Synthesis and Electrochemical Characterization of Coatings on LiFePO$_4$ Nanoparticles

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Introduction

Since its discovery in 1997[1], lithium iron(II) phosphate (LiFePO$_4$) has become a key cathode material in lithium ion batteries (LIBs). The flat voltage plateau during discharging/charging, the good stability provided by the olivine crystal structure and the low cost due to the abundant elements make LiFePO$_4$ (LFP) a promising candidate for industrial lithium ion batteries applications.

During lithiation, either the phase separation or the solid solution phase forms (see Figure 1). Kinetically, the size relationship between the lateral transport rate and the insertion rate influences the type of intermediate phases (see Figure 2). The phase separation is energetically favorable at room temperature, where the rate performance is limited by the slow motion of phase boundary. Considering the application condition of LIBs, the formation of the solid-solution phase is desirable.

![Figure 1. Phase diagram of LiFePO$_4$][2]

![Figure 2. Scheme of the motion of lithium ions][3]

Objective and Hypothesis

Our objective is to alter the type of active particles during discharging/charging by tuning the lithium ions transport on the interface.

It has been reported that the interface diffusion can be separated from the bulk diffusion by conducting experiments on LFP nanoparticles[3].

Within LFP particles, electrons migrate via a small polaron hopping mechanism[4]. The strong binding energy between lithium ions and electrons makes the motion of Li$^+$ and electrons coupled[4].

To investigate the transport of Li$^+$ on the LFP interface, our hypothesis is that the lithium ions and the electrons are also coupled on the interface. Therefore, the ion transport can be adjusted by the electron transport.

Method

LiFePO$_4$ nanoparticles are used to obtain the interface diffusion. A layer of materials with different conductivity are coated on the LFP particles.

The synthesis of LiFePO$_4$ nanoparticles is based on the hydrothermal synthesis. The routine is shown below:

Carbon and ZnO coatings are achieved by the thermal decomposition of glucose and Zn(OAc)$_2$, respectively.

Ag layers are coated on the particles by the reduction reaction between AgNO$_3$ and (NH$_4$)$_2$SO$_4$. TiO$_2$ coatings are obtained by the sol-gel reaction of Ti(OOC$_2$H$_5$)$_4$.

Results

![XRD](C-coated LFP) ZnO-coated LFP TiO$_2$-coated LFP Ag-coated LFP

The electrodes with PAA as binder show great improvement on the rate performance compared with the case where PVDF is used as binder.

![Size Analysis](normalized discharge capacity vs. cycles)

Conclusion

- Coating LiFePO$_4$ nanoparticles with C, Ag, TiO$_2$, and ZnO are successfully done by using wet-chemical and mechanical methods.
- The LFP water-based electrodes with PAA as binders show excellent rate performance.
- The discharge capacity of C-coated LFP water-based electrodes made of the optimized recipe is outstanding.
- The diffusion coefficient is measured by performing cyclic voltammetry at different sweep rates and temperatures. The calculated diffusion coefficient of the pristine LFP is in the order of $10^{-15}$ cm$^2$/s$^2$, while that of C-coated LFP is in the order of $10^{-13}$ cm$^2$/s$^2$ and those of other coated samples are in the order of $10^{-14}$ cm$^2$/s$^2$.

Outlook

- The synthesis of Ag coating needs to be optimized to get rid of the formation of Ag clusters.
- Operando-XRD measurements of coated LFP nanoparticles are needed to visualize.
- The CV measurements have to be repeated on the electrodes with different parameters.

Reference