

Surface-modified meso-carbon microbeads anode for dry polymer lithium-ion batteries

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Abstract

A high-anode performance for dry polymer lithium-ion batteries was obtained in the surface-modified meso-carbon microbeads (MCMB). MCMB and polyvinylchloride (PVC) mixture was heated at 700 °C for 6 h under inert atmosphere. By this treatment, the surface of MCMB is covered with low-crystalline carbon material derived from PVC pyrolysis. The surface-modified MCMB electrode applied to dry polymer electrolytes shows a reversible capacity of 300 mAh g⁻¹, which is comparable to those obtained in the liquid electrolyte systems.

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1. Introduction

Lithium polymer batteries have been considered as a promising technology, for it is able to satisfy the requirements of future applications such as stand-by power and electric vehicles (EV) [1]. The polymer batteries reported previously have used a lithium metal anode and an oxide cathode to attain a high-energy density [2,3]. Generally, formation of lithium dendrites during charging the lithium metal anode remains one of the major issues of battery with liquid electrolyte [4]. Even in the case of polymer electrolyte, this phenomenon exists, although it was shown to be less important than in liquid electrolyte. Dolle et al. reported the visual dendrite growth on lithium and copper sheet at 80 °C in lithium/polymer batteries with help of in situ scanning electron microscope [5,6].

A significant improvement in lithium/polymer electrolyte interface has been achieved by use of polymer electrolytes with an inorganic filler [7]. However, the polymer battery with large amount of metallic lithium is not a practical choice, if considering the abuse of large scale batteries for EV or hybrid electric vehicles (HEV). It seems necessary to explore alternative anodes other than lithium metal for polymer batteries. Yang et al. have proposed alloy anodes, which consist of Sn (or SnSb) and

Li_{2.6}Co_{0.4}N. This new concept anode for polymer electrolyte showed the initial reversible capacity as high as 800 mAh g⁻¹, but the capacity gradually decreased to 400 mAh g⁻¹ after 10 cycles [8]. More recently, Liu et al. reported the composite anode of Li_{2.6}Co_{0.4}N/Co₃O₄ for polymer batteries with less capacity fading by cycling. The initial capacity recorded 600 mAh g⁻¹, but the capacity fading was not suppressed adequately [9]. Effort for searching a higher reversible anode for polymer electrolyte is still necessary.

The chemical reactivity of anode and polymer electrolyte is another factor for choosing a safe anode material. Reaction tendency between the anode candidates and polymer electrolyte were examined by a differential scanning calorimetry. The reaction heat of the Li_{2.6}Co_{0.4}N/Co₃O₄ composite anode is 1.2 J(mAh)⁻¹, which is much lower compared to that of lithium metal anode of 5 J(mAh)⁻¹. Whereas, the reaction heat of the graphite anode and polymer was estimated as low as 0.9 J(mAh)⁻¹ by our preliminary experiment. Thus, the carbon anode is found most attractive with respect of the safety issue. However, only few papers have been reported on the polymer batteries with carbon materials anode. Tsumura et al. reported brief results for natural graphite and surface-modified graphite anode in polymer electrolyte [10]. It is commonly recognized that the interface resistances between the graphite and the polymer electrolyte are quite large and it is difficult to pass a large current. This is due to poor compatibility between the carbon and polymer electrolyte.

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In this study, the compatibility of carbon anode against polymer electrolyte has been improved by the surface modification of MCMB by low-crystalline carbon. This is achieved by pyrolysis of carbon precursors mixed with MCMB particles. Our earlier study on silicon/carbon composite anode reveals that PVC among several carbon precursors results in the good result [11]. Therefore, the electrochemical behaviors of the MCMB modified by pyrolysis of PVC have been examined in polyethylene oxide (PEO)-based electrolyte system.

2. Experimental

MCMB (Osaka Gas Chemicals Co. Ltd.) was used as the starting material. PVC (Aldrich) as a carbon precursor and counterpart of the composite has the average molecular weight of about 62,000. MCMB and PVC in 7:3 weight ratio were mixed with THF and then dried at 60 °C for 1 h. The dry powder was pressed into a tablet and heated at 700 °C for 6 h under argon gas flow to produce surface-modified MCMB. The product was examined by X-ray diffraction (XRD) using Cu K α radiation, Raman spectroscopy and scanning electron microscope (SEM) observation.

The composite electrode with polymer electrolyte was prepared as follows. Li(CF₃SO₂)₂N (Fluka) was dissolved into anhydrous acetonitrile (AN), then the surface-modified MCMB and acetylene black were added into the solution. Next, PEO (Aldrich: Mw = 6 × 10⁵) was dissolved and stirred for 3 h. The ratio of MCMB, acetylene black, Li(CF₃SO₂)₂N, and PEO

was 52:10:10:28 in wt% (MCMB: 20 mg). The Li/O ratio in PEO/Li(CF₃SO₂)₂N electrolyte was 1/18. The anode slurry was spread on a copper foil with a thickness of about 20 μ m, dried at 120 °C under vacuum for 3 h to remove AN completely, and finally pressurized to make a sure contact in the whole system. The graphite materials of TIMCAL SFG-44 and TIMCAL KS-6 were compared with MCMB.

The polymer electrolyte sheet as a separator was prepared following the previously reported method [12]. A given weight of PEO (Mw = 6 × 10⁵) and Li(CF₃SO₂)₂N (Li/O = 1/18) with 10 wt% of BaTiO₃ was added into AN. After strong stirring overnight, the viscous solution was cast in a Teflon dish. After AN was slowly and completely evaporated, the obtained film was further dried at 90 °C under vacuum for 8 h. The conductivity of the polymer electrolyte was as high as 5 × 10⁻⁴ S cm⁻¹ at 60 °C, which is comparable to the previously reported value [13].

The electrode performance was examined using a coin type cell (CR2025). Lithium metal was used as the counter electrode. Porous nickel foam was inserted between the back-side of MCMB electrode and the cathode can to increase internal pressure and make sure the contact of components. The active area of the electrode was 1.54 cm² and the thickness of PEO electrolyte was about 300 μ m. The cells were galvanostatically charged and discharged in the voltage range of 0.01–2.0 V. A current density of 0.05 mA cm⁻² (1/20C) was applied and temperature was kept at 60 °C. Cyclic voltamograms (CV) were measured by Solartron 1287 potentiostat.

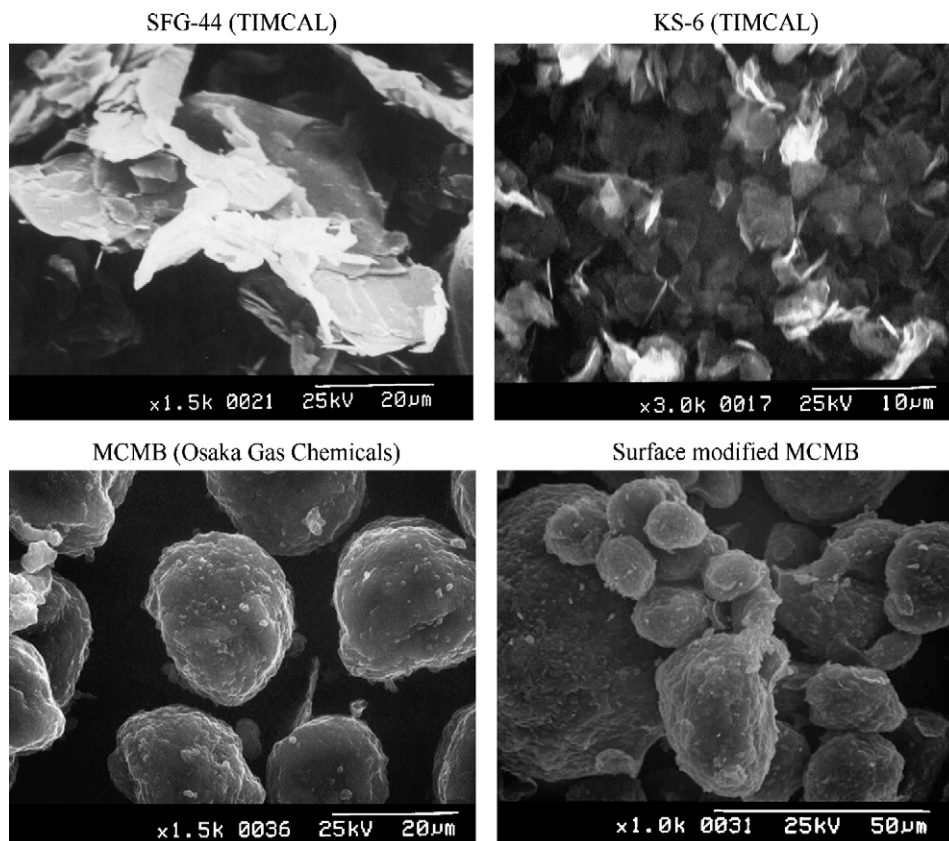


Fig. 1. SEM photos of artificial graphites SFG-44, KS-6, MCMB before and after the modification.

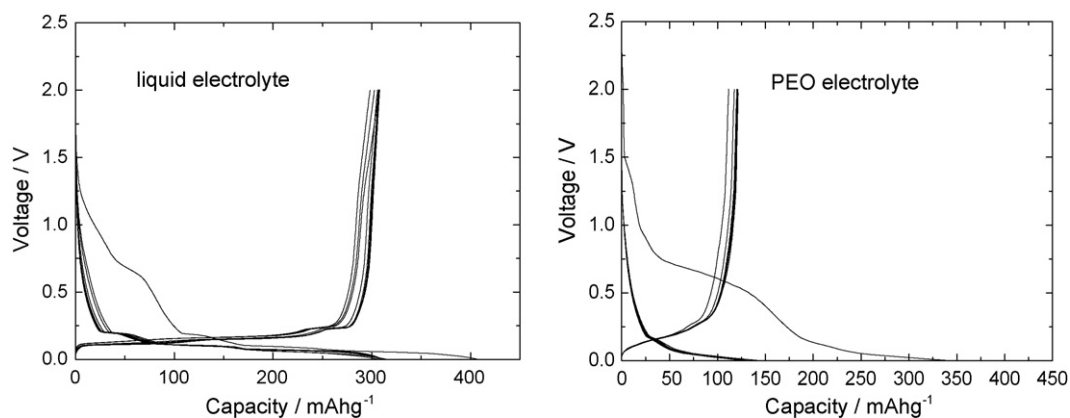


Fig. 2. Charge–discharge curves of artificial graphite SFG-44 in EC-DEC-LiClO₄ at room temperature and in PEO-Li(CF₃SO₂)₂N at 60 °C.

3. Results and discussion

Lithium intercalation performances of several types of synthetic graphite were compared in the cells with liquid electrolytes and polymer electrolytes. The plate type TIMCAL SFG-44 (average diameter; 15 μm), the flake-shape graphite TIMCAL KS-6 (average particle size; 5 μm) and the spherical MCMB (particle size; 20–30 μm) were examined. SEM images of these artificial graphites are shown in Fig. 1. Charge–discharge performances of these graphite anodes are

shown in Figs. 2–4, where 1 M LiClO₄ in ethylene carbonate and diethyl carbonate (50:50 vol.%) was used as the liquid electrolyte. The operation temperatures were fixed at room temperature for the liquid electrolyte cells and at 60 °C for the polymer electrolyte cells. These synthetic graphite materials show a high capacity of about 300 mAh g⁻¹ and a good cyclic performance in the liquid electrolyte cells. However, all the cells with polymer electrolytes exhibit small capacities as much as 100 mAh g⁻¹ and the first cycle efficiencies become less than 40%. The large irreversible capacity is due to the reaction of

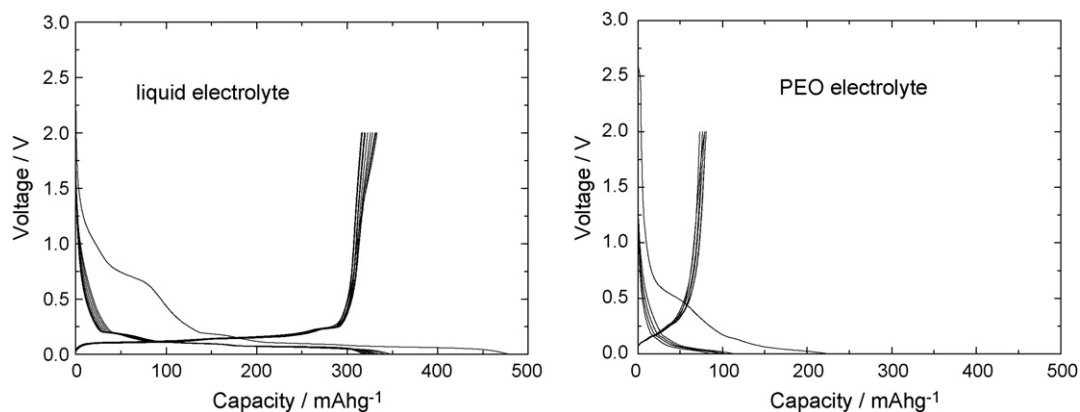


Fig. 3. Charge–discharge curves of artificial graphite KS-6 in EC-DEC-LiClO₄ at room temperature and PEO-Li(CF₃SO₂)₂N at 60 °C.

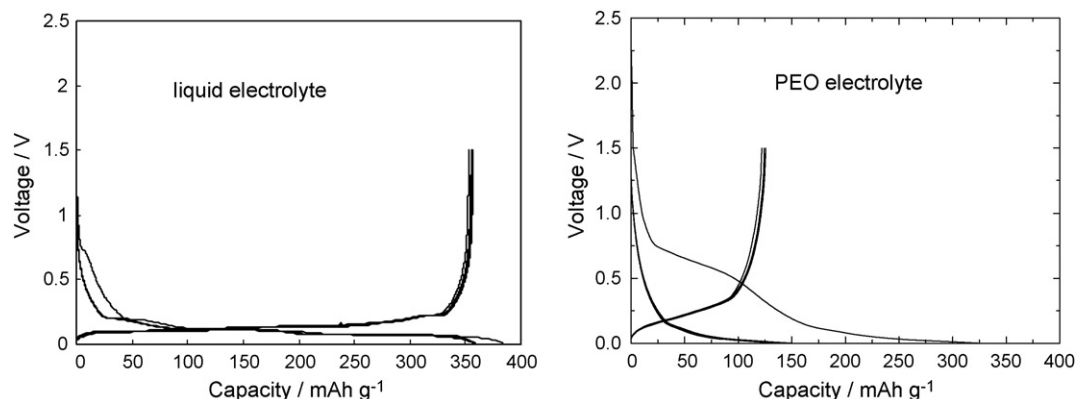


Fig. 4. Charge–discharge curves of artificial graphite MCMB in EC-DEC-LiClO₄ at room temperature and PEO-Li(CF₃SO₂)₂N at 60 °C.

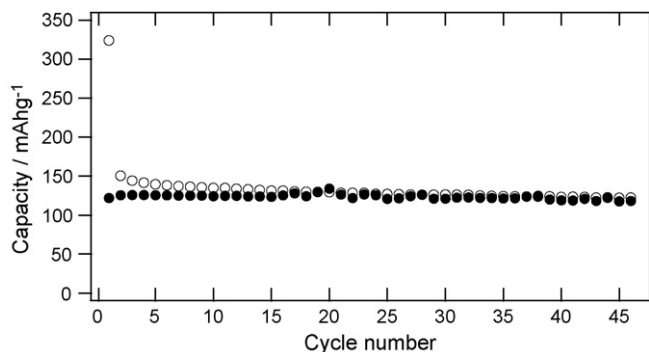


Fig. 5. Charge (○) and discharge (●) capacity change by cycling of MCMB thick electrode with polymer electrolyte at 60 °C.

the polymer electrolyte and the carbon electrode, which is also shown from the voltage profile in the first cycle.

The reaction between the graphite anode and the electrolyte is well known for liquid electrolyte. In 1970, Dey and Sullivan reported the electrochemical decomposition of propylene carbonate (PC) on graphite at potentials positive to lithium deposition (~ 0.8 V vs. Li/Li^+) [14]. Currently, electrolytes based on ethylene carbonate (EC) have been used for the graphite electrode. The exceptional compatibility of the solvent EC with graphite is related to the properties of the formed protective films (solid electrolyte interface, SEI) [15]. The compatibility of the graphite with the polymer electrolyte is also important to obtain high performance. The MCMB electrode showed an excellent cycling performance with the PEO-based polymer electrolyte as shown in Fig. 5. The high reversibility of the MCMB electrode shows that it has a protective layer on the surface to suppress further reaction as in the EC-based liquid electrolyte.

The reversible capacity of MCMB as much as ca. 120 mAh g^{-1} is much lower than that with liquid electrolyte. One possible reason for the low capacity is attributed to small active contact area between electrode and electrolyte and/or the lithium low-diffusion rate through the interface layer and the electrode. To reduce the lithium diffusion length, a thin film electrode was prepared and examined. The charge–discharge curves of such anode with the polymer electrolyte at 60 °C are shown in Fig. 6, where MCMB of 4.7 mg was loaded and the thickness of the electrode was around $50 \mu\text{m}$. This is equivalent to one

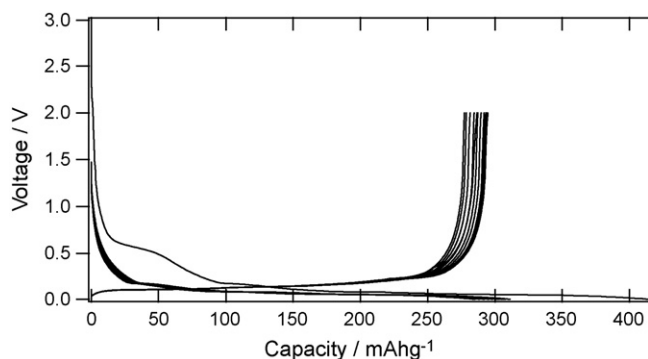


Fig. 6. Charge and discharge curves of non-modified MCMB thin electrode with a thickness of about $50 \mu\text{m}$ in a polymer electrolyte system at 60 °C.

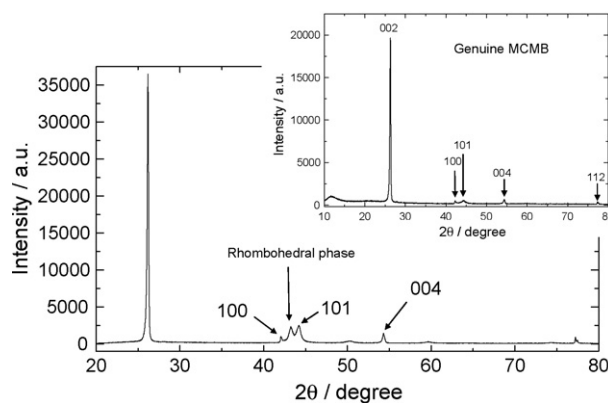


Fig. 7. X-ray diffraction patterns of modified MCMB by thermally decomposed PVC. The inset shows the pattern of non-modified MCMB.

or two layers of single MCMB particles. The reversible capacity is enhanced to 280 mAh g^{-1} , which is comparable to that in liquid electrolyte system. These results suggest that the lithium diffusion in the polymer electrolyte infiltrated in electrode plays an important role in the kinetics. The electrode structure mainly determines the utilization of the active material.

The thinner electrode containing non-modified MCMB shows improved capacity, while it shows capacity fading upon cycling due to large amount of lithium intercalation as 280 mAh g^{-1} . This is directly attributed to the nature of the interface between MCMB and PEO electrolyte. In order to optimize the surface structure of graphite, there is a report that amorphous carbon was coated on graphite to achieve improved performance in propylene carbonate-based liquid electrolytes [16]. The modified graphite anode reduced the charge-transfer resistance and the thickness of SEI film. In our study, the MCMB was modified by pyrolyzed carbon from PVC [17]. This method is quite simple that the mixture of MCMB and PVC was heated at 700 °C. Our preliminary result showed that PVC mainly decomposes near 300 °C and no chlorines remain in the products, which is supported by the literature [18].

The SEM image of non-modified MCMB showed a smooth surface, while the surface-modified MCMB by decomposed PVC as shown in Fig. 1 consists of small particles on the original MCMB spheres. PVC is known to be carbonized through the liquid phase during heat treatment in two steps from 200 to 350 and 350 to 550 °C with evolution of hydrocarbons [17]. It was considered that PVC-derived pitch carbon coated the MCMB particles at 700 °C.

The XRD pattern of the surface-modified MCMB is shown in Fig. 7. The modified MCMB shows an extra diffraction peak near $2\theta = 43^\circ$, but other features are kept unchanged after the modification. This shows that major part of MCMB is not affected by the modification. The newly appeared diffraction corresponds to the peak of rhomboidal phase of graphite. Such diffraction was also observed in the MCMB ground by a high-speed ball milling. PVC was pyrolyzed to form low-crystalline carbon layer on MCMB. At the same time, chlorine in PVC works as an etchant to clean the MCMB surface. This chemically corrosive nature of chlorine is considered quite strong and comparable

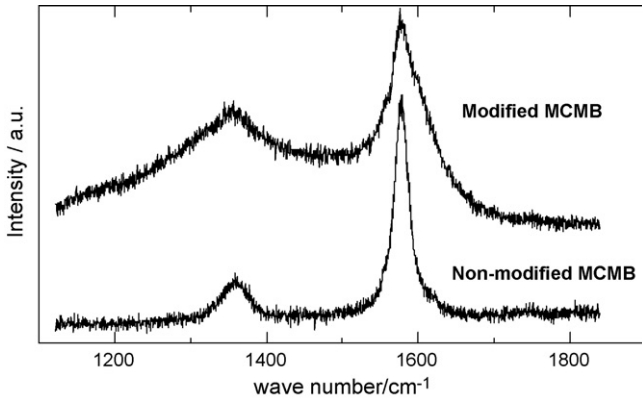


Fig. 8. Raman spectra of non-modified and modified MCMB which were obtained by argon-ion laser at the wave length of 488 nm.

to the ball milling power. This chemical effect is considered to cause the structural distortion of the surface and leads to transform of the hexagonal to the rhombohedral phase. Broad bands indicating the low-crystalline carbons are not present in the pattern. The main phase of the composite is MCMB and the ratio of surface low-crystalline carbon to the MCMB is negligible.

Fig. 8 compares the Raman spectra of the modified and non-modified MCMB. Both spectra show two peaks at 1580 and 1360 cm^{-1} which are called as G-band and D-band, respectively. The D-band corresponds to the conversion of a sp^2 to a sp^3 hybridized carbon [19]. Therefore, the relative increase in the intensity of D-band to G-band reflects a less resonance of graphitic structure and can be interpreted as the destruction of the two-dimensional structure. The R -value is defined as the intensity ratio of the peak intensity at 1360 and 1580 cm^{-1} ,

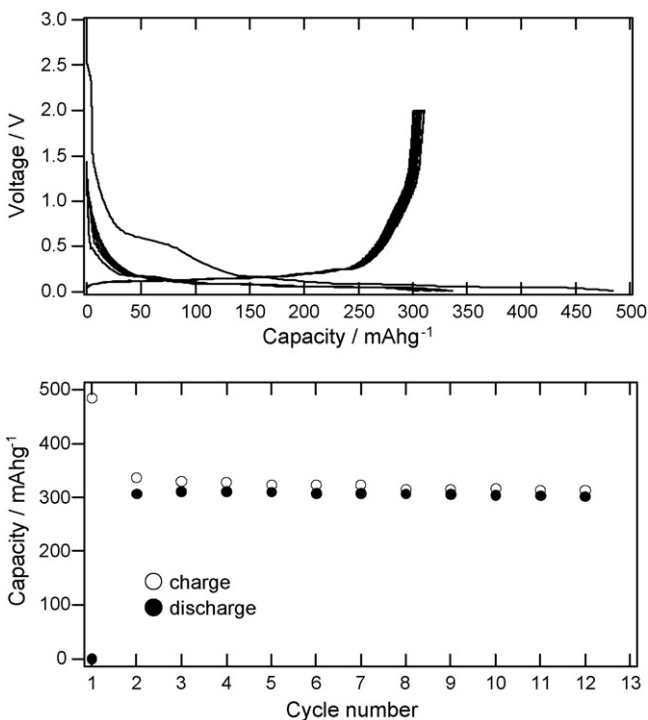


Fig. 9. Charge and discharge curves of modified MCMB by thermally decomposed PVC in polymer electrolyte system at 60 °C.

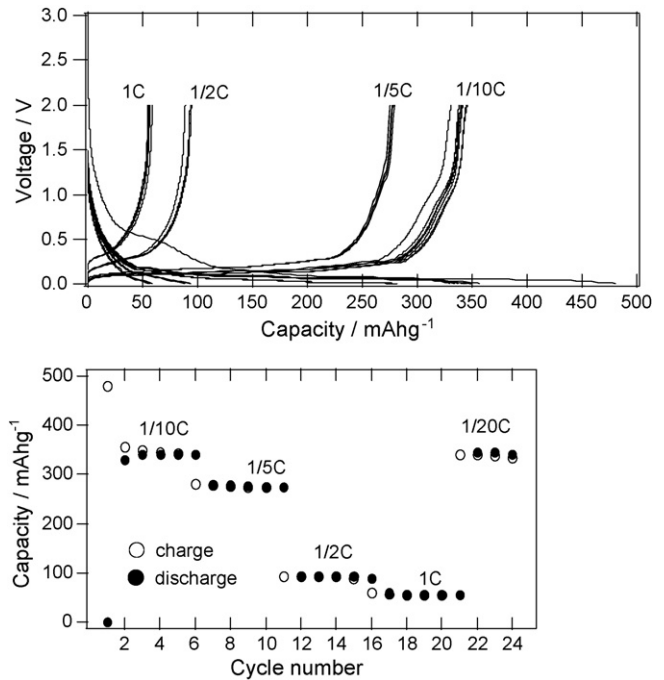


Fig. 10. Rate capability of the modified MCMB in polymer electrolyte system at 60 °C. The current densities in the form of C -rate are indicated in the figure.

which is known as an indicator of crystallinity in the near surface region [20]. The R -values are 0.24 for the as-received MCMB and 0.53 for the modified MCMB, respectively. These values are comparable with those reported previously and show that low-crystalline carbon exists on the surface of the modified MCMB.

Fig. 9 shows charge–discharge curves for the surface-modified MCMB with PEO electrolyte at 60 °C, where the applied currents were 1/20C and the thickness of the electrode was estimated about 50 μm . The first charge–discharge efficiency is 64% for the modified MCMB anode, while it is 69% for the non-modified MCMB anode. After the second cycle, the efficiency was become more than 95% and the capacity fading was

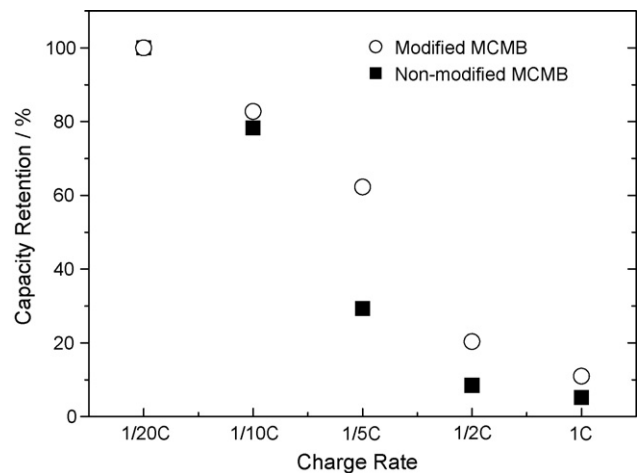


Fig. 11. The comparison of the rate capability of non-modified and modified MCMB. The capacity retention values against C -rate are calculated, on the basis that the capacity at 1/20C is 100%.

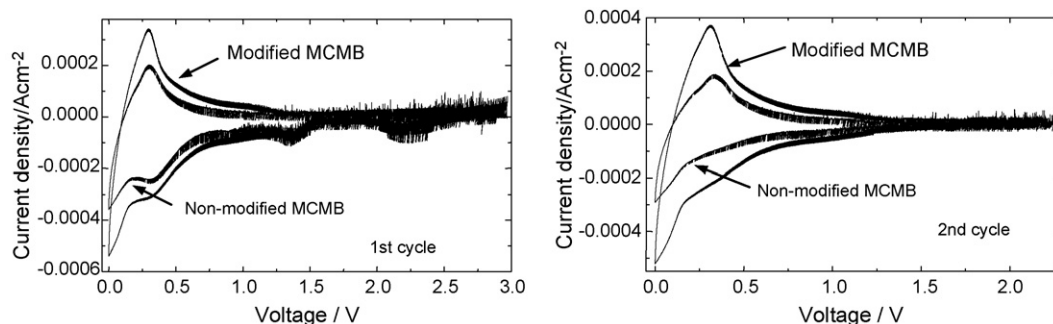


Fig. 12. Cyclic voltammograms of non-modified and modified MCMB in polymer electrolyte system. The scanning rate is 0.3 mV s^{-1} . The left and right figures show the first and second cycle, respectively.

hardly observed. The improvement of the efficiency was considered to be a decrease of the active edge sites at the surface of MCMB. The reversible capacity of about 300 mAh g^{-1} is close to that obtained in the liquid electrolyte system. The improvement of the compatibility of the interface is found quite effective for the high performance of MCMB with polymer electrolyte.

The rate capability of the modified MCMB anode with the polymer electrolyte was examined at 60°C . The typical results are shown in Fig. 10, where the loaded active material was 2.7 mg and several charge currents as $1/10C$, $1/5C$, $1/2C$ and $1C$ were applied in turn. At a high-current density such as $1/2C$ (about 0.25 mA cm^{-2}), a discharge capacity of 100 mAh g^{-1} is obtained. The charge–discharge coulombic efficiency is almost 100% even under high rate as $1C$. The comparison of rate performances before and after the modification of MCMB is summarized in Fig. 11. The difference becomes remarkable at $1/5C$ rate and higher. The surface modification is also effective for improvement of the rate performance of MCMB anode.

Fig. 12 shows the cyclic voltammogram (CV) of the non-modified MCMB and the modified MCMB in the first and second cycles at 60°C , where the scanning rate was set at 0.3 mV s^{-1} . The first lithium insertion into the non-modified and the modified MCMB show four peaks in the curve. The two peaks at 2.4 and 1.4 V correspond to the reaction between the polymer electrolyte and the MCMB, because the peaks disappear in the following lithium extraction process and in the second cycles. These reactions at higher voltages were not observed for the surface-modified MCMB heated with PVC at 800°C in the liquid electrolyte [21]. The irreversible reaction mechanism against polymer electrolyte is not discussed further, but it should be related to the formation of SEI layer by decomposition of PEO. Both non-modified and modified MCMB show a shoulder on the curve near 0.4 V and sharp peak near 0.0 V during lithium insertion in the first cycle, while in the second cycle, the peak at 0.4 V almost disappears and remains as a broad band in the non-modified MCMB. The peak near 0.4 V corresponds to a small plateau in the potential profile at ca. 0.5 V as shown in Fig. 9.

The high-speed ball milling of MCMB in dodecan solvent, shows a similar CV profile of the modified MCMB. The ball milled MCMB also showed the distorted surface structure confirmed by Raman and X-ray studies. The low-crystalline carbon shows a similar electrode potential profile in lithium insertion and extraction. Therefore, the peak near 0.4 V may correspond

to lithium intercalation of the distorted carbon on the MCMB surface. These characterizations of the surface-modified MCMB suggest that the surface is covered by pyrolyzed disordered carbon and this surface layer makes more compatible interface with PEO for the lithium insertion and extraction. This is considered due to the physical enlargement of the electrode surface area, which leads to the larger electrode/electrolyte interface to bear a large current. Or, surface of MCMB particle covered by the disordered carbon might have improved chemical affinity to the polar PEO polymer.

4. Conclusion

Several types of synthetic graphite were examined as the anode in the polymer electrolyte cell. The cast thin MCMB anode showed a high-reversible capacity of 260 mAh g^{-1} . The reversibility of MCMB was improved by coating the MCMB surface with thermally decomposed carbon of PVC. The first charge and discharge coulombic efficiency was 64% and the reversible capacity was about 300 mAh g^{-1} , which are comparable to those of the MCMB anode with liquid electrolyte. These performances can solve the problems when lithium-ion polymer batteries are considered for the practical applications. Further effort to reduce the operation temperature of the MCMB which corresponds to the better interface between MCMB and the electrolyte, will accelerate the development of the dry lithium polymer battery.

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