Toward practical application of functional conductive polymer for a high-energy lithium-ion battery design

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Abstract

Silicon alloys have the highest specific capacity when used as anode material for lithium-ion batteries, however, the drastic volume change inherent in their use causes formidable challenges toward achieving stable cycling performance. Large quantities of binders and conductive additives are typically necessary to maintain good cell performance. In this report, an only 2% (by weight) functional conductive polymer binder without any conductive additives was successfully used with a micron-size silicon monoxide (SiO) anode material, demonstrating stable and high gravimetric capacity (> 1000 mAh/g) for ~500 cycles and more than 90% capacity retention. Prelithiation of this anode using stabilized lithium metal powder (SLMP®) improves the first cycle Coulombic efficiency of a SiO/NMC full cell from ~48% to ~90%. The combination enables good capacity retention of more than 80% after 100 cycles at C/3 in a lithium-ion full cell.

SiO active material

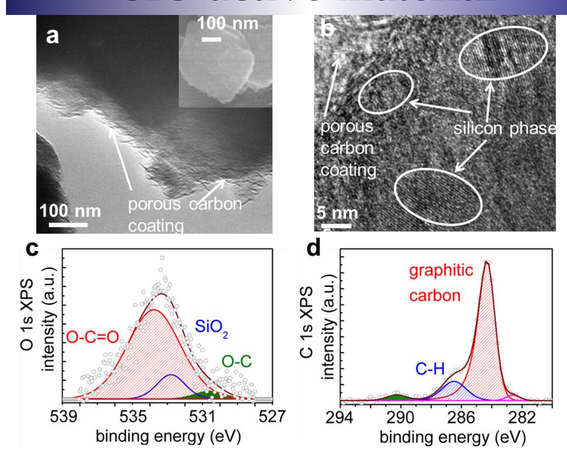

***Figure 1*:** (a) (b) TEM image of the carbon-coated SiO particle (c)(d) XPS spectra was acquired simultaneously at the outer surface of the SiO materials.

Interaction between binder and SiO

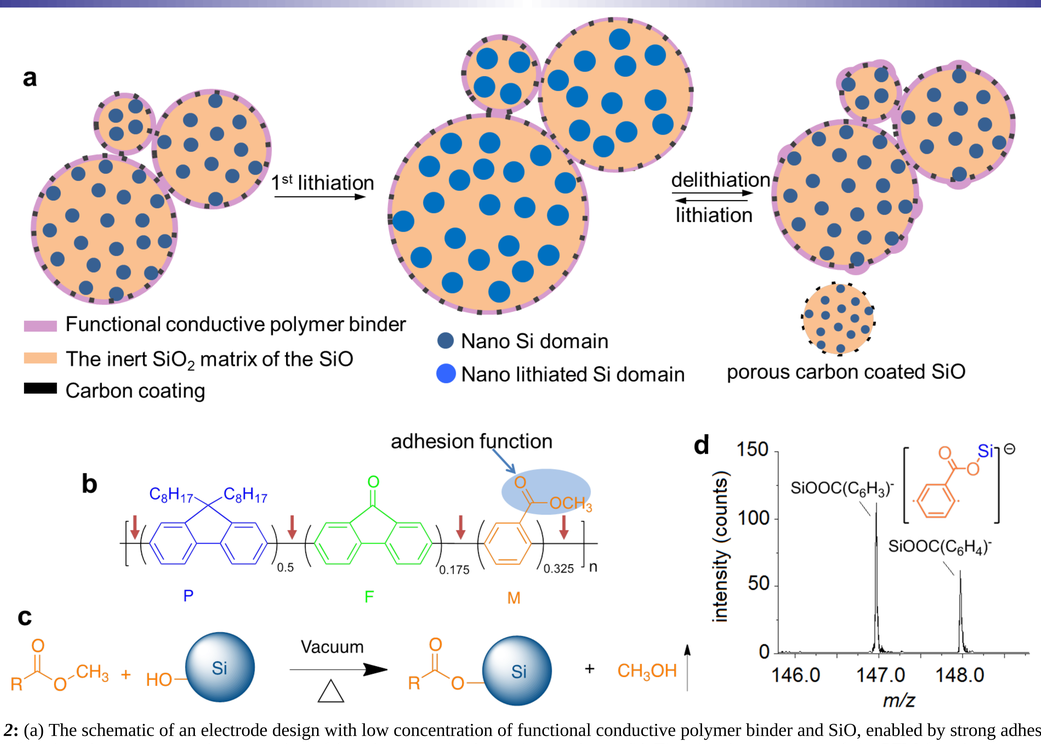

***Figure 2*:** (a) The schematic of an electrode design with low concentration of functional conductive polymer binder and SiO, enabled by strong adhesion of covalent functionality and electronic conduction of functional conductive polymer binder. (b) The chemical structure of the PFM functional conductive polymer binder. The red arrows indicate the most likely chemical bonds to be broken during the ionization process in the TOF-SIMS measurement. The blue shadow highlights the ester group that forms adhesion bonds with the SiOH surface. (c) The trans-esterification reaction between the ester functional group of the PFM binder and the SiOH surface group, which provides strong adhesion, during the electrode drying process. (d) The TOF-SIMS result of the binder and active materials interface that shows the evidence of chemical bonding between the binder and the active materials.

Performance of half cell

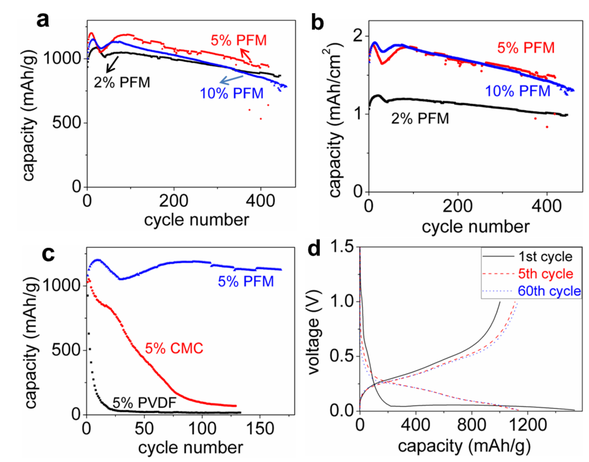

***Figure 3*:** (a) Galvanostatic cycling performance of SiO anodes with 2%, 5%, and 10% by weight of a PFM binder using lithium counter electrodes at a C/10 rate (200 mA/g). (b) The same data from (a) plotted in areal loading. (c) Comparison of the electrochemical performance of SiO electrodes made with 5% by weight of PVDF, CMC, and PFM binders using lithium counter electrodes at a C/10 rate. (d) 1st, 5th, and 60th cycle potential vs. the capacity curves of a 2% PFM/SiO electrode.

Most of the reactive Si phases in the SiO material are enclosed in the SiO_2 matrix (Figure 1a, b, c). 10% highly porous carbon coating (Figure 1a, d) improves the conductivity of the active material.

The polar ester functional group in PFM is designed for the adhesion with the SiO_2 surface on the SiO particles (Figure 2a, b). The formation of this strong chemical bond between the SiO and PFM can be observed in the TOF-SIMS results (Figure 2c, d). The functional conductive polymer binder PFM enables SiO electrode to maintain a reversible capacity of 1,000 mAh/g for over 400 cycles with a 2% to 10% PFM binder (Figure 3a, b), indicating obvious advantage compared to the conventional binders (Figure 3c).

A calendar machine was used to pressure-activate the Stabilized lithium metal powder (SLMP) particles (Figure 4a). This operation breaks the lithium carbonate (Li_2CO_3) shell and allows lithium to be in direct electrical contact with the SiO materials in the anode. The shape change of SLMP could be seen before (Figure 4b) and after pressure-activation of the SLMP. When it makes contact with the electrolyte, the SLMP on the SiO electrode releases lithium which spontaneously migrates to SiO. SEI formation is induced, and partial lithiation of the SiO also occurs, indicated by the disappearance of SLMP in Figure 4c. SLMP successfully enhanced the 1st cycle efficiency of PFM/SiO/NMC full cell to ~90%. SLMP enabled the NMC/SiO full cell to maintain a reversible capacity of ~110 mAh/g after more than 100 cycles at C/3 (Figure 4d, e).

Full cell with SLMP

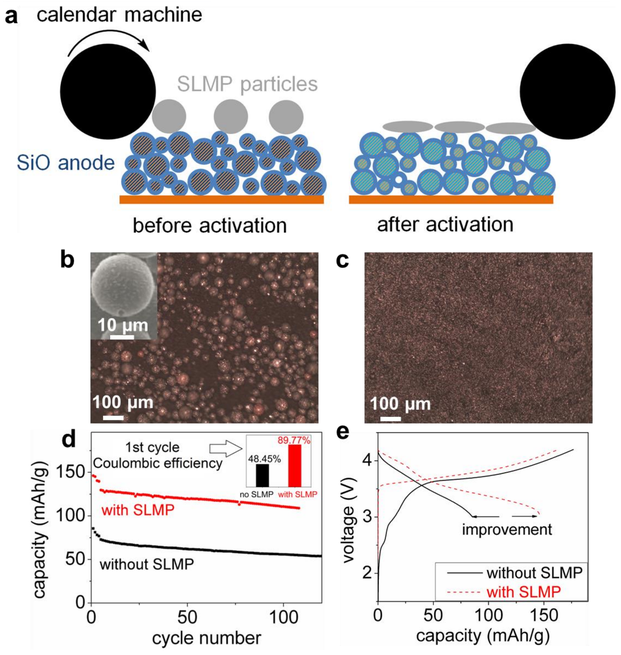

***Figure 4*:** (a) Schematics of the utilization of SLMP for the SiO electrode. SLMP particles are loaded on to the SiO anode. Rolling compression was used to crush the Li_2CO_3 shell of SLMP to release lithium metal and laminate it on the surface of SiO electrode. This process is called SLMP activation. (b) SLMP particles loaded on the SiO electrode before activation. The inset shows the SEM image of a single SLMP particle. (c) The SiO electrode surface after electrolytes are added onto the SiO electrode with activated SLMP after 12 hours. This shows the disappearance of SLMP and indicates the successful prelithiation of the SiO electrode. (d) SiO/NMC full cell performance with or without the SLMP capacity-enhancement additive, two cycles at C/20, two cycles at C/10, and then C/3. (e) The first cycle voltage curves of the two cells.

Conclusions

- Conductive polymer (PFM) is shown to enable excellent cycling performance of SiO anode
- Stabilized lithium metal powder (SLMP) successfully enhanced the 1st cycle efficiency of PFM/SiO/NMC full cell to ~90%.
- The combined strategy of using functional conductive polymer and SLMP is the key to enable a high-energy SiO-based lithium ion battery.

Acknowledgements

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