Oxidative processes in LiFeBO₃

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Lithium-ion battery is a promising power source in large-scale devices, such as electric vehicles and plug-in hybrid electric vehicles. This prospect of powering large-scale devices motivates a comprehensive survey of new cathode materials that have high energy densities. LiFeBO₃, with a 30% larger theoretical capacity and 10% larger energy density than LiFePO₄, has emerged recently as a new candidate. This promising material, however, suffers from poor rate capability and low operation voltage. Knowledge about the (de)lithiation processes of LiFeBO₃ is a key to fully "unlock" the potential of such a battery material and also its substituted variants.

Characterizations of the LiFeBO₃ (de)lithiation processes have been severely complicated by the difficult-to-eliminate degradation process upon air exposure. Degradation of LiFeBO₃ immediately occurs when nano-LiFeBO₃ is exposed to air, resulting in the creation of a lithium-deficient degraded phase (Li_dFeBO_3)[1], [2]. This difficult-to-eliminate degradation process makes it extremely difficult to fabricate pure LiFeBO₃-based electrode and complicates the analysis of the (de)lithiation processes. It is difficult to distinguish between LiFeBO₃, partially delithiated LiFeBO₃ ($Li_{1-x}FeBO_3$) and degraded LiFeBO₃ (Li_dFeBO_3) by diffraction techniques only, since they possess similar crystal structures/cell-volumes and thus difficult-to-distinguish diffraction "fingerprints".

The subtle volume change between LiFeBO₃ and "FeBO₃" poses another challenge in charactering the (de)lithiation processes. The lattice parameter variation was estimated to be only ~ 1% according to pervious density functional theory (DFT) calculations[3]. Delithiation of LiFeBO₃ was first reported to occur through a solid-solution mechanism with a continuum of phases $Li_{1-x}FeBO_3$, based on the shifts of the reflections in the X-ray diffraction patterns with a peak width Δd/d of ~2%[1]. This peak width is however even greater than the predicted lattice parameter variation (~1%) and thus limiting the significance of the results.

In order to provide insights into the (de)lithiation processes of LiFeBO₃ during electrochemical cycling, we have used a wide range of complementary structural probes to characterize such processes both in situ and ex situ (in situ X-ray absorption/diffraction, ex situ nuclear magnetic resonance and ex situ pair distribution function analysis). Of particular note is that these structurally similar phases (LiFeBO₃, $Li_{1-x}FeBO_3$ and Li_dFeBO_3) that are difficult to distinguish in diffraction can be easily distinguished in ⁷Li NMR spectra (Fig. 2).

(De)lithiation of LiFeBO₃ was demonstrated to proceed reversibly through a combination of two-phase reaction between LiFeBO₃ and Li_tFeBO_3 (t ~ 0.5), as well as a solid-solution reaction between Li_tFeBO_3 and $Li_{t-x}FeBO_3$ (0 < x < t). We also observed that the solid-solution reaction between Li_tFeBO_3 and $Li_{t-x}FeBO_3$ begins well before the two-phase reaction (LiFeBO₃-Li_tFeBO_3) is complete, rather than occurring in a typically sequential manner.

Another finding is a reversible low-voltage process (< 2 V) occurring to the degraded LiFeBO₃ (Li_dFeBO_3). It explains the origin of the commonly observed extra capacity below 2 V during the first discharge. Interestingly, lithiation of the degraded LiFeBO₃ does not produce LiFeBO₃, which distinguishes the degraded phase from a partially delithiated LiFeBO₃ phase.

In summary, our studies have provided fundamental insights into the oxidative processes in LiFeBO₃ (degradation and delithiation), and can serve as strong basis for further exploration of LiFeBO₃ and its substituted variants.
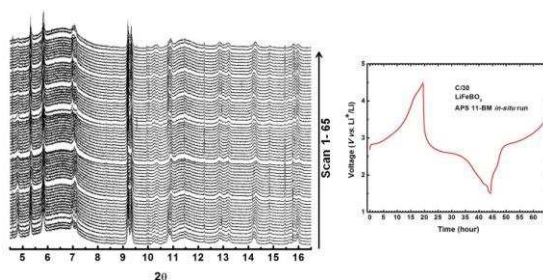

Figure 1. In situ XRD patterns of LiFeBO₃ during cycling (left) and its corresponding electrochemistry (right). Data were collected with a wavelength of ~0.41 Å.
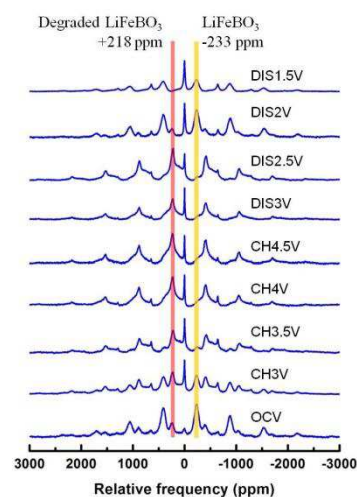

Figure 2. ⁷Li magic angle spinning (MAS) NMR spectra of LiFeBO₃ samples at different stages of cycling (CH: charge, DIS: discharge).

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