Effect of lithium content on LiMnPO_4 and its electrochemical property for lithium ion batteries

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Recently, many research groups have reported the effect of lithium content on the structure and electrochemical performance of cathode material, such as layered structure LiNi_{0.5}Mn_{0.5}O_2, spinal structure LiMn_2O_4 and also olivine family member, LiCoPO_4 [1-4]. Meanwhile, Li_3PO_4 also worked as a good SEI film on the cathode surface which may prevent the contact between electrolyte and LiCoPO_4 avoiding side reactions between them at high charge and discharge voltage. All of the reported results showed that appropriate excess lithium could contribute to the electrochemical performance of the above cathode materials to some extent for different mechanisms.

In this article, we have reported the synthesis and electrochemical characterization of LiMnPO_4 material prepared via a citric acid-assisted sol–gel route without any additional treatment, investigated and discussed the effects of the amount of Li relative to the pristine composition LiMnPO_4 on the structure and electrochemical properties for the first time.

The X-ray diffraction patterns of nominal Li_{1+x}MnPO_4 (x=0.8, 1.0, 1.2, 1.4) powders are presented in Fig. 1. An olivine-type structure is formed and all of the peaks can be indexed to an orthorhombic structure with space group Pnma for standard sample. When x=0.8, a minor phase Mn_2P_2O_7 was formed. With lithium excess in the nominal composition, in “Li_{1.2}MnPO_4” or “Li_{1.4}MnPO_4”, three additional phases of Mn_3O_4, Li_2O and Li_3PO_4 appear.

FESEM images (Fig. 2) of Li_{1+x}MnPO_4 (x=0.8, 1.0, 1.2, 1.4) powders sintered at 550 ºC showed uniform particle dimensions distributed around 100~200nm for all of the powders. When x=1.4, the particle shows strawberry morphology composed of some primary particles with around 10 nm size.

Fig. 3 (a) Initial discharge-charge profiles and (b) the cycling performance and (c) direct current resistance as a function of cell voltages for Li_{1+x}MnPO_4 (x=0.8, 1.0, 1.2, 1.4).

The electrochemical property (Fig. 3) shows that Li_{1.2}MnPO_4 sample delivers the highest capacity and cycling stability. Li_2O and Li_3PO_4 may act as not only a good lithium ionic conductor but also excellent solid electrolyte separation layer to stabilize the LiMnPO_4 electrode surface, while Mn_3O_4 may act as an in site additive to enhance the electronic conductivity.

References

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