

Structure and Electrochemical Properties of Doped Iron Phosphates

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New positive electrode materials for lithium-ion batteries have been recently developed that offer increased promise for the future. Important criteria for include low cost, low toxicity and good safety properties. Although these needs have been met to some degree in emerging layered manganese/nickel oxides, they still exhibit problems inherent to their composition. One other exciting class that has garnered much interest is transition metal phosphates. These framework or “polyanion” structures, first explored extensively by Goodenough et al.,¹ are based on frameworks built of PO₄ tetrahedra and MO₆ octahedra. They exhibit a favorable increase in the Li insertion potential of up to 2 V compared to the corresponding oxide, owing to the inductive effect of the PO₄³⁻ moiety. This is especially important for Fe whose oxide potential lies at low values. In particular, much interest has been shown in LiFePO₄ with an olivine structure (Figure 1), and a theoretical capacity of 170mAh/g. This framework displays extensive interconnection of octahedra with M2 site cations (the Fe cations) forming a network of corner-shared octahedra in the (010) plane. The octahedral M1 site (Li) cations share edges along the [100] direction.

Unfortunately, owing to its negligible electronic conductivity of about 10⁻⁸ S/cm, the theoretical capacity of LiFePO₄ (170mAh/g) is only partially accessible even at slow rates although raising the temperature markedly improves transport. LiFePO₄ coated with a thin carbon layer deposited from solution exhibited very good capacities at 80°C in conjunction with a polymer electrolyte. Our approach is to induce nucleation of LiFePO₄ within a conductive carbon web, simultaneously “wiring” the embedded particles with electronic injection sites, and restricting particle size growth. These metal phosphate/carbon matrix composites are prepared by a solid-state method that uses simple inorganic precursors and a carbon gel as the matrix precursor,³ resulting in materials with tap densities are between 1.4 and 1.5 g/cc. Electronic conductivities of the composites range from 1 x 10⁻³ S/cm (7% carbon) to 1.4 x 10⁻¹ (14% carbon) Impressive electrochemical results can be achieved in room temperature cells. Optimized materials can achieve extremely stable capacities of about 160 mAhg⁻¹ (C/5), with good rate capability (Figure 2).⁴

Another interesting approach to the problem of electronic conductivity relies on doping the Li⁺ sites with a metal such as Mg²⁺, Al³⁺, Nb⁵⁺ and Zr⁴⁺. Y.-M. Chiang et al. demonstrated that this resulted in materials with greatly enhanced electronic conductivity, up to 2 x 10⁻² S/cm for pressed pellets densified at high temperature. Our experiments using Chiang’s approach and Zr as the dopant, have produced deep black materials of composition Li_{0.99}Zr_{0.01}FePO₄ that display conductivities of up to 3.0 x 10⁻⁴ S/cm for pellets densified at room temperature. The mechanism of the conductivity enhancement and the possible role of occluded carbon have yet to be completely elucidated, however, and will form part of the subject of this talk. With respect to electrochemical properties, comparison of data taken directly from reference X, with our data on

LiFePO₄/carbon matrix electrodes at similar percentages of active material is shown in Figure 2. The upper curves represent LiFePO₄/C electrodes with 14% carbon (75% active LiFePO₄ in the electrode), and 7% carbon (83% active). This data is compared to electrodes described in reference 5 containing 78% active Li_{0.99}Nb_{0.01}FePO₄. Actual current densities are similar (see Figure caption). Despite the apparent increase in electronic conductivity, the electrochemical performance of the material is not dramatically enhanced compared to poorly conductive LiFePO₄ embedded in a conductive medium. The question of the limiting factors in rate response in this material will be addressed using electrochemical data on our Zr-doped LiFePO₄.

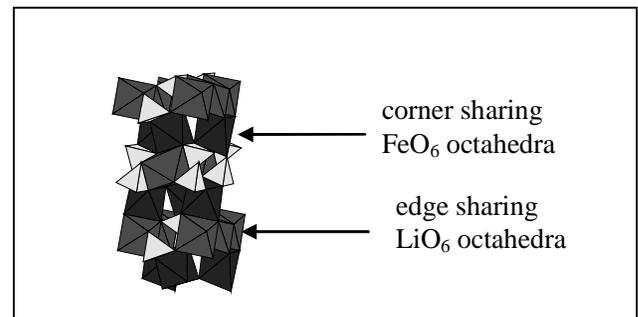


Figure 1. Structure of LiFePO₄ showing connectivity of framework components.

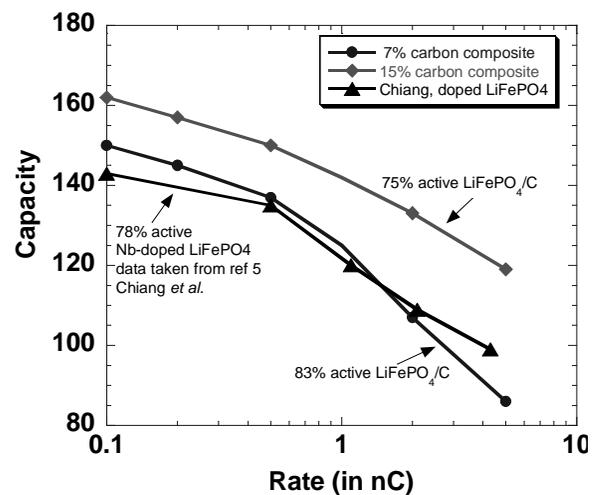


Figure 1. Comparison of electrochemical performance as a function of rate for our LiFePO₄/C materials (75% active and 83% active; C/2 rate ~ 85mA/g); and data reported for Li_{0.99}Nb_{0.01}FePO₄, taken from reference 3 (78% active; C/2 rate ~ 75 mA/g)

References

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