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Combustion Synthesis of Lithium Manganese Phosphate

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Lithium metal phosphates with the olivine structure are among the most promising cathode materials for lithium ion batteries. Both LiFePO_4 and LiMnPO_4 are potentially less costly and safer than the transition metal oxides currently used, making them attractive for high power applications such as hybrid electric vehicles (HEVs). While particle size engineering and carbon coating technologies have recently overcome the rate limitations of the native LiFePO_4 , the performance of LiMnPO_4 is still sub-optimal. Both materials have theoretical capacities of 170 mAh/g, but the higher discharge potential of LiMnPO_4 compared to LiFePO_4 (~4V and 3.45V vs. Li/Li^+ , respectively) leads to a higher specific energy for the former, providing an incentive to develop it further. A significant factor in the poor discharge characteristics of LiMnPO_4 is its very low electronic conductivity (10^{-16} S/cm). One strategy to overcome this limitation is make LiMnPO_4 nanoparticulate to decrease the diffusion distance, as has been done with the polyol process used by High Power Lithium, Ltd. Further improvements to the rate capability are still needed, however. We have recently shown that the electrochemical performance of LiFePO_4 is highly dependent on the quality of the carbon coatings on the particles. Furthermore, we have recently developed a combustion method for the production of olivines or olivine/carbon composites, in which the amount of the graphene component of the carbon is increased over that formed during conventional synthesis. The sp^2/sp^3 ratio of disordered carbon is a structural characteristic that correlates closely with the electronic conductivity of the composites and with rate capability of the olivine.

Nanoparticulate LiMnPO_4 can be prepared in one step by glycine-nitrate combustion (GNC), without the need for further calcination. The reaction is self-propagating and can be carried out within a minute, resulting in particles of 30-40 nm average size. For this paper, we will discuss the effects of varying synthetic parameters such as the fuel to nitrate ratio, use of different precursors, and sources of carbon, on the physical properties of the LiMnPO_4 produced. The electrochemical behavior of these samples will be compared to those synthesized hydrothermally.

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