

## Carbon anode thin films for lithium batteries



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### ABSTRACT

This paper describes a simple method to create carbon anode films for potential applications to the research field of lithium batteries. Carbon films were prepared using DC magnetron sputtering with post-annealing process in the range from room temperature (RT) to 700 °C. Half cells assembled with lithium foils as the counter electrode and 1 M LiPF<sub>6</sub> in EC:DMC (1:1 v/v) electrolytic solution was used to evaluate the discharging capacity of prepared anode thin films. We showed that carbon film deposited at RT can be more suitable for an anode material than that of higher temperature annealed films above 400 °C. A variety of analysis methods including X-ray diffraction spectrometry (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were utilized to evaluate the defect density of the films; for example, the more defects on the film were identified when the carbon film was treated at a low temperature such as RT. It is envisioned that DC magnetron-sputtering with optimized process conditions can be useful for fabricating carbon based film anodes.

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### 1. Introduction

Much attention has been paid to the lithium rechargeable ion batteries (LIBs), which have great utilization for application in mobile IT device due to their advantages of high energy density, moderate rate capability, and long cycle life [1–4]. Furthermore, rechargeable solid state lithium batteries are considered to be a next generation power source due to guaranteed safety properties. Inorganic solid electrolytes can be classified as oxide and sulfide based systems. However, recently oxide based systems such as garnet structure are regarded as more promising one because of easy handling and adoption of lithium metal anode, although it shows relatively low ionic conductivity [5]. Lithium metal, which is originally used as anode materials for its highest specific capacity (3.86 Ah/g) and good cyclability, needs special packaging layer to protect it from moisture in atmospheric conditions. One of simple packaging methods is to encapsulate the lithium using metal coated pouch by special adhesives; however, this method cannot

perfectly prevent side-attack of moisture through the polymer based adhesives. A more advanced packaging includes the use of the organic/inorganic multi-layers as a protective coating material. However a perfect sealing using this method is also difficult, since it cannot often fully cover the large particles, pin-holes or hill locks. Thus, it is necessary to find alternative materials for substituting conventional lithium anode. Although tin based composites have drawn attraction for alternative anode materials, however it is also required to overcome cyclability and initial irreversible capacity issues [6–9]. Carbon can reversibly intercalate or de-intercalate lithium ions without significant swelling under prolonged cycling unlike other lithium metal alloys, which show several hundred percents of volume expansions. It can deliver many advantages, including no dendrite formation, process compatibility and relatively low packaging regulations [10–12]. Carbon is refractory and hardly vaporized material condensing in amorphous state (at low substrate temperature), and its anode properties depend on the condensation conditions. There are many approaches for carbon coating, but the carbon properties are mainly depend on the ratio of  $sp^2$  and  $sp^3$ , caused by deposition methods and process parameters [13–16]. Especially, there are few reports of the carbon thin film for study of anode application in lithium batteries and also controversial issues on the use of carbon film fabricated using DC

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magnetron sputtering by variation of substrate temperature for real adaptation [17]. In this paper, we demonstrate a simple fabrication method for anodic carbon films using DC magnetron sputtering method with variation of chamber pressure and post-annealing temperatures. The film structure was analyzed using XPS, Raman and XRD as well as charge/discharge performance and the results were also compared to those of previously reported works.

## 2. Experimental

### 2.1. Fabrication of carbon thin films

Ti (300 nm) and Pt (250 nm) were consecutively deposited by direct current (DC) sputtering method onto ceramic substrates in a vacuum chamber, in which platinum functions as a current collector, and the titanium as an adhesive layer. The substrate was wet-cleaned to remove the surface contaminations. Before deposition, the vacuum chamber was evacuated to a base pressure of  $6 \times 10^{-4}$  Pa. Carbon films were also DC-magnetron-sputtered onto a current collector with an applied power of 130 W using a 3 inch graphite target with a round shape. The electrode area was a  $1 \text{ cm}^2$  and total film thickness was controlled to 1 micrometer. Argon gas (purity of 5 N) was used as a process gas, and the sputtering pressure was maintained at 0.8 Pa, 1.33 Pa and 2.13 Pa, respectively. The obtained carbon films were heat-treated at 400 °C and 700 °C under Ar atmosphere and their performance were compared to that of room temperature condition.

### 2.2. Electrochemical analysis

For the electrochemical measurements of carbon anode films, half cells were assembled with lithium foils (Battery grade) as the counter electrode and 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC) : diethyl carbonate (DMC) (1:1 v/v) electrolytic solution. All cells were assembled in the dry-room below  $-60$  °C of the dew point and cycled at  $4 \mu\text{A}$  constant current in the range from 2 V to 0 V vs.  $\text{Li/Li}^+$  using galvanostat apparatus.

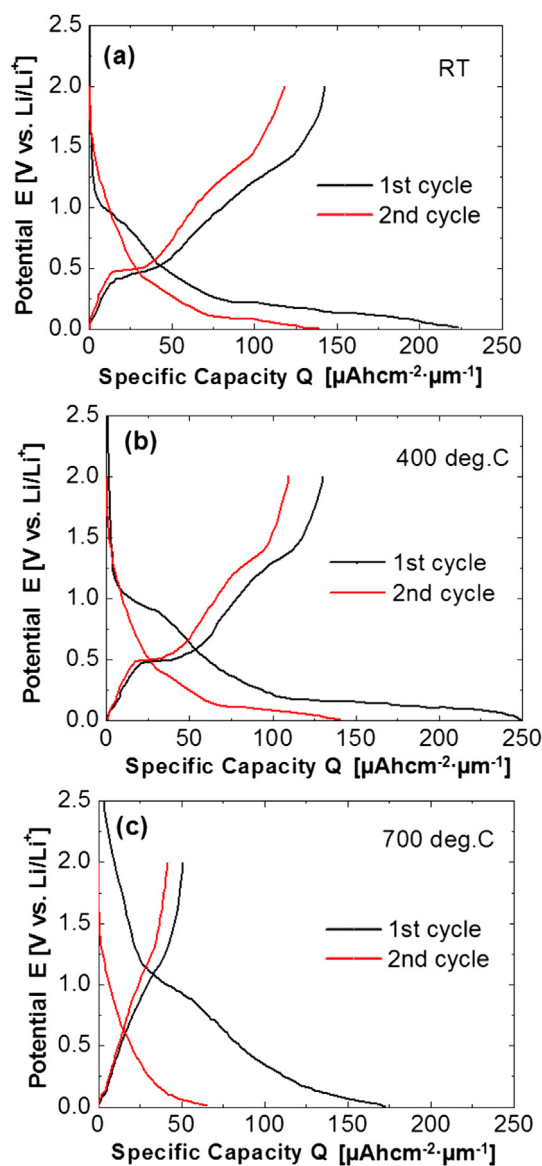
### 2.3. Spectroscopic analysis

The film texture was analyzed by x-ray diffraction spectrometer (XRD, RINT/DMAS-2500, Rigaku). X-ray photoelectron spectra (XPS, ESCALAB 220i-XL, VG scientific instrument) were obtained to characterize chemical states of carbon films with monochromatic Al  $K\alpha$  irradiation. Raman spectroscopy measurements were performed in a backscattering geometry with a JY LabRam HR fitted with a liquid nitrogen cooled CCD detector.

## 3. Results and discussion

### 3.1. Electrochemical tests of carbon anode films

Various half-cells fabricated using different carbon anode films prepared at process pressure of 0.8, 1.33 and 2.13 Pa, respectively, were used for electrochemical tests. However, the half-cells with the carbon film prepared at 2.13 Pa only show reasonable charge/discharge behaviors (see Fig. 1). Charge/discharge profile of the half-cells consisting of three different carbon anodes prepared at a process pressure of 2.13 Pa are presented in Fig. 1(a)–(c) with varying post-annealing at room temperature (RT), 400 °C, and 700 °C, respectively in a furnace. A constant current of  $4 \mu\text{A}$  was also applied within the range from 2 V to 0 V vs.  $\text{Li/Li}^+$ . In the case of the carbon film deposited at RT (Fig. 1(a)), a large plateau could be observed at 1 V vs.  $\text{Li/Li}^+$  during the first discharge, and similar results could also be found for half-cells with carbon films treated



**Fig. 1.** Charge and discharge profiles of carbon films treated at (a) room temperature, (b) 400 °C and (c) 700 °C at 2.13 Pa. The applied current was  $4 \mu\text{A}$  in the range from 2 V to 0 V vs.  $\text{Li/Li}^+$ .

at 400 °C, and 700 °C, respectively. This result is related to the initial irreversible capacity and such phenomenon is generally known to be related to the solid-electrolyte-interface (SEI) at graphitic carbon electrodes [18–20]. For the RT deposited film, a next plateau at 0.23 V vs.  $\text{Li/Li}^+$  could be observed in the discharge profile. For the first charging process of the half-cell with RT deposited carbon film, a first, second and third plateaus could be observed at 0.12, 0.5 and 1.3 V vs.  $\text{Li/Li}^+$ , respectively. The discharge profile at a second cycle showed a gradual decrease in the potential, followed by a plateau at 0.1 V vs.  $\text{Li/Li}^+$ . The charge profile at a second cycle showed analogous shape to that of the first one. These plateaus are described as a co-existence of lithium intercalation/de-intercalation phase transition, however it is estimated that lithium intercalation sites in a carbon layer are randomly exist by the effect of disordered structural change, resulting in not apparent staging phenomena.

The half-cells with RT and 400 °C treated carbon films showed similar charge/discharge profiles. The only difference between both cells were that a longer plateau at a lower potential (0.18 V vs.  $\text{Li/Li}^+$ ) was found in the first discharge profile of the 400 °C annealed

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