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Electrochemically stabilised quinone based electrode composites for Li-ion batteries

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ABSTRACT

In order to improve the stability and kinetics of organic materials for lithium batteries, composites between a quinone derivative of calyx[4]arene and carbon black were prepared. Two different approaches were used, the first relying on covalent grafting and the second on electrochemical grafting of the quinone derivatives on the carbon black support. The properties of prepared composites were investigated using XRD, FTIR, TGA and NMR, while their electrochemical stability was studied using classical galvanostatical cycling. It was found that the efficiency of the electrochemical stabilisation of organic molecules depends on the surface properties of the substrate. Interestingly, within the same compositional range, the covalently and electrochemically grafted quinone derivatives of calyx[4]arene showed similar cycling stability. Composites with approximately 20 wt.% of active organic material showed excellent cycling stability within 100 cycles with a delivered capacity of about 60 mAh g^{-1} of composite (more than 300 mAh g^{-1} per quinone).

1. Introduction

Rechargeable Li-ion batteries are penetrating into various domains of our everyday activities, and, according to predictions, they will become the main electrochemical storage device for electricity produced from renewable sources [1]. Current Li-ion battery technologies use inorganic insertion materials. Among various reasonable alternatives to be developed within the next years, redox active organic molecules [1–6] are one possibility. One of the greatest advantages is their wide accessibility and the large variety of possible atom arrangements. The latter offer immense possibilities using intuitive synthesis approaches, which, in the final stage of development, may lead to interesting recipes for preparation of electrode active materials with finely tuned properties. Other expected advantages of electro-active organic molecules over the existing technologies are a weaker environmental impact due to low temperature synthesis and much larger availability compared to most inorganic materials. Smaller and lighter organic molecules or those with multiple functional groups also meet requirements for high gravimetrical and volumetric energy density. Probably the biggest present issue is their cycling instability, which is due to the significant solubility of organic molecules in electrolytes used in contemporary Li-ion batteries.

In one of the earliest systematic studies, Poizot et al. proposed a new class of sustainable lithium batteries based on organic compounds that can be derived from biomass [2,3]. Later on, they focused on organic molecules containing carbonyl functional groups and found several candidates for both high and low redox materials that led to the design of the first all organic lithium ion battery. It was, however, within a limited output voltage [5,6]. In further attempts to increase the operation voltage, Poizot et al. proposed N-cyclic structures, where they were able to demonstrate only a limited number of cycles, however, with an improved voltage output [7]. Meanwhile, various reports on the electrochemical activity of quinone based electroactive materials showed a higher operation voltage during galvanostatic cycling [8–11]. Furthermore, quinone based organic molecules are known redox materials in biological electron-transport systems. Theoretically, two electrons can be reversibly exchanged with a capacity of about 500 mAh g^{-1} if the simplest 1,4-benzoquinone is considered [11]. Typically, all quinone derivates are soluble in the electrolytes commonly used in Li-ion battery technology, although their solubility can be reduced but not completely hindered [11].

Other literature reports the use of polymers [12–14] and radical polymers [15–17] or organic radicals as possible electro-active materials in Li-ion batteries. While polymers offer reasonably stable electrochemical behaviour during lithium battery operation,

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very limited numbers of organic molecules are not soluble in the electrolytes typically used in lithium batteries. To overcome this problem, we have recently proposed that soluble organic molecules can be grafted onto the surface of an insoluble substrate [10]. We demonstrated the principle by grafting a quinone derivative of calix[4]arene onto the surface of two different substrates: (a) nanosized silica particles with a specific surface area of 200 m^2g^{-1} and (b) selected carbon black samples with a specific surface area of 1080 m^2g^{-1}. Although this approach has several limitations, they can in principle be remedied using appropriate innovative approaches. For example, the decreased energy density due to grafting on inactive substrate can effectively be restored by using smaller (lighter) organic molecules or very high surface area substrates or both. Alternatively, a high loading of redox active molecules could be achieved by constructing similar electrode composites as proposed recently in Li–S batteries [18]. The next potential problem – the difficulty of achieving efficient grafting of certain molecules of interest onto a substrate can be solved using so-called electrochemically assisted covalent modification of substrates. Namely, in the literature it has been shown that during electrochemical treatment, strong interactions between organic molecules and carbon surface can be established [19]. By the use of appropriate candidates for each specific case, one could probably achieve a robust linkage between the carbon surface and grafted organic molecule. Such covalently attached organic molecules should be very stable even in harsh chemical environments. At least in its originally proposed version, the method is simple, rapid and requires only basic electrochemical equipment [19].

In this work, we study the possibility of using the electrochemical grafting method for the stabilisation of a calix[4]arene quinone derivate (CQ) on carbon black (CB) or on activated carbon black (CBA). We compare three different electrode composites: (a) a composite containing a physical mixture of CQ and CB, (b) a composite containing a physical mixture of CQ and CBA and (c) a composite with chemically grafted CQ on CBA. Interactions between the carbon substrate and CQ molecules in as prepared composites were studied by means of various characterization techniques and the cycling stability of the prepared composites was checked using classical galvanostatic cycling. Besides getting a deeper insight into the structure-performance correlations in organic battery materials, a practical aim of this work was also to simplify the procedure of electrode composites preparation using soluble organic molecules as an active material.

2. Experimental

Composites preparation: Activated carbon black CBA was made according to the literature [25], with some modifications. 1 g of carbon black (Ketjenblack ECP600JD, surface area 1300 m^2g^{-1}) was added to 50 ml of CH_3CN solution containing 0.5 g of 4-aminobenzoic acid in a nitrogen-filled flask. Later on, 2 ml of isopentyl nitrite was added drop wise with a syringe under vigorous stirring. The mixture was kept stirring at room temperature for 3 days. After the reaction, the mixture was filtered and washed with CH_3CN by sonication twice. Then it was dried on air for 1 day and ground with a mortar and pestle to obtain black powder.

Quinone derivative of calix[4]arene (CQ) was synthesised according to the procedure proposed by Chung [26]. A more detailed description of the synthesis, including the presentation of intermediate products as well as details of the grafting of CQ onto carbon black, was published in our previous paper [10].

Electrochemically active composites (83%) and a solution of the ethylene–propylene–diene monomer rubber (EPDM) in hexane (17%) were homogenised in a mortar and pestle. To prepare the electrodes, the slurry 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 24 h before use. "Coffee bag" batteries were assembled in which the working electrodes were the composites with 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). The current density in the galvanostatic experiments was 48 mA per gram of CQ and batteries were cycled between 2.0 and 4.0 V versus metallic lithium.

X-ray diffraction patterns were collected on a Siemens D-5000 diffractometer in reflection (Bragg–Brentano) mode using Cu Kα radiation, monochromatised by a secondary graphite monochromator. The data were collected in the range between 5 and 75° in steps of 0.04° and the integration time of 1 s per step.

FTIR spectra were measured on a Bruker IFS 66/S spectrometer. A few milligrams of our material and 200 mg of dried KBr were homogenised in a mortar and pestle. Then pellets were compressed using a hydraulic press and IR spectra were measured in nitrogen atmosphere.

^{1}H magic-angle spinning (MAS) NMR spectra were recorded on a 600 MHz Varian NMR system, operating at ^{1}H Larmor frequency of 599.688 MHz and using rotation synchronised Hahn-echo pulse sequence. The sample rotation frequency was 20 kHz, the repetition delay between consecutive scans was 10 s and the number of scans was 16. Chemical shifts of ^{1}H signals were referenced to the signal of tetramethylsilane.

Thermogravimetric measurements were performed on a Mettler Toledo TGA/SDTA 851e Instrument. From 1 to 2 mg of the sample was placed in a 70 μL alumina crucible. A heating rate of 10 K min^{-1} and temperature range from 25 to 600 °C were used in measurements, performed under air atmosphere. In measurements carried out under inert atmosphere, the furnace was purged with Ar for half an hour at 25 °C. After purging, a heating rate of 2 K min^{-1} was used in a temperature range from 25 to 900 °C. In all measurements, the gas flow rate was 100 mL min^{-1} and the baseline was automatically subtracted.

3. Results and discussion

As mentioned in Section 1, we compare the properties of three distinctly different electrode composites consisting of carbon black (CB) with a surface area of 1300 $m^2 g^{-1}$ and a model organic molecule – a calix[4]arene quinone derivative (CQ).

The composites were prepared in the weight ratio 1:1 in the following way: (a) a simple physical mixture of CB and CQ (composite "CB + CQ" in Fig. 1); (b) a physical mixture of activated carbon black (CBA) and CQ (composite "CBA + CQ" in Fig. 1) and (c) chemically grafted CQ on the activated carbon black (composite "CBACQ" in Fig. 1).

3.1. Thermogravimetry

Both physical mixtures were used as prepared for further characterization, while the CBACQ composite was thoroughly washed several times before characterization. Due to the extensive washing, the quantity of CQ in the CBACQ composite could only be determined after the preparation of the composite using a suitable method, for example thermogravimetry.