Investigation of Charge Storage Mechanism of a Novel High Entropy Oxide Anode for Lithium Ion Batteries

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Abstract

As increasing energy storage demands for electric cars and mobile applications, advanced renewable technologies are expected to continue to grow in the future and have receive lots of attention. The most commonly used energy storage devices are Lithium-ion batteries (LIBs) with intercalation-based anode (such as Graphite) which exhibit high reversibility and low cost. However, lower theoretical capacity of graphite (~372 mA h g^{-1}) cannot meet the requirements for high-energy-density applications. Conversion-type anode such as $ZnMn_2O_4$ exhibits much higher theoretical capacity (784 mA h g^{-1}) than graphite, but it suffers from severe volume expansion resulting in poor cycling stability.

High entropy oxide (HEO) has been proposed and synthesized since 2015, and it has been found that the high configuration entropy can stabilize five elements with equiatomic amount in a single-phase rock salt system. Since then, several HEOs with different structures and elements have been synthesized, and HEOs with various properties can be designed. Sarkar et al used $(Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2})O$ as electrode of Lithium battery and showed high specific capacities (770 mAh g^{-1} at 0.1 A g^{-1}) and high stability with a capacity retention of ~100% up to 300 cycles. This result demonstrated that the entropy stabilization leads to significant benefit for the cycling stability.

Here we proposed a new single-phase HEO with spinel-structured $(Ni,Co,Mn,Fe,Ti)_3O_4$ as anode for lithium ion batteries. The microstructure was studied by SEM, EDX, TEM, and EXAFS. Based on the concept of entropy structure stabilization, the $(Ni,Co,Mn,Fe,Ti)_3O_4$ anode provided a reversible capacity of 560 mA h g^{-1} after 100 cycles with an excellent capacity retention of 100% up to 100 cycles at current density of 100 mA g^{-1}. The charge storage mechanism was investigated carefully by in operando X-ray diffraction (XRD), transition X-ray microscopy (TXM), and X-ray absorption spectroscopy (XAS).

Keywords – high entropy oxide, lithium ion batteries, transition X-ray microscopy, X-ray absorption spectroscopy, X-ray diffraction