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Short communication

Electrochemical studies of graphitized mesocarbon microbeads as an anode in lithium-ion cells

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Abstract

The electrochemical performance of negative electrodes (anodes) made from mesocarbon microbeads (MCMB) in lithium-ion cells has been studied systematically via a variety of electrochemical techniques. The MCMB anodes have a stable lithium intercalation capacity of 325 mAh g^{-1} on high-rate charge–discharge cycling. Cyclic voltammetry shows only one reduction peak and one oxidation peak, which correspond to lithium-ion intercalation and de-intercalation, respectively. The diffusion of lithium ions in MCMB electrodes is characterized by ac impedance measurements.

Keywords: Mesocarbon microbeads; Lithium-ion battery; Anode; ac impedance

1. Introduction

Various graphitic and non-graphitic carbons have been extensively investigated as anode materials for lithium-ion batteries. The application of carbon anodes in lithium-ion batteries significantly reduces safety concerns compared with the use of lithium metal [1,2]. The advantages of carbonaceous anodes over lithium metal are many. First, there is no possibility of the development of lithium dendrites on the surface of the electrode, because lithium ions are inserted into the carbon structure. Second, the reaction rate is limited by the diffusion of lithium ions. Therefore, reaction rates at high temperature are much lower than those with lithium metal. Third, the carbonaceous anodes do not melt under normal conditions, which does happen with lithium metal anodes.

The critical property for carbon anodes in organic electrolyte is the formation of a passivation layer on the surface of the lithiated carbon. This passivation layer ensures that the electrode has sufficient stability and reversibility to undergo long-term cycling without irreversible capacity loss [3–8]. In general, two types of carbons, can be used for lithium storage, namely, graphitized carbon and non-graphitzed carbon. Non-graphitizable carbon, or hard carbon, has large lithium insertion capacity but suffers large irreversible capacity. The irreversible capacity requires excess cathode material to provide lithium-ion resources, which results in a low specific energy of the battery pack. The irreversible capacity for graphitized carbon is much smaller. Graphitized mesocarbon microbeads (MCMB) represent an industrial benchmark for the lithium-ion battery industry. MCMB materials have good capacity at low voltage and good cycleability. Thus, it is important to characterized systematically the electrochemical properties of MCMB materials as anodes in lithium-ion cells.

In this investigation, the electrochemical performance of a MCMB electrode is evaluated by means of electrochemical techniques. The kinetics of lithium-ion insertion in MCMB are characterized by ac impedance spectroscopy.

2. Experimental

The MCMB was supplied by Osaka Gas Co., Japan. This material was graphitized at 2800 °C. The morphology of the MCMB particles was observed by scanning electron microscope. X-ray diffraction was performed on MCMB powders using a Phillips PW1730 diffractometer with Cu Kα radiation. Particle-size analysis was undertaken with a Malvern Laser Particle-Size Analyzer. Teflon cells were assembled for electrochemical characterization of MCMB electrodes using lithium foil as counter electrodes. The MCMB

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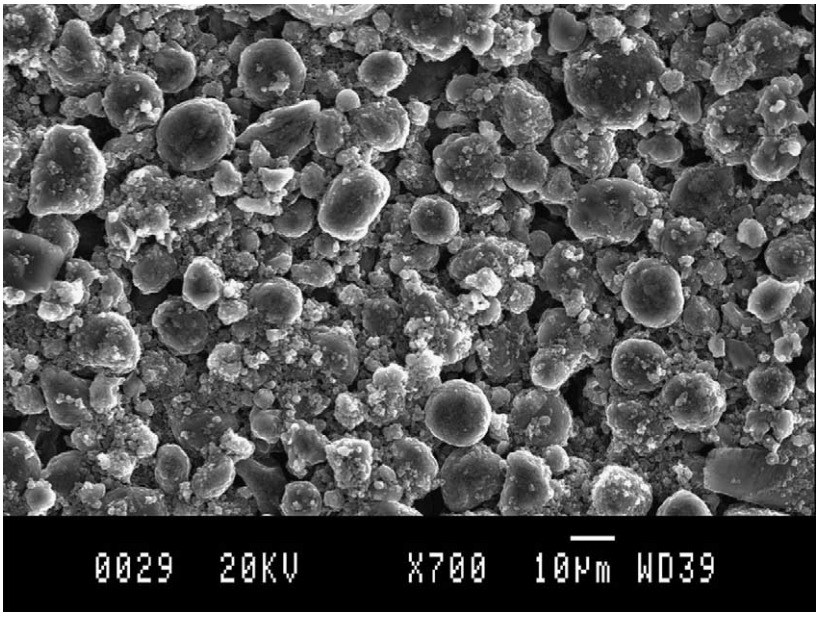

Fig. 1. Scanning electron micrograph of MCMB carbon particles.

electrodes were made by dispersing 95 wt.% active material and 5 wt.% poly-vinylidene fluoride (PVDF) binder in dimethyl phthalate solvent to form a slurry, which was then spread on to copper foil. The thickness of the electrode was controlled at 60–80 μm with a loading of 2–3 mg. The cells were assembled in an argon-filled glove-box (Mbraun, Unilab, USA). The electrolyte was 1 M $LiPF_6$ in a 1:1 (by volume) mixture of ethylene carbonate (EC) and dimethyle carbonate (DMC) provided by MERCK KgaA, Germany. The cells were galvanostatically charged and discharged in the voltage range 0.05–1.5 V versus Li/Li^+. Measurements of ac impedance were made on MCMB electrodes using an EG & G Princeton Applied Research Electrochemical Impedance Analyzer (model 6310). Before ac impedance measurements, the cells were pre-cycled galvanostatically between 0.05 and 1.5 V for five cycles to establish and stabilize the solid electrolyte interface (SEI) between the electrolyte and MCMB carbon electrode. The cell was potentiostatically conditioned to a certain potential and equalibrated for 3 h. The ac impedance spectra were obtained by applying a sinewave of 5 mV amplitude over the frequency range 100 kHz to 1 mHz.

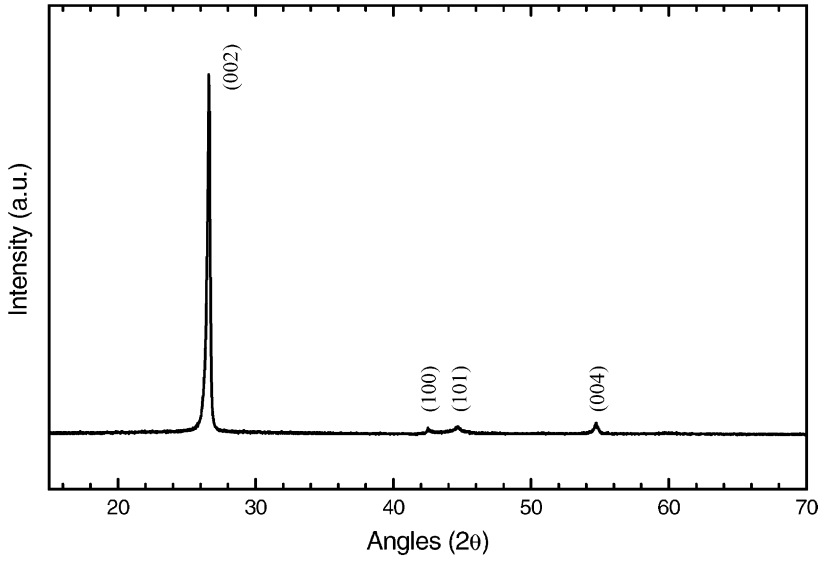

Fig. 2. X-ray diffraction pattern of MCMB powder.

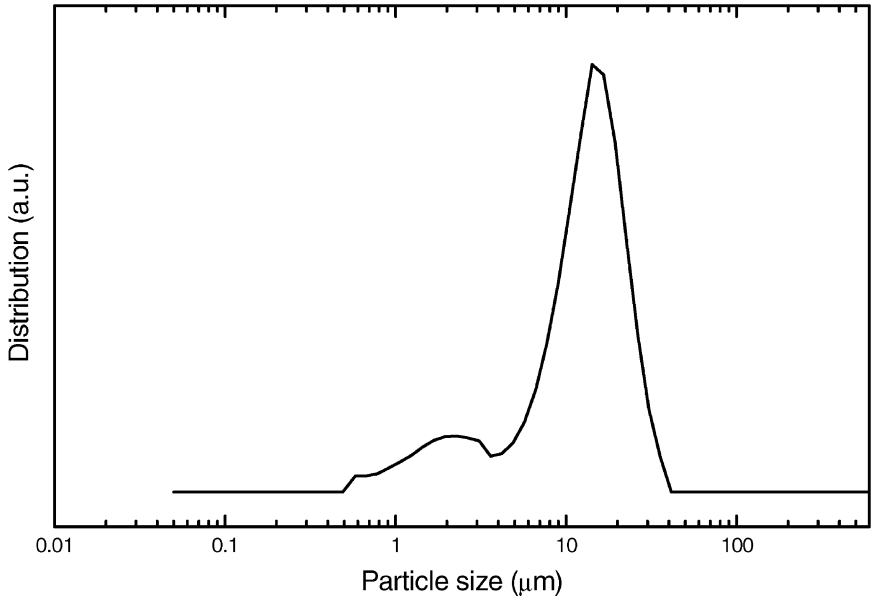

Fig. 3. Particle-size distribution of MCMB carbon powders.

3. Results and discussion

3.1. Physical characterization of MCMB

The morphology of MCMB particles was observed by scanning electron microscopy. An electron micrograph of MCMB particles is shown in Fig. 1. The MCMB agglomerates have a spherical shape, which consists of many small graphite particles. The spherical agglomerates have an average particle size of 10–15 μm. A substantial amount of small non-spherical graphite particles are also present. The co-existence of large spherical agglomerates and small particles would allow the electrode to have higher packing density according to the principle of powder packing. This will increase the energy density when MCMB carbons are used as anode materials in lithium-ion batteries. The X-ray diffraction pattern of MCMB is shown in Fig. 2. The MCMB is a very well graphitized carbon with a strong (0 0 2) diffraction line. The d space of $d_{0\,0\,2}$ equals 3.351 Å, which is the same as perfect graphite ($d_{002} = 3.35$ Å). Using a laser particle-size analyzer, the average particle size d_{50} of MCMB was found to be around 13.2 μm. The particle-size distribution is shown in Fig. 3 and it can be seen that there are two distribution peaks. A small portion of MCMB

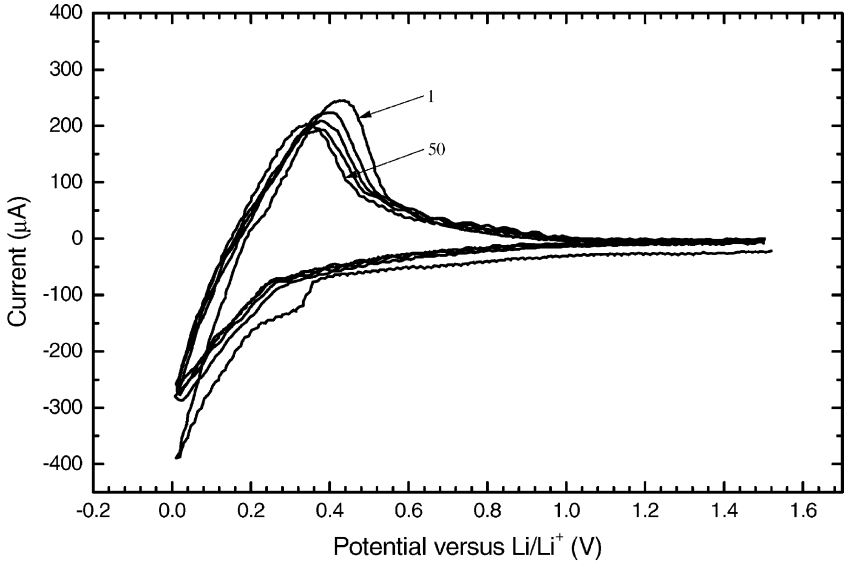

Fig. 4. Cyclic voltammograms of MCMB carbon electrode.

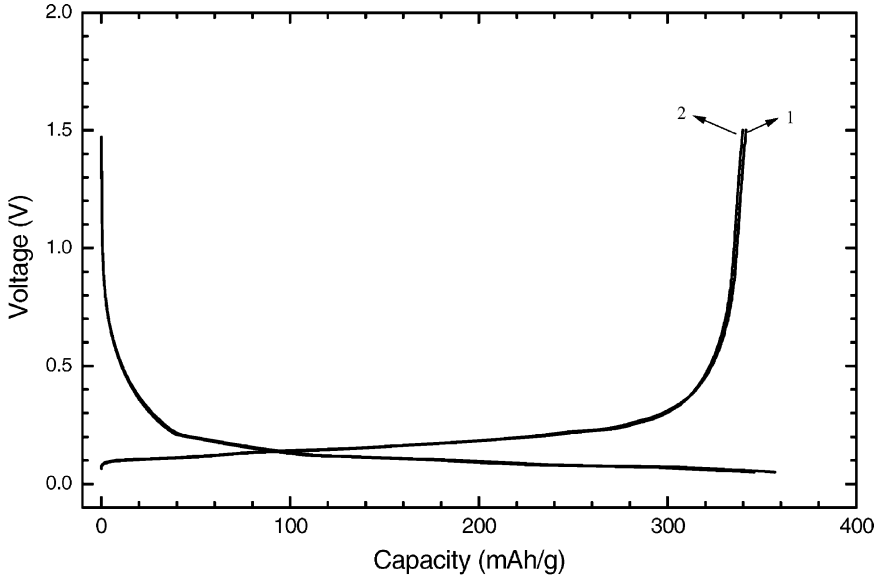

Fig. 5. First and second charge–discharge curves of MCMB electrode.

particles has a small average particle size of ∼2 μm. This is consistent with scanning electron microscopic observations.

3.2. Electrochemical testing of MCMB as anodes in lithium-ion cells

Cyclic voltammograms of MCMB electrodes in lithium-ion cells, in which a lithium foil was used as the counter electrode and reference electrode are shown in Fig. 4. In the first scanning cycle, there is a small hump in the potential range 0.24–0.33 V, which is related to the formation of a passivation film on the surface of the MCMB electrode [9,10]. The passivation layer is usually called the solid electrolyte interface. In the subsequent scanning cycle, this broad lithium insertion peak disappears. Therefore, the passivation film on the surface of the MCMB electrode appear to be formed during the first cycle and remains stable on subsequent cycles. The potential of the lithium-ion insertion peak in the cyclic voltammetric curves is very close to 0.0 V versus Li/Li^+ reference electrode. Whereas the potential of lithium extraction is in the range 0.3–0.4 V versus lithium reference electrode. There exists a voltage hysteresis between lithium extraction and lithium insertion. Previously, it was reported [11] that the hysteresis during lithium insertion and extraction in ball-milled carbon might be related to interstitial carbon atoms. MCMB carbon is, however, a well graphitized carbon. There is no interstitial carbon in the graphite crystal structure. Therefore, it seems

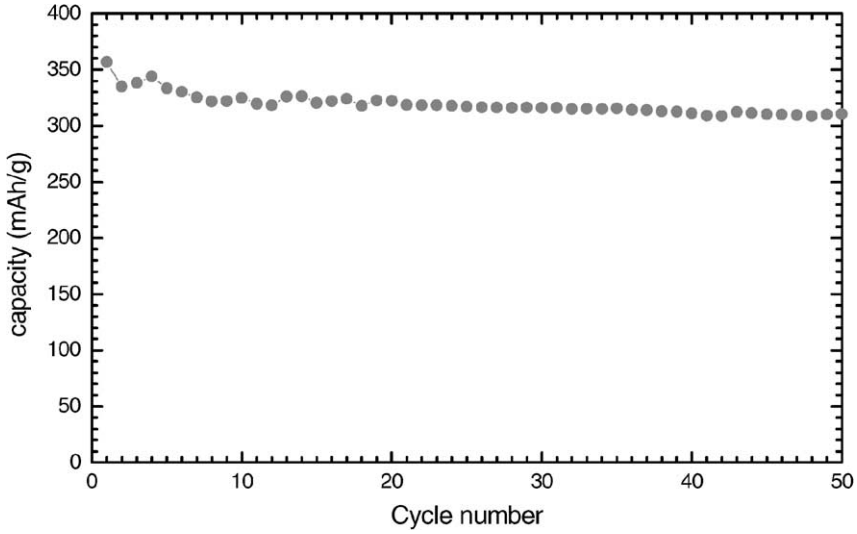

Fig. 6. Lithium insertion capacity vs. cycle number.

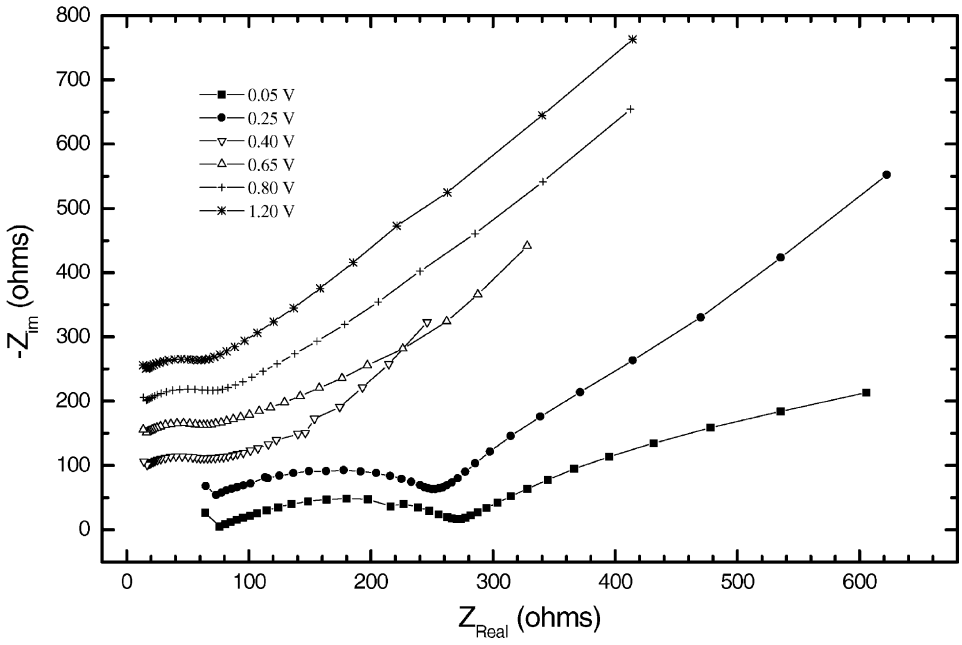

Fig. 7. ac impedance spectra of MCMB electrode at different potentials.

likely that a different mechanism induces the slight voltage hysteresis between lithium intercalation and lithium de-intercalation in the (MCMB) electrode.

Discharge and charge curves of the MCMB e1ectrode are shown in Fig. 5. The electrochemical potential for lithium insertion is below 0.2 V, and the potential for lithium extraction is mainly located between 0.1 and 0.4 V. This is in good agreement with the result of the cyclic voltammetry tests. In the first cycle, there is 25–30 mAh g^{-1} irreversible capacity between lithium insertion and extraction, which is quite small compared with other carbonaceous materials. This irreversible capacity is probably used to form the passivation layer on the surface of the electrode. MCMB anodes have a low lithium insertion potential and a small irreversible capacity on the first cycle, which is desirable for anode materials for lithium-ion batteries. The variation of lithium insertion capacity with cycle number for MCMB anodes is presented in Fig. 6. MCMB electrodes are very stable on cycling and can deliver an average reversible lithium storage capacity of 325 mAh g^{-1}.

3.3. ac impedance studies on MCMB carbon electrode

ac impedance spectra of MCMB electrodes were obtained. Gawano static cycling was performed for five cycles and then stopped at a potential of 1.5 V. The ac impedance measurements were then performed at each step by potentiostatically discharging the electrode to the desired potential from 1.5 to 0.1 V. The Nyquist complex plane impedance plots are presented in Fig. 7. A semicircle is observed in the high-frequency regime, which can be assigned to the charge-transfer impedance on the MCMB electrode vertical line electrolyte interface. An inclined line at an approximate 45 °C angle to the real axis corresponds to the lithium-diffusion process within the MCMB electrode.

The ac impedance spectra for the MCMB electrode can be modeled by the modified Randles equivalent circuit presented in Fig. 8. R_e is the electrolyte resistance, and C_f and R_f are the capacitance and resistance, respectively, of the passivation film formed on the surface of the electrode.

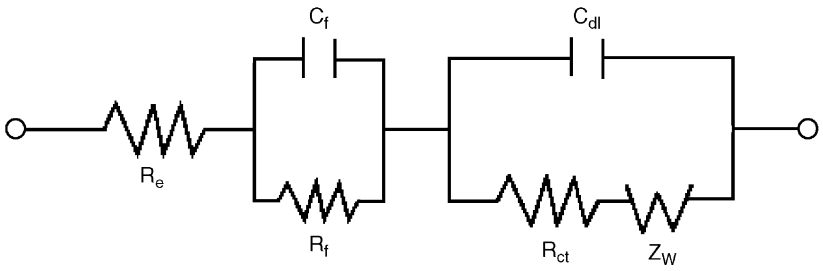

Fig. 8. Randles equivalent circuit for MCMB electrodelelectrolyte interface.

Table 1
Kinetic parameters of MCMB electrode

Electrode potential (V)	R_e (Ω cm^{-2})	R_{ct} (Ω cm^{-2})	i_0 ($\times 10^{-4}$, A cm^{-2})	C_{dl} (μF)
1.20	75.85	194.15	1.32	3.2
0.80	73.21	173.69	1.48	3.6
0.65	17.78	58.20	4.14	4.3
0.40	18.34	50.69	5.04	4.9
0.25	18.34	52.23	4.9	4.8
0.05	17.92	43.21	5.94	5.8

C_{dl} and R_{ct} are the double-layer capacitance and charge-transfer resistance, respectively, Z_w is the Warburg impedance related to the diffusion of lithium ions into the bulk of the MCMB electrode. The exchange current density i_0 can be deduced from the equation: $i_0 = RT/nFR_{ct}$. The kinetic parameters of the MCMB electrode are summarized in Table 1. MCMB electrodes demonstrate relatively higher R_e and R_{ct} at potentials of 1.20 and 0.80 V. In the lower potential range, the R_e and R_{ct} values are almost invariable. Since the MCMB electrode has been cycled for five cycles prior to the ac impedance measurement, a stable surface layer should be established. The decrease of R_{ct} at low potential indicates that the charge-transfer resistances are not influenced by the Li^+ ion concentration in the MCMB host. This is favorable for battery operation.

4. Conclusions

The electrochemical properties of mesocarbon microbeads electrode (anodes) have been investigated. MCMB carbon is a well graphitized carbon. Cyclic voltammograms show a couple of redox peaks, which correspond to lithium insertion and extraction, respectively. The MCMB anode can deliver a reversible capacity of 325 mAh g^{-1}. The kinetics of Li^+ ion insertion in the MCMB host have been characterized by ac impedance measurements. In the lower potential range, the charge-transfer resistance of the MCMB electrode is independent of the state of lithiation.

Acknowledgements

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