

Lithium position and occupancy fluctuations in a cathode during charge/discharge cycling of a lithium-ion battery

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Lithium-ion batteries are undergoing rapid development to meet the energy demands of the transportation and renewable energy-generation sectors. The capacity of a lithium-ion battery is dependent on the amount of lithium that can be reversibly incorporated into the cathode. Neutron diffraction provides greater sensitivity towards lithium relative to other diffraction techniques. In conjunction with the penetration depth afforded by neutron diffraction, the information concerning lithium gained in a neutron diffraction study allows commercial lithium-ion batteries to be explored with respect to the lithium content in the whole cathode. Furthermore, neutron diffraction instruments featuring area detectors that allow relatively fast acquisitions enable perturbations of lithium location and occupancy in the cathode during charge/discharge cycling to be determined in real time.

Here, we present the time, current, and temperature dependent lithium transfer occurring within a cathode functioning under conventional charge-discharge cycling. The lithium location and content, oxygen positional parameter, and lattice parameter of the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ cathode are measured and linked to the battery's charge/discharge characteristics (performance). We determine that the lithium-transfer mechanism involves two crystallographic sites, and that the mechanism differs between discharge and charge, explaining the relative ease of discharging (compared with charging) this material. Furthermore, we find that the rate of change of the lattice is faster on charging than discharging, and is dependent on the lithium insertion/extraction processes (e.g. dependent on how the site occupancies evolve).

Using *in situ* neutron diffraction data the atomic-scale understanding of cathode functionality is revealed, representing detailed information that can be used to direct improvements in battery performance at both the practical and fundamental level.