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# Modelling the morphological background to capacity fade in Si-based lithium-ion batteries

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## ABSTRACT

Understanding the fundamental processes at the electrode/electrolyte interface during charge and discharge will aid the development of high-capacity Li-ion batteries (LIBs) with long lifetimes. Finite Element Methodology studies are here used to investigate the interplay between morphological changes and electrochemical performance in Si negative electrodes. A one-dimensional battery model including Solid Electrolyte Interphase (SEI) layer growth is constructed for porous Si electrodes in half-cells and used for simulating electrochemical impedance response during charge and discharge cycles. The computational results are then compared with experimental investigations. The SEI layer from the electrolyte decomposition products, different depending on the presence or absence of the fluoroethylene carbonate (FEC) additive, covers the electrode surface porous structure and is leading to an increasing polarization observed in the Nyquist plots during cycling. A continuous reformation of the SEI layer after each cycle can be observed, leading to consumption of  $\text{Li}^+$ . The electrolyte composition also results in a variation of electrode porosity, which affects the performance of the cell. A more stable porous network is formed when using the FEC additive, rendering a reduction in polarization due to improved Li diffusion inside the electrode composite.

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## 1. Introduction

Silicon-containing anodes for Li-ion batteries (LIBs) have received considerable attention, largely because Si has almost ten times ( $\sim 3600$  mAh/g) the gravimetric capacity of the current commercial standard, graphite ( $\sim 372$  mAh/g). However, the corresponding large volume expansion that occurs during cycling can exceed 300% [1,2], causing electrode failure during battery cycling. Studies on morphological aspects of particle fracture mechanisms demonstrates, however, that cracking can be reduced or eliminated by reducing particle size and controlling electrode morphology (e.g., by employing nanosized particles, nanowires, etc.) [3–6] or by using complex electrode architectures [7–12].

One considerable difficulty associated with the large volume changes is the challenge of forming a stable solid electrolyte interphase (SEI) on the Si electrode. The natural SEI film formed on Si anodes, which mainly comprises solvent reduction products [7], is not self-passivating. A significant number of studies target

different electrolyte additives which can suppress the fracture mechanisms and provide a more stable SEI on the anode surface [13,14]. Among all these additives, fluoroethylene carbonate (FEC) demonstrates to be one of the most promising candidates as it significantly improves the cyclability of batteries based on silicon anodes. Xu and coworkers [14] added 10 wt% of fluoroethylene carbonate (FEC) to a lithium hexafluorophosphate ( $\text{LiPF}_6$ ) based ethylene carbonate:diethylene carbonate (EC:DEC) electrolyte (LP40) and thereby significantly improved the long term cycling performance. The SEI formed during initial cycling consists of large amounts of FEC decomposition products, but can prevent the continuous degradation of EC and DEC and thereby provide a more homogeneous SEI layer. Although the exact decomposition schemes and products are still debated, it is generally agreed that the SEI layer formed from FEC contains large amount of LiF and FEC-derived polymer species [13–17]. The SEI formed using FEC-containing and FEC-free electrolytes will cause substantial differences in the porous electrode structure, also affecting polarization. Without FEC, electrode cracks can be observed after cycling. It could be concluded that not only the SEI thickness affects the electrode behavior, but also the homogeneity of the SEI coverage. High magnification SEM images confirmed that the SEI for FEC

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containing cells is uniformly covering the Si particles while a porous electrode structure is preserved. On the contrary, the SEI formed using FEC-free LP40 electrolyte severely damaged the porous structure, which led to a dramatic increase in impedance and rapid capacity decay. Moreover, larger polarization was observed for the lithiation process of the electrodes as compared to delithiation. Similar results were obtained by Oumellal et al. [18] and Radvanyi et al. [19] who suggested that this could be attributed to kinetic restrictions due to limited diffusion of  $\text{Li}^+$  through the composite electrode.

Electrochemical impedance spectroscopy (EIS) has become an increasingly popular technique as a diagnostic tool in the study of the lithium-ion batteries [20–23]. EIS is able to resolve multiple electrochemical processes which exhibit different time constants. However, the interpretation of EIS data relies heavily on equivalent circuit modelling, which represents an oversimplification of the electrochemical behavior in complex systems where porous-electrode effects, non-linear responses, etc., are not truly captured. In a physical-electrochemical EIS model [21,23], on the other hand, the spatial parameters and material properties can be directly correlated to cell impedance.

The interpretation of electrochemical data with respect to the morphological changes is presently not well understood. There have been studies on the experimental aspects to understand the structural details related to composition and chemical structure, however, none of these have been aspected with the theoretical framework to understand the electrochemical response for such cells where morphological changes can render signatures in the electrochemical response. To better grasp the influence between these structural changes in the electrode and their corresponding electrochemical response, a physical-electrochemical model which generate EIS data - directly comparable to experimental counterparts - will constitute a route forward. To date, this has not yet been implemented for Si-based electrodes.

The objective of this current study is to demonstrate the influence of a growing SEI film on the Si anode, along with the changing electrode porosity due to volume expansion and SEI formation. Theoretical and experimental analysis on EIS data are conducted to fundamentally understand the effects of the electrode morphology evolution during continuous cycling. The theoretical battery model constructed using finite element methodology (FEM) has therefore included effects of SEI growth and exposure of new surface and changing electrode porosity as functions of cycling. These porosity changes are modelled as dependent of the state of charge. Thus, the relationship between porosity and tortuosity due to SEI formation in Si electrodes can be explored theoretically by modelling these features in the EIS spectra. The simulated EIS spectra are then compared with experimental counterparts to understand the cumulative effects of these phenomena.

## 2. Experimental

### 2.1. Sample preparation

The silicon electrodes consisted of 80 wt% Si nanoparticles (average particle size 50 nm, Alfa Aesar), 12 wt% carbon black (SUPER C65, TIMICAL), and 8% sodium carboxymethyl cellulose (CMC-Na, DS = 0.9, Mw = 700000, Sigma Aldrich). The electrode slurry was prepared by 1 h ball-milling in a water-ethanol solution ( $\text{H}_2\text{O}:\text{EtOH} = 7:3$ ) and was casted on copper foil. Circular electrodes (20 mm in diameter) were punched out and dried at  $120^\circ\text{C}$  for 12 h under vacuum inside an Argon-filled glovebox ( $\text{O}_2 < 2$  ppm,  $\text{H}_2\text{O} < 1$  ppm). The average mass loading of silicon was  $0.76\text{ mg}/\text{cm}^2$ . The thickness and estimated porosity of the coating was  $12\text{ }\mu\text{m}$  and 67%. Si/Li half-cells in the format of pouch-cells were used to

evaluate the electrochemical performance of silicon anode. Such cells were prepared by layer-by-layer stacking one silicon anode, two layers of the Solupor<sup>®</sup> separator (Lydall Performance Materials) soaked with the electrolyte of interest, and one piece of lithium metal. Two electrolytes were used in this study: commercial LP40 (1 M LiPF<sub>6</sub>, EC:DEC = 1:1, Merck) and FEC/LP40 containing 90 wt% LP40 and 10 wt% FEC (99%, Aldrich).

### 2.2. Electrochemical and morphological characterizations

The electrochemical characterizations, consisting of galvanostatic cycling, EIS and cyclic voltammetry (CV), of the silicon half-cells with LP40 and FEC/LP40 electrolytes respectively, were performed on a Bio-Logic VMP2 potentiostat. A pre-cycling step, during which the batteries were cycled at a current density of 150 mA/g (Si) with a limited discharge capacity (2000 mAh/g of Si) and a cut-off voltage of 0.9 V vs. Li/Li<sup>+</sup> for the charging process, was applied prior to long-term cycling. For long-term cycling up to 100 cycles, the applied current density was 500 mA/g and the batteries were galvanostatically cycled between 0.12 V (cut-off for the discharge/lithiation) and 0.9 V (cut-off for the charge/delithiation). EIS was performed on various samples: the assembled battery prior to cycling (OCV, open circuit voltage, sample), one battery discharged to 0.9 V during the pre-cycling step (0.9 V sample), and batteries after the pre-cycling, and after 10, 20, 50 and 100 cycles, respectively. The frequency range used was 200 kHz to 100 mHz, and the voltage amplitude applied was 10 mV. The CV measurements were carried out for a scan rate of 0.1 mV/s between 0 and 1.5 V for the battery after the pre-cycling, and after 10, 20, 50 and 100 cycles, respectively. The surface and cross-section morphology of the silicon electrodes after cycling with LP40 and FEC/LP40 electrolyte, respectively, were investigated using a scanning electron microscopy (SEM) Zeiss 1550 instrument. The samples were carefully washed three times with dimethyl carbonate (DMC) prior to the measurements to remove electrolyte residues.

## 3. Simulations

### 3.1. Mathematical description

The Li-Si battery chemistry has been modelled using isothermal conditions, assuming  $\text{Li}_{15}\text{Si}_4$  being the highest lithiated phase at 298 K. A lithium half-cell with Si anode has been constructed using the Battery and Fuel Cell (BFC) module in COMSOL Multiphysics 5.1 for simulation of the battery charging profile. The half-cell lithium battery model consists of the cell cross section in one dimension, implying that edge effects in length and height are neglected. The cell has the following geometry:

- $x = 0$  : Negative current collector boundary.
- $0 < x < \delta_n$  : Porous Si-electrode ( $\text{Li}_x\text{Si}_y$ ). Thickness:  $35\text{ }\mu\text{m}$ .
- $\delta_n < x < \delta_s$  Separator (1 M LiPF<sub>6</sub> salt in 1:1 EC:DEC as electrolyte, either with or without FEC). Thickness:  $50\text{ }\mu\text{m}$
- $\delta_s < x < \delta_p$ : Counter electrode (lithium foil). Thickness:  $25\text{ }\mu\text{m}$

For the electronic current balance, a potential of 0 V is set on the counter electrode boundary ( $x = \delta_s$ ). At the working electrode current collector/feeder ( $x = 0$ ), the current density (harmonic perturbation) is specified. The inner boundaries facing the separator ( $x = \delta_n$  and  $x = \delta_s$ ) are insulating for electronic currents. To maintain the ionic charge balance in the electrolyte, the current collector boundaries ( $x = 0$  and  $x = \delta_p$ ) are ionically insulating. Insulating conditions also apply to the material balances.

The SEI formation process can generally be describe by a passivation model that considers both reaction and diffusion

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