

### A Simple, Versatile Sol-Gel Method for the Synthesis of High-Performance LiMPO<sub>4</sub> (M=Fe, Mn, Co)

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The olivine-type LiFePO<sub>4</sub> has attracted great attention in recent years as a promising cathode material for rechargeable lithium-ion batteries [1]. However, for all its advantages, a major limitation is its poor rate performance, which is believed to be due to the material's intrinsic low electronic conductivity. One approach to overcoming this limitation is synthesis of nanocomposites consisting of small particles of LiFePO<sub>4</sub> and an electronic conductive phase, typically carbon [2-6]. For such a composite, phase purity of the active material, particle size, amount of carbon, form of carbon contact, and even the structure of carbon influence its electrochemical performance. These factors are all largely synthesis route dependent, and consequently, the performance of resultant LiFePO<sub>4</sub> electrodes is strongly synthesis route dependent as well. Solution based sol-gel methods, which are capable of producing gel precursors where multiple reactants are homogeneously mixed at the molecular level, are versatile methods for the synthesis of phase-pure nano-sized or submicron materials. This has been shown for various oxides. However, sol-gel methods for the synthesis of high-performance LiFePO<sub>4</sub> have not been adequately explored, despite the fact that its multi-element nature would make sol-gel methods appear particularly attractive for its synthesis.

Here we report a simple, versatile sol-gel method for the synthesis of carbon-coated LiFePO<sub>4</sub> as high-performance cathode. The method consists of two simple steps: (1) dissolve lithium acetate, iron (II) acetate and phosphoric acid in ethylene glycol to form a molecularly homogeneous, monolithic organo-gel; (2) directly heat the gel in nitrogen atmosphere to form carbon-coated, phase-pure LiFePO<sub>4</sub>. The LiFePO<sub>4</sub> formed are 200 – 300 nm particles with rather uniform size distribution and with 1 – 3 wt% surface carbon coating. Fig. 1 shows the morphology of the synthesized LiFePO<sub>4</sub> obtained by heating a 0.75 M precursor gel at 700 °C in N<sub>2</sub> for 12 hrs. The material has 1.8 wt% carbon coated on its surface, as detected by a combustion method.

The synthesized material exhibits excellent electrochemical properties and rate performance. The material yields a specific capacity of 165 mAh/g when charged to 4.0 V at a C/100 rate, with nearly perfect reversibility in discharge, as shown in Fig. 2. Fig. 3 shows specific discharge capacities versus cycle number of the material cycled at a 2C rate. A capacity around 150 mAh/g is achieved for initial cycles, and the material also exhibits good cycling performance. For the electrochemical tests, composite electrodes of a composition of 75:15:10 (active material:carbon:binder) with thickness of 150 – 200 μm and active material loading of 15 – 20 mg/cm<sup>2</sup> are used. These parameters along with the high specific capacities achieved at high rates demonstrate the excellent rate capability of the synthesized LiFePO<sub>4</sub>.

The method reported here is also versatile in that other lithium transition metal phosphates such as LiMnPO<sub>4</sub>,

LiCoPO<sub>4</sub> and solid solutions of different lithium transition metal phosphates with favorable physical characteristics can be synthesized by the method as well. This presentation will describe the method in detail and the influence of synthesis parameters on electrochemical performance of LiFePO<sub>4</sub>. Physical characteristics and electrochemical performance of other lithium transition metal phosphates synthesized by the method will also be presented and the advantages of the method demonstrated.

#### References

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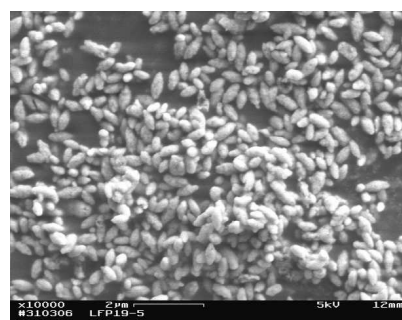


Fig.1. Morphology of carbon-coated LiFePO<sub>4</sub> synthesized from heating a 0.75 M gel at 700 °C.

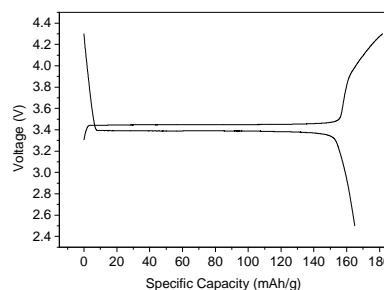


Fig. 2. Charge and discharge profiles of the synthesized LiFePO<sub>4</sub> at C/100 charge/discharge rate.

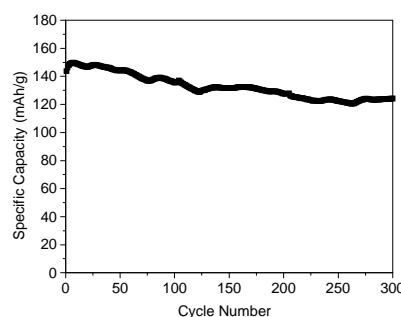


Fig. 3. Cycling Performance of the synthesized LiFePO<sub>4</sub> at 2C charge/discharge rate.