Atomic and electronic structure peculiarities vs. electrochemical performance of high energy density insertion cathode materials in high power ion batteries

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The raising demands for the safe high-energy density batteries employed in emerging electrical vehicles and high-capacity energy storage devices empower the search for low-cost and environmental friendly intercalation cathode materials that offer high power density and user safety in rechargeable ion-exchange batteries.

The application of the multivalent intercalation cathode materials pared with metal electrode is one of the promising strategies for increasing the battery energy density1. Among various candidates, Mg with its two valence electrons possesses high volumetric specific capacity of 3833 mAh cm^{-3}, doesn't generate dendrite growth, is safe to handle in an ambient atmosphere and largely availability throughout the planet2. The promising host material candidates for multivalent intercalation that display higher voltages are variants of manganese oxide. The investigated MgMn2O4 spinel and (Mg1-xNa2)Mn2O4 birnessite phases possess high specific capacities of 130 - 100 mAh/g and 210 mAh/g, respectively. Both materials in charged state, i.e. demagnesiated, exhibited microstructure, where the initially single-crystalline particle structure had changed into the patchwork of small regions with variously orientated crystallites, which was observed by HAADF- and ABF-STEM imaging. Evaluation of the ELNES data showed changes of the Mn valence towards Mn2+ and Mn3+, indicating the presence of Mn3O4 spinel phase in both materials. Upon galvanostatic magnesiation (battery discharge) both spinel and birnessite phases resembled their initial crystalline structures, however, leaving voids and defects behind with damage being more prominent in the birnessite. The degradation of both materials through the permanent change of the crystal structure led to the battery failure.

Another promising class of high energy density intercalation cathode material candidates is Li-rich oxyfluorides Li1+xMO2F with M=Ti, Mn, Fe, Co, Ni3-5 that possess the theoretical capacity range of 220-465 mAh/g. Here, the charge balance compensation of Li-excess is achieved through the O2- anion partial substitution by the F-. The theoretical capacity values of Li-rich oxyfluorides are in the range of 220-465 mAh/g. These materials crystallize in the disordered rocksalt structure and were so far obtainable only by mechanochemical synthesis route, which produced a large fraction of the amorphous phase. In our study, we have for the first time successfully synthesized Li1.5FeO2F0.5 via conventional ceramic synthesis. The produced material had high degree of crystallinity and achieved the higher capacity than the mechanochemically prepared material. The nanoscale distribution of F, atomic structure observations and Fe valence variations were monitored in the pristine materials prior cycling by means of EDS-, HAADF-, and EELS-STEM analysis. By correlating the TEM and in operando XAS analysis of Fe-K the higher capacity of the ceramic-route synthesized cathode material was attributed to the presence of structural defects.

References
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