

## LiFeO<sub>2</sub> – tunnel: The First Multiple Electrons Transfer Fe Based Cathode Compound

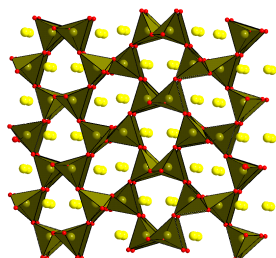
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A systematic investigation of the possibility of Fe based cathodes with 2 Li per 1 Fe atom electrochemical cycling was undertaken. In such cathodes, both the Fe<sup>2+</sup>/Fe<sup>3+</sup> as well as the Fe<sup>3+</sup>/Fe<sup>4+</sup> redox couples are to be utilized. To identify appropriate candidate compounds for Fe<sup>2+</sup>/Fe<sup>4+</sup> multiple electrons transfer chemistry, the following model compound selection criteria were used:

- 1) Rigid tunnel crystal structures were considered in order to provide structural stability during 2 electron transfer on charge/discharge cycling.
- 2) Fe<sup>3+</sup> oxidation state in the initial compound to minimize structural stresses during cycling between Fe<sup>2+</sup> and Fe<sup>4+</sup> oxidation states.
- 3) Structures with unusually large (for Li compounds) tunnels to accommodate multiple Li ions per Fe and to decrease repulsion between Fe and Li ions in the fully lithiated state.

Our study was focused on 2 model structures with Fe exclusively in octahedral, LiFeTiO<sub>4</sub>, or tetrahedral, LiFeO<sub>2</sub> (Fig. 1), environments. The target compounds were prepared via ion exchange from appropriate intermediate phases with larger alkali cations. The structural motifs were preserved during the ion exchanges as confirmed by powder X-ray diffraction (PXD) measurements.

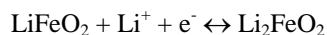


**Figure 1.** Crystal structure model of tunnel LiFeO<sub>2</sub>. FeO<sub>6</sub> octahedra are highlighted. Li atoms are shown as yellow spheres.

Chemical Li deintercalation from LiFeTiO<sub>4</sub> by an I<sub>2</sub> solution in acetonitrile resulted in the Li<sub>0.33(5)</sub>Fe<sub>1.00</sub>Ti<sub>1.00</sub>O<sub>4</sub> stoichiometry as determined by inductively coupled plasma (ICP) spectroscopy. PXD measurements showed that the crystal structure was preserved on Li deintercalation. Extraction of 0.7 Li<sup>+</sup> per LiFeTiO<sub>4</sub> formula unit by a mild oxidizing agent is indicative of an unexpectedly low Fe<sup>3+</sup>/Fe<sup>4+</sup> potential, which was also confirmed electrochemically. Chemical Li intercalation into LiFeTiO<sub>4</sub> resulted in phase decomposition.

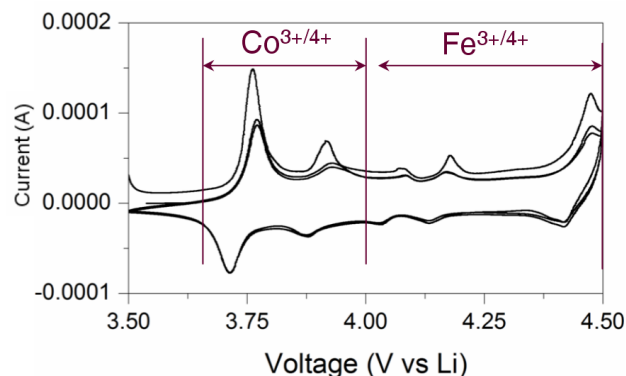
During electrochemical cycling, intercalation of Li into the tunnel phase LiFeO<sub>2</sub> can theoretically result in the Li<sub>2</sub>FeO<sub>2</sub> stoichiometry, while a complete Li deintercalation would formally lead to the “FeO<sub>2</sub>” tunnel

compound, as shown below.



Unlike layered structures, which collapse before all Li can be removed, tunnel structures are known to sustain complete Li deintercalation. The theoretical specific capacity of LiFeO<sub>2</sub> for the case of 2 Li cycling is 526.6 mAh/g, much greater than conventional Li-ion cathode materials

Co doped LiFe<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub> (x = 0.01, 0.05, 0.10, 0.20) samples were prepared to improve electronic conductivity. Cyclic voltammetry (CV) measurements revealed multiple electrochemical processes (Fig. 2) during the charge/discharge cycle of these doped materials. We attribute the peaks at 3.75 and 3.9 V to Co<sup>3+/4+</sup> redox couple, while the Fe<sup>3+/4+</sup> redox couple is the only feasible explanation for the charging peak at 4.5 V. Reaction with the EC:DMC electrolyte begins at 4.6 V, most likely due to holes occupying O states in the band structure with formation of active peroxide (O<sub>2</sub>)<sup>2-</sup> species. Li intercalation events are observed on CV during the material discharge. The CV results confirm the validity of the approach and feasibility of oxide cathode material utilizing Fe<sup>3+/4+</sup> redox couple.



**Figure 2.** Electrochemical measurements results for LiFe<sub>0.9</sub>Co<sub>0.1</sub>O<sub>2</sub> (C/5 cycling rate, LiPF<sub>6</sub> in EC:DMC electrolyte).

Chemical Li intercalation into the LiFeO<sub>2</sub> tunnel structure resulted in Li<sub>1.57(5)</sub>Fe<sub>1.000</sub>O<sub>2</sub> stoichiometry without destroying the structure. Li intercalation occurs at ~2.4 V, as was determined electrochemically.

Thus, the new tunnel LiFeO<sub>2</sub> polymorph is the very first compound demonstrating accessibility of both redox couples, Fe<sup>2+</sup>/Fe<sup>3+</sup> as well as Fe<sup>3+</sup>/Fe<sup>4+</sup>, in one compound for electrochemical cycling.