A Novel Process to Improve ICE of SiO$_2$@C Composite Anode Materials for the Lithium Ion Batteries

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**Highlights**
- SiO$_2$@C composite was synthesized by simple and cost-effective one-pot synthesis process
- To improve ICE, we have developed a coating technique on the anode electrode surface
- The thickness of the coating layer on the electrode surface can be controlled

1. Introduction

With the widespread use of electric vehicles and renewable energy storage facilities in the Si-based anodes are widely considered in lithium ion batteries because of their large theoretical capacity and low reaction potential of approximately 0.4 V Li/Li$^+$ [1]. However, the initially high capacity of these anodes is drastically reduced by microstructural distortions or disintegrations caused by large volume changes (about 300 times) during the intercalation/deintercalation of lithium ions [2]. To overcome these issues, SiO$_2$ is getting focus due to its high specific capacity (i.e., $\geq$800 mAh g$^{-1}$) and more stable cyclability than Si because of its lower volume expansion resulting from providing SiO$_2$ buffers to restrain huge volume changes of Si [3]. Most approaches (hydrothermal, sol-gel, evaporation technique) they use to synthesize SiO$_2$ required complicated, multi-step and high temperatures processes [4]. Meanwhile, silicon oxide anode materials have a initial high irreversibility, namely poor initial Coulombic efficiency (ICE). The low ICE observed in the first cycle can be attributed to the formation of a solid-electrolyte interphase (SEI) layer triggered by electrolyte decomposition and the irreversible product (Li$_2$SiO$_4$, Li$_2$O). In full cell, the problem affects energy and powder density due to the loss of lithium ions in the cathode. In order to control the ICE, in a general way, most of negative electrode was treated by a simple ex-situ pre-lithiated process. However, this method has been reported to deteriorate the cyclic performance because a strong current flows to the electrode for a short time and damages the electrode surface [5,6].

In this study, we ideally designed SiO$_2$@C composite using a simple and cost-effective one-pot synthesis process based on the mineralization of SiO$_2$ with simultaneous fabrication of multiple carbon matrices. Also, we have developed a coating technique for anode electrode by decomposing the electrolyte to solve poor ICE. This technique enables significant improvements on the electrochemical performances of SiO$_2$@C. At 0.1 A g$^{-1}$, SiO$_2$@C composite delivers a discharge capacity of $\sim$851 mAh g$^{-1}$, and surprisingly, after apply to coating technique for anode electrode, its ICE is exhibited to 92.7%, while bare electrode is 44.2% of the ICE measured at 0.1 A g$^{-1}$. Furthermore, the SiO$_2$@C composite applying coating technique has highly stable cyclability over 600 cycles with a Coulombic efficiency $\sim$98.8%.

2. Methods

The SiO$_2$@C composite was synthesized by modifying our previous study [7]. The as-prepared SiO$_2$@C for the anode electrode was subjected to electrochemical characterization using CR2032 coin-type cells, with a metal lithium foil as the counter electrode. The electrode in the cells was prepared by mixing 70 wt% SiO$_2$@C powder with 20 wt% conductive carbon blacks of Super-P (SP, TIMCAL, Super P Li), 10 wt% Na–CMC (sodium carboxymethyl cellulose, Sigma Aldrich Co.) binder, and appropriate amounts of water to form a uniform slurry. The electrolyte used was a solution of 1.2 M LiPF$_6$ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (3:7 v/v, Panaxetec) containing 3% vinylene carbonate additive. The electrodes were dried in a vacuum oven at 80 °C for 24 h before being transferred into an Ar-filled glove box.
for cell assembly. The coin cells were charged and discharged between 0.01–1.5 V (vs. Li/Li+) by applying a constant current of 100 mA/g and 500 mA/g at 25 °C for electrochemical characterization. To improve the ICE, we designed a module that can simply be shorted using various resistors. In this process, the thickness of the coating layer on the electrode surface can be controlled using time and resistance parameters.

3. Results and discussion

Figure 1a shows the comparison of the specific capacity and ICE of SiOₓ@C composite by coating technique. At the shorting time of 14 h with 500 Ω resistor, the initial charge and discharge capacities are 867 mAh g⁻¹ and 804 mAh g⁻¹, respectively, leading to an optimal ICE of 92.7%. The ICE was significantly increased, which is seen as a result of coating by the electrolyte decomposition on the electrode surface. In Figure 1b, the cyclic performance of the SiOₓ@C composite measured at current density of 0.5 A g⁻¹ was maintained up to 520 mAh g⁻¹ over 600 cycles, and each cycle exceeded 98.8% coulombic efficiency. These data indicated that the coating technique by ideal design of module enables excellent electrochemical performances of SiOₓ that can meet the demands of large-scale applications.

![Figure 1](image.png)

**Figure 1.** (a) Comparison of the specific capacity and ICE depend on coating technique. (b) Cycling performance of SiOₓ@C composites applying coating technique during 600 cycles.

4. Conclusions

In summary, we prepared the ideally designed SiOₓ@C composite using a simple and cost-effective one-pot synthesis process based on the mineralization of SiOₓ with simultaneous fabrication of the multiple carbon matrix. The approach is found to be promising for the cost-efficient fabrication of SiOₓ@C composite anodes. Also, we have developed a coating technique on anode electrode surface by decomposing the electrolyte to solve poor ICE. As a result, the cyclic stability and high capacity of the SiOₓ@C composite was possible by synergetic impact of incorporation of carbon and silicon into the SiO₂ matrix and excellent coating technique on the electrode surface.

References

Keywords
Lithium ion batteries; Anode, Silicon oxide; Coating technique