

Si-Doped Carbon Xerogels for Li/Na-ion Batteries



Joseph Carabetta*, Nathalie Job

*joseph.carabetta@uliege.be



Objective

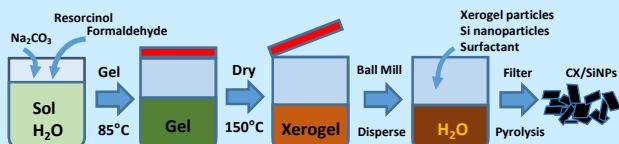
Silicon as an alloying-type anode material for Li/Na-ion batteries is a promising material due to the high specific capacity (~4200 mAh/g for Li⁺) and relative abundance in nature. However, it has been thoroughly observed that silicon degrades during cycling due to the large volumetric difference (~400%) between its charged and discharged states. This instability causes unstable SEI formation and pulverization of the silicon, which leads to a premature failure of the anode.

Therefore, a carbon xerogel (CX) support structure was synthesized via a sol-gel process, which provides a support structure and electronic/ionic conductivity for silicon nanoparticles (SiNPs) due to the unique 3D mesoporous network.

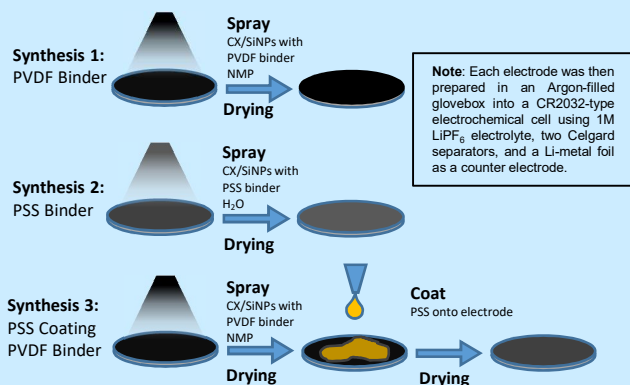
Additionally, syntheses have been made using a protective ionomer, poly(sodium 4-styrenesulfonate) (PSS), as a binder. This unique polymer is able to infiltrate the CX/SiNPs composite and further protect the composite material from degradation due to its mechanical flexibility, high ionic conductivity, and good wetting properties.

Synthesis

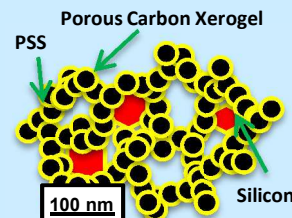
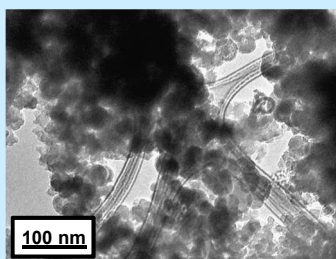
Active Material Preparation: via a resorcinol-formaldehyde sol-gel xerogel synthesis followed by doping with SiNPs in a green aqueous environment and subsequent pyrolysis.



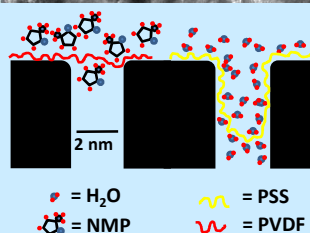
Electrode preparation: via manual spray coating of the CX/SiNPs active material using (1) a PVDF Binder, (2) a PSS Binder, and (3) a PVDF binder with a PSS coating.



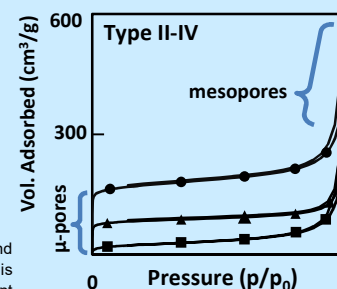
Characterization



TEM image (left) and sketch (above) of SiNPs dispersed throughout the carbon xerogel

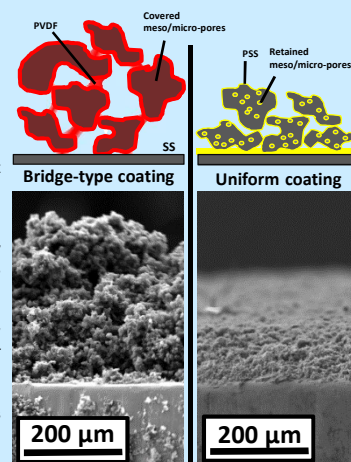


A schematic showing a comparison of the PVDF and PSS binder covering the micropores of the CX is shown above. The physical size of the solvent molecules influences the morphology of the binder on the CX surface. Since the NMP molecule can't easily fit within a micropore, the micropore surface area of the CX with the PVDF binder is measured less by N₂ adsorption compared to the CX with the PSS binder, as shown in the N₂ isotherm data.

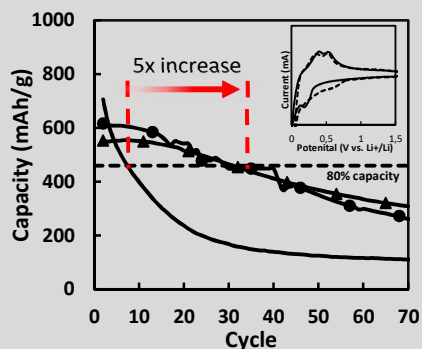


N₂ adsorption isotherms are shown above for the CX powder (●), CX powder with a PSS binder (▲), and the CX powder with a PVDF binder (■). All samples were collected post-spraying.

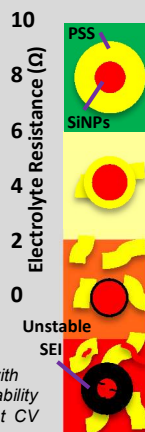
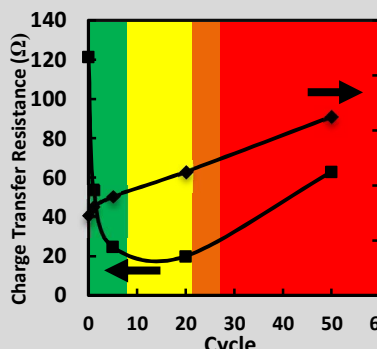
Additionally, a difference in coating morphology was observed between the use of PSS or PVDF as a binder. A possible theory is that a bridge-type coating forms on the CX/SiNPs when a PVDF binder compared to a thinner, uniform coating when a PSS binder is used. This change in grain morphology could be explained by considering that the binder is located either on the external surface covering the micropores (PVDF) or the binder follows the contour of the micropores (PSS). There are two points which support this theory: (1) As observed by the N₂ isotherms, microporosity is reduced with PSS and lost with PVDF and, (2) given that the available micropore volume of the CX is ~3-10x larger than the volume of PVDF or PSS available (as measured by Hg porosimetry and t-plot analysis), the PVDF binder must be located on the external surface of each grain rather than filling the micropores. Therefore, PVDF is more available to mechanically bind grains to each other, via bridges on their external surface, and less so for PSS since some is located within the micropores.



Results & Discussion



Galvanostatic cycling at a rate of C/10 between 1.5V and 0.005V vs. Li⁺/Li for the CX/SiNPs active material with 10 wt% SiNPs. PVDF Binder (—), PSS Binder (▲), PSS Coating/PVDF Binder (●). A 5x increase in cycle stability @ 80% the initial capacity was measured as compared to an electrode with only a PVDF binder. Inset CV diagram shows the 1st cycle (—) and 5th cycle (---) for an electrode with a PSS coating/PVDF binder.



CX/SiNPs anodes that included PSS as a binder or coating exhibit a period of stable reversible capacity followed by a period of gradual loss of capacity. This phenomenon may be due to the loss of PSS into the electrolyte.

A constant increase in the electrolyte resistance may be caused by the poisoning of the electrolyte with PSS.

A decrease in charge transfer resistance (CTR) reaches a minimum as the layer of PSS becomes thinner followed by an increase of the CTR as the SiNPs pulverize and form an unstable SEI.