ELECTROCHEMICAL CHARACTERISTICS OF CARBON-SILICON COMPOSITE ELECTRODES FOR THE ANODE OF LITHIUM SECONDARY BATTERY

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Introduction

Graphite has been commonly employed as an anode material for lithium ion batteries because of its low and flat working voltage and better cycle performance compared with the metal oxides. During charge process, a lithium ion reacts with the six atoms of carbon. Thus, theoretical maximum storage capacity of graphite can be calculated as 372 mAh/g [1].

In order to increase the specific capacity of the lithium secondary batteries, silicon is considered as one of the promising alternative anode materials. According to the electrochemical reactions between silicon and lithium, silicon can alloy with lithium up to 4.4 Lithium per silicon at high temperature. Theoretical capacity of silicon, therefore, is about 4,000 mAh/g. However, silicon is difficult to applied due to the problems as follows: the first one is poor cyclability caused by severe volume expansion and the second one is the high irreversible capacity at first cycle [2].

Here, the purpose of this study is accomplishment of high capacity of anode material with good cycle performance through silicon coating on the graphite surface. In the present study, preparation of highly dispersed silicon on the graphite anode is tried. In the carbon-silicon composite system, we expect that silicon acts lithium alloying reactants during charge-discharge process and also carbon matrix play a role as the lithium intercalation sites and conducting medium between silicon particles as well.

Experimental

Commercial synthetic graphite was used as the raw material with an average particle diameter of c.a. 10 micro-meter (MCMB1028, Osaka gas). In this study, the employed coating technique for the preparation of silicon-graphite composite is a gas-suspension spray coating method. All the graphite particles consists bed are all just suspended in upwarding flow gas. For spray coating, the atomized liquid droplet from the spray nozzle which was placed at the bottom of the bed contact the suspending graphite particles and spread over on the surface of the particles. The wetted particles are extensively dried through solvent evaporation. The repeated motion of the particles through the spray zone allows a continuous coating of material to build up and, finally uniform

coating particle can be prepared. The precursor containing silicon was employed as a coating solute and ethanol mixture used for the solvent. After particles were coated, they were calcined in a furnace in the range of 400~800℃ under an inert atmosphere.

Electrode for half-cells of lithium ion batteries were manufactured with the samples prepared under different conditions and their electrochemical properties were compared. Negative electrodes were fabricated by mixing a slurry containing 6 wt.% polyvinylidiene fluoride (PVDF) binder, 3 wt.% acetylene black as the conductor, and 91 wt.% active materials. The metals-coated carbon electrode does not contain acetylene black. The graphite, in the presence of some acetone was mixed in a vortex mixer at 5000 rpm. A slurry containing carbonaceous material was spread to form a 100 ㎛ thick sheet on a copper foil by dipping. The sheet was allowed to dry at ambient temperature for a day, followed by drying in an oven at 80℃. The composite was then pressed at 110~120℃ in a roll press. The pressed composite was cut into 2×2 cm pieces and dried in a vacuum at 110℃ for 24 hours. All cells were assembled in a dry-room (max. moisture 〈 5%). The counter electrodes were lithium metal foils of 75 ㎛ thickness, while the separator was a polypropylene film. The electrolyte employed in this study was 1M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC), propylene carbonate (PC) and dimethyl carbonate (DMC).

Silicon coated graphites, prepared by gas suspension coating, were characterized in terms of i) inductively coupled plasma (ICP ; Ash Thermo Jarrel POLYSCAN 61E) ii) X-ray diffractommetry (XRD using a RIGAKU RINT/DMAS-2500) with a CuK α source, iii) scanning electron micrography (SEM employing a Hitachi S-4200), iv) BET surface area measurement (ASAP : Micromeritics ASAP-2010).

Typical charge-discharge cycling tests for the silicon-coated graphites were carried out using a galvanostatic cycling at various charge-discharge rates between 0 and 1.2V vs. Li/Li^+ and cyclic voltammetry tests were carried out between 0 and 2V at the scan rate of 0.1mV (Won A Tech WBC3000). The AC impedance measurements for the metal-coated graphites were carried out under an open-circuit condition in a frequency range from 0.1 to 106 Hz. The perturbation amplitude was ±5mV. The employed experimental set-up consists of a frequency response analyzer and a potentiostat / galvanostat (ZAHNER IM6).

Results and Discussion

The specific charge capacities and discharge capacities of bare synthetic graphite and silicon-coated graphites are shown in Figure 1. The reversible capacity of bare MCMB showed about 280 mAh/g, but the reversible capacity of the silicon-coated graphite increased with increase of coating amount and then reached up to 450 mAh/g for 10 weight % silicon coated graphite. The enhancement of specific capacity attributed to the alloying formation between silicon and lithium during cycles.

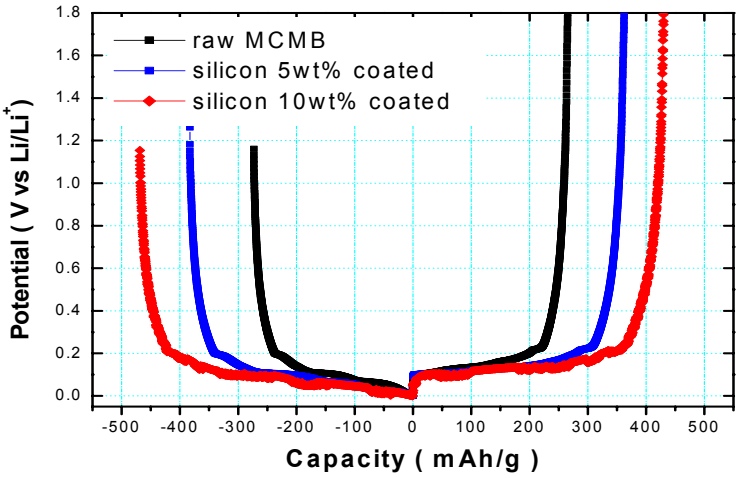

Figure 1. Charge-discharge curves for bare and silicon coated graphite. Bare and Si coated MCMB at 10th cycle with 0.2 mA/cm2 current density.

The cycle performance of half cells for the electrodes containing bare and 10 wt% silicon coated MCMB is given in Figure 2. Used Electrolyte was 1M $LiPF_6$ in EC-EMC-DMC(1:1:1 in v/v). For the 10wt% silicon coated graphite, the discharge capacity of 450mAh/g maintained by 20 cycles and then greadually decreased until 55 cycles and then rapidly decreased with cycles probably due to the dentrite formation. The cycle performance pattern for bare MCMB showed almost the same with the silicon coated graphite. This result suggests that the silocon coated graphite prepared by gas suspension spray method has higher capacity and good cycle performance as well.

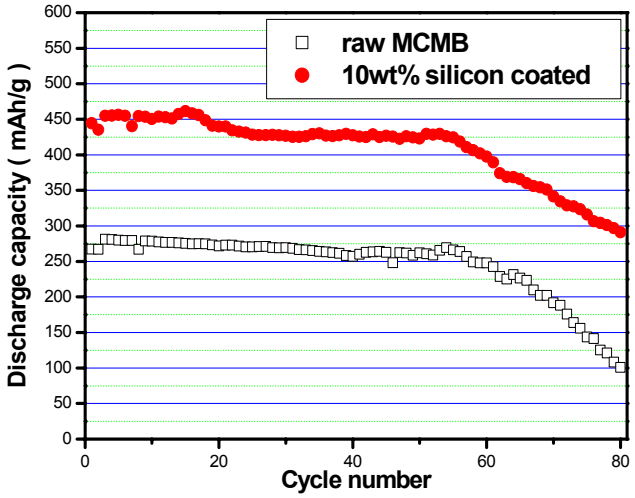

Figure 2. Cycle performance of half cells with the anodes containing bare and 10 wt% silicon coated MCMB at C/5 rate. Electrolyte of 1M $LiPF_6$ in EC-EMC-DMC(1:1:1 in v/v).

The CV(Cyclic Voltammogram**)** diagram for the cells from bare MCMB, 5wt% and 10wt% silicon-coated MCMB presented in Figure 3. The evidence of the SEI(solid electrolyte interface) film formation could be found in the figure. For bare MCMB, very small peak was observed at the potential range of 0.15-0.18 V vs Li/Li+ both in first cycle. However, in case of the silicon-coated graphite, SEI peaks due to the interfacial reaction between the silicon and the electrolyte are clearly exist at the same potential range. Much stronger peak was observed with increase of silicon coating amount. As to silicon-coated graphite, Li ions deintercalation peak get higher with increase of silicon coating amount. These results can be explained that discharge rate and capacity increased with the silicon coating amount.

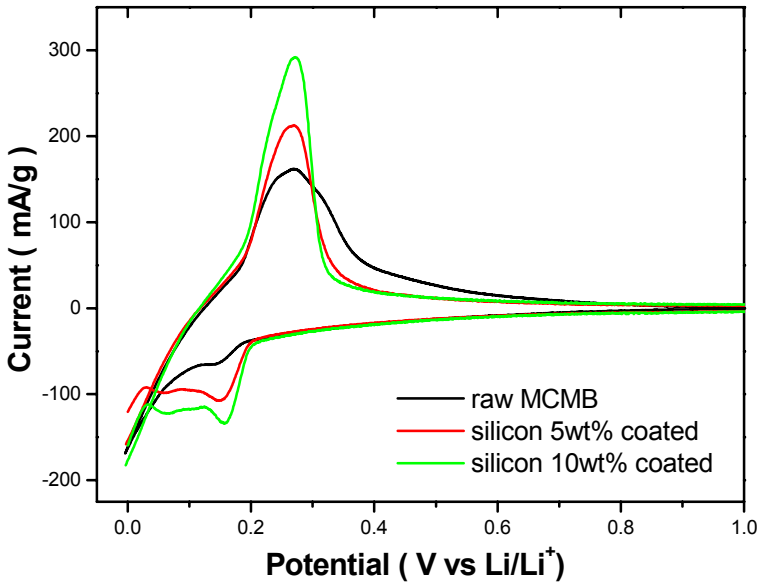

Figure 3. Cyclic voltammograms of the Si coated graphite. Potential range from 0.0 to 1.2V with scan rate of 0.1mV/s. Lithium metal served both as counter and reference electrodes in 1M $LiPF_6$/EC-EMC-DMC(1:1:1 in v/v).

Figure 4 shows Coulombic efficiency and Irreversible capacity of silicon coated graphite for four different kinds of electrolytes. The values of electrochemical performance are dependent on the species and composition of the solvents in the electrolyte. In case of EC:EMC:DMC 1:1:1 showed the highest charge capacity and irreversible capacity. By contrast, EC: DEC 1:2 showed the lowest charge and irreversible capacity. Those result probably related to the wetbility or SEI film characteristics, which may possibly lead the difference in electrochemical performance such as specific capacity and irreversible capacities.

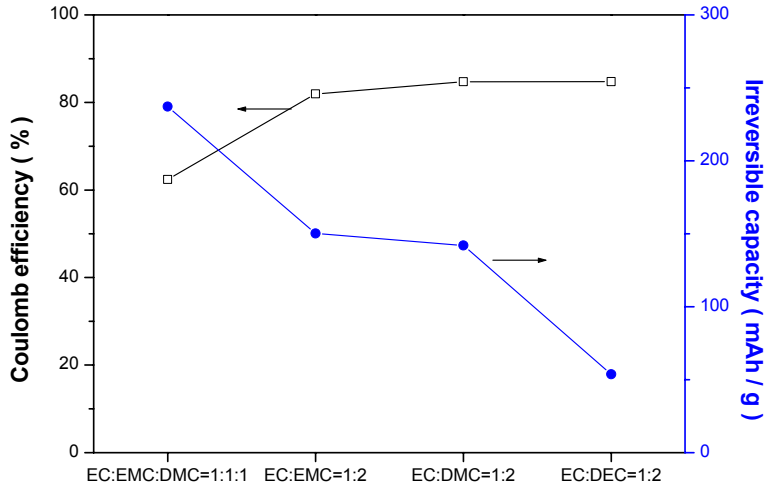

Figure 4. Coulomb efficiencies and irreversible capacities of silicon-coated grahites under various electrolytes**.**

Conclusions

Nano-sized silicon coated -graphite particles were prepared by a gas suspension spray method and they showed the high specific capacity and good cycle performance. It is found that the improvement of electrochemical performance is due to the formation of nano-sized amorphous silicon layer on the surface of graphite particles. The silicon-coated graphites have high irreversible capacity due to the SEI formation at 1st cycle. However, the capacity loss could be lessened to a certain level by controlling the characteristics of electrolyte. Further study should be needed to find the relationship between the electrochemical performance and electrolyte properties.

References

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[2] Bourderau S, Brousse T, Schleich DM. Amorphous silicon as a possible anode material for Li-ion batteries. Journal of Power Sources 1999;81/82:233-236.

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