

Ex situ (TEM) and *in situ* (EIS) investigation of the electrolyte decomposition layer in silicon electrodes for Li-ion batteries

K. Van Havenbergh^{1,2*}, K. Driesen², J.-S. Bridel², S. Turner¹, S. Put² and G. Van Tendeloo¹

¹EMAT, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium

²Umicore Research, Kasteelstraat 7, 2250 Olen, Belgium

*Corresp. author, email: kristof.vanhavenbergh@ua.ac.be

It is generally accepted that Li-ion batteries will become the most important energy storage solutions in an energy transition that is currently taking place, where hydrocarbons as privileged fuel are being replaced with sustainable energy sources. To replace the actual graphite based anode, several studies have been initiated over the past 15 years to implement alloy-based systems, but without success. Si has a ten times higher intrinsic capacity than graphite, because of an alloying reaction with lithium rather than an intercalation of lithium between graphene layers. The drawback of an alloying reaction is that it is accompanied by a drastic volume increase up to 300% (10% in graphite)¹. Due to this volume change, during every lithiation and delithiation, freshly exposed silicon surfaces will continuously react with the electrolyte and create new decomposition products that accumulate at the surface, resulting in irreversible capacity loss. As these interphase reactions are key points to obtain a good capacity retention, it is essential to monitor and analyze their formation closely in order to be able to propose new strategies.

Electrochemical impedance spectroscopy (EIS) is an ideal technique to study *in situ* interphase phenomena. Valuable information about the formation of surface coatings (decomposition layer and/or additional coatings), during the lithiation and delithiation process, can be gathered. However, a Li-ion battery is a very complex system and various electrode components (such as polymeric binder, conductive carbon, surface coatings, decomposition layers,...) contribute to the impedance signal. Based on impedance spectroscopy solely, it is very difficult to assign every internal process to its corresponding impedance signal. Transmission electron microscopy (TEM) is well-suited to this challenge, because the surface coatings of individual silicon particles can be investigated after a certain cycling time. This is definitely no straightforward experiment, since contact with air and water needs to be avoided at all times during transfer from battery to electron microscope, in order to avoid side reactions of the surface coatings.

In this contribution, the evolution of surface coatings on silicon nanopowders will be presented through an electrochemical impedance spectroscopy and transmission electron microscopy study. Electrodes in three-electrode-type cells were cycled and studied *in situ* with EIS (Fig 1a). TEM measurements were performed by stopping battery cycling at several stages in the lithiation-delithiation process. Samples were introduced inside the electron microscope using a dedicated vacuum-transfer sample holder. Electron energy-loss spectroscopy (EELS) and high-resolution transmission electron microscopy (HRTEM) imaging were performed at low acceleration voltage (80-120 kV) in an aberration-corrected instrument (Fig 1b). These experiments allow us to correlate the evolution of the interphase resistance with the thickness and nature of the decomposition layer.

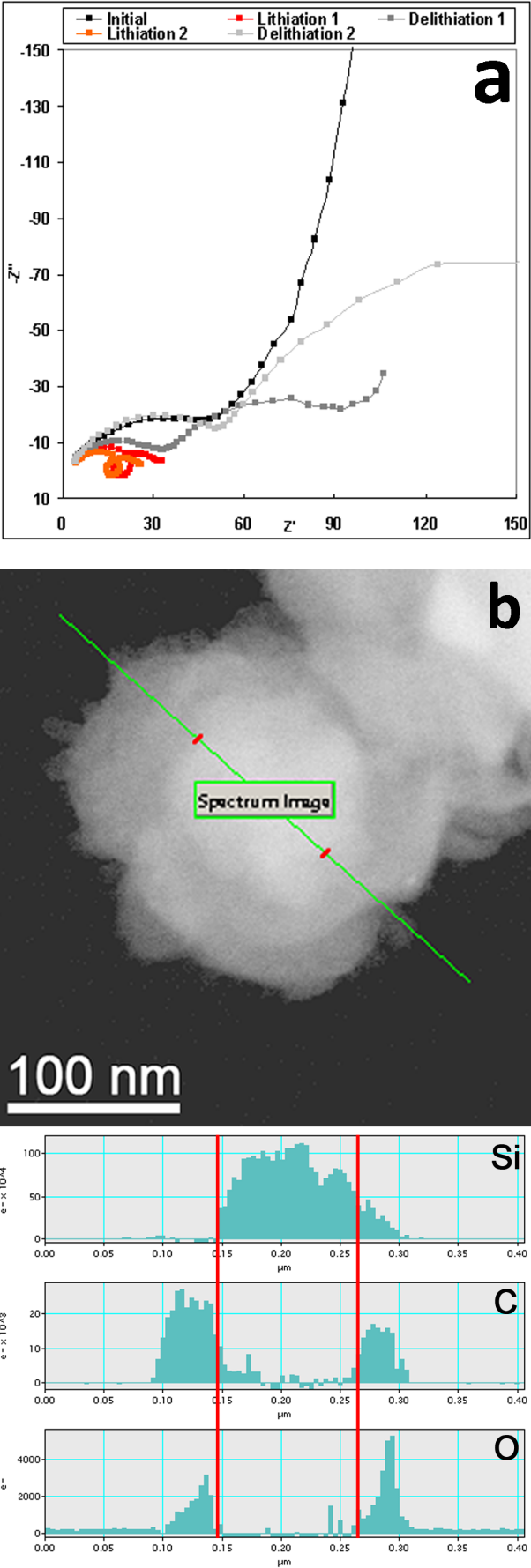


Figure 1: a) Electrochemical impedance spectra, recorded at several cycling stages; b) TEM EELS spectrum image showing the elemental composition of a cycled silicon particle.

¹ R. Teki *et al* (2009) *Small*, 5, 2236

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