

Insights into Structural Evolution of a Solid Electrolyte Interphase Using Thin Window Si Membrane Negative Electrodes

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Silicon has emerged as one of the most promising anode materials for high-performance Li-ion batteries because of its exceptional theoretical specific capacity of 4200 mAh g⁻¹, which is more than 10 times the theoretical capacity of graphite (372 mAh/g) [1,2]. However, practical use of Si as a negative electrode is hampered by high volume expansion of up to 400 % on full lithium insertion, pulverization of the material, and growth of a solid electrolyte interphase (SEI) [1,2]. Physico-chemical stability of the SEI at the interface between Si and the liquid electrolyte is a crucial factor in achieving a long cycle life. In this work, we focus on phase structural evolution of the SEI during lithiation of electron transparent *c*-Si anodes, which allow correlation of electrochemical properties with the structure on the same electrode feature. We have chosen for this study *p*-doped thin window <100>-oriented single crystalline planar *c*-Si membranes as model electrodes suitable for monitoring lithiation processes and characterization by high-resolution analytical S/TEM. A LiClO₄ solution in a 1:1 mixture by volume of ethylene carbonate (EC) : diethyl carbonate (DEC) was employed as a nonaqueous electrolyte due to its low viscosity and anodic stability.

Electrochemical measurements were carried out in a three-electrode custom-designed PTFE cell. The working electrode was a 3 mm diameter *c*-Si membrane that had nine 35 nm-thick windows. The membranes were connected to the current collector by a Cu lead. The counter and reference electrodes were made from a lithium foil. Cyclic voltammetry of the Si membranes in a 1M electrolyte was carried out from open circuit voltage and between 0.01 V and 2.0 V vs. Li/Li⁺ with the sweep rate of 0.1 mV sec⁻¹. Lithiated membranes were held 17 h at 0.15 V. After electrochemical lithiation, the samples were transferred for examination in a TEM. A glove bag purged with an UHP Ar was used to prevent the samples from being exposed to an ambient environment during the transfer. Low-dose BF- and DF- TEM, STEM, HRTEM, SAED, EELS and EDXS were applied *ex situ* to characterize the morphology, crystallinity and local chemical compositions of the passivation films formed during lithiation/delithiation of the membrane anodes. Soaking of a control Si membrane into the electrolyte for 24 hours without processing did not reveal the growth of the SEI.

The positions of the reduction peaks at 1.5 V, 1.3 V and 0.6 V in a cyclic voltammogram (Fig. 1) were in good agreement with the positions of the reduction peaks obtained for a 1 M LiClO₄/EC: dimethyl carbonate (DMC, 1:1 by vol.) with a Pt electrode [2] and can be attributed to decomposition of the electrolyte. Our findings suggest that the SEI consists of an inner “inorganic” layer composed of Li₂O, Li₂CO₃, LiOH, as well as Li_xSiO_y formed from a native oxide and an outer preferentially “organic” layer comprising mostly alkyl carbonates (Fig. 1b) [2,3]. Si lithiation with the formation of a Li_{1.7}Si phase occurs at 0.33 V [4] and an increase of the current intensity below 0.3 V can be attributed to lithiation of the Si matrix. The oxidation peaks at 0.7 V and 1.5 V can be attributed to delithiation of Si and SiO_x, respectively [5]. For the 2nd cycle, the reduction peak at 1.5 V is not as prominent as for the 1st cycle. However, reduction current is still detected suggesting that the SEI continues to grow during the 2nd cycle.

Observed SEI features include various morphological shapes, such as dendritic sponge aggregates impregnated with a liquid electrolyte (Fig. 2a). By soaking a lithiated Si membrane in DMC, web-like organic-inorganic structures grown on the *c*-Si surface and agglomerates of LiClO₄ nanocrystallites were found (Fig. 2b). *Ex situ* BF-TEM (Figs. 2a-b) and HRTEM (Fig. 2c) studies indicate that dynamically evolving SEI growth profoundly dominates over *c*-Si lithiation. An island-like growth of such loose nonuniform SEI films can cause a rise of the interfacial impedance and low Coulombic efficiency, thus essentially hampering the potential of Si anodes to be practically realized.

References: [1] V.P. Oleshko, *et al.*, *Microsc. Microanal.* **22**(Suppl.3), (2016) 1556. [2] R. Marom, *et al.*, *J. Electrochem. Soc.*, **157**(2010) A972. [3] M. Hess, *Electrochimica Acta*, **244** (2017) 69. [4] J. Wen, R. A. Huggins, *J. Solid State Chem.*, **37**(1981) 271. [5] Q. Sun, *et al.*, *Appl. Surf. Science*, **254** (2008) 3774

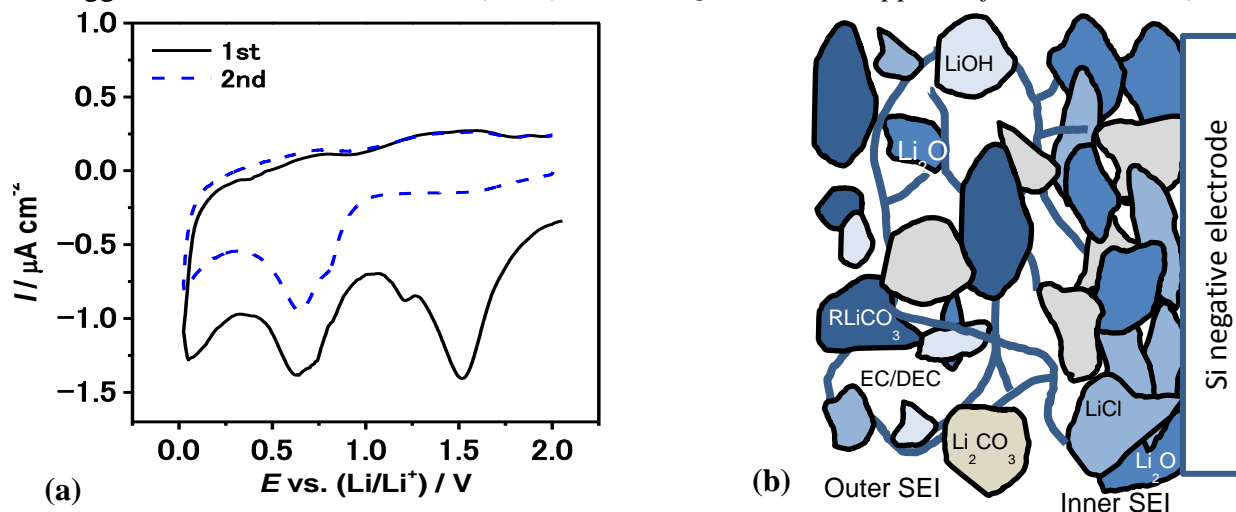


Fig. 1. (a) Cyclic voltammogram of a thin window *c*-Si membrane in a 1M LiClO₄/EC: DEC electrolyte at 0.1 mVs⁻¹ scan rate. (b) Schematic model of an SEI comprising a 10 to 100 nm thick outer organic-inorganic polymeric layer and a 2 – 10 nm-thick inner inorganic layer, respectively.

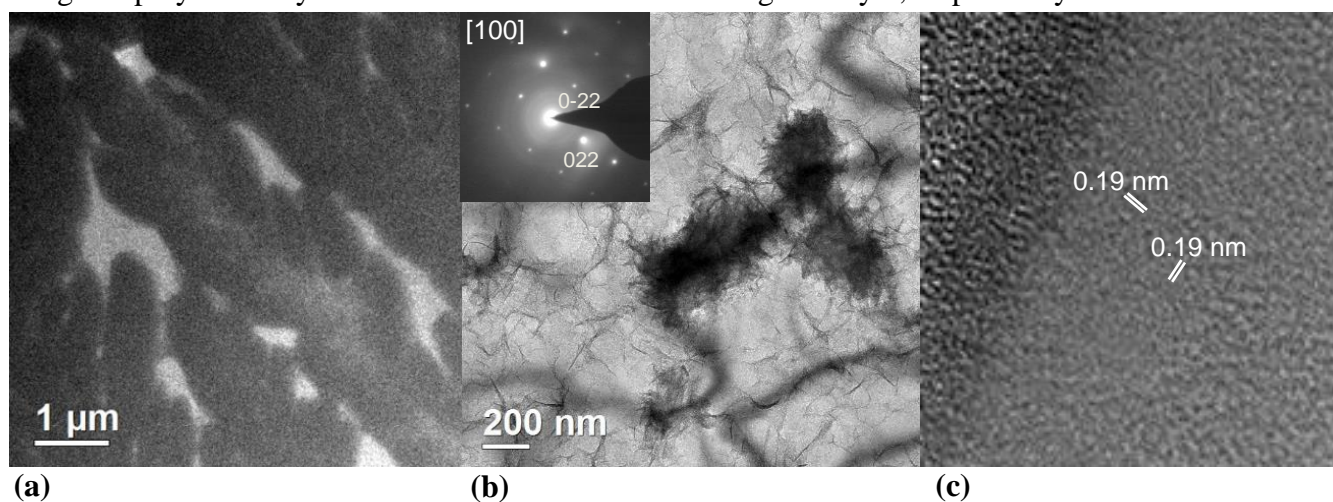


Fig. 2. *Ex situ* low-dose BF-TEM. (a) Dendritic sponge aggregates impregnated with a liquid electrolyte in an outer SEI layer after 17 h at 1.5 V cutoff. (b) Web-like aggregated structures formed after drying the electrolyte. SAED pattern (upper inset) of a lithiated *c*-Si membrane at [100] zone axis. (c) HRTEM, a densified inner SEI layer of the lithiated membrane, (002) Si lattice fringes are barely visible through the amorphous SEI film.