

Short communication

Effect of carbon coating on electrochemical performance of hard carbons as anode materials for lithium-ion batteries

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Abstract

Surface modification by a soft-carbon coating is used to improve the electrochemical performance of hard carbons as the negative-electrode (anode) material in lithium-ion batteries. The coating process involves simple heat-treatment of a mixture of coal-tar pitch and hard carbon powders at 1000 °C. The carbon coating significantly reduces the reaction of lithium with surface functional groups or absorbed species caused by air exposure. This is attributed to the effective suppression of the diffusion of both air and water into the hard carbon by the soft-carbon coating, and the better resistance of soft carbon to air. As a result, the charge–discharge coulombic efficiency during cycling, as well as during the first cycle, is improved. © 2007 Elsevier B.V. All rights reserved.

Keywords: Hard carbon; Carbon coating; Irreversible capacity; Air exposure; Negative-electrode material; Lithium-ion battery

1. Introduction

Various carbon materials have been extensively investigated as negative-electrode (anode) materials for lithium-ion batteries. Currently, graphite is commonly used in commercial lithium-ion batteries that are used as power sources for portable electronic devices. Graphite anodes have limited reversible capacity and are highly sensitive to electrolyte solutions. Propylene carbonate (PC)-based electrolytes are not compatible with graphites because of rapid electrolyte decomposition and exfoliation of the graphite structure [1–3]. Nevertheless, PC is still an attractive electrolyte due to its low melting point (–55 °C).

Hard carbons have attracted much attention as candidate anode materials due to their high Li-ion storage capacity [4–9]. The working potential of Li-ion cells with hard carbons is significantly wider than that of cells using pure graphite. It is known, however, that the gradual potential change with time can be an advantage for practical uses since it permits estimation of the remaining capacity [10]. Hard carbon has been used as a nega-

tive electrode in a cell of high power density for transportation applications such as electric vehicles (EV) and hybrid electric vehicles (HEVs) [11]. Moreover, hard carbons are stable during charge–discharge cycling in PC-based electrolytes. Nevertheless, a main disadvantage of hard carbons is a high irreversible capacity, which is generally attributed to two reactions [12], namely: (i) the reaction of lithium with electrolyte to form a passivating layer; (ii) the reaction of lithium with surface functional groups or absorbed species that result from air exposure.

A surface modification has been used to reduce the large irreversible capacity observed with bare hard carbon. This has involved coating a soft carbon on the surface of hard carbons by a chemical vapour deposition (CVD) process [13], a thermal vapour decomposition (TVD) process [14], and a pressure-pulsed chemical vapour infiltration (PCVI) method [15]. In our previous studies [16,17], carbon was successfully coated on graphite powder by simple heat-treatment of mixtures of graphite and soft carbon precursors, such as polyvinyl chloride and coal-tar pitch, in which carbonization takes place via a liquid phase. This reduces significantly the initial irreversible capacity of the graphite, even in PC-based electrolyte. In practice, if the sensitivity of the anode material to water can be decreased, lithium-ion batteries can be more easily manufactured since the

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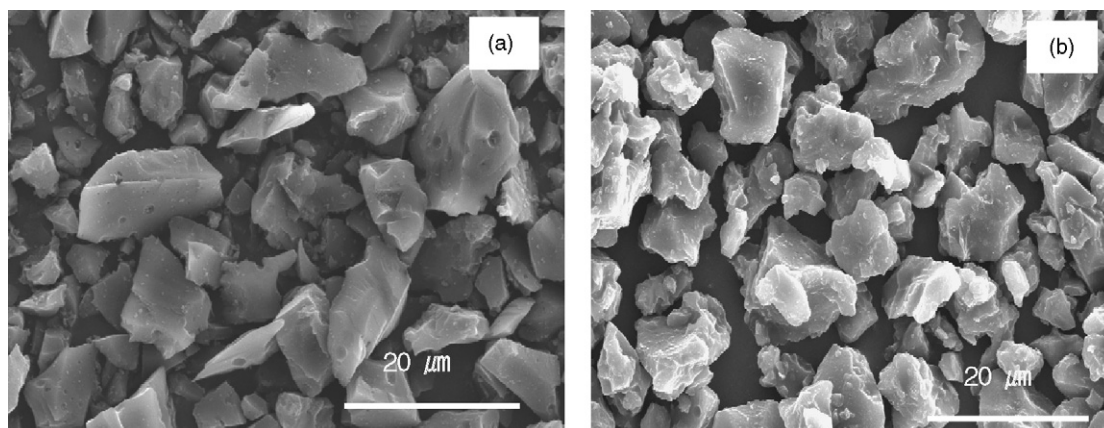


Fig. 1. Scanning electron micrographs for (a) as-received and (b) carbon-coated hard carbon.

requirement to control the water content in the manufacturing environment can be lowered [18]. In this work, an attempt has been made to improve the electrochemical performance of a hard carbon, especially in terms of surface modification to resist the interactions with air, by coating with soft carbons.

2. Experimental

Hard carbons were used as received (Kureha Corp., Japan). The carbon coating process was performed by mechanically mixing the hard carbon in a planetary ball mill (pulverisette 7,

Fritsch) with 30 wt.% coal-tar pitch, and then heating the mixture in a alumina boat to 1000 °C for 1 h under an argon flow for pyrolysis of the coal-tar pitch. The carbon-coated samples were obtained by repeating the above procedure, i.e., double-coating.

Coin-type test cells were assembled for electrochemical characterization of bare- and carbon-coated hard carbons using lithium foil as counter electrodes. The hard carbon electrodes were made by dispersing 90 wt.% active material and 10 wt.% poly-vinylidene fluoride (PVDF) binder in an *N*-methyl-2-pyrrolidone (NMP) solvent. The resultant slurries were spread on a copper foil, dried at 120 °C under vacuum overnight to

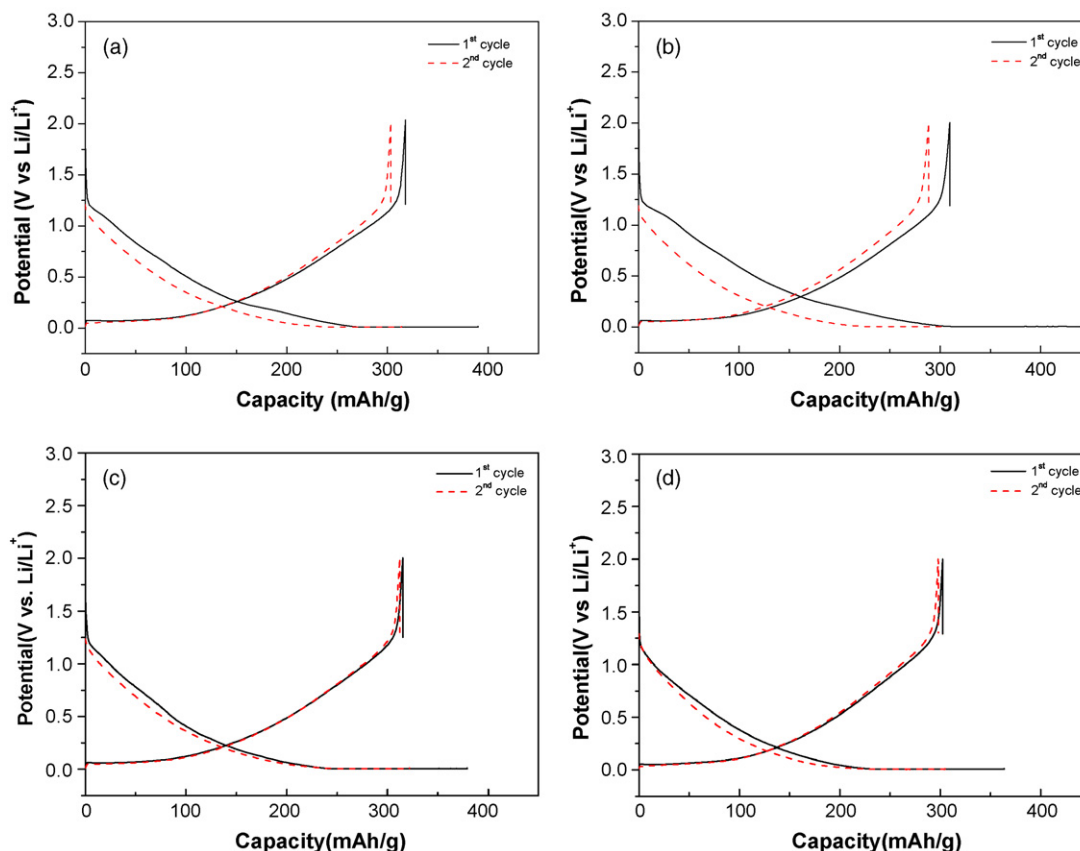


Fig. 2. Charge–discharge curves for first and second cycles of (a) as-received hard carbons; (b) as-received sample post-treated at 800 °C for 1 h under Ar flow, followed by air exposure (90% RH) for 1 week; (c) carbon-coated hard carbon; (d) carbon-coated hard carbon, followed by air exposure (90% RH) for 1 week.

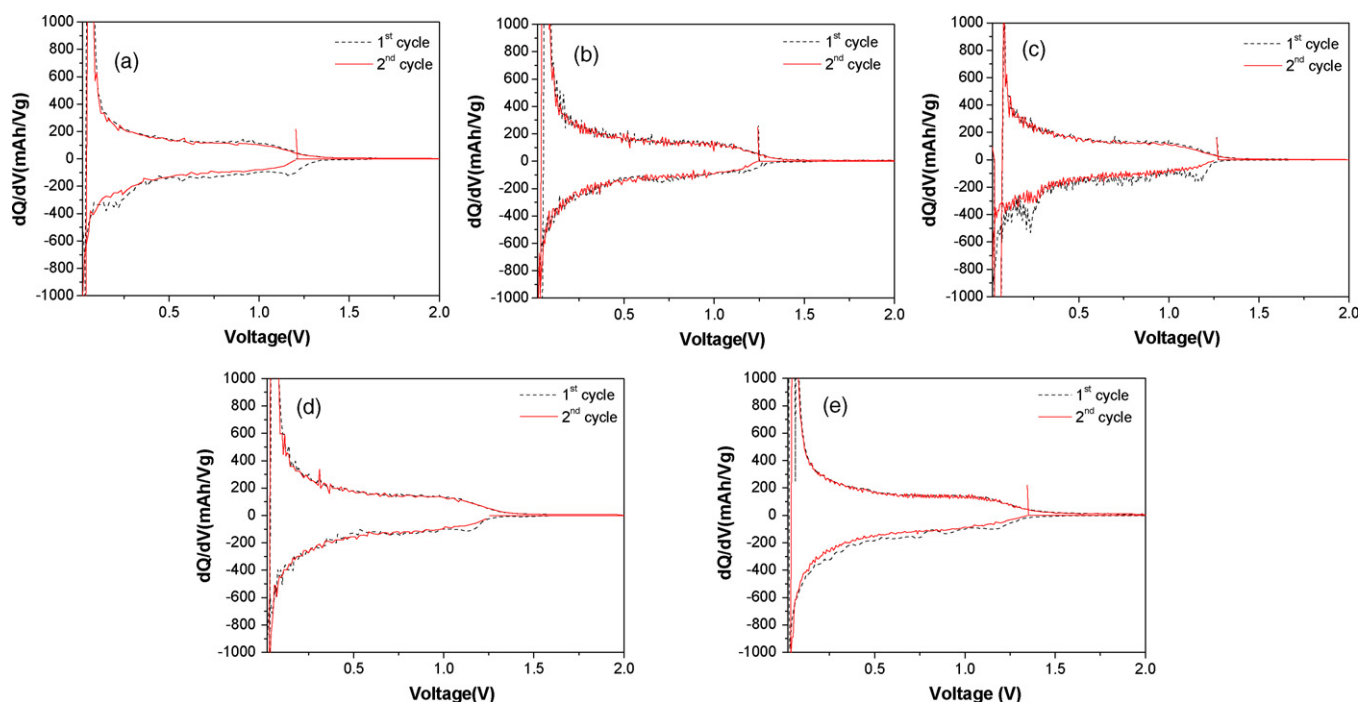


Fig. 3. Differential capacity vs. voltage for first and second cycles for: (a) as-received hard carbon; (b) as-received sample post-treated at 800 °C for 1 h under Ar flow; (c) as-received sample post-treated at 800 °C for 1 h, followed by air exposure (90% RH) for 1 week; (d) carbon-coated hard carbon; (e) carbon-coated hard carbon, followed by air exposure (90% RH) for 1 week.

remove the NMP, and then pressed into a sheet. It should be noted that in order to investigate the resistance to air exposure, both types of samples, i.e., bare- and carbon-coated hard carbons, were exposed to air with a relative humidity (RH) of 90% at 25 °C for a week before electrode fabrication. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v, provided by Cheil Industries Inc., South Korea). Half-cells were assembled in an argon-filled glove-box.

The cells were galvanostatically charged and discharged in the voltage range 0.01–2.0 V versus Li/Li⁺ at a current density of 0.3 mA cm⁻². Measurements of ac impedance were made on bare- and carbon-coated sample electrodes as a function of cell potential.

3. Results and discussion

Scanning electron micrographs of as-received and carbon-coated hard carbon powders are presented in Fig. 1. The as-received powder consists of sharp-edged particles, while carbon-coated powder shows the morphology of shapeless pebbles. The charge–discharge curves for the first two cycles of as-received and carbon-coated electrodes are given in Fig. 2. The distinct features with the as-received hard carbons are: (i) the charge (i.e., intercalation) curve during the second cycle is at lower potentials compared with that during the first charge; (ii) the potential gap between the two curves increases after the sample has been exposed to air (90% RH) for a week (Fig. 2(a) and (b)). For the carbon-coated electrode, the potential gap

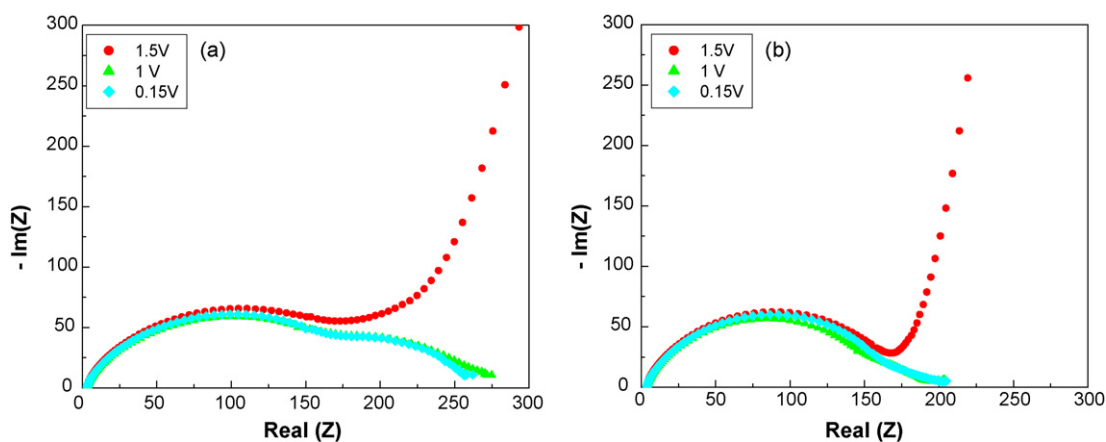


Fig. 4. Nyquist plots obtained at various electrode potentials during first charge for (a) bare and (b) carbon-coated hard carbons, exposed to air (90% RH) for a week.

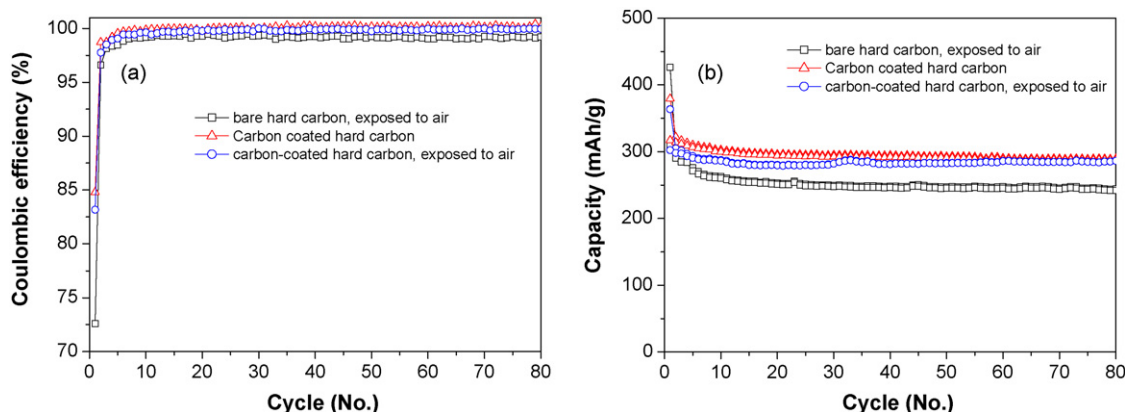


Fig. 5. (a) Charge–discharge coulombic efficiencies and (b) capacity retention as a function of the cycle number for bare and carbon-coated hard carbon.

between the initial two charge curves is quite small and appears to increase insignificantly even after air exposure under such a high humidity condition (Fig. 2(c) and (d)). It should be noted that the air exposure process for the bare sample was performed after heat-treatment of as-received hard carbons at 800 °C for 1 h under a flow of argon.

The above-mentioned features are better revealed in the plots of the differential capacity versus voltage for the first and second cycles of the same cells, as shown in Fig. 2. The differential capacity curve of the first cycle of the bare hard carbons have two major peaks, which are close to 1.2 and 0.25 V, as shown in Fig. 3(a) and (c). The peak near 1.2 V has been attributed [19,20] to the decomposition of electrolyte, i.e., the formation of a passivating layer, whereas peak near 0.25 V is due to the reaction of lithium with surface functional groups or absorbed species that result from air exposure [12]. A trace of the differential capacity peak near 0.25 V is absent in the cell with as-received hard carbon, that is post-treated at 800 °C for 1 h, as shown in Fig. 3(b). This is consistent with the finding that irreversible capacities of hard carbons have been reduced by post-treatments [21]. When post-treated bare hard carbons were held under 90% RH for a week, the irreversible peaks, especially that near 0.25 V, are intensified (Fig. 3(c)). This behaviour results from the diffusion of more air and water deep into the micro pores of the hard carbons. As a consequence, a trace of the 0.25 V peak can also be observed even in the second charge differential capacity curve, as shown in Fig. 3(c).

On the other hand, in the case of the carbon-coated sample, no evidence of the 0.25 V peak is seen (Fig. 3(d)), and moreover, a trace of the 0.25 V peak is not evident even after exposure to 90% RH for a week (Fig. 3(e)). This result suggests that the carbon coating might suppress the diffusion of air and water into hard carbons.

Nyquist plots obtained for the bare- and carbon-coated hard carbons, exposed to 90% RH for a week, at various potentials during the first charge reaction are shown in Fig. 4. At potentials lower than 1.0 V, two semicircles are observed. The semicircle in the high-frequency region corresponds to formation of a solid electrolyte interface (SEI) film on the surface of the carbon, whereas the semicircle in the low-frequency region relates to the charge-transfer process at the carbon|electrolyte interface

[22]. It appears that the resistance of the surface film on bare hard carbon is larger than that on carbon-coated hard carbon. This is attributable to the lower amount of surface filming products formed on the carbon-coated sample, as can be estimated by comparing the differential capacity peak intensities near 1.2 V for both electrodes (Fig. 3(c) and (e)). The increase in film resistance is probably because the coal-tar pitch as a carbon precursor is carbonized through a liquid phase and thus the resultant surface coated carbon has a dense structure compared with hard carbon. From these results, it is found that the coulombic efficiencies during cycling, as well as on the first cycle, are improved by carbon-coating treatment. This is shown in Fig. 5, in which the electrochemical performance of the carbon-coated sample is only slightly affected despite the fact that it was subjected to the high humidity condition for a week.

4. Conclusions

A soft carbon coating has been applied to a hard carbon by simple mechanical mixing and heating of hard carbon with coal-tar pitch powders. The carbon-coating dramatically inhibits the initial irreversible reactions of hard carbons, caused by air exposure, and this improves the charge–discharge coulombic efficiency on the first cycle and during cycling. When exposed to air, the soft carbon coating effectively suppresses the diffusion of air and water into the hard carbon and, moreover, the soft carbon appears to be more resistant to air exposure than the bare hard carbon. This may be responsible for the improved electrochemical performance of carbon-coated samples.

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