

Effect of Additive on Electrodeposition of Si-O-C Composite Anode for Lithium Secondary Batteries

Hiroki Nara¹, Tokihiko Yokoshima¹, Mitsutoshi Otaki², Mika Nakamura², Toshiyuki Momma^{1,2}, Tetsuya Osaka^{1,2}¹ Faculty of Science and Engineering Waseda University, 3-4-1, Okubo, Shinjuku-ku, Tokyo, 169-8555, Japan² Department of Advanced Science and Engineering Waseda University, 3-4-1, Okubo, Shinjuku-ku, Tokyo, 169-8555, Japan

Silicon is one of promising materials as a candidate of graphite anode in lithium-ion batteries (LIBs) because of its high theoretical capacity of 4200 mAh/g, which is ~ 11 times higher than that of graphite. However silicon anode has a critical problem that when silicon reacts with lithium, its volume expands ~ 4 times larger than that before lithiation and the lithiated silicon shrinks after delithiation. This volume change causes pulverization of silicon active material, resulting in capacity fade. To solve the problem, some attempts have been proposed such as a formation of thinner film^[1], nano-, micro-structure such as nano-wired structure^[2], core-shell structure, porous structure^[3], alloying with the third metallic elements^[4], and so on. Among them, we have proposed Si-O-C composite anode prepared by electrodeposition process.^[5,6] The electrodeposition method was introduced based on the assumption that, to form the composite of Si with an organic/inorganic compound withstands the stress during the anode operation. Organic/inorganic compounds formed by the reduction of the organic solvent, as in the formation of a resultant solid electrolyte interphase (SEI) layer on anodes in Li ion batteries, are well known to exhibit permeability to Li⁺ ion as well as chemical/electrochemical stability. Based on these considerations, to realize a Si and organic/inorganic compound which would buffer the stress and exhibit Li⁺ permeability, the electrochemical co-reduction of Si and the solvent was performed directly on the current collector. The Si-O-C anode showed excellent cycle durability, that is the Si-O-C anode delivered ca. 800 mAh/g-Si even over 7000 cycles. In this paper, to improve the charge-discharge properties further with expectation of a variation of organic compound phase, we introduced an additive into bath for electrodeposition of Si-O-C anode.

The electrolytic solution for the deposition of the composite contains 0.5 M SiCl₄ and 0.5 M tetrabutylammonium perchlorate / propylene carbonate (PC) + additive. The additives, added to the electrolytic solution with the amount of ca. 1 vol.%, are fluoroethylene carbonate (FEC), vinylene carbonate (VC), and ethylene carbonate (EC). The electrochemical cell equipped with a Li reference electrode, 1.0 cm² Cu foil as a working electrode and Pt counter electrode was set up. A constant cathodic current of 1.0 mA/cm² was applied to pass a charge of 2.0 C/cm² for the deposition.

Figure 1 shows linear sweep voltammogram on the various baths. The figure indicates that additive affects the potential to start the silicon deposition. The onset potentials on only PC, PC+FEC, PC+EC, and PC+VC were 1.32, 1.07, 1.18, and 1.12 V vs. Li, respectively. The difference of the potential would vary the composition of Si-O-C anode. The difference of the composition was roughly confirmed by EDX. Figure 2 shows the coulombic efficiency of the Si-O-C anode electrodeposited from various baths. As the results, the Si-O-C anode electrodeposited from the bath containing FEC

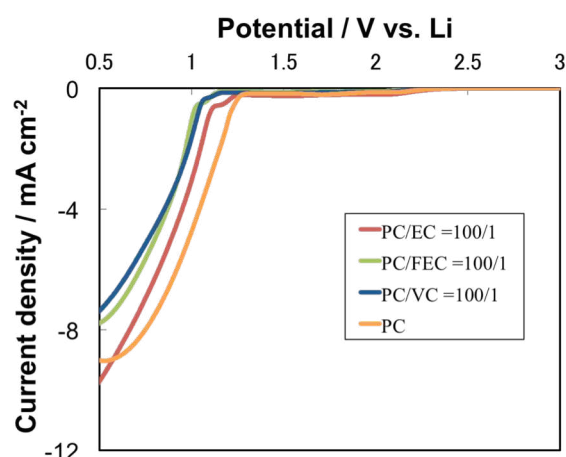


Fig. 1 Linear sweep voltammogram to cathodic direction on Si-O-C deposition from various baths: only PC, FEC+PC, EC+PC, and VC+PC with SiCl₄ as silicon source. Scan rate; 2 mV/sec.

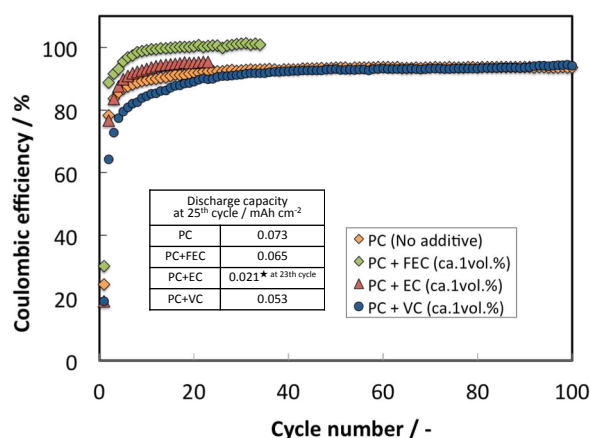


Fig. 2 Coulombic efficiency of Si-O-C anode electrodeposited by various baths: only PC, FEC+PC, EC+PC, and VC+PC with SiCl₄ as silicon source. The Si-O-C anodes were cycled with cut off potential of 0.01 – 1.2 V vs. Li/Li⁺, constant current of 25 μ A/cm².

showed higher coulombic efficiency at 1st cycle compared with others and best coulombic efficiency which was almost 100% after 10 cycles. In the presentation, characterization of the Si-O-C anodes will be discussed in detail.

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