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Communication—Fabrication of a Uniformly Tin-Coated Three-Dimensional Copper Nanostructured Architecture by Electrodeposition

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Communication—Fabrication of a Uniformly Tin-Coated Three-Dimensional Copper Nanostructured Architecture by Electrodeposition

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A three-dimensional copper nanostructure architecture (3DC1) coated uniformly with a tin film was fabricated by electrodeposition. In these trials, a pyrophosphate bath was used for tin plating, and the effects of polyethylene glycol and formaldehyde additives on the morphology of the deposited tin were investigated. Relatively large tin particles were electrodeposited in an inhomogeneous manner over the 3DC1 surface when using a plating bath without additives. In contrast, 3DC1 coated with a uniformly thick tin film was fabricated by employing a bath with the additives.

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Since three-dimensional (3D) nanostructured metal architectures typically exhibit large specific surface areas as well as superior electrical conductivity values, their application as electrodes in functional devices such as supercapacitors,[1] fuel cells[2] and batteries[3] have been widely researched. Among these potential uses, the application of 3D copper nanostructured architectures as current collectors in lithium ion battery anodes is one of the most attractive. Consequently, numerous studies have investigated possible tin-based lithium ion battery anodes, including nanoporous copper formed by de-alloying aluminum from an Al-Cu alloy,[4] nanoporous copper generated by electrodeposition using hydrogen bubbles as a template[5-7] and copper nanopillars fabricated by electrodeposition through a porous alumina membrane.[8] Although these 3D copper nanostructured architectures are very effective at improving electrode functions, their manufacture requires many steps and is therefore complex. In contrast, our group has previously developed a very straightforward electrodeposition method for the fabrication of these architectures, in which an organic additive is simply added to the electrodeposition bath.[9] This process of making 3D copper nanostructure architectures by one-step electrodeposition (the resulting products henceforth being designated as 3DC1) can be expected to have practical applications in the manufacture of various objects, such as current collectors for tin-based lithium ion battery anodes. To ensure the high performance of such anodes, the uniformity of the tin film on the 3DC1 substrate is important. Unfortunately, in general, it is difficult to form metal films with uniform thicknesses on uneven substrates such as 3DC1 by electrodeposition.

In this study, therefore, the conditions associated with the electrodeposition of tin on 3DC1 were examined with the aim of fabricating uniformly tin-coated 3DC1.

Experimental

3DC1 was fabricated on a pure copper plate (JIS C1201P) with an exposed surface area of 10 cm^2 (3.3 × 3 cm) using a plating bath (0.85 M $CuSO_4 \cdot 5H_2O$ + 0.55 M H_2SO_4 + 3×10^{-4} M polyacrylic acid (mean molecular weight 5000; PA-5000)) under galvanostatic conditions (1 A dm^{-2}) without agitation at 25°C.[9] The amount of charge applied was 38 C (3.8 C cm^{-2}). The continuous electrodeposition of tin was conducted on the resulting 3DC1, employing a pyrophosphate bath[10] (0.25 M $Sn_2P_2O_7$ + 1 M $K_4P_2O_7$) as the basic tin plating bath, together with polyethylene glycol (mean molecular weight 600: PEG600) and formaldehyde (HCHO) as additives.[11] The composition of the tin plating bath with additives was 0.25 M $Sn_2P_2O_7$ + 1 M $K_4P_2O_7$ + 0.005 M HCHO + 1.2 g dm^{-3} PEG600. The electrodeposition of tin was carried out under galvanostatic conditions at 25°C without agitation, applying 3 C of charge and with a pure tin plate as the anode. The phase structure of the resulting tin-deposited 3DC1 was evaluated by X-ray diffraction (XRD; SmartLab, Rigaku) operating in thin film mode. The surface and cross-sectional morphologies of the tin-deposited 3DC1 were examined using a field emission-scanning electron microscope (FE-SEM; JSM-7000F, JEOL). Elemental mapping analysis was also carried out with an energy dispersive spectroscope (EDS) attached to the FE-SEM. A cross-section polisher (SM-09010, JEOL) was used to prepare cross-sectional samples for FE-SEM analysis.

Results and Discussion

Figure 1 shows surface and cross-sectional SEM images of the 3DC1 before and after the electrodeposition of tin using different plating baths at an applied current of 0.1 A. In the present study, since the surface area of the 3DC1 was unknown, applied current was used as the electrochemical reaction rate parameter rather than applied current density. The 3DC1 evidently consists of thin, sheet-like copper deposits approximately 5 μm thick (Figs. 1a and 1b). Tin grains several μm in size are evident on the 3DC1 surfaces following the tin deposition process in the basic plating bath not incorporating additives (Figs. 1c and 1d). In contrast, distinct tin deposits are not evident on the 3DC1 sample treated in the tin plating bath with additives (Figs. 1e and 1f). Therefore, it appears that the tin film applied to the 3DC1 in the case of the bath with additives had a uniform thickness and was very thin. The deposition of tin on the 3DC1 was confirmed by XRD analysis, and Figure 2 presents the XRD patterns of 3DC1 before and after tin deposition using the plating bath with additives. Strong diffraction peaks assigned to face-centered-cubic copper are present at 44° and 51° in the XRD pattern prior to tin deposition (Fig. 2a). On the contrary, in addition to the copper diffraction peaks, a small, broad diffraction peak attributed to a β-Sn phase is seen at 30° in the pattern acquired after the electrodeposition of tin (Fig. 2b). Thus, tin (β-Sn) was undoubtedly deposited on the 3DC1. To clarify the uniformity of the tin deposition on the 3DC1, an EDS mapping analysis was also carried out.

Figure 3 summarizes the results of elemental mapping analysis of cross-sections of the 3DC1 before and after tin electrodeposition. Prior to tin deposition, copper is present within the 3DC1 cross-section while tin, as expected, is not detected (Figs. 3a–3c). After tin deposition using a bath without additives, tin is distributed inhomogeneously on and within the 3DC1 (Figs. 3d–3f). The high concentrations of tin

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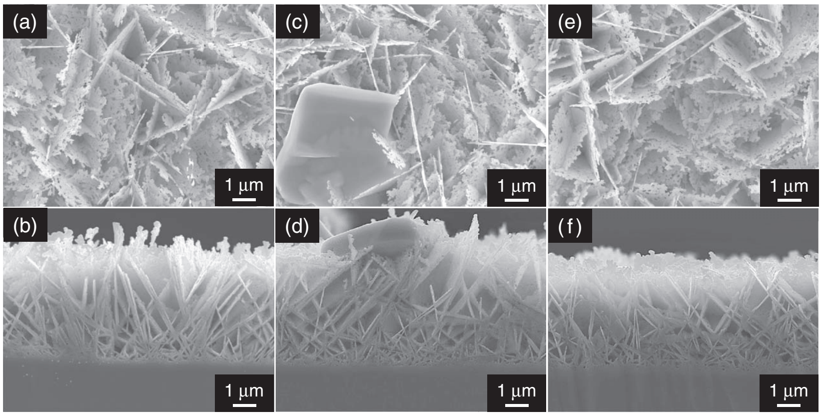

Figure 1. Surface and cross-sectional SEM images of 3DC1 before and after tin electrodeposition using different tin plating baths: (a) surface of 3DC1 prior to tin deposition, (b) cross-section of (a), (c) surface of 3DC1 after tin deposition using a tin plating bath without additives, (d) cross-section of (c), (e) surface of 3DC1 after tin deposition using a tin plating bath with additives and (f) cross-section of (e).

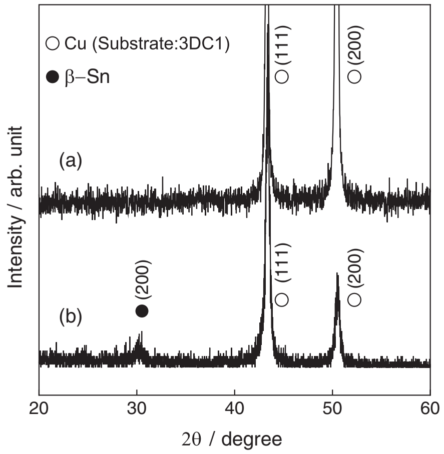

Figure 2. XRD patterns acquired from (a) untreated 3DC1 and (b) 3DC1 following electrodeposition of tin using a tin plating bath with additives.

evident on the 3DC1 surface correspond to deposited tin grains (Figs. 3d and 3f). In contrast, a homogeneous distribution of tin over the cross-section is seen following the electrodeposition of tin using a bath with additives (Figs. 3g–3i). These results indicate that tin was homogeneously deposited on and in the 3DC1 both in the horizontal and vertical directions. Since distinct deposits of tin are not observed in the surface and cross-sectional SEM images (Figs. 1e and 1f), a very thin tin film must have formed over the sheet-like copper of which the 3DC1 was composed. Thus, 3DC1 uniformly coated with a tin film (Sn@3DC-1) was successfully fabricated by electrodeposition.

Summary

The effects of electrodeposition conditions on the morphology of the resulting tin layer on 3DC1 were studied. The fabrication of 3DC1 coated with a uniform tin film (Sn@3DC-1) was achieved under galvanostatic conditions using a pyrophosphate bath containing polyethylene glycol and formaldehyde. This material is expected to have applications to lithium ion battery anodes.

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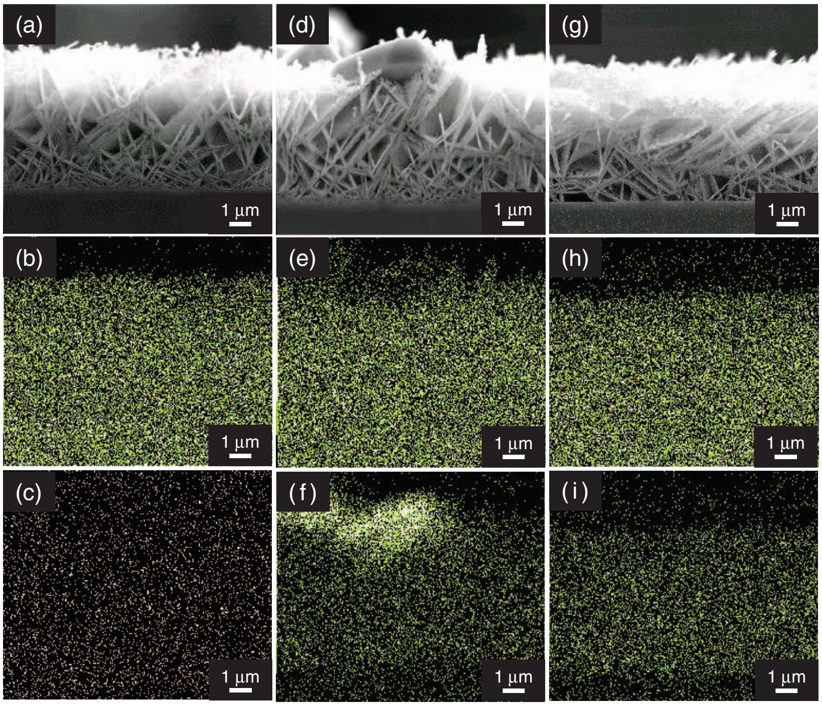

Figure 3. EDS mapping of 3DC1 cross-sections before and after electrodeposition of tin using different plating baths: (a) SEM image of 3DC1 before tin deposition, (b) copper and (c) tin mapping images of (a), (d) SEM image of 3DC1 after tin deposition using a plating bath without additives, (e) copper and (f) tin mapping images of (d), (g) SEM image of 3DC1 after tin deposition using a plating bath with additives, (h) copper and (i) tin mapping images of (g).

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