

Redox chemistry in the Li-Fe-P-O system

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Intense research over the last few years in the Li-battery community has been focused on trying to bypass the poor intrinsic electronic conductivity of LiFePO_4 in order to implement it in real commercial electrochemical cells. Various strategies have been proposed, the most successful consisting in conductive carbon “nanopainting” at the surface of LiFePO_4 particles [1-3]. In the meantime, Chiang’s group proposed to dope LiFePO_4 with pentavalent or tetravalent metals such as Nb or Zr [4] which brought much controversy [5]. We undertook as well a long and fastidious study on how to produce efficient carbon coating on LiFePO_4 particles from a straightforward process that may be implemented to a cheap industrial production [6]. Meanwhile we decided to investigate in much detail the reproducibility of Yamada’s and Chung’s type syntheses that both used $\text{Fe}^{\text{II}}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (carbon-containing precursor) as the Fe source. We prepared several series of samples of “nominal” compositions $\text{Li}_{1-x}\text{Nb}_x\text{FePO}_4$ ($0 \leq x \leq 0.05$) using various sources for Nb, Fe, Li and P and investigated in details the particles formed by HRTEM. Our study reveals with much consistency, in agreement with Subramanya Herle [3] and Ravet [5], that LiFePO_4 could not be doped with Nb. Instead, if any of the precursors of the synthesis ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{Nb}(\text{OC}_6\text{H}_5)_5$, ...) contains carbon, residual carbon was systematically found by chemical analysis. It was observed as i) a thin (~10 nm) coating at the surface of LiFePO_4 particles and ii) an amorphous “Nb,P,C,O” web. Depending on the more or less reductive nature of the synthesis atmosphere, thin Fe_2P layers were observed as well. On the other hand, all the samples synthesized from NbCl_5 and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were virtually “carbon-free” and showed very poor electrochemical activity. For both $\text{Li}_{0.99}\text{Nb}_{0.01}\text{FePO}_4$ and $\text{Li}_{0.95}\text{Nb}_{0.05}\text{FePO}_4$ carbon-free nominal compositions, NbOPO_4 particles were clearly identified from HRTEM, XRD and from their electrochemical signature.

References

1. N. Ravet, J. B. Goodenough, S. Besner, M. Simoneau, P. Hovington, M. Armand, *The 1999 Joint International Meeting*, (1999). Hawaii, Oct. 17- 22.
2. A. Yamada, S. C. Chung, K. Hinokuma, *J Electrochem Soc*, 148(3), p. A224-A229, (2001)
3. H. Huang, S. C. Yin, L. F. Nazar, *Electrochemical and Solid State Letters*, 4(10), p. A170-A172, (2001), P. Subramanya Herle, B. Ellis, N. Coombs & L.F. Nazar, *Nature Materials*, 3, 147-152, March 2004
4. S. Y. Chung, J. T. Bloking, Y. M. Chiang, *Nature Materials*, 1(2), p. 123-128, (2002) ; S. Y. Chung, Y. M. Chiang, *Electrochem Solid-State Lett.*, 6(12), A278-A281 (2003)
5. N. Ravet, A. Abouimrane & M. Armand, *Nature Materials*, 2, 702, Nov. 2003
6. A. Audemer, C. Wurm, S. Gwizdala, M. Morcrette, and C. Masquelier, *World Patent #WO04001881* (2003)

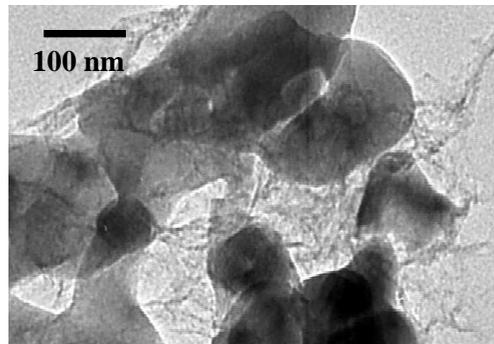


Figure 1: Carbon coating at the surface of LiFePO_4 particles

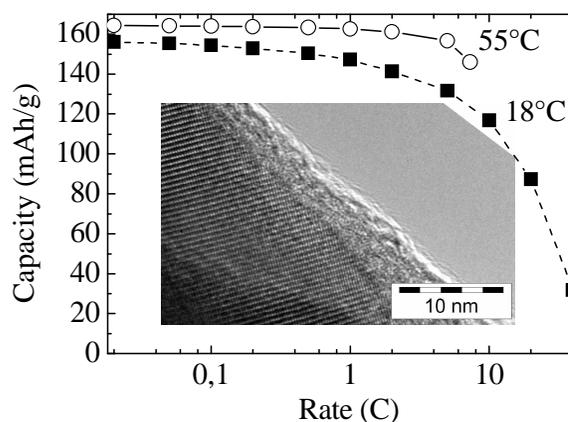


Figure 2: Signature plots at 18°C and 55°C and HRTEM micrograph of an optimized LiFePO_4/C electrode

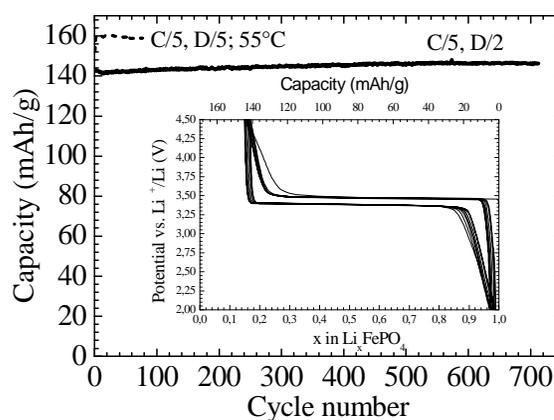


Figure 3: Long term cycling of a plastic LiFePO_4/C electrode vs. Li in coin-type cell.
C : charge, D : discharge

