doi:10.1246/cl.2010.610

Surface Thiolation of MCMB to Support Sn Nanoparticles for Anode Materials of Lithium Ion Batteries

Yong-Tae Kim
School of Mechanical Engineering, Pusan National University, Busan 609-735, Korea

(Received January 6, 2010; CL-100017; E-mail: yongtae@pusan.ac.kr)

In this study, we suggest a unique approach with which it is possible to enhance the capacity and cycle performance of composite anode materials for lithium ion batteries. We introduced surface thiol groups onto mesocarbon microbeads (MCMB), and these functional groups efficiently obstructed the agglomeration between Sn nanoparticles in the composite formation. This resulted in the high dispersion of Sn nanoparticles with very small size. Half-cell tests showed that highly dispersed Sn nanoparticles enabled us to enhance the capacity by improvement of mechanical stress tolerance in the charge/discharge process.

Sn or Sn oxide materials have been intensively investigated for lithium ion battery anodes, because they could overcome the relatively small capacity of graphite.[1] The poor cycle performance resulting from large volume changes during charge/discharge is, however, the main drawback for commercialization.[2] To solve this problem, many efforts have been made to prepare very small Sn metal or oxide nanoparticles and homogeneous composite with carbon materials.[3–8] In many cases, it was quite difficult to form small well-dispersed nanoparticles of active materials on carbon. This is because the weak electronic interaction between Sn and carbon leads to a serious agglomeration of Sn particles, and the composite materials are thereby vulnerable to volume change. Such poor dispersion is an important reason that enhanced cycle performance has not been obtained in spite of significant increases in capacity. In this study, we introduced a unique approach, the surface thiolation of carbon materials, to obtain highly dispersed Sn nanoparticles. Surface thiol groups, which have a great affinity with metal, have successfully prevented agglomeration between Sn nanoparticles in the composite process (see scheme in Figure 1); thus, highly dispersed Sn nanoparticles were obtained on mesocarbon microbeads (MCMB), and the capacity and cycle performance can thereby be improved.

Thiolation of the MCMB (Osaka Gas, Japan) was conducted by a method based on the formation of amide bonds, as reported in a previous study.[9] An amount of MCMB and $SnCl_2 \cdot 5H_2O$ (Aldrich) equivalent to 25% weight ratio of Sn to carbon was suspended by sonication in 40 mL of deionized water. Subsequently, this Sn precursor was simultaneously reduced and supported on the MCMB using $NaBH_4$ (Kanto Chemical) and then washed with deionized water and ethanol several times. After evaporation and drying, we obtained 25 wt % Sn nanoparticles supported on S-MCMB, which is referred to as Sn/S-MCMB. Likewise, Sn nanoparticles supported on untreated MCMB was abbreviated to Sn/MCMB. X-ray diffractometry (XRD, M18XHF-SRA, MAC Science Co.) analysis was carried out using a Cu Kα source at room temperature. Slurry for anode casting was prepared by mixing the Sn/S-MCMB or Sn/MCMB powder with 10 wt % carbon black (Denka, Japan) and 10 wt % poly(vinylidene fluoride) (PVdF) in *N*-methylpyrrolidone (NMP) solution (Kureha, Japan). Coin cells (2016 type) were assembled in a glove box, which consisted of the Sn/S-MCMB or Sn/MCMB electrode and lithium foil as a counter and quasi-reference electrode and two sheets of PP separator (Celgard, USA) soaking in 1 M $LiPF_6$ dissolved in a 1:1:1 (in vol %) EC:DMC:EMC solvent (Cheil, Korea) as the electrolyte.

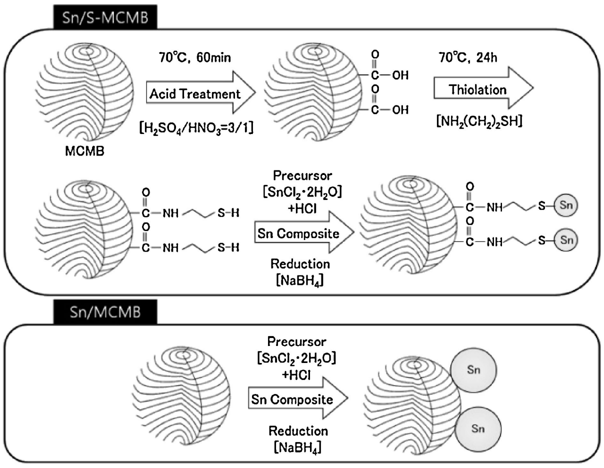

Figure 1. Schematic diagram of the thiolation of MCMB and the formation mechanism of more homogenous composite for Sn/S-MCMB than for Sn/MCMB.

A lattice structure of Sn nanoparticles supported on both MCMB and S-MCMB was characterized by XRD measurement. As shown in Figure 2, a perfectly different XRD pattern was exhibited between Sn/MCMB and Sn/S-MCMB. Peaks corresponding to Sn(200) and Sn(101) were shown at $2\theta = 30.7$ and 32.1°, respectively, for Sn/MCMB, whereas there was no peak corresponding to the crystal lattice of Sn in the case of Sn/S-MCMB. This is because the introduction of surface thiol groups resulted in the formation of amorphous Sn nanoparticles composed of an insufficient number of atoms to create diffraction, which was demonstrated in our earlier studies.[10,11] In the XRD pattern for Sn/S-MCMB, a very broad peak was shown at $2\theta = 33.9°$ corresponding to $SnO_2(101)$; this means that Sn nanoparticles on S-MCMB were partially oxidized. Since the standard reduction potential for Sn/Sn^{2+} is -0.14 V versus a standard hydrogen electrode (SHE), the surface of Sn can easily be oxidized, especially in water. From XRD measurements, we identified that the Sn nanoparticles on S-MCMB were composed of a small number of atoms, enough to eliminate the diffraction pattern; these were highly dispersed, and their surfaces were oxidized.

The charge/discharge performance was drastically changed by surface thiolation, as shown in Figure 3a. The most different

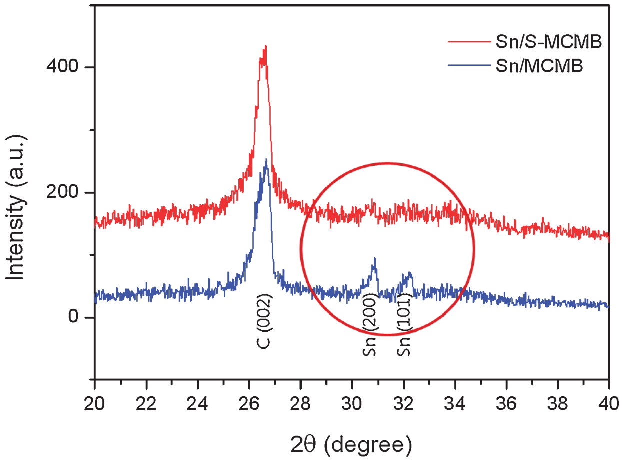

Figure 2. XRD patterns of Sn/S-MCMB and Sn/MCMB.

point is that in the case of Sn/S-MCMB, potential plateau regions around 0.4 V (vs. Li/Li^+) corresponding to Li_7Sn_3, Li_5Sn_2, and $Li_{13}Sn_5$ phase changes, which were clearly shown for Sn/MCMB and vanished in the charge/discharge curve, and the charge/discharge potential was generally higher than Sn/MCMB.[2] These differences are attributed to the amorphous structure in which no phase change during charge/discharge clearly occurred and to the considerable surface oxide formation which can increase the charge/discharge potential by irreversible reaction.[12,13] These results indicate that surface thiolation is definitely efficient for the enhancement of the dispersity of Sn nanoparticles on MCMB, while it could be disadvantageous from the standpoint of the charge/discharge potential.

The capacity and cycle performance was, however, enhanced by surface thiolation. As shown in Figure 3b, in the early cycle, Sn/S-MCMB showed about 450 $mA\,h\,g^{-1}$ of discharge capacity, while Sn/MCMB obtained no more than 350 $mA\,h\,g^{-1}$. This is because most of the Sn atoms in very tiny and well-dispersed nanoparticles on MCMB resulting from surface thiolation can effectively participate in the charge/discharge. In particular, Sn/S-MCMB demonstrated enhanced cycle performance. The average fading rate in discharge capacity was 0.39 $mA\,h\,g^{-1}$ per unit cycle, which was a considerably better value compared to 0.81 $mA\,h\,g^{-1}$ for Sn/MCMB. This implies that the smaller nanoparticles are more tolerant to mechanical stress due to relatively small volume change during the charge/discharge process.

In summary, the surface thiolation of MCMB led to the formation of tiny well-dispersed Sn nanoparticles on MCMB. Half-cell tests demonstrated that the capacity and cycle performance of Sn/S-MCMB was considerably enhanced in spite of higher charge/discharge potential than Sn/MCMB. Therefore, surface thiolation is a useful technique to form tiny well-dispersed Sn nanoparticles on MCMB which have good tolerance to mechanical stress and can enhance the capacity and cycle performance of lithium secondary batteries.

This work was supported by National Research Foundation of Korea Grant funded by the Korean Government (2009-0076509) and a creativity program by Korea Institute of Science and Technology, Republic of Korea.

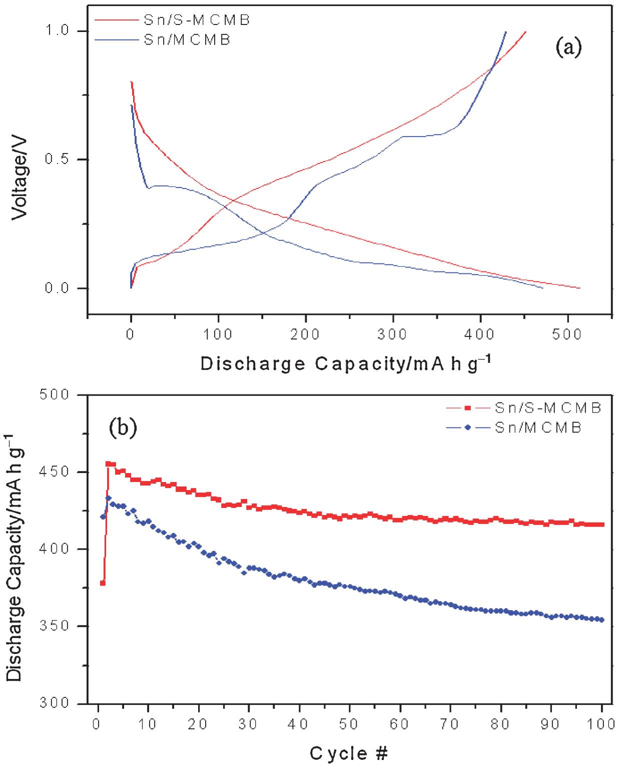

Figure 3. (a) Charge/discharge curves and (b) cycle performance of Sn/S-MCMB and Sn/MCMB with a current density of 10 $mA\,mg^{-1}$ in a voltage range of 0.005 to 1 V (vs. Li/Li^+).

References

1 Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, *Science* **1997**, *276*, 1395.
2 J. Yang, Y. Takeda, N. Imanishi, O. Yamamoto, *J. Electrochem. Soc.* **1999**, *146*, 4009.
3 H. Nara, Y. Fukuhara, A. Takai, M. Komatsu, H. Mukaibo, Y. Yamauchi, T. Momma, K. Kuroda, T. Osaka, *Chem. Lett.* **2008**, *37*, 142.
4 B. Veeraraghavan, A. Durairajan, B. Haran, B. Popov, R. Guidotti, *J. Electrochem. Soc.* **2002**, *149*, A675.
5 Z. Yuan, F. Huang, J. Sun, Y. Zhou, *Chem. Lett.* **2002**, *31*, 408.
6 H. Li, Q. Wang, L. Shi, L. Chen, X. Huang, *Chem. Mater.* **2002**, *14*, 103.
7 H. Morimoto, S. Tobishima, H. Negishi, *J. Power Sources* **2005**, *146*, 469.
8 M.-S. Park, G.-X. Wang, Y.-M. Kang, D. Wexler, S.-X. Dou, H. K. Liu, *Angew. Chem., Int. Ed.* **2007**, *46*, 750.
9 Y.-T. Kim, K. Ohshima, K. Higashimine, T. Uruga, M. Takata, H. Suematsu, T. Mitani, *Angew. Chem., Int. Ed.* **2006**, *45*, 407.
10 Y.-T. Kim, T. Uruga, T. Mitani, *Adv. Mater.* **2006**, *18*, 2634.
11 Y.-T. Kim, T. Mitani, *J. Catal.* **2006**, *238*, 394.
12 J. Dahn, I. Courtney, O. Mao, *Solid State Ionics* **1998**, *111*, 289.
13 F. Robert, P. Lippens, J. Olivier-Fourcade, J. Jumas, F. Gillot, M. Morcrette, J.-M. Tarascon, *J. Solid State Chem.* **2007**, *180*, 339.