Facile Topotactic Delithiation from LiFePO$_4$

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The high cost, toxicity, safety hazards, and chemical instability of the conventional LiCoO$_2$, LiNiO$_2$, and LiMn$_x$O$_{2-y}$ based cathode materials prohibits their use in lithium cells for large-scale or biomedical applications. As part of an intensive search for alternative materials, LiFePO$_4$ has been shown to have great advantages in cost, stability, and safety with no significant shift in the high energy density of the conventional materials. However, its inherently poor electronic conductivity and resultant poor current maintenance has presented major drawbacks to practical implementation. Here we demonstrate that the inherently slow kinetics can be easily compensated for by the acceptable external anodic overvoltage, under which the charging speed becomes astonishingly fast and competitive with that of the conventional LiMn$_x$O$_y$.

The current response to the stepwise constant voltage of 4.2V vs. Li/Li$^+$ at 25°C was integrated to give the time-dependent capacity consumption, this is summarized in Fig. 1. Both LiFePO$_4$ and LiMn$_x$O$_y$ have fast kinetics in lithium extraction under these experimental conditions. It can be seen that LiFePO$_4$ consumes most of its theoretical capacity (170 mAh/g) within 10 minutes followed by the quick saturation after 30 minutes. It is quite astonishing that the reaction speed is competitive with and even faster than that of the conventional LiMn$_x$O$_y$. In contrast, the capacity consumption of Li$_3$MnPO$_4$ under identical experimental conditions was almost negligible. Based on these results, a 30 minute potentiostatic oxidation at 4.2V vs. Li/Li$^+$ was followed by galvanostatic discharge at the C/20 rate, the discharge curves are shown in Fig. 2. The large discharge capacity with the expected profiles was confirmed both for LiFePO$_4$ and LiMn$_x$O$_y$. The negligibly small discharge capacity of Li$_3$MnPO$_4$ can be explained by examining Fig. 1, where the 30 minutes oxidation could extract less than only 5% of the total lithium. Figure 3 is the accelerating test of Fig. 1 with chemical delithiation using NO$_2$BF$_4$ as an oxidizer, where we can recognize the host frameworks of FePO$_4$ and 3-MnPO$_4$ are robust enough to tolerate the non-equilibrium conditions at 5.1V and the very slow kinetics with the significant loss of long-range order in Li$_3$MnPO$_4$.

The inherent low electronic conductivity of LiFePO$_4$ has been recognized as a major problem that limits the charge-discharge reaction kinetics, and makes it unsuitable for high-power operations. However, our experiments have shown that this intrinsic problem can be easily compensated for by the acceptable external oxidation power in the charging process by satisfying the following intrinsic criteria: (i) open circuit voltage with an appropriate over-voltage margin to the electrolyte oxidation, (ii) structural integrity under the strong non-equilibrium state induced by the over-potential, and (iii) moderate electrochemical activity easily enhanced to the practical level by efficient carbon coating. Unfortunately, olivine Li$_3$MnPO$_4$ satisfies none of these conditions.

Details of these experiments will be presented in the poster and rationalized with the accurate structural data obtained by the neutron diffraction study.

Fig. 1. The integrated current responses to the stepwise anodic overvoltages of 4.2 V vs. Li/Li$^+$ applied to (a) LiFePO$_4$, (b) LiMn$_x$O$_y$, and (c) Li$_3$MnPO$_4$, which represents the time-dependent anodic capacity consumption.

Fig. 2. The galvanostatic discharge curves at the C/20 rate after 30 minutes potentiostatic oxidation at 4.2V vs. Li/Li$^+$ for (a) LiFePO$_4$, (b) LiMn$_x$O$_y$, and (c) Li$_3$MnPO$_4$.

Fig. 3 X-ray diffraction patterns before/after the 30 minute chemical oxidation of (a) LiFePO$_4$, (b) LiMn$_x$O$_y$, and (c) Li$_3$MnPO$_4$, using NO$_2$BF$_4$ as the oxidizer (5.1V vs. Li/Li$^+$). This corresponds to the accelerating test of Fig. 1.