

Charge–discharge properties of surface-modified carbon by resin coating in Li-ion battery

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Abstract

The effect of an epoxy resin coating on the electrochemical performance of Li-ion batteries is investigated. Mesocarbon microbeads (MCMB), which constitute a promising carbon anode material for rechargeable Li-ion batteries is used as a starting carbon material. The surface coating of the MCMB is carried out by refluxing in a dilute H₂SO₄ solution and mixing in the epoxy resin-dissolved tetrahydrofuran (THF) solution. After heat treatment at 1000–1300 °C, the resin coating layer on the MCMB is converted to an amorphous phase which is identified by means of a high resolution transmission electron microscope (HRTEM) and a electron energy loss spectroscopy (EELS) analyses. The Brunauer–Emmett–Teller (BET) surface area of MCMB is increased by the formation of the amorphous epoxy resin coating layer. The electrochemical performance of the MCMB, such as the charge–discharge capacity and cycleability, is enhanced by the surface modification through epoxy resin coating. The reasons for the improvement of electrochemical performance are discussed in terms of the results from HRTEM observation, EELS analysis, and cyclic voltammetry © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Li-ion battery; Surface modification; Electrochemical reaction; Carbon electrode

1. Introduction

The crystallographic parameters of carbon and its chemical composition, such as surface functional groups and additives, are generally regarded as critical for the electrochemical performance in Li-ion batteries. Many extensive investigations and reviews have been reported on the relationship between the microstructure and chemical composition of carbon and its Li-intercalation behaviour [1–5]. Several subsidiary reactions between electrode and electrolyte are responsible for the attenuation of electrochemical performance such as a capacity loss (or irreversible capacity) and poor cycleability. Since a negative electrode is the lithium source in a lithium-ion cell, its capacity loss is especially detrimental to the specific energy of the cell and has to be minimized for optimum cell performance.

One of the events causing a capacity loss is the formation of thick interfacial layers (or a passivation layer) on carbon surfaces during the first few lithium-intercalation/de-inter-

calation processes, especially at the first reduction. The formation of these surface layers accompany electrolyte decomposition and are significantly dependent on the type of electrolyte and carbon. It is believed that these surface films are the ternary graphite intercalation compounds containing both lithium and electrolyte solvent Li_x(solv)_yC₆, called ‘solvated compounds’, are thermodynamically unstable and irreversible in the intercalation/de-intercalation process [6]. In addition, the capacity loss results from reduction of carbon surface complexes, impurities such as H₂O and O₂, residue compounds, etc. It has been reported that a large portion of the capacity loss could come from the reactions of Li with active sites such as surface hydroxyls, carbon radicals and adsorbed water, which commonly exist in carbons treated at low temperature [7,8].

A number of practical means to enhance cell performance have been considered [9–12]. A partial oxidation in an oxidizing atmosphere has been found to improve both intercalation capacity and cycleability. The removal of adsorbed water and surface hydroxyls during heat treatment in vacuum at about 1000 °C is also found to increase the carbon electrode performance. A mild oxidative thermal treatment at about 600 °C in air is also effective to reduce the

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irreversible capacity and increase the lithium intercalation capacity.

This study examines the effects of carbon surface modification by epoxy resin coating on the electrochemical performance. This treatment of the surface coating is expected to affect the charge–discharge capacity and cyclability associated with the formation of the passivation film on the carbon surface. Commercial mesocarbon microbeads (MCMB) are surface-modified by coating an epoxy resin and the electrochemical behaviour is discussed with respect to several physical and electrochemical properties such as Brunauer–Emmett–Teller (BET) surface area, micro structure, and cyclic voltammetric behaviour.

2. Experimental

The surface treatment was performed by epoxy resin coating MCMB (Osaka Gas Ltd.) carbon. MCMB powders were refluxed for 2 h in a 0.3 M H_2SO_4 solution and mixed in 20 wt.% epoxy resin dissolved tetrahydrofuran (THF) solution with stirring for 24 h. After separation from the solution, the coated MCMB powders were dried in a vacuum oven for 24 h and then heat treated at 1000–1300 °C for 2 h in flowing N_2 gas. Carbon electrodes, which served as anodes in lithium-ion half-cells, were prepared by wet mixing the MCMB powders. A conductor (Vulcan Xc-72R, 3 wt.%) and a binder dissolved in a solvent (polyvinylidene fluoride (PVDF) were dissolved in *N*-methyl pyrrolidinone (NMP)). The resulting slurry was rolled on to a copper foil current-collector, dried at 100 °C for 20 h in a vacuum dry oven, and then pressed at about 1.5 MPa using unidirectional pressure. The carbon electrodes thus formed had a thickness of 0.2–0.4 nm and a surface area of 10 cm^2 .

Electrochemical experiments were carried out in 10 cm^3 , three-electrode cylindrical glass-cells in which electrodes and separators (Celgard 2400) were placed vertically and the lithium foils were used as counter and reference electrodes. The electrolyte was prepared by dissolving 1 M LiPF_6 in a mixture of 50% ethylene and 50% diethyl carbonate by volume. The half-cells were fabricated in a dry argon-atmosphere glove box. Electrochemical tests were performed using a potentiostat–galvanostat (EG and G Inst. 263A). The cells were discharged at a constant current ($C/10$ rate) to a cut-off voltage of 10 mV versus Li/Li^+ . Charging was at the same rate up to 20 V versus Li/Li^+ . Cyclic voltammograms, were recorded at a scan rate of $5 \mu\text{V s}^{-1}$ in the range 0.0–0.3 V for analyzing the intercalation process of lithium ions into the coated MCMB.

The BET surface area was determined by nitrogen adsorption (Shimadzu, Micromeritics 2400). The morphology of the carbon electrodes was examined by a high resolution transmission electron microscope (HRTEM, JEM 3000F, JEOL Ltd.) operated at 300 kV.

3. Results and discussion

The charge–discharge behaviour of a Li/carbon (MCMB) half-cell is shown in Fig. 1 as potential versus capacity for the first cycle for untreated MCMB and coated MCMB heat treated at 1000 and 1300 °C. The coated MCMBs show higher charge–discharge capacities than that of a raw MCMB. The discharge–charge capacities of the coated MCMBs heat treated at 1000 and 1300 °C are 324/245 and 320/239 mA g^{-1} , respectively, while the capacity the untreated MCMB is 308/223 mA g^{-1} . Also, the voltage (IR) drop of the coated MCMBs at charge was lower than that of untreated MCMB by about 0.1 V.

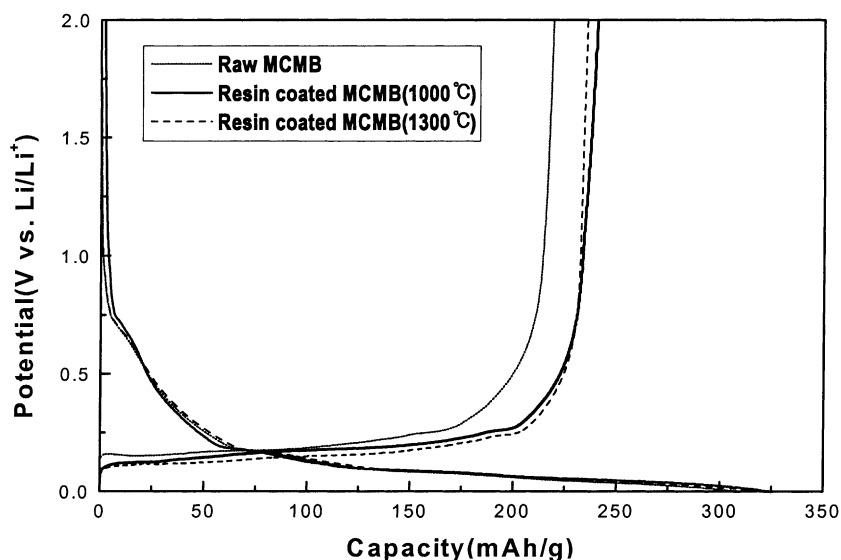


Fig. 1. First charge–discharge profiles of untreated (raw) MCMB and resin coated MCMBs (heat-treated at 1000 and 1300 °C).

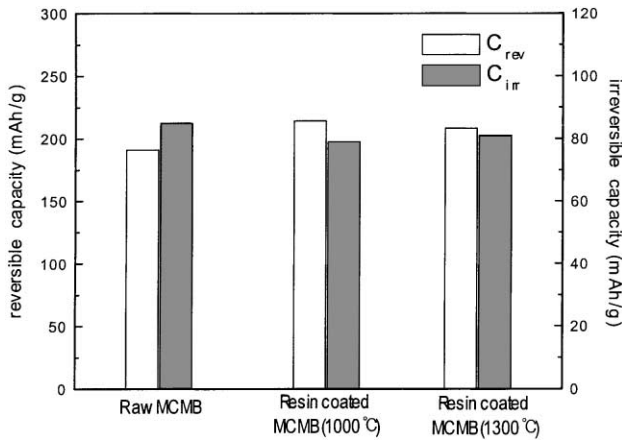


Fig. 2. Reversible (C_{rev}) and irreversible (C_{irr}) capacities of untreated (raw) MCMB and resin coated MCMBs (heat-treated at 1000 and 1300 °C).

The reversible and irreversible specific charges for untreated and coated MCMB are shown in Fig. 2. The reversible capacities of the coated MCMBs (heat treated at 1000 and 1300 °C) are higher than that of untreated MCMB by 19–23 mAh g⁻¹, while the irreversible capacity of the coated MCMBs are lower than that of untreated MCMBs by 4–7 mAh g⁻¹. The variation of the BET specific surface area with respect to the epoxy resin coating of MCMB is given in Fig. 3. The coated MCMB without heat treatment has a lower surface area than that of an untreated counterpart. By contrast, the coated MCMB with heat treatment exhibits higher surface area and its surface area increases as the heat-treatment temperature increases. Generally, the surface area of a disordered carbon synthesized at low temperature is higher than that of a well-graphitized carbon which is generally heat treated over 2000 °C. The surface area of the coated MCMB appears to be increased by the surface film which would be a disordered carbon structure when synthesized at low temperature of 1000 or

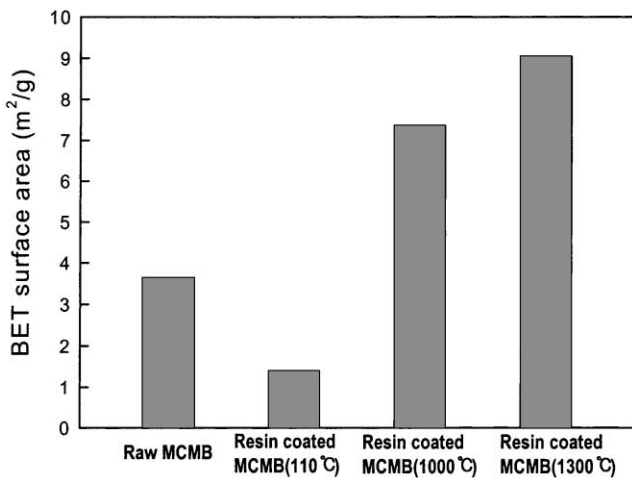


Fig. 3. BET surface area of untreated (raw) MCMB and epoxy resin coated MCMBs. Numbers in parentheses are heat-treatment temperatures.

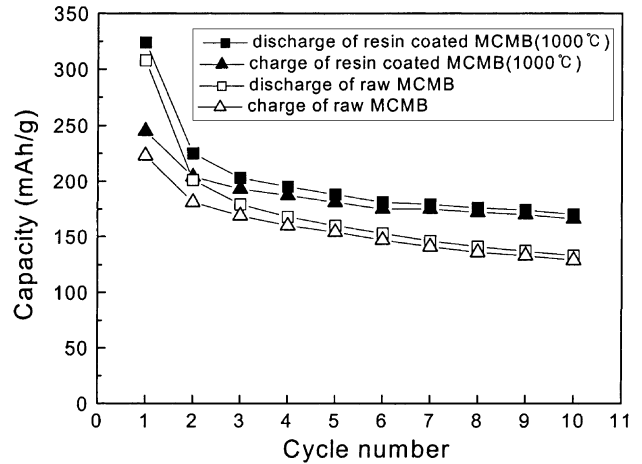


Fig. 4. Cycleability as charge–discharge capacity vs. cycle number for untreated (raw) MCMB and epoxy resin coated MCMB (heat-treated at 1000 °C).

1300 °C. Thus, one of main reasons for the enhanced discharge capacity of the resin-coated MCMB is probably due to the increase in the surface area.

The charge–discharge capacities versus cycle number by the 10th cycle for untreated MCMB and coated MCMB (heat treated at 1000 °C) are given in Fig. 4. The coated MCMB displays higher charge–discharge capacity and better cycleability than untreated MCMB. For both untreated and coated MCMB, the capacity losses on the first cycle, which are attributed primarily to the formation of a solid-electrolyte interphase (SEI), are very high but decrease significantly after the second cycle. The rate of capacity loss of the coated MCMB is relatively lower than that of untreated MCMB as the cycle number increases. The capacity loss of the coated and untreated MCMBs from the second to the 10th cycle is 23 and 36.5%, respectively.

In order to examine the surface morphology and the structure of the coated MCMB, the microstructure was observed by HRTEM. The lattice image of the coated MCMB which is heat treated at 1300 °C is shown in Fig. 5. As expected, the microstructure of MCMB shows regular ordering of the basal planes and closely resembles that of graphite. The epoxy resin coating covers the surface of the MCMB as an irregular and discontinuous film with a thickness of several nanometers. In particular, the valley-like surface area where carbon layers overlap each other, is filled with a thick layer of resin. The microstructure of the coating is clearly different from that of MCMB in that it lacks ordered layers.

The structure of the epoxy resin coating was analyzed by electron energy loss spectroscopy (EELS). The EELS spectra obtained from the coated and untreated MCMBs are given in Fig. 6. Curve A is the spectra obtained at an area of MCMB without a coating and shows the typical EELS pattern for graphite, which has sharp energy loss peaks associated with σ -bonds (σ^*) and π -bonds (π^*) at 284 and 291 eV, respectively [13]. Curve B is the spectra

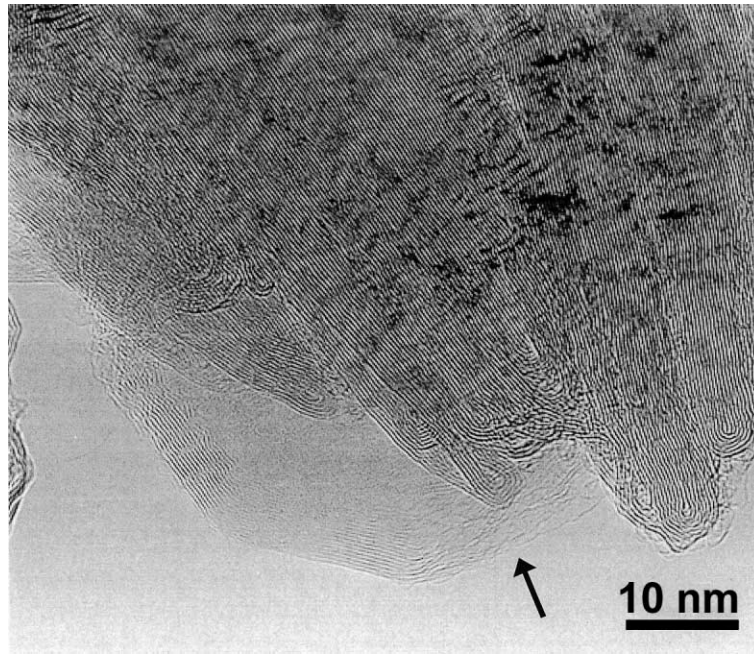


Fig. 5. HRTEM micrograph of epoxy resin coated MCMB (heat-treated at 1300 °C).

obtained at the coating (indicated by an arrow in the figure) and has weak energy loss peaks of σ^* and π^* . This indicates an amorphous carbon structure.

In order to examine the detailed microstructure of the epoxy resin coatings, carbons were fabricated by pyrolyzing the epoxy resin in N_2 gas at 1000 °C which is a similar heat-treatment temperature for the epoxy resin coated MCMB. The microstructure of the carbon obtained by pyrolyzing the epoxy resin is presented in Fig. 7 and shows graphene sheets which are less than 50 Å in size and are stacked roughly in

parallel fashion, but with random orientations between each layers. The selected area electron diffraction (SAED) pattern in the left box is a diffuse ring pattern, which indicates that the structure of carbon is amorphous.

Consequently, the charge–discharge capacity of MCMB is enhanced by the epoxy resin coating. Two major reasons can be considered for the improved electrochemical performance of carbon electrode by epoxy resin coating. One of the causes of capacity loss is the formation of a thick passivation layer accompanying the electrolyte decomposition which is markedly dependent on the type of electrolyte and carbon structure. The formation of this passivation layer and subsequent self-discharge occurs only in the prismatic plane, rather than in the basal plane of graphite [14]. The epoxy resin coating layer of amorphous structure covering the prismatic plane may retard the formation and growth of passivation layer by acting as a reaction barrier between the electrolyte and graphite, and thus improve the charge–discharge capacity. Cyclic voltammograms obtained from untreated MCMB and the epoxy resin coated MCMB are given in Fig. 8. There are three oxidation and reduction peaks (marked as 1r–3r and 1o–3o) which represent the formation and decomposition of lithiated carbons, respectively. These three main peaks in the spectra of the coated MCMB are shifted to lower potentials in reduction and higher potentials in oxidation, compared with those for untreated MCMB. This is probably due to the retardation of the Li–C reaction by the amorphous layer formed by the epoxy resin coating which plays a role as a barrier for the Li-ion diffusion.

Another reason for the improved electrochemical performance of the coated MCMB would be from the enhance-

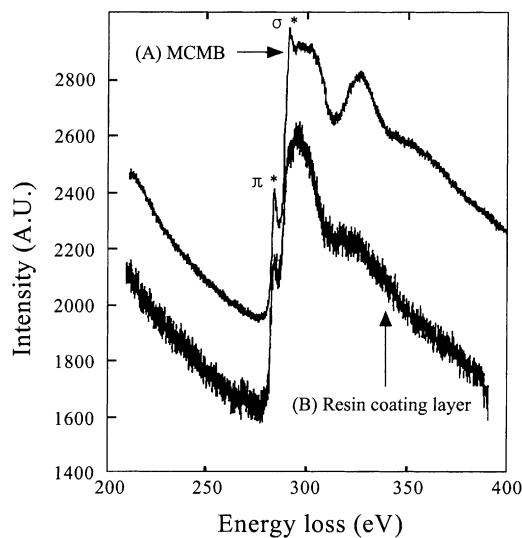


Fig. 6. EELS spectra for (A) MCMB matrix and (B) epoxy resin coating layer.

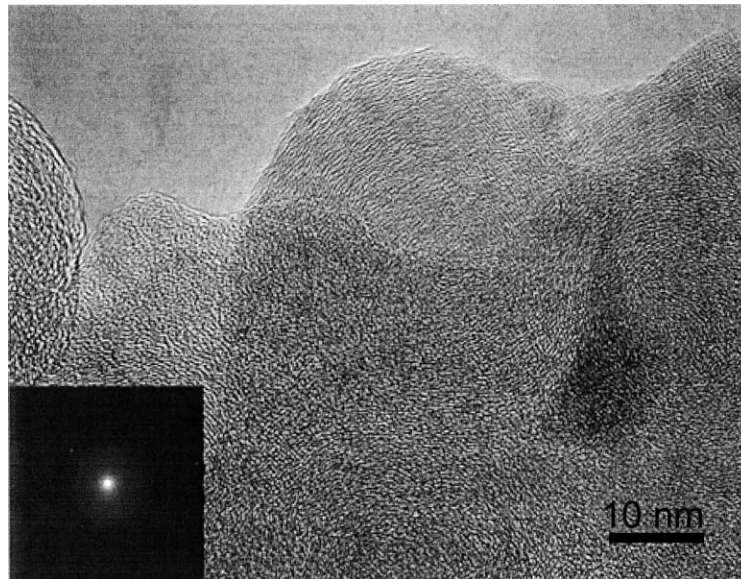


Fig. 7. HRTEM micrograph of carbon obtained by pyrolyzing epoxy resin.

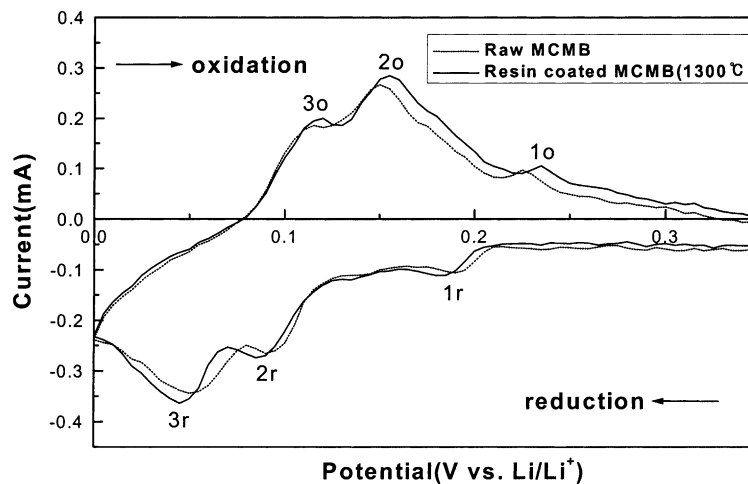


Fig. 8. Cyclic voltammograms for the untreated (raw) MCMB and epoxy resin coated MCMB (1300 °C).

ment of surface mechanical properties by the formation of the amorphous film. The amorphous carbon film on graphite substrate greatly improves the surface mechanical properties such as hardness and toughness [15]. Thus, this improvement may increase delamination resistance during the repeated intercalation/de-intercalation process, and subsequently enhances cell cycleability and stability.

4. Conclusions

The present study examines the effects of surface modification by coating with epoxy resin is on the electrochemical performance of MCMB as an anode in Li-ion batteries. The results are summarized as follows.

1. The epoxy resin coated MCMB shows higher reversible capacity, lower irreversible capacity, and better cycleability than untreated MCMB.
2. The epoxy resin coating layers on MCMB covered the surface as irregular and discontinuous films and are identified as an amorphous structure by HRTEM and EELS analyses. The BET surface-area of MCMB is increased by the epoxy resin coating.
3. Two reasons for the enhancement of the cell performance by the epoxy resin coating have been considered. First, the coating plays an important role as a barrier for carbon reacting with electrolyte and retarding the formation of a passivation layer. Second, the coating as an amorphous film on the MCMB substrate improves the surface mechanical properties and resists surface

delamination during Li-intercalation/de-intercalation process.

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