



Short communication

Electrochemical behavior of a silicon monoxide and Li-powder double layer anode cell

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ABSTRACT

A new technique for synthesizing double layer anodes with silicon monoxide and Li powder has been developed to reduce the initial capacity loss of silicon monoxide anodes. Double layer anode (DLA) cells are fabricated using Li emulsified powders on a Cu foil and silicon monoxide powders on a Cu mesh collector and their electrochemical behaviors are studied. The DLA cells show reduced initial irreversibility and enhanced coulombic efficiency. The coulombic efficiency of the first cycle of the DLA cell is over 100% and its capacity remains as 700 mAh g^{-1} up to 20 cycles. SEM observation shows that the Li-powder layer in DLA compensated for the initial irreversible loss and vanished after several cycles.

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1. Introduction

Silicon is one of the most attractive anode materials for lithium ion batteries, due to its high theoretical capacity of about 4004 mAh g^{-1} [1]. However, the drastic change in volume that silicon undergoes during charge/discharge cycles has often 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 carbon-coated silicon monoxide as an alternative anode material has been proposed, because of its large capacity of over 1200 mAh g^{-1} , long cycle life, and low charge–discharge potential [3–8]. However, it has been shown that the SiO composites still have 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 $5\text{SiO} + 6\text{Li} = \text{Li}_2\text{O} + \text{Li}_4\text{SiO}_4 + 4\text{Si}$. The first charge results in the formation of nano-sized clusters of amorphous silicon surrounded by lithium oxide and lithium silicate, and the reaction that produces the lithium oxide and lithium silicate is irreversible and, in turn, causes the capacity loss in subsequent discharge cycles [10–12]. In a previous study, a carbon-coated silicon monoxide anode cell which was pre-doped chemically with Li powders showed an improvement in its initial coulombic efficiency of 5% [13]. In the

present study, a new physical method of improving the irreversible capacity of SiO is suggested. Instead of the chemical pre-reaction between SiO and Li, the SiO and Li-powder layers were fabricated independently. The two layers were connected and formed a double layer anode (DLA) together. The lithium powders in the DLA were positioned to compensate for the Li loss in the irreversible reaction between SiO and Li during cycling. Therefore, the Li-powder layer acts as a reservoir of lithium ions during the initial discharge processes, whereas the SiO layer acts as an active electrode.

2. Experiments

2.1. Double layer anode fabrication

The working electrodes were prepared by casting a slurry containing 90 wt% of carbon-coated SiO and 10 wt% of polyvinylidene fluoride (PVDF) as a binder, both dissolved in N-methyl-2-pyrrolidone (NMP), onto a piece of copper mesh. The working electrodes were then dried under vacuum at 120°C for 3 h. The average particle size of SiO was 8–12 μm . The SiO active material layer of the DLA had a thickness of 80 μm and weight of 10 mg.

Lithium powders, synthesized by the Droplet Emulsion Technique (DET), were emulsified into the DMC [14]. The emulsified lithium powder was coated onto the copper foil by the tape casting method. The lithium powder electrode was positioned on the back side of the SiO working electrode. Then, the copper mesh and foil current collectors were welded to ensure their electrical connection. A schematic illustration of the DLA is shown in Fig. 1

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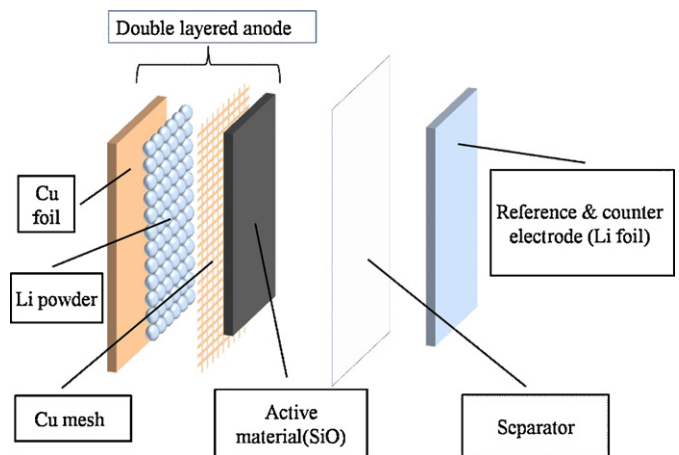


Fig. 1. Schematic illustration of the SiO and lithium powder double layer anode (DLA) cells.

[15]. For comparison, mono SiO layer anode (MLA) cells without a Li-powder layer were also fabricated. The lithium powder layer was fabricated using lithium powder with a mean particle size of 10–15 μm and had a thickness of 40 μm and weight of 1.8 mg.

2.2. Test cell assembly

Coin-type DLA/Li-foil cells (CR2032) were assembled in an argon-filled glove box. The electrolyte present was 1 M LiPF_6 in a mixture with a volume ratio of EC:DMC:EMC = 1:1:1 (Technosemichem, Republic of Korea). Lithium foils were used as the counter and reference electrodes. After the cell was assembled, the coin cells were aged for 24 h. Electrochemical tests were performed by galvanostatically charging/discharging the cells 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). The morphology change of the DLA was observed by SEM (Hitachi S-4300, Japan) before and after the cycling test.

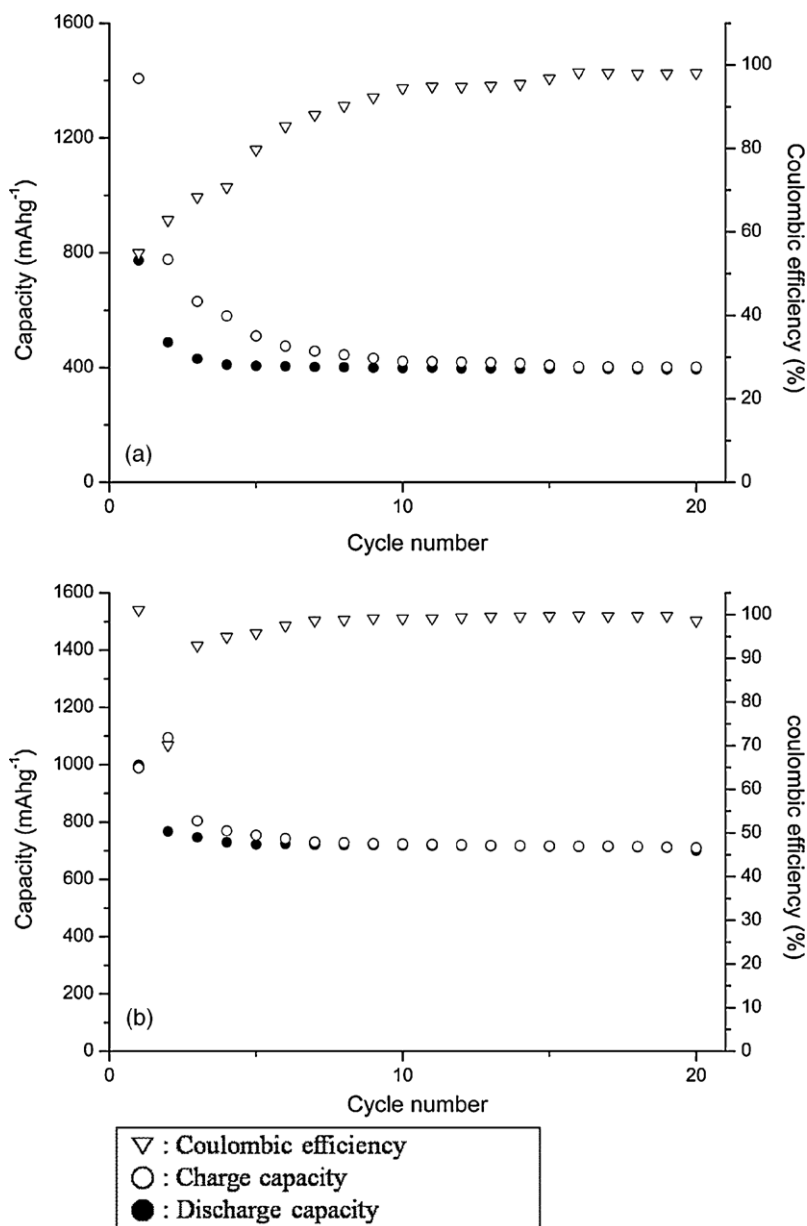


Fig. 2. Variation of the specific capacities and coulombic efficiency profiles for the MLA cell and the DLA cell with the cycle number.

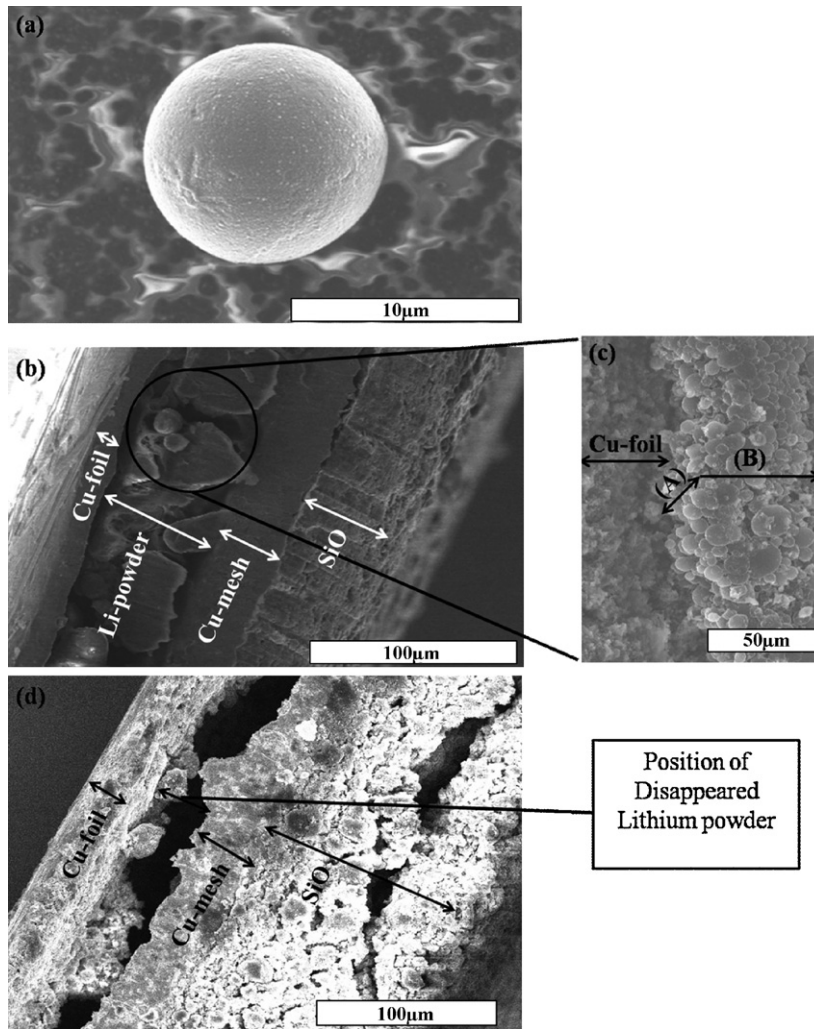


Fig. 3. SEM images of Li emulsified powder (a), DLA (SiO + Li-powder) before cycle test (b), magnified part of Li-powder layer in DLA (c), and DLA after 10 charge and discharge cycles (d). In (c), (A) denotes the thickness of lithium powder layer and (B) denotes the width of lithium powder electrode. The total width of the Li-powder layer is 13.7 mm.

3. Results and discussion

Fig. 2 shows the specific capacities and coulombic efficiencies of the DLA cell as a function of the cycle number. The specific charge and discharge capacities of the MLA cell in the 1st cycle

were 1410 and 773 mAh g⁻¹, respectively, and, therefore, its efficiency was 54.92%. The charge and discharge capacities of the MLA cell decreased continuously up to 10 cycles and reached almost a steady state. After 20 cycles, the charge and discharge capacities of the MLA cell were 394 and 402 mAh g⁻¹, respectively, and its effi-

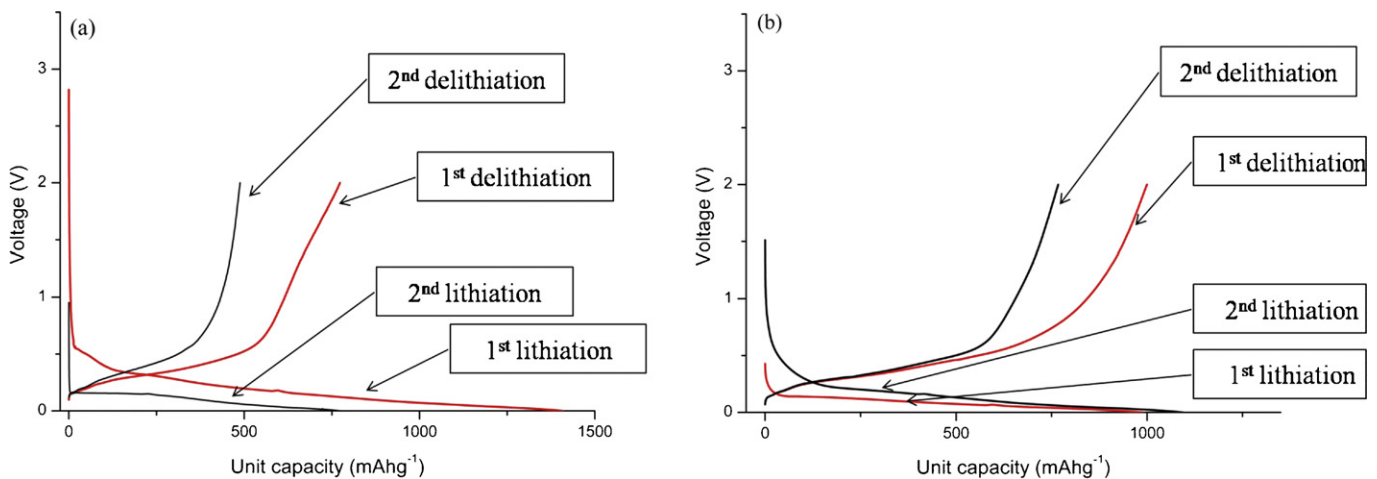


Fig. 4. Voltage profiles: (a) mono layer electrode; (b) double layer electrode.

Table 1
Summary of cycle performances of MLA and DLA cells.

Cycle number	Mono layer anode			Double layer anode		
	Charge capacity (mAh g ⁻¹)	Discharge capacity (mAh g ⁻¹)	Coulombic efficiency (%)	Charge capacity (mAh g ⁻¹)	Discharge capacity (mAh g ⁻¹)	Coulombic efficiency (%)
1st	773	1410	54.92	989	1000	101.07
2nd	488	776	62.88	1090	767	70.10
3rd	431	630	68.31	804	747	92.89
10th	399	422	94.44	724	718	99.12
20th	394	402	98.05	700	710	98.61

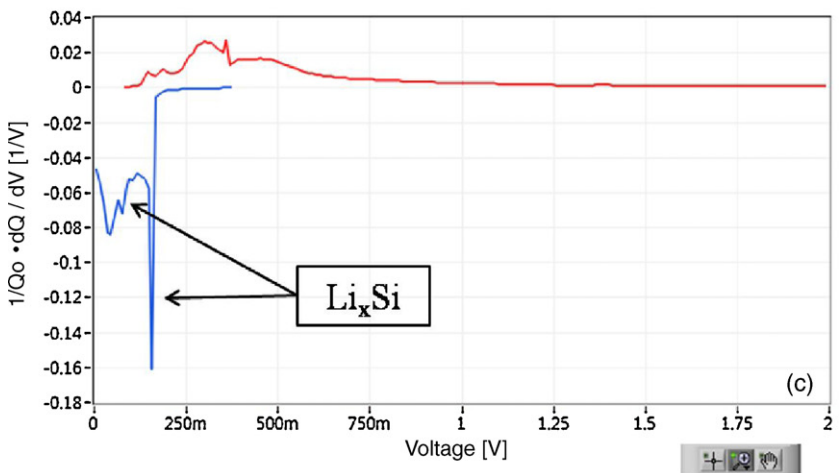
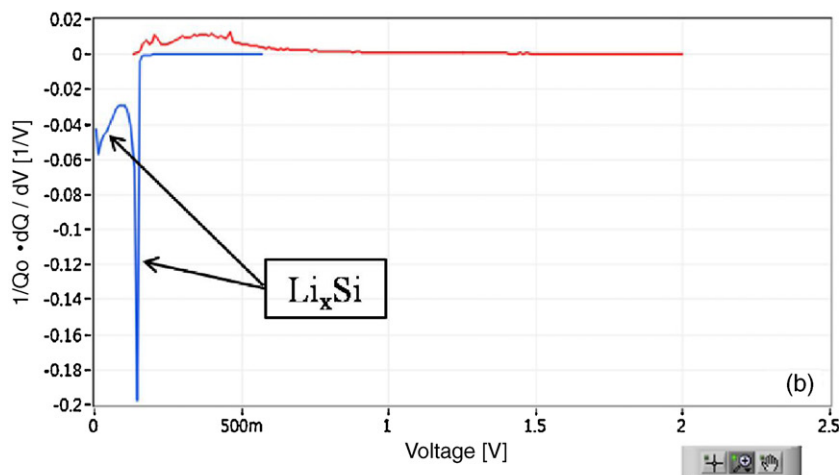
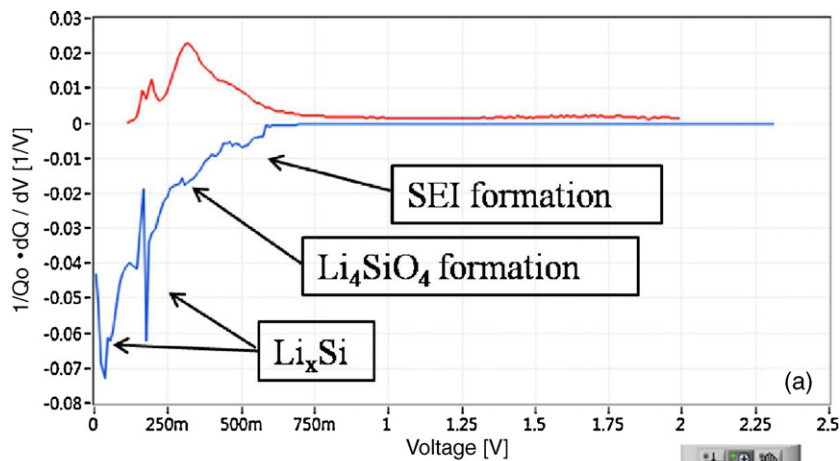


Fig. 5. Differential capacity curves: (a) 1st cycle of MLA cell; (b) 2nd cycle of MLA cell; (c) 1st cycle of DLA cell.

ciency was 98%. In contrast, the charge and discharge capacities of the DLA cell were 989 and 1000 mAh g⁻¹, respectively, and its efficiency was 101% in the 1st cycle. That is, the very first discharge capacity loss of the DLA cell was reduced dramatically. However, though it was higher than that of the MLA cell, the efficiency of the 2nd cycle was only 70% and it did not approach 100% until the 10th cycle. After 10 cycles, the capacity of the DLA cell remained at about 700 mAh g⁻¹ and its efficiency was about 100%. The cycle performances of the MLA and DLA cells are summarized in Table 1. Based on these results, it may be concluded that no capacity loss was observed for the DLA cell in the 1st cycle, because the reserved lithium in the DLA dissolved into the electrolyte during discharge. The reason that the efficiency dropped after the 2nd cycle may be due to the shortage of Li in the DLA. As shown in Fig. 2, the irreversible capacity of the MLA cell in the 1st cycle was 637 mAh g⁻¹. The weight of the active material in the MLA cell used for the test was 10 mg. Therefore, the irreversible capacity of the test cell was about 6.37 mAh. In the case of the DLA cell, the amount of lithium powder which was positioned on the back side of SiO was 1.8 mg. The theoretical capacity of the reserved lithium powder in the DLA was 6.95 mAh. Therefore, the Li in the DLA might be drained at the 1st cycle, in which case there would be no Li left to compensate for the capacity loss after the 2nd cycle. That is, because of the quantity of lithium powder in the DLA cell, capacity loss might be observed after the 2nd cycle.

The morphology of the DLA in the cross sectional observation by SEM is shown in Fig. 3. The emulsified lithium powder used for the Li-powder layer is shown in Fig. 3(a). Fig. 3(b) shows the morphology of the double layer anode and Fig. 3(c) shows a magnified image of the Li-powder layer before the cycling test. Fig. 3(d) shows the morphology of the DLA after 10 cycles. After 10 cycles, the lithium powder layer in the DLA, whose initial thickness was around 40 μm, disappeared (Fig. 3d). The vanished Li-powder layer may act as a reservoir for the irreversible reaction of lithium ions with SiO during the 1st charge process and, therefore, the initial coulombic efficiency of the DLA cell was more than 100%.

Fig. 4 shows the voltage profiles of the MLA and DLA cells. There were two differences between the MLA and DLA cells. The first was the rest potential after the cell aging process and the second was the specific capacities of the 1st and 2nd cycles. In the case of the MLA cell, the initial potential was 2.82 V, whereas that of the DLA cell was 0.42 V. This means that the small amount of lithium powder reacted with SiO during the aging process in the DLA cell. Therefore, similar to the result obtained in the case of the pre-doping method [13], the rest potential of the DLA cell was decreased compared with that of the MLA cell. This behavior also affects the specific capacity of the DLA cell. The 1st specific charge capacity of the MLA cell was 1410 mAh g⁻¹ (Fig. 4a), whereas that of the DLA cell was only 989 mAh g⁻¹ (Fig. 4b). That is, the lithium powder reacted with SiO during the aging process to form lithium silicate. This can be more clearly understood by the analysis of the cyclic voltammetry or differential capacity plot.

Fig. 5 shows the differential capacity plots of the MLA (Fig. 5a and b) and DLA (Fig. 5c) cells. There was an SEI formation peak at approximately 500 mV in the dQ/dV plot of the 1st cycle cathodic curve of the MLA cell and, near 300 mV, a lithium silicate formation peak was observed. In the 2nd cycle of the MLA cell, there were no SEI or lithium silicate formation peaks during the cathodic reaction (Fig. 5a and b). Compared with Fig. 5a and b, the dQ/dV curve of the DLA cell was very similar to the 2nd cycle curve of the MLA cell (Fig. 5c). In the case of the DLA cell, no SEI or lithium sili-

cate formation peaks were observed. This means that the DLA cell did not react with the lithium ions originating from the cathode to form lithium silicate and an SEI during the 1st cycle. In consideration of the rest potential obtained from the voltage profile, it can be inferred that a small amount of lithium powder reacted with SiO during the cell aging process. It could be concluded that a chemical reaction between Li and SiO occurred during the cell aging process, though the Li-powder layer and SiO layer were stacked physically. The products from the pre charge/discharge reaction, such as lithium silicates and the SEI, however, were only formed in small amounts and this mostly during the cycling process.

4. Conclusions

The initial irreversible capacity loss of the SiO anode cell can be remarkably reduced by using a SiO/lithium double layer anode. The coulombic efficiency of the DLA cell was almost 100% in the 1st cycle, but only 70% in the 2nd cycle, because all the lithium powder in the anode layer was completely dissolved in the 1st cycle. At the 3rd cycle, the coulombic efficiency of the DLA increased to about 92% and attained about 100% at the 10th cycle. The capacity of the DLA cell remained at 700 mAh g⁻¹ after the 10th cycle, whereas that of the MLA cell was 400 mAh g⁻¹. SEM observations showed that the Li-powder layer was dissolved to compensate for the initial irreversible capacity loss of Li during cycling. The greater the amount of lithium powder in the DLA cell, the smaller the capacity loss of the SiO active material. Based on the comparison of the rest potentials and the dQ/dV curves of the DLA and MLA cells, it can be inferred that some of the Li reacted chemically with SiO during the aging process, though the SiO layer and Li-powder layer were stacked physically.

Acknowledgements

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