

Effect of electrolyte additive on cycle performance of electrodeposited Si-O-C composite anode for lithium secondary battery

Tokihiko Yokoshima¹, Mitsutoshi Otaki², Takanori Kato², Hiroki Nara¹, Toshiyuki Momma^{1,2}, Tetsuya Osaka^{1,2}

1. Research Institute for Science and Engineering, Waseda University, Shinjuku, Tokyo 169-8555, Japan

2. Department of Applied Chemistry, School of Advanced Science and Engineering, Waseda University, Shinjuku, Tokyo 169-8555, Japan

Silicon shows high theoretical capacity so that it is one of the promising materials as anode of lithium secondary battery with high energy density and high capacity. Si as anode shows the capacity fading due to large volume change during charge-discharge cycles. It is a serious problem for practical use. We have proposed a Si-O-C composite anode electrodeposited from an organic solution showing high discharge capacity of ca. 830 mAh/g of Si even at 7,000th cycle [1-4]. It is indicated that decomposed product of organic electrolyte and/or part of Si-O-C composite film anode acted as matrix phase, and this matrix inhibited the volume change of anode films. At tens of charge-discharge cycle, however, cycle retention is not high compared with that of conventional carbon anode. Additive in the electrolyte of LIB cell is effective to maintain the capacity retention because of formation of SEI on the Si anode [5,6]. In this study, effect of electrolyte additive on cycle performance of electrodeposited Si-O-C film anode was investigated. The method of effective addition was also discussed.

The propylene carbonate (PC) containing 0.5 M SiCl₄, 0.5 M TBAClO₄ (TBA: tetrabutyl ammonium) was used as electrodeposition bath for preparation of Si-O-C composite film anode. Cu foil was used for the substrate, and counter electrode and reference electrode were Pt wire and Li in TBAClO₄, respectively. Current density and quantity of electricity were 1 mA/cm² and 2 C. The half-cell was used for measurement of electrochemical properties. The working electrodes were Si-O-C anode prepared by electrodeposition. The both counter electrode and reference electrode were Li foil. The electrolyte was 1 M LiClO₄ (EC:PC 1:1 in volume). Constant current charge-discharge test was carried out under the rate of 25 μA/cm² between 0.01 – 1.2 V vs. Li/Li⁺.

First, effect of additive in the electrolyte on discharge capacity of electrodeposited Si-O-C anode was investigated. In this investigation, vinylene carbonate, VC, and fluoroethylene carbonate, FEC, were used for additive to form the SEI on the anode films. Concentration of both additives was 1 vol %. The discharge capacity after several charge - discharge cycles were compared. From the results, discharge capacity of the Si-O-C anode using the electrolyte containing additive, decreased dramatically compared with that using no additive electrolyte. In the case of VC, discharge capacity is less than 10 mAh/g of silicone, which is less than 1 percent of that of conventional Si-O-C. In the case of using FEC, discharge capacity is less than 400 mAh/g of silicone. At the first charge, the thickness dramatically increased and microstructure dramatically changed because of acting lithium [4]. It is suggested that these additives was inhibited to react anode and lithium by decomposed reaction of the additive on the Si-O-C surface. It is indicated that this inhibiting causes very low capacities.

Next, effect of additive in the electrolyte on cycle

performance of electrodeposited Si-O-C anode was investigated. For improving the cycle performance, initial treatment were carried out. Lithiation (lithium reacting) and delithiation (removing external lithium) were carried out as initial treatment in this investigation. Figure 1 shows effect of initial treatment on discharge capacity of Si-O-C anode using the electrolyte containing additive was investigated. The discharge capacities with initial treatment show high value compared with that without the treatment. Figure 2 shows capacity retention of Si-O-C anode using the electrolyte with or without additive. In this investigation, initial treatment for both of Si-O-C anode was carried out. From the fig.2, cycle retention was improved using VC and FEC. Using the additive electrolyte is effective to maintain the cycle retention. It is thought that SEI from decomposing the additive were formed, and that SEI protected Si-O-C anode surface as same as the case of conventional carbon anode.

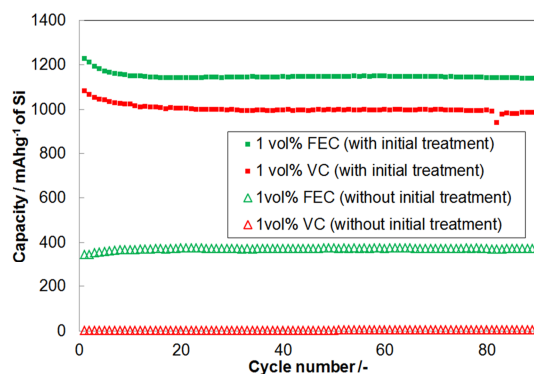


Fig. 1 Discharge capacity of electrodeposited Si-O-C composite anode using electrolyte containing VC or FEC with or without initial treatment.

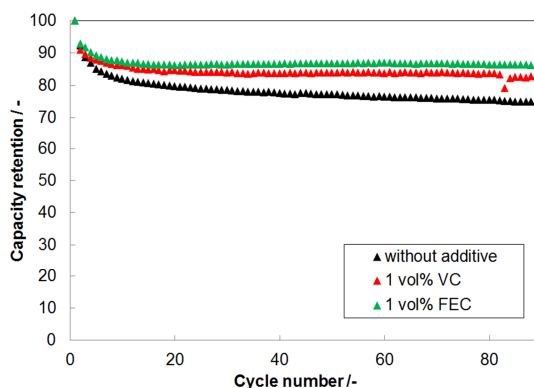


Fig. 2 Capacity retention of Si-O-C composite film anode using the electrolyte with or without additive.

References

- [1] T. Momma, et al., *Electrochem. Commun.*, **13** (2011) 969-972.
- [2] H. Nara, et al., *Energy Environ. Sci.*, **5** (2012) 6500-6505.
- [3] T. Hang, et al., *J. Power Sources*, **222** (2012) 503-509.
- [4] T. Yokoshima, et al., *Abstract of 16th Int'l Meeting on Lithium Batteries (IMLB2012)*, P3-80 (2012).
- [5] L. Chena, et al., *J. Power Sources*, **174** (2007) 538-54.
- [6] V. Etacheri, et al., *Langmuir* **28** (2012) 965-976

Acknowledgment

This work was partly supported by "Research & Development Initiative for Scientific Innovation of New Generation Batteries" from NEDO, Japan, and the Grant-in-Aid for specially promoted research "Establishment of electrochemical device engineering"