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Comparison of LiMnPO₄ made by Combustion and Hydrothermal Syntheses

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Among the olivine-structured metal phosphate family, LiMnPO₄ exhibits a high discharge potential (4V), which is still compatible with common electrolytes, making it interesting for use in the next generation of Li ion batteries. The extremely low electronic conductivity of this material severely limits its electrochemical performance, however. One strategy to overcome this limitation is to make LiMnPO₄ nanoparticulate to decrease the diffusion distance. Another is to add a carbon or other conductive coating in intimate contact with the nanoparticles of the main phase, as is commonly done with LiFePO₄.

The electrochemical performance of LiFePO₄ is highly dependent on the quality of the carbon coatings on the particles [1-2], among other variables. Combustion synthesis allows the co-synthesis of nanoparticles coated with carbon in one step. Hydrothermal synthesis is used industrially to make LiFePO₄ cathode materials [3] and affords a good deal of control over purity, crystallinity, and particle size. A wide range of olivine-structured materials has been successfully prepared by this technique [4], including LiMnPO₄ in this study.

In this paper, we report on the new synthesis of nano-LiMnPO₄ by a combustion method. The purity is dependent upon the conditions used for synthesis, including the type of fuel and precursors that are chosen. The fuel to nitrate ratio influences the combustion temperature, which determines the type and amount of carbon found in the LiMnPO₄ composites. This can further be modified by use of carbon structural modifiers added during a subsequent (optional) calcination step.

Figure 1 shows a transmission electron microscopy (TEM) image of the spherical nano-sized LiMnPO₄ particles typically formed by combustion synthesis. The average particle size is around 30 nm, in agreement with values obtained by the Rietveld refinement of XRD patterns. The small size of the particles cause the peak broadening evident in the pattern of combustion formed LiMnPO₄, shown in Figure 2. Figure 2 also shows a pattern of hydrothermally prepared LiMnPO₄, which is sub-micron in size.

In this presentation, we will show how the crystallographic parameters, particle size, particle morphology, and carbon content and structure impact the electrochemical properties of the LiMnPO₄/C composites produced by these methods.

References

1. N. Ravet, Y. Chouinard, J.F. Magnan, S. Besner, M. Gauthier, M. Armand, *J. Power Sources*, **97-98**, 503 (2001).
2. J. D. Wilcox, M.M. Doeff, M. Marcinek, and R. Kostecki, *J. Electrochem. Soc.*, **154**, A389 (2007).
3. J. Chen and M. S. Whittingham, *Electrochem. Commun.*, **8**, 855 (2006).
4. J. Chen, S. Wang, and M. S. Whittingham, *J. Power Sources* **174**, 442 (2007).

Acknowledgments

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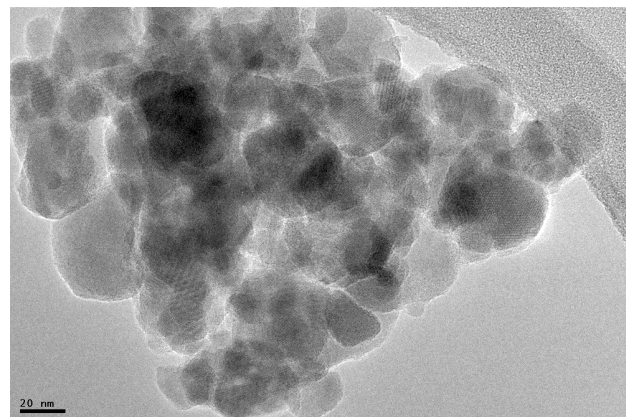


Figure 1. TEM image of nanosized LiMnPO₄ by combustion synthesis

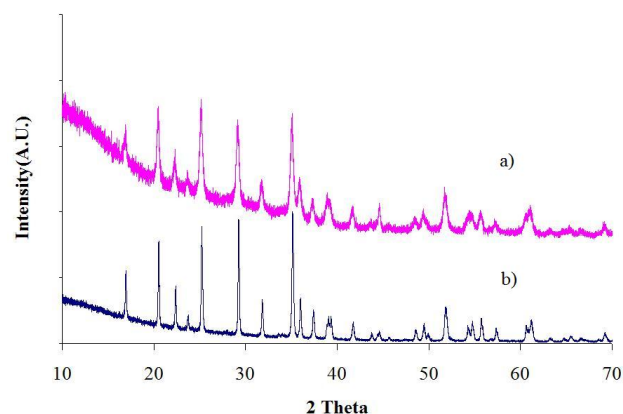


Figure 2. X-ray diffraction patterns of a) nanometric LiMnPO₄ made by combustion synthesis and b) hydrothermally prepared sub-micron LiMnPO₄.