

# Cycling performance of LiCoPO<sub>4</sub> cathodes: reasons for capacity fading and effect of the electrolyte composition.

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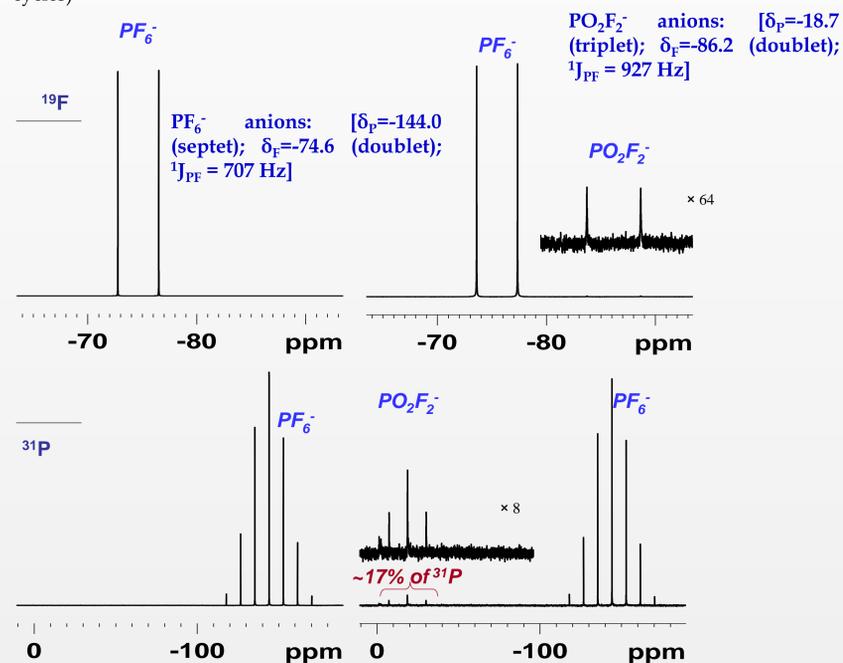
The reasons for capacity fading of LiCoPO<sub>4</sub> cathodes in 1M LiPF<sub>6</sub> EC/DMC 1:1 electrolyte solutions were investigated using <sup>19</sup>F-, <sup>31</sup>P-NMR and XPS spectroscopy. The origin of the poor performance of LiCoPO<sub>4</sub> cathodes in LiPF<sub>6</sub> containing electrolyte solutions is a nucleophilic attack of F<sup>-</sup> anions in solution on the P atoms, resulting in the breaking of the P-O bonds of the phosphate anions and the formation of soluble LiPO<sub>2</sub>F<sub>2</sub> moieties. Markedly enhanced cycling performance of a LiCoPO<sub>4</sub>/C cathode was observed in a 1M LiPF<sub>6</sub> in fluoroethylene carbonate (FEC)/dimethyl carbonate (DMC) electrolyte solution compared to 1M LiPF<sub>6</sub> in ethylene carbonate (EC)/DMC electrolyte solution. Further improvement was achieved by the addition to the electrolyte solution of 0.5-1% of trimethyl boroxine (TMB) additive. Capacity retention of LiCoPO<sub>4</sub> electrode in this electrolyte comprises 90% with faradaic efficiency of 98% after 100 cycles.

Why the capacity of LiCoPO<sub>4</sub> electrodes fades in LiPF<sub>6</sub> containing electrolyte solutions?

## NMR spectroscopy analysis of the electrolyte solution in the LiCoPO<sub>4</sub>/Li cells after their cycling

### Standard electrolyte solution

An identical spectrum was obtained for the electrolyte solution rinsed from cycled LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>/Li cells (11 days, 14 cycles)

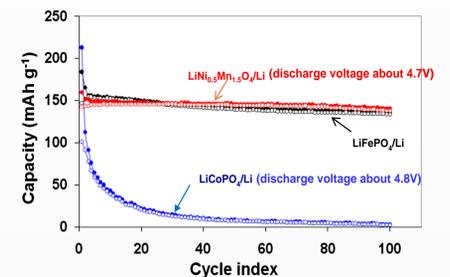


### Electrolyte solution rinsed from cycled LiCoPO<sub>4</sub>/Li cells (11 days, 75 cycles)

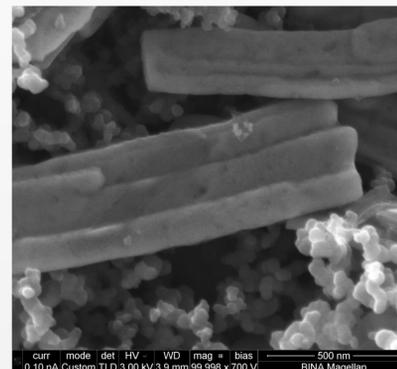
Why LiFePO<sub>4</sub> possesses a much higher stability toward HF attack during cycling than LiCoPO<sub>4</sub>?

LiCoPO<sub>4</sub>/Li cells identical to the cycled cells were left on the shelf for a prolonged period, similar to the whole period of the cycling experiments reported herein.

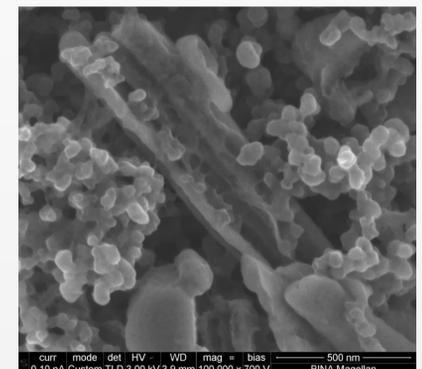
The electrolyte rinsed from these cells did not contain difluorophosphates.



We ascribe this result to the extremely low chemical stability of the delithiated CoPO<sub>4</sub> phase [1, 2]. The reason for such instability may be the fact that, unlike the other olivines, in CoPO<sub>4</sub>, Co<sup>3+</sup> exists in a high-spin configuration [2].



SEM image of the pristine LiCoPO<sub>4</sub> electrode.

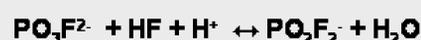


SEM image of LiCoPO<sub>4</sub> electrode cycled in 1M LiPF<sub>6</sub> in EC/DMC 1:1 electrolyte solution

Thus, LiCoPO<sub>4</sub> active material dissolves in 1M LiPF<sub>6</sub> in EC/DMC 1:1 electrolyte solution

Both type of cells (LiCoPO<sub>4</sub>/Li and LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>/Li) with the cathodes of the same capacity were cycled with equal current density between 3.5 and 5.2V. Thus, the time of the cycling was proportional to the charge which passed through the cells.

### Proposed mechanism:



### An important note :

All these fluorophosphate species (namely, POF<sub>3</sub> and Li salts of both fluorophosphate anions, L<sub>2</sub>PO<sub>3</sub>F and LiPO<sub>2</sub>F<sub>2</sub>) may be formed in the electrolyte solution by the hydrolysis of PF<sub>6</sub><sup>-</sup> anions in the presence of traces of water:



The content of these species in the electrolyte solution in this situation is limited by water concentration, which usually does not exceed tens of ppm. However, according to our estimation, about 17% of phosphorus atoms in the electrolyte solution after cycling of LiCoPO<sub>4</sub>/Li cells were in the form of PO<sub>2</sub>F<sub>2</sub><sup>-</sup> anions!

In our case, when phosphate-containing cathode material is in contact with a standard electrolyte solution containing HF contamination, (and hence, active F<sup>-</sup> species), every step of the formation of the P-F bond is accompanied by release of one water molecule that generates a new portion of HF in the reaction with PF<sub>6</sub><sup>-</sup>. In this case, traces of water start a chain process that may lead to the full degradation of the cathode material due to the dissolution of difluorophosphate lithium salts.

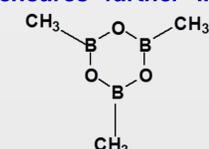
What is the source of oxygen in the structure of PO<sub>2</sub>F<sub>2</sub><sup>-</sup> anions: LiCoPO<sub>4</sub> or organic carbonates?

To discriminate between these two possibilities, we tested the solutions rinsed from LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>/Li cells (discharge voltage about 4.7V) after cycling performed with the electrodes of the same capacity as for LiCoPO<sub>4</sub> electrodes and the same current density.

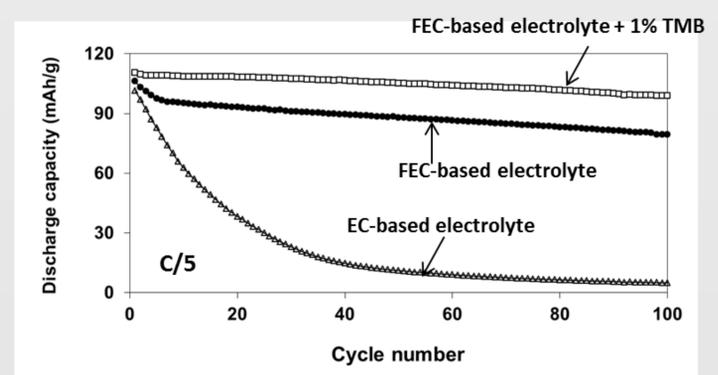
For LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>/Li cells which were cycled for the same time (see NMR spectra) no fluorophosphate species were observed besides the PF<sub>6</sub><sup>-</sup> anions.

Thus, the main source of difluorophosphate species in the electrolyte after cycling LiCoPO<sub>4</sub>/Li cells is decomposition of LiCoPO<sub>4</sub>.

The use of 0.5-1% of TMB additive ensures further improvement of cycling performance of the cells.



Trimethyl boroxine (TMB)



## Conclusions

- The fast capacity fading of LiCoPO<sub>4</sub> cathodes in LiPF<sub>6</sub> containing electrolyte solutions is induced by a nucleophilic attack of F<sup>-</sup> anions due to the presence of HF on the P atoms of the olivine compound in the delithiated (charged) state. This attack leads to the breakdown of the P-O bonds of the phosphate anions with the formation of the soluble in the electrolyte solution salt LiPO<sub>2</sub>F<sub>2</sub>.
- FEC-based electrolyte solution demonstrates dramatically improved discharge capacity retention and faradaic efficiency during charge-discharge cycling of LiCoPO<sub>4</sub>/Li cells compared to the EC-based electrolyte.
- The use of 0.5-1% of TMB additive ensures further improvement of cycling performance of the cells. Capacity retention of LiCoPO<sub>4</sub> electrode in this electrolyte comprises 90% with faradaic efficiency of 98% after 100 cycles.