Investigating Charge Compensation in Li $_{(1-x)}$ FePO$_4$

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In its application as a cathode material for Li-ion batteries, LiFePO$_4$ shows good thermal stability, high theoretical energy density and low production costs. However, wider application of this material is still limited by poor transport of the charge carriers and poor Li ion transport within the LiFePO$_4$ lattice [1]. This has lead to concerted research efforts how the electronic structure of LiFePO$_4$ changes during the extraction (delithiation) and insertion (lithiation) of Li atoms in LiFePO$_4$ lattice. A simplified picture of charge compensation in LiFePO4 holds that removing Li atoms from the lattice results in the Fe ion being oxidized from Fe^{2+} to Fe^{3+}. However, this simple ionic picture does not take into consideration the covalency and hybridization between Fe and O atom.

We report on investigations of the near edge fine structures (ELNES) at the O-K and Fe L$_{2,3}$ edges in order to understand the charge compensation during the delithiation of LiFePO$_4$.The Fe-2p and O 1s spectra have also been analyzed with the aid of ligand-field multiplet model and density functional theory methods. Figure 1(a) shows the O-K edge before and after delithiation. The O-K edge is characterized by a pre-edge peak below 530 eV after delithiation. The pre-edge peak at the O-K edge has been variously interpreted as transitions to empty oxygen 2p which have been hybridized with the Fe 3d states or due to local atomic rearrangements arising from radiation damage from the electron beam [2, 3, 4]. Therefore, our study also included a series of experiments to determine the extent into which radiation damage influences the intensity of the pre-edge peak. The behavior of the O K-edge corroborates the trends in the Fe L$_{2,3}$ edge. Figure 1(b) shows the changes in the fine structure of the Fe L$_{2,3}$ edge with before and after delithiation. The changes in the fines structure the transition metal edge are due to the changes in the valency at the iron site as a result of the delithiation process. Due to covalency and hybridization effects, the local changes at the O atom can be correlated to changes in electronic structure around at the Fe atoms. These results point towards both Oxygen and Iron atoms being involved in the charge compensation process during delithiation.

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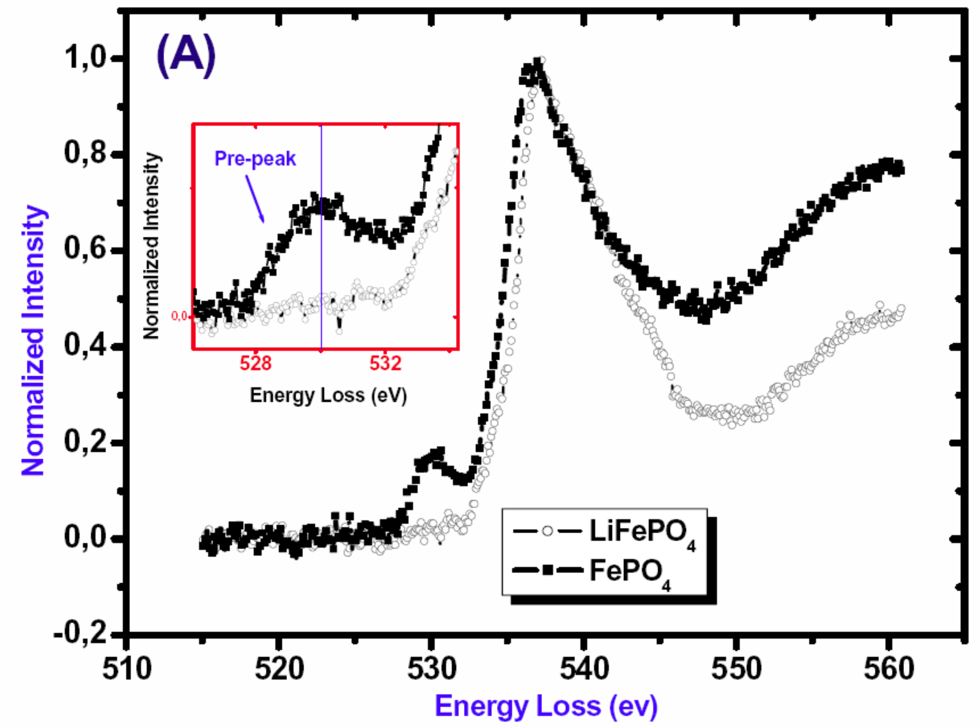

Figure 1(a). O-K absorption edges of undelithiated $LiFePO_4$ and delithiated $FePO_4$. Inset shows an expanded view of the pre-peak.

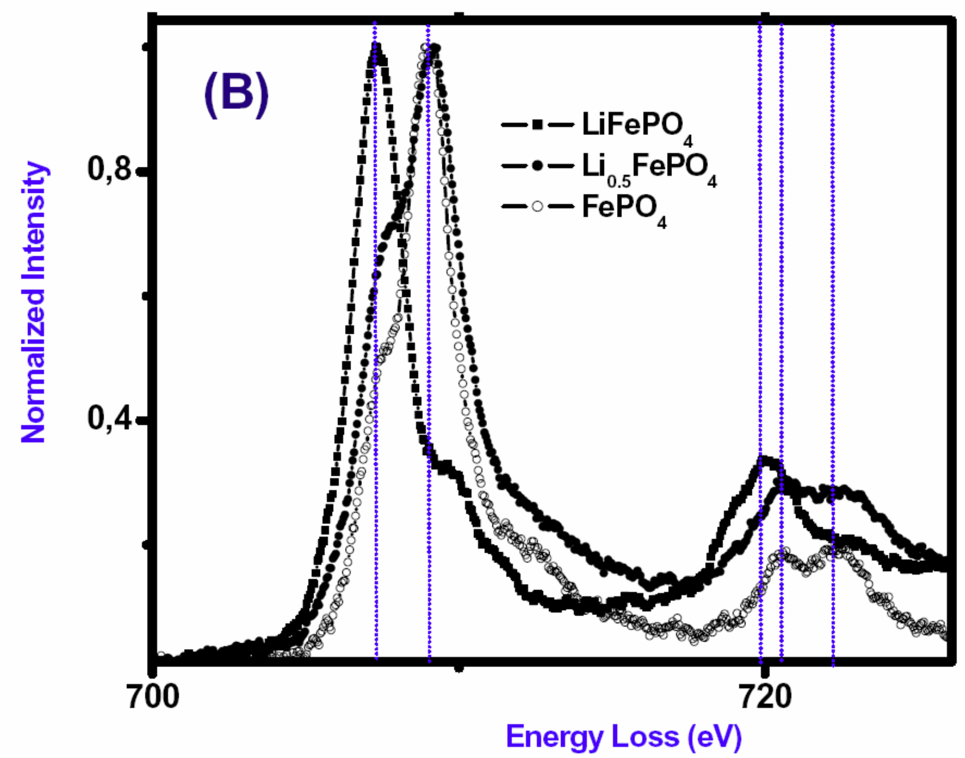

Figure 1(b). Fe $L_{2,3}$ edges of undelithiated $LiFePO_4$, partially delithiated $Li_{0.5}FePO_4$ and delithiated $FePO_4$. The peak features are indicated by the dotted vertical lines.

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