

In-situ Raman spectroscopy of high capacity 3D Si nanowire electrodes

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In-situ Raman spectroscopy is one of the most advanced methods to study the relationship between structural and electrochemical data during electrode cycling.[1] But the formation of a thick solid-electrolyte-interface (SEI) layer imposes challenges on Raman measurement as the signal from the electrode material with increasing background fluorescence is blocked. Herein, we present the in-situ Raman spectroscopy on high capacity 3D silicon nanowire (SiNW) electrodes (Fig 1a) during charging and discharging. An optimized setup (Fig 1b) in LP30® electrolyte vs. Li/Li⁺ was used to evaluate a maximum signal response from the electrode at a laser excitation wavelength of 514 nm. For pure SiNWs the Si signal exhibits a drop of intensity already at 0.5 V (Fig 1c) due to SEI formation. In the fully lithiated state, the Raman measurements show an unprecedented observation of peaks resulting from the electrolyte, its decomposition products, e.g. Li₂CO₃ and LiF (Ref. [2]) and so far unassigned peaks of the cycled Si electrode, e.g. lithium silicides. To reduce SEI formation, dedicated electrodes were conformally coated with a conductive carbon coating. The potential dependent crystallinity changes of the electrode are supported by in-operando synchrotron X-ray diffraction.

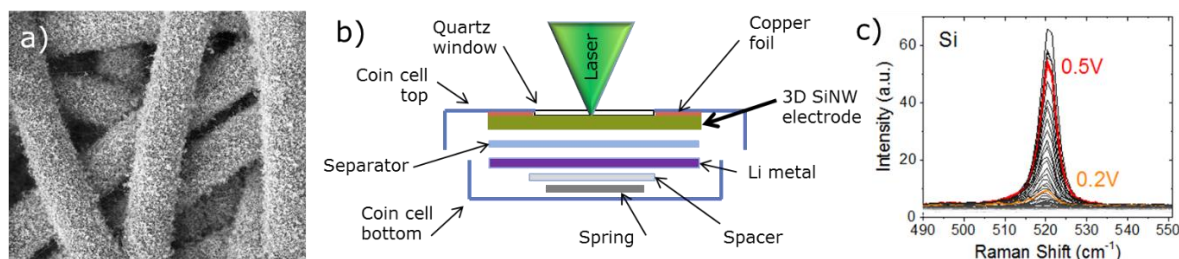


Figure 1: SiNW electrode in a half-cell setup vs. Li. a) Binder-free 3D SiNW electrode on carbon mesh. b) SiNW electrode in an in-situ coin cell housing. c) Si peak development during 1st lith. cycle.

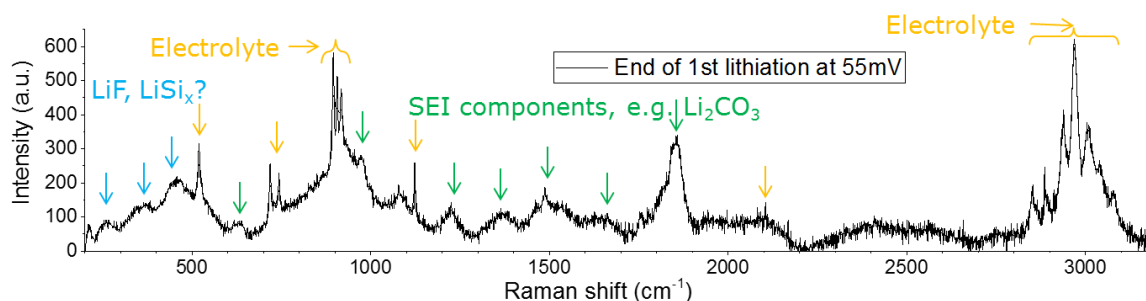


Figure 2: Detailed Raman measurement of SiNW electrode in fully lithiated state.

References:

- [1] Z. Zeng, N. Liu, Q. Zeng, S.W. Lee, W.L. Mao, Y. Cui, In situ measurement of lithiation-induced stress in silicon nanoparticles using micro-Raman spectroscopy, *Nano Energy*. 22 (2016) 105–110.
- [2] C.K. Chan, R. Ruffo, S.S. Hong, Y. Cui, Surface chemistry and morphology of the solid electrolyte interphase on silicon nanowire lithium-ion battery anodes, *J. Power Sources*. 189 (2009) 1132–1140.