Short communication

Electrochemical behavior of a lithium-pre-doped carbon-coated silicon monoxide anode cell

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ABSTRACT

Owing to high energy density, silicon monoxide is an attractive anode material for lithium ion secondary batteries. However, its huge irreversible capacity during initial cycling makes it difficult to use in lithium secondary batteries. A new technique for lithiation in the silicon monoxide has been developed using Li powders. The electrochemical behavior of the lithium powder pre-doped carbon-coated silicon monoxide (OG) anode cell was studied. The cells showed reduced initial irreversibility and enhanced coulombic efficiency. The behavior of the cells was analyzed by X-ray diffraction and electrochemical testing methods.

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1. Introduction

Silicon is one of the most attractive anode materials for lithium ion batteries. The capacity of silicon is theoretically about 4004 mAh g^{-1} [1]. However, often drastic changes in the volume that silicon undergoes during charge–discharge cycles have prevented silicon anodes from being used in lithium ion secondary batteries. To help overcome this problem, various modifications, such as the use of nano-structured silicon anodes, the synthesis of composites with other materials, and the use of carbon coatings, have been suggested [2]. The use of silicon monoxide as an alternative anode material has been proposed because of its large capacity at over 1200 mAh g^{-1}, long cycle-life, and low charge–discharge potential [3–8]. However, it has been shown that a carbon-coated SiO composite still has a huge irreversible capacity of over 45% during the 1st and 2nd cycles [9]. In the case of SiO, the reaction between SiO and lithium is governed by $5SiO + 6Li = Li_2O + Li_4SiO_4 + 4Si$. The first charge results in the formation of nano-sized clusters of amorphous silicon surrounded by lithium oxide and lithium silicate. Unfortunately, the reaction that produces the lithium oxide and lithium silicate is irreversible [10–12]. On the other hand, a method of pre-lithiation using lithium powder was reported by Jarvis et al. [13]. In the present study, a technique for lithiation in the OG using Li emulsified powders has

been developed and the electrochemical behavior and cycle characteristics of Li-deposited carbon-coated SiO composite anodes are investigated. The irreversible capacity of the cell is found to be significantly reduced. The electrochemical properties of the cell are investigated as well.

2. Experiments

A mixture of silicon monoxide (Shinetsu, Japan) and graphite was ball milled in order to carbon coat the surface of the silicon monoxide. Natural graphite (size of 20 μm, spherical type) was mixed with SiO of the same weight ratio. The weight ratio of ball to materials was 5:1 and milled for 30 min at 1200 rpm. The coated layer was identified by HR-TEM (JEM 2100F, JEOL) and EDX. The TEM sample was made by FIB (focused ion beam) ion beam milling method. Platinum and tungsten was coated on the specimen to protect the graphite-coated layer before ion milling.

Electrodes were prepared by casting a slurry containing 90 wt% of the carbon-coated SiO (hereafter referred to as "OG") and 10 wt% of polyvinylidene fluoride (PVDF) as a binder, both dissolved in N-methyl-2-pyrrolidone (NMP), onto a piece of copper foil. The electrodes were then dried under vacuum at 120 °C for 3 h. Lithium powders, synthesized by the droplet emulsion technique (DET), were coated onto the electrodes [14]. The total weight of the lithium powder coating was 0.04 mg. The electrodes were pressurized and soaked in the electrolyte for 24 h to induce the reaction between the lithium and the OG. Next, the samples were heated at 60 °C for
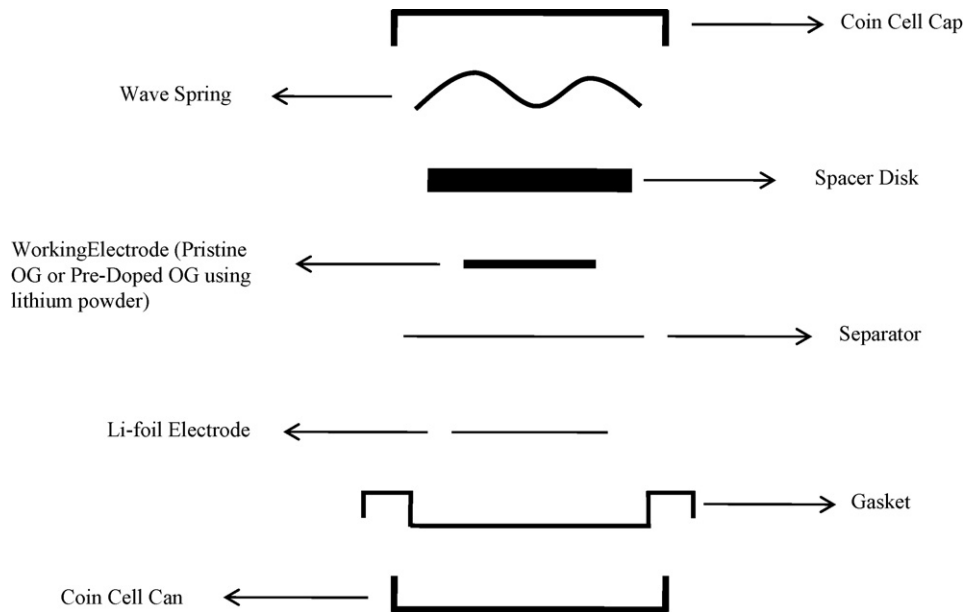
Fig. 1. The schematic diagram of the CR2032 cell specimen.

48 h to stabilize them. Finally, they were washed by DMC to remove any remaining lithium powder and salt.

Coin-type Li-pre-doped OG/Li-foil cells (CR2032) were assembled in an argon-filled glove box. The schematic diagram for the coin cell specimen is shown in Fig. 1. The electrolyte present was 1 M of LiClO$_4$ in a mixture with the ratio of EC:DMC:EMC = 1:1:1 (V:V:V) (Technosemichem, Republic of Korea). Lithium foils were used as the counter and reference electrodes. The rest potential was measured at 25 °C, 12 h after cell fabrication [15]. Electrochemical tests were performed by galvanostatically charging/discharging the cell in the range of 0–2 V, at a constant current density of 0.1 mA cm^{-2}, using a WBCS 3000 instrument (Wanatech Inc. Republic of Korea).

Pristine electrodes without pre-lithiation, electrodes without pre-lithiation but after 10 cycles of charge–discharge, and lithium-pre-doped electrodes prior to cycling were examined and compared with an X-ray diffractometer using Cu K$_\alpha$ radiation. The scan rate was 2° per minute over a 2θ range of 20–80°.

3. Results and discussion

Silicon monoxide was ball milled with graphite to increase electrical conductivity. The coated graphite layer was confirmed by HR-TEM and EDX (Figs. 2 and 3). The graphite layer was coated on the silicon monoxide surface to a thickness of 30–60 nm (Fig. 2). The surface coating of carbon was identified by EDX spectrum 1 (Fig. 3a), while the matrix was Silicon monoxide (Fig. 3b, silicon 51.08 at% and oxygen 48.92 at%). The tungsten peaks represent the protecting material for the specimen preparation.

The assembled cell was aged at 25 °C for 12 h. The rest potential was measured after aging. The average rest potential of the pristine electrodes was found to be 3.15 V (see Table 1). By contrast, the average rest potential of the pre-doped cell was found to be

Table 1
Rest potentials (measured 12 h after cell assembly).

Sample	Pristine SiO–C composite electrode	Pre-doped SiO–C composite electrode
Rest potential (V)	3.15	1.84
Error margin (%)	3.53	9.09

1.84 V. The reduced rest potential value confirms that the lithium had previously been successfully doped into the OG electrode.

The typical X-ray diffraction patterns of the pristine electrodes, the electrodes after 10 cycles, and the pre-doped electrodes are shown in Fig. 4. The diffraction peaks corresponding to the silicon and carbon can be observed in the pattern given for the pristine electrodes (Fig. 4a). By contrast, the peaks due to the lithium silicate and lithium oxide are visible in the diffraction pattern given for the electrodes after 10 cycles (Fig. 4b). The identical peaks can also be observed in the pattern given for the pre-doped but no cycling electrodes (Fig. 4c). XRD patterns, therefore, confirm that lithium silicate and lithium oxide may form in the OG by cycling or by pre-lithiation process. It also confirms that pre-lithiation occurred in the OG by a new technique.

The voltage profiles of the very 1st charge–discharge cycle are shown in Fig. 5. The initial charge and discharge capacities of the pristine electrodes are found to be 1192 mAh g^{-1} and 809 mAh g^{-1}, respectively. The coulombic efficiency is 67.7% for the initial charge–discharge stage (Fig. 5a). The initial capacity of the pre-doped electrodes is higher than that of the pristine electrodes. The charge and discharge capacities of the pre-doped electrodes are
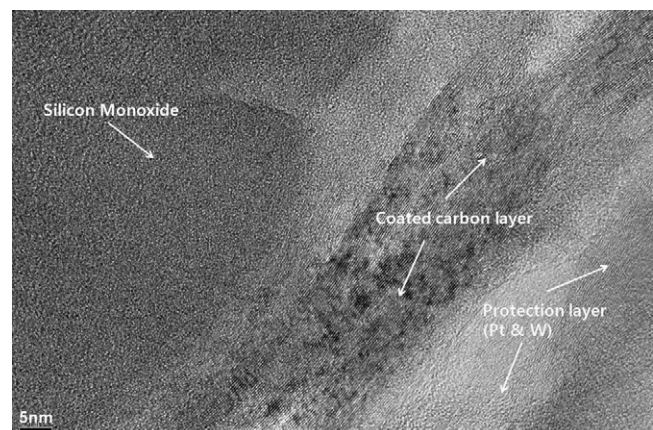

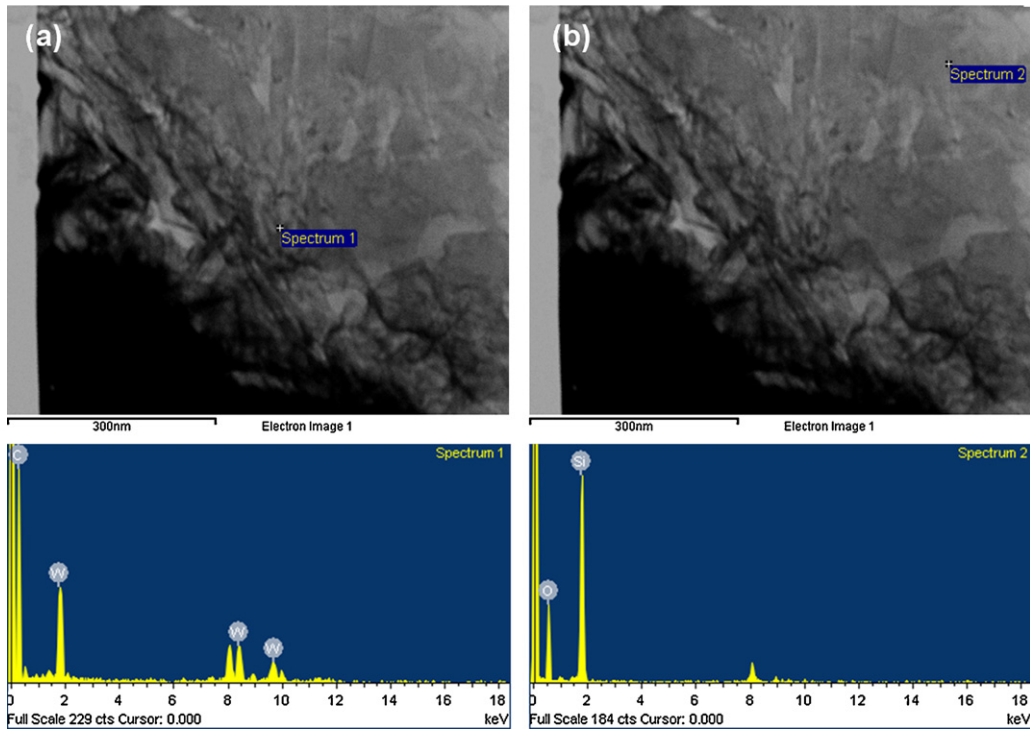**Fig. 2.** HR-TEM image of carbon-coated silicon monoxide.

Fig. 3. EDX analysis of the: (a) carbon-coated layer and (b) silicon monoxide active material.
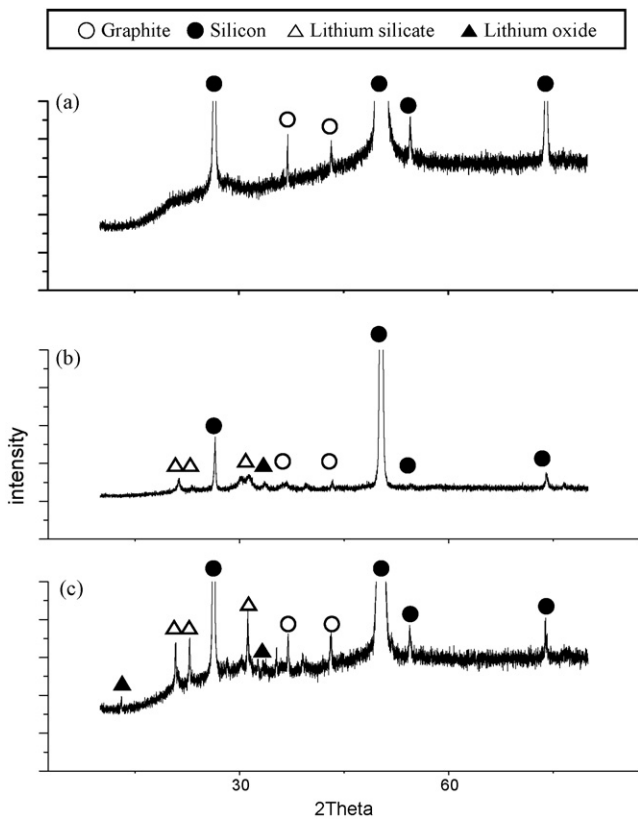

Fig. 4. X-ray diffraction patterns of the: (a) pristine electrode (without lithiation and before cycling), (b) electrode after the 10th charge–discharge (without lithiation and after 10 cycling) and (c) pre-doped electrode (with lithiation sand before cycling).
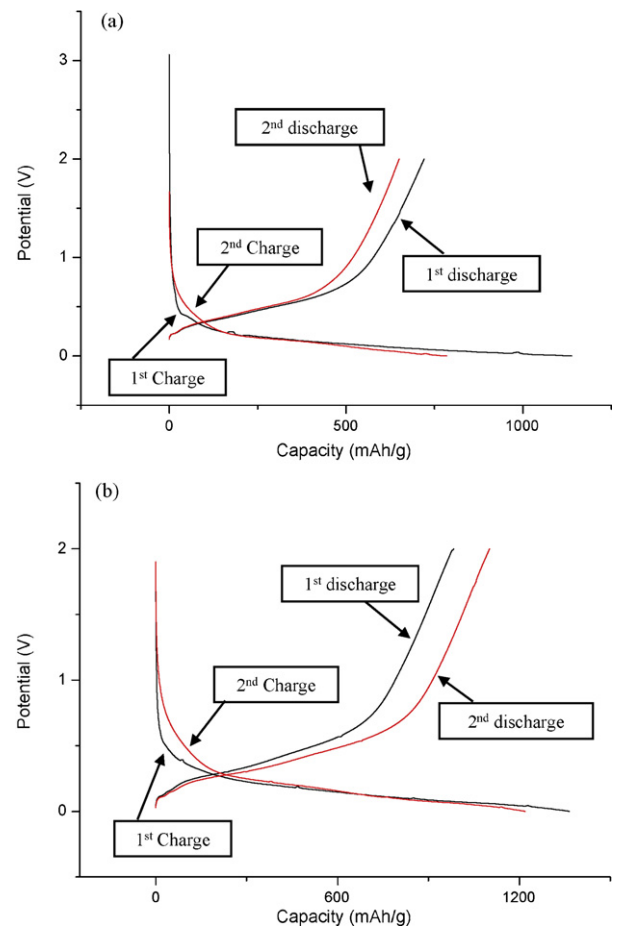

Fig. 5. Voltage profile of the: (a) pristine electrode and (b) pre-doped electrode.
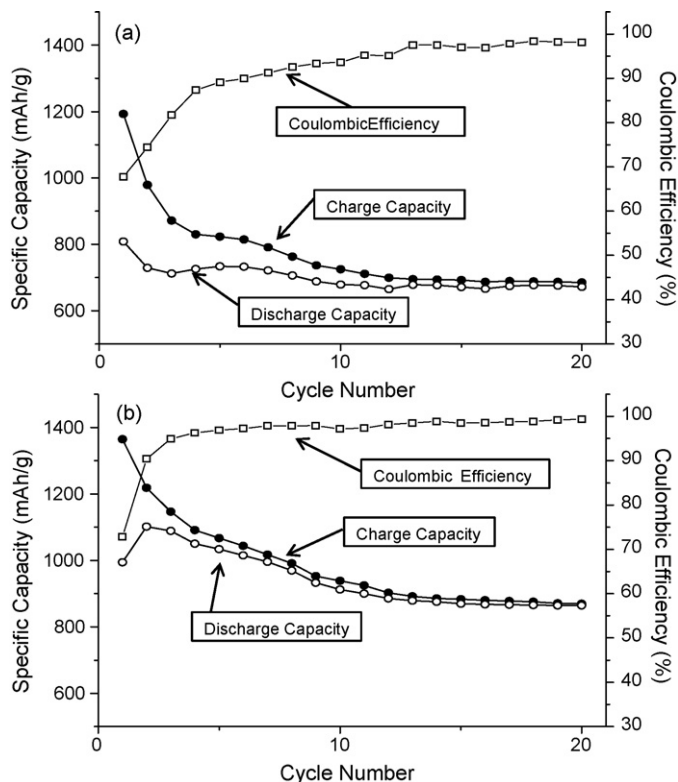
Fig. 6. Specific capacity and coulombic efficiency as a function of cycle number for the: (a) pristine electrode and (b) pre-doped electrode.

1364 mAh g^{-1} and 994 mAh g^{-1}, respectively. The coulombic efficiency of the pre-doped electrodes is 72.8%. A higher coulombic efficiency level found here compared with that of the pristine electrodes (Fig. 5b) suggests that the pre-doped lithium powder had already reacted with the oxide and then had subsequently formed the lithium silicate and lithium oxide. The net result is that the irreversible capacity has decreased by about 5% (in the case of the pristine electrode, the irreversible capacity was 67.7%. However, in the case of the pre-lithiated electrode, the irreversible capacity was 72.8%).

The specific capacity and coulombic efficiency as functions of the number of cycles are given in Fig. 6. The initial coulombic efficiency of the pristine electrodes is 67.7%. After the 9th cycle, the efficiency has increased to 93.4% (Fig. 6a). The coulombic efficiency during the 2nd to 6th cycle interval is under 90%. By contrast, in the case of the pre-doped electrodes, the coulombic efficiency is much higher than that of the pristine electrodes through all cycles (Fig. 6b). While the initial efficiency hovers at 72.8%, it drastically increases to over 90% level just after the 2nd cycle has elapsed. The higher coulombic efficiency can be explained by observing that the irreversible reaction that forms the lithium silicate and lithium oxide has scarcely occurred during the initial charge. This is because most of the lithium silicate and lithium oxide had already formed during the pre-doping treatment. The factors responsible for capacity degradation with cycle-life may result from particle fractures, the loss of electrical contact between the electro-active species and the current-collector, and the loss of electrolytes.

Based on reduced irreversible capacity calculations, nearly 35% of the Li, which is equivalent to 0.54 mAh was used to form Li silicate and Li oxide during pre-doping process. This means that only 0.014 mg out of the initial 0.04 mg of Li was effectively involved in reacting with OG during the first cycle. This amount represents

less than 16% (equivalent to 0.24 mAh, which is in turn equivalent to 0.006 mg) of the lithium involved in the 2nd cycle. This finding means that lithium powder and OG reacted not only during the first cycle but also during the second cycles, with more than 50% of the total lithium initially present being used up by pre-lithiation reaction. Since the main purpose of the present research is to reduce the irreversible reaction through pre-lithiation, the total amount of Li that collects at the cathode is critically important. The efficiency of pre-lithiation process may depend on the reaction conditions. Temperature and reaction time may be the principle processing parameters in this experiment. If a suitable range of reaction temperature and time could be found the efficiency of the pre-lithiation reaction could be increased. Further research is needed to enhance the reaction efficiency. However, the present finding demonstrates that pre-lithiation process by Li powder reduces the irreversible initial capacity and renders support for using OG as a new anode material in high capacity Li rechargeable batteries.

4. Conclusions

A large initial irreversible capacity of the OG can be drastically reduced by a lithium pre-doping method. The pre-doping technique for the OG using Li emulsion powders has been developed. The rest potential of the pre-doped OG cell was found to be 1.84 V, while that of the non-lithiated electrodes was 3.15 V. The lithium silicate and lithium oxide were formed by lithium pre-doping method and identified by XRD patterns. The initial coulombic efficiency of the pre-doped electrodes was found to be higher than that of the pristine electrodes by almost 5% and it was rather increased in the 2nd cycle by almost 16%. About 35% of the lithium was estimated to be reacted with the OG during doping process. It is predicted that increasing the amount of lithium powder used in the pre-doping stage or enhancing lithiation reaction will dramatically improve the irreversible capacity of the OG.

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