

The degradation origin of all-solid-state thin-film Li-ion micro-batteries

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In practice, Li-ions batteries (LIB) will inevitably suffer from capacity losses during charge and discharge cycling. Regrettably, in comparison with conventional liquid-electrolyte based LIB, all-solid-state LIB are more complex systems, and understanding the degradation mechanisms is therefore even more complicated. Herein, a novel approach is presented, based on *in situ* Neutron Depth Profiling (NDP) to investigate the degradation mechanisms within all-solid-state thin film $\text{LiCoO}_2/\text{Li}_3\text{PON}/\text{Si}$ batteries under operando conditions. Important aspects of the long-term degradation mechanism are elucidated. It is experimentally found that the strongest capacity losses occur in the initial cycles, more particularly during the first charging process. It is concluded from the NDP studies that, after the first charging process, a Li-immobilization layer is immediately present in the solid-state electrolyte adjacent to the silicon anode, as shown in Figure 1. Furthermore, the *in situ* NDP results revealed that the Li-ions immobilized interfacial layer further growing into electrolyte upon cycling. The formation of this interface layer is explained in terms of the immobilization of moveable Li-ions together with Si migration into Li_3PON , leading to large initial capacity losses. Insights gained from this NDP work shed light on the aging of thin film all-solid-state Li-ions batteries and facilitate potential interface modifications for better all-solid-state battery performance.

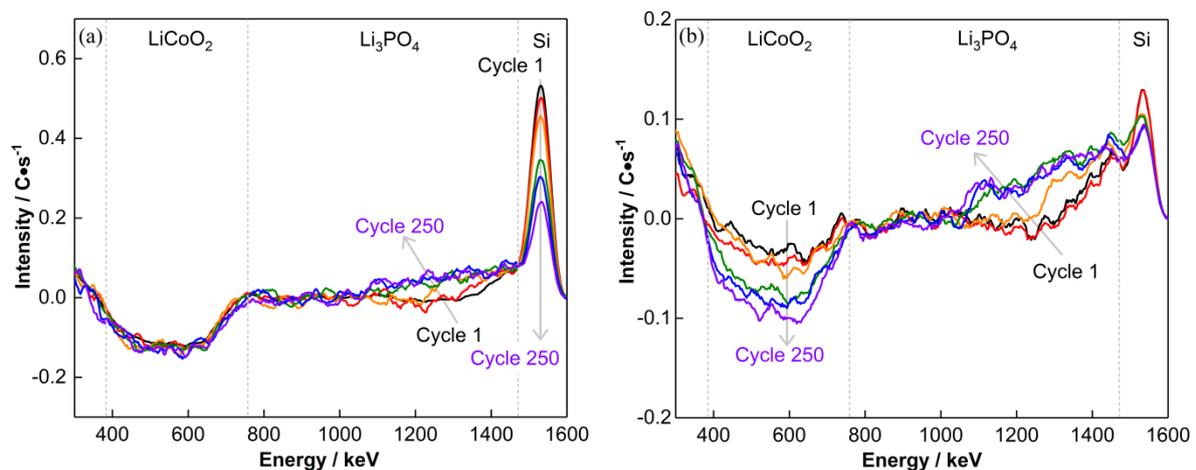


Figure 1. The difference NDP plots at the charged (a) and discharged (b) state of which the signal of the pristine (discharged) $\text{LiCoO}_2/\text{Li}_3\text{PON}/\text{Si}$ battery is subtracted. The *in situ* measured NDP spectra are given for the 1st (black), 2nd (red), 10th (orange), 50th (green), 100th (blue) and 250th (purple) cycle.