

THE ELECTROCHEMICAL CHARACTERISTICS OF SURFACE-MODIFIED CARBONACEOUS MATERIALS BY GAS SUSPENSION COATING WITH TIN OXIDES AND COPPER

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Introduction

In the carbon-metallic system, we expect that the carbon matrix acts as a lithium intercalation site, and also that metallic compounds on the carbon surface have a role as an artificial passivating film or an electronic conducting agent in the electrode. We employed the fluidized-bed chemical vapor deposition(CVD) technique to coat various metals on carbon surface, which will be used as alternative anode materials for lithium secondary battery.

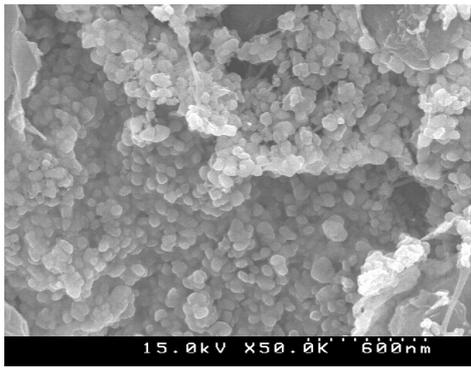
Experimental

Tin oxide and copper were coated on the synthetic graphite, MCMB by fluidized-bed CVD, and three different kinds of samples were prepared. Cu(hfac)₂ and (CH₃)₄Sn were employed as organometallic precursors, respectively. The surfaces of the samples prepared have different compositions as follows: S0 of raw MCMB; S1 of 1.37wt.% of tin oxide; S2 of 0.93wt.% of tin oxide; S3 of 1.83wt.% of tin oxide and 0.14wt.% of copper. The electrodes for half-cells of lithium ion batteries were manufactured with these samples prepared and their electrochemical properties were compared. All cells were assembled in a dry-room (max. moisture < 5%). The counter electrodes were lithium metal foil of 75 μm thickness and the separator was the polypropylene-based film. The used electrolyte was 1 mole lithium hexafluorophosphate(LiPF₆) in ethylene carbonate/ethyl methyl carbonate/

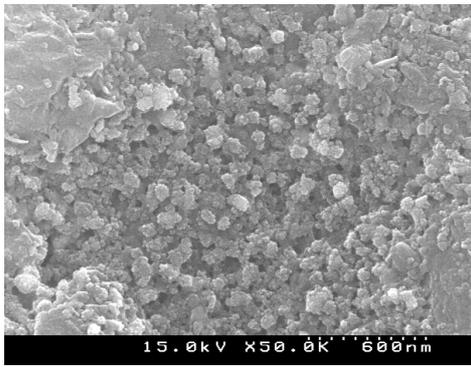
dimethylene (EC: EMC: DMC, 1:1:1, Merck).

Results and Discussion

As shown in Figure 1, scanning electron micrography was employed to explain the difference in surface morphology between the tin oxide coated electrode before the charge-discharge experiment and the one after 30 cycles. The pores in Figure 1 (b) represent that the oxygen atoms in tin oxide react with lithium and form tin during cycles. Fig. 2 shows the comparison of XRD spectra of tin oxide-coated graphite before the charge-discharge experiment and the one after 30 cycles. As shown in the figure, the tin oxide peaks disappeared after the cycles, while the reduced tin peaks appeared. The tin oxide coated MCMB, S1 and S2 gave the higher discharge capacities than that of the raw material at initial cycles, but it swiftly decreases after 10 cycles(Figure 3). However, the copper-tin coated sample, S3, maintained higher cycling performance than that of raw MCMB possibly due to the buffering effect of copper from severe volume changes of tin oxide. Figure 4 compared the AC impedance and electrochemical voltage spectroscopy curves between S0 and S3. The higher peaks of spectra of S3 represent higher reduction reaction and lower impedance leads to the higher discharge capacity as shown in Figure 3.



(a)



(b)

Figure 1. Scanning electron micrography of tin oxide coated carbon (a) before charge-discharge experiment and (b) the one after 30 cycles.

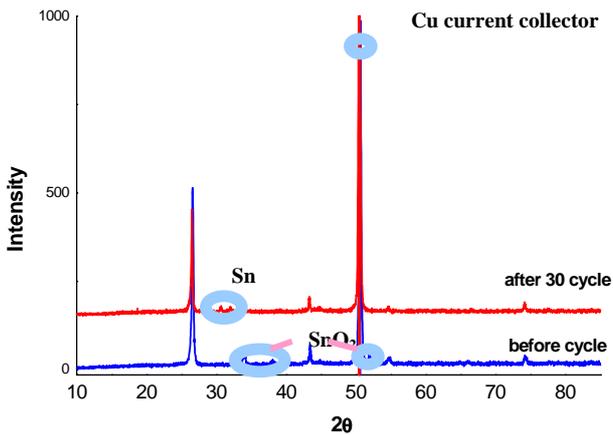


Figure 2. X-ray diffraction diagrams of tin oxide coated electrodes before and after the cycling of charge-discharge test.

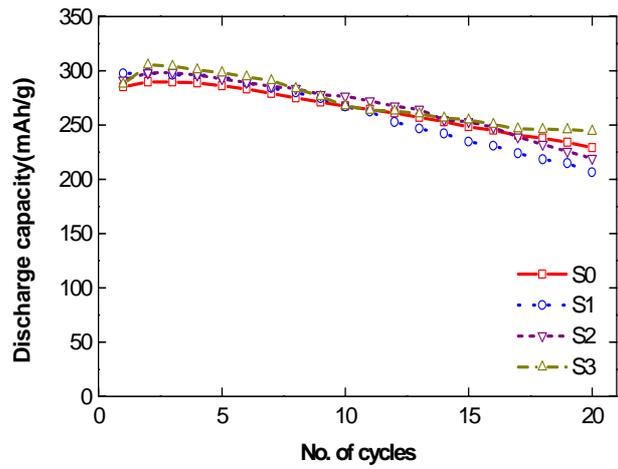
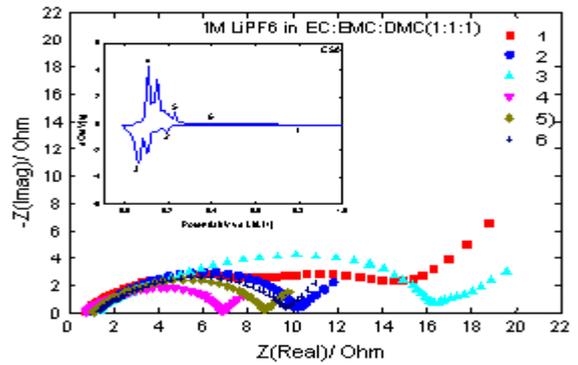
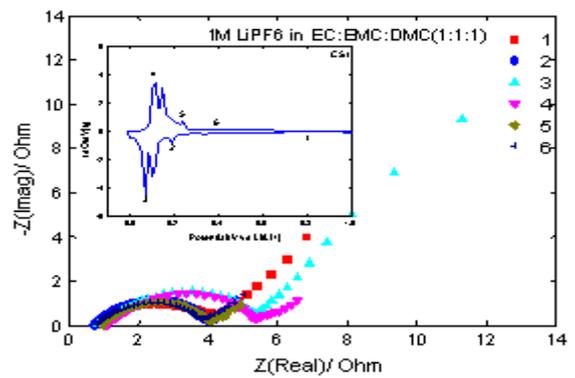


Figure 3. Comparison of cycling performance of the samples which be coated tin oxide and copper by fluidized-bed CVD and the raw MCMC electrode (1M LiPF₆ in EC:EMC:DMC, 1:1:1) .



(a)



(b)

Figure 4. Nyquist of S0, (a) and S3, (b) at 2nd cycle.