

Impact of SEI lithium salts on cycling ability and effect of complexant additives.

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Li-ion batteries are undoubtedly the most popular and mature electrochemical storage devices. Numerous studies deal with the development of new materials and electrolytes for such systems [1-3]. However, there are several factors that limit the development of this technology, and one of the key questions is the limitation of the life time. Efficient cycling of lithium-ion batteries is associated with the formation of a passivation layer at the electrodes surface, referred to as the SEI (Solid Electrolyte Interphase) [4]. The quality of this film is decisive for battery performance: it must prevent solvent intercalation in the electrode, limit electrolyte degradation upon cycling, but still allow an optimal transport of Li^+ ions between the electrode and the electrolyte.

The SEI covering electrodes in lithium-ion batteries consists of a variety of lithium compounds, either organic or mineral, which have a direct effect on battery performance, however impacts of lithium salts formed on SEI during cycling is not well known. In this presentation the impact of various salts present in the SEI is investigated to determine which compounds are the most detrimental to cycling on graphite and LiNiMnCoO_2 (NMC) electrodes in half-cell and in full cell into a three electrode configuration.

The SEI components considered in this study are lithium fluoride LiF , lithium carbonate Li_2CO_3 , lithium hydroxide LiOH , lithium oxide Li_2O and lithium methoxide LiOCH_3 . These salts are formed during cycling of electrolyte PC/EC/DMC (1:1:3, %w) using LiPF_6 .

Results show that these lithium compounds have very diverse effects on battery efficiency, NMC being more sensitive to salt addition than graphite. Mineral compounds, LiOH and Li_2O are shown to degrade battery performance by forming a resistive film at the electrodes surface. On the contrary, lithium alkoxides LiOCH_3 and carbonate Li_2CO_3 are beneficial to cycling and seem to favour the formation of a polymeric coating on the SEI which promotes faradic efficiency.

In this presentation, focus was made on lithium fluoride because of its preponderance within the SEI and its high solubility in EC/PC/3DMC, 0.35 mol.L^{-1} [5, 6], compared to other lithium compounds. As a result, several concentrations of LiF were studied in the reference electrolyte, below or close to solubility limit, to determine the effect of this salt on cycling performance.

Finally, a complexant additive such as Glyme has been tested to improve performance of electrolyte with SEI lithium salts as additives to counter and to limit the negative effects of these salts.

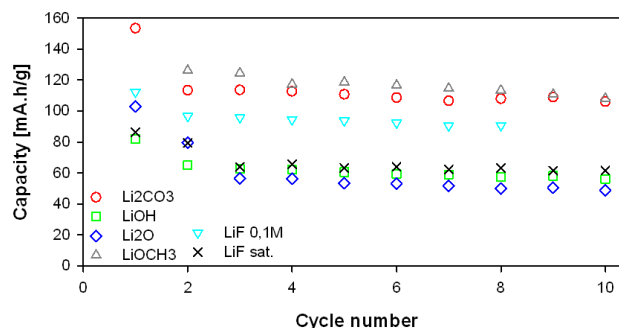


Fig 1: Discharge capacity after 10 cycles on NMC, according to the nature of LiX content in the electrolyte EC/PC/DMC (1:1:3, %w) + 1M LiPF_6 + lithium salt.

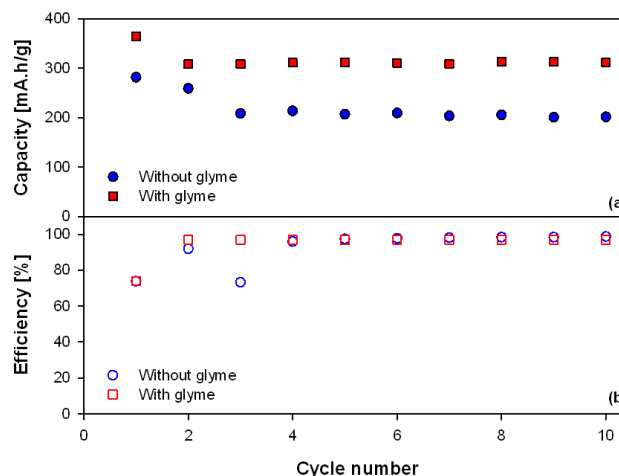


Fig 2: Comparative capacity (a) of graphite electrode and efficiency (b) of electrolyte with saturated lithium fluoride in EC/PC/DMC (1:1:3, %w) + 1M LiPF_6 + sat. LiF without and with Glyme at $T = 25^\circ\text{C}$.

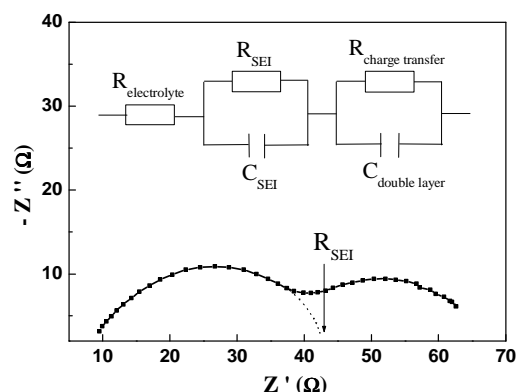


Fig 3: Equivalent circuit and Nyquist plot of graphite/ Li cell after 20 cycles in 0.20 mol.L^{-1} LiF electrolyte.

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