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To cite this article: Haiqing Xiao *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **242** 042014

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Study on the Fading Mechanism of SiO₂-based Anodes Using Styrene Butadiene Rubber and Carboxymethyl Cellulose as Binders for Lithium-ion Batteries

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Abstract. Three kinds of SiO₂-based electrodes and one graphite electrode were fabricated using styrene butadiene rubber (SBR) and carboxymethyl cellulose (CMC) as binders. The cycling results showed that the more amount of SiO₂ in the electrodes was, the faster the capacity of the electrode dropped and the lower coulombic efficiency of the electrode performed. Thus, it was the fading of SiO₂ resulted in the SiO₂-based anodes reversible capacity dropping. In order to analyze the fading mechanism of the SiO₂-based anodes, SiO₂ electrode was done 10% capacity lithiation/delithiation cycling, during which the volume change of the electrode should be negligible. The results showed that the voltage difference between the maximum and minimum values of the SiO₂ anode cell kept increasing, which indicated that the SiO₂ anode fading happened. The SEM images of SiO₂ anodes illustrated that before cycling, the surface of SiO₂ particles were smooth and tidy, and the SiO₂ particles' edge was sharp, while the surface of SiO₂ particles became roughness, the edge was blurry, and there were fewer conductive additives on the SiO₂ particles' surface after cycling, which implied that electronic conductivity of the electrode became worse after cycling. It can be concluded that electronic conductivity played an important role in the electrode. We believe that boosting the electronic conductivity of the SiO₂-based electrode is one of the important methods to improve the cell cycle performance.

1. Introduction

Lithium-ion batteries (LIBs) are currently widely used in consumer electronics such as laptops, mobile phones, medical devices, and electric vehicles (EVs) due to high gravimetric and volumetric energy, high power density, long cycle life, and low self-discharge [1-4]. Though the specific capacity is limited to ca. 372 mAh/g, graphitic carbon is the major anode material in today's LIBs because of its superior cycling stability and very small volume expansion of only 10% during Li uptake/release [5].

Silicon (Si) is expected to be one of the promising anode materials for future high-capacity anodes in LIBs because it theoretically has very high capacity (ca. 4200 mAh/g) [5-10]. However, Si anodes suffer from volume changes of more than 300%, and the mechanical stress leads to the degradation of the Si particles during cycling, resulting in poor cycle stability [5, 11, 12]. Recently, silicon suboxides (SiO) have attracted considerable attention due to their improved cyclability compared to Si. During



cycling and reaction of Li with SiO, formation of irreversible Li oxide and Li silicate after the first cycle decreased the specific capacity and initial coulombic efficiency, but acted as a volume buffer matrix to cyclable Li_xSi which in turn saw improved cycling performance and capacity retention^[4, 13, 14]. Although the volume expansion of SiO upon electrochemical lithiation is certainly suppressed in comparison to silicon, the reported expansion percentage is still close to 200% of the initial volume, and SiO also has capacity fading upon cycling^[13, 15, 16]. Decrease of the particles size or carbon coating can improve the electrochemical reversibility of SiO-based materials^[4, 13, 15-17]. Feng et al.^[13] noted that suitable binders can effectively improve the integrity of the electrode by enabling consistent contact among the active material, the conducting additive, and the current collector. Much more research is needed to understand the electrochemical of SiO-based anodes.

Previous reports showed that water-based binders such as styrene butadiene rubber (SBR) and carboxymethyl cellulose (CMC) effectively improve the cycling stability of silicon electrode^[5, 18-20]. Recently, it was reported that using SBR and CMC to fabricate SiO-based anodes also showed beneficial effect in enhancing capacity retention^[4, 13, 16, 17]. In this study, the electrochemical behavior of SiO-based electrodes using SBR and CMC as binder was investigated.

2. Experimental

2.1 Materials

SBR emulsion (JSR TRD105A, 40.7%, w.t.) is from JSR Corporation, Japan. CMC sodium salt (Aldrich), Mw 250000, D. S. 0.90. The 4% (w.t.) CMC solution was made by dissolving 4 g CMC in 96 g deionized water. Isopropyl alcohol is from Aldrich. The 10% (w.t.) isopropyl alcohol solution was made by mixing 10 g isopropyl alcohol with 90 g deionized water. Conductive carbon black: TIMCAL SUPER C65. SiO (micro-size particles) and Graphite (SPG6) are commercially available from Bosch.

2.2 Slurry and electrode casting

SiO particles, graphite particles, conductive carbon black, CMC and 10 % isopropyl alcohol solution were first mixed and milled by ball mill for 6 hours. Then the SBR emulsion was added and milled over night. The mixture slurry was casted into thin film on copper foil by a fixed-thick blade. The films were first dried in room temperature for 3 h and then further dried at 60 °C under 10^{-2} Torr pressure for 24 h. The electrodes were compressed to around 40 μm thick using a rolling mill. Four kinds of electrodes were prepared: SiO/C65/CMC/SBR is 80/10/5/5 (w.t.), SiO/Graphite/C65/CMC/SBR is 18.4/73.6/2/3/3 (w.t.), SiO/Graphite/C65/CMC/SBR is 4.6/87.4/2/3/3 (w.t.), SPG6/C65/CMC/SBR is 92/2/3/3 (w.t.), named "100% SiO", "SiO/C is 20/80", "SiO/C is 5/95", "100% Graphite", respectively.

2.3 Coin cell fabrication and testing

The anodes were fabricated into standard 2325 coin cells with lithium film as counter electrodes done in an argon-filled glove box. A mixture of 70% 1.2 M LiPF_6 in EC: DEC (3:7 weight ratio) and 30 % FEC was added as electrolyte. The coin cell performance was evaluated in a thermal chamber at 30°C with a Maccor Battery Test System. Cycling procedure includes two formation cycles of C/25 rate, followed by C/3 rate cycles with constant voltage during each discharge step.

3. Results and discussion

3.1 The role of isopropyl alcohol during slurry processing



Figure 1. The photos of the anodes plates: a: the "SiO/C is 5/95" anode using water as solvent during slurry. b: the "SiO/C is 20/80" anode using water as solvent during slurry. c: the "100% Graphite" anode using water as solvent during slurry. d: the "SiO/C is 20/80" anode using 10 % isopropyl alcohol solution as solvent during slurry.

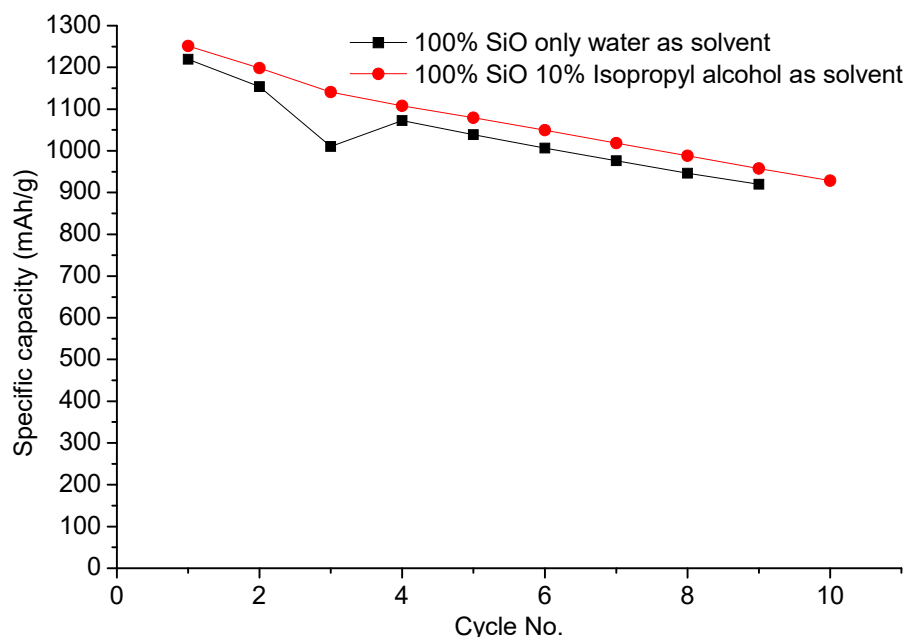


Figure 2. The specific capacities of the "100% SiO" anodes using water or 10% Isopropyl alcohol as solvent during slurry processing

In this study, at first only water was used as solvent during slurry process when using SBR and CMC as binders. Poor soakage of slurry coating on the copper foil resulting in active materials contraction and reunion during drying was observed for the "SiO/C is 5/95" (Figure 1a) and "SiO/C is 20/80" anodes (Figure 1b). A large amount of pits appeared on the slurry coating surface for the "100% Graphite" anode after drying (Figure 1c). After many times experiments, we found that using 10% isopropyl alcohol solution as solvent during slurry could obtain perfect slurry coating (Figure 1d).

There was no significant difference observed for the "100% SiO" anodes plates' morphology and the cycling performance (Figure 2) between using isopropyl alcohol and without using it. So, 10% isopropyl alcohol solution was used as solvent during slurry process for all the anodes.

3.2 The cycling performance of SiO-based anodes

Dimov et al. ^[21] reported that SBR and CMC content are the most influential parameters for the improved cycle life of Si/C electrodes, and it is clear that CMC and SBR mixture has a favorable influence on the cycle life probably due to the increased strength of the electrode film. Buqa et al. ^[19] reported that as low as 1-2% of SBR mixed with 1-2% Na-CMC as a binder is sufficient to assure a good electrochemical performance of nano-silicon/graphite electrodes. Thus, the ratio of SBR and CMC was kept as 1:1 (w.t.) for SiO-based anodes in this study. It was reported that SiO-based anodes suffer from poor electronic conductivity ^[4]. In order to increase the conductivity of the anodes, the amount of conductive additives and binders for the "100% SiO" anodes was 10% (w.t.) and 10% (w.t.) of total anodes materials weight, respectively. Graphite has electrical conductivity, so the amount of conductive additives and binders for SiO/Graphite composite anodes was 2% (w.t.) and 6% (w.t.) of total anodes materials weight, respectively. The cycle performance of anodes was showed in Figure 3, and the coulombic efficiencies of the anodes were illustrated in Figure 4.

The "100% Graphite" anode showed highly cycling stability. The specific capacity of the "100% Graphite" anode was around 357 mAh/g at the first cycle, and kept around 362 mAh/g after 100 cycles (Figure 3). On the contrary, though the initial specific capacity of the "100% SiO" anode reached around 1250 mAh/g, its specific capacity dropped to around 170 mAh/g after 100 cycles, which was much lower than the "100% Graphite" anode. The specific capacity of the "SiO/C is 20/80" anode was around 580 mAh/g at the first cycle, which was much higher than the "100% Graphite" anode, and showed much fast dropping in the first 40 cycles, then its dropping trend slowed down. The specific capacity of the "SiO/C is 20/80" anode was around 10% lower than the "100% Graphite" anode after 100 cycles. The initial specific capacity of the "SiO/C is 5/95" anode was around 413 mAh/g, which was 15% higher than the "100% Graphite" anode. The specific capacity of the "SiO/C is 5/95" anode kept dropping slowly during cycling, at last, it was around 370 mAh/g after 100 cycles, which was only 2% higher than the "100% Graphite" anode. It can be concluded that the more amount of the SiO in the anode was, the faster specific capacity of the anode dropped during cycling.

The first cycle coulombic efficiencies of the "100% SiO", "SiO/C is 20/80", "SiO/C is 5/95" and "100% Graphite" anodes were 65.5%, 73.6%, 77.7% and 80.6% (Figure 4), respectively. During cycling, the "100% Graphite" anode showed significant good coulombic efficiency, which was higher than 99% from 4 cycles and then higher than 99.9% from 30 cycles. The "100% SiO" anode showed relatively low coulombic efficiency, which was lower than 98% in the first 40 cycles and lower than 99.2% all through the first 100 cycles. Among the four anodes, the coulombic efficiency of the "100% Graphite" anode was the highest followed with the "SiO/C is 5/95" and the "SiO/C is 20/80" anodes, and that of the "100% SiO" anode was the lowest all through cycling. It is well known that low coulombic efficiency indicates there is reversible capacity lost during each lithiation/delithiation cycling. The results in this study showed that "100% Graphite" anode performed pretty good coulombic efficiency, and the more SiO that the anode contained, the lower coulombic efficiency the anode had during cycling. Combining the results in Figure 3 and 4, it can be concluded that it was the fading of SiO resulted in the reversible capacity dropping of SiO-based anodes.

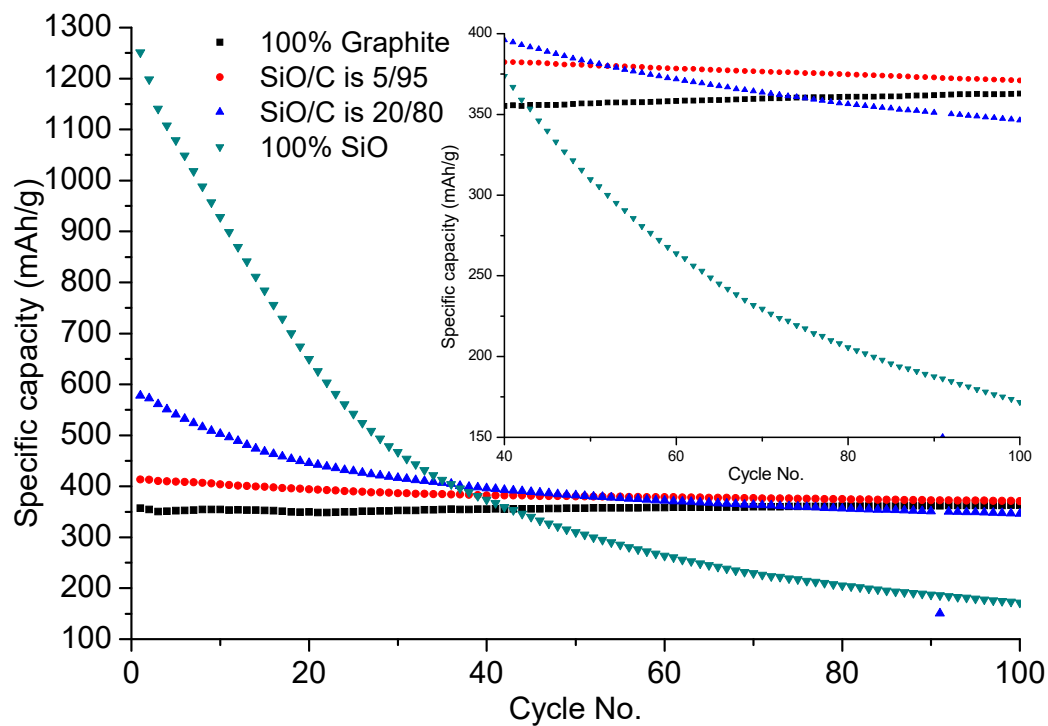


Figure 3. The cycle performance of the SiO-based anodes

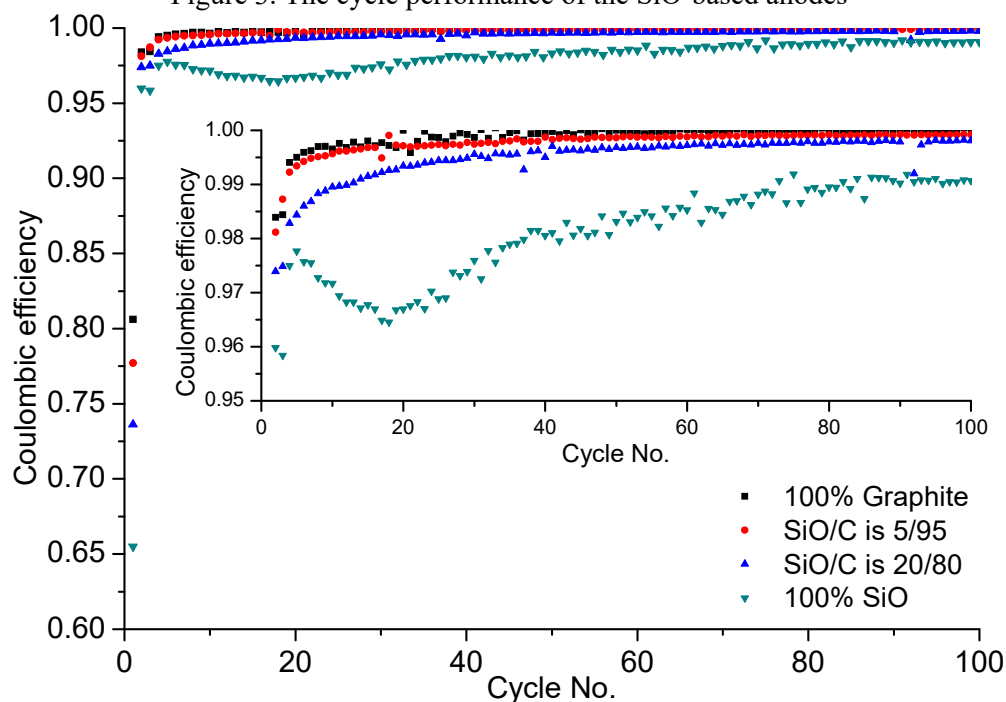


Figure 4. The coulombic efficiency of the SiO-based anodes

3.3 The voltage changes of half cells with "100% SiO" anode during 10% capacity lithiation-delithiation cycling

Many studies were taken to reveal the capacity fading mechanism of SiO-based anodes, and several explanations were reported in previous studies, such as particle pulverization, SEI reparation, serious

volume change during full depth of charge-discharge, and loss of electric contact between active materials and current collector^[4, 17, 22-25]. In the present study, the half cell with the "100% SiO" anode was lithiated to 50% theory capacity and then done 10% delithiation/lithiation cycling under 1C (1C=1.3 mA/g) rate for 1000 cycles. Because the anode was only done 10% capacity discharge-charge cycling after formation, the anode volume change should be negligible, and the SEI should be stable. As we all known, when the anode of the half cell is lithiated, the voltage of the cell will decrease, while the anode is delithiated, the voltage of the cell will increase. If the anode keeps stable during 10% capacity lithiation/delithiation cycling, the voltage difference between the maximum and minimum values of the cell would be stable too. In the present study, the results (Figure 5) showed that voltage difference between the maximum and minimum values of the cell kept increasing all through the 1000 cycles, which indicated that the SiO anode fading happened under the 10% capacity lithiation/delithiation cycling condition.

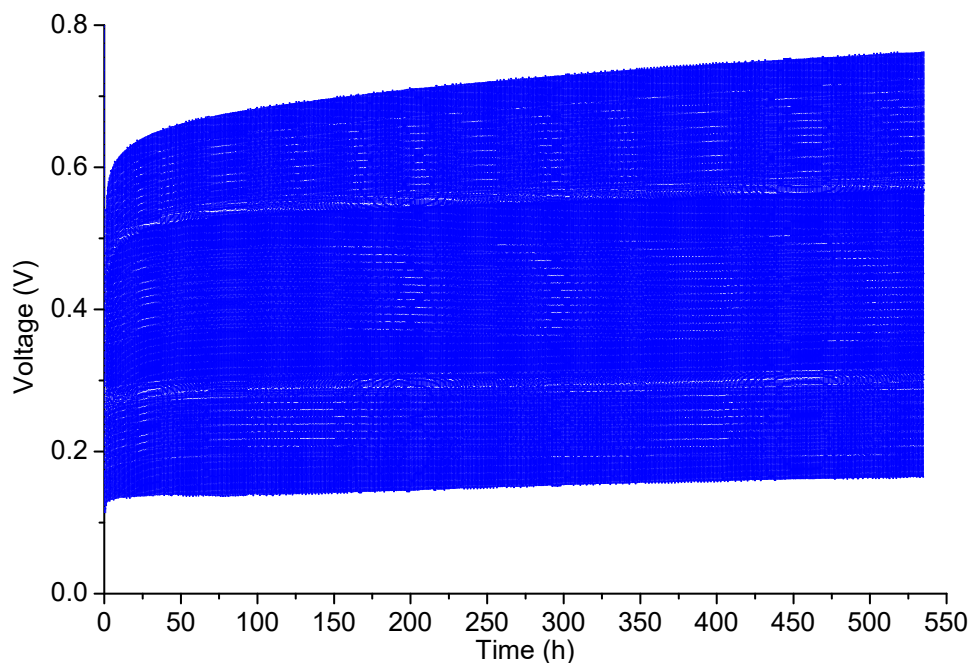


Figure 5. The voltage changes of SiO anode half cell during cycling

3.4 Surface morphology of SiO anodes

SEM analysis was used to examine the microstructure of the SiO anode. Both the surface of the SiO anode before cycling (Figure 6a, b) and that after cycling (Figure 6d, e) did not show any crack, which proved the inference that the volume expansion could be negligible during 10% capacity discharge-charge cycling. However the SiO particles' surface morphology changed a lot after cycling. It can be seen (Figure 6c) that the SiO particles' surface was smooth and tidy, and the edge of them was sharp before cycling, while their surface was rough and their edge was fuzzy after cycling (Figure 6f). Such kind of phenomena was also observed in the Graphite-Si/SiO_x/C system by Yuan et al.^[17]. The conductive additives distribution patterns also changed. There were fewer conductive particles on the active particles after cycling than that before cycling (Figure 6c, f). All these features may make the conductivity of the anodes worse, which can lead to poor cycling performance. In other words, the loss of electric contact between active particles was one of the crucial factors caused the SiO-based anodes fading.

On the other hand, better electrode conductivity for SiO-based anodes can lead to better cycle performance. Feng et al.^[13] prepared SiO-based electrodes with SiO (or SiO/C), conductive carbon black and binder at a weight ration of 70:20:10, one of which used SBR/CMC (SCMC, 3:5 by weight)

as the binder. Comparing their results with the results in the present study, we can find that increasing the conductive additives weight ratio from 10% to 20% can significantly enhance the capacity retention. They also concluded that carbon layer on the surface of SiO can enhance the electronic conductivity and structure stability of the active phase, which is the important reason for the improved cycling performance^[13]. Zhao et al.^[26] reported that only 2% (by weight) conductive polymer binder without any conductive additives was used with a micron-size SiO anode, demonstrating excellent cell performance. In conclusion, enhancing the electronic conductivity of the SiO-based electrode is one of the important methods to improve the cell cycle performance.

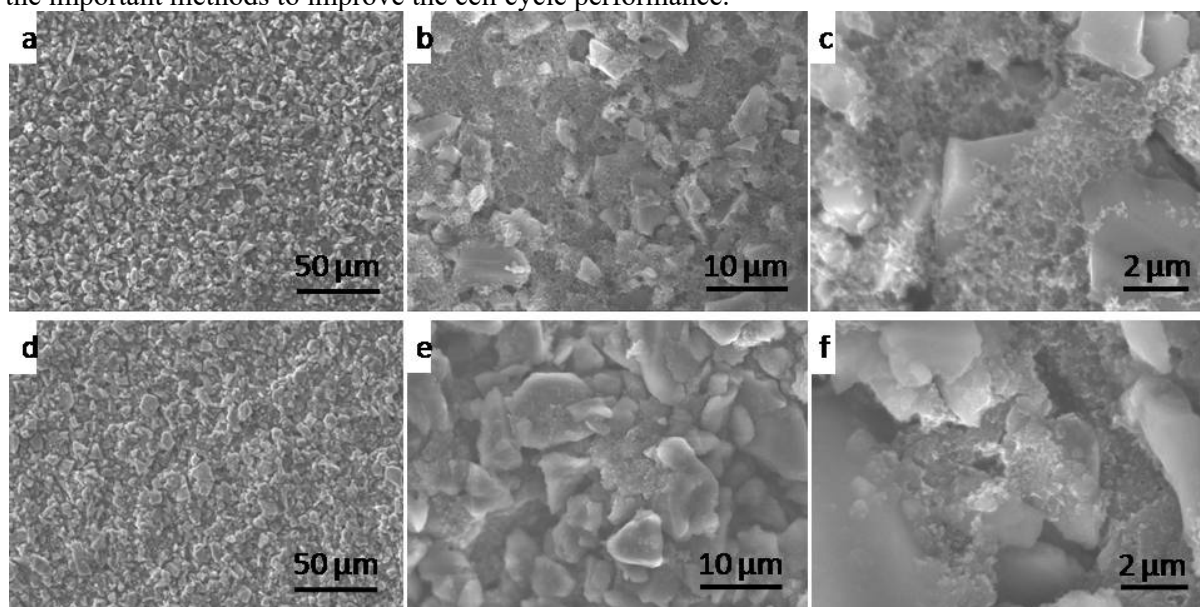


Figure 6. SEM images of SiO anodes before and after 10% capacity discharge-charge cycling. a, b, c: Images of SiO anode before cycling. d, e, f: Images of SiO anode after cycling.

4. Conclusion

Three kinds of SiO-based and one graphite electrodes were fabricated and their cycle performance was studied. The results showed that the more amount of SiO in the electrodes was, the faster the capacity of the electrode dropped and the lower coulombic efficiency of the electrode performed. Thus, it was the fading of SiO resulted in the reversible capacity dropping of SiO-based anodes. During 10% capacity lithiation/delithiation cycling, the voltage difference between the maximum and minimum values of the SiO anode cell kept increasing, which indicated that the SiO anode fading happened. The SEM images of the SiO anodes implied that electronic conductivity of the electrode became worse after cycling. We can conclude that electronic conductivity plays an important role in the electrode and enhancing the electronic conductivity of the SiO-based electrode is one of the important methods to boost the cell cycle performance.

Acknowledgments

This work was financially supported by National key R & D program of China (2017YFF0210002).

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