

Improved anode performance of thermally treated SiO/C composite with an organic solution mixture

Chil-Hoon Doh^a, Hye-Min Shin^a, Dong-Hun Kim^a, Yoon-Cheol Ha^a, Bong-Soo Jin^a, Hyun-Soo Kim^a, Seong-In Moon^a, Angathevar Veluchamy^{a,b,*}

^a Advanced Battery Division, Korea Electrotechnology Research Institute, Changwon 641-120, Republic of Korea

^b Central Electrochemical Research Institute, Karaikudi 630 006, India

Received 16 November 2007; received in revised form 28 November 2007; accepted 29 November 2007

Available online 4 December 2007

Abstract

A pristine composite anode material comprising of silicon monoxide and graphite was prepared through ball milling process and made in the form of a slurry using a simple solution mixture consisting of propylene carbonate (PC) and acetone (AC) and then heat treated. Cycle life study of the pristine composite and heat treated organic slurry composite showed the charge capacity values as 318 and 500 mAh g⁻¹, respectively at 100th cycle. Analysis of change of delithiation capacity with cycling and delithiation current between 0.3 and 0.6 V from cyclic voltammogram (CV) along with scanning electron microscope (SEM) and X-ray diffraction (XRD) of the electrodes/composites leads to conclude thermal processing of the organic slurry treated pristine composite converts dispersed active materials of the pristine composite into a compact structure trapped/wrapped with carbon particles (Cx, x varies from 1 to 3) providing apparently a resistor like behaviour and makes the anode deliver a stable reversible capacity with cycling.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Ball milling; SiO/C organic slurry composite; Propylene carbonate; Acetone; Heat treatment; Anode; Li-ion battery

1. Introduction

The alloy forming property of silicon and tin with lithium has evoked interest among the battery researchers to develop high capacity anodes for lithium ion battery in order to replace the graphite anode which has only 372 mAh g⁻¹ as its specific capacity. Even though these elements have the tendency to form alloys such as Li₂₂Si₅ and Li₂₂Sn₅ with theoretical capacities of 4190 and 990 mAh g⁻¹, respectively, their practical application is hampered as they show large crystallographic volume differences between the lithiated and delithiated compounds [1–3]. The repetitive volume changes during cycling causes

anode particle fracture which leads to the loss of electrical contact between the particles limiting cycle life performance of the cell. In the case of silicon based anodes the volume changes has been minimized by modifying the active materials as intermetallic alloys, compounds, nano-sized active materials or composite materials so as to provide high specific capacity with cycle life [4–7]. Despite a number of silicon based anodes with high specific capacity were reported, they could not meet the requirements of industrial applications either due to multi step synthesis procedures or due to unsolved problems such as large irreversible capacity during initial cycles and capacity degradation upon extended cycling.

In order improve the cycle performance, carbon coating over silicon based anode materials were carried out using various carbon sources. Dimove et al. [1,2] have deposited carbon over silicon through thermal vapour deposition using benzene or toluene as carbon source

* Corresponding author. Address: Advanced Battery Division, Korea Electrotechnology Research Institute, Changwon 641-120, Republic of Korea. Tel.: +82 055 280 2527; fax: +82 055 280 1590.

E-mail address: veluchamy.a@gmail.com (A. Veluchamy).

and nitrogen as a carrier gas and noted uniform deposition of lithium over silicon nano-domains during initial cycles and formation of lithium dead spots in the later cycles. Coal tar pitch has been considered as a carbon coating material for the nano-sized Si phase prepared through the reduction of SiO by Al and also for the composite Ni₂₀Si₈₀ alloy/graphite, both composites were synthesized using ball milling process. In these electrodes the carbon coating was supposed to provide superior performance due to enhanced electronic and ionic conduction of the electrode [8,9]. Kim et al. [10] used organic materials such as trisodium citrate dihydrate and polyvinyl alcohol (PVA) along with other chemicals for the preparation of carbon coated Si–Cu₃Si–Cu composite. Spherically structured Si/C composite containing nano silicon and fine graphite particles embedded in carbon matrix has been synthesized by spray drying technique using phenol formaldehyde resin as a carbon source [11]. The materials such as copper (II) D-gluconate [12], furfuryl alcohol [13], tetraethoxy silane [14], citric acid in ethanol solution [15] and a process involving several organic chemicals [16] were also reported for the preparation of carbon coated anode materials.

The prime requirement for an anode to deliver long cycle life is to make them degrade less capacity with cycling. This may be made possible if the composite has a rigid structure along with sufficient porosity and flexibility to accommodate the volume change. So far this has been achieved through a process called carbon coating which uses invariably organic compounds for that purpose.

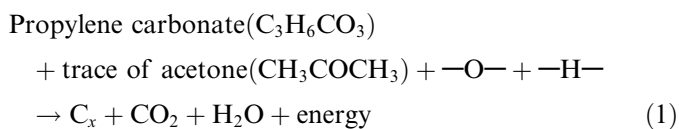
For the first time in the present investigation a simple and cheap compound, propylene carbonate has been chosen for enhancing the performance of silicon based anode material for the following reason. Propylene carbonate has a density of 1.189 g/mL. Due to its viscous nature it is used as a plasticizer in solid polymer electrolyte for use in lithium ion battery [17]. It is combustible with a flash point 135 °C and has autoignition temperature 455 °C. It is supposed that this polar, aprotic organic compound could attach well with SiO/C composite as the composite has also residual charges due to the presence of adsorbed water molecules and physically and chemically attached oxygen. The direct use of propylene carbonate with the composite and heat treatment does not improve the performance of the anode composite. This may be due to the viscous nature of propylene carbonate which could prevent easy penetration and uniform distribution over the composite material. In order to make propylene carbonate to interleave well between the composite particles acetone was used as a thinner along with propylene carbonate.

This paper presents the synthesis of SiO/C composite using ball milling and thermal treatment of the composite with an organic solution mixture made of propylene carbonate and acetone. Analysis of the electrode/electrode materials through X-ray diffraction (XRD), scanning electron micrographs (SEM), cyclic voltammetry (CV) and cycle life study has been performed to understand the fac-

tors responsible for better cycle life performance of the electrode.

2. Experimental

Appropriate quantities of SiO (Aldrich, –325 mesh) and graphite (Sodiff New Materials Co., Ltd., Korea, –400 mesh) weighing equal proportion were placed along with stainless steel (SS) balls in a 200 ml stainless steel vial. The weight ratio of SS ball to material was maintained at 10:1 and the vial was filled with argon gas. The contents in the vial were milled for 15 h using a ball mill at 350 rpm. The milled sample is denoted as composite ‘A’. Slurry was prepared by mixing 2.5 g of the composite ‘A’ and 5 ml of the solution made of propylene carbonate (PC) and acetone (AC) in the ratio 1:1 (v/v) in a beaker using a magnetic stirrer. During stirring the volume of the slurry got reduced probably due to the evaporation of acetone. The slurry was poured into an alumina boat and heated in a furnace at a rate of 5 °C under an argon atmosphere and maintained at 750 °C for 3 h and then spontaneously cooled down to reach room temperature. The thermal decomposition of the organic molecules [15] under argon atmosphere in the presence of SiO/C composite may be represented by the equation



The components –O– and –H– come from trace of adsorbed water molecules and also from physically/chemically attached –O– from SiO and graphite. C_x denotes the variation of x value of carbon from 1 to 3. The material obtained after thermal treatment of the slurry appeared as agglomerated clusters possibly due to wrapping up of C_x carbon particles which was then crushed into powder using a mortar and denoted as composite ‘B’. A viscous mass was prepared by mixing the composites ‘A’ and ‘B’ independently with 15 wt.% polyvinylidene difluoride (PVDF) dissolved in *N*-Methyl-2-pyrrolidinone using an agitator. The viscous mass was then coated on a copper foil and dried in a hot air oven at 110 °C for 1 h and pressed using SS roller to reduce the thickness to ~75%. Finally the film was annealed at 110 °C for 12 h in vacuum.

The active material coated copper foil was cut in the form of a circular disc of diameter 1.4 cm and coupled with lithium foil counter electrode separated by polypropylene separator, celgard membrane 2700 in a coin cell. The electrolyte (received from Techno Semichem. Ltd., Korea) is 1 M LiPF₆ with 2 wt.% of vinylene carbonate (VC) dissolved in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) mixed in 1:1 (V/V) ratio. Coin cells were assembled in a dry room maintained at ~21 °C with dew point temperature ~–65 °C. The anode was cycled between 0 and 1.5 V versus Li⁺/Li at a constant current

of 0.253 mA cm^{-2} using charge–discharge analyzer, Toyo System Ltd., Japan.

The composite powders were examined using a Philips 1830 X-ray diffractometer with nickel filtered Cu $K\alpha$ radiation at a scan rate of $0.04^\circ/\text{s}$ over a 2θ range of $10\text{--}80^\circ$. The surface morphology of the active material coated on copper foil was scanned using Hitachi S-4800 scanning electron microscope.

3. Results and discussion

The XRD pattern obtained for SiO, graphite (C) and the composite 'A', and the composite 'B' are presented in Fig. 1. The pattern for composite 'A' shows that the graphite considered for ball milling is crystalline one and SiO is an amorphous variety. Thermally treated organic slurry composite powder shows a slight enhancement of the amplitude of the peak at 26° showing that the crystalline nature of the graphite is slightly improved. This improved crystalline nature of the graphite implies that the graphite in the resultant structure is reinforced to provide compactness to the electrode material. Also the XRD pattern suggests that the ball milling as well as the heat treatment with organic solutions have not produced formation of any new compound.

The SEM pictures of the electrode-A and electrode-B are shown in Fig. 2. It is evident from the SEM pictures that the electrode-B has larger particles with voids and interspaces compared to the particle arrangement in the electrode-A. The partial removal of oxygen as well the trace of hydrogen present in the composite could have effected bonding rearrangement within the particles invoking reinforcement and compactness to the resultant structure in concomitant with trapping/wrapping of formed C_x particles.

The comparative curves showing the values of specific capacity with cycle number for the electrode-A and electrode-B are given in Fig. 3. The figure illustrates that the electrode-A exhibits higher charge/discharge capacity values until 53rd cycle and then the capacity falls below the

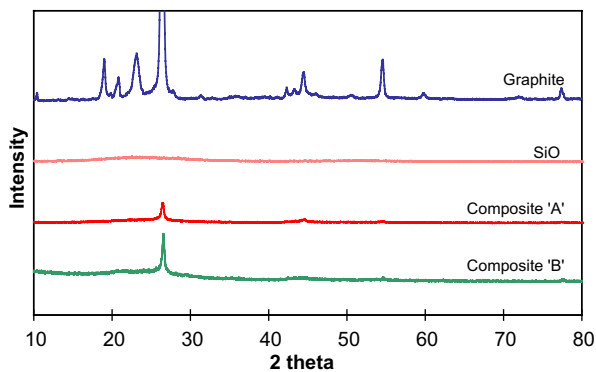


Fig. 1. XRD patterns of SiO; Graphite (C); composite 'A' – ball milled SiO/C; composite 'B' – obtained after the thermal treatment of the slurry made of SiO/C, PC and AC.

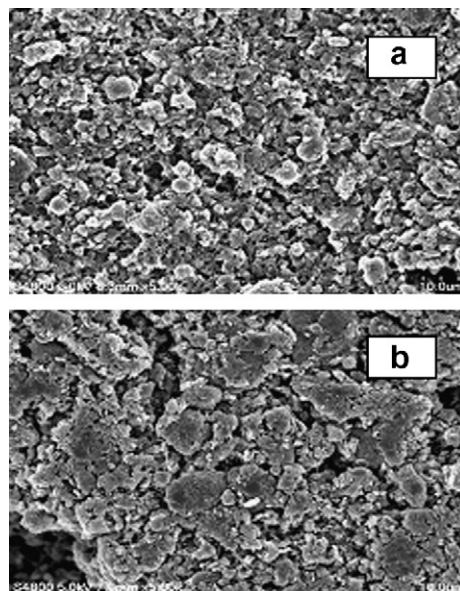


Fig. 2. SEM micrographs of samples, a – electrode-A; b – electrode-B.

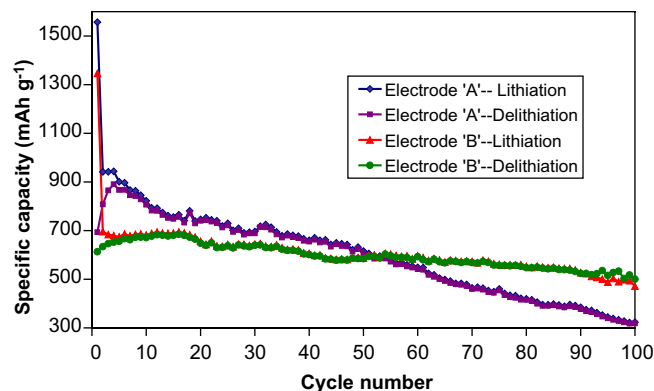


Fig. 3. Specific capacity as a function of cycle number for electrode-A and electrode-B.

value of the electrode-B. The initial irreversible capacities (863 mAh g^{-1} for the electrode-A and 733 mAh g^{-1} for electrode-B) denote the utilization of these capacities for the formation of Li_2O which acts as a buffer component for improving the cycle behaviour [3]. Again the lower initial irreversible capacity value of the electrode-B compared to the electrode-A by a value, 130 mAh g^{-1} suggests the reduction of equivalent amount of chemically/physically attached oxygen in the composite 'B' compared to the oxygen present in the composite 'A' after thermal treatment (1). Further, the electrode-B has lower initial irreversible capacity, 733 mAh g^{-1} compared to the value 863 mAh g^{-1} of the electrode-A. The lower initial irreversible capacity corresponds to the formation of lower buffer component, Li_2O . Even though the electrode-B has lower buffer component compared to the electrode-A, it shows better cycle behaviour, possibly due to the structural rearrangement associated with partial removal of oxygen and wrapping/trapping of formed C_x with the composite particles

enabling the formation of reinforced flexible structure which makes the electrode-B to withstand the volume changes during cycling. For both the electrodes, the irreversible capacity decreases with cycling and the coulombic efficiency tend to reach $\sim 99\%$ after few cycles. It may be noted from 1st to 4th cycle for the electrode-A, the charge capacity value increases from 693 to 890 mAh g⁻¹ and for the electrode-B from 613 to 652 mAh g⁻¹. The charge capacity increase values calculated as 197 and 39 mAh g⁻¹ may be termed as the charge capacity recovery values for the respective electrode-A and electrode-B. The attributes of the electrode-B such as lower charge capacity recovery and lower capacity degradation with cycling also reflect the structural rearrangement that occurred during thermal treatment with organic solution.

The cyclic voltammograms of the electrode-A and electrode-B scanned between 0 and 1.5 V at a scan rate of 0.1 mV s⁻¹ is shown in Fig. 4. The delithiation process displayed in the 5th cycle is considered for discussion. The delithiation process of the electrode-A is associated with an increase of current with potential whereas the electrode-B shows first an increase up to 0.3 V, then exhibits nearly a stable current between 0.3 and 0.6 V. This shows an overpotential dependent current flow through the electrode-A which is possible for an electrode with a loosely bound dispersed structure. The electrode-B nearly does not show increase of current as the potential is scanned from 0.3 to 0.6 V, illustrating that the electrode-B behaves apparently like a resistor over this narrow potential range. The resistor like behaviour illustrates the compact nature of the structure which could stream line the current flow with a tolerable volume changes during charge/discharge process. This is well supported by the SEM micrographs which show the presence of large interspaces and voids among the agglomerated particles. These voids and interspaces could accommodate enough electrolytes for easy lithium ion diffusion. Since the capacity degradation is less with cycles it may be presumed that the electrode has a flexible structure with sufficient pores to buffer the volume changes during charge/discharge cycles.

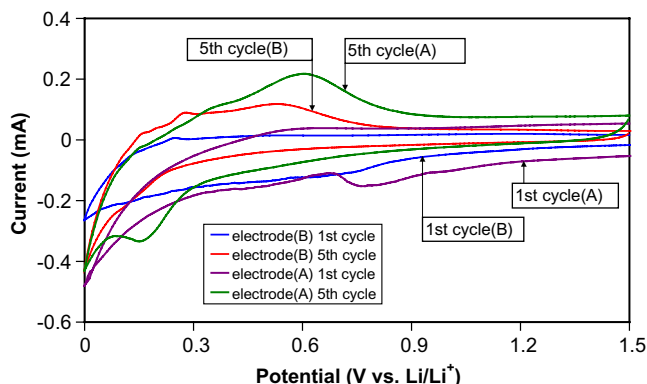


Fig. 4. Cyclic voltammogram for electrode-A and electrode-B at 0.1 mV s⁻¹.

4. Conclusions

For the first time a simple organic solution mixture consisting of propylene carbonate and acetone has been reported for the slurry preparation and thermal treatment of SiO/C composite as anode material for lithium ion battery. The pristine composite has higher charge capacity recovery as well as higher capacity degradation with cycling. On the other hand thermally treated slurry composite shows low charge capacity recovery and stable capacity with cycling. The appearance of voids and interfaces appearing in SEM micrographs was attributed to agglomeration of the composite particles following structural rearrangement during partial removal of chemically/physically present oxides and trace of hydrogen. Even though the thermally treated composite has lower Li₂O buffer component, exhibits higher cycle stability possibly attributed to the reinforced flexible structure trapped/wrapped with C_x particles/layers. The resistor like behaviour as evident from cyclic voltammetry study shows the constant current flow over a narrow potential range from 0.3 to 0.6 V during delithiation explains the compactness of the electrode structure. Hence it may be concluded that further study on silicon based electrodes with this simple and cheap organic solution could arrive a better composite composition for developing a high cycle capacity anode for lithium ion battery.

Acknowledgements

This work has been carried out at Division of Advanced Batteries supported by NGE program (Project No. 1001653) of KERI, Korea. One of the authors A. Veluchamy wishes to thank the Korean Federation of Science and Technology Societies, Korea for awarding Brain Pool Fellowship and also thanks CECRI/CSIR, India for granting leave.

References

- [1] N. Dimov, K. Fukuda, T. Umeno, S. Kugino, M. Yoshio, J. Power Sources 114 (2003) 88.
- [2] N. Dimov, S. Kugino, M. Yoshio, *Electrochim. Acta* 48 (2003) 1579.
- [3] C.H. Doh, H.M. Shin, D.H. Kim, Y.D. Jeong, S.I. Moon, B.S. Jin, H.S. Kim, K.W. Kim, D.H. Oh, A. Veluchamy, *J. Alloys compd.* Available online 28 July 2007.
- [4] C.H. Doh, N. Kalaiselvi, C.W. Park, B.S. Jin, S.I. Moon, M.S. Yun, *Electrochem. Commun.* 6 (2004) 965.
- [5] N. Jayaprakash, N. Kalaiselvi, D.H. Doh, *Intermetallics* 15 (2007) 442.
- [6] M.S. Yun, K.Y. Jeong, E.W. Lee, B.S. Jin, H.S. Kim, S.I. Moon, C.H. Doh, *Korean J. Chem. Eng.* 23 (2006) 230.
- [7] M.S. Yun, K.Y. Jeong, E.W. Lee, C.H. Doh, *Bull. Korean Chem. Soc.* 27 (2006) 175.
- [8] H.Y. Lee, S.M. Lee, *Electrochem. Commun.* 6 (2004) 465.
- [9] H.Y. Lee, Y.L. Kim, M.K. Hong, S.M. Lee, *J. Power Sources* 141 (2005) 159.
- [10] J.H. Kim, H. Kim, H.J. Sohn, *Electrochem. Commun.* 7 (2005) 557.
- [11] L. Chen, X. Xie, B. Wang, K. Wang, J. Xie, *Mater. Sci. Eng. B* 131 (2006) 186.

- [12] S. Yoon, S.I. Lee, H. Kim, H.J. Sohn, J. Power Sources 161 (2006) 1319.
- [13] T. Morita, N. Takami, J. Electrochem. Soc. 153 (2) (2006) A425.
- [14] T. Zhang, J. Gao, H.P. Zhang, L.C. Yang, Y.P. Wu, H.Q. Wu, Electrochem. Commun. 9 (2007) 886.
- [15] S.H. Ng, J. Wang, K. Konstantinov, D. Wexler, S.Y. Chew, Z.P. Guo, H.K. Liu, J. Power Sources 174 (2007) 823.
- [16] Y. Kwon, G.S. Park, J. Cho, Electrochim. Acta 52 (2007) 4663.
- [17] T.J. Benedict, S. Banumathi, A. Veluchamy, R. Gangadharan, A.Z. Ahamad, S. Rajendran, J. Power Sources 75 (1998) 171.