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Short communication

Electrochemical reactivity of pyrolytic carbon film electrodes in organic carbonate electrolytes

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ABSTRACT

The electrochemical reactivity of polyimide-derived pyrolytic carbon film electrodes in a standard organic carbonate lithium-ion battery electrolyte was studied and quantified. An oxidative heat treatment at 900 °C under CO_2 atmosphere was found to lower the reactivity of disordered carbons towards electrolyte oxidation. Cyclic voltammetry and potentiostatic measurements of the carbon film electrodes demonstrate the beneficial effect of the CO_2 heat treatment in the potential range between 4.2 and 4.8 V vs. Li/Li^+ i.e., at potentials where high-energy Li-ion positive composite electrodes operate.

1. Introduction

Lithium-ion battery composite electrodes commonly incorporate 1–10% wt. of carbon black additives in their formulation [1–3]. The promising new positive electrode materials for high-energy Li-ion batteries e.g., $LiMnPO_4$ [4], $LiNi_{0.5}Mn_{1.5}O_4$ [5], $x\ Li[Mn_{1/2}Ni_{1/2}]O_2 \cdot y\ LiCoO_2 \cdot z\ Li[Li_{1/3}Mn_{2/3}]O_2$ $(x + y + z = 1)$ [6], which operate at relatively high potentials require new electrode material formulations for stable performance in organic carbonate electrolytes.

Interfacial processes at Li-ion positive composite electrodes have been studied quite extensively [7,8]. Organic carbonate-based electrolytes undergo oxidation at the surface of positive electrodes at potentials exceeding 4.2 V vs. Li/Li^+, which often leads to degradation of the electrode active and passive components [7,8]. These processes result in gradual electrolyte degradation, surface film formation and gas evolution during cell operation, which affect electrochemical performance and lifetime of Li-ion cells.

These studies, however, tend to focus on the electrochemical properties of the electrode active material itself, often ignoring the fact that carbon black (CB) conductive additives constitute 80–98% of the composite electrode surface area. Investigations of interfacial properties of CB additives in Li-ion negative electrodes are manifold [3,9]. Corresponding studies of electrochemical properties of carbons at potentials of lithium-ion positive electrodes are limited and relate mainly to anion intercalation into graphite [10,11].

Organic carbonate electrolytes begin to undergo oxidative decomposition on carbonaceous surfaces at potentials above 4.2 V [12]. Electrolyte decomposition products adversely affect the electrochemical impedance of the electrode and they are responsible for lithium inventory shift and premature failure of Li-ion cells.[12,13] The goal of this work was to study the electrochemical response of a model pyrolytic carbon film electrode in an organic carbonate electrolyte at potentials that correspond to the operation range of high-energy Li-ion positive electrodes, and to evaluate the effect of carbon dioxide heat treatment on the carbon interfacial reactivity

2. Experimental

Highly disordered carbon film electrodes were produced by temperature-programmed pyrolysis of high purity Kapton HN sheets (Goodfellow Cambridge Limited, thickness 0.125 mm) under a constant nitrogen flow ca. 10 ml/min in a tubular furnace. A linear temperature ramp from room temperature to 900 °C over 180 min was applied followed by 60 min at 900 °C. The oxidative CO_2-surface treatment was conducted at 900 °C under CO_2 flow. Film carbon samples were slowly cooled down under nitrogen flow to room temperature and transferred into a glove box (Nexus II, VAC — H_2O, $O_2 < 1$ ppm) where all electrochemical measurements were carried out.

The specific surface area of the carbon films was measured using the Brunauer–Emmet–Teller (BET) method (Micromeritics TriStar™ II 3020) after degassing at 200 °C for 60 min under vacuum. Raman

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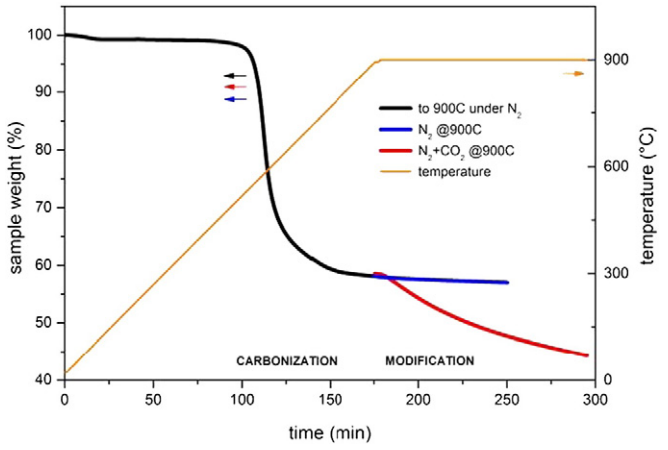

Fig. 1. TGA profiles of the Kapton thin film during the pyrolysis under N_2 and heat post-treatment at 900 °C under CO_2.

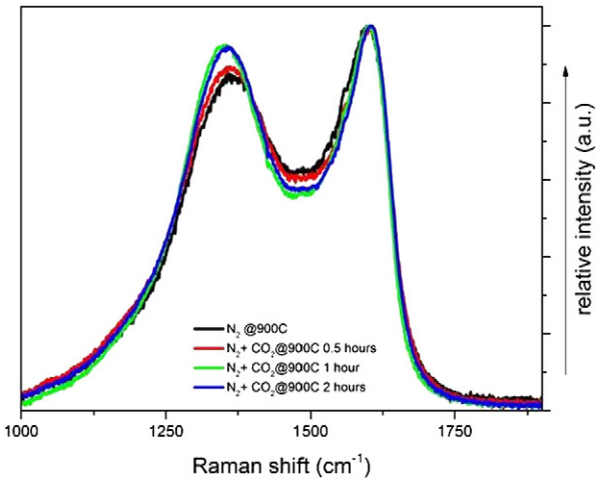

Fig. 3. Raman spectra of the pristine pyrolytic carbon black thin film and after 0.5, 1 and 2 h of heat treatment at 900 °C under CO_2.

spectra of the pyrolytic carbon films were collected using a Raman microscope system (Labram, Horiba Jobin Yvon USA, Inc.) in the back-scattering configuration [7,14]. Electrochemical measurements were performed in a three electrode beaker cell filled with 1 M $LiPF_6$, ethylene carbonate (EC): diethyl carbonate (DEC) (1:2 weight ratio) electrolyte (Novolyte Technologies, Inc.). High purity lithium foil (FMC Lithium) was used as counter and reference electrodes.

Cyclic voltammetry (CV) scans were carried out at a scan speed of 1 mV/s and quasi steady-state potentiostatic step (PS) measurements were performed at 125 mV increments with a 60 min polarization time at each step. All potentials are relative to a Li/Li^+ reference electrode.

3. Results and discussion

The pyrolysis process of the precursor polyimide layer at 900 °C under nitrogen leads to formation of a disordered carbonaceous film [15–17]. Fig. 1 shows a TGA plot of the initial pyrolysis and subsequent heat treatment processes under N_2 or CO_2. The early weight loss of the polyimide precursor film at T > 550 °C corresponds to the burning-off of the oxygen groups and subsequent carbonization of the sample. At 860 °C the pyrolysis process is completed and no further weight loss is observed under nitrogen. The pyrolytic carbon films have a relatively high surface area of 20 m^2/g and moderate electronic conductivity ca. 89 Scm^{-1}.[15–17] The dangling bonds at the edges of the carbon layers are saturated mostly by hydrogen. However, oxygen and nitrogen that originate from the polyimide precursor can also be taken up during carbon black formation and bound to the edges of the carbon layers.

The resultant carbon film is dense and homogenous with a few pin holes and cavities (Fig. 2A). Prolonged (2 h) heat treatment at 900 °C under nitrogen does not alter the carbon film surface area, morphology, electronic conductivity and electrochemical reactivity.

The post-pyrolysis heat treatment at 900 °C under CO_2 results in a reverse Boudouard reaction [18],

$$C_{(s)} + CO_{2(g)} \rightarrow 2CO_{(g)} \quad (1)$$

with mild carbon surface oxidation, including removal of surface chemical functional groups, sp-coordinated surface carbon atoms, and gradual formation of pores and an increase in surface area upon prolonged heat treatment.

The rate of carbon oxidation depends on the type of carbon e.g., disordered vs. graphitic, CO_2 pressure and temperature [19,20]. The rate of carbon black oxidation at 900 °C is also directly proportional to the surface area per unit of carbon mass. Typically, 2 hour-long heat treatment at 900 °C under CO_2 leads to ca. 13% loss of the carbon black mass and significant increase of the surface area from 20 to 194 m^2/g. Interestingly, the post-pyrolysis heat treatment at 900 °C under CO_2 does not affect the carbon film electronic conductivity, which indicates that the oxidation reaction occurs mainly at the carbon surface.

The SEM image of the CO_2 heat-treated carbon film (Fig. 2B) displays increased roughness and porosity that is evenly distributed across the carbon film surface. The Raman spectra of the modified carbon films (Fig. 3) consist of two broad peaks at around 1600 and 1365 cm^{-1}, which correspond to the graphite G- and D-bands, respectively. The D/G peak integrated intensity ratio in disordered carbons, which accounts

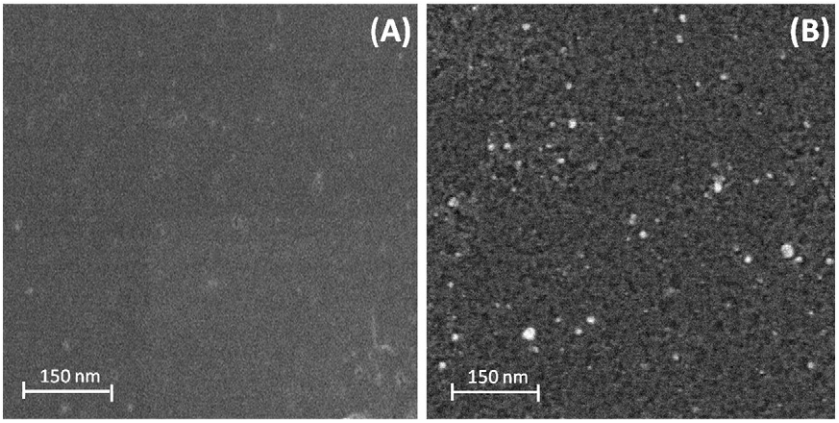

Fig. 2. SEM images of pristine (A) and after 1 h of CO_2 heat-treatment (B) pyrolytic carbon black films.