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Published in:
Journal of the Electrochemical Society

Published: 01/01/2019

Document Version:
Final Published version, also known as Publisher’s PDF, Publisher’s Final version or Version of Record

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Publication record in CityU Scholars:
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Published version (DOI):
10.1149/2.0321903jes

Publication details:

Citing this paper
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Download date: 09/09/2019
Probing the Reversibility of Silicon Monoxide Electrodes for Lithium-Ion Batteries

Tian Tan, Pui-Kit Lee, and Denis Y. W. Yu

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Silicon monoxide (SiO) is a promising anode material for lithium-ion batteries (LIBs) with a reversible capacity of more than 1000 mAh g\(^{-1}\), much higher than that of graphite. However, it suffers from two major issues. First, it undergoes a large volume expansion of about 200% during lithiation, which leads to pulverization of the particles and electrode cracking. Second, the material has a low first cycle efficiency (FCE) due to the formation of inactive lithium silicate in the material. Some of the mechanical problems can be suppressed by the reduction of particle size and utilization of a stronger binder. In this study, we investigate the factors affecting the initial reversibility of SiO to develop insights to improve the material.

Previous works indicate that the lithiation of SiO results in the formation of lithium oxide and lithium silicate such as Li\(_2\)SiO\(_3\), Li\(_2\)SiO\(_4\), Li\(_3\)SiO\(_4\), as well as lithiated silicon (Li\(_3\)Si).\(^{5-7}\) The material shows low FCE (65.1–82.1%), as the Li-ions are trapped mainly as Li\(_2\)O and lithium silicate inside it. The amount of oxygen in SiO\(_x\) has been found to be an important factor affecting its FCE - Kim et al. discovered that the increase of oxygen atomic ratio in SiO\(_x\) leads to a decrease in FCE,\(^{8}\) while Yang et al. showed that the reduction of SiO\(_x\) by mechanochemical/thermal reduction with Li metal can improve the FCE.\(^{9}\) Prelithiation by methods such as electrochemical discharging of SiO with Li, direct contact between the SiO electrode and Li metal, and coating Li metal onto the polypropylene separator can increase FCE.\(^{10}\) However, these methods typically require the use of glove box or dry room for the processing of the Li metal and are not practical for mass production.

To understand and quantify the reversibility of SiO, we adopted the “depth of discharge” (DOD) test here that we have previously developed to the study of Si electrodes.\(^{11}\) The detailed procedure of the test can be found in our previous publication, but in brief, electrodes are discharged to different degree of lithiation, and then charged subsequently to monitor the reversible capacity. Here, we first performed the DOD tests on SiO materials to understand the contributions to its reversibility. Then, the effects of carbon-coating and disproportionation were studied. Amorphous SiO can be disproportionated into nanocrystalline Si domain and SiO\(_2\) cluster above 850 °C, thus changing the capacity and efficiency of the material.\(^{12,13}\)

### Experimental

**Materials.**—SiO and carbon-coated SiO (SiO@C with 3 wt% C) were provided by Osaka Titanium Technologies Co., Ltd., Japan. The Si:O ratio is 1:1.2. All other chemicals were of analytical grade and used as received.

<table>
<thead>
<tr>
<th>Material</th>
<th>Loading (mg cm(^{-2}))</th>
<th>Packing density (g cm(^{-3}))</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO</td>
<td>0.98±1.02</td>
<td>~1.2</td>
<td>44~46</td>
</tr>
<tr>
<td>SiO@C</td>
<td>0.95±1.05</td>
<td>~1.2</td>
<td>40~49</td>
</tr>
<tr>
<td>d-SiO@C-900°C</td>
<td>0.94±1.00</td>
<td>~1.2</td>
<td>40~48</td>
</tr>
<tr>
<td>d-SiO@C-1000°C</td>
<td>0.97±1.07</td>
<td>~1.2</td>
<td>41~47</td>
</tr>
</tbody>
</table>

\(^{9}\)E-mail: denisyu@cityu.edu.hk

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Results and Discussion

Material characterizations.—Figure 1a displays the SEM image of the pristine SiO particles. The particles are irregular in shape, but the average particle size is about 1 μm. Carbon-coating the material results in material with similar morphology and size (Figure 1b). Figures 1c and 1d show similar appearance of the SiO@C material after disproportionation at 900 °C and 1000 °C, respectively. These images indicate that the heat-treatment process did not alter the morphology and shape of the materials.

The XRD patterns of pristine SiO, SiO@C, d-SiO@C-900 °C, and d-SiO@C-1000 °C powders are shown in Figure 2. The SiO material is amorphous, as no crystalline peaks can be observed. Carbon-coated SiO also shows an amorphous structure. In contrast, Si peaks can be observed after 900 °C disproportionation and the intensity of the Si peaks increases at higher temperature (1000 °C). This suggests that during the high-temperature annealing, SiO is disproportionated into Si and SiO2 regions, similar to that observed by Park et al.14

TGA was conducted to obtain the ratio of SiO2 in the pristine sample. During the heat-treatment to 1000 °C, SiO will react with oxygen in air to form SiO2. According to the TGA data (Figure 3), the weight increase is about 30.5%. This corresponds to a starting material of SiO1.12. The SiO ratio is consistent with that of Hirata et al., where the analyses were carried out on materials from the same source.12

The XRD patterns of SiO, SiO@C, d-SiO@C-900 °C, and d-SiO@C-1000 °C powders are shown in Figure 2. The SiO material is amorphous, as no crystalline peaks can be observed. Carbon-coated SiO also shows an amorphous structure. In contrast, Si peaks can be observed after 900 °C disproportionation and the intensity of the Si peaks increases at higher temperature (1000 °C). This suggests that during the high-temperature annealing, SiO is disproportionated into Si and SiO2 regions, similar to that observed by Park et al.14

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Depth of discharge tests on SiO.—SiO powders were first tested to understand the contributions to its discharge and charge capacities. Identical cells were made and discharged to different capacity limits under the DOD test, and then were charged to 2 V vs. Li/Li+. An upper cutoff potential of 2 V vs. Li/Li+ is chosen here as we intend to study the fundamental charge-discharge mechanism of SiO including the investigation of the amount of reversible and irreversible capacities from the conversion reaction (Li2O). Figure 4a shows the 1st discharge and charge curves of the SiO batteries discharged to 500, 1000, 1500 mAh g−1 and 0.01 V vs. Li/Li+. Since the first discharge curves for all cells overlapped each other, only the curve corresponding to a full discharge is plotted in Figures 4a–4d and the end points of different cells are marked as “X”. SiO shows a slanted 1st discharge profile, which is characteristic of the amorphous SiO and consistent with other works.5,6,15 We note that the subsequent charge capacity depends on the depth of discharge – a higher charge capacity is obtained when the material is discharged deeper initially. In the charge curves, the slanted region between 0.2 V and 0.65 V vs. Li/Li+ is attributed to the removal of lithium from the Li-Si alloy. The small capacity between 0.65 V and 2 V vs. Li/Li+ is attributed to the partial removal of lithium from Li2O formed during the previous lithiation.

To determine the contributions to the reversible and irreversible capacities, we can plot the initial charge capacity vs. discharge capacity for different cells as in Figure 4e. The data show a linear pattern which can be fitted with a straight line. In addition, the fitted line is deviated from the origin with a non-zero x-intercept. From our previous analysis, the slope of the line represents the intrinsic efficiency of the material, which is the proportion of lithium that can be extracted reversibly from the material.13 On the other hand, the non-zero x-intercept represents the amount of capacity that is completely irreversible. For the SiO material charged to 2 V vs. Li/Li+ in this work, the measured slope is 80% with an x-intercept of 264 mAh g−1 (Table II.) This suggests that on top of an irreversible capacity of 264 mAh g−1 during first discharge, an extra 20% of the Li remained in the material after charging to 2 V. If a cutoff potential of 1 V vs. Li/Li+ is considered, as in a practical battery, the intrinsic efficiency (slope) of SiO is reduced to 75%, and the amount of irreversible capacity is increased to 399 mAh g−1 because the Li2O component is regarded as irreversible with a lower cutoff potential. Compared to crystalline Si materials, which has an intrinsic efficiency of 90% and an x-intercept
of 55 mAh g$^{-1}$. SiO has a much lower intrinsic efficiency (more Li trapped in the material) and a larger irreversible capacity.

Previous work by Kim et al. has suggested that during the lithiation of SiO, Li$_{3.75}$Si, Li$_2$O and Li$_4$SiO$_4$ are formed. Among the reaction products, Li$_4$SiO$_4$ is suspected to be completely inactive, whereas Li$_2$O can be charged and discharged to a certain degree and contributes significantly to the conversion reaction of oxide materials such as NiO, SnO$_2$, etc. These are consistent with results from our DOD test. Our work suggests that there are 2 contributions to the irreversible capacity of SiO: 1) the formation of an inactive matrix of lithium silicate, represented by the x-intercept; 2) the efficiency of the delithiation of Li$_{3.75}$Si and Li$_2$O, represented by the slope of the DOD test (see Figure 4e). To further analyze the results, we hypothesize a reaction mechanism during lithiation of SiO as following:

$$\text{SiO} \rightarrow a\text{Li}_{3.75}\text{Si} + b\text{Li}_2\text{O} + c\text{Li}_4\text{SiO}_4 + d\text{SiO}_2$$

Where “Li$_{3.75}$Si/Li$_2$O” is partially reversible (with an efficiency given by the slope of the DOD test) and “Li$_4$SiO$_4$” is irreversible (corresponding to the x-intercept of DOD test). Capacity corresponding to solid electrolyte interphase (SEI) formation can be included in the coefficient “c” as part of the irreversible component. Since the measured capacity of our SiO sample at full discharge (1804 mAh g$^{-1}$) is smaller than the theoretical capacity of 2459 mAh g$^{-1}$ (assuming 20% Li$_2$O product based on Kim et al.), we speculate there is a por-

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**Table II. Summary of slope and x-intercept from DOD test of SiO, SiO@C and disproportionated SiO@C.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Slope</th>
<th>x-intercept (mAh g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO</td>
<td>80% ± 0.5%</td>
<td>264 ± 5</td>
</tr>
<tr>
<td>SiO@C</td>
<td>93% ± 0.2%</td>
<td>310 ± 4</td>
</tr>
<tr>
<td>d-SiO@C-900°C</td>
<td>88% ± 0.2%</td>
<td>246 ± 2</td>
</tr>
<tr>
<td>d-SiO@C-1000°C</td>
<td>87% ± 0.1%</td>
<td>189 ± 1</td>
</tr>
</tbody>
</table>
tion of SiO₂ in the material that are not reacted (4th compound). The compositions of the product “a”, “b”, “c”, and “d” in Equation 1 can be estimated using results from the DOD test. Specifically, the coefficient “c” corresponds to the x-intercept of the DOD test (264 mAh g⁻¹) based on the assumption that Li₄SiO₄ is irreversible. The total first discharge capacity obtained can be converted into the value of “y”. The remaining three coefficients can be solved as there are 3 relationships corresponding to the balance of chemical elements of Li, Si and O.

The fitted parameters for SiO based on the obtained 1st discharge capacity and the x-intercept of the DOD test is shown in Table III, and the reaction is estimated to be:

\[
\begin{align*}
\text{SiO}_1& \rightarrow 3.10 \text{Li}^+ + 3.10 \text{e}^- \rightarrow 0.63 \text{Li}_3\text{SiO}_4 + 0.15 \text{Li}_2\text{O} \\
+ 0.11 \text{Li}_2\text{SiO}_3 + 0.26 \text{SiO}_2
\end{align*}
\]

The result suggests that for every mole of SiO₁,₂, the products after lithiation are 0.63 moles Li₃SiO₄, 0.15 moles Li₂O, 0.11 moles Li₂SiO₃ and 0.26 moles SiO₂. A total of 3.10 moles of Li⁺ is inserted, corresponding to the first discharge capacity of 1804 mAh g⁻¹. The measured first charge capacity is 1250 mAh g⁻¹, corresponding to an extraction of 2.14 moles of Li⁺. This is consistent with Equation 2, where 80% (= slope of DOD test) of Li in “Li₃.75Si/Li₂O” is reversible (i.e. 0.8 × (0.63 × 3.75) + (0.15 × 2)) = 2.13, and all Li in Li₄SiO₄ is irreversible. In addition, most of the Li is removed from the Li₃Si component formed after lithiation, which is also consistent with the charging curve (Figure 4a) where most of the capacity originates from a potential range below 1 V vs. Li/Li⁺.

Effect of carbon coating.—SiO is coated by a layer of carbon by chemical vapor deposition. The amount of carbon coating is 3 wt%. The SiO@C material was made into electrodes and tested in the same way as SiO. Figure 4b shows the discharge-charge curves during 1st cycle. With carbon coating, both discharge and charge capacities increase, suggesting that a larger portion of the lithium is trapped in the form of Li₄SiO₄.

By carrying out the same analysis using Equation 1, the composition after lithiation of SiO@C can be estimated from the discharge capacity and the irreversible capacity (x-intercept of DOD). The reaction is estimated to be:

\[
\begin{align*}
\text{SiO}_1& \rightarrow 3.47 \text{Li}^+ + 3.47 \text{e}^- \rightarrow 0.67 \text{Li}_3\text{SiO}_4 + 0.20 \text{Li}_2\text{O} \\
+ 0.13 \text{Li}_2\text{SiO}_3 + 0.19 \text{SiO}_2
\end{align*}
\]

Carbon coating increases the amount of lithiated reactants (a, b and c) and decreases the amount of unreacted SiO₂ after discharge (Table III).

To investigate the reason for the higher capacity after carbon coating, electrochemical impedance spectroscopy (EIS) measurement was carried out. All electrodes used for the EIS tests have similar active material loading of about 1.05 mg cm⁻². As shown in Figure 5a, the impedance plots consist of a semicircle in high-frequency region which is related to the charge transfer process, and a sloping line in low-frequency region which is ascribed to the solid-state Li diffusion inside active material. These curves are fitted with an equivalent circuit model as given in Figure 5b, where Rs, RSEI and RCT represent the internal resistance, resistance from SEI and charge-transfer resistance, respectively. CPE, C₀ and Cₓ are related to constant phase element, double layer capacitance and interaction capacitance, and ZW is the Warburg resistance corresponding to the lithium diffusion process. It can be seen that carbon coating decreases the charge-transfer resistance (Rₓ) from 33.8 Ω to 10.7 Ω. These results indicate that the incorporation of carbon layer can significantly improve the electrical conductivity, thus increasing the initial discharge (204 mAh g⁻¹) and charge capacities.

Carbon coating also increases the slope of the DOD test and the reversible capacity to 93%. This is consistent with the first charge capacity of 1605 mAh g⁻¹, corresponding to an extraction of 2.75 moles of Li from SiO@C. Apart from lithium removal from Li₃SiO₄, we also observe higher reversibility from Li₂O, leading to higher intrinsic efficiency. This is consistent with the additional capacity from a potential above 0.65 V vs. Li/Li⁺ as seen in the charge curves in Figure 4b.

Effect of disproportionation.—The microstructure of SiO is still controversial. There are two mainstreams of the structural model, one is the random bonding (RB) model and another is random mixture (RM) model. The RB model assumes a random network of silicon and oxygen in SiO, while the RM model assumes that there are 2 separate phases including Si and SiO₂. A modified RM model was also proposed by Hirata et al. where SiO acts as a transition layer between amorphous Si and SiO₂. When SiO is heat-treated, it will disproportionate to Si and SiO₂. The amount of crystalline Si and SiO₂-based amorphous suboxide will increase as the temperature increases. This is consistent with our XRD results, where the Si and SiO₂ peaks are observed when SiO@C is heat-treated. The peak intensities are higher at higher annealing temperature. Park et al. reported a better FCE and cycle performance with disproportionated SiO (d-SiO). This prompts us to use the DOD test to investigate the effect of disproportionation on the reversibility of SiO.

The 1st cycle discharge-charge curves for the d-SiO@C-900 °C and d-SiO@C-1000 °C are shown in Figures 4c and 4d, respectively. With disproportionation, we observe the initial discharge curves shift to lower potential. This is attributed to the discharge of the crystalline

Table III. Estimated amount of products after first lithiation. “a”, “b”, “c” and “d” are coefficients as given in Equation 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO</td>
<td>0.63</td>
<td>0.15</td>
<td>0.11</td>
<td>0.26</td>
</tr>
<tr>
<td>SiO@C</td>
<td>0.67</td>
<td>0.20</td>
<td>0.13</td>
<td>0.19</td>
</tr>
<tr>
<td>d-SiO@C-900 °C</td>
<td>0.62</td>
<td>0.14</td>
<td>0.10</td>
<td>0.28</td>
</tr>
<tr>
<td>d-SiO@C-1000 °C</td>
<td>0.54</td>
<td>0.03</td>
<td>0.08</td>
<td>0.38</td>
</tr>
</tbody>
</table>
are shown in Figure 6. SiO electrode shows a small drop in capacity during the first 10 cycles. Cycle efficiencies during the initial 10 cycles are also lower than SiO@C electrode, suggesting that there are some more Li trapped in the electrode with cycling. SiO@C shows higher charge capacity, better cycle efficiencies and also better cycle performance. Disproportionation decreases the available capacity, with slightly worse cycle performance than the SiO@C material.

Conclusions

We have applied the depth of discharge test to study the contributions to the irreversibility of SiO electrodes. Our results suggest that the amount of irreversible capacity of SiO depends on the type of reaction products. Using the obtained capacities from electrochemical depth of discharge tests, we can estimate the proportion of the reaction products. Even though some simple assumptions have to be made during the analyses, the trends are consistent with our experimental observations. Specifically, carbon coating the material leads to higher reactivity of SiO with Li due to improved electrical conductivity and reversibility of the Li2O conversion reaction. Though, the amount of inactive lithium silicate is also increased. Disproportionation reduces the irreversibility of SiO by forming some inactive SiO; in the material, though the overall capacity is reduced. Our results suggest that there are opportunities to further improve the first cycle efficiency of SiO by finding ways to control the reaction products during initial lithiation process.

Acknowledgments

The work described in this paper was supported by a grant from the Research Grants Council (CityU 21202014) of the Hong Kong Special Administrative Region, China.

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References


Cycle performance of SiO samples.—Cycle performance of the 4 types of electrodes were tested at 150 mA g⁻¹, and the results