The impact of charge/discharge rate on capacity fade on composite structured cathodes in lithium ion batteries

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We develop a cohesive understanding the effect of rate of cycle on the composite structure of a lithium ion battery. Electrochemical techniques are used to evaluate capacity, resistance, and rate capability. Together, capacity and resistance measurements are used to segregate chemical-induced degradation (associated with resistance rise and capacity loss) from mechanical-induced degradation (primarily associated with capacity loss) in the cathode for different c-rate cycling. Meanwhile, rate capability measurements reveal the impact of chemical and physical degradation on utilization of the electrodes at various c-rates. Raman spectroscopy is used to directly measure Li\(^+\) inventory losses caused by film growth on the composite anode surface and evaluate how it contributes to capacity loss measured electrochemically. Lastly, microscopy techniques assess mechanical damage in LiCoO\(_2\) particles in the form of micro-cracks and dislocation defects which are thought to impede solid-state Li ion diffusion. This was demonstrated through diffusivity measurements using galvanostatic intermittent titration techniques.

Through the use of various testing techniques, it is determined that chemical degradation accounts for the entirety of capacity loss at slow c-rates. Meanwhile, at high c-rates it is both chemical and mechanical degradation that contributes to fade; where mechanical degradation plays an increasing role as c-rate is raised. Pointedly, higher c-rates effectively increase the strain rate for lithiation of LiCoO\(_2\) particles resulting in diffusion induced stresses that can lead to micro-crack formation, defect generation, and eventual particle fracture. Ultimately, micro-crack and defect formation limits electrode utilization at moderate to high c-rates resulting in reduced discharge capacity. To this end, diffusivity measurements using galvanostatic intermittent titration techniques are presented.

By showing that Li inventory can be accounted for fully using the Raman techniques and quasi-equilibrium rates, we can assign mechanical effect and damage accumulation on cycling to the cathode loss of capacity, and ascribe a mechanical impact of the damage to the composite on the microscale, including the loss of solid state diffusivity observed as the composite undergoes successive charging and discharging.