revealing molecular structure–performance relationships and unraveling the main degradation mechanisms.

Here, we address the electrochemical behavior of promising polyquinone-based material PBQM (Scheme 1) which has an impressive theoretical capacity of ~446 mAh $g^{-1}$, exceeding that of $LiFePO_4$ by a factor of 2.5. PHQM, also known as bakelite, is a readily available heavy industry material, which can be easily prepared from cheap precursors following the well-known procedure.[†,8,9]



**Scheme 1**

Cyclic voltammogram[‡] of the PBQM // Li cell measured within the 1.0–3.7 V potential range is shown in Figure 1(*a*). One can

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[†] 1,4-Dihydroxybenzene (5.5 g, 50 mmol) and paraformaldehyde (2.3 g, 75 mmol) were dissolved in acetic acid (25 ml) with addition of $H_2SO_4$ (0.5 ml) and refluxed for 3 h. To obtain PBQM, the formed black precipitate of PHQM was washed thoroughly with deionized water, dried and then stirred vigorously in THF with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (11.2 g, 50 mmol) within 16 h. The precipitate was collected by filtration and subjected to Soxhlet extraction with THF for 12 h to remove all low-molecular-weight impurities. The dried PBQM was characterized by elemental analysis, FT-IR and solid state $^{13}$C NMR spectroscopy (see Online Supplementary Materials). The obtained results were fully consistent with the molecular composition and structure of PBQM.[8]

[‡] The electrochemical performance of PBQM was evaluated in laboratory prototypes of the pouch-type lithium batteries. The cathode composite consisted of 55 wt% of PBQM, 40 wt% of conductive carbon black (Timical Super C65, MTI Corporation, USA) and 5 wt% of PVDF polymer binder (Kynarflex HSV 900, Arkema France). All components were dispersed in NMP (99%, Aldrich) to obtain ~12% suspension, which was homogenized mechanically (Isolab Homogenizer, Light Duty). The obtained cathode slurry was applied onto the current collector (25 μm thick Al-foil) using tape coating. The resulting films were dried at 120–200 °C *in vacuo*. The cathode (1.5 × 1.5 cm), polypropylene separator (Celgard 2325, France) and lithium anode (1.5 × 1.5 cm, Russia) were assembled in a pouch-type lithium batteries using a standard 1 M $LiPF_6$ solution in ethylene carbonate/dimethyl carbonate (1 : 1 v/v) (Sigma–Aldrich) mixture as electrolyte. The assembly of the pouch batteries was carried out inside an MBraun argon glove box using Henkelman Mini Jambo vacuum packager for the case sealing.

The electrochemical performance of the batteries was evaluated using Elins P30 potentiostat (Russia) and Neware battery analyzer (BTS-5V10mA, China) by cyclic voltammetry measurements and charge/discharge cycling at different current rates (from *C*/20 to *C*/2).

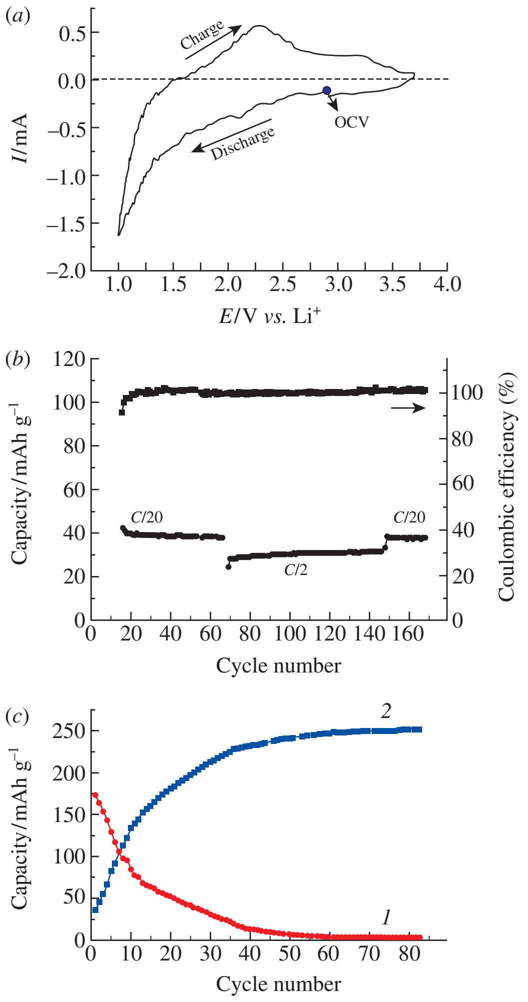

**Figure 1** (*a*) Cyclic voltammogram of the PBQM//Li cell recorded in the 1.0–3.7 V potential window (voltage sweeping rate 2 mV $s^{-1}$). (*b*) The discharge capacity and coulombic efficiency of PBQM//Li battery *vs.* the cycle number under cycling rates *C*/20 and *C*/2 within the controlled potential windows (0.5–2.0 V). The first 15 formation cycles are not shown. (*c*) The discharge capacity (*1*) and irreversible capacity (*2*) of the PBQM//Li battery *vs.* the cycle number while charging/discharging in the 0.5–4.0 V potential range with *C*/20 current rate.

identify a weak anodic peak at 3.25 V and a stronger peak at 2.30 V *vs.* Li/$Li^+$. These peaks can be tentatively attributed to the oxidation of each benzoquinone moiety first to semiquinone and, finally, to hydroquinone dianion. Figure 1(*b*) shows the cycling behavior of the PBQM//Li battery with different sweeping rates. We found that *C*/20 charge/discharge rate gives better performance compared to *C*/2. Coulombic efficiency of the charge–discharge process for each cycle was virtually equal to 100%, thus indicating complete reversibility of the electrochemical reaction while charging/discharging the battery within 10% of the theoretical capacity. It should be emphasized that the battery showed no signs of the capacity fading after 160 charge/discharge cycles. Figure 1(*c*) shows the evolution of the discharge capacity of the PBQM//Li battery while cycling (current rate of *C*/20) within the expanded potential window (0.5–4.0 *vs.* Li/$Li^+$) resulting in a substantially deeper charge/discharge of the device (40% of the theoretical capacity). It is notable that the initial discharge capacity was increased to 175 mAh $g^{-1}$, thus pointing towards the potential of PBQM being applied as high-capacity cathode material. For comparison, the reference $LiFePO_4$//Li batteries delivered initial discharge capacity of 140–150 mAh $g^{-1}$ under the same conditions. Unfortunately, very fast deterioration of the performance of the PBQM//Li battery was observed and the discharge capacity has fallen down to zero just after 60 cycles. This degradation was accompanied by a rapid growth of the irreversible capacity due to deep intercalation of lithium ions and, presumably, partial disintegration of the PBQM-based composite cathode. The total irreversible capacity approaches 250 mAh $g^{-1}$, which amounts up to more than 50% of the theoretical capacity.

We have applied density functional theory (DFT) quantum chemical calculations in order to rationalize how the degree of lithium intercalation in PBQM affects the battery performance and stability under charge/discharge cycling. In particular, we considered a model of short oligomer chains with 5–6 repeating units $C_6H_3O_2(CH_2C_6H_2O_2)_5H$ (Figure 2) and calculated the structure and the formation energy of various lithiation products. All calculations were performed at the Joint Supercomputer Center of RAS using Perdew, Burke and Ernzerhof (PBE) density functional[10] and Stevens, Basch and Krauss (SBK) pseudopotential[11] with extended basis set for valence electrons realized in PRIRODA software package.[12] This approach allows one to describe accurately the interactions of $Li^+$ with organic molecules.[13]

The isolated PBQM polymer has a regular structure with a zigzag arrangement of $CH_2$ and phenylene units between them with a periodicity of 10.15 Å [Figure 2(*a*)]. The addition of just one Li atom per PBQM repeating unit causes some relatively small changes in the polymer structure: carbonyl groups of adjacent quinoid moieties move closer to each other while forming energetically favorable Li–O coordination bonds [Figure 2(*b*)]. The period of the structure corresponds to 10.0 Å, which is very similar to that of the non-lithiated polymer. The accumulated

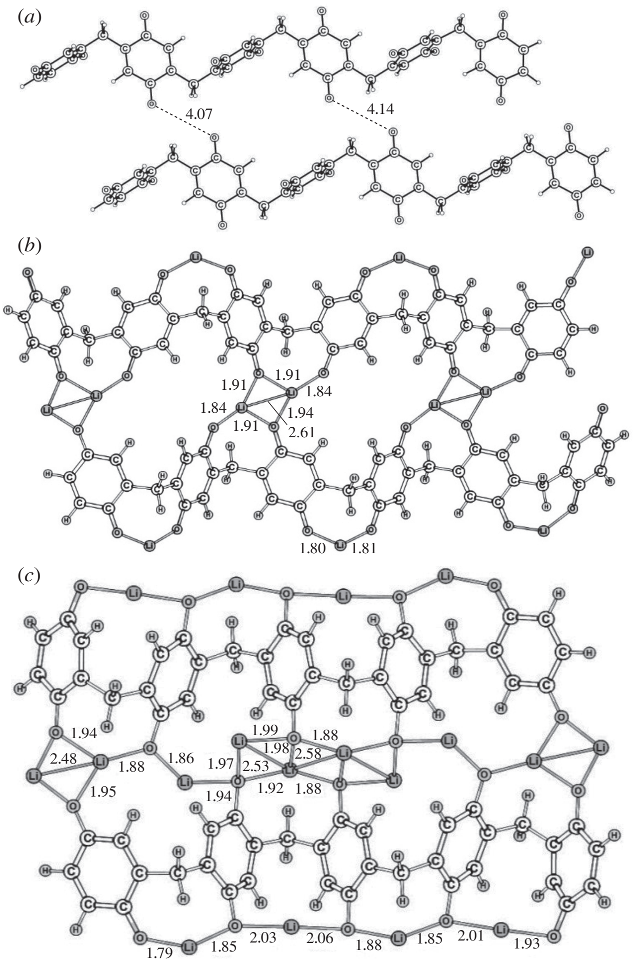

**Figure 2** Computed 3D geometry of the (*a*) non-lithiated PBQM chain and the polymer chains with (*b*) one or (*c*) two intercalated Li atoms per repeating unit. The values are given in Å.

energy in a single lithiated PBQM chain is 1.96 eV per Li atom. However, supramolecular interactions of the neighboring polymer chains induce the formation of additional Li–O coordination bonds [one per Li atom, see Figure 2(*b*)], which increase the stored energy up to 2.77 eV per Li atom. This value corresponds well to the battery open circuit voltage (OCV) [see Figure 1(*a*)].

A stoichiometric lithiation of PBQM, corresponding to the addition of two Li atoms per each benzoquinone ring, leads to the formation of two coordination Li–O bonds by every CO group [Figure 2(*c*)]. The accumulated energy in the fully lithiated PBQM chains amounts to 1.73 eV per Li atom. At potential about 1.7 V, the current changes a sign of the CVA curve [see Figure 1(*a*)]. It should be emphasized that the high degree of lithiation of PBQM results in a strong conformation change: the polymer chains shrink and the period of the structure becomes reduced substantially down to 8.49 Å.

In the course of lithium deintercalation while charging the battery, highly compact structure shown in Figure 2(*c*) is transformed to a less compact structure shown in Figure 2(*b*). This is accompanied by a considerable chain expansion with increase in the half of O–O distances from 3.2 to 6.8 Å. Apparently, this process associated with a strong conformational change has a high energy barrier and, therefore, can be in part responsible for the observed irreversibility of the deep lithium intercalation in PBQM.

Most importantly, repeatable shrinkage of the PBQM structure under deep lithiation while discharging the battery followed by strong expansion of the active material under discharge should lead to unavoidable loss of the cathode integrity. Similar or even more dramatic effects are observed in silicon anodes, which also undergo strong volume change under lithiation.[14]

In conclusion, the revealed complicated conformational dynamics of PBQM under deep lithiation/delithiation was considered as a main cause of the rapid battery failure under cycling observed experimentally. Further design of organic cathode materials should be focused on more rigid electroactive polymer structures, which can be pre-screened efficiently using DFT computational methods.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.09.032.

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