Influence of electrolyte, additives and cycling conditions on the chemistry of the Solid Electrolyte Interphase layer formed on a-Si:H films

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It is commonly known that few nanometer thick Solid Electrolyte Interphase layer (SEI) formed on the surface of negative electrode, due to the reductive decomposition of electrolyte, is a good Li-ion conductor and electrical insulator. The SEI layer properties can significantly influence the electrode long term stability and capacity upon cycling.

The particularities of Si negative electrode are great volume variations (expansion/contraction) induced by electrochemical lithiation/de-lithiation, respectively. These volume changes lead to SEI layer cracking and exposure of new parts of the Si electrode surface to the electrolyte. To avoid this effect, electrolyte additives like vinylene carbonate (VC) and monofluoroethylene carbonate (FEC), have been recently used for their polymerizable features and the possibility of forming a SEI layer with better mechanical properties able to accommodate volume variations [1, 2]. VC and FEC additives can also improve the thermal stability of SEI layer due to preferential formation of polymeric species at the expense of salt species [3]. Several studies point out the improvement of electrochemical performances in presence of additives, but few have been dedicated to the understanding of the role of additives in SEI layer/Si chemical properties.

Our previous studies on amorphous Si thin film electrodes (a-Si:H) in PC/LiClO₄ 1M performed by X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) showed that lithium can be trapped in the bulk of electrode material [4]. ToF-SIMS negative-ion depth profile of a-Si:H cycled electrode showed that the Li ion profile followed the SiO₂ ion signal, indicating a great affinity of lithium for oxygenated species. It was also shown that the SEI layer formed on the Si electrode cycled in PC/LiClO₄ 1M was thicker than in EC:DMC (1:1)/LiPF₆ 1M electrolytes. NMR analysis of post-mortem Si composite electrodes performed by Oumellad et al. [5] showed that a poor cycling performance of the Si electrode was due to the formation of a thick SEI layer and to the effect of lithium trapping.

To understand the influence of PC/LiClO₄– and EC:DMC/LiPF₆–based electrolytes on the chemical stability of a-Si:H thin film (of 100 nm by PECVD) upon cycling, a thorough study was carried out by means of ToF-SIMS and XPS techniques. The influence of VC and FEC additives as well as the different anodic cut-off potential was also investigated.

Fig. 1a shows Si capacity evolution and coulombic efficiency with different anodic cut-off potentials ($E_{cut-off}$ =800, 900 and 1000 mV). The best cycling stability was obtained by limiting anodic cut-off to 800 mV. Fig. 1b displays the Si⁻³ ion signal in ToF-SIMS profile collected for a-Si:H electrodes cycled in EC:DMC (1:1)/LiPF₆ 1M with FEC additive.





A significant increase in ToF-SIMS sputtering time (~800 s), after 100 cycles, is observed with respect to a lower time (~300 s) after only 1 and 20 cycles. This indicates modification of the chemical nature of the Si matrix and/or Si electrode pulverization induced by cycling. The increase in the electrode volume suggests modification of the electrode morphology with formation of Si particles enrobed with SEI layer or Si swelling and trapping of SEI inside the Si porous structure. The modified morphology can facilitate diffusion of Li ions into the bulk of Si electrode material and decrease mechanical stress.

Considerable higher ToF-SIMS sputtering times were observed on a-Si:H cycled in PC/LiClO₄–based electrolytes showing significantly thicker SEI layer and trapping of the SEI inside the open and porous structure, without significantly affecting the Si electrode capacity. More details concerning the influence of electrolyte composition and cycling conditions on the electrochemical performance of the Si electrode and its surface and bulk modifications will be presented.

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