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The Impact of Carbon Structure and Morphology on the Electrochemical Performance of LiFePO₄/C Composites

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The morphology, structure, and quantity of the carbon in LiFePO₄/C composites used as electrodes in Li ion batteries are critical determinants of its electrochemical performance. For example, we have recently shown that there are strong correlations between carbon sp²/sp³ ratios and the pressed pellet conductivities and rate capabilities of coated LiFePO₄ samples. While it is most common and convenient to incorporate carbon directly during LiFePO₄ synthesis by mixing in organic additives, this presents a dilemma; graphite, the most electronically conductive form, is typically produced at temperatures much higher than can be used for production of the olivine. Judicious selection of organic precursors and the use of graphitization catalysts can improve structure, but the carbon produced is still very disordered. Combustion synthesis, in contrast, affords a way of decoupling carbon production from that of LiFePO₄. The combustion temperature and carbon content are determined by the fuel:nitrate ratio, where the fuel is, e.g., an organic complexing agent. During subsequent calcination, the LiFePO₄ phase is formed. Interestingly, LiFePO₄/C composites produced this way also contain long C fibers that can act as nano-wires for the transfer of electrons during the electrochemical process.

Another parameter relevant to electrochemical performance is the carbon content in the composite materials. High carbon contents (above about 1-2 wt. %) have an adverse effect on tap density and energy density and are therefore undesirable, although they may result in good rate performance. Using a simple bricklayer model, it can be shown that very little carbon is necessary to improve the pressed pellet conductivities (and by correlation the rate capability) of LiFePO₄/C composites, provided that the electronic conductivity of the carbon is sufficiently high. This can be achieved by manipulation of synthetic parameters, as will be discussed in this presentation.