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Effect of boron doped fullerene C_{60} film coating on the electrochemical characteristics of silicon thin film anodes for lithium secondary batteries

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ABSTRACT

In this work, boron doped fullerene (B:C_{60}) films were prepared by the radio frequency plasma assisted thermal evaporation technique for use as a coating material for the silicon thin film anode in lithium secondary batteries. Raman and XPS analyses revealed that the boron atoms were well inserted into the fullerene film lattices. The effect of the B:C_{60} film on the electrochemical characteristics of the silicon thin film was studied by charge–discharge tests, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The B:C_{60} coated silicon film exhibited a high reversible capacity of more than 1200 mAh g^{-1} when cycled 50 times between 0 and 2 V at a current density of 1200 μA cm^{-2} (1.5 C). The film also showed good rate capacity at different current densities and a more improved coulombic efficiency of 87.7% in the first cycle in comparison with that of the C_{60} coated film electrode.

1. Introduction

Fullerene C_{60}, as one allotrope of carbon, constitutes a versatile class of molecules, due to its special characteristics related to the practice of doping [1,2]. Doping C_{60} with impurity atoms has an effect on the electronic structure of the fullerene C_{60} cages and, as a result, it is a promising material for electronic applications. One of the most widely used doping atoms for fullerenes is boron, since it can form a stable structure with them [3,4]. The structural and optical properties of boron doped fullerene C_{60} (B:C_{60}) thin films have been studied by several researchers [5,6]. Theoretically, boron can improve the conductivity of carbon materials, since it lowers their Fermi energy level [7,8], however, no practical applications of B-doped C_{60} (B:C_{60}) have yet been found.

As an anode material for lithium secondary batteries, silicon can be a suitable candidate, since it can store more lithium and deliver a higher theoretical capacity of 4200 mAh g^{-1}, as compared with that of graphite carbon with a theoretical capacity of 372 mAh g^{-1} [9]. However, it is well known that silicon based anodes suffer from severe mechanical disintegration caused by the effect of the huge volume expansion during the alloying/de-alloying reaction with lithium ions, resulting in rapid capacity fading, which certainly limits their application [10]. Another issue is the low electrical conductivity of silicon based materials which affects their rate capability at high current density [11,12]. It is well known that the rate capability of electrodes is highly dependent on the kinetic property of Li-ion transport at the electrode/electrolyte interphase [13,14].

One promising way to improve the electrochemical performance of silicon anodes is to cover their surface with a carbon coating layer which is more conductive and can facilitate the Li-ion transport, hence the Li-ion kinetic property can be improved [15–17]. Previously, it has been reported that the electrochemical performances of silicon film anodes were enhanced by coating their surface with C_{60} films as carbon sources using plasma assisted evaporation technique [18,19]. Under the excitation to the generated plasma process, the C_{60} molecules can be cross-linked each other to form some kind of polymeric phase and this new structure of C_{60} greatly affects its electrical property [20]. This unique property of plasma deposited C_{60} thin film cannot be found in the other form of carbon such as graphite or diamond [21]. By adjusting the appropriate process parameter in the plasma assisted deposition process, the structural and electrical property of C_{60} films especially its conductivity can be controlled, as reported in our previous work [18,22].

In the present work, we evaluated the use of a boron doped C_{60} (B:C_{60}) film as a coating material for silicon film anodes in lithium secondary batteries. The effect of the surface modification using B:C_{60} coating layer on the electrochemical characteristics of silicon

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thin film anodes was investigated in comparison with those of bare silicon anodes and C_{60} coated anodes. Our expectation is that the B:C_{60} coating layer can modify the kinetic property of the Li-ions transfer at the electrode/electrolyte interface, which is the main factor determining the electrochemical performances.

2. Experimental

2.1. Thin film deposition

Two sequential thin film deposition processes were carried out in the experiments. Firstly, silicon thin films were prepared by radio frequency plasma enhanced chemical vapor deposition (rf-PECVD) on to 20 μm copper substrates. The CVD chamber was evacuated using a turbo pump, reaching a base pressure of 10^{-5} Torr. The flow rates of argon as a carrier gas (30 sccm) and silane as a precursor gas (10 sccm) were adjusted by a mass flow controller (MFC), allowing a working pressure of 8.0×10^{-2} Torr to be obtained. The substrate temperature and deposition time were then set at 150 °C and 30 min, respectively.

In the second deposition process, B:C_{60} films were deposited onto the silicon thin film by a radio frequency (rf) – plasma assisted thermal evaporation technique. The C_{60} powder used as an evaporation source was placed in a tungsten boat put in the center of the deposition chamber. The deposition chamber was operated at a base pressure of 1.0×10^{-5} Torr by a rotary pump. After heating the C_{60} powder inside the boat, the feeding gas (argon gas containing 1 vol.% B_2H_6) entered the chamber and formed a mixture gas with the evaporated C_{60}. During the deposition of the thin film, the working pressure was 2.5×10^{-5} Torr and various plasma powers of 50, 100 and 200 W were used to control the boron doping concentration. The substrate temperature was adjusted to a constant value of 150 °C and the films were deposited for 20 min. From the cross sectional SEM image the thickness of Si film was estimated about 300 nm. For the comparison study, un-doped C_{60} thin film was also coated onto the silicon film anodes under the same process conditions as those used for the deposition of the B:C_{60} film.

2.2. Structural and electrochemical characteristics

The structural characteristics of the films were examined by Raman spectroscopy and X-ray photo electron spectroscopy (XPS). The Raman measurements were collected using a Nicolet Almega XR Dispersive Raman Spectrometer (Thermo Electron Corporation, USA) with the 633 nm line of an Ar laser. The XPS data were measured by a VG Scientific ESCALAB 200R. The electrical conductivity of the film samples was estimated by Hall measurements. The electrochemical characteristics of the B:C_{60} coated silicon thin films were examined using half cells, which were fabricated by placing a polyethylene separator between the fullerene coated silicon thin films used as a working electrode and the lithium metal used as a counter electrode. The liquid electrolyte was 1 M $LiPF_6$ in ethylene carbonate, ethyl methyl carbonate and dimethyl carbonate (1:1:1 volume ratio). The half cells (2 cm × 2 cm) were then sealed in a polyethylene bag. All the cells were fabricated in a dry room (maximum moisture content of less than 5%). The charge–discharge tests were conducted at current densities of 100, 300, 600, 900 and 1200 μA cm^{-2} (ca. 0.3 C, 0.6 C, 0.9 C, 1.2 C and 1.5 C) with a cut off voltage of 0–2 V versus Li/Li^+ using MACCOR battery tester series 4000 at room temperature. For the determination of specific capacity of the thin film electrodes, the weights of material were calculated as follows:

$$C = \frac{Q}{A \times [(d_1 \times \rho_1) + (d_2 \times \rho_2)]},$$

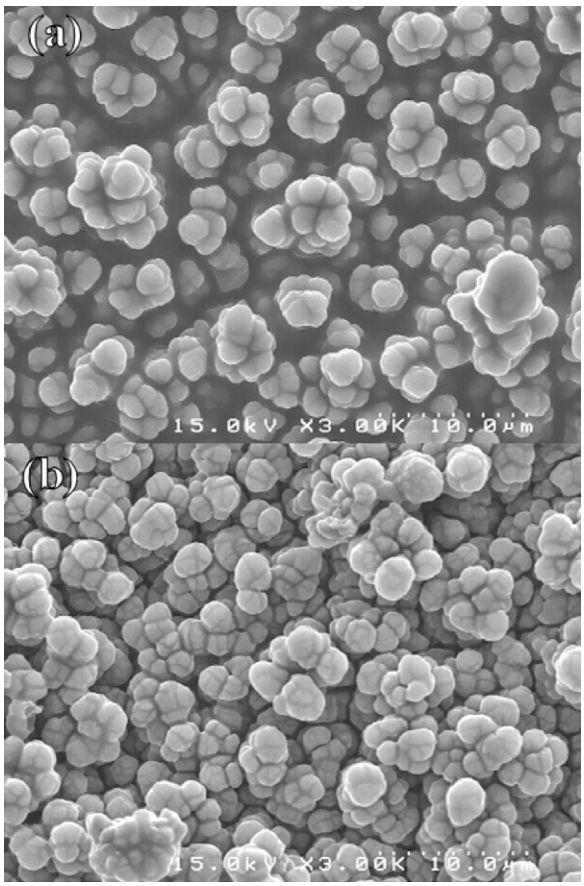

Fig. 1. SEM image of B:C_{60} films deposited at plasma powers of (a) 50 and (b) 200 W.

where C (in mAh g^{-1}) is the specific capacity, Q (in mAh) is the capacity which obtained from the MACCOR battery tester, A is the area of thin film electrode (4 cm^2 in this work), d_1 is the thickness of Si film (300 nm as estimated by SEM image), ρ_1 is the density of Si film (2.33 g cm^{-3}), d_2 is the thickness of C_{60} coating film (100 nm as estimated by SEM image), ρ_2 is the density of C_{60} film (1.6 g cm^{-3}). From this procedure, the average total mass density mass per square area of thin film materials was about 0.1 mg cm^{-2} in which the mass density of silicon was 0.08 mg cm^{-2} and the rest was the C_{60} film.

The half cells were also tested by electrochemical impedance spectroscopy (EIS) using a Zahner IM 6 with an amplitude of 5 mV and a frequency range between 0.01 Hz and 10^6 Hz. The impedance data were then fitted with a simple equivalent circuit using the commercial software, Zview. Cyclic voltammetry (CV) measurements were done in the range of 0–2 V at scanning rates of 0.02, 0.03, 0.04, 0.06 and 0.08 mV s^{-1}.

3. Results and discussion

3.1. Structural characteristics of B:C_{60} thin film

. 1 shows the SEM images of the as-deposited B:C_{60} thin film. It can be seen that the B:C_{60} thin films deposited at plasma powers of both 50 and 200 W have a rough surface, as shown in Fig. 1a and b, respectively. However, the morphology of the B:C_{60} film deposited at a plasma power of 50 W is rather different from that of the 200 W-sample; its surface is less dense with bigger gaps between the granules. These morphology differences between the two samples may be related to the different boron concentrations on their surface, as will be shown by the XPS analysis. From the cross sec-