

Cycling performance of LiCoPO₄ cathodes: reasons for capacity fading and effect of the electrolyte composition.

D. Aurbach, E. Markevich, R. Sharabi, K. Fridman, H. Gottlieb, G. Salitra.

Department of Chemistry, Bar-Ilan University
Ramat Gan 52900 Israel

G. Semrau and M. A. Schmidt

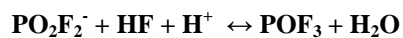
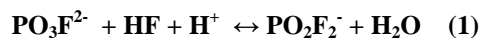
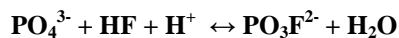
BASF SE

Ludwigshafen 67056, Germany

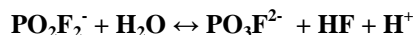
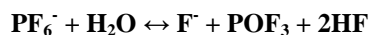
High voltage Li-ion batteries attracted high attention as potential power sources for the electric vehicles due to the highest energy density of all the commercialized rechargeable batteries. LiCoPO₄ with an olivine possesses high operating voltage (red-ox potential of 4.8 V vs. Li/Li⁺), flat voltage profile, and a high theoretical capacity of about 170 mAh/g. However, LiCoPO₄ has shown a fast fading of discharge capacity upon charge-discharge cycling

With the use of ¹⁹F and ³¹P NMR spectroscopy analysis we showed that the main reason for the capacity fading of LiCoPO₄ cathodes in the LiPF₆ containing electrolyte solutions is the nucleophilic attack of F⁻ anion on P atom, resulting in the breaking of the P-O bonds of the phosphate anions (Fig. 1).

The fluorophosphate species (namely, POF₃ and Li salts of both fluorophosphate anions, L₂PO₃F and LiPO₂F₂), which are known to be soluble in the electrolyte solution are formed according to the following proposed mechanism:



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:



Here we present the electrolyte solution which ensures stable cycling of the carbon-coated unsubstituted LiCoPO₄ cathodes. Cycling results of LiCoPO₄/Li cells in two electrolyte solutions (1M LiPF₆ in EC/DMC, "EC-based", and 1M LiPF₆ in fluoroethylene carbonate (FEC)/DMC, "FEC-based") are shown in Fig. 2.

For the cells cycled in the FEC-based electrolyte solution (green and red curves), a much better capacity retention and higher coulomb efficiency, compared to the cells cycled with EC-based solution (blue and pink curves) is observed. The increase of the active cathode mass : electrolyte volume ratio and, as a result, LiCoPO₄: HF molar ratio, improves the cycling performance of the cells. Indeed, both the capacity retention and coulomb efficiency were improved when the volume of the electrolyte solution in the cells cycled with the FEC-based electrolyte solution was decreased from 15 μL/mg (green curve) to 5 μL/mg (red curve) of electrode active mass.

Further improvement of the cycling behavior of LiCoPO₄/Li cells was achieved by the use of trimethyl

boroxine (TMB) additive taken in amount of 0.5-1 weight % (black curve).

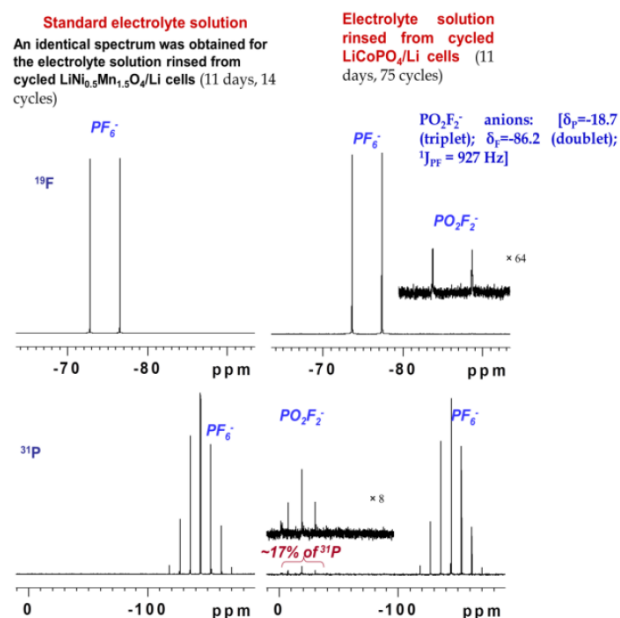


Fig.1 ¹⁹F and ³¹P NMR spectra of a standard electrolyte solution and an electrolyte solution which was rinsed with DMC from LiCoPO₄/Li cells after cycling.

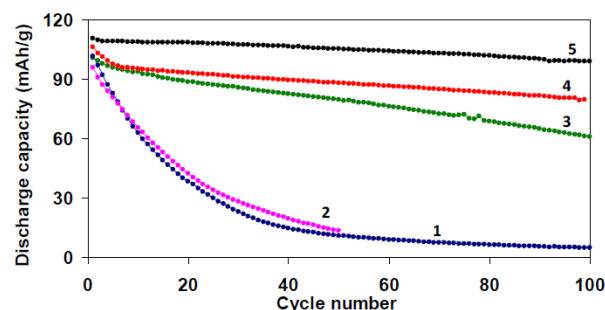


Fig.2 Curves of discharge capacity vs. cycle number obtained upon galvanostatic cycling (C/5 h rates) of LiCoPO₄ electrodes (30 °C).

1) and 2) 1M LiPF₆/EC-DMC 1:1 solution taken in amount of 15 μL/mg and 5 μL/mg of active electrode mass, respectively;

3) and 4) 1M LiPF₆/FEC-DMC 1:4 solutions taken in amount of 15 μL/mg and 5 μL/mg of active electrode mass, respectively;

5) 0.5% of TMB in 1M LiPF₆/FEC-DMC 1:4 solution taken in amount of 5 μL/mg of active electrode mass.

Conclusions

The fast capacity fading of LiCoPO₄ cathodes in LiPF₆ containing electrolyte solutions is induced by a nucleophilic attack of F⁻ anions due to the presence of HF on the P atoms of the olivine compound in the delithiated (charged) state which leads to the formation of the soluble in the electrolyte solution salt LiPO₂F₂. FEC-based electrolyte solution demonstrates dramatically improved cyclic characteristics of LiCoPO₄/Li cells compared to the EC-based electrolyte. The decrease of the electrolyte volume: electrode active mass ratio leads to a significantly improved cycling behavior of LiCoPO₄ electrodes, suggesting that this type of cathode material is extremely sensible to the HF contaminant in LiPF₆-containing electrolyte solutions. The use of 0.5-1% of TMB additive ensures further improvement of cycling performance of the cells.