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Investigation the role of Co^{2+} in LiFePO_4 cathode material during batteries operation by In-situ XANES technique

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Rechargeable lithium ion batteries are amongst the most advanced electrical energy storage system available today. Many families of compounds have been developed for use as cathode materials in Li-ion batteries such as layered oxides LiMO_2 ($M = \text{Co}, \text{Ni}, \text{Mn}, \text{or V}$), manganese spinel (LiMn_2O_4), and phospho-olivines LiMPO_4 ($M = \text{Fe}, \text{Mn}, \text{Co}, \text{or Ni}$). Lithium iron phosphate (LiFePO_4) have become the most interesting cathodes materials for lithium ion batteries because of their inexpensive, environmental friendly, high theoretical capacity (170 mAh/g) and long cycle life and high safety. However, LiFePO_4 inherently show poor electronic conductivity causing low rate performance. Many approaches have been used to improve conductivity of this material, e.g. carbon coating and nano-sizing. These also include isovalent doping which significantly increasing conductivity of the material.[1-3] Co is an element widely chosen as dopant due to the increasing of rate capability. However, there is not clearly evident showing mechanism of Co^{2+} incorporating with the improving rate capability during batteries operation. Here, we study the electronic structure change of Co^{2+} -doped LiFePO_4 materials during battery operation by in-situ X-ray absorption near edge structure (XANES). The materials were synthesized by the solid-state reaction. The single phase of LiFePO_4 was confirmed by X-ray diffraction. The in-situ Co and Fe K edge XANES were measured during charge-discharge to observe the oxidation state of Co^{2+} . The XANES result indicate that the oxidation state of Co^{2+} do not incorporate in phase transition during batteries operation. It only provides the improvement in conductivity of LiFePO_4 material.

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