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Electrochemical behavior of SiO_X@C anode material for lithium-ion battery

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Highlights

- SiOx@C was synthesized by facile solution-reaction.
- Citric acid acts as a chelating agent, and it transformed to carbon after heating.
- SiO_X@C with citric acid showed ~1300 mAh/g of initial discharge capacity.

1. Introduction

With the development of technology from mobile electronic device to energy storage system (ESS), the demand for high-capacity energy storage has been increasing continuously. Currently, carbon-based material has been widely used as the anode of lithium-ion batteries due to their inherent stability. However, due to its low capacity (372 mAh/g, LiC_6), various research have been conducting to find alternative materials. One of the alternative materials is silicon which has high theoretical capacity (~4200 mAh/g, $Li_{22}Si_5$), but its excessive volume expansion up to 400% during charging process prevents practical use.

To solve this problem, SiO_X (Silicon Suboxide, X<2) has been approached for its capacity, cyclic performance, and stability. It has sufficient capacity to replace the carbon-based material, but irreversible product of Li_4SiO_4 is generated. Nevertheless, Li_4SiO_4 plays positive role in suppressing volume change [1].

In previous studies, our group conducted various SiO_X anode experiments, and acquired over 800 mAh/g of initial discharge capacity. For additional capacity enhancement, we focused on the disproportion reaction of SiO_X, increasing heat-treatment temperature to 900°C. Disproportionated SiO_X produces additional nanocrystalline Si on amorphous SiO_X layer, and it gives additional capacity improvement [2]. In addition, citric acid is introduced for chelating agent. Chelation reaction is occurred between $SiCl_4$ and citric acid [3], then reaction between $SiCl_4$ and ethylene glycol proceeds relatively slowly. In this experiment, the effect of citric acid addition were studied through comparison.

2. Methods

13mL of ethylene glycol (99.5%, Samchun Co.) was prepared with a certain amount of citric acid (anhydrous, 99.5%, Daejung Co.), and it was stirred for 7 days at room temperature. Amount of citric acid was determined by weight ratio of $SiCl_4$, which were 1:0.08 (7.4 wt%) and 1:0.1 (9.1 wt%). After that, it was mixed into solution of 50mL benzene (99.5%, Daejung Co.) and 20ml $SiCl_4$ (99%, Wako Co.) to obtain agglomerated white precursor powder. The precursor powder was heat-treated at 900°C for 3 hours in vacuum furnace, then black-brown color SiO_X@C powder was obtained. For comparison, reference sample of SiO_X@C was also synthesized through same route without citric acid.

Electrodes were prepared by mixing 70 wt% of SiO_X@C powder, 20 wt% of Super-P (TIMCAL), 10 wt% Na-CMC (Sigma Aldrich Co.), and an appropriate amount of water added to form a slurry, then they were stored overnight in a vacuum oven at 80°C. During coin cell assembly process, dried slurries were moved to Ar glove box, and 1.2 M $LiPF_6$ in ethylene carbonate(EC), dimethyl carbonate (DMC) (3:7 v/v), and 3% vinyl carbonate (VC) (Panaxetec) was used as the electrolyte.

3. Results and discussion

Figure 1 is initial charge-discharge performance of SiO_X@C, with different amount of citric acid. For electrochemical characterization, the coin cells were charged and discharged between 0.01 and 1.5 V of

potential window, by applying a constant current of 100 mA/g at room temperature. SiO_X@C with 7.4 wt% of citric acid shows 1370.4 mAh/g of initial discharge capacity and 47.8 % of initial coulombic efficiency. SiO_X@C with 9.1 wt% of citric acid shows 1228.3 mAh/g of initial discharge capacity and 46.6 % of initial coulombic efficiency, and SiO_X@C are 1183.5 mAh/g and 47.6%. Addition of 7.4 wt% of citric acid was more contributed to capacity increase.

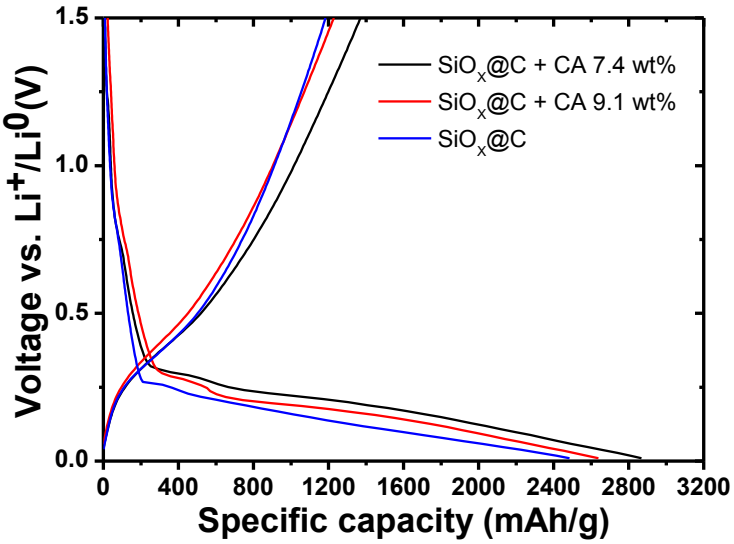

Figure 1. The initial charge-discharge curve of the SiO_X@C

4. Conclusions

In this study, SiO_X@C anode material was synthesized by solution reaction method and heat-treatment of 900°C. All samples showed significant increase of capacity compared to previous experiments, and SiO_X@C added with citric acid by 7.4 wt% showed an initial capacity of 1370.4 mAh/g. These result were achieved by using disproportion reaction of SiO_X, which provide nanocrystalline Si in anode material. Also, introduction of citric acid was successfully applied, contributing to additional capacity enhancement. Nonetheless, low initial reversibility properties have been found, but it seems to be able to improve ICE through additional research.

References

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Keywords
lithium-ion battery; silicon suboxide; anode material