

Non-equilibrium Phase Transformation in Li-ion Battery through Simulation and In-situ Studies

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Two-phase transformation in lithium-ion battery (LIB) materials such as LiFePO_4 , representing a flat potential at a low discharge rate, has been demonstrated to be one of the most critical factors in determining battery discharging rate and capacity. During rapid discharge (e.g., 20C), however, the flat potential is replaced with a downward curve. It is hypothesized that a non-equilibrium phase transformation occurs due to sluggish lithium ion diffusion across the miscibility gap, which distorts and shifts to higher lithium compositions. This non-equilibrium behavior could have significant implications to high-rate battery kinetics and new material design.

Despite recent significant advances in understanding intercalation dynamics and miscibility gap, theoretical and quantitative investigation of the non-equilibrium phase transformation in battery materials still remains elusive. Initial viability studies by our group have produced a 'mushy-zone' approach^{1,2} to confirm the non-equilibrium phase transformation. It has showed a significant effect of this non-equilibrium phenomenon: there is a strongest dependence of two-phase miscibility gap width and position on the high-rate discharge of LiFePO_4 -based materials. This paper, based on our recent simulation developments¹⁻⁶, will investigate the non-equilibrium phenomenon and determine under which conditions (e.g., discharge rate and particle geometry, electrode composition, transport anisotropy) the non-equilibrium effects are most significant, as well as quantification of the effects. In addition, two complementary in-situ techniques – in-situ XRD and micro-Raman – have been combined to validate the non-equilibrium phase transformation model at different length scales. We have developed unique transparent LIB housings which enable in-situ XRD and micro-Raman studies⁷ on an operating LIB electrode. The different results obtained from the two in-situ techniques have revealed phase transformation phenomena at different length scales. The in-situ XRD picks up the electrode-level phase transformation information (thus averaged over multiple particles), while the micro-Raman collects only particle-level phenomena (as the Raman laser beam size is only 1.5 μm).

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