Conductive Coatings on Small Crystallite Size LiFePO₄

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Many recent developments in new cathode materials for lithium-ion batteries have focussed on lithium metal phosphates. The most prominent member of the family, olivine-type $LiFePO_4^{-1}$ has good lithium ion mobility,² but poor inherent electronic conductivity. ($\sigma \sim 10^{-9}$ S/cm). This limits its electrochemical response. Two approaches to improve the response are to a) limit particle size; b) to include conductive phases, thus increasing its capacity to near theoretical values.³ It was also reported that the inherent conductivity of the lattice can be altered by doping it with a supervalent ion. Compositions were described as black *p*-type semiconductors with conductivities of $\sim 10^{-2}$ S/cm arising from minority Fe³⁺ hole carriers.⁴ We have recently shown that a nano-network of metal-rich phosphides is responsible for the enhanced conductivity. Microstructure control can be used to manipulate electron transport.⁵

This talk will summarize and compare our recent efforts to control particle size and conductivity through different synthetic methods that employ organic additives. These have been applied to a wide range of solution and solid state processing of

 $Li_{1-x}M_yFePO_4$ materials. Bulk conductivities in the range from 10^{-1} to 10^{-3} S/cm, similar to those previously reported in the literature,⁴ were achieved in many cases. A combination of Mossbauer, X-ray diffraction, STEM on these materials, and carbon-free olivines will be presented along with our electrochemical studies on the performance of these materials as cathodes in Li-ion batteries.

References

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