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Anode Properties of Cu-Coated Si Thick Film Electrodes Prepared by Electroless Deposition and Gas-Deposition

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Thick film electrodes of Cu-coated Si particles were fabricated by an electroless deposition and a successive gas-deposition, and were evaluated their electrochemical properties as an anode of Li-ion battery. The discharge capacity and its retention at the 1000th cycle were 570 mAh g^{-1} and 61%. The excellent cycle life performance is attributed to an enhanced electrical conductivity due to the Cu-coating and a reversible conversion reaction between Li and Cu_2O which was formed on the Cu surface. The high capacity retention is caused by a high fracture toughness of the coated Cu which can effectively relax a stress induced by volume expansion of Si as a buffer matrix.

Key Words : Si anode material, Electroless Deposition, Gas-deposition, Lithium Rechargeable Battery

1 Introduction

Si-based anode materials with much higher energy density than graphite have been intensively studied for Li-ion battery in electric vehicles. In the formation of Li-Si alloy ($Li_{4.4}Si$), the volume per Si atom is approximately four times larger than that of the parent Si atom, i.e., a 400% volume expansion of the Si lattice takes place. The violent volumetric change generates a compressive stress, which induces the breakup of the electrode and the electrical isolation of the active material. This phenomenon significantly lowers a discharge capacity of Si electrodes.

In this regard, we have prepared thick film electrodes of Ru-coated Si by a combination of an electroless deposition (ELD) and a successive gas-deposition (GD) method,[1-4] and revealed that the film electrodes exhibited an excellent cycle life performance[5] and a conversion reaction between RuO_2 and Li[6-8] contributed to the electrode reaction of the composite electrode. Elemental Ru is, however, not suitable for practical use because of its rarity and expensiveness. Therefore, it is required to replace Ru with common metals such as Cu in the film electrodes. In this study, we prepared film electrodes of Cu-coated Si by using the ELD and GD, and investigated the electrochemical performance of the film electrodes.

2 Experimental

ELD of Cu on Si was performed in acid and basic baths to change the oxidation condition of the coated Cu. In the ELD using acid bath, $CuSO_4 \cdot 5H_2O$ was dissolved an aqueous solution of 0.1 mol L^{-1}(M) H_2SO_4. After a commercial Si powder (Wako pure chemical Industries, Ltd., 99％, diameter: 0.1~100 µm) was also added in the solution under a vigorous stirring with condition of pH 1, a reducing agent of sodium boron hydride ($NaBH_4$) was added to the solution. As for the ELD using basic bath, $CuSO_4 \cdot 5H_2O$ and a complexing agent of $(NH_4)_2SO_4$ were dissolved an aqueous solution of 0.2 M KOH with pH 9. The Si powder was also added in the solution with the stirring, and then the reducing agent of $NaBH_4$ was added to the solution. By the reduction of Cu^{2+} ions in the acid and basic bath, Cu and Cu-O can be coated on the Si powder, respectively. The composition ratio of the coated Si powder was studied by inductively coupled plasma atomic emission spectroscopy (ICP-AES), which revealed that the radio Cu:Si is 4:96 wt%. The crystal structure of the coated Si powder was investigated by using an X-ray diffractometer (XRD-6000 Shimadzu Co., Ltd.).

For gas-deposition, Cu foil substrates (20 µm thickness; 99.9%, Nilaco Co., Ltd.) were set up in a vacuum chamber with a guide tube.[1-4] An aerosol consisting of an Ar gas (differential pressure 7×10^5 Pa) and active material powders of the coated Si was generated in the guide tube, and gushed from a nozzle to the Cu substrate in the chamber with a base pressure of 8 Pa. Thick films of the active material powders with weight of about 0.035 mg were deposited on the substrate. The film thickness of the electrodes was estimated to be about 4 µm by a cross-sectional observation using a confocal scanning laser microscope (CSLM, VK9710 Keyence Co., Ltd.). The surface morphology and element distribution were observed using scanning electron microscope (SEM, JSM-5200; JEOL Ltd.) and energy dispersive X-ray analysis (EDX, EDS-54033MCK; JEOL Ltd.).

Electrochemical measurements were carried out with a beaker-type three-electrode cell. The working electrodes used were the deposited thick film electrodes. Both counter and reference electrodes were Li metal sheets (Rare Metallic, 99.90％) with the thickness of 1 mm. As an electrolyte, we used 1 M $LiClO_4$-dissolved propylene carbonate (PC, Kishida Chemical Co., Ltd.). Cyclic voltammetry measurements were carried out using an electrochemical measurement system (HZ-3000 Hokuto

Denko Co., Ltd.) at a scan rate of 0.001 mV s^{-1} in the potential range between 0.005—3.400 V vs. Li/Li^+. Constant current charge-discharge tests were performed under a constant current of 0.05 mA (1.7 *C*) at 303K with the cutoff potentials being 0.005 V vs. Li/Li^+ for charge and 3.400 V vs. Li/Li^+ for discharge.

3 Results and Discussion

Figure 1 shows XRD patterns of coated Si powders prepared by the ELD in the aqueous solution containing Cu^{2+} ions with (a) acid condition and (b) basic condition. In the acid condition, we observed diffraction peaks of cubic Si (JCPDS No.27-1402) and Cu (JCPDS No.04-0836) as shown in Fig. 1(a). This means that metal Cu was coated on the Si powder by reducing of Cu^{2+} ions in the acid bath. In the basic condition, a Cu_2O (JCPDS No. 05-0667) peak was also observed in addition to the peaks of Cu and Si. We obtained two kinds of coated Si powders with different oxidation conditions of Cu. Hereafter, we call the coated Si powders prepared in the acid and basic baths Cu-coated Si and Cu_2O-coated Si, respectively.

Figure 2 depicts a charge-discharge (Li insertion-extraction) curve at the first cycle for the GD-film electrodes of Cu-coated Si. For comparison, the figure also displayed the charge-discharge curves of the GD-film electrodes of pristine Si and Ru-coated Si, which have been previously studied. In the all cases, potential plateaus appeared at about 0.1 and 0.4 V vs. Li/Li^+ in the charge and discharge processes. The potential plateaus are attributed to alloying and de-alloying reactions of Li-Si. Thus, we revealed that the electrode reactions in the Ru-coated and Cu-coated Si thick films are mainly based on the Li-Si alloying and de-alloying. Large irreversible capacities at the first cycle are attributed to the formation of solid-electrolyte interface layer and lithium oxide.

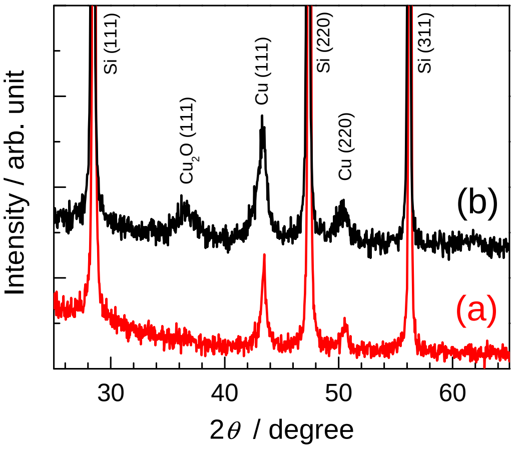

Fig. 1 XRD patterns of coated Si powders prepared by ELD in aqueous solution containing Cu^{2+} ions with (a) acid condition of pH 1 and (b) basic condition of pH 9.

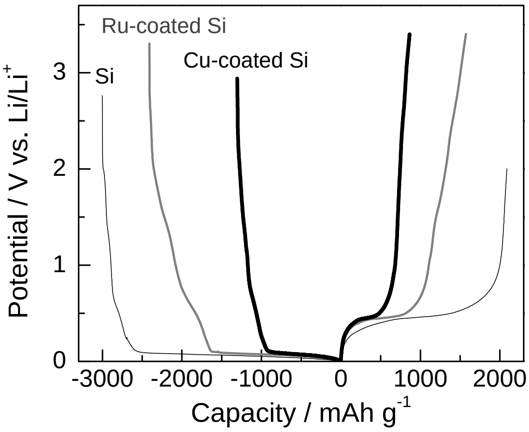

Fig. 2 Charge-discharge curves at the first cycle for the GD-film electrodes of Si, Ru-coated Si, and Cu-coated Si.

Figure 3 presents dependence of the discharge capacity on the cycle number for the GD-film electrodes of the pristine Si, Ru-coated Si, and Cu-coated Si. Although the pristine Si electrode showed a large discharge capacity (Li-extraction) of about 2000 mAh g^{-1} at the initial cycle, the electrode continued to show a significant capacity decay until 100th cycle. In case of the Cu-coated electrode, the initial discharge capacity of 870 mAh g^{-1} was not excellently large as a next-generation anode. However, the discharge capacity of 570 mAh g^{-1} was maintained even at the 1000th cycle. Note that the capacity is much larger than that of the theoretical value of graphite (372 mAh g^{-1}). At the 1000th cycle, the capacity retention of the Cu-coated Si electrode is 61%, which is remarkably higher compared with the Ru-coated Si electrode of 37%. Meanwhile, the Cu_2O-coated Si electrodes exhibited a lower capacity retention of 31%. The reason is probably a lowered electrical conductivity of the electrode because the Cu_2O-coated Si should contain a large amount of Cu_2O, and the electrical resistivity of 1×10^4 Ωcm in Cu_2O is extremely higher than that of 2×10^{-6} Ωcm in Cu.

In our previous study with a GD-film electrode of Ru, we have revealed that Ru was oxidized to RuO_2 during a few charge-discharge cycles in the $LiClO_4$-PC electrolyte, and that the Ru electrode exhibited an excellent cycle life performance due to a conversion reaction between RuO_2 and Li. In this study, we consider that the excellent cycle life performance of the Cu-coated Si electrode, as well as the Ru-coated Si electrode, is caused by a contribution of Cu-O (copper oxides) to the electrode reaction. Figure 4 compares cyclic voltammograms of Cu-coated Si and

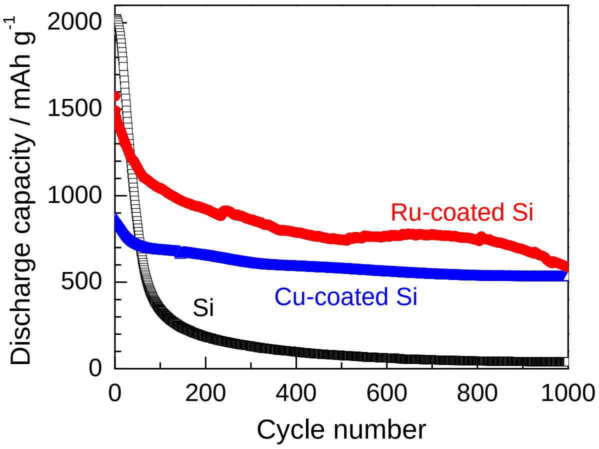

Fig. 3 Dependence of discharge capacity on cycle number for the GD-film electrodes of Si, Ru-coated Si, and Cu-coated Si.

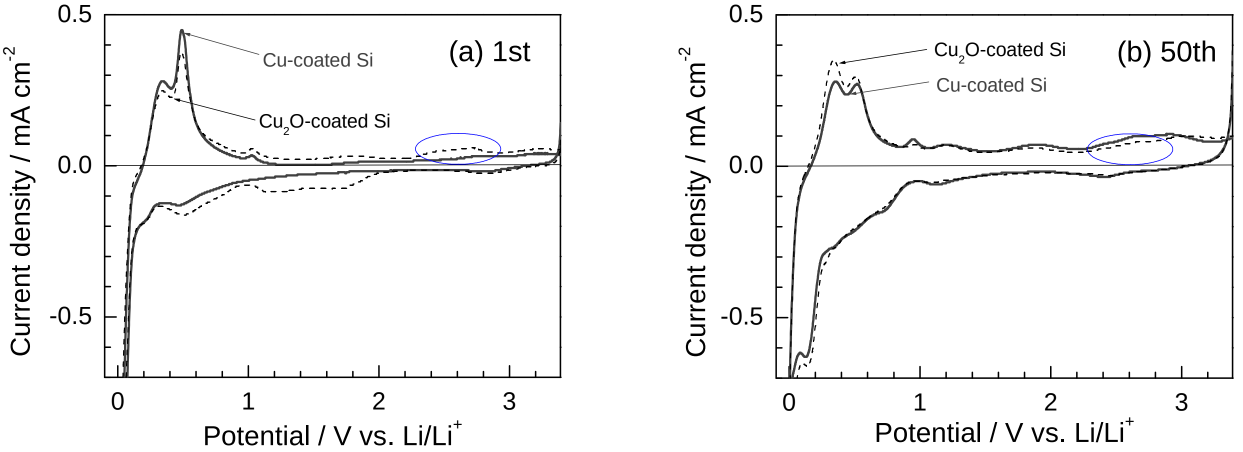

Fig. 4 Cyclic voltammograms of the GD-film electrodes of Cu-coated Si and Cu_2O-coated Si (a) at the first cycle and (b) at 50th cycle.

Cu_2O-coated Si electrodes (a) at the first cycle and (b) at 50th cycle. Both Cu-coated Si and Cu_2O-coated Si electrodes show two anodic peaks at 0.34 and 0.48 V vs. Li/Li^+ at the first cycle shown in Fig. 4(a), which indicates de-alloying reactions in Li-Si alloys. A small anodic peak at 1.03 V vs. Li/Li^+ is presumably due to an extraction of Li from silicon oxide which is partially formed on a surface of the Si powder. Only for the Cu_2O-coated Si, a broad anodic and cathodic peaks appeared in the range of 2.2-2.8 V and 1.1-1.8 V vs. Li/Li^+. It has been reported that the broad peak indicates a conversion reaction[9-11] between Cu_2O and Li, and that the reaction of Cu_2O on Li insertion and extraction is described as the following two-step reactions[6,8,9]:

$$Cu_2O + 2Li^+ + 2e^- \rightleftarrows 2Cu + Li_2O \qquad (1)$$

$$Li^+ + e^- + Cu/Li_2O \rightleftarrows Li/Cu/Li_2O \qquad (2)$$

At the 50th cycle, both the two electrodes showed the broad peaks of the reversible conversion reaction in the potential range as shown in Fig. 4(b). The result suggests that a surface of Cu in the Cu-coated Si was oxidized to Cu_2O by the surface effect during the cycling, and that the formed Cu_2O contributes to the electrode reaction.

The results of SEM and EDX mapping for the Cu-coated Si electrode figured out that Si particles of the electrode are partially covered by Cu. This implies a matrix structure, a coated-Cu layer encapsulates Si particles like a net. The more excellent capacity retention in the Cu-coated Si than Ru-coated Si can be discussed in relation to the mechanical property of the coated materials. The Mohs hardness of 3 in Cu is much lower than that of 6.5 in Ru. This means that the fracture toughness of Cu is very high. We consider that the coated Cu can play a role as a buffer matrix to relax a stress caused by the large volume expansion of Si during the Li-Si alloying. Therefore, the electrode showed higher capacity retention than the Ru-coated Si electrode because the relaxation effectively prevents the active materials from breaking up and being electrically isolated.

4 Conclusion

The thick film electrodes consisting of Cu-coated Si particles were fabricated by the ELD and the GD, and were evaluated their electrochemical properties as the anode for Li ion battery. The discharge capacity and the capacity retention at the 1000th cycle were 570 mAh g^{-1} and 61%. The CV results suggest that the surface of Cu in the Cu-coated Si electrode was oxidized to Cu_2O during the charge-discharge processes. The excellent cycle life performance of the Cu-coated Si electrode is attributed to the reversible conversion reaction between Cu_2O and Li on the surface. The higher capacity retention was obtained in the Cu-coated Si electrode because the stress relaxation effectively prevents the active materials from breaking up and being electrically isolated. The results indicate that Cu can be replaced with Ru as a more suitable coating material in the electrodes of anode for Li-ion battery.

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