

CARBON/METAL COMPOSITE ANODES FOR LITHIUM SECONDARY BATTERIES

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Introduction

Carbon/metal composite anodes having larger specific energy density than graphite were prepared and tested for lithium secondary batteries. Especially tin has been reputed to show very large volumetric energy density but the poor cycle performance. The latter disadvantage prevented it from its commercial application. In this study, we tried to make new carbon-metal composite anode materials having better cycle performance than its mother metal itself, maintaining larger specific capacity than graphite.

Experimental

The carbon-metal composite materials were prepared through heat treatment of graphite(MCMB6-28) and/or naphthalene isotropic pitch with metal precursors such as SnO, tetraphenyltin and SiO. The details of preparation conditions were described in Table 1. In order to confirm the final products, x-ray diffraction was performed. ESCA measurements were carried out to analyze the surface compounds of powders. The composite electrode was prepared by mixing the active material with PVDF binder in the ratio of 10 wt%. The mixed slurry was coated on copper foil followed by vacuum drying on 120°C for 6 hours. The composite electrode was used as an working electrode and Li metal sheet was used as the counter electrode.

Results and Discussion

MCMB6-28 and SnO – As shown in Fig. 1, the profiles and capacity of lithium deinsertion of A, B, C (denoted in Table 1) are very similar with simply mixed one, and it show favorable capacity and profiles. On the other hand, the profiles of lithium insertion exhibit some difference. The samples B and C showed only graphite and tin metal peaks in diffraction patterns while sample A, there was some other diffraction peaks which are ascribed to a deformed phase of SnO. And as shown in differential capacity plots(Fig. 3), sample B and C show the peaks due to graphite and tin while simply mixed sample did the decomposition reaction of SnO to Sn metal and lithium-oxygen compound ascribed to an irreversible reaction occurred at near 1.0 V vs. Li/Li⁺[1].

However in sample A, the peak regarded as a decomposition reaction is shown in 0.8 V and it means the different bonding energy between Sn and oxygen with SnO. In XPS analysis (Fig. 4), the different kinds of surface bonding energy of Sn 3d_{5/2} was confirmed between sample A and SnO (486.8eV). The step-by-step etching with argon exposed tin metal bonding peak (484.9 eV) in both samples. In spite of the changes in bonding states of tin after heat treatment, small loss of tin metal was confirmed during heat treatment.

Naphthalene isotropic pitch(NIP) and tetraphenyltin(TPT) – The composite material prepared from NIP and TPT heat-treated at 1000°C showed the reasonable reversible capacity and cyclability(Fig 5). The smaller particle size of metal is believed to the better cycle performance. So far encapsulation of metal by carbon is believed to enhance cyclability of carbon-metal composite material.

MCMB6-28 and SiO – Silicon showed quite different behavior with those of tin. Silicon reacts with carbon to form carbide phase that is inactive with lithium ion and it means the loss of active material. As shown in Fig.6, the reversible capacity of composite material decreased as the increase of the heat treatment temperature. So, the control of particle size and heat treatment is important factors for carbon/silicon composites.

Conclusions

The larger capacity than graphite was obtained in composites of carbon with tin or silicon and in the aspect of energy density, the enhancement become greater. And although tin was heat treated over its melting point, it was confirmed that very small loss of tin occurred as well as tin did not segregate during heat treatment. But the improvement of cycle performance is still necessary for commercial use.

References

- [1] I. A. Courtney, J. R. Dahn, J. Electrochem. Soc. 144(1997)2045

Table 1. Processing conditions of composite materials

Sample	Precursors	Mixing ratio in wt	Heat treatment temperature	Heating rate and holding time	Reversible capacity in first cycle ^a
A	MCMB6-28, SnO	1 : 1	800 °C	10°C/min, 1hour	428 mAh/g
B	MCMB6-28, SnO	1 : 1	900 °C	10°C/min, 1hour	429
C	MCMB6-28, SnO	1 : 1	1000 °C	10°C/min, 1hour	420
D	MCMB6-28, SnO	1 : 1	1000 °C	10°C/min, 10hour	395
E	MCMB6-28, SnO	4 : 1	1000 °C	10°C/min, 1hour	328

^a: the reversible capacity of simply mixed – 440 mAh/g

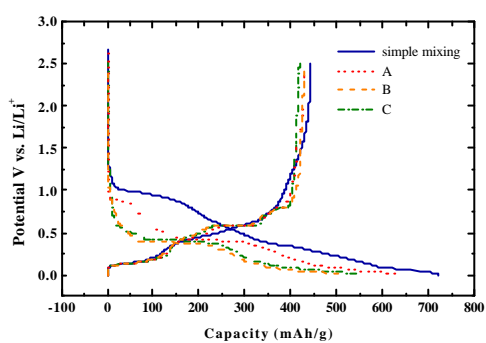


Figure 1. The first cycle charge/discharge profiles of composite anodes. (test rate : 50 mA/g, electrolyte : 1M LiPF₆ in EC:DEC (1:1 in vol))

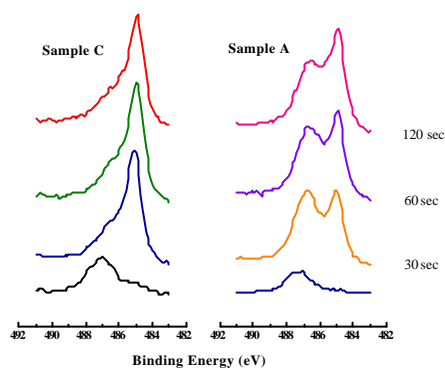


Figure 4. XPS analysis of 3d_{5/2} of Sn

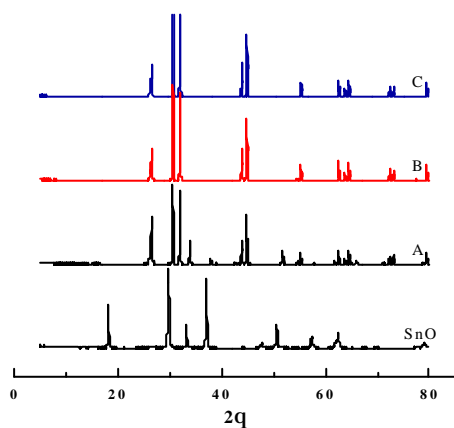


Figure 2. XRD diffraction patterns

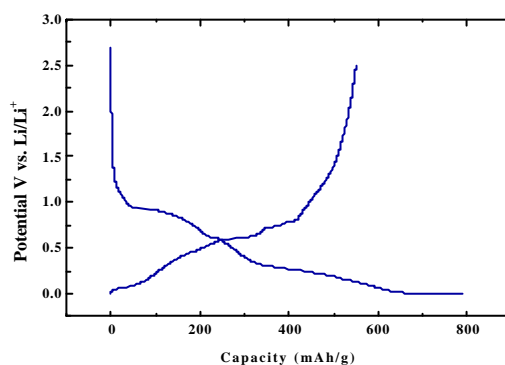


Figure 5. The first charge/discharge profile of composite anode prepared from NIP and TPT (PTFE used as binder in this sample)

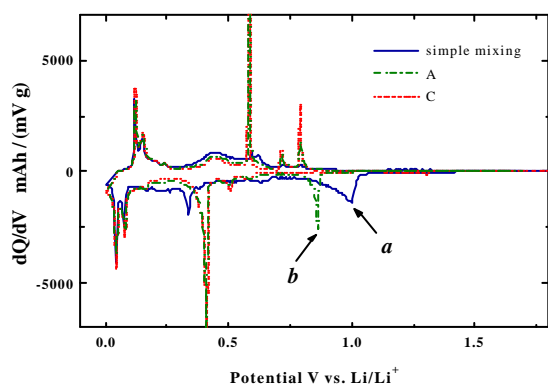


Figure 3. Differential capacity plot of composite electrodes.

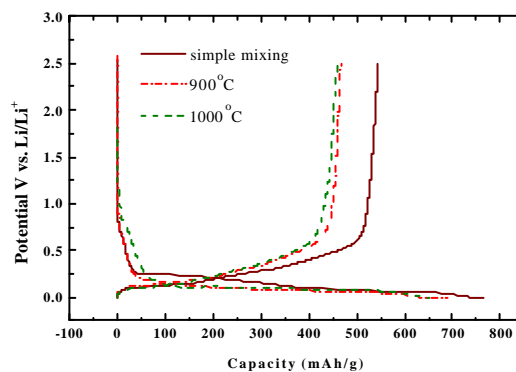


Figure 6. The first charge/discharge profiles of composite electrode prepared with MCMB6-28 and SiO