

THE EFFECT OF WATER BINDER ON ELECTROCHEMICAL PROPERTIES OF SILICON OXIDE AS THE ANODE MATERIAL FOR LITHIUM ION BATTERIES

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Among new anode materials proposed for lithium-ion batteries (LIBs), silicon (Si) is considered the most promising candidate for replacing graphite. It is the second most abundant element in the earth's crust. This material is environmentally friendly with an ultra-high theoretical capacity ($4200 \text{ mAh}\cdot\text{g}^{-1}$). However, sharp volume changes of Si during the lithiation / delithiation process ($\sim 400\%$) and the high cost of producing a nanostructured silicon seriously prevent its wide use [1-3].

Recently, silicon oxides have been considered as promising substitutes for elementary silicon due to their extremely large reserves, low cost, and ease of synthesis [4]. In addition, they show smaller volume change upon cycling compared to elementary Si ($\sim 200\%$). Li_2O and lithium silicates generated during the first lithiation process can restrain large volume changes and as a result, improved cycling stability can be realized. Despite these advantages, silicon oxides also have a number of shortcomings, viz.:

- silicon oxides are insulators with low intrinsic electrical conductivity, which reduces their electrochemical activity;
- although the coefficient of volumetric expansion is not as large as in the case of elementary silicon, its influence cannot be completely excluded;
- the initial Coulombic efficiency (ICE) of silicon oxides is relatively low due to the irreversible formation of lithium silicates and Li_2O in the first cycle.

Thus, if the solution to the third problem lies in the area of improving the properties of the material itself (in particular, a number of authors propose to solve it by the preliminary lithiation of a sample), the first two problems may be directly related to the microstructure of the electrode, in particular, to the properties of the binder material.

The use of water-soluble systems for the electrode preparation process allows creating multiple silicon-oxygen bonds, which prevent mechanical destruction of the electrode upon cycling and, as a consequence, lead to an increase in the battery cycling life [5,6]. This paper deals with the electrochemical behavior of silicon oxide electrodes with various water-based binders.

1. Experimental

Silicon oxide SL450A-SOCQ (IOPSILION, China) was used as an active material for batteries together with various binders. Sodium carboxymethyl cellulose (CMC), styrene-butadiene rubber (SBR) (Shandong Gelon Lib Co. Ltd., China) and polyacrylic latex (LA136D) (Indigo, China). The presence of hydrophilic cyanoamide groups with high polarity in LA136D made it possible to ensure sufficient bond strength between the active material, the conductive agent and the current collector. The adhesion of the anode material to a copper foil was measured with an adhesion meter HI-0350 (Shanghai Hengyi Testing Instruments Co. Ltd., China).

The electrode mass was prepared by mixing silicon oxide, acetylene black (Super P, Alfa Aesar), and a polymer binder composition. The silicon oxide: Super P: polymer binder ratio was 93:2:5 (by weight). Deionized water was used as a solvent for the binders. After mixing for several hours, the electrode mass was applied to a copper foil (9 μm thick) by doctor blade). The electrodes were pre-dried at $t = 80\text{ }^{\circ}\text{C}$, compacted with a roller and cut to fit the dimensions of the CR2016 element. The final drying of the electrodes was carried out under vacuum at a temperature of $120\text{ }^{\circ}\text{C}$ for 48 hours. All LIB assembly operations were performed in a dry glove box. The humidity in the box did not exceed 1ppm. A 1 M solution of LiPF_6 in the mixture of ethylene carbonate, dimethyl carbonate and ethyl methyl carbonate (1:1:1 by mass, Dongguan Shanshan Battery Material Co. Ltd, China) were used as an electrolyte

together with a Celgard 2325 separator. Electrochemical characteristics of half-cells were obtained in the CCCV mode on electrochemical testing units by Neware Technology Limited (China). The operating voltage range upon cycling was 0.01-2.0 V. The analysis of the impedance spectra was made on a CHI electrochemical module (CH Instruments Inc., USA) using a ZPlot software.

2. Results and discussion

LA136D binder is a "sticky" polymer that provides better contact of the material to the Cu-collector. An increase in the LA136D content of the electrode mass leads to an increase in adhesion forces between the electrode material and the copper foil.

The initial specific capacity of silicon oxide (Fig. 1) is 600 to 650 mAh·g⁻¹ at a current density of 44.7 mA·g⁻¹ (the first 5 cycles of lithium intercalation into the structure of silicon oxide were carried out in two stages: (i) cycles at 44.7 mA·g⁻¹, (ii) cycles at 44.7+ 8.9 mA·g⁻¹). In the 1st cycle, the formation of a SEI layer consisting of oxides, fluorides, and lithium silicates (Li₂O, LiF, Li₂SiO₄, Li₂SiO₃, Li₂Si₂O₅, Li₆Si₂O₇) is observed.

Table. 2. Physicochemical and electrochemical parameters of the electrodes

| Binder compositions, % | Q, mAh·g ⁻¹ | | Coulombic efficiency in the first cycle, % | Physical parameters of electrode | | | Average voltage (current density 44.7 mA·g ⁻¹) | | |
|------------------------|------------------------|--------|--|----------------------------------|--------------------------|-------------|--|-------|-------|
| | 1-st | 5-th | | δ , μm | d , g·cm ⁻³ | Porosity, % | 5th | 15th | 75th |
| CMC: SBR (2:3) | 623.34 | 626.5 | 86.90 | 70±2 | 0.821 | 22.36 | 0.176 | 0.199 | 0.286 |
| CMC: LA136D (2:3) | 641.57 | 647.06 | 86.40 | 65±2 | 0.748 | 29.30 | 0.174 | 0.209 | 0.281 |
| LA136D (5:0) | 595.74 | 600.37 | 89.89 | 70±2 | 0.733 | 30.72 | 0.193 | 0.223 | 0.348 |

The formation of SEI requires lithium ions, so the coulombic efficiency in the 1st cycle does not exceed 86-89%. The main parameters of the electrodes are presented in Table. 2.

In 2nd to 5th cycles, a slight increase in specific capacity occurs indicating a pretreatment of the electrode material. In this case, the Coulombic efficiency of silicon oxide in a half-cell increases to 99%.

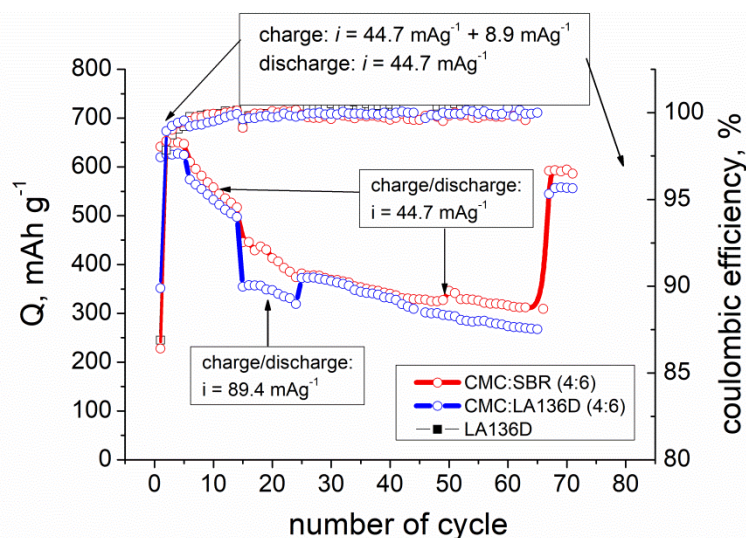


Fig. 1. Dependence of the specific capacity of electrodes with different water-soluble binders on the number of cycle

Next 10 (6th to 15th) cycles have been carried out at a current density of intercalation/deintercalation of lithium ions of 44.7 mA·g⁻¹ (without additional charge at $i = 8.9 \text{ mA}\cdot\text{g}^{-1}$). Here, a sharp drop in the specific capacity can be noted, amounting at $1.7 \pm 0.1\%$ per cycle. A further increase in the current density to $I = 89.4 \text{ mA}\cdot\text{g}^{-1}$ leads to an even greater decrease in the specific capacity, which is 320 to 400 mA·g⁻¹ (16th to 25th cycles) when various binder materials are used. Increasing the current density above 90 mA·g⁻¹ (at the same charge/discharge currents) is not advisable since the practical capacity of the material becomes lower than the specific capacity of the graphite electrode. The subsequent decrease in the current density ($I = 44.7 \text{ mA}\cdot\text{g}^{-1}$) upon cycling (26 - 75 cycles) does not cause a noticeable increase in the specific capacity. It should be however noted that the decrease in specific capacity slows down and is $0.4 \pm 0.1\%$ per cycle. Control cycling (76 - 80 cycles) at the current density of 44.7+8.9 mA·g⁻¹ shows the recovery of specific capacity values to

590 mA·g⁻¹ in the case of the CMC : LA136D binder composition, which allows us to conclude that the electrode material is incompletely worked through at a high rate of intercalation of lithium ions. The decrease in the specific capacity of silicon oxide after 80 cycles is 97, 65 and 60 mA·g⁻¹ in the case of CMC: SBR, LA136D and CMC: LA136D binders, respectively. A sharp decrease in the specific capacity of silicon oxide can be explained by several factors: silicon oxides are insulators with low intrinsic electrical conductivity, therefore, with a significant content of active material in the electrode, it is necessary to use low current densities when lithium ions are intercalated into the material structure;

- ❖ the particle size of the starting material is very large (52.7 μm), which limits the diffusion rate of lithium ions into the bulk. As a consequence, at the current density $I > 10$ mA·g⁻¹, an incomplete electrode charge process and a decrease in specific capacity are observed.

The use of various functional groups in the composition of binder materials makes it possible to obtain electrodes with a high degree of elasticity, good adhesion and cohesion of the material, as well as multiple silicon-oxygen bonds. This not only prevents the electrode from "cracking" during significant volume changes, but also contributes to its self-recovery.

It was also noted that when using two-stage charge ($i = 44.7+8.9$ mA·g⁻¹) in the case of SiO_x electrodes, higher specific capacities are achieved upon cycling process. Here, no sharp decrease in the specific capacity of the material after the 5-th cycle is observed (Fig. 3). The specific capacity values slowly drop with increasing discharge current density.

Considering the behavior of silicon oxide upon cycling in the cyclic voltammetry (CV) mode in the voltage range from 0.0 to 1.0V, it can be noticed that a peak at 0.08V in the cathodic area and a counter-peak at 0.35V in the anodic area are observed corresponding to the intercalation/deintercalation of lithium ions to/from amorphous silicon (Fig. 3). In this voltage range, the formation of electrochemically inactive reaction products (Li₂O, Li₂SiO₄, Li₂SiO₃, Li₂Si₂O₅, Li₆Si₂O₇) occurs.

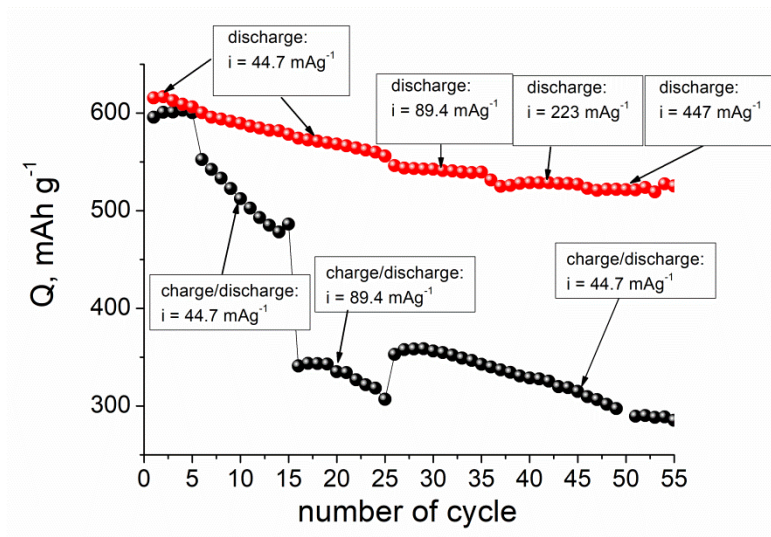


Fig. 2. Dependence of the specific capacity of SiO_x electrodes on the cycle number at different current loads

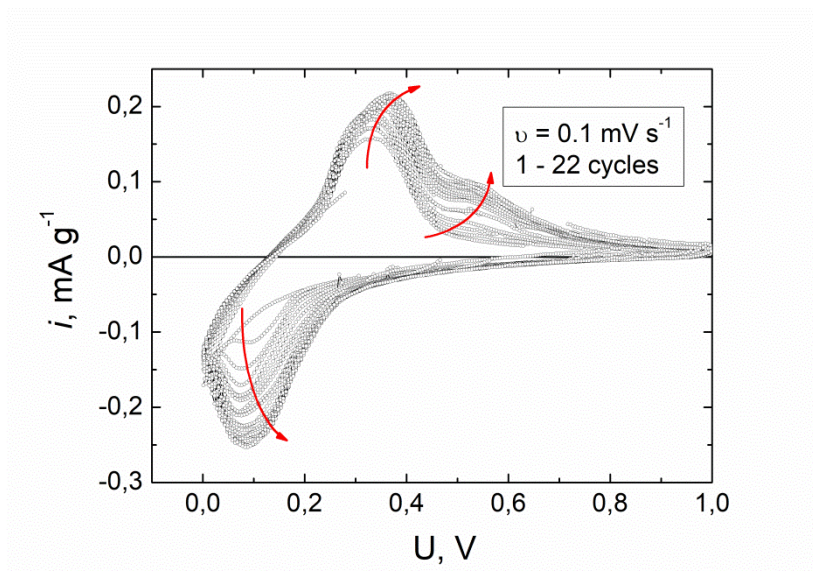


Fig. 3. CV curves of SiO_x electrodes at the scanning rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$

Moreover, the appearance and increase of a peak at 0.54 V is observed upon cycling, which is associated with the deintercalation of lithium ions from the crystalline phase of $\text{Li}_{15}\text{Si}_4$ at 0.14 V . This process leads to an increase in the irreversible capacity of the electrode material. In this regard, some authors recommend limiting intercalation potentials of lithium ions ($0.1 \text{ V vs. Li}^+/\text{Li}$) for improving the battery life to avoid the formation of a crystalline phase. It is noted that an increase in the specific capacity of silicon oxide is observed upon cycling at $0.1 \text{ mV}\cdot\text{s}^{-1}$, which occurs more slowly than if the CCCV mode is used. This is associated

with a high potential sweep rate during the intercalation / deintercalation of lithium ions, which leads to a partial formation of amorphous silicon in the initial cycles. Upon cycling electrodes in the CV mode, the amount of silicon involved in the insertion/ deinsertion process of lithium ions increases.

3. Conclusion

Electrochemical properties of silicon oxide with water-soluble binders have been studied. It is shown that the use of a combination of CMC and LA136D binder materials allows saving 90% of the electrode capacity upon cycling for 85 cycles in various charge / discharge modes. It is noted that increasing the LA136D content of the electrode leads to an increase in material adhesion. At the same time, this fact does not affect the specific capacity of the material at a low discharge current density. It can be concluded that the specific capacity of the material strongly depends on the magnitude of the intercalation current of lithium ions.

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