

Enhancement of Li doping/undoping reaction rate of carbonaceous materials by coating with an evaporated metal film

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Abstract

A novel method for enhancing the charge/discharge rate of the graphite anode of Li-ion batteries has been developed. The method involves covering the surface of the carbon material with a film of an appropriate metal. Simple vacuum evaporation was found to be effective in covering the entire surface of a carbon fiber sample. The metals examined were Ag, Au, Bi, In, Pb, Pd, Sn and Zn. All the metals exhibited a more or less rate-enhancing effect, but Ag, Sn and Zn were the most effective. The effect was dependent on the film thickness. The effects of heat-treatment were also studied with an eye toward obtaining a stable cycleability. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The production amount of Li-ion secondary batteries is still increasing rapidly because of their superior performance in satisfying the demands of various handy electronic appliances. The high rate charge/discharge cycleability, however, is not sufficient as compared to that of Ni–Cd or Ni–MH batteries. Since future appliances will require more power, improved high rate performances are required. The limitation in the high rate performance of the present Li-ion batteries is considered to be due to the insufficient electrochemical reaction rate of the active materials, especially due to that of the anode material of carbon.

Attention has been paid to the surface condition of the carbon anode with respect to the reaction rate and an improvement of the surface condition has been undertaken by heat-treatment and related technologies [1–4]. An example of an effective method is mild oxidation where surface contamination or a reaction-retarding layer is burned off, resulting in the exposure of a preferable reactive surface [2,3]. However, the newly-formed surface is still the surface of carbon so that the SEI formed on the mild oxidation-treated surface is believed to be not so different from that formed on an untreated surface.

In the present paper, we would like to report a novel method involving covering the carbon surface entirely with an evaporated metal film on which a different type of SEI is proposed to be formed [5]. Since this is a newly discovered method, no sound methodology has been established yet. However, we have accumulated some experimental results and in this paper we would like to disclose the most advanced results together with an issue to be solved.

2. Experimental

2.1. Carbon fiber materials

Two types of a pitch-based mesophase carbon fiber felt (Melblon, produced by Petoca) were examined: a fiber heat-treated at 950°C having a disordered structure, and a fiber heat-treated at 3100°C having a well-graphitized structure. Both of the samples were heated at 150°C in vacuo for 5 h in order to remove the physisorbed water and contaminants, and used as a pristine sample. The fiber felt was cut into pieces 2 mm thick and 1 × 1 cm² and sandwiched between two sheets of a 50 mesh Ni grid or a Ni expanded metal. The rims of the sheets were spot-welded at several points to maintain a good electrical contact. A Ni wire was spot-welded on one sheet of the Ni

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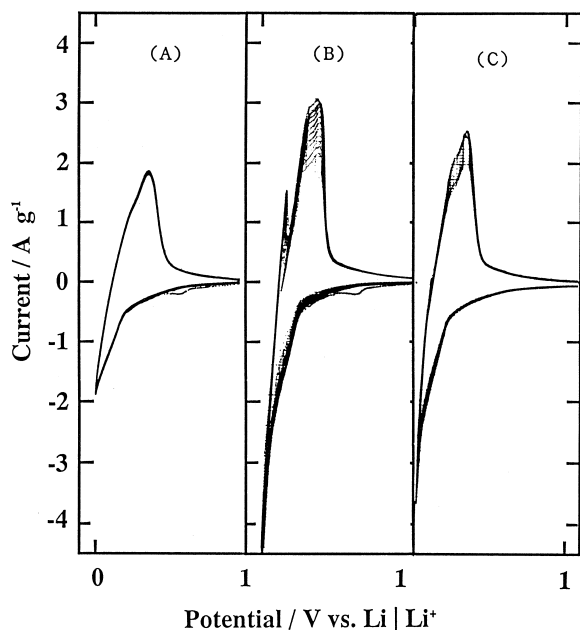


Fig. 1. Cyclic voltammograms of a graphitized carbon fiber with and without an evaporated Pd film in EC/DMC containing 1 M LiClO₄. The repeated CV curves were obtained with a voltage scan rate of 1 mV/s. (A) Bare carbon fiber; (B) covered with a 150 Å-thick Pd film; (C) covered with a 500 Å-thick Pd film.

grid or expanded metal in advance, which was used as a lead wire.

2.2. Metal film evaporation

Several pieces of 2 × 2 cm sample sheets of 2 mm thickness were mounted in a vacuum evaporation chamber, evacuated to 10⁻⁸ Torr for 5 h. The source of metal contained in a tungsten crucible was melted using a tungsten wire heater, and then the metal was allowed to evaporate on the carbon surface at an ambient temperature. The evaporation rate and the thickness of the film were controlled by adjusting the supplying power to the heater and by monitoring the change in the thickness of the deposit with a quartz crystal micro balance mounted in the chamber near the sample holder. In order to facilitate the homogeneous distribution of the metal film thickness, the carbon felt sample in the chamber was rotated so as to expose both sides of the felt face equally to the evaporation crucible during the evaporation.

2.3. Electrochemical measurements

A cylindrical Pyrex glass cell (35 mm outer diameter) with a three-electrode system was used for obtaining the linear sweep cyclic voltammograms (CV) and constant current charge/discharge characteristics. The CVs were recorded repeatedly with a 20-cycles voltage scan with a Hokuto-Denko Potentiogalvanostat. Pure metallic Li foils

were used as reference and counter electrodes. A solvent of propylene carbonate (PC), a mixture of PC and ethylene carbonate (EC) (1:1 v/v), or a mixture of EC and dimethyl carbonate (DMC) (1:1 v/v), all of which contained 1 M LiClO₄, was used as the electrolyte. All the measurements were conducted in a glove box containing dry argon at room temperature. SEM pictures were obtained with a JEOL JSM 5200 S.E. Microscope and X-ray diffraction (XRD) patterns were measured with a Rigakudenki RINT 2200 Diffractometer.

3. Results and discussion

3.1. Comparison of the effects of precious metals

The criterion of choosing the metal for evaporation was based on (1) Li can be absorbed in the metal by forming a Li alloy, and (2) the metal should be soft to facilitate Li movement inside the metal. We presumed that the Li taken into the metal from the electrolyte through a Li doping reaction could be incorporated into carbon by moving across the metal/carbon interface. A metal which cannot form a Li alloy was supposed to be difficult for assisting

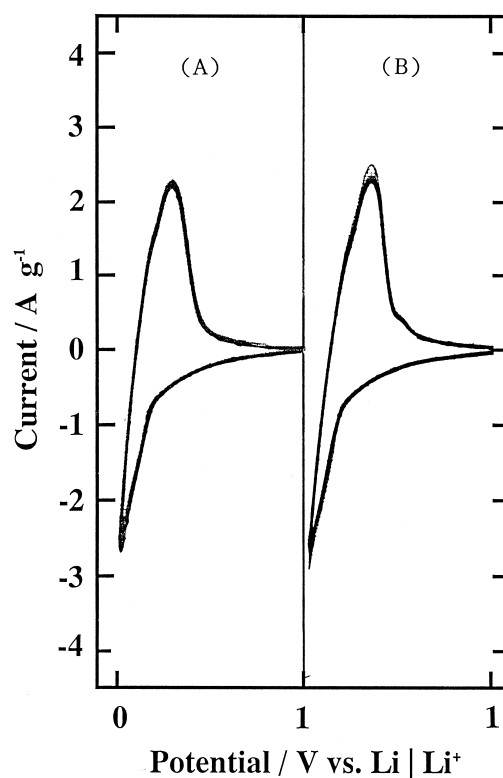


Fig. 2. Cyclic voltammograms of a graphitized carbon fiber with an evaporated Au film in EC/DMC containing 1 M LiClO₄. The repeated CV curves were obtained with a voltage scan rate of 1 mV/s. (A) Covered with a 150 Å thick Au film; (B) covered with a 300 Å thick Au film.

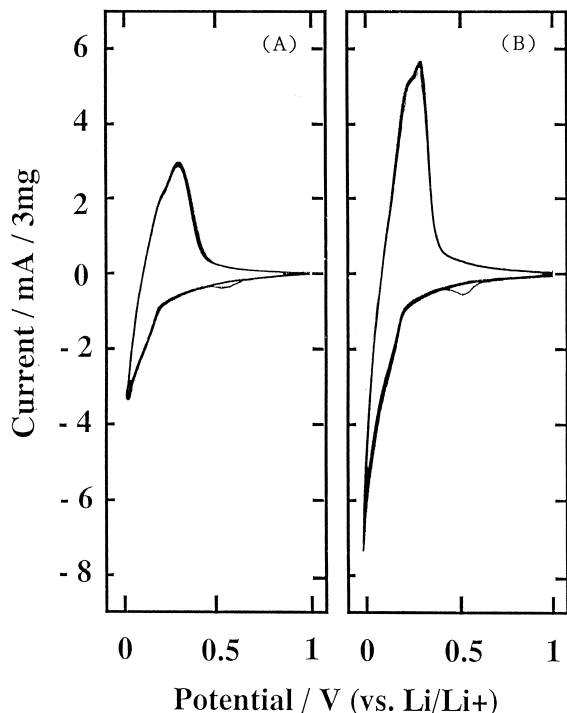


Fig. 3. Cyclic voltammograms of a graphitized carbon fiber with and without an evaporated Ag film in EC/DMC containing 1 M LiClO₄. The repeated CV curves were obtained with a voltage scan rate of 1 mV/s. (A) Bare carbon fiber; (B) covered with a 400 Å-thick Ag film.

an enhancement of the charge/discharge rate because of inadequate Li activity in the metal. In addition, in a metal which has a poor affinity with Li, the diffusion rate of Li was supposed to be slow. Since Au, Ag, and Pd are chemically very stable and can form Li alloys, they were expected to give hopeful results. Concerning the SEI, however, it was difficult to predict what types of chemical entities are formed on the surface of the metal selected.

An example will be shown first for Pd. Due to its high affinity for Li, Pd was expected to give markedly positive results. The CVs obtained were in accordance with the expectation, as shown in Fig. 1, where the CVs are compared for carbon with and without a Pd evaporated film. As shown in Fig. 1(B) for the sample covered with a 150 Å-thick Pd film, the anodic peak due to the deintercalation of Li from carbon is obviously enhanced, accompanied by a splitting of the peak into two sub peaks, showing that the intercalation rate is enhanced significantly. The enhanced peak in Fig. 1(B), however, depressed progressively during the charge/discharge cycles. This may be due to the gradual deterioration of the film structure caused by the repeated crystal form change by the alloy formation and disappearance during the repetition of Li intercalation and deintercalation. Such a diminution was suppressed when the film thickness was increased up to 500 Å as seen in Fig. 1(C). Rapid peak depression was recognized also in a study with a single fiber [6].

The study with a Pd film suggested that a softer metal may exhibit a better cycle performance. The movement of Li in metal is presumably easy in a soft metal. Au was chosen as a candidate, which was expected to give better results. The results are shown in Fig. 2(A) which exhibits much improved characteristics. The enhanced peak height increased with increasing film thickness, but the cycle stability was reversed; an example is shown in Fig. 2(B). The degeneration of the peak was ascertained by XRD to be due to a rigid alloy formation.

In contrast to Au, Ag gave a very hopeful result as is shown in Fig. 3, where no progressive suppression of the peak is seen [7]. With a 400 Å thick film, the most improved performance was observed. As in the case of Au, a too thick film gave rather poor results, implying that the movement of Li in Ag is presumably not fast enough. This was ascertained by measuring CVs with an Ag film evaporated on a Ni plate, where the CVs were measured with a varied voltage scan rate.

3.2. Comparison of the effect of Sn, Pb, and Zn

An important issue in the case of Ag, Au, and Pd is their unrealistic price in accordance with practical use. In an attempt to apply the present method to practical use, we surveyed cheaper metals. Based on the knowledge accumu-

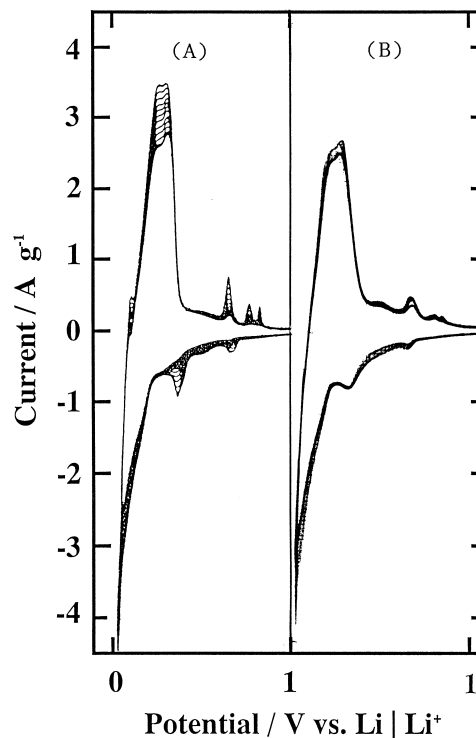


Fig. 4. Cyclic voltammograms of a graphitized carbon fiber with a 150 Å thick Sn film in EC/DMC containing 1 M LiClO₄. The repeated CV curves were obtained with a voltage scan rate of 1 mV/s. (A) Without heat-treatment; (B) the sample fiber was heated at 250°C for 30 min and offered to the CV measurement.

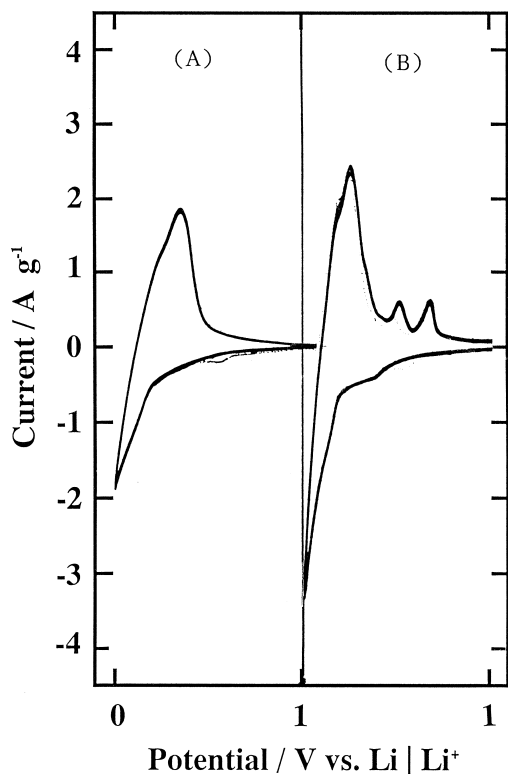


Fig. 5. Cyclic voltammograms of a graphitized carbon fiber with and without an evaporated Zn film in EC/DMC containing 1 M LiClO_4 . The repeated CV curves were obtained with a voltage scan rate of 1 mV/s. (A) Bare carbon fiber; (B) covered with a 300 Å-thick Zn film.

lated with precious metals, we selected Pb, Sn, and Zn as candidates.

In the case of Pb, a carbon fiber covered with a 300 Å-thick Pb layer was investigated. The peak enhancement was obvious, but the diminution of the peak height was significant. Such a rapid progressive peak depression appeared to be inherent to this metal because it could not be suppressed even by varying the film thickness.

In the case of Sn, however, promising results were obtained after heat treatment. As shown in Fig. 4(A), a significant increase in the peak height could be seen for a 100-Å thick Sn film, but unfortunately, the peak height progressively decreased. The significant peak enhancement and splitting imply that a Sn film is quite effective in enhancing the reaction rate. Several small spike peaks newly formed on both the cathodic and anodic branch were attributed to the doping/undoping of Li in Sn, which was ascertained by comparing with the CVs of a Sn film evaporated on a Ni plate.

We attempted to suppress the peak depression by annealing the film. Sn is easy to be melted (m.p. 231.8°C). A Sn film-covered sample was annealed at a temperature slightly higher than the melting point for 30 min and then used in the CV test. As shown in Fig. 4(B) the depression was decreased by the treatment. A more effective method

is to make the covering film amorphous by oxidizing the evaporated Sn through mild oxidation followed by electrochemical reduction. These results will be shown elsewhere [5].

Zn was found to give a stable enhancing effect without any after-treatment. An example is shown in Fig. 5. Even in the absence of peak splitting, the peak is significantly high and stable during the cycling as seen in the figure. In summary, Sn and Zn are considered to be hopeful candidates for practical use.

3.3. Behavior of In and Bi

Bi and In are more expensive than Sn and Zn, but are still interesting because of their softness which is considered to play an important role in the enhancing effect. When we applied In on a graphitized carbon fiber, the Li undoping peak height was substantially emphasized, but progressive peak depression was observed as seen in Fig. 6(A). Since In gives rise to an amorphous oxide, we attempted to make it amorphous by the same procedure described in the case of Sn. The treatment was found to be quite effective in stabilizing the peak, the results being shown in Fig. 6(B). A deep negative current peak at about 0.7 V is ascribed to the reduction of oxidized In. Small

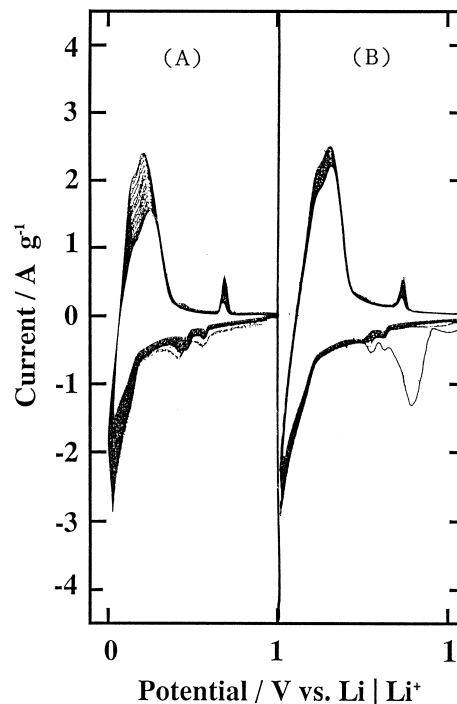


Fig. 6. Cyclic voltammograms of a graphitized carbon fiber with a 200 Å thick In film in EC/DMC containing 1 M LiClO_4 . The repeated CV curves were obtained with a voltage scan rate of 1 mV/s. (A) Without heat-treatment; (B) the sample fiber was heated at 400°C for 10 min and used for the CV measurement.

additional peaks appearing repeatedly are due to the Li doping/undoping in In.

Similar results were obtained with Bi, where a peak enhancement, progressive peak height depression, and stabilization by mild oxidation were also found.

4. Conclusion

Covering the entire surface of a graphitic carbon fiber with an evaporated metal film has proven to be a promising technique for improving the charge/discharge reaction rate to a great extent. The most reasonable explanation of the effect is that a new SEI is formed on the metal surface, which helps the electrochemical reaction to proceed.

Since a zinc metal film capacitor is mass produced by vacuum evaporation on an insulating film, vacuum evaporation of a metal such as Zn or Sn is considered to have practical significance. Evaporation on a powder material is to be investigated for commercialization. A constant current cycle test with an actual type of the electrode is necessary as a next stage. Evaporation of a corresponding oxide is also attractive. We are now undertaking the study of oxide evaporation.

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