



Electrochemically stabilised quinone based electrode composites for Li-ion batteries

Klemen Pirnat^a, Robert Dominko^{a,*}, Romana Cerc-Korošec^b, Gregor Mali^a, Bostjan Genorio^b, Miran Gaberscek^{a,b}

^a National Institute of Chemistry, Hajdrihova 19, SI-1000, Ljubljana, Slovenia

^b Faculty of Chemistry and Chemical Technology, University of Ljubljana, Askerceva 6, SI-1000, Ljubljana, Slovenia

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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).

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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 gravimetric 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 derivatives 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,

* Corresponding author. Tel.: +386 4760362; fax: +386 4760422.

E-mail address: Robert.Dominko@ki.si (R. Dominko).

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 $200\text{ m}^2\text{ g}^{-1}$ and (b) selected carbon black samples with a specific surface area of $1080\text{ m}^2\text{ g}^{-1}$. 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 derivative (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 $1300\text{ m}^2\text{ g}^{-1}$) 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 $\text{Cu K}\alpha$ 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.

^1H magic-angle spinning (MAS) NMR spectra were recorded on a 600 MHz Varian NMR system, operating at ^1H 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 ^1H 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 $70\ \mu\text{L}$ 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 $1300\text{ m}^2\text{ g}^{-1}$ 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.

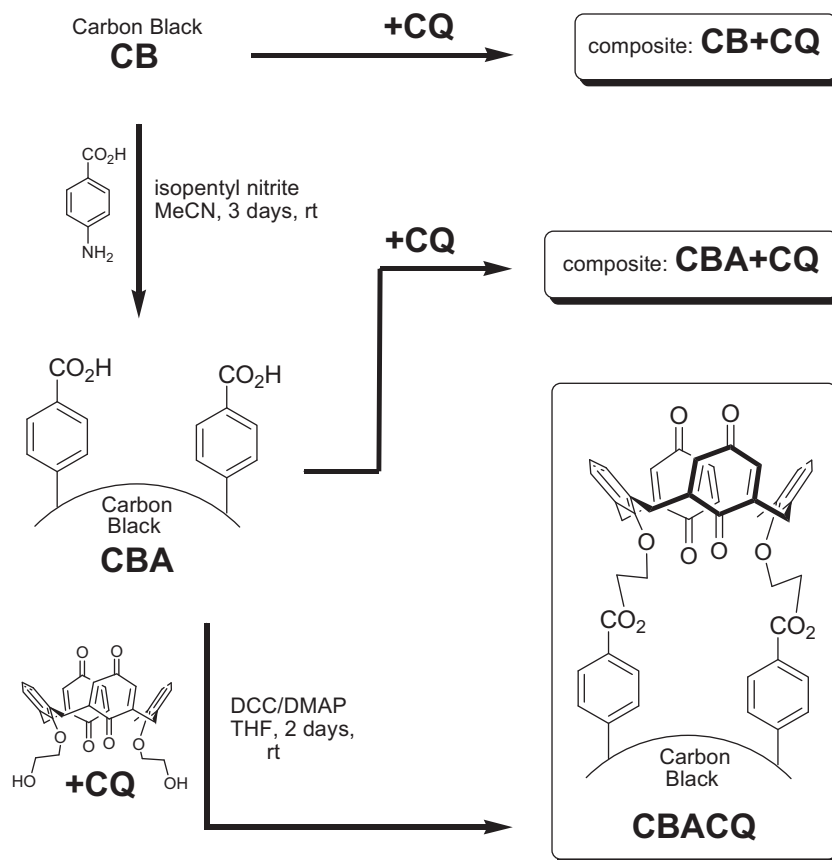


Fig. 1. Schematic presentation of the composites used in this study.

For easier comparison, Fig. 2a shows the thermogravimetric curves (under dynamic air atmosphere) of all three composites and also of the starting materials. Pure CQ and the physical mixtures of CQ with carbon black or activated carbon black start to lose weight at around 100 °C. After the first step, from 100 to 150 °C, CQ exhibits another well-resolved step in the interval from 200 to 220 °C. After that, CQ gradually decomposes in a wide range extending up to 500 °C. The mixture of CB and CQ shows a similar behaviour to CQ but with slightly less pronounced transitions. The mixture CBA + CQ is slightly more stable after the first step, but it starts to decompose rapidly beyond ca. 280 °C. The composite with grafted CQ (CBACQ) shows enhanced thermal stability at lower temperatures: it starts to lose weight at about 50 degrees higher temperatures (at around 150 °C) with respect to both physical mixtures. We presume that in CBACQ the enhanced thermal stability is due to the chemical bonding of CQ molecules on CBA, causing the observed temperature lag of the decomposition process.

The quantity of grafted CQ in the CBACQ composite was estimated on the basis of dynamic TG curves obtained under inert atmosphere (Fig. 2b). In the temperature range from 350 to 900 °C, the mass loss of CBACQ is between the mass loss of CBA and CQ. Presuming that the mass loss of the final material, CBACQ, is a linear combination of both mass losses of the individual components (at the same temperature) and that the sum of mass fractions of both components is equal, 17 wt.% of grafted CQ in CBACQ was estimated. Using the same procedure, the estimated amount of CQ in CB + CQ and in CBA + CQ was approximately the same, that is, about 42 wt.%. This value is in agreement with the data for physical mixture if we take into account non-homogeneities that can occur within small amounts of sample (approx. 4 mg of composite was analysed).

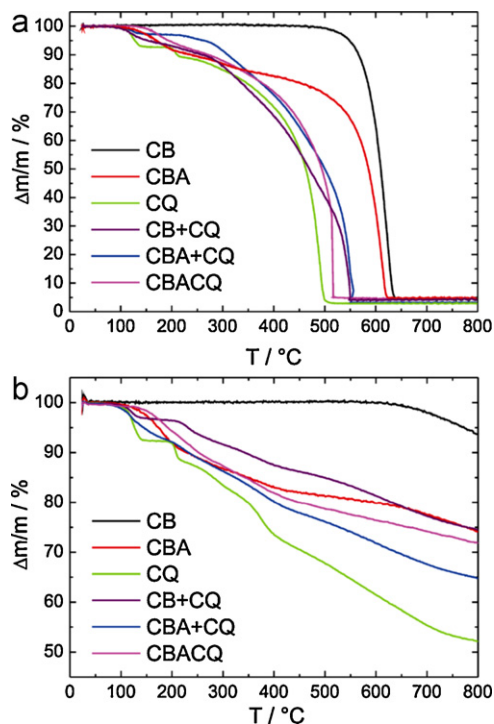


Fig. 2. Thermogravimetric curves of composites and starting materials (a) in air and (b) in argon.

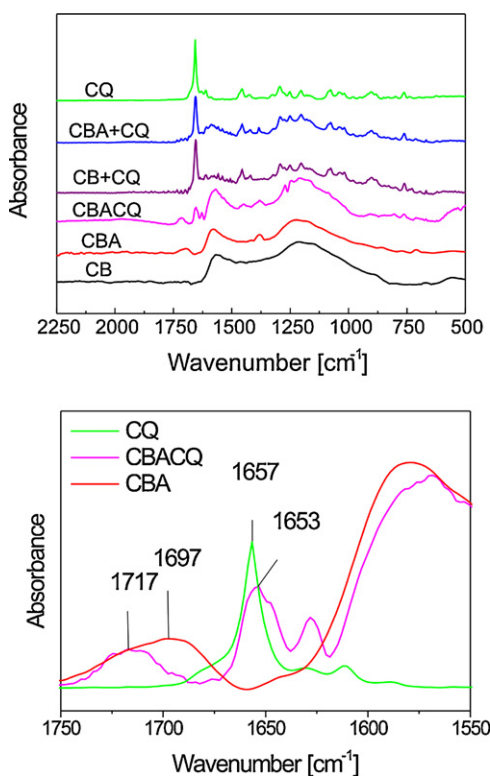


Fig. 3. FTIR spectra of composites and starting materials used in this study.

3.2. FTIR spectroscopy

FTIR spectra of all three composites, i.e. CB+CQ, CBA+CQ and CBACQ, are shown in Fig. 3. For easier discussion, we also show FTIR spectra of the entering materials: CB, CBA and CQ. Based on a peak-to-peak comparison, the FTIR spectra of CB+CQ and CBA+CQ are practically identical. In both spectra, the most intensive signal at 1657 cm^{-1} can be ascribed to quinone stretching, while we do not see any adsorption peak from the carbonyl group of carboxylic acid. Unlike the spectrum for pure CQ, these spectra exhibit a broad peak at 1575 cm^{-1} . FTIR spectra of CB and CBA also contain broad contributions (at 1570 cm^{-1} and 1220 cm^{-1}). The CBA spectrum contains two additional adsorption bands at 1697 cm^{-1} and at 1381 cm^{-1} , both due to carboxyl groups.

This difference is in agreement with one of the present goals, namely to activate the surface of carbon black with carboxylic functional groups for chemical or electrochemical grafting of the CQ molecule. The biggest difference with respect to the other spectra is observed in the case of chemically grafted CQ on the surface of CBA (CBACQ). With respect to the spectra of starting materials, the spectrum of CBACQ exhibits two major differences: (a) appearance of C=O stretching from the ester bond at 1717 cm^{-1} and (b) the carboxyl group band at 1697 cm^{-1} becomes much weaker compared to the CBA starting material (Fig. 2b). The adsorption peak at 1653 cm^{-1} in CBACQ can be ascribed to the slightly shifted quinone stretching, which appears at 1657 cm^{-1} in the CQ starting material. Based on the present set of FTIR measurements, we can ascribe the changes in the spectrum of CBACQ to the formation of an ester bond between the activated carbon black and the quinone derivative of calix[4]arene. Conversely, the spectra of physical mixtures of CQ with either CB or CBA show the expected behaviour of true mixtures of the starting materials (no new bonds were formed).

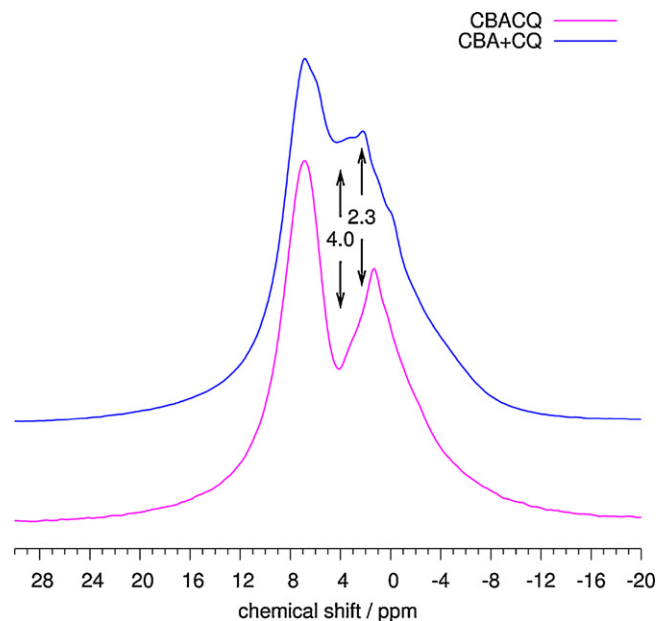


Fig. 4. ^1H MAS NMR spectra of CBA+CQ and CBACQ composites.

3.3. Solid state NMR

NMR was used for the determination of differences between CBA+CQ and CBACQ composites. ^1H MAS NMR spectra of CBA+CQ and CBACQ composites are shown in Fig. 4. Both spectra are composed of several overlapping resonances. The most prominent contributions in both spectra resonate at approximately 7 ppm and belong to protons from aromatic rings. Additionally, there is a broad shoulder between 0 and 4 ppm in CBA+CQ, and a broad peak at approximately 1.3 ppm in CBACQ. The latter peak belongs to protons from aliphatic chains. NMR signals originating from various sites in various aromatic rings or from various sites in the aliphatic part of the quinone derivative of calix[4]arene molecules cannot be resolved from one another for several reasons. Traditionally, ^1H solid-state NMR spectra are relatively poorly resolved because of strong homonuclear dipolar proton–proton interactions. These interactions lead to inhomogeneous line-broadening, which cannot be removed using slow or medium-fast MAS. In our particular case, the lines can be additionally broadened due to distribution of chemical shifts. Although a reliable decomposition of the two proton NMR spectra into individual contributions cannot be performed, the comparison of the spectra still shows that there are major differences between them at about 4 and 2.3 ppm. Protons resonating at these two chemical shifts can be assigned to hydroxyl groups (2.3 ppm) and to either small clusters of water molecules or water molecules bonded to hydroxyl groups (4 ppm). Protons from bulk water usually resonate at about 4.8–5 ppm. Differently, quickly exchanging protons in the ‘clusters’ of only few hydrogen-bonded water molecules or in water molecules hydrogen-bonded to hydroxyl groups can exhibit chemical shifts close to or even smaller than 4 ppm [20].

^1H MAS NMR spectra thus show that the CBACQ composite contains less water molecules and less OH groups than the CBA+CQ composite. In fact, the reduced amount of water molecules in the former material is probably induced by the reduced amount of OH groups, making the composite less hydrophilic. The reduced amount of OH groups themselves suggests that in the CBACQ composite the quinone derivative of calix[4]arene most probably reacted with the activated surface of carbon black and indeed

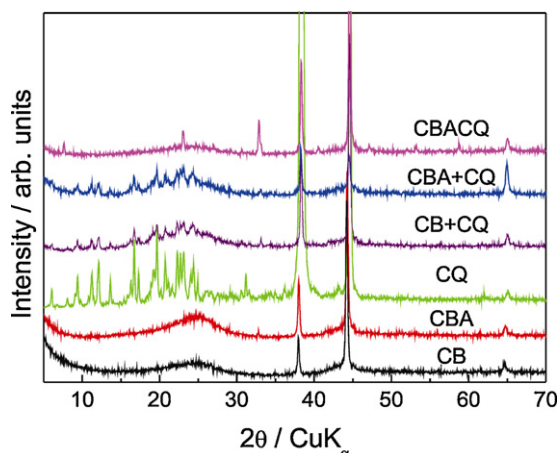


Fig. 5. X-ray diffraction patterns of composites and starting materials used in this study.

formed bonds with the carboxylic groups of the benzoic acid molecules.

3.4. X-ray diffraction

Derivatives of calix[4]arenes are known for their various conformations [21] but once they are grafted to certain surfaces, a loss of the degrees of freedom is expected [22,23]. We examined all three prepared battery composites (the physical mixtures and the grafted CQ) together with the corresponding starting materials using X-ray diffraction (Fig. 5). The diffraction peaks at 38.3° , 44.5° and at 64.7° are from the sample holder. As expected, the starting CB and CBA samples show only a broad diffraction peak close to 26° , which is a typical diffraction peak for hard carbons [24]. The crystal structure of the active quinone derivative of calix[4]arene (CQ) used in our work has not been resolved yet; one can see numerous diffraction peaks at low angles, in particular in the range $15 < 2\theta < 25$. Similar patterns are observed in CB+CQ and CBA+CQ, however with a lower intensity of diffraction peaks due to the presence of carbon black. After the CQ molecule has been grafted on the surface of activated carbon black, one can observe a changed pattern with only three major diffraction peaks. This probably happens due to “freezing-in” of the calix[4]arene molecules [22], which results in a higher symmetry of the CBACQ composite.

All of the above results consistently support the initial hypothesis, namely that CQ is grafted on the activated carbon black, while in the other two composites CQ merely forms physical mixtures with carbon black. One may expect that the grafted CQ molecules will be more stable during the electrochemical operation, where various forces occur due to rapid transport of species and, of course, due to main and side electrochemical reactions.

3.5. Electrochemical characterization

The calculated capacities during charge/discharge presented in Fig. 6 are based on the total mass of composites (including the active material, the linker and the added carbon black). In the physical mixtures, we observe three different regimes in the charge/discharge process, while the CBACQ composite exhibits only two regimes. The particularly inclined region above 3 V versus lithium reference most probably corresponds to charging of the CB surface. This assumption is in agreement with the observed variations in the capacities obtained in this region. Namely, this capacity is considerably higher in CBACQ, which contains much more CB (more than 80 wt.%) than both physical mixtures, CBA+CQ and

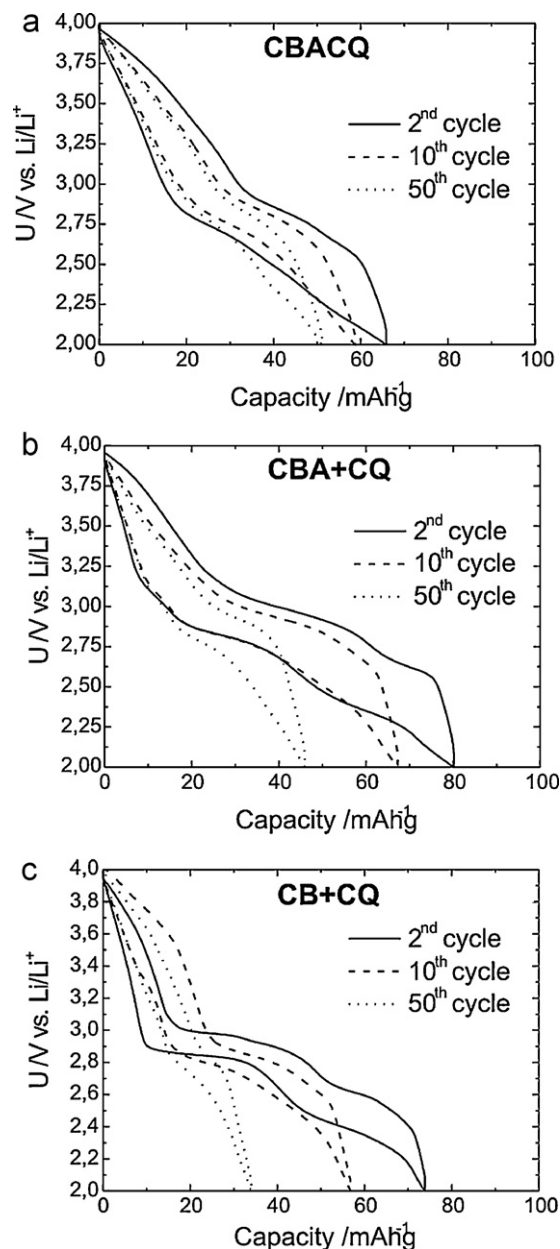


Fig. 6. Oxidation–reduction curves for (a) covalently grafted CQ on activated carbon black, (b) physical mixture of CQ and CBA in weight ratio 1:1 and (c) physical mixture of CQ and carbon black in weight ratio 1:1.

CB+CQ (about 50 wt.%). In the lower part of the charge–discharge curves (between 2 V and 3 V), we observe two well defined plateaus in the formation cycles for both physical mixtures, while the sample with grafted CQ shows only one poorly resolved plateau. Based on the literature [11] and our previous results [10], the plateau close to 3 V is due to a reversible electrochemical reaction of quinone with lithium, while the origin of the low voltage plateau is still unclear. We note, however, that during the cycling process, the capacity of the low voltage plateau is reduced substantially from cycle to cycle. By contrast, the capacity fading of the middle voltage plateau (at 3 V) can be correlated with the composite used in the experiment – the least fading was observed in the case of composite with grafted CQ (CBACQ). Correspondingly, this sample also shows the best overall cycling stability (Fig. 7). Analysis shows that, in fact, in CBACQ the capacity fading in the formation cycles is mainly due to the capacity loss obtained within the low voltage plateau. In other words, the

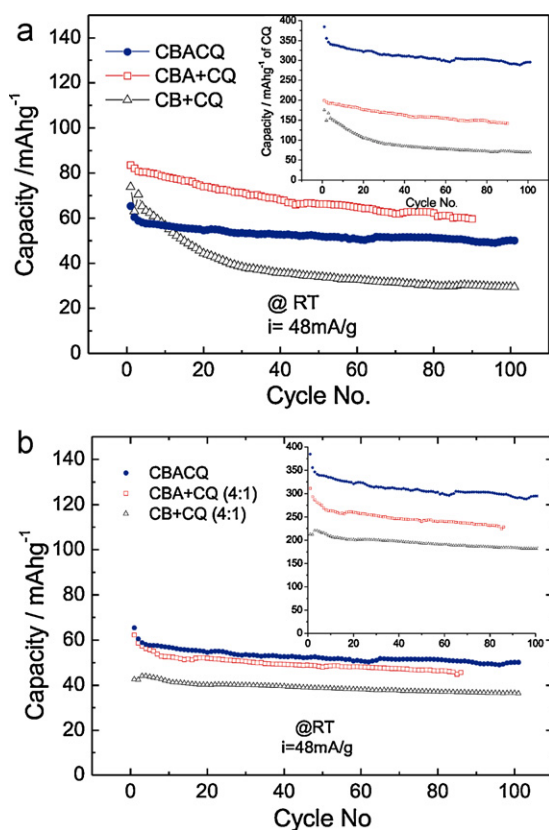


Fig. 7. Galvanostatic cycling with a constant current between 2 and 4V versus lithium reference for chemically grafted composite and physical mixtures; (a) physical mixtures with 50 wt.% of CQ and (b) physical mixtures with 20 wt.% of CQ. The capacity presented in the inset figure was calculated based on the amount of CQ.

electrochemical reaction of quinone seems to be completely stable during the whole cycling experiment.

During testing of present and similar composites, we have observed that the content of CQ in the composites, in particular in the physical mixtures, also affects, quite systematically, the capacity fading. Typically, at relatively high loadings, such as in the present physical mixtures (about 50 wt.%), the initial capacity fading was much more expressed than in parallels with a smaller content of CQ. This effect can be seen by comparing Fig. 7a (50% of CQ in composite) and Fig. 7b (20% of CQ). Obviously, the decrease in CQ content improved the cycling stability of both physical mixtures, which becomes comparable to that of the grafted (CBACQ) sample. Even more interestingly, if the capacity is normalised to the content of CQ (see insets in Fig. 7), then one observes a significant increase in the capacity of both physical mixtures when the content of CQ is decreased. It seems as if by appropriate tuning of composition, the electrochemical performance (cycling stability, capacity) of the simple mixtures would become completely comparable to that of the grafted sample. This is highly unexpected if we recall that CQ is soluble in the present organic solvents and if we take into account the results above that clearly showed no interactions between CQ and carbon in the simple physical mixtures. The very good performance of such non-interacting mixtures is also in contradiction with our previous work [10] in which we showed that in the case of a silica substrate, only the grafted sample exhibited good electrochemistry; the mixtures, on the contrary, only showed a supercapacitive behaviour.

In order to explain the unexpectedly good performance of the present physical mixtures, we assume that in these particular mixtures a process takes place that resembles the “electrochemical grafting” described previously in non-battery electrochemical

systems [19]. Such grafting can occur on substrates having appropriate surface groups. By nature of preparation, the activated carbon (CBA) has a higher number (density) of such surface groups, so it can in principle graft a higher number of CQ molecules than the non-activated carbon (CB). This is indirectly but consistently confirmed by the present electrochemical results. We even assume that if one were able to prepare a CQ+CBA (but also CQ+CB) mixture with optimized CQ:surface group ratio, there should be no difference between the performance of such an optimized mixture and the chemically prepared grafted sample (CBACQ). Preparation of such optimized mixtures is a matter of extensive further research.

4. Conclusions

Many organic materials exhibit poor cycling performance due to their inherent solubility in conventional Li battery electrolytes. One of the strategies that significantly improve their cycling performance is grafting onto solid, insoluble substrates with preferably high surface areas. Besides the chemical grafting demonstrated in our previous paper and in one of the present samples (CBACQ), one can also try to exploit the electrochemical grafting – a principle known for more than a decade. The present results indicate, indirectly but coherently, that the success of electrochemical grafting depends on the surface properties of substrate – the activated carbon performed better than the non-activated (probably due to a higher surface density of active groups appropriate for electrochemical grafting). The possibility of electrochemical grafting significantly simplifies the grafting procedure, because it only requires preparation of initial mixtures of active organic molecules and an appropriate solid substrate; the grafting is then carried out “in situ” during the electrochemical cycling.

In order to achieve capacities of practical importance using the grafting or electrochemical grafting principle, it is necessary to further optimize the surface functionalization of solid substrates – together with maximization of their specific surface, minimization of the molecular weight of organic molecule and maximization of the number of its active groups.

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