

Comparison of SiO_x vs. Si Electrodes from a Multi-Nuclear-Solid-State-NMR Standpoint

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Silicon-containing anodes are one of the main candidates to replace conventional graphite anodes due to their superior theoretical capacities (up to 4000 mAh/g).^[1] However, one of the major drawbacks is their tendency to expand significantly upon lithiation.^[2] Silicon monoxide (SiO_x), a nano-sized mixture of Si and SiO₂, has shown promising cycling behavior compared to pure silicon due to the formation of irreversible lithium silicates during the first charge cycle.^[3] It is hypothesized that the silicates act as a buffer towards the volumetric expansion. Grey et. al have successfully elucidated the lithiation mechanism of pure silicon electrodes showing that repeated transitions between amorphous and crystalline lithium silicide phases could be linked to capacity fade.^[4] However, the phase changes in SiO_x electrodes are still not fully understood. For this reason, this current study focuses on gaining more insight into the electrochemical cycling process of SiO_x electrodes utilizing both ²⁹Si MAS-NMR (850 MHz, spinning speed 23kHz) and in-situ ⁷Li NMR (200 MHz, static).

Electrode slurries (70 wt% SiO_x/Si, 20 wt% carbon black, 10 wt% sodium alginate binder) were cast onto a porous cellulosic substrate instead of copper foil to increase the amount of active material inside the coin cell and to mitigate RF penetration issues for in-situ NMR measurements. Interestingly, ²⁹Si MAS-NMR reveals that the lithiated silicon domains (Li_xSi_y) that are formed during the lithiation process appear at different chemical shift values in silicon (broad resonance at 300 ppm) compared to silicon monoxide anodes (broad resonance at -100 ppm). We hypothesize that the lithiated silicon domains in SiO_x have less of a metallic character than in the case of lithiation of pure silicon due to its nano-sized particles and therefore show a less pronounced Knight shift. In-situ ⁷Li NMR shows that the electronic environments of lithium in the associated lithium silicide phases are not equivalent between the two anode materials. A peak at -10 ppm, which corresponds to the highest lithiated phase Li₁₅Si₄, is observed for the pure silicon anode but is absent in the SiO_x sample. This indicates that the highly lithiated silicon domains in SiO_x anodes are interspersed finely enough to result in a different lithium chemical shift trend.

In comparison, not only the formation of irreversible silicates but also the nature of its lithium silicide composition could be the reason for the low volumetric expansion of SiO_x anodes compared to pure silicon anodes.^[3]

References:

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