Surface modification of carbonaceous material by fluidized-bed spray coating method

Wonchang Choi[a], Joong Kee Lee*, Dongjin Byun[a], Byung Won Cho and Dalkeun Park

Eco-Nano Research Center, KIST, Seoul 130-650 KOREA

[a]Dept. of Materials Science & Engineering, Korea University, Seoul 136-701 KOREA

Low rate capability of carbonaceous anode for lithium secondary batteries is attributed to relatively low insertion of lithium ion to carbon material, which depends on largely surface characteristics of the carbon [1-2]. To improve the charge-discharge reaction rate of anode, graphite particles were coated with metals by fluidized-bed spray coating method, and their electrochemical characteristics were investigated.

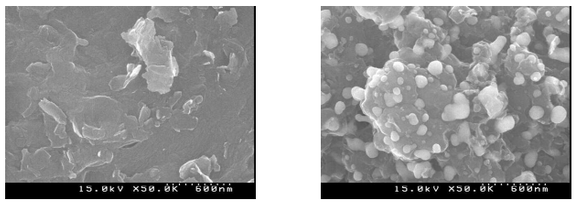
Commercial synthetic graphite with average particle diameter of about 10 μm (MCMB 1028, Osaka gas) was used as raw material. Ethanol-based metal nitrate solutions silicon solutions were sprayed to the graphite particles to coat the surface with metal or silicon, and coated particles were calcined in the furnace in the range of 500 $^{\circ}$C under H_2 atmosphere after coating process.

Coating amount was controlled by processing time and concentration of metal solutions. Metals-coated graphite, prepared by FBSC method, was characterized by ICP, XRD, SEM, BET. The electrodes for half-cells of lithium ion batteries were manufactured and their electrochemical properties were compared. The graphite electrodes containing 6wt.% polyvinylidiene fluoride (PVDF) binder and 91 wt.% active materials were prepared by dipping method. Typical charge-discharge cycling tests for the metal-coated synthetic graphite were carried out using galvanostatic cycling at various C rates between 0 and 1.2Vvs. Li/Li^+ and cyclic voltametry tests were carried out between 0 and 2V with the scan rate of 0.1mV. The AC impedance measurements for the metal-coated graphite were carried out in a frequency range from 0.1 to 10^6 Hz.

Fig. 1 present the dispersion of particles prepared by fluidized-bed spray coating method for silver. The particles of silver are about 100nm in diameter and have a spherical shape.

Fig. 2 shows a family of Nyquist plots measured from during the course of Li intercalation. Each samples were measured at the point of the oxidation peak of potential range. The diameters of slightly depressed semicircles represent the charge transfer resistance from electrochemical reactions. It was observed that the diameters of semicircle for all the surface-modified graphite electrodes were smaller than that of the raw synthetic graphite electrode. It was confirmed that coating of metal provided the surface of carbon electrode with increased conductivity during lithium intercalation.

Fig. 3 shows the change in discharge capacities with different C-rates. The results showed that the silver-coated MCMB exhibited the highest rate capability. It can be construed that the artificial SEI films which were formed on the metal coated film at the first cycle play an important role to enhance the rate capability. [3].



(a) (b)

Fig. 1. Scanning electron micrography of surface-modified graphite : (a) raw graphite ; (b) silver-coated graphite.

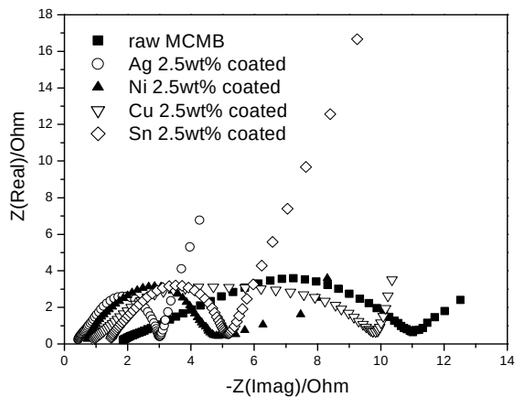


Fig. 2. Nyquist plots of surface-modifies graphite at 1st cycle at oxidation peak

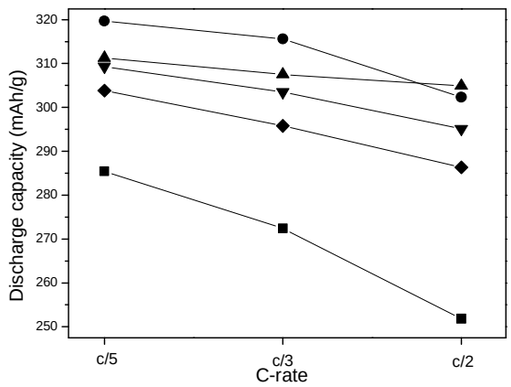


Fig. 3. C-rate effect of surface-modified MCMB1028. MCMB (■), Ag2.5 (●), Ni2.5 (▲), Cu2.5 (▼), Sn2.5 (◆).

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