

Structural Analysis of Highly Durable Si-O-C or Sn-O-C Composite Anodes for Lithium Secondary Battery by Means of Electrodeposition

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Progress of lithium ion batteries (LIBs) has encouraged development of electric devices whose power consumption has become higher. Recently, a circumstance surrounding energy devices has been changing. Namely, the applications of LIBs to electric vehicles and stationaries for a grid arose. Therefore the development of LIBs is subjected to strong requirements such as safer, longer life, lower cost, higher energy density, and higher power.

Our group has developed novel materials with higher energy density for next generation energy devices on the basis of nano- and meso- electrochemistry. In the field of lithium secondary batteries, tin or silicon, which have higher theoretical capacity compared with a conventional graphite anode (silicon: ca.4200 mAh/g, tin: 994 mAh/g, graphite: 372mAh/g) are promising material for the anode. However, those materials have a crucial problem of capacity fading due to their large volume change during charge discharge cycling. To improve the problem, we developed the anode by introducing nano- and meso- structures.

As for tin anode system, we have overcome the problem by alloying with an inactive metal against to lithium¹⁻⁵ or introducing pores in nano- and meso- scale⁶, resulting in improvement on the cycle durability. In the case of NiSn alloy, the discharge capacity was ~600 mAh/g of NiSn at 70th cycle. In the case of mesoporous Sn, the discharge capacity was ~430 mAh/g of Sn at 100th cycle.

Recently, we have proposed novel anode fabricated by electrodeposition from an organic solution with the idea that a deposit would be composed of silicon-based inorganic phase and organic phase formed by cathodic reaction at the interface of anode and electrolyte (Fig. 1). The silicon anode has succeeded in achieving outstanding cycle durability. The silicon anode delivered high discharge capacity of over 1000 mAh/g of Si during over 4000 cycles and sustained in the following cycles up to 7000 cycles with the discharge capacity of ~800 mAh/g of Si (Fig. 2).^{7,8} The outstanding property is considered to be due to Si-O-C composite which is composed of amorphous SiO_x and organic phases. Furthermore, to enhance the capacity per unit area, we tried to increase the thickness of the Si-O-C film by using a current collector,

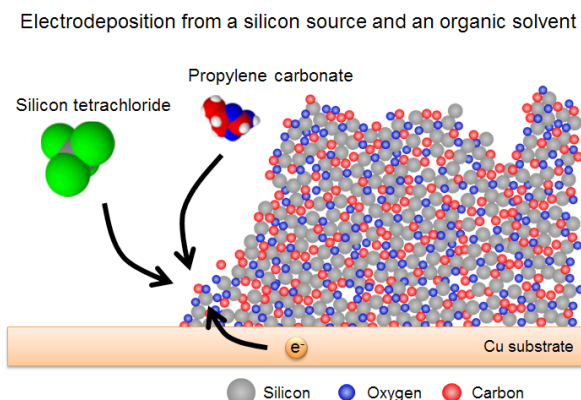


Fig. 1. Schematic illustration of electrodeposition from an organic electrolyte solution containing metal source.⁷

which has a nanocone structure.⁹ As the result, we have succeeded in the increase of the capacity per unit area up to ca. 13 times larger.

In same way, we have also investigated tin-based anode fabricated by electrodeposition from an organic solution.¹⁰ In the presentation, the chemical structures of the Si-O-C and the Sn-O-C composite anode will be discussed in detail.

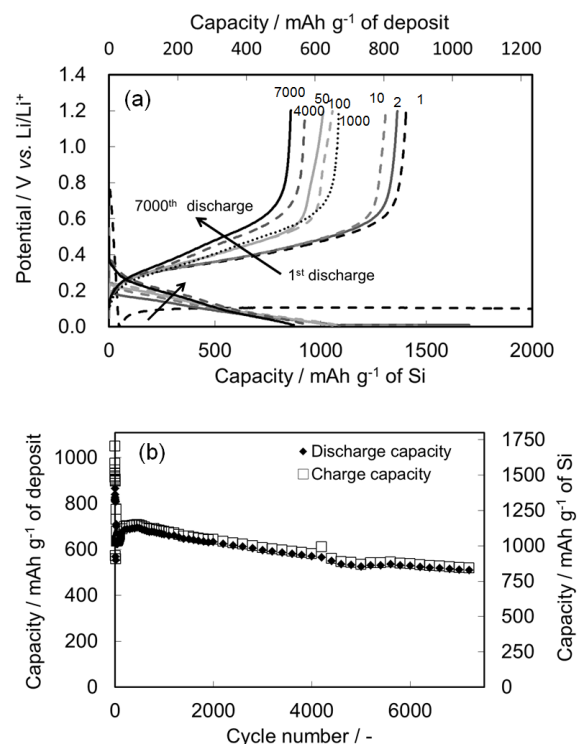


Fig. 2. Potential profiles of SiOC composite anode for Li battery during charge-discharge cycling at various cycle numbers (a) and plots of charge-discharge capacity against the number of cycles (b). The capacity values were normalized with respect to the weight of initial deposit or the calculated amount of Si in the deposit. The applied current density was 250 $\mu\text{A cm}^{-2}$ (1.0 C-rate).⁷

References

1. T. Momma, N. Shiraishi, A. Yoshizawa, T. Osaka, A. Gedanken, J. J. Zhu and L. Sominski, *J. Power Sources*, 2001, **97-8**, 198-200.
2. H. Mukaibo, T. Momma, M. Mohamedi and T. Osaka, *J. Electrochem. Soc.*, 2005, **152**, A560-A565.
3. H. Mukaibo, T. Momma and T. Osaka, *J. Power Sources*, 2005, **146**, 457-463.
4. H. Mukaibo, T. Osaka, P. Reale, S. Panero, B. Scrosati and M. Wachtler, *J. Power Sources*, 2004, **132**, 225-228.
5. H. Mukaibo, T. Sumi, T. Yokoshima, T. Momma and T. Osaka, *Electrochem. Solid-State Lett.*, 2003, **6**, A218-A220.
6. H. Nara, Y. Fukuhara, A. Takai, M. Komatsu, H. Mukaibo, Y. Yamauchi, T. Momma, K. Kuroda and T. Osaka, *Chem. Lett.*, 2008, **37**, 142-143.
7. T. Momma, S. Aoki, H. Nara, T. Yokoshima and T. Osaka, *Electrochem. Commun.*, 2011, **13**, 969-972.
8. H. Nara, T. Yokoshima, T. Momma and T. Osaka, *Energy Environ. Sci.*, 2012, **5**, 6500-6505.
9. T. Hang, H. Nara, T. Yokoshima, T. Momma and T. Osaka, *J. Power Sources*, 2013, **222**, 503-509.
10. M. Jeong, H. Nara, T. Yokoshima, T. Momma and T. Osaka, the 222nd Meeting of ECS, Honolulu, Hawaii, 7-12 October, 2012.