Lithium-Ion Batteries

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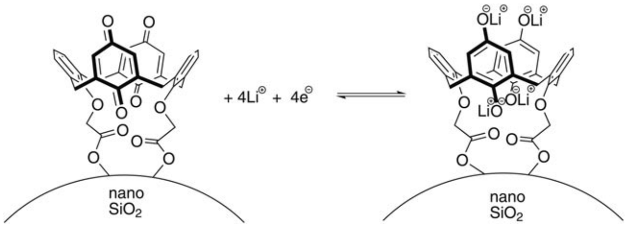
Electroactive Organic Molecules Immobilized onto Solid Nanoparticles as a Cathode Material for Lithium-Ion Batteries**

*Bostjan Genorio, Klemen Pirnat, Romana Cerc-Korosec, Robert Dominko, and Miran Gaberscek**

Li-ion batteries are considered very promising energy-storage devices for a variety of applications including large-scale batteries.[1] Given the large quantities of energy to be stored in such applications, the amount of cathode materials will be in the order kilograms per battery unit. This will not only raise concerns about the finite quantity of some resources on the earth and its environmental intolerance but also about overall CO_2 management.[2] To overcome such problems efficiently, Armand, Chen, and co-workers[2–4] recently suggested a new class of sustainable lithium batteries based on organic compounds. The other available literature mainly reports on the use of polymers as possible electroactive materials in Li-ion batteries[5,6] or totally organic polymer based rechargeable batteries.[7] Indeed, certain redox active centers of organic molecules (and also polymers) offer almost unlimited combinations of atomic arrangements and many possibilities for substitutions; this allows for fine tuning of the desired properties. Herein, our primary focus is the use of "monomer" organic molecules as an active material for Li-ion batteries. The reversible capacity of certain organic compounds, such as $Li_xC_6O_6$, can reach values as high as 580 $mA\,h\,g^{-1}$,[3] but their operating voltage is typically quite low (about 2 V vs. Li). However, the most critical problem associated with utilization of organic materials in batteries is the high solubility of many interesting organic molecules in the aprotic electrolytes commonly used in the Li-ion batteries. Although soluble molecules can act as a charge carrier,[8] the operation of a battery using such molecules is diffusion-limited. Besides that, the use of soluble organic molecules in a long-term cycling process may be questionable. Herein we propose, for the first time, that this problem can be overcome by grafting (anchoring) of soluble electroactive organic molecules onto the surface of an appropriate insoluble substrate. The essence of this approach is the strong attachment of organic molecules to a suitable substrate. This attachment not only makes the organic molecule stable during the electrochemical operation but also allows tuning of its electrochemical properties (e.g. its redox potential). Unlike in batteries, such an approach is commonly used in the related fields of sensors[9,10] and supercapacitors.[11]

We demonstrate this concept by grafting a quinone derivative of calix[4]arene (CQ) onto the surface of two different substrates: 1) nanosized silica particles with a specific surface area close to 200 $m^2\,g^{-1}$ and 2) carbon black. The electronic wiring between the grafted CQ and the current collector is established by further addition of carbon black. Scheme 1 shows the hypothetical mechanism of grafting of one CQ on silica nanoparticle and the proposed electrochemical reaction. The proposed binding nature of CQ onto silica is supposed to result in excellent electrochemical stability of such organic–inorganic hybrid system. The choice of CQ was based on proven redox activity of quinone[8] and on its known conformational mobility.[12] That is, although CQ is a relatively large molecule with a molecular weight of 568.5 $g\,mol^{-1}$, it can accommodate itself on a substrate surface, thus acquiring an optimal geometry. CQ has two quinone units, each having two redox active sites. If the proposed four-electron reaction mechanism[13] can be fully realized, a theoretical capacity of 189 $mA\,h\,g^{-1}$ is expected.



Scheme 1. A quinone derivative of calix[4]arene grafted on a silica nanoparticle and the proposed redox reaction.

By grafting CQ to an insoluble substrate, we inevitably lose part of this capacity. A simple estimation shows that if a monolayer of CQ on a 200 $m^2\,g^{-1}$ specific surface area is formed, a total capacity of 39 $mA\,h\,g^{-1}$ (normalized per 1 g of CQ//substrate) will be obtained (Figure S1 in the Supporting Information). Of course, using substrates with a larger specific surface area or employing electrochemically active organic molecules with a lower molecular weight can be expected to increase the capacity to much higher values in future research.

Most importantly, as shown below, the partial loss of capacity is crucially compensated by the gain in electrochemical activity and stability during cycling.

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[*] K. Pirnat, Dr. R. Dominko, Prof. Dr. M. Gaberscek
Laboratory for Materials Electrochemistry
National Institute of Chemistry
Hajdrihova 19, Ljubljana (Slovenia)
Fax: (+386) 1-476-0422
E-mail: miran.gaberscek@ki.si
Homepage: http://www.ki.si

Dr. B. Genorio, Dr. R. Cerc-Korosec, Prof. Dr. M. Gaberscek
Faculty of Chemistry and Chemical Technology
University of Ljubljana
Askerceva 5, Ljubljana (Slovenia)

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The general electrochemical performance of CQ grafted on silica nanoparticles is shown in Figure 1. In the potential window from 2.5 to 3.5 V, pure silica is not electrochemically active (Figure 1 a, solid line), whereas CQ grafted on the silica shows a typical reversible behavior at a potential close to 3 V versus metallic lithium (dashed line). Although there is some variation of capacity with cycling, the cycling stability is very much improved relative to nongrafted materials. To independently confirm that grafting indeed occurs, we performed a detailed thermal analysis of the prepared samples (see the Supporting Information).

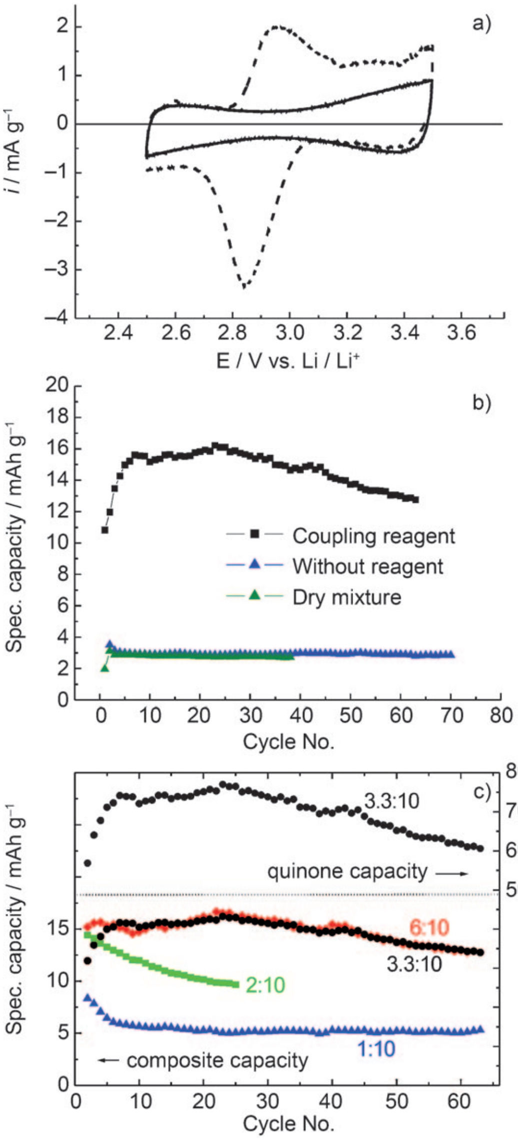

Figure 1. Electrochemical characterization of various samples prepared in this study. a) Cyclovoltammetry scans for pure silica (solid line) and CQ-silica composite (dashed line); scan rate 0.05 mV s^{-1}. b,c) Galvanostatic cycling with a constant current of 3 mA per 1 g of composite or pure CQ in the voltage window between 2.0 and 4.0 V versus Li reference.

In principle, without grafting the present material cannot be utilized because of the high solubility of CQ. This behavior is seen directly in two samples in which silica and CQ were simply mixed by a mortar and pestle and also in the case when the composite was prepared according to the reaction scheme but without addition of the coupling reagent 1,1′-carbonyldiimidazole (CDI) (Figure 1 b, green and blue triangles). The very low capacity in these two materials is not a result of CQ activity but rather of charging/discharging of the double layer around carbon black/silica nanocomposite (mimicking the behavior of electrochemical capacitors).

At least theoretically, it is expected that a maximum specific capacity will be obtained when a full monolayer of CQ on all silica particles is formed. In search for this maximum, we prepared several composites with the nominal CQ content of 1, 2, 3.3, and 6 g per 10 g of silica. A saturation of the composite capacity value was observed already in the sample with the ratio of 3.3:10 (Figure 1 c). If we normalize the capacity per known content of CQ, we get the upper curve in Figure 1 c, that is, about 42 % of the theoretical capacity (189 mA h g^{-1}). The incomplete utilization is either due to inability to exploit all four electrons or due to less than 50 % of silica surface coverage by CQ. In any case, although the SiO$_2$//CDI//CQ system is a good model system to prove the feasibility of the grafting concept, other systems with higher capacity need to be explored for potential use in practice.

Among various solid substrates with relatively high specific surface area, we have tested several materials such

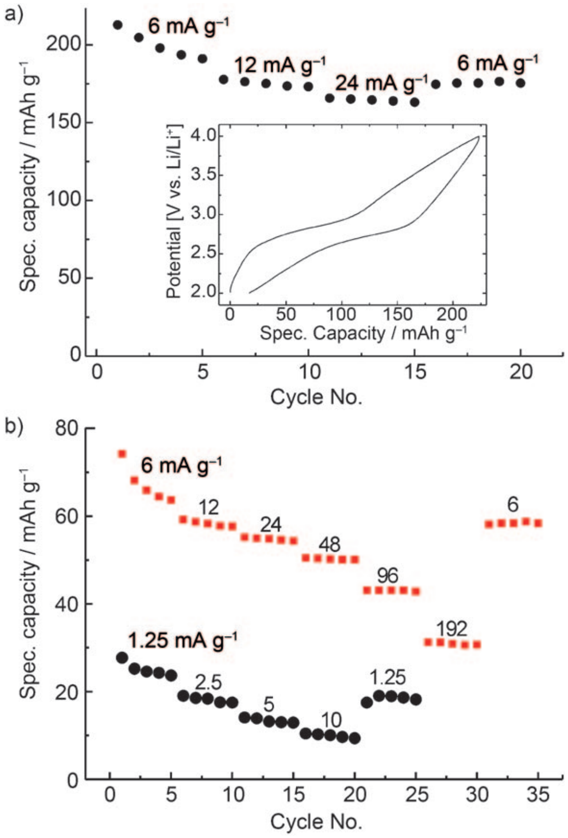

Figure 2. a) Cycling performance and 2nd cycle (inset) of CQ grafted on the surface carbon black (calculated per mass of pure CQ).
b) Comparison of cycling performance of SiO2//CDI//CQ (black circles) and CQ on CB (red squares) (calculated per mass of whole composite).

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as hydroxymethyl cellulose, active carbon, and carbon black (CB). Especially the latter gave quite interesting preliminary results. As seen from Figure 2, the capacity, and especially the rate performance of CQ grafted on CB, is greatly enhanced with respect to the SiO_2//CDI//CQ system. The grafting mechanism in this case is less clear—a hypothetical scenario is proposed in the Supporting Information. Most importantly, the much better rate performance is ascribed to the much better electronic conductivity resulting from the use of carbon black substrate. If in future the mass of carbon black support could be substantially decreased, the specific capacity could be increased from the present 60–70 $mA\,h\,g^{-1}$ (Figure 2b) towards the limiting case of 189 $mA\,h\,g^{-1}$ (Figure 2a). The utilization of all four instead of two electrons would add an additional factor of 2 to the capacity of CB/CQ composite.

Herein, we demonstrated, for the first time, that it is possible to exploit soluble "monomer" organic molecules as electrode active materials for Li-ion batteries. The essence of our approach consists of grafting such soluble organic molecules to an insoluble substrate. This can be considered as an introduction of a new family of batteries—batteries based on soluble active molecules. Our approach also represents a significant step forward towards batteries with increased ordering of constituent phases on nano- and even molecular level (self-assembled monolayers of redox active molecules on high-surface area solid-state substrates). Using low molecular weight organic molecules with four or more exchange sites and high surface area substrates, capacities higher than known in present cathodes could be achieved.

Experimental Section

Grafting of electroactive organic molecules onto solid nanoparticles: Quinone derivative of calix[4]arene (CQ) was synthesized according to a procedure published elsewhere.[9] A more detailed description of the synthesis, including the presentation of intermediate products, is given in the Supporting Information. Grafting of CQ onto the SiO_2 surface has been achieved as follows (see Schemes S1–4 in the Supporting Information): CQ (10 mg, 0.02 mmol), CDI (10 mg, 0.06 mmol), 4-dimethylaminopyridine (DMAP) (1 mg, 0.01 mmol), and SiO_2 (100 mg) were suspended in dichloromethane (DCM) (5 mL) using ultrasound for 1 min. The suspension was stirred for 2 days at room temperature under inert atmosphere, filtered using a PTFE filter (0.2 μm), and washed twice with DCM (2 × 50 mL). The solid residue was then dried under vacuum for 24 h at room temperature. Grafting of CQ onto carbon black was carried out using the same basic concept, with a slight modification as described in the Supporting Information.

Preparation and electrochemical analysis of chemical modified composite materials for Li-ion batteries: CQ//CDI//SiO_2 or CQ//CB (80 mg) composite materials, acetylene carbon black (20 mg), and 5 wt% solution of ethylene–propylene–diene monomer rubber (EPDM) (20 mg) in cyclohexane were homogenized in a mortar with pestle to obtain a homogeneous suspension. To prepare the electrodes, the suspension was transferred onto several Al current collectors (2 cm in diameter) and left to dry at room temperature. The electrodes were then transferred and kept in a glovebox (< 1 ppm water) for at least 48 h before use. "Coffee bag" batteries were assembled in which the working electrodes were the composites with grafted organic molecules while a lithium foil served as a counter electrode. The electrodes were separated with a glass wool separator soaked with 1 M solution of $LiPF_6$ in a mixture of ethylene carbonate/diethyl carbonate (EC/DEC = 1:1). The electrochemical measurements were conducted using a VMP3 potentiostat/galvanostat (Bio-Logic, France). Cyclic voltammograms were measured with a scan rate of 0.05 $mV\,s^{-1}$ in the potential window between 2.5 and 3.5 V versus metallic lithium when SiO_2 and carbon black were used as substrates, respectively. The current density in the galvanostatic experiments was adjusted per mass of the composite and batteries were cycled between 2.0 and 4.0 V versus metallic lithium. The obtained capacities are given per mass of the composite unless stated differently.[14]

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