

Characteristics of surface films formed at a mesocarbon microbead electrode in a Li-ion battery

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Abstract

An investigation is made on the interfacial phenomena of commercially available mesocarbon microbeads (MCMB) as the carbon lithium electrode in an electrolyte, which consists of 1 M LiPF₆ dissolved in an equal mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Once the charge–discharge of lithium (Li) proceeds, a surface film is formed on the MCMB carbon electrode, and its thickness increases with cycle number. The growth of the surface film with cycle number is observed by a scanning electron microscope and the surface resistance by means of AC impedance measurements. A continuous decrease in the charge capacity with cycle number is found and is related to film growth. The surface films are composed of solvated Li compounds, as shown by surface-sensitive Fourier transform infrared (FT-IR) spectroscopy. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lithium-ion battery; Mesocarbon microbeads; Electrochemical properties; Carbon electrode

1. Introduction

As most carbons, including graphite, can insert lithium (Li) reversibly with high capacity, have good electronic conductivity and low electrochemical potential with respect to Li metal, they are attractive candidates as anode materials for rechargeable Li-ion cells. The types of carbonaceous materials studied for the Li-ion cell range from completely layered graphites to non-graphitizable hard carbons. Structural variations of carbonaceous materials play an important role in the electrochemical performance of the Li-intercalated carbon, such as capacity reversibility, cycleability, and stability. Recent works by many research groups [1–5] have demonstrated that disordered carbons, obtained typically by pyrolyzing organic precursors such as phenolic resins, petroleum pitch, coal tar pitch, sugar, and poly(vinylchloride) (PVC) at low temperature, can intercalate Li with very high capacity. Graphite has a nearly perfect layered structure and is able to intercalate Li to a stoichiometry of LiC₆. Unfortunately, practical graphi-

te electrodes typically have specific charges far below the theoretical maximum ($\sim 300 \text{ mA h g}^{-1}$). This implies that the real electrochemical reaction is more complicated and involves the formation of Li_xC₆ as described by the equation: $x\text{Li}^+x\text{e}^- + 6\text{C} \leftrightarrow \text{Li}_x\text{C}_6 (0 < x < 1)$. Several subsidiary reactions between the electrode and the electrolyte are responsible for the attenuation of electrochemical performance such as capacity loss (or irreversible capacity) and poor cycleability. Since the negative electrode is the Li source in a Li-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 causes of capacity loss is the formation of a thick interfacial layer (or a passivation layer) on the carbon surface during the first few Li intercalation–de-intercalation processes, especially during the first reduction. The formation of this surface layer accompanies electrolyte decomposition and is markedly dependent on the type of electrolyte and carbon. It is believed that these surface films are ternary graphite intercalation compounds, which contain both Li and electrolyte solvent, i.e., Li_x(solv)_yC₆, so-called solvated compounds, which are thermodynamically unstable and irreversible in the intercalation–de-intercalation process [6,7]. In addition, the capacity loss results from reduction of carbon surface complexes, impu-

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urities such as H₂O and O₂, residue compounds, etc. It has been reported that a large portion of the capacity loss could originate from the reaction of Li with active sites such as surface hydroxyls, carbon radicals, and adsorbed water, which frequently exist in carbons treated at low temperature [8–10]. In the present study, a study is made of the electrochemical performance of Li-ion half-cells, which consist of mesocarbon microbeads (MCMB) electrodes vs. Li metal, and of the formation of surface films by Fourier transform infrared spectroscopy (FT-IR) analysis, scanning electron microscopy (SEM), and impedance spectroscopy.

2. Experimental

Mesocarbon microbeads (MCMB2528, Osaka Gas) were used as a negative electrode in the Li-ion half-cell. The first two digits in the number for the carbon designation indicate the particle size (in μm), the second two digits indicate the heat-treatment temperature. That is, MCMB2528 means that the particles are smaller than 25 μm and the heat-treatment temperature is 2800 J. The carbon electrodes were prepared by a wet mixing of 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). This slurry-state mixture was rolled on to a copper foil current-collector, dried at 100 J for 20 h in a vacuum dry oven, and then pressed at about 1.5 MPa using a unidirectional pressure. The carbon electrodes thus formed had a thickness of 0.2 to 0.4 mm and a surface area of 1.0 cm².

Electrochemical experiments were carried out in a 10-ml, three-electrode cylindrical glass-cell in which the electrodes and the separators [Celgard 2400] were placed vertically. Li foils were used as the counter and reference electrodes. The electrolyte was prepared by dissolving 1 M LiPF₆ in a mixture of 50% ethylene and 50% diethyl carbonate by volume. Half-cells were fabricated in a dry

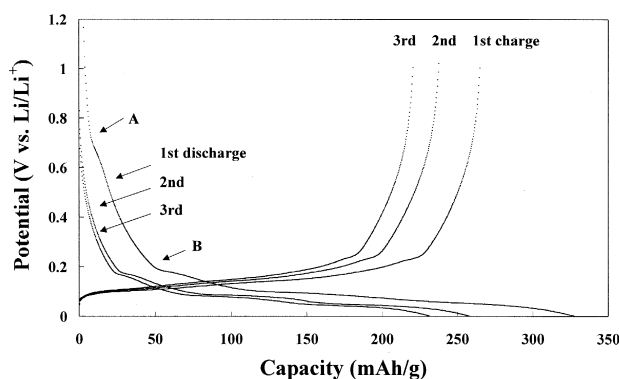


Fig. 1. Charge–discharge behaviour of Li/MCMB half-cell.

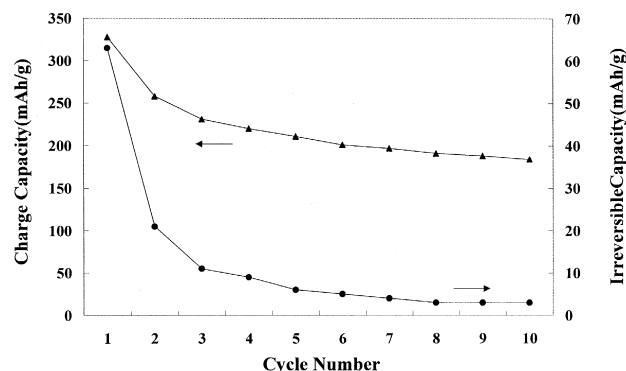


Fig. 2. Charge capacity and irreversible capacity as cycle number. Symbols of solid triangle (\blacktriangle) and circle (\bullet) are charge capacity and irreversible capacity, respectively.

argon-atmosphere glove box. The electrochemical tests were performed using a potentiostat/galvanostat (EG and G Inst. 263A). The cells were discharged at constant current (C/10 rate) to a cut-off voltage of 10 mV vs. Li/Li⁺. Charging was performed at the same rate up to 1.5 V vs. Li/Li⁺. In this paper, the counter-electrode is Li metal and the discharge process is the intercalation of Li into carbon. Cyclic voltammograms were measured 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 Li ions into MCMB carbons.

Impedance spectra were obtained by using a Solartron 1260 impedance analyzer, which was performed at 25°C on fully charged cells using an applied signal of 50 mV(rms) over the frequency range from 1 mHz to 1 MHz. The morphology of the carbon electrodes was observed with a scanning electron microscope (JSM 5800).

3. Results and discussion

The charge–discharge behaviour of a Li/carbon (MCMB) half-cell is shown in Fig. 1 as potential vs. capacity for the 1st to 3rd cycle. The current density was 50 $\mu\text{A m g}^{-1}$ and the cut-off voltage was 10 mV for discharge and 1.0 V for charge. The discharge capacity is about 330 mA h g⁻¹ on the 1st cycle, which corresponds to the formation of the compound LiC₆. The capacity decreases to 260 and 235 mA h g⁻¹ on the 2nd and 3rd cycles, respectively. On the 1st discharge curve, two distinct inflection points occur at about 0.75 V (point A) and 0.2 V (point B), respectively. The inflection point of A is mainly due to the formation of solvated Li intercalation compounds followed by solvent decomposition, which results in capacity loss. The reaction of solvated Li intercalation is hindered once the SEI film is formed with an appropriate thickness [11]. Thus, the inflection point of A on the 1st discharge curve disappears on the 2nd cycle. Below a potential of 0.2 V vs. Li/Li⁺ (inflection point B), the primary reaction is the formation of Li_xC₆ and gives

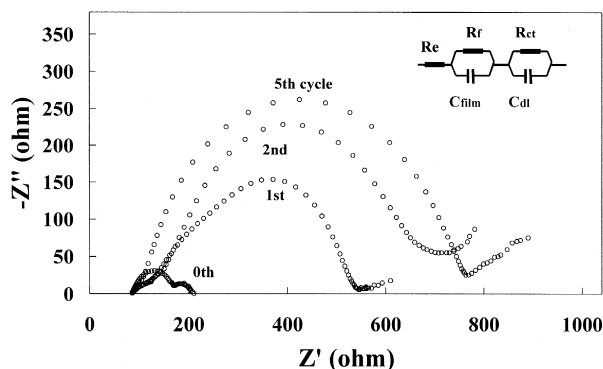


Fig. 3. Nyquist plots of impedance obtained for Li/MCMB carbon cell in (EC+DEC+LiPF₆) in frequency range 1 mHz–1 MHz at different cycle numbers. The equivalent circuit is given.

rise to a potential plateau, which is reversible in the subsequent cycle. At the same time, a significant loss of charge occurs below the point B because the intercalated Li may partially participate in the formation of solvated Li intercalation compounds by so-called self-discharge [11–15].

The charge capacity (intercalation) and the irreversible capacity (defined as the difference between the 1st charge and discharge cycles) vs. cycle number are presented in Fig. 2. Both the charge capacity and the irreversible capacity of the 1st cycle are very high and decrease significantly after the 2nd cycle. This phenomenon seems to be associated with the formation of irreversible surface layers, which accompany the solvated Li intercalation, which is mainly formed on the 1st discharge and irreversible subsequent charge. In order to evaluate the surface resistance of the electrode with respect to the formation of the irre-

versible surface layers, AC impedance measurements were performed. The overall resistance consists of the sum of the electrolyte resistance (R_e), the surface film resistance (R_f) and the charge-transfer resistance (R_{ct}), as shown in Fig. 3. The resistance of the surface film is attributed to the formation of a passivation layer on the surface of the electrode. The resistance of the surface film (R_f) for an uncycled electrode is very low, but increases significantly on the 1st cycle, and moderately on subsequent cycles. This demonstrates that once the passivation films are formed on the first discharge, they continue to grow and affect the subsequent capacity by remaining on the surface of electrode without being dissolved or decomposed into the electrolyte. The large increase in the resistance of the surface film on the first cycle suggests that solvated Li compounds are formed on the initial discharge and account for the high irreversible capacity on the first cycle in Fig. 2.

Electron micrographs of MCMB electrodes before and after charge–discharge are shown in Fig. 4. Before examination, the specimen was separated from the cell in a glove box, washed with ethanol, and dried in a vacuum oven at 60°C. Compared with an uncycled specimen, the carbon subjected to charge–discharge is covered by a surface film with a thickness that increases with cycle number. The surface films develop a significant thickness as cracks are observed after 10 cycles. Such surface films are usually formed by the reaction between Li ions and the organic electrolyte during charge–discharge [16,17]. Once formed, the surface films do not dissolve, but grow to a detectable thickness, as shown in Fig. 4c and d.

It is known that surface films are formed on a Li electrode in polar aprotic solvents by precipitation of

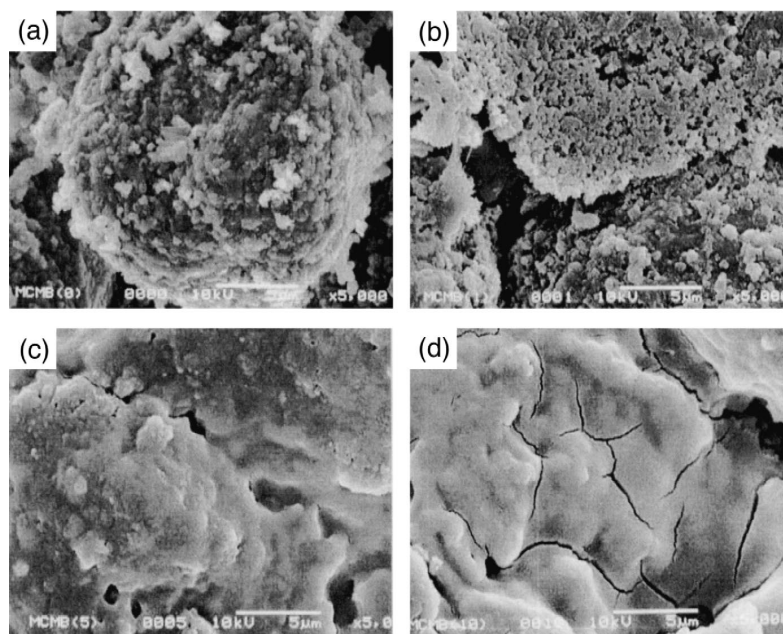


Fig. 4. Electron micrographs of MCMB carbon electrodes (a) before charge–discharge, (b) after 1 cycle, (c) 5 cycles, (d) 10 cycles.

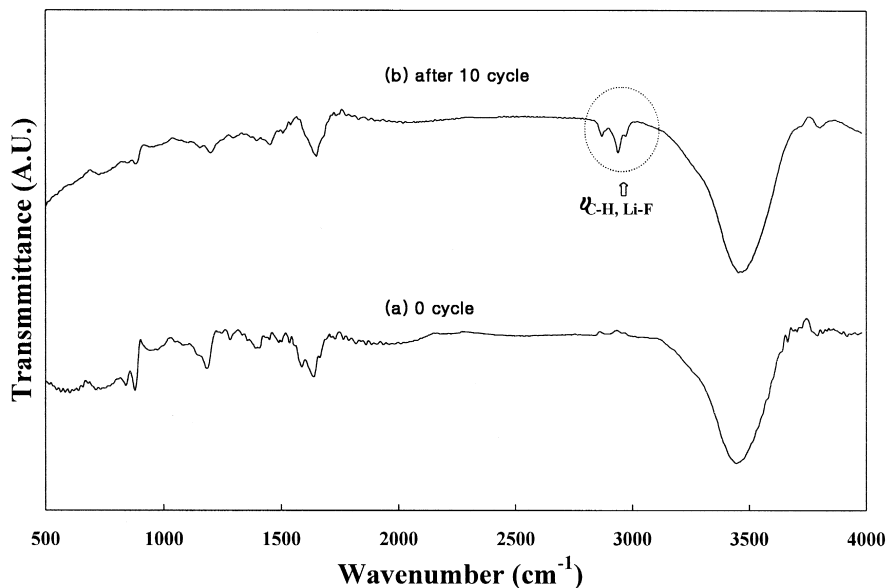


Fig. 5. FT-IR spectra for MCMB electrodes: (a) before and (b) after 10th cycle of charge–discharge.

species, which are the reaction products between the Li and the electrolyte components. The films control the electrochemical behaviour of Li in solutions [18]. Also, surface films similar to those formed on Li electrodes at low potential are found on graphite electrodes in solutions (e.g., propylene carbonate (PC), ethylene carbonate (EC), methyl formate (MF), LiAsF_6 or LiClO_4) and affect the reversibility of Li intercalation [7,19–22]. Therefore, it is concluded that the surface films shown in Fig. 4 were formed on the MCMB carbon by precipitation of the reaction products between lithiated carbon and the electrolyte components EC, DEC, and LiPF_6 .

In order to investigate the chemical composition of surface films, surface sensitive FT-IR in a transmittance mode was performed. Two FT-IR spectra obtained from MCMB carbon electrodes before and after the 10th cycle in an electrolyte solution, which is 1 M LiPF_6 dissolved in a solvent of EC/DEC (50/50 by volume) are compared in Fig. 5. The samples were prepared in a manner similar to that used for the electron micrographs in Fig. 4. Spectrum

5(a) relates to the electrode before the electrochemical process. Spectrum 5(b) was obtained from the electrode after the 10th cycle and exhibits a significant difference to the spectrum in 5(a), i.e., there are some extra peaks in the wave number range 2850–2950. These peaks are relevant to C–H and Li–F compounds [7], which are attributed, respectively, to the reduction of EC/DEC and LiPF_6 solutions during the charge–discharge process. Thus, the surface films formed on the MCMB electrode are related to reduction products of the solvents (EC + DEC) and a lithium salt (LiPF_6).

The cyclic voltammogram of the carbon electrode is shown in Fig. 6. There are three oxidation and reduction peaks (marked as 1,2,3), which represent the formation and decomposition of lithiated carbons, respectively. According to previous studies of lithiation of carbon fibres and graphites [22–25], these peaks correspond to the potentials of two-phase coexistence. That is, peaks 1, 2, and 3 are the equilibrium potentials of the dilute stage 1 (or called 1') and stage 4 (LiC_{36}), stage 3 (LiC_{18}) and stage 2 (LiC_{12}), and stage 2 and stage 1 (LiC_6), respectively. The reduction and oxidation peaks 3 are not clearly defined in this cyclic voltammogram, probably because the MCMB2528 is not perfectly graphitized as a layered graphite.

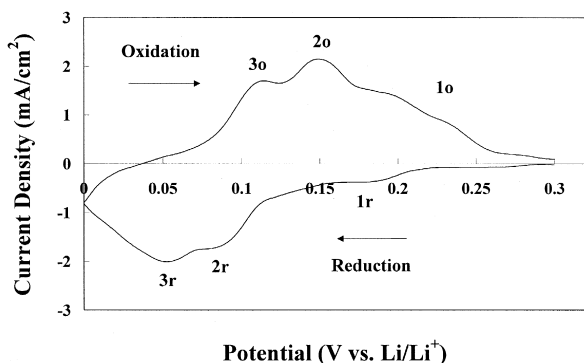


Fig. 6. Cyclic voltammogram for MCMB electrode in (EC + DEC + LiPF_6) electrolyte. Scan rate = $5 \mu\text{V s}^{-1}$.

4. Conclusions

As electrochemical reactions during charge–discharge occur in the Li/MCMB carbon cell in electrolyte solutions of EC + DEC + LiPF_6 , surface films (or passivation films) form on the carbon electrode. Once the surface films are formed on the 1st discharge, these grow continuously during subsequent charge–discharge cycling, without dis-

solution into the electrolyte solutions, and cause a reduction in charge capacity. The continuous reduction of charge capacity with cycling is related to growth of the surface film. Also, AC impedance spectroscopy measurements confirm the growth of the surface film by an increase in the surface resistance of the carbon electrode with cycling.

Evidence of the growth of the surface film growth with cycling is identified by SEM micrographs. The high irreversible capacity on the first cycle is due to the surface film, which is comprised of insoluble solvated Li compounds. According to FT-IR spectra analysis, the surface films are formed from the reduction products of the solvents (EC + DEC) and the lithium salt (LiPF_6) that are used in this study.

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