Source of Additional Capacities Seen in Metal Oxide/Fluoride Electrodes

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Metal fluorides/oxides (MF_x/M_xO_y) are promising electrode candidates for lithium-ion batteries (LIBs) that operate via conversion reactions.[1] These conversion-type reactions are associated with much higher energy densities as compared with the reactions based on intercalation chemistry that are typically used in commercially available LIBs. These metal salts (MF_x/M_xO_y) can also exhibit significant additional reversible capacity beyond the theoretical estimate based on the maximum electron transfer from available redox metal centers.[2 3 4 5 6] However, the difficulty in characterizing structures at the nano-scale, particularly at buried interfaces, has meant that the mechanism accounting for the additional capacity remains unclear. This study employs high-resolution multinuclear (^{1}H, ^{6}Li/^{7}Li, ^{17}O, ^{19}F) multidimensional solid-state NMR techniques, complemented by real-time detection using X-ray based methods (e.g. Figure 1), in order to characterize two model systems, RuO_2 and TiF_3. The results illustrate the origin of additional capacities found in metal oxides/fluorides used as electrodes in LIBs.

Short- and long-range structure and valence changes along with the different chemical phases present in the solid-electrolyte interface (SEI) are determined as a function of charge. The experiments, in conjunction with theoretical calculations, show that in the RuO_2/Li system a major contribution to the extra capacity is due to the generation of LiOH and its subsequent reversible combination with extra Li to form Li_2O and LiH (Figure 2). In the TiF_3/Li system, the additional capacity is mainly due to reversible SEI formation. In both cases, surface-OH and initial electrolyte decomposition serve as the source of H.

This study illustrates that the characterization of the source of additional capacities in metal oxide/fluoride electrodes provides a comprehensive understanding of the chemical phase composition and their spatial distribution at the interface between the electrode and electrolyte. This study also demonstrates a protocol with which to study the amorphous SEI that exists in essentially all battery systems.

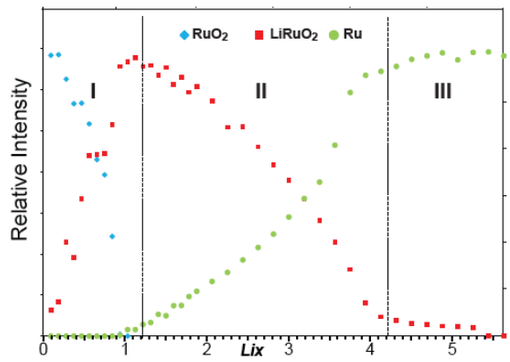

Figure 1. Evolution of chemical phases following the discharge process of the RuO_2/Li battery system, derived from the refinement of *in situ* pair distribution analysis.

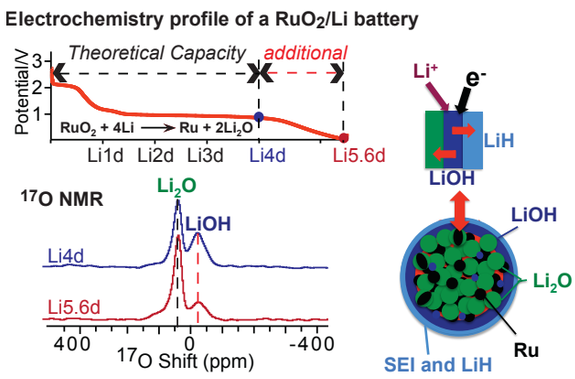

Figure 2. Schematic illustration of the source for additional capacities found in RuO_2 electrodes for LIBs.

References

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