

Investigation of SEI layer formation mechanism in Mn-based batteries

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Even after 30 years of discovery, Li-ion batteries still suffer from capacity fade with repeated charge-discharge cycles. It is extremely crucial to understand the ageing mechanisms of batteries in order to improve their cyclability and life. Because of its thermodynamic instability due to their LUMO being lower than anode's electrochemical potential, organic electrolytes undergo reduction on the surface of anode to form SEI layer. A stable SEI prevents further decomposition of electrolyte once it has formed [1]. Recently there has been much interest in developing and optimizing various Mn-based cathodes such as NMO, NMC, layered Li_2MnO_3 and combination of these compounds owing to their higher capacity, rate capability, low cost and environment friendly nature [2,3]. However, the cycling performance of these cathodes pose serious problems. Mn dissolution occurs when Mn^{3+} ions from the cathode undergo disproportionation reaction to form Mn^{2+} and Mn^{4+} . Mn^{2+} is soluble in electrolyte which after diffusing through it gets lodged in the anode SEI which has been found to increase the rate and amount of SEI formation [4]. There have been many but no comprehensive theory proposed to explain the formation of SEI [5]. There is active debate on the state of Mn and its effect on SEI layer. Few groups claim that Mn^{2+} exists in its ionic form and have proposed an ion-exchange mechanism in SEI layer [6]. On the other hand some claim that Mn(0) is deposited in an unidentified state different from atomic scale, nanometre scale or mesoscale Mn(0) clusters [7]. The key motivation for this work is a transient approach which is necessary to analyse the evolution of SEI to confirm either of these observations. We report cycling and characterization data of graphite half-cells and graphite- LiMn_2O_4 cells for different number of cycles. Our present work focusses on analysing the transient evolution of SEI, in presence of Mn ions in the latter and in absence of it in the former, which would be crucial to propose a comprehensive mechanism.

We have employed a combined characterization approach, elemental composition and bond characterization which provides information on different compounds formed from decomposition of electrolyte. In addition to it, we have performed corresponding DFT calculations to validate our hypothesis of most favourable mechanism. By altering the rate control step using additives, we can further enhance the lifetime of manganese-based Li-ion batteries.

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