



## Short communication

Improvement of cycle behaviour of SiO/C anode composite by thermochemically generated Li<sub>4</sub>SiO<sub>4</sub> inert phase for lithium batteries

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## ABSTRACT

A new anode composite material is prepared by thermal treatment of a blend made of silicon monoxide (SiO) and lithium hydroxide (LiOH) at 550 °C followed by ball milling with graphite. X-ray diffraction pattern confirms the presence of Li<sub>4</sub>SiO<sub>4</sub> in the thermally treated (SiO + LiOH) material. The electrode appears to be smooth and glassy as evident from observation with a scanning electron microscope (SEM), possibly due to the presence of nano-silicon and Li<sub>4</sub>SiO<sub>4</sub> particles, and exhibits superior performance with a charge capacity of ~333 mAh g<sup>-1</sup> at the 100th cycle with a low-capacity fade on cycling. Cyclic voltammograms of the electrode predict high power capability. On the other hand, the electrode comprising of only SiO and C prepared through ball milling, devoid of Li<sub>4</sub>SiO<sub>4</sub>, shows hard crust particulates in the electrode exhibiting low charge–discharge capacities with cycling.

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## 1. Introduction

The search for a high specific capacity anode as an alternative for low-capacity graphite (372 mAh g<sup>-1</sup>) used in lithium-ion batteries has opened up a new area of research based on tin and silicon, which have specific capacity values of 4190 and 990 mAh g<sup>-1</sup> corresponding to Li<sub>22</sub>Si<sub>5</sub> and Li<sub>22</sub>Sn<sub>5</sub> alloys, respectively [1,2]. Despite exhibiting high initial capacities, the crystallographic volume changes of these electrodes during cycling cause premature cell failure. In the case of silicon-based composites, a reasonable level of cycle capacity has been achieved employing dual composites comprising Si or SiO with graphite. Improvements in performance have been reported by adding metal powders [3], silicon alloys [4], silicon compounds [5] and carbon coatings to the composites [1,6]. Silicon oxide-based composite anodes perform better than silicon-based ones as the former generate a buffer component Li<sub>2</sub>O along with nano-silicon during initial cycling that

reduces electrode strain [6]. It has been disclosed [7] that the high performance of a SiO-based composite is due to the formation of silicate in the electrode during the initial lithiation process that acts as a volume buffer in addition to its role as an electroactive species [7]. Even though different mechanisms have been reported to explain the high cycleability of SiO, the study by Schulmeister and Mader [8] showed that commercially produced SiO is not a single-phase compound but a mixture of amorphous SiO<sub>2</sub> and amorphous Si. Such investigations portray the difficulties in proposing any plausible mechanism to explain the charge–discharge process of SiO-based electrodes. Further improvement in electrode performance was made by incorporating/generating inert materials such as Li<sub>2</sub>O [9], Al<sub>2</sub>O<sub>3</sub> [10] and SiO<sub>2</sub> [11], either during synthesis or in the first lithiation process. The interdependency of sustainable reversible capacity and initial irreversible capacity (Li<sub>2</sub>O) of the electrode materials has also been reported for a SiO/C composite [6]. Anode composite materials consisting of nano-sized silicon and Li<sub>4</sub>SiO<sub>4</sub> [12] and also the Li-doped SiO material Li<sub>x</sub>SiO [13] are capable of delivering high capacity with a flat plateau in cycle-life performance.

This paper reports a simple method for preparing a precursor material by thermal treatment of SiO with LiOH at around 550 °C, followed by ball milling with graphite powder. An electrode prepared with this composite is compared with a normally prepared

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SiO/C composite electrode through techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), charge–discharge analysis and cyclic voltammetry (CV).

## 2. Experimental

Equimolecular quantities of lithium hydroxide monohydrate LiOH·H<sub>2</sub>O (Aldrich) and SiO (–325 mesh, LTS Chemicals Inc.) were mixed in a mortar and then heated to 550 °C for 3 h in an argon atmosphere. Graphite (C) was then added to maintain the weight ratio of C and SiO at 1:1 and ball-milled for 15 h. The composite was named as ‘A’. In order to understand the behaviour of the new composite ‘A’ another composite ‘B’ was prepared by just ball milling SiO and C in a weight ratio of 1:1 for 15 h.

The composite powders ‘A’ and ‘B’ were then examined by means of a Philips 1830 X-ray diffractometer with nickel-filtered Cu K $\alpha$  radiation at a scan rate of 0.04° s<sup>–1</sup> over a 2 $\theta$  range of 10–80°. The surface morphology of the active material coated on copper foil was examined with a Hitachi S-4800 scanning electron microscope. Hereafter, for the sake of convenience, lithium hydroxide monohydrate (LiOH·H<sub>2</sub>O) will be referred as LiOH.

The composites so obtained were independently mixed with 15 wt.% of polyvinylidene difluoride (PVDF) in N-methyl-2-pyrrolidinone using an agitator. The viscous masses were then coated on different copper foils and dried in a hot air oven at 110 °C for 1 h and pressed using a stainless-steel roller to reduce the thickness to ~75%. Finally, the copper foils coated with electrode materials were annealed at 110 °C for 12 h in vacuum and cut in the form of circular disc of diameter 1.4 cm.

The disc thus cut were denoted electrodes ‘A’ and ‘B’ and independently coupled with a lithium foil counter electrode separated by a polypropylene separator, and a celgard membrane 2700 in a coin cell. The electrolyte (Techno Semichem. Ltd., Korea) was 1 M LiPF<sub>6</sub> with 2 wt.% vinylene carbonate (VC) dissolved in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) mixed in 1:1 (v/v) ratio. The cells were assembled in a dry room maintained at ~21 °C with dew point temperature of about –65 °C. The anodes were cycled between 0 and 1.5 V versus Li<sup>+</sup>/Li at a constant current of 0.253 mA cm<sup>–2</sup> using a charge–discharge analyzer (Toyo System Ltd., Japan).

## 3. Results and discussion

### 3.1. X-ray diffraction analysis

The XRD patterns of graphite (C), SiO, LiOH, heat-treated (SiO+LiOH) and ball-milled material made of heat-treated (SiO+LiOH)/C are presented in Fig. 1. The data show that graphite and LiOH are crystallites, and SiO is amorphous. The constituents C, SiO and LiOH are noted in figure as (a)–(c). The precursor material obtained by heating (SiO + LiOH) at 550 °C does not show peaks corresponding to LiOH but exhibits new peaks. Examination with the JCPDS file shows that the new peaks are related to the compound Li<sub>4</sub>SiO<sub>4</sub>. Also the base line above the horizontal line between 2 $\theta$  values of 20° and 30° suggests the presence of SiO in the heat-treated materials. In the sub-section of Fig. 1, XR-2 the material (d) = (b) + (c) heated to 550 °C exhibits a peak at 2 $\theta$  = 32° that is ascribed to Li<sub>4</sub>SiO<sub>4</sub> and not to Li<sub>2</sub>O as there exists no other peak that can be attributed to Li<sub>2</sub>O. This observation leads to the conclusion that all the Li<sub>2</sub>O has reacted with SiO at 550 °C to form Li<sub>4</sub>SiO<sub>4</sub>. There are also several minor peaks for Li<sub>4</sub>SiO<sub>4</sub>. Hence, it may be proposed that before the melting point ~450 to 470 °C, the lithium hydroxide is dehydrated to form Li<sub>2</sub>O as represented by reaction (1). The reaction of Li<sub>2</sub>O with SiO may be represented by reaction (2):

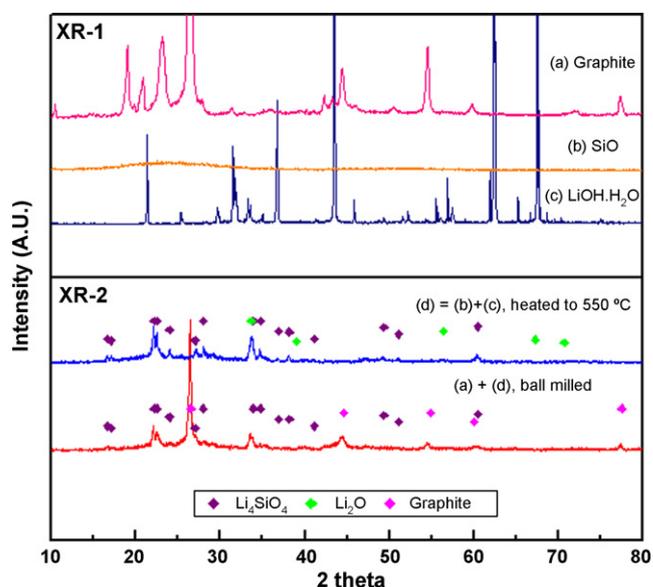


Fig. 1. XRD pattern of materials: (a) graphite; (b) SiO; (c) LiOH; (d) (b) + (c) heated at 550 °C in argon atmosphere; (a) + (d) ball-milled composite material.



Reaction (2) includes the formation of nano-silicon in addition to Li<sub>4</sub>SiO<sub>4</sub> and SiO in the precursor material (d). Li<sub>4</sub>SiO<sub>4</sub> is a compound with a high negative change in free energy ( $\Delta G^\circ_{298\text{K}} = -2366$  kJ/mole) [14] and is considered to be an electrochemically inactive species in the composite [12]. The XRD pattern of the ball-milled materials (d) with graphite (a) shows a reduction in the peak heights of both graphite and Li<sub>4</sub>SiO<sub>4</sub> and this implies that the particles have undergone size reduction during ball milling.

### 3.2. Scanning electron micrographs

Scanning electron micrographs of electrodes ‘A’ and ‘B’ are presented as (A) and (B) in Fig. 2. The proposed reaction (2) states that electrode ‘A’ has two additional component, viz., Li<sub>4</sub>SiO<sub>4</sub> and nano-silicon, with a lesser quantity of SiO compared with electrode (B). This difference in the components may be responsible for the marked difference in the micrographs of the two composites. The particles in electrode ‘A’ appear to be smooth and glassy, whereas electrode ‘B’ is composed of hard crust particulates. The smooth glassy structure of ‘A’ may be due to the presence of a strain-free particle arrangement which may be expected to deliver flat-plateau cycle behaviour compared with electrode ‘B’.

### 3.3. Specific capacity–voltage profile

The typical specific capacity–voltage profile for the electrode ‘A’ is presented in Fig. 3. The discharge and charge capacity values are 862, 470 and 440 and 475, 464 and 437 mAh g<sup>–1</sup>, respectively, for the 1st, 10th and 30th cycles. These values suggest that, the large difference in capacities on the first cycle is attributable to the formation of Li<sub>2</sub>O. In the 10th and 30th cycles, however, the negligible difference in the discharge–charge cycle suggests that in addition to graphite, the presence of lithium silicate Li<sub>4</sub>SiO<sub>4</sub> in the composite has contributed to the improvement in cycling behaviour.

### 3.4. Cycle/capacity behaviour

The variation of specific capacity with cycle number for electrodes ‘A’ and ‘B’ is presented in Fig. 4. For both electrodes, the

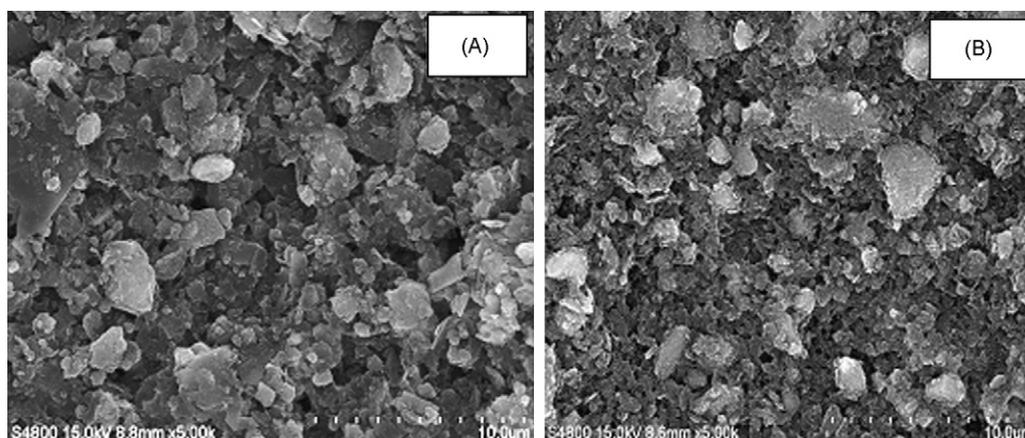


Fig. 2. Scanning electron micrographs of electrode 'A', heat-treated (SiO + LiOH)/C; electrode 'B', SiO/C.

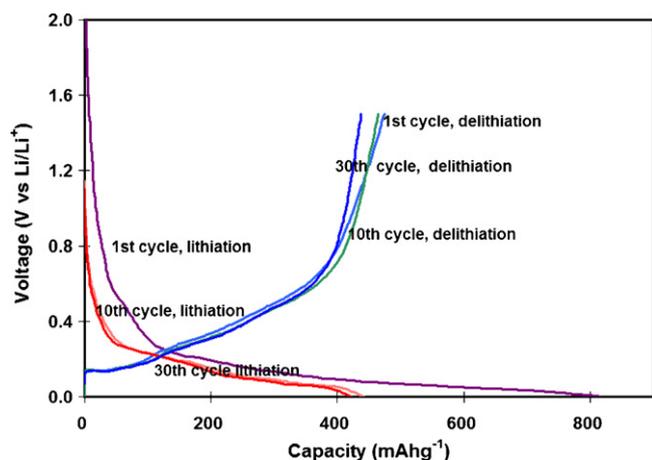


Fig. 3. Typical voltage-specific capacity profile of heat-treated (SiO + LiOH)/C electrode 'A' at different cycle numbers.

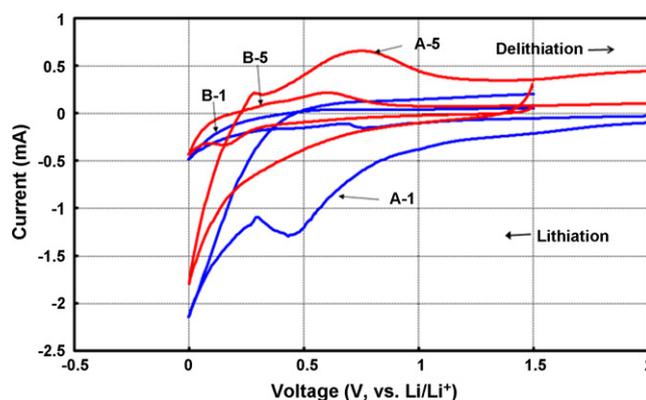


Fig. 5. Cyclic voltammograms for electrodes scanned at  $0.1 \text{ mV s}^{-1}$ ; A-1 and A-5 are 1st and 5th cycles of the heat-treated (SiO + LiOH)/C electrode 'A' and B-1 and B-5 are 1st and 5th cycles of SiO/C electrode 'B'.

reduction in discharge capacity in the second cycle is attributed to the consumption of part of the lithium that has been inserted into  $\text{Li}_2\text{O}$  during first discharge process [6]. Data obtained from Fig. 4 is presented in Table 1. The irreversible capacity  $387 \text{ mAh g}^{-1}$  (44%) given by electrode 'A' is considerably lower than that, namely,  $\sim 863 \text{ mAh g}^{-1}$  (55%), of electrode 'B'. Electrode 'A' also exhibits a lower initial lithiation capacity ( $862 \text{ mAh g}^{-1}$ ) than electrode 'B'. The reduction in initial capacity and also the irreversible capacity are attributed to the reduction of a quarter of the SiO in the composite 'A', that is converted into  $\text{Li}_4\text{SiO}_4$  during precursor formation. The amount of SiO present in the composite has a direct relationship with irreversible capacity and initial specific capacity, which is in agreement with an early report [9]. The slightly higher charge capacity shown by electrode 'A', even at the 100th cycle, may be attributed to the buffer action provided by  $\text{Li}_4\text{SiO}_4$ .

### 3.5. Cyclic voltammograms (CV)

The cyclic voltammograms (CV) of electrode 'A' and 'B' are presented in Fig. 5. Comparison of the low delithiation current peak of

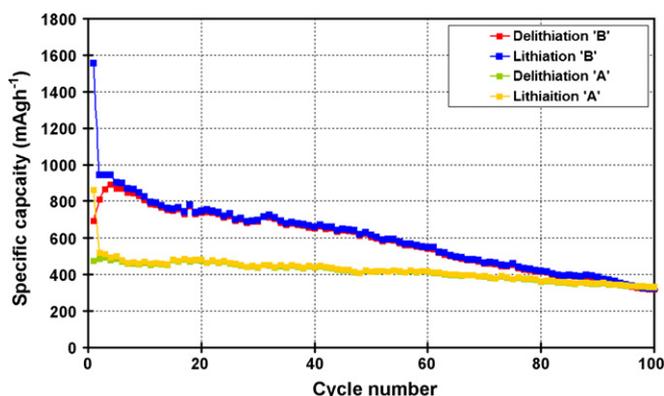


Fig. 4. Profile of specific capacity versus cycle number: delithiation 'B' and lithiation 'B' represent charge and discharge curves, respectively, for SiO/C electrode 'B'; delithiation 'A' and lithiation 'A' represent charge and discharge curves for heat-treated (SiO + LiOH)/C electrode 'A'.

Table 1  
Capacity values obtained from Fig. 4 for two different composite electrodes.

Composition of the electrodes	Initial lithiation capacity ( $\text{mAh g}^{-1}$ )	Initial delithiation capacity ( $\text{mAh g}^{-1}$ )	Irreversible capacity ( $\text{mAh g}^{-1}$ )	Charge capacity at 100th cycle ( $\text{mAh g}^{-1}$ )
Heat-treated (SiO + LiOH) with C electrode 'A'	862	475	387 (44%)	333
SiO with C electrode 'B'	556	693	863 (55%)	318

'B' and the high delithiation current of 'A' is sufficient to explain the superior properties of electrode 'A', which contains  $\text{Li}_4\text{SiO}_4$  along with a lower active silicon ( $\text{SiO} + \text{Si}$ ) content (see reaction (2)). The high peak current values noted in the CV, such as A-5 and B-5 for the delithiation current at 5th cycle suggest that electrode 'A' would have better lithium-ion diffusion process supporting its suitability for high-power battery applications. This possibly due to the presence of lithium environment/buffer action provided by  $\text{Li}_4\text{SiO}_4$  in the composite.

#### 4. Conclusions

This study has reported for the first time a thermochemical procedure to prepare a precursor containing  $\text{Li}_4\text{SiO}_4$  and  $\text{SiO}$ , possibly along with nano-silicon particles, by heating  $\text{SiO}$  and  $\text{LiOH}$  at  $550^\circ\text{C}$ . The electrode containing a heat-treated ( $\text{SiO} + \text{LiOH}$ )/C composite shows sustainable capacity up to 100 cycles with a low rate of degradations. The superior property of the composite is achieved at the cost of initial capacity since quarter of the active material  $\text{SiO}$  has been converted to  $\text{Li}_4\text{SiO}_4$ . The presence of  $\text{Li}_4\text{SiO}_4$  is considered to provide better lithium-ion diffusion and thereby makes the electrode a candidate for high-power anodes in lithium-ion battery application.

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