Modelling of lithium ion batteries employing Monte Carlo and Mesoscale Simulations

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In the current investigation the modeling of the two half cells ($LiMn_2O_4$ and $LiCoO_2$ cathode and carbon anode) of the battery using Monte Carlo method, followed by modeling of the complete cell had been carried out. It also takes into account the effect of electrolyte and temperature variations on various battery parameters like open circuit potential, cell current, cell voltage and free energy of Li^+ intercalation/deintercalation. Estimation of open circuit potential (OCV) of Lithium ion batteries becomes vital as it is a crucial parameter in (i) estimating diffusion coefficient of lithium in the electrode material during charge/discharge process, (ii) obtaining entropy of the reaction and internal energy calculations and (iii) understanding thermal runaway problems. The strong dependence of OCV with the state of charge (SOC) of the battery and temperature makes the prediction more difficult. To avoid computational tediousness, Monte Carlo technique coupled with mesoscale simulation is employed to predict OCV of cathodic half cell and anodic half cell. The effect of solvents employed, electrolytes utilized, temperature of the cell are incorporated to predict the actual OCV of the battery under operating conditions via mesoscale simulations. The open circuit potential (OCV) of spinel $LiMn_2O_4$ and $LiCoO_2$ were predicted in solid phase as well as a half cell by employing Monte Carlo technique coupled with mesoscale simulation. The temperature dependence of OCV in solid phase and $OCV_{experimental}$ was also predicted. A qualitative agreement with the existing literature data for OCV (solid phase) and OCV(experimental) for $LiMn_2O_4$ were established. The possible trend in surface potential, $E_{visdrag}$ and desolvation energy of Li ion with SOC and temperature was predicted. Although there exists a hysteresis between solid phase OCV versus experimental data for $LiMn_2O_4$ (which is true for other cathode materials like $LiFePO_4$, $LiCoO_2$ etc.), this mV variation leads to severe performance issues at high power or current discharge rate. Temperature effect on solvation of lithium ion also contributes for the material degradation and low performance of the battery. Current methodology is generic in nature and can be extended to analyze the OCV (solid phase as well as experimental) by varying the input parameters like system potential, interaction energies (NN and NNN), ionic radius, radius of the solvent, dielectric constant etc. It can be applied to understand the trend in OCV at different temperatures and for different materials (cathode as well as anode). By further incorporating the applied current density or power and time (kinetic Monte Carlo), the performance of the lithium ion battery can be predicted with ease.