Metastable Intermediate in Li_xFePO_4
Structure, Electrochromism, and Transport Properties

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In Li_xFePO_4, the ground state phase separation and metastable solid solution are energetically competitive, and the solid solution phase is induced in a non-equilibrium electrochemical reaction. However, until now, there has been no discussion or experimental report of the crystal structure, optical and transport properties of the metastable solid solution phase due to the following extreme technical difficulties. First, the solid solution phase Li_xFePO_4 is metastable during electrochemical process and disappears within a few seconds after relaxation. We overcame this limitation by quenching Li_xFePO_4 (x = 2/3) at 350 °C to room temperature. This quenched phase remained stable for a couple of weeks, which enabled sufficient time to measure the several intrinsic properties. Second, conductive carbon may form during sintering at high temperature from possible carbon sources such as polyolefin worn from jars, organic solvent used in milling and carbon-containing precursors (e.g., oxalate $FeC_2O_4{\cdot}2H_2O$). Finally, impurities such as Li_3PO_4, $Li_4P_2O_7$ and Fe_xP resulting from off-stoichiometric mixing or the carbon reduction effect above 800 °C will largely increase the apparent optical absorption and conductivity of Li_xFePO_4 by several orders of magnitude. The scattering of the conductivity data resulting from the above extrinsic effects has troubled and confused scientists for a long time. In our present study, pure carbon-free $LiFePO_4$ and $FePO_4$ were prepared using carbon-free precursors and controlling sintering parameters, and the intrinsic superstructure [1], optical properties [2], and conductivity [3] of quenched single phase Li_xFePO_4 (x = 2/3) was evaluated.

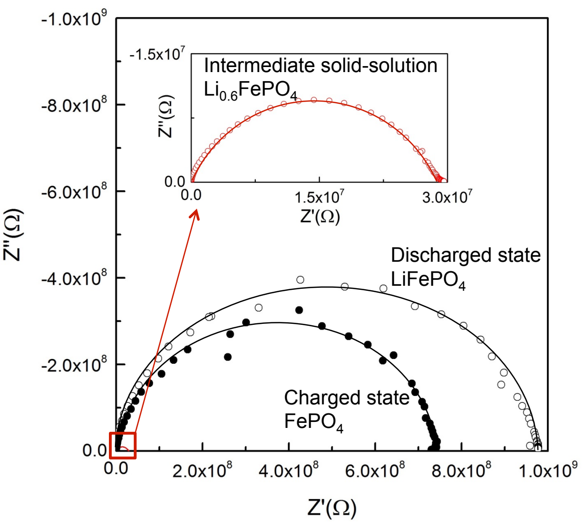

Figure 1 Nyquist plots for thermodynamically stable $FePO_4$, $LiFePO_4$, and the isolated intermediate solid solution $Li_{0.6}FePO_4$. The non-equilibrium solid solution $Li_{0.6}FePO_4$ shows approximately two orders of magnitude lower resistance than the equilibrium end members $FePO_4$ and $LiFePO_4$.

[1] S. Nishimura, R. Natsui, A. Yamada, *Angew. Chem. Int. Ed.* 54 (2015) 8939–8942.
[2] S. Furutsuki, S. C. Chung, S. Nishimura, Y. Kudo, K. Yamashita, A. Yamada, *J. Phys. Chem. C*, 116 (2012) 15259-15264
[3] J. Lu, G. Oyamad, S. Nishimura, A. Yamada, submitted, (2015)