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Electrodeposition of cohesive carbon films on aluminum in a LiCl–KCl–K_2CO_3 melt

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Abstract

Electrodeposition of carbon on an aluminum electrode was studied in a LiCl–KCl–K_2CO_3 melt. A cyclic voltammogram for an aluminum electrode indicates that the cathodic current is due to the reduction of CO_3^{2-} ions. Carbon films on aluminum substrates were obtained by potentiostatic electrolysis, and the cohesiveness of the films depended on the potential. SEM observations showed that the morphology of the deposited carbon film depends on the electrolytic conditions. Raman spectroscopy, XPS and XAES measurement showed that the film consisted of carbon in the sp^2 state.

1. Introduction

The electrochemical formation of carbon films from molten halide can be considered as one of the candidates for electrochemical CO_2 fixation processes. CO_2 fixation can be achieved through the following two steps: First, CO_2 gas is supplied to molten halide containing oxide ions to form carbonate ions as follows:

$$CO_2 + O^{2-} \rightarrow CO_3^{2-} \tag{1}$$

Then, Cathodic reduction of carbonate ions:

$$CO_3^{2-} + 4\,e^- \rightarrow C + 3\,O^{2-} \tag{2}$$

This takes place to form various types of carbon film on the cathode depending on the electrolytic conditions.

To exemplify the possibility of the latter step, electrodeposition of carbon on a nickel was carried out, and various types of carbon films were obtained depending on the electrolytic conditions [1]. However, the cohesiveness of deposited carbon was not good and the characterization of carbon was incomplete.

If a cohesive carbon film on a metal substrate is obtained, the corrosion resistance and/or thermal resistance of the surface of the metal substrate may be greatly improved because the corrosion resistance or thermal resistance of carbon is superior to that of metal.

This has been achieved successfully by the reduction of carbonate ions using an aluminum electrode in a LiCl–KCl–K_2CO_3 melt. In the following, the experimental procedures and detailed discussion of the obtained film will be provided.

2. Experimental details

The experimental arrangement is shown in Figure 1. A LiCl–KCl eutectic melt (LiCl:KCl = 58.5:41.5 mol %; Wako Chemical Co., Ltd) was used as electrolyte. The electrolyte temperature was 723 K. Anhydrous K_2CO_3 (Wako Chemical Co., Ltd) was used as the CO_3^{2-} ion source and the concentration of K_2CO_3 was 1.0 mol %. The working electrode was a rectangular sheet of aluminum (10 mm × 5 mm × 0.5 mm; Nilaco Corp., 99.6%). The working electrode was mechanically polished with abrasive paper followed by a 0.3 μm alumina polishing suspension (Baikowsi Corp.) to obtain a mirror-like surface and washed ultrasonically in acetone. The counter electrode was a 5 mm diameter glassy carbon rod (Tokai Carbon Co., Ltd). The reference electrode was a 1 mm diameter silver wire immersed in a LiCl–KCl melt containing 1 mol % of AgCl, placed in a glass tube with a thin bottom to maintain electrical contact with the melt. The potential of this reference electrode was calibrated with reference to a dynamic reference electrode. The dynamic reference electrode was prepared by electrodepositing Li metal on a nickel wire (Nilaco Corp., 99.35%) [2]. All potentials are given with reference to this dynamic reference electrode potential.

Cyclic voltammetry and potentiostatic electrolysis were conducted using a potentio/galvanostat (Hokuto Denko Co., Ltd, model HA-301) combined with a function generator (Hokuto Denko Co., Ltd, model HB-104) and a coulomb/ampère-hour meter (Hokuto Denko Co., Ltd, model HF-201). The character of the films was investigated by SEM, Raman spectroscopy, XPS and XAES measurements.

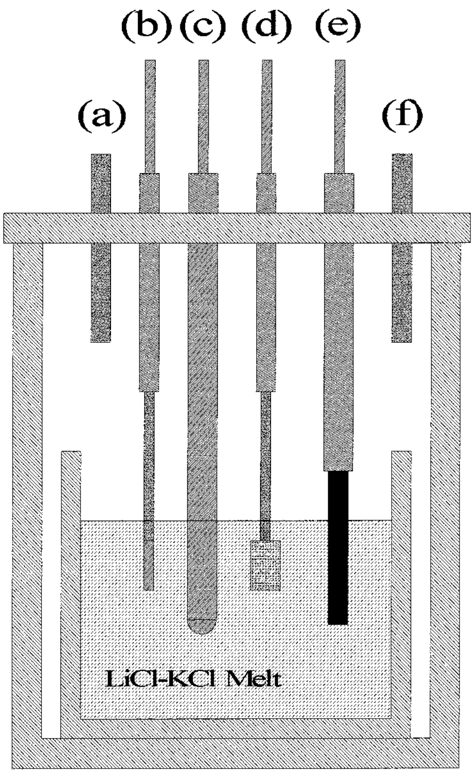

Fig. 1. Schematic representation of the experimental apparatus for electrodeposition of carbon from a LiCl–KCl–K_2CO_3 melt. (a) argon gas inlet, (b) dynamic reference electrode (Ni wire), (c) reference electrode, (d) working electrode, (e) counter electrode and (f) argon gas outlet. Thermocouple is not shown.

3. Results and discussion

3.1. *Cyclic voltammetry*

Cyclic voltammetry was carried out on an aluminum electrode in a LiCl–KCl–K_2CO_3 melt. Before adding K_2CO_3, a blank measurement was performed, as shown by the dashed line in Figure 2. In this voltammogram, the cathodic current arising at about 0.6 V is due to Li–Al alloy formation and the anodic current is due to the dissolution of Li from the alloy. The anodic current arising at 1.5 V is due to the dissolution of the Al substrate.

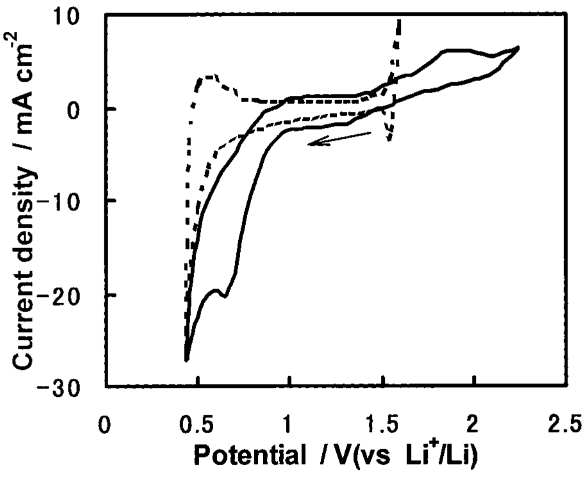

Fig. 2. Cyclic voltammograms for an aluminum electrode in a LiCl–KCl (dashed line) and a LiCl–KCl–K_2CO_3 melt (solid line). Potential scan rate 0.05 V s^{-1}. Key: (——) LiCl–KCl–K_2CO_3; (– – –) LiCl–KCl.

The solid line in Figure 2 shows a voltammogram after adding K_2CO_3. The cathodic current peak at about 0.7 V corresponds to the reduction of CO_3^{2-} ions and the anodic current peak at about 2.0 V is due to oxidation of the deposited carbon.

3.2. *Potentiostatic electrolysis*

The preceding results show that the reduction of CO_3^{2-} ions occurs around a potential of 0.7 V. In order to confirm the reaction around this potential, potentiostatic electrolysis at 0.60, 0.70, 0.80, 0.90, 1.00, 1.10 and 1.20 V was conducted.

On the one hand, when the potential was more negative than 0.80 V, the deposits were rough and coarse, and easily stripped from the aluminum electrode when rinsed in distilled water to remove the salt. On the other hand, when the potential was more positive than 0.90 V, the deposits were smooth and fine, and hardly stripped from the electrode when rinsed in distilled water to remove the salt. When the potential was more positive than 1.10 V, the current density was almost zero and deposits were not obtained on the electrode.

Figure 3 shows SEM images of the surface of the cohesive deposits obtained by potentiostatic electrolysis at 0.90, 1.00 and 1.10 V, respectively for 100 C cm^{-2}. The morphology of the deposits depended on the potential, that is, the surface of the deposit became smoother as the potential was more positive.

3.3. *Characterization of the deposits*

To characterize the deposits obtained by the reduction of CO_3^{2-} ions in the melt, the samples electrodeposited under various applied potentials mentioned above were investigated by Raman spectroscopy, XPS and XAES measurement. Since significant differences were not observed among these samples, only the results of the deposited film obtained by potentiostatic electrolysis at 1.00 V for 100 C cm^{-2} is discussed in detail in this section.

3.3.1. *Raman spectroscopy*

Raman spectroscopy is a widely used method giving information about different bonds of carbon atoms. This method is applicable for bulk samples. Figure 4 shows the Raman spectrum of the deposited film. The spectrum shows two broad peaks at about 1586 cm^{-1} (G peak) and at about 1351 cm^{-1} (D peak). The D peak is attributed to a particle size effect [3] and the linear relationship between the magnitude of I_D/I_G and the inverse crystalline size is obtained where I_D and I_G are the peak intensities of the D and G peaks, respectively. The I_D/I_G intensity ratio of the deposited carbon film

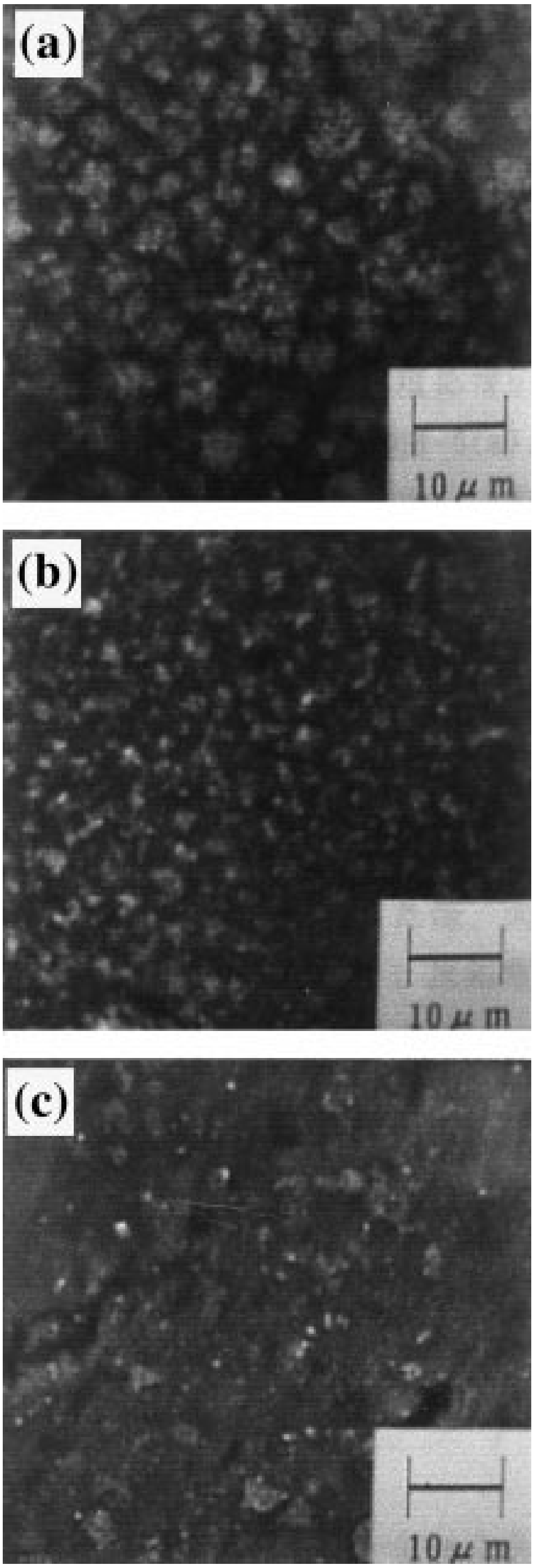

Fig. 3. SEM images of the deposit obtained by potentiostatic electrolysis in a LiCl–KCl–K_2CO_3 melt. Potential: (a) 0.90, (b) 1.00 and (c) 1.10 V vs Li^+/Li; charge 100 C cm^{-2}.

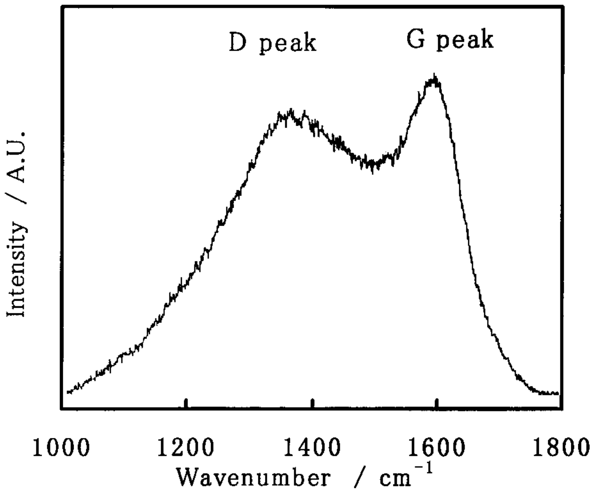

Fig. 4. Raman spectrum of the deposited carbon film obtained by potentiostatic electrolysis at 1.00 V vs Li^+/Li for 100 C cm^{-2}.

was estimated as 0.98. The linear relationship [3] yields a crystalline size of about 5 nm for the deposited film.

The position of the peaks brings information concerning bond-angle disorder and bonding in the crystallites. The downward shift of G and D peaks is a sensitive indication that carbon is changing from one with bond-angle disorder to one containing threefold-coordinated crystallites [4]. As the peak positions of the deposited carbon had graphite-like values (D peak at about 1350 cm^{-1} and G peak at about 1600 cm^{-1}), the deposited film is considered to be sp^2-hybridized carbon.

3.3.2. *XPS and XAES spectroscopy*

XPS and XAES (X-ray excited AES) provide information concerning the chemical state of atoms in the near surface region of a solid. AES is the preferential methods for investigation of the chemical interaction on the surface of carbon films.

Figure 5 shows the C 1s core level emission from the deposited carbon film. The background was subtracted by Shirley's method [5]. The left shoulder of the spectrum lies in the slightly higher binding energy range so that several peaks are considered to be convoluted. Three features are evident at 284.3, 286.1 and 288.8 eV, respectively in Figure 5. The first originates from the carbon–carbon bond, the second occurs due to single-bonded carbon–oxygen interaction and the third demonstrates the double carbon–oxygen bond. The spectrum shows that the surface of the deposited carbon was oxidized.

Figure 6 shows the C KVV spectra of the deposited carbon film and natural graphite flake as the reference.

The C KVV spectrum is convoluted by the partial density-of-state components [6, 7]. The spectrum shapes for sp^2 and sp^3 hybridization have different characteristic features and are useful to identify sp^2 and sp^3 states of carbon atoms in solids [8].

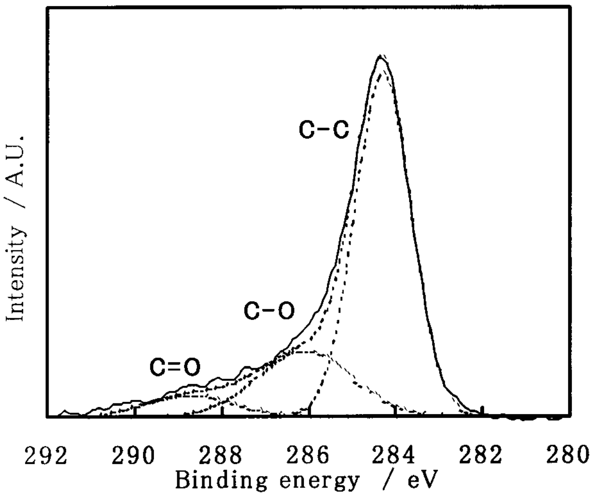

Fig. 5. C 1s core level emission from the deposited carbon film. Background subtracted by Shirley's method. Three features of binding energy are evident; C–C at 284.3, C–O at 286.1 and C=O at 288.8 eV, respectively.

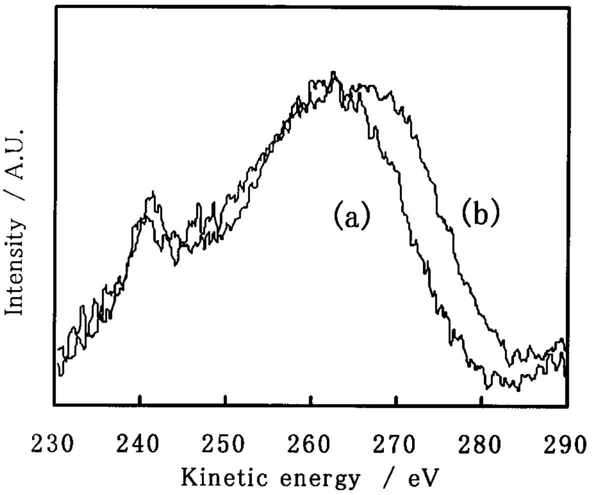

Fig. 6. C KVV spectra of (a) deposited carbon film and (b) natural graphite flakes as reference. Background subtracted by Shirley's method.

The right shoulder of the deposited carbon film lies in a lower kinetic energy range than the natural graphite flake, because the ratio of the sp^2 state in the surface of the deposited carbon film is decreased. A similar tendency is shown in the C KVV spectrum of oxidized graphite surfaces [9], so that the surface of the deposited carbon film was considered to be oxidized by air when the film was taken out of the electrolytic cell, and the transition from the sp^2 to the sp^3 state occurred at the surface of the carbon film.

4. Conclusions

Carbon films on aluminum were obtained by electrodeposition in a LiCl–KCl–K_2CO_3 melt. Various morphologies and cohesiveness of the deposits were obtained depending on the potential. A cohesive film on aluminum substrate was obtained by potentiostatic electrolysis at 0.90, 1.00 and 1.10 V vs Li^+/Li.

All the carbon films obtained in this study were in the sp^2 state, though the surfaces of the films were partially in the sp^3 hybridized state due to oxidation by air.

Acknowledgments

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