

# Electrochemical Characteristics of Diamond-Like Carbon/Cr Double-Layer Coating on Silicon Monoxide-Graphite Composite Anode for Li-Ion Batteries



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## ABSTRACT

The electrochemical behavior of a SiO<sub>x</sub>-graphite composite anode with a diamond-like carbon (DLC)-Cr double-layer coating and employed in a Li-ion secondary cell was studied to determine whether the coating improved the electrochemical characteristics of SiO<sub>x</sub>. The DLC layer was coated through plasma-enhanced chemical vapor deposition, and the Cr layer was formed by physical vapor deposition. The formation of the coating layer was confirmed by transmission electron microscopy, Raman spectroscopy, and electron microprobe analysis. The charge capacity of a coated-anode cell (591 mA·h·g<sup>-1</sup>) was found to be higher than that of a bare-anode cell (517 mA·h·g<sup>-1</sup>) after the 1st cycle. Further, the 50th-cycle capacity retention of the coated-anode cell (83%) was higher than that of the bare-anode cell (59%) at a 0.5 C-rate. The electrochemical characteristics of the coated-anode cell were investigated by impedance analysis, energy-dispersive X-ray spectroscopy, and scanning electron microscopy. Because of good mechanical properties of the DLC-Cr coatings and high electrical conductivity of Cr, double layer coating enhances the electrochemical behavior of SiO<sub>x</sub> as a supplementary coating material.

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## 1. Introduction

Silicon monoxide-based materials are considered as promising alternatives to graphitic ones for use in lithium-ion batteries (LIBs) because of their high specific capacity (2400 mA·h·g<sup>-1</sup>) [1]. Irreversible products such as Li<sub>2</sub>O and Li<sub>4</sub>SiO<sub>4</sub> are formed during the initial lithiation reaction in LIBs, but these products act as buffer materials against the volume expansion of Si, which can expand by up to 400% [1–5].

However, SiO<sub>x</sub> also undergoes a volume expansion of approximately 200% during cycling [3–5]. In order to overcome this problem, SiO<sub>x</sub>-graphite composites have been synthesized that exhibit a capacity as high as 1200 mA·h·g<sup>-1</sup> as well as stable cyclability [6,7]. Although its positive characteristics, SiO<sub>x</sub>-graphite composites has various problems related to them, including an unstable solid-electrolyte interface (SEI) layer and low electrical conductivity as well as volume expansion.

In this study, we coated a diamond-like carbon (DLC)/Cr double layer as an inactive layer on a SiO<sub>x</sub>-graphite composite anode

to enhance the electrochemical behavior of SiO<sub>x</sub> when used as an anodic material. DLC has a metastable structure with amorphous carbon which consists of sp<sup>2</sup>-bonds and sp<sup>3</sup>-bonds, and is used for a wide range of industrial applications such as protective coatings because of its chemical inertness and hardness [8–13]. Further, Cr has high electrical conductivity (~7.9 × 10<sup>6</sup> S·m<sup>-1</sup>), and DLC-Cr coatings are used in a number of applications owing to their mechanical and tribological properties being superior to those of plain DLC coatings [14].

Therefore, it is expected that a DLC-Cr coating layer would have a positive effect on SiO<sub>x</sub> performance owing to the following three factors: 1) the high Young's modulus of the DLC-Cr layer would suppress the volume expansion of SiO<sub>x</sub> during cycling; 2) its high electrical conductivity would enhance the capacity of a SiO<sub>x</sub> electrode; and 3) its chemical stability would induce stable cycling for the electrode. [14–17]. To apply a DLC-Cr layer on a SiO<sub>x</sub> anode, DLC was coated on a SiO<sub>x</sub> electrode by plasma-enhanced chemical vapor deposition (PECVD) and then Cr was coated on the DLC-coated SiO<sub>x</sub> electrode by physical vapor deposition (PVD). In this study, the effect of a DLC-Cr double layer as an inactive layer on a SiO<sub>x</sub> anode was investigated by a cycle test, an impedance test, high-resolution transmission electron microscopy (HRTEM), and scanning electron microscopy (SEM). This paper proved that double layer (Cr-DLC)

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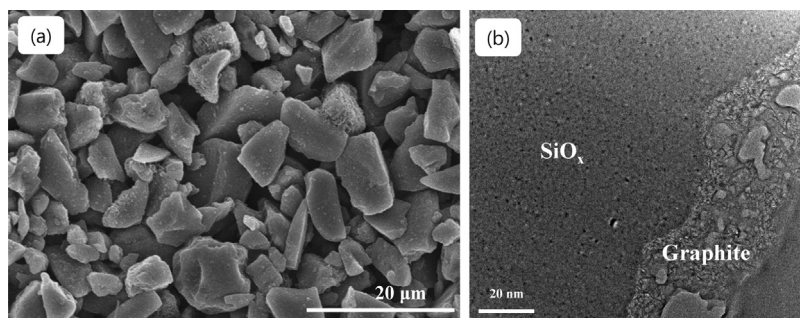


Fig. 1. SEM and TEM images of  $\text{SiO}_x$ -graphite composite powder particles.

enhances the electrochemical behavior of  $\text{SiO}_x$  anode as like (1) stable cycle behavior and (2) superior capacity at high C-rates.

## 2. Experimental

### 2.1. Preparation of the electrodes

The  $\text{SiO}_x$ -graphite composite was fabricated by ball milling a mixture containing the two components in an equal weight ratio for 30 min at 1200 rpm. The components and structure of the composite were identified by high-resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM). Electrodes were fabricated using the mixture, which was made up of 90 wt.% active material and a solution containing 10 wt.% polyvinylidene fluoride (PVDF) in *n*-methyl-2-pyrrolidinone (NMP). The slurry was coated onto a piece of copper foil. After the electrode was dried at 120 °C for 3 h in vacuum, it was compressed by roll-press. Hydrocarbon source gas  $\text{C}_2\text{H}_2$  gas is adopted to form the layer of DLC on the electrodes. PECVD is used to coat DLC layer on the  $\text{SiO}_x$  electrode at 100 °C for 5 min. Next, a layer of Cr was coated on the DLC coated electrode by physical vapor deposition (PVD). The two deposition processes were performed at Dongwoo Surface Tech Co., Ltd, Korea. Raman spectroscopy is used to identify the composition and structure of the DLC layer deposited on the electrodes. The characteristics of the DLC/Cr double layer coated on the  $\text{SiO}_x$ -graphite composite electrodes were investigated using HRTEM and electron microprobe analysis (EPMA).

### 2.2. Test-cell assembly

The cell assembly (CR2032) process was carried out in an Ar-filled box. Lithium cobalt oxide (Samsung SDI, Republic of Korea) was used as the cathode material.  $\text{LiPF}_6$  (1 M) in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume, Techno SemiChem Co. Ltd., Republic of Korea) was used as the electrolyte, and polypropylene was used as the separator. The anode and cathode areas were about 2.01 and 1.54  $\text{cm}^2$ , respectively. The anode area was kept larger than that of cathode for ensuring cell stability. The amounts of anode and cathode used were 3.762 and 27.13  $\text{mg}\cdot\text{cm}^{-2}$ , respectively. After assembling the cell, it was aged for 24 h. The total capacities of the anode and cathode were  $\sim 6.95$  and  $\sim 6.89$  mA, respectively, assuming that the capacities were calculated using the limiting area of the cathode.

The cells were electrochemically tested by galvanostatically charging and discharging them between 2.75 and 4.3 V at a constant current density of 0.5 C (i.e.,  $\sim 2.0$   $\text{mA}\cdot\text{cm}^{-2}$ ). A WBCS 3000 instrument (WonATech Inc., Republic of Korea) was employed for this purpose. The cells were also tested at various C-rates for determining their rate capabilities. Alternating current (AC) impedance measurements were performed over frequencies ranging from

$10^{-2}$  to  $10^5$  Hz by using AC voltage with an amplitude of 5 mV. The measurements were performed using a Solartron SI 1280B potentiostat (TekNet Electronics, USA). The impedance data were then processed using the ZView software (Scribner Associates Inc., USA) and fitted to an equivalent electrical circuit. Energy-dispersive X-ray (EDX) spectroscopy and SEM (S-4300, Hitachi Ltd., Japan) were used to observe the morphologies and compositions, respectively, of the electrodes after cycling.

## 3. Results and discussion

### 3.1. Characterization of DLC-Cr double layer-coated $\text{SiO}_x$ -graphite composite anode

Fig. 1(a) shows SEM images of  $\text{SiO}_x$ -graphite composite powder particles, which were  $\sim 10$   $\mu\text{m}$  in size. Both graphite as well as  $\text{SiO}_x$  can be observed in the cross-sectional TEM image in Fig. 1(b). Fig. 2 shows the Raman spectra of a DLC (or amorphous hydrogenated carbon (a:C:H))-coated anode; the spectra were analyzed by Gaussian-Lorentzian fitting. DLC could be identified on the electrode, with the two main peaks at 1350 and 1582  $\text{cm}^{-1}$  matching the D (disorder) and G (graphite) peaks [18–21], respectively. This proved that the electrode was coated with DLC. It is known that G peak is due to the bond stretching of all pairs of  $\text{sp}^2$  in C=C chains or aromatic rings. On the other hand, the D peak is caused by the breathing mode of the  $\text{sp}^2$  sites in only aromatic rings and not those in C=C chains [19].

Fig. 3 shows a TEM image of the cross-section of a coated  $\text{SiO}_x$ -graphite composite anode prepared using a focused ion beam. The double layer consisting of Cr and DLC as inactive materials can

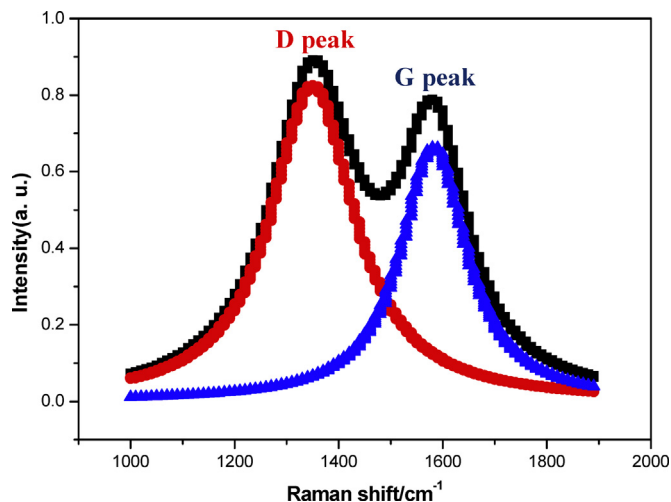


Fig. 2. Raman spectra of a coated  $\text{SiO}_x$ -graphite electrode.

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