ELECTROCHEMICAL STUDY OF SiO INITIAL EFFICIENCY FOR LITHIUM ION BATTERIES

Il Won Seong, Jee Ho Yom, Sung Man Cho, Woo Young Yoon*

Department of Materials Science and Engineering, Korea University, 1, 5Ga, Anam-dong,
Sungbuk-Gu, Seoul, 136-701, Republic of Korea
E-mail address: wyyoon@korea.ac.kr

Abstract— **A new method of preparing anodes for rechargeable lithium batteries using silicon monoxide and Li powder is reported herein. Although SiO anode materials show good cyclability and high capacity, their initial irreversibility limits their commercial use. In this study, we present a double-layered anode in which the Li powder is partly composed of SiO to compensate for the initial irreversible loss. The efficiencies in the 1st and 2nd cycles of this doubled-layered cell were ~90.17% and 98.50%, respectively. This double layered anode approach represents a breakthrough that enables the use of SiO in high-capacity Li rechargeable batteries.**

Keywords—lithium; electrochemical reaction; lithium ion batteries; SiO; irreversible capacity

I. INTRODUCTION

Lithium-ion (Li-ion) Batteries are now the most widely used secondary battery systems for portable electronic devices [1]. However, the gravimetric capacities ($mAh \cdot kg^{-1}$), and volumetric energy densities ($Wh \cdot l^{-1}$) of these cells must be further enhanced to meet the demands for miniaturization and other advances in the portable device industry and to further their use in aerospace, military, and automobile applications like hybrid electrical vehicles (HEV) or electrical vehicles (EV). This can be achieved by replacing the electrode materials in the cathodes and anodes [2].

Many researchers have recently focused their attention on finding alternative anode materials with higher gravimetric and volumetric capacities than graphite [1–12], among which, silicon monoxide (SiO) has been extensively investigated [3,15−17]. Although SiO has a large lithium (Li) insertion capacity, it shows a very low initial coulombic efficiency [15]. During the first charging reaction, SiO reacts with Li ions to produce lithium oxide (Li_2O) and lithium silicate (Li_4SiO_4) [15]. The reaction between SiO and Li has been reported as (1):

$$5SiO + 6Li \rightarrow Li_2O + Li_4SiO_4 + 4Si \qquad (1)$$

The first two products (i.e., Li_2O and Li_4SiO_4) act as inactive matrices and reduce the volume changes of silicon (Si), which is the active material of the cell [16]. This is the main reason for the excellent cycle performance and high capacity of SiO as an anode material [17]. However, the reaction that produces (Li_2O) and (Li_4SiO_4) is irreversible, and any reacted Li causes a permanent loss in the cathode capacity. This initial irreversible reaction is therefore unavoidable but unacceptable for secondary cells.

In our previous studies, we suggested two different ways to improve the irreversible capacity, i.e., through a pre-chemical reaction with Li and by using Li powder. A carbon-coated SiO anode cell that was subjected to chemical reaction with Li powder prior to cell fabrication showed an improvement in its initial coulombic efficiency of ~15.78% compared to that of the standard SiO anode [18]. An anode cell employing a double-layer of SiO and Li powder (as an alternative to chemical pre-reaction) showed an even greater initial efficiency of 98.18% [19]. Similarly, Li powder was coated on a separator and used as a reservoir layer. Despite the improved initial efficiency of SiO, the reservoir layer may block or damage the Li ion pathway of the separator [20]. Kim et al. demonstrated improved initial coulombic efficiency for a pre-lithiated SiO anode half-cell compared to full cells with various cathodes [21]. However the pre-lithiation process required a dedicated cell for pre-lithiation only. The cell was then disassembled to use the pre-lithiated anode. This process is too complicated as a means to overcome the SiO initial irreversible capacity. Consequently, the pre-lithiation process is essential for reducing the irreversible capacity of SiO anodes. Under these conditions, the Li powder layer acts as a Li ion reservoir to compensate for Li loss in the initial cycle. Although the prior chemical reaction and Li reservoir approaches to compensate for the initial irreversible Li loss both reduce the initial irreversible capacity of the SiO anode cell, fabrication of complex electrodes by these methods is difficult, and even higher efficiencies are thus required for the secondary cell. Furthermore, the difference in the initial efficiency of the two types of electrodes has not yet been fully understood.

In the present study, the double-layered structure of the SiO anode results in almost 100% initial coulombic efficiency. An anode is synthesized by simply dispersing Li powder uniformly onto the tape-cast surface of a SiO electrode.

II. EXPERIMENTAL

A. Reservoir electrode preparation

A mixture of SiO (Aldrich, 325 mesh) and graphite was ball-milled. Natural graphite (DAG, Sodiff, size: 20 μm, spherical type) was mixed with SiO in a 1:1 weight ratio. The ball-to-material weight ratio was 5:1 and milling was

performed for 30 min at 1200 rpm. The electrodes were prepared by a tape casting method with a slurry containing 90 wt% of the mixed powder and 10 wt% of polyvinylidene fluoride (PVDF) as the binder, which were dissolved in *N*-methyl-2-pyrrolidone (NMP) and deposited onto a piece of copper foil. The electrodes were then dried under vacuum at 120 °C for 3 h.

The Li powder was prepared by a droplet emulsion technique (DET) [22]. Figure 1 shows a schematic of the DET method and a SEM image of the prepared lithium powder. Silicon oil (Shinetsu, 100cs) was heated to 200°C in the oil bath and filled into the mixing chamber. Melted lithium metal from the other bath was introduced into the mixing chamber. The impeller was then rotated at a rate of over 25,000 rpm for 5 min to generate the lithium metal emulsion. When the mixing chamber valve was opened, the emulsion quickly cooled down and the melted lithium droplets solidified. The cooled emulsion was filled into a separating funnel and washed out with normal hexane. The final lithium powder product was dried for 24 h under argon atmosphere. All the processes were carried out in an argon filled glove box.
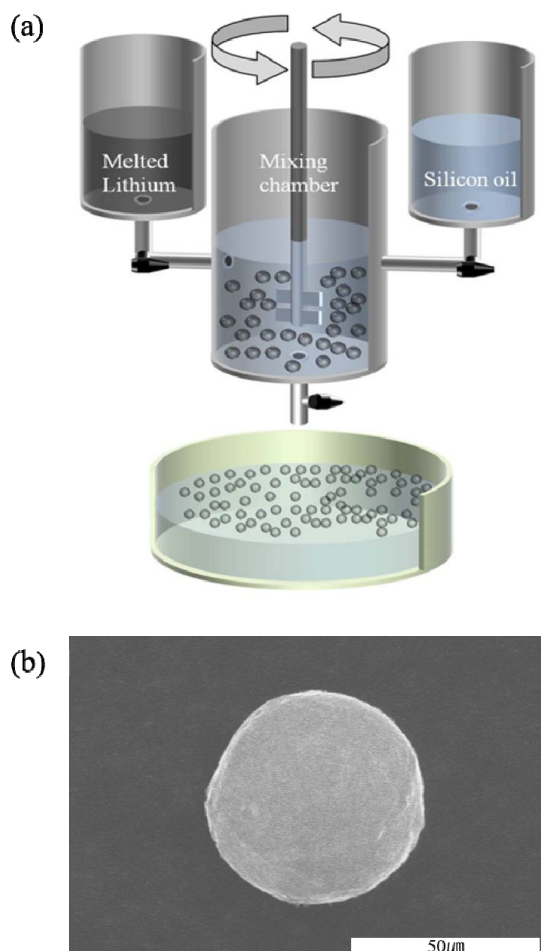
Figure 1. Schematic of (a) droplet emulsion setup and (b) SEM image of manufactured lithium powder.

A reservoir electrode was prepared by the following steps. Lithium powder was dispersed in dimethyl carbonate (DMC) in an aluminum dish. The SiO electrode was soaked in the Li powder–DMC suspension for a few seconds and dried for 5 h in a glove box. Finally, in order to improve the attachment between the Li powder and the SiO layer, the electrode was pressed at 20 kg·cm^{-2}.

B. Cell performance characterization

The sample was characterized by X-ray diffraction (XRD, Rigaku RINT-2000) with Cu-Kα radiation and high-resolution transmission electron microscopy (HRTEM, JEM-2010) in order to identify the formed phases. The XRD analysis was carried out at a scan speed of 2° min^{-1} over the 2θ range of 20°–80°. The TEM samples were prepared using the focused ion beam (FIB) milling method. Coin-type cells (CR2032) were assembled in an argon-filled glove box. The anode consisted of dispersed Li or a pure SiO–natural graphite mixed electrode and the cathode was a commercially available lithium cobalt oxide (LCO) electrode. The electrolyte was LiPF$_6$ (1 M) in a mixture of ethylene carbonate (EC):dimethyl carbonate (DMC):ethyl methyl carbonate (EMC) in a 1:1:1 ratio (v:v:v) (Technosemichem, Republic of Korea). After cell assembly, the cell was aged for one day at 40 °C. The electrochemical tests were performed by galvanostatically charging/discharging the cell in the 2.75–4.2 V range at a constant current of 0.1 C-rate using a WBCS 3000 instrument (Wonatech Inc., Republic of Korea).

III. RESULTS AND DISCUSSION

The pure SiO anode is black due to the carbon conductive agent. The double-layered electrode, however, was characterized by a metallic patina. Figure 2 shows the schematic structure of the double-layered anode/LCO cathode cell. The Li powder (mean size of 10 μm) sample was synthesized by DET [22] and spread homogeneously on the SiO electrode surface.
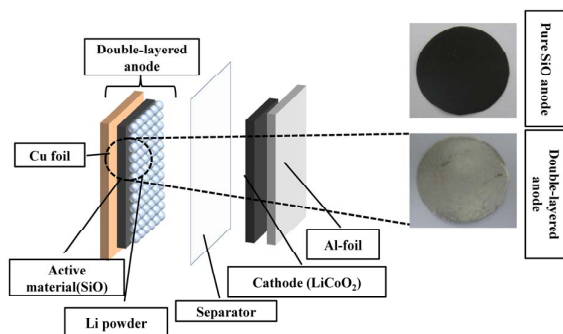
Figure 2. Schematic structure of the double-layered anode cell and photographs of pure SiO anode and double-layered anode.

The cross-sectional SEM images of the bare SiO electrode and double-layered electrode are presented in Fig. 3. Compared to the bare and double-layered electrodes, the thickness of the SiO active material layer was around 38 μm. In the case of the double-layered anode (Fig. 3b), the lithium powder layer was well deposited on the SiO active materials

in mono- or bi-layers. The thickness of the lithium powder layer was 7.74 µm. The morphology of the lithium powder in the double-layered anode was hemispherical. The lithium powder particles were initially spherical, but during the pressing process, the powder particles underwent deformation. However, without pressing, the lithium powder could be electrically isolated. Thus, during the electrochemical charge/discharge process, the powder does not work as a Li reservoir as hoped; moreover it acts to resist lithium ion migration.
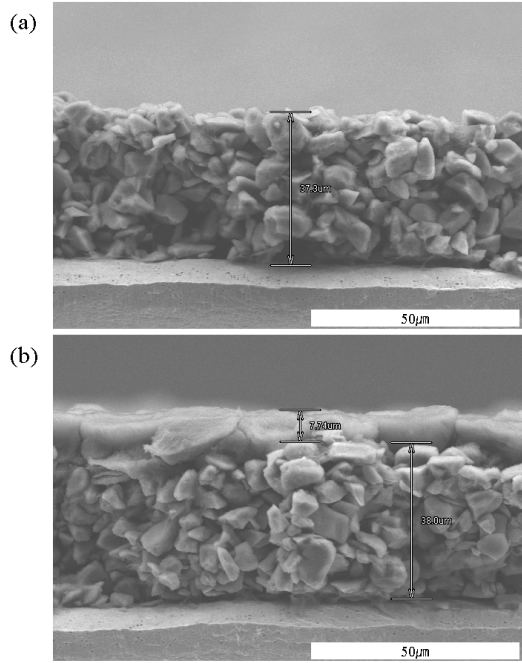

Figure 3 Cross-sectional SEM image of (a) bare SiO electrode and (b) double-layered electrode.

Figure 4 shows the relationship between the amount of Li added and the initial efficiency of the cell. The straight line represents the calculated value of the Li weight capacity and the points represent the experimental results. The initial value for the pure SiO anode is 60.32%. Our calculations show that about 1 mg of Li is able to fully compensate the initial capacity loss. The empirical results can be compared to the theoretical capacity of the Li loaded electrode, calculated using formula (2):

$$E_{theo\ rev} = 100 \times [1-(C_{irrev}-C_{Li})/C_{anode}] \qquad (2)$$

Here, $E_{theo\ rev}$ is the theoretical coulombic efficiency, and C_{irrev}, C_{Li}, and C_{anode} are the irreversible capacity, added Li capacity, and total anode capacity, respectively. The efficiency of the double-layered anode cell with 0.5 mg Li agreed well with the estimated value, but samples with more than 0.5 mg Li showed only small increases and appeared to be saturated at about 90% efficiency. That is, for the sample loaded with >0.5 mg Li, either a certain amount of the Li powder remains on the surface or some of the reacted Li cannot contribute to

compensation during the cycles. If any Li powder remains on the surface, it may compromise the cell safety. The anode cell prepared with about 1.3 mg Li had an initial efficiency of 91%. This means that 90% of the Li reacts with SiO and the remaining 10% does not contribute to improving the efficiency.
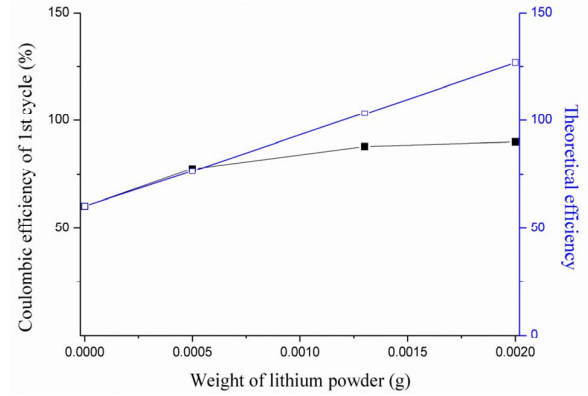
Figure 4 Coulombic efficiency as a function of the Li powder added. Straight line represents the theoretical efficiency and the marked points are the experimental results

.

Figure 5 shows the specific capacity and coulombic efficiency of the pure SiO anode and the double-layered anode cell as a function of the number of cycles. In the case of the pure SiO cell, the coulombic efficiencies at the 1st and 2nd cycles were 60.3% and 93.63%, respectively.
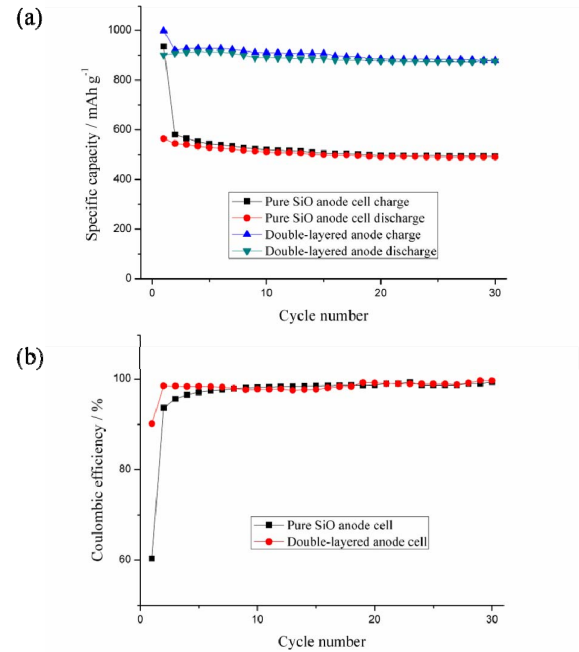
Figure 5(a) Cycle performance of the double-layered anode cell and the pure SiO anode cell, and (b) coulombic efficiency of both cells. The inset

After 30 cycles, the capacity remained at 86.8% of the initial value. In contrast, in the case of the doubled-layered cell, the efficiencies at the 1st and 2nd cycles were approximately 90.17% and 98.50%, respectively. Therefore, the remaining capacity after the 30th cycle was more than 97% of the 1st discharge capacity, with a value of 876.7 mAh·g^{-1}. Consequently, Li addition beneficially influences the initial efficiency and cyclability of the cell. To the best of our knowledge, this is the highest initial efficiency reported for a SiO electrode. The initial capacity loss of <10% is acceptable when compared to the initial efficiency of the graphite electrode commercial cell.
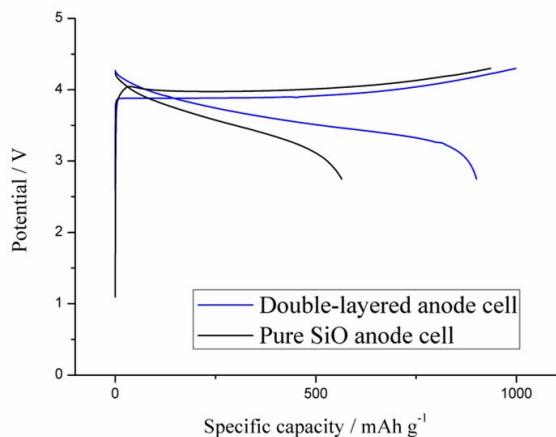

Figure 6 Voltage profiles of Li-added SiO and the reference/lithium cobalt oxide cells.

Figure 6 presents the voltage profiles of the pure SiO anode cell and the double-layered anode cell. The rest potentials for the reference and Li-added cells were 1.09 V and 2.59 V, respectively. In a previous report, the variation of the capacity of Li powder based on the reaction with SiO and formation of a solid electrolyte interface (SEI) during the aging process was examined [19]. The 1st charge capacity of the reference cell was 935.88 mAh·g^{-1} and the discharge capacity was 565 mAh·g^{-1}. The coulombic efficiency of the reference electrode was 60.3%. In contrast, the 1st charge and discharge capacities of the Li-added cell were 998.7 mAh·g^{-1} and 901 mAh·g^{-1}, respectively, with a coulombic efficiency of 90.17%.

Figure 7 shows the changes in the XRD patterns of the pure SiO electrode and the double-layered electrode before and after the 1st cycle. The pattern of the pristine SiO electrode presented no peaks of crystalline phases (Fig. 4a). Although the double-layered electrode includes a Li layer, the pattern was similar (Fig. 4b) since Li cannot be detected through the XRD technique. A small peak corresponding to Li oxide was found at around 2θ = 20°. After the 1st cycle, peaks of crystalline Si, Li$_2$O, and Li$_4$SiO$_4$ were observed for both electrodes (Fig. 4c and d). This means that there is almost no

chemical reaction in the double-layered electrode prior to cycling. The XRD pattern of the pre-chemically reacted electrode resembles that shown in Fig. 4c [18]. It displays peaks of Si, Li$_2$O, and Li$_4$SiO$_4$. Although the products are identical, the efficiency of the pre-chemically reacted cell is not as high as that of the reported double-layered anode cell [19] or the present double-layered anode cell. The Li powder in the latter two electrodes acts as a reservoir to compensate the initial loss of electrochemically reacted Li instead of undergoing a pre-chemical reaction.
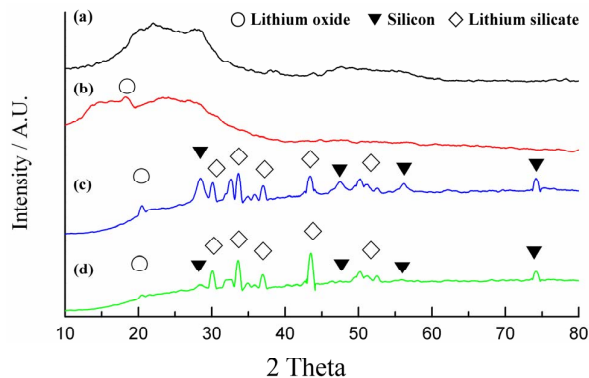
Figure 7 XRD diffraction patterns of (a) commercial SiO powder, (b) double-layered anode, (c) pure SiO after the 1st cycle, and (d) double-layered anode after the 1st cycle.
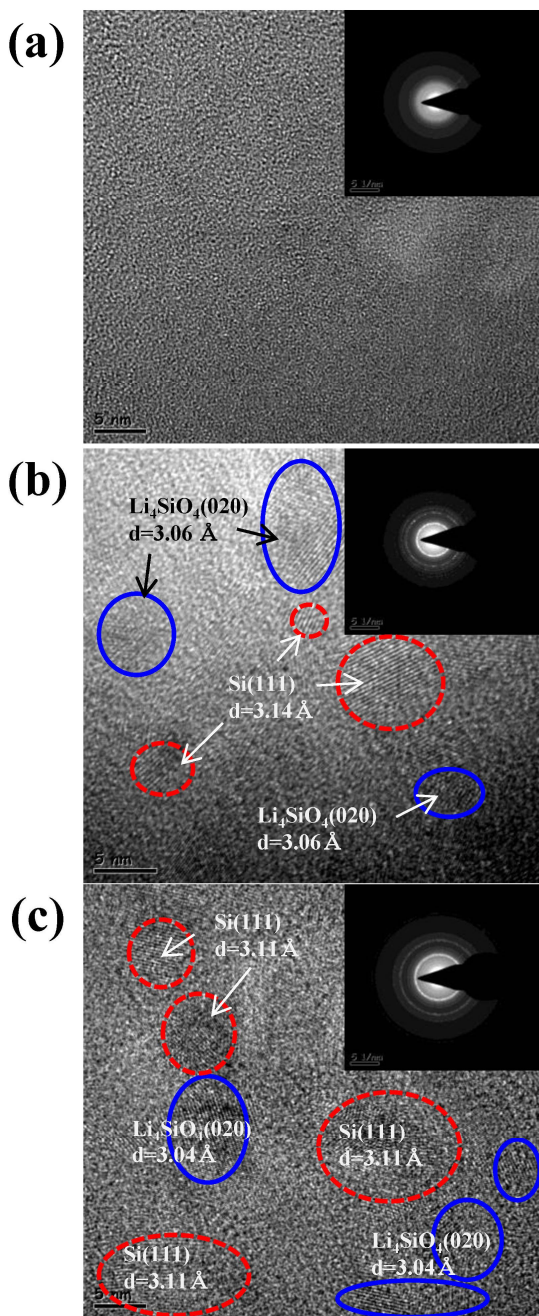
Figure 8 shows the TEM and selected area electron diffraction (SAED) images of pure SiO powder and the pure and double-layered anodes after the 1st cycle. The pure SiO anode presents an amorphous phase (Fig. 5a). After the 1st cycle, however, the pure SiO electrode changes to a composite phase consisting of nanosized Si particles, crystalline Li$_4$SiO$_4$, and non-crystalline Li silicates. The SAED lattice fringes shown in the inset of Fig. 5b confirm the presence of monoclinic Li$_4$SiO$_4$ [15]. Figure 5c shows the TEM image of the double-layered electrode after the 1st cycle, which is similar to that shown in Fig. 5b. The arrangement (i.e., the relative position) of the phases, as well as that of the products themselves, is similar in both electrodes, but the arrangement is different in the pre-chemically reacted anode [18]. The differences between the chemical and electrochemical reactions may account for the difference in the initial efficiency of the different types of electrodes from prior reports. This difference indicates that the products of the reactions as well as the arrangement of the products affect the initial efficiency. However, further research is needed to fully understand this reaction behavior.

IV. CONCLUSIONS

Li powder physically attached to a SiO electrode successfully reduces the initial irreversible capacity of SiO. The Li powder acts as a reservoir for the Li ions originating at the cathode, leading to a coulombic efficiency of >90% in the 1st cycle for the double-layered anode cell. TEM demonstrated

different morphologies of the electrochemically reacted and chemically reacted SiO electrode components. In other words, these morphological differences may be directly related to the initial efficiency of the pre-chemically and electrochemically reacted electrodes.

(a)

(b)

Li$_4$SiO$_4$(020) d=3.06 Å

Si(111) d=3.14 Å

Li$_4$SiO$_4$(020) d=3.06 Å

(c)

Si(111) d=3.11 Å

Li$_4$SiO$_4$(020) d=3.04 Å

Si(111) d=3.11 Å

Si(111) d=3.11 Å

Li$_4$SiO$_4$(020) d=3.04 Å

Figure 8 HR-TEM images of (a) pure SiO powder, (b) pure SiO anode after the 1st cycle, and (c) double-layered anode after the 1st cycle. The insets are the SAED patterns for each sample.

References

[1] J. M. Tarascon, M. Armand, "Issues and challenges facing rechargeable lithium batteries", Nature, **404**, 359-367 (2001).

[2] M. Miyachi, H. Yamamoto, H. Kawai, T. Ohta, M. Shirakata, "Analysis of SiO anodes for lithium-ion batteries" J. Electrochem. Soc., **152,** A2089-A2091 (2005).

[3] A. Netz, R. A. Huggins," Amorphous silicon formed in situ as negative electrode reactant in lithium cells", Solid State Ionics, **175**, 215-219 (2004).

[4] M. Miyachi, H. Yamamoto, H. Kawai, "Electrochemical properties and chemical structures of metal-doped SiO anodes for Li-ion rechargeable batteries", J. Electrochem. Soc., **154** (4), A376-380 (2007).

[5] M. N. Obrovac and L. J. Krause, "Reversible cycling of crystalline silicon powder," J. Electrochem. Soc., **154**, A103–A108 (2007).

[6] H. Kim, B. Han, J. Choo and J. Cho, "Three-dimensional porous silicon particles for use in high-performance lithium secondary batteries," Angew. Chem. Int. Ed., **47**, 10151–10154 (2008).

[7] Z. P. Guo, J. Z. Wang, H. K. Liu and S. X. Dou, "Study of silicon/polypyrrole composite as anode materials for Li-ion," J. Power Sources, **146**, 448–451 (2005).

[8] C. Chan, H. Peng, G. Liu, K. McIlwrath, X. Zhang, R. Huggins and Y. Cui, "High-performance lithium battery anodes using silicon nanowires," Nature Nanotech., **3**, 31–35 (2008).

[9] A. Netz, R. A. Huggins and W. Weppner, "The formation and properties of amorphous silicon as negative electrode reactant in lithium systems," J. Power Sources, **95**, 119–121 (2003).

[10] S. E. Hayes, H. Eckert, W. R. Even Jr. and R. Guidotti, "Structural and electrochemical characterization of glassy carbon prepared from silicon-doped polymethacrylonitrile/divinylbenzene copolymer," J. Electrochem. Soc., **146**, 2435–2442 (1999).

[11] A. M. Wilson, B. M. Way, J. R. Dahn and T. V. Buuren, "Nanodispersed silicon in pregraphitic carbons," J. Appl. Phys., **77**, 2363–2369 (1995).

[12] T. Hasegawa, S. R. Mukai, Y. Shirato and H. Tamon, "Preparation of carbon gel microspheres containing silicon powder for lithium ion battery anodes," Carbon, **42**, 2573 –2579 (2004).

[13] W. R. Liu, M. Yang, H. Wu, S. M. Chiao and N. Wu, "Enhanced cycle life of Si anode for Li-ion batteries by using modified elastomeric binder," Electrochem. Solid State Lett., **8**, A100–A103 (2005).

[14] U. Kasawajjula, C. Wang and A. J. Appleby, "Nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells," J. Power Sources, **163**, 1003–1039 (2007).

[15] X. Yang, Z. Wen, X. Xu, B. Lin and S. Hung, "Nanosized silicon-based composite derived by in situ mechanochemical reduction for lithium ion batteries," J. Power Sources, **164**, 880–884 (2007).

[16] A. Veluchamy, C. Doh, D. Kim, J. Lee, D. Lee, K. Ha, H. Shin, B. Jin, H. Kim, S. Moon and C. Park, "Improvement of cycle behaviour of SiO/C anode composite by thermochemically generated Li$_4$SiO$_4$ inert phase for lithium batteries," J. Power Sources, **188**, 574–577 (2009).

[17] M. Mamiya, H. Takei, M. Kikuchi and C. Uyeda, "Preparation of fine silicon particles from amorphous silicon monoxide by the disproportionation reaction," J. Cryst. Growth, **229**, 457–461 (2001).

[18] I. W. Seong and K. T. Kim, W. Y. Yoon, "Electrochemical behavior of a lithium-pre-doped carbon-coated silicon monoxide anode cell," J. Power Sources, **189**, 511–514 (2009).

[19] I. W. Seong and W. Y. Yoon, "Electrochemical behavior of a silicon monoxide and Li-powder double layer anode cell," J. Power Sources, **195**, 6143–6147 (2010).

[20] S. Hwang and W. Yoon, "Effect of Li powder-coated separator on irreversible behavior of SiOx-C anode in lithium-ion batteries," J. Electrochem. Soc., **161**, A1753–A1758 (2014).

[21] H. Kim, S. Choi, S. Lee, M. Seo, J. Lee, E. Deniz, Y. Lee, E. Kim and J. Choi, "Controlled prelithiation of silicon monoxide for high performance lithium-ion rechargeable full cells," Nano Lett., **16**, 282–288 (2016).

[22] W. Yoon, J. S. Paik, D. LaCourt and J. H. Perepezko, "The effect of pressure on phase selection during nucleation in undercooled bismuth," J. Appl. Phys., **60**, 3489–3494 (1986).