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Electrochemical Two-Step Delithiation/Re-Lithiation of $LiCoPO_4$ observed by *in situ* XRD, *in situ* XAS, and *ex situ* $^7Li/^{31}P$ NMR spectroscopy

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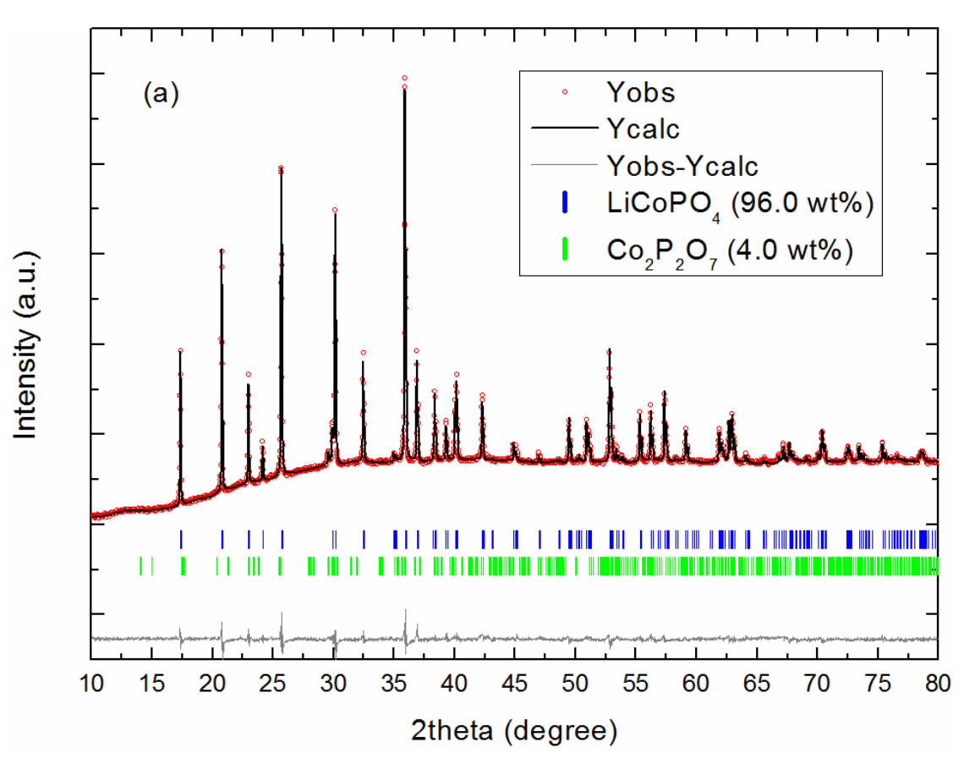
$LiCoPO_4$ was synthesized by a solid-state method. *In situ* XANES experiments were evaluated based on full-cycle experiments confirming the predominantly reversible character of the redox reaction. *In situ* XRD measurements were performed to follow structural changes during cycling indicating the existence of an intermediate phase upon cycling. The local phosphorous and lithium environments were studied by *ex situ* ^{31}P and ^7Li NMR at different states of charge proving the existence of an intermediate phase of the composition $Li_{2/3}CoPO_4$. Based on these findings a model of the (de)lithiation process of $LiCoPO_4$ is developed and discussed.

Synthesis and Characterization by XRD, SEM, and TEM

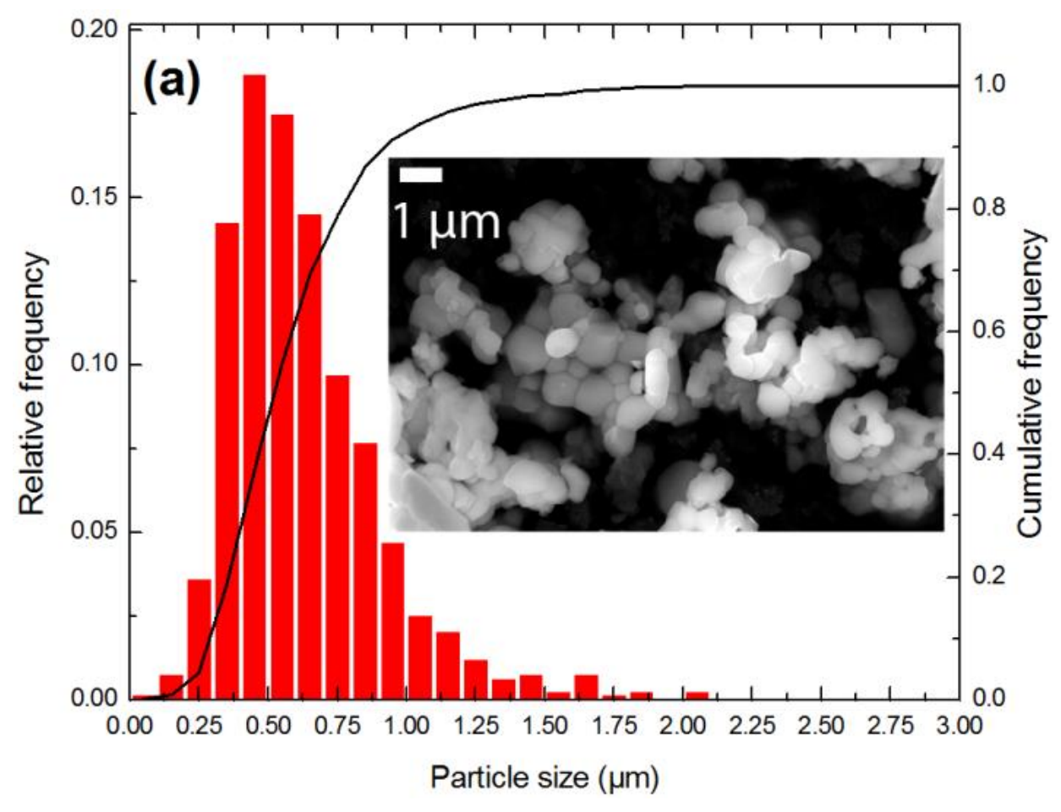
$LiCoPO_4$ was synthesized by a solid-state reaction by mixing stoichiometric amounts of $(NH_4)Co(PO_4) \cdot H_2O$ and Li_2CO_3 which were then ground in a mortar. The powder was calcined in air for 16 hours at 600°C, reground, and again calcined in air for 8 hours at 600°C.

XRD



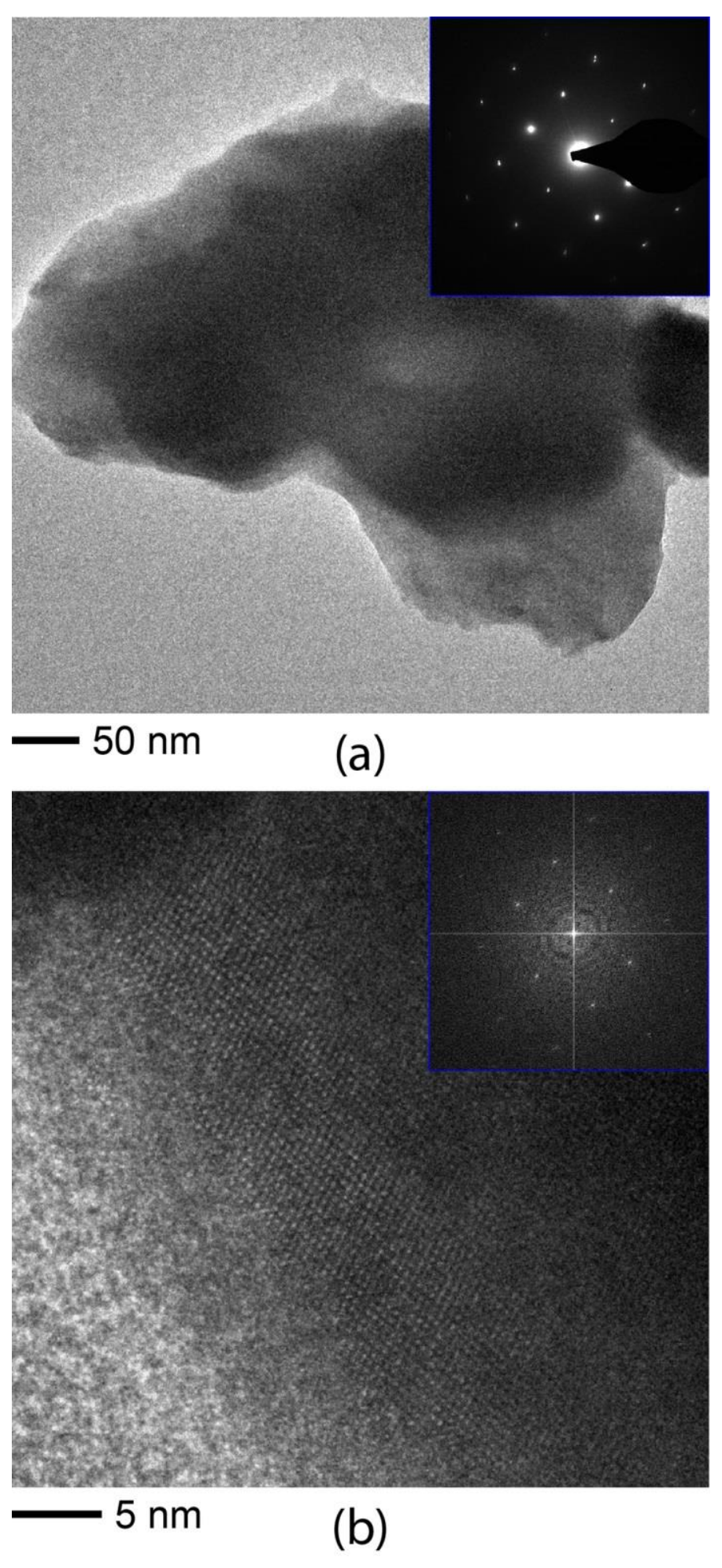
- olivine structure
- narrow size distribution
- minor impurity of $Co_2P_2O_7$ (4 wt%)

SEM



Space group	Pnma
a (Å)	10.20275(5)
b (Å)	5.92186(3)
c (Å)	4.69982(3)
V (Å³)	283.960(3)
R_{Bragg}	7.32
R_F	7.12
χ^2	5.54
d50 (µm)	0.577

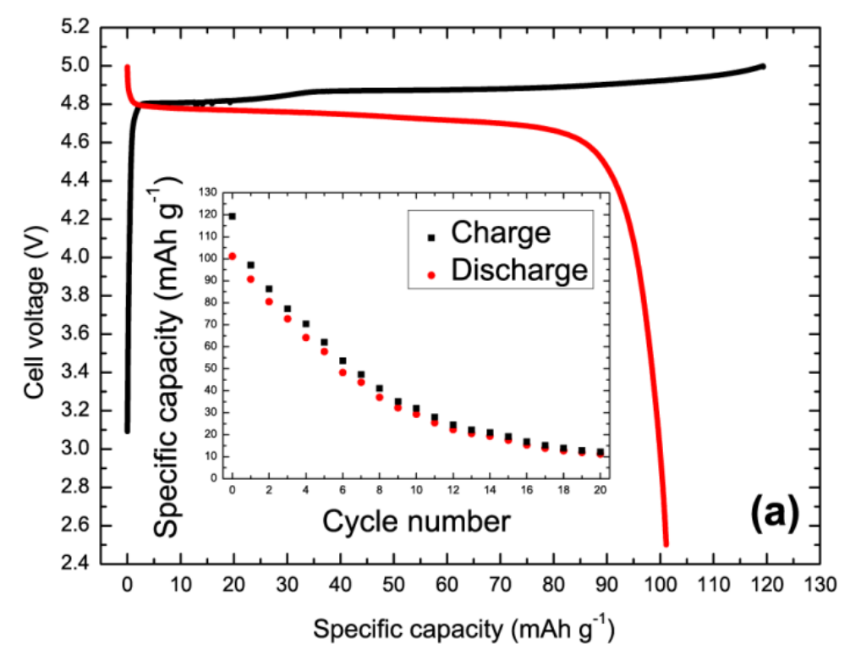
TEM



(a)

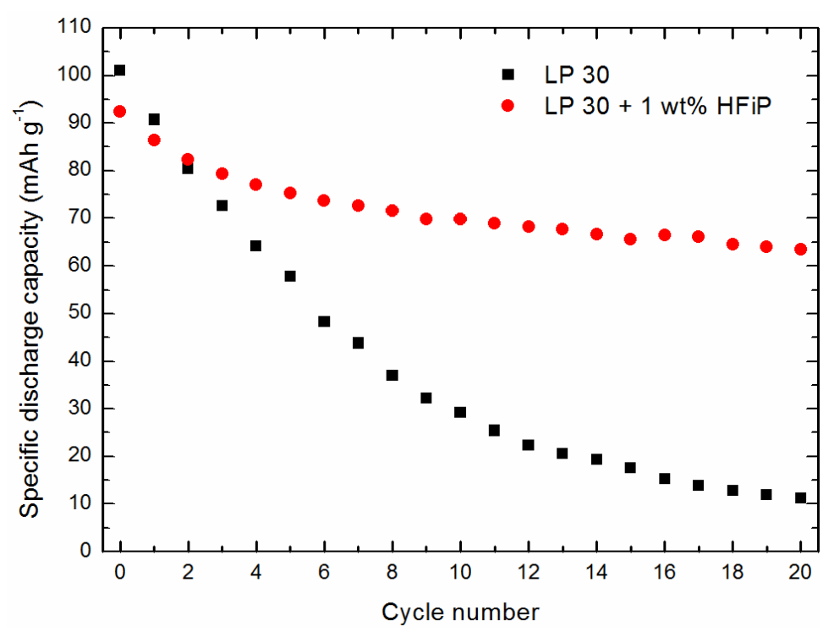
(b)

Electrochemical Characterization



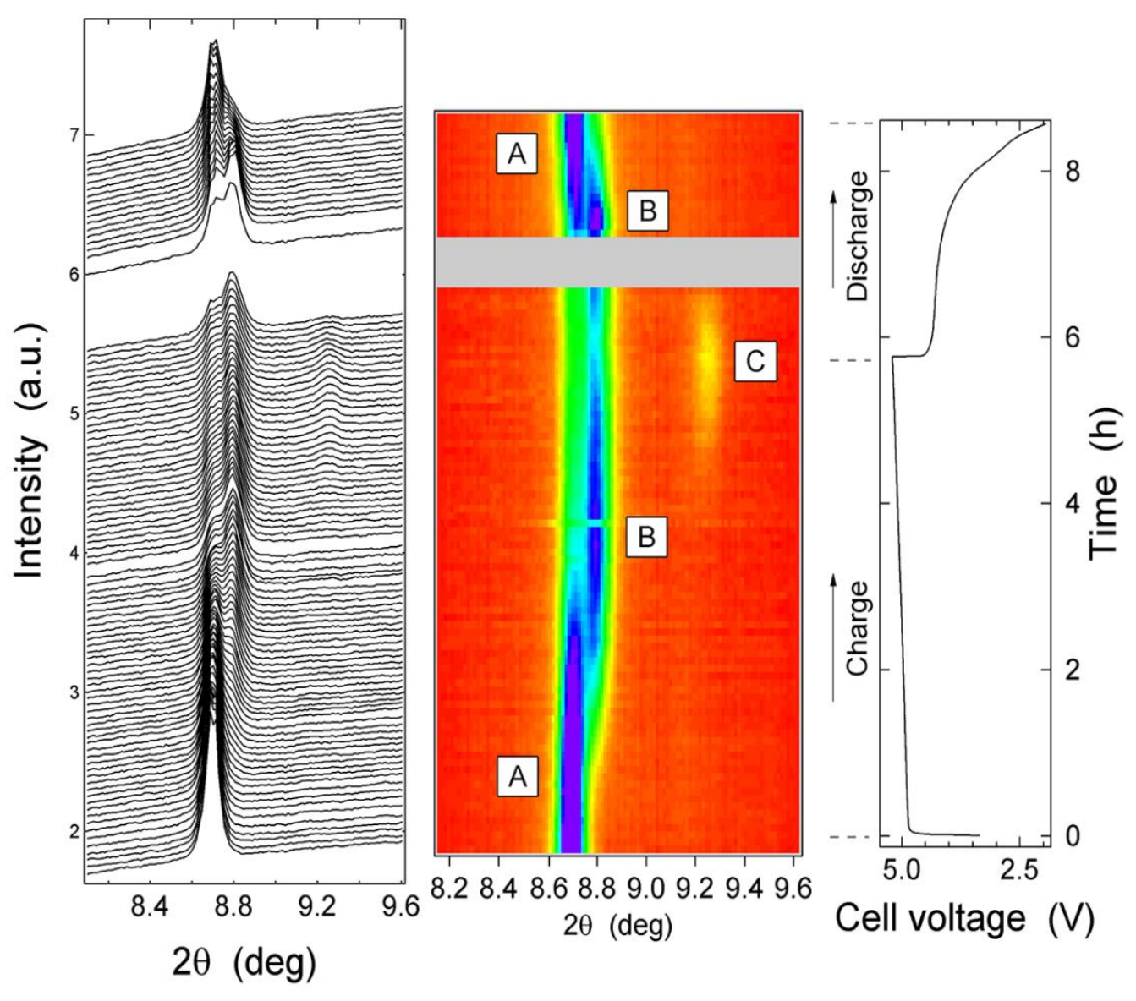
→ two plateaus in charge profile

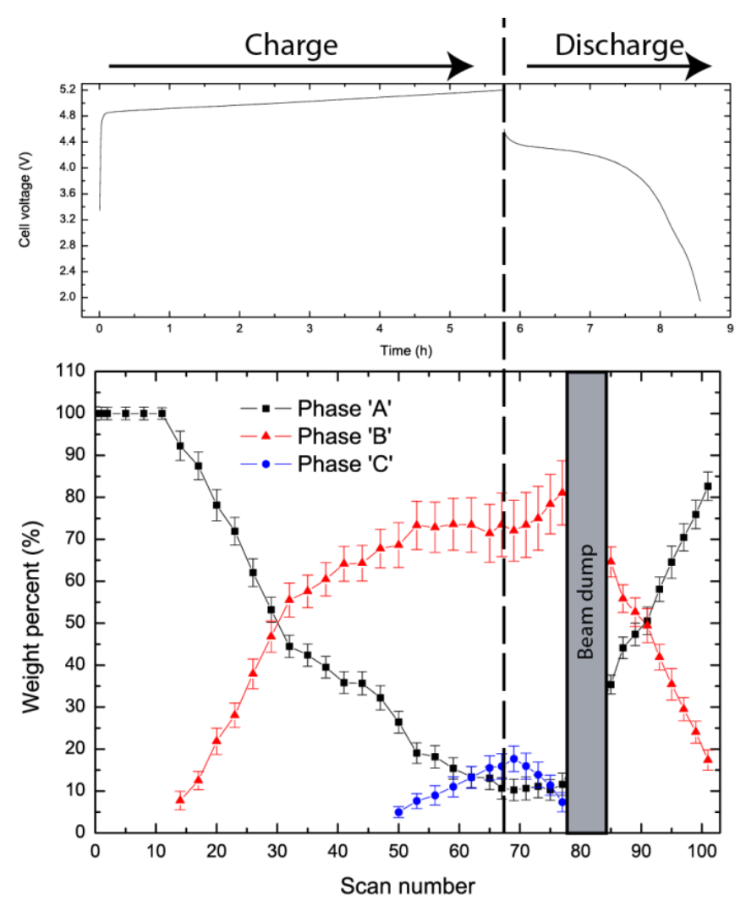
→ strong capacity fading during cycling

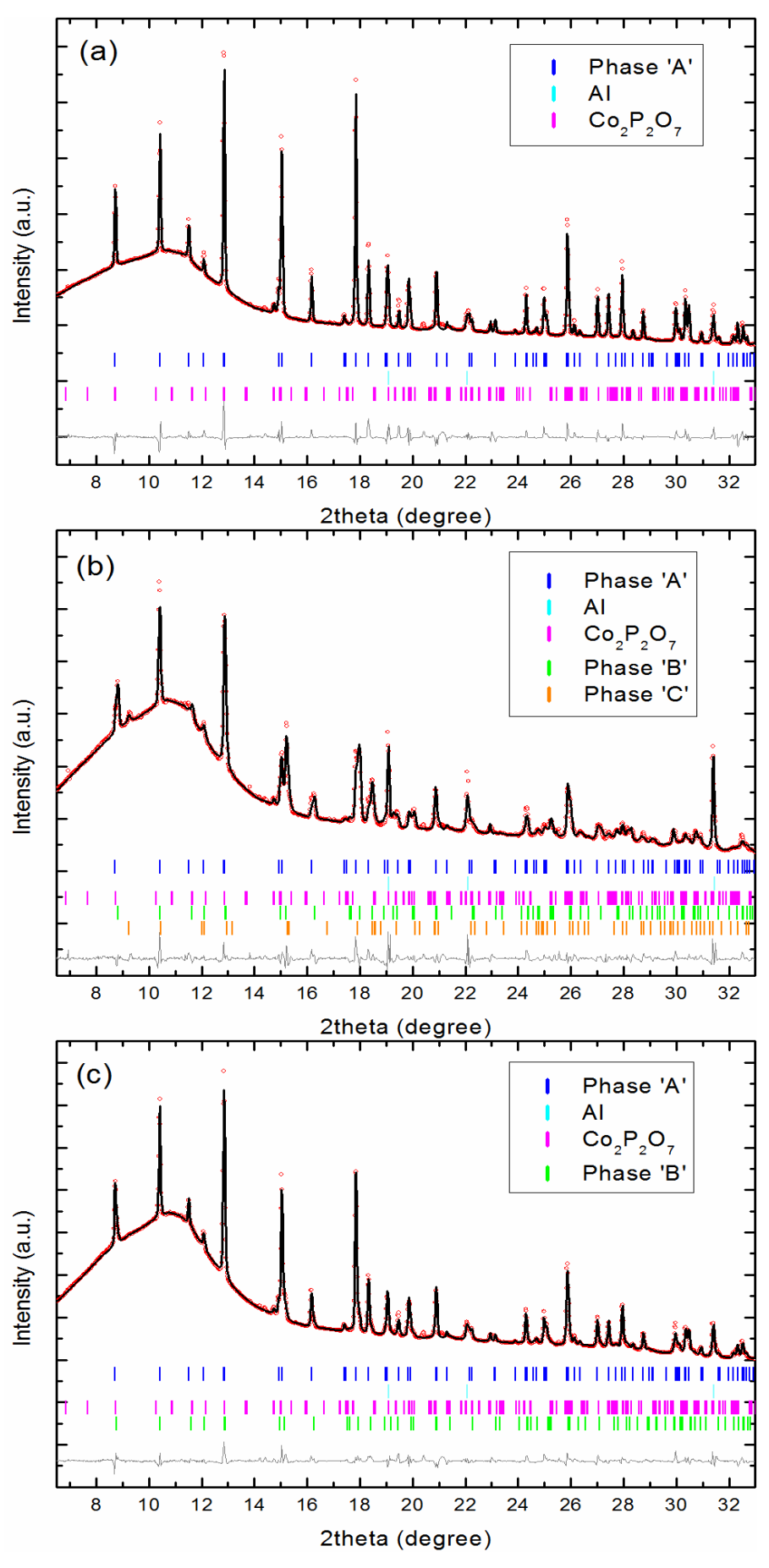


→ improved cyclic stability by addition of HFiP

In Situ XRD



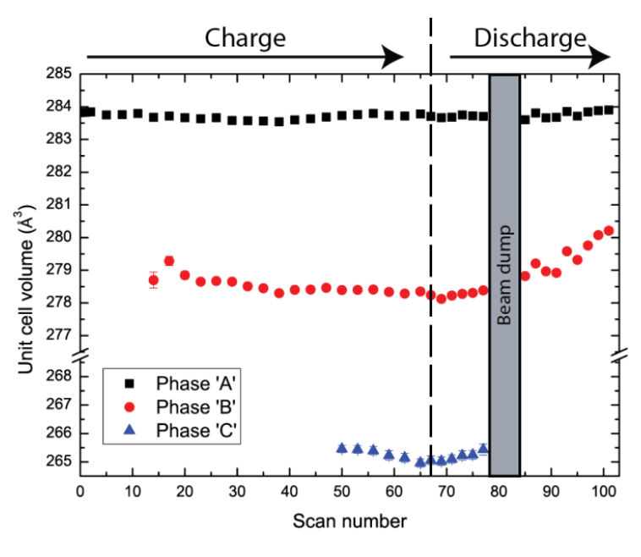


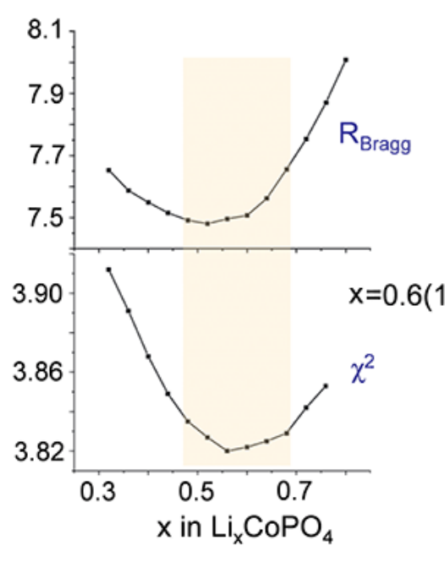


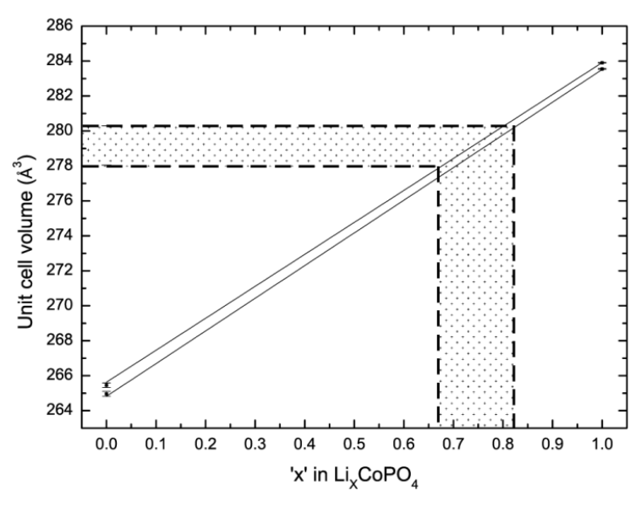
	Space group	a (Å)	b (Å)	c (Å)	V (Å³)
Phase 'A'	Pnma	10.20048(17)	5.92127(10)	4.69949(9)	283.848(9)
Phase 'B'	Pnma	10.08597(71)	5.85849(30)	4.71872(46)	278.823(37)
Phase 'C'	Pnma	9.63743(286)	5.81302(159)	4.73839(124)	265.456(128)

XRD reveals the presence of an intermediate phase during delithiation and relithiation. The composition of this intermediate phase is difficult to estimate from the applied charge due to side reaction of the electrolyte.

Overall, a two-phase reaction with two subsequent two-phase steps is observed. The volume changes of all three phases during cycling are small.

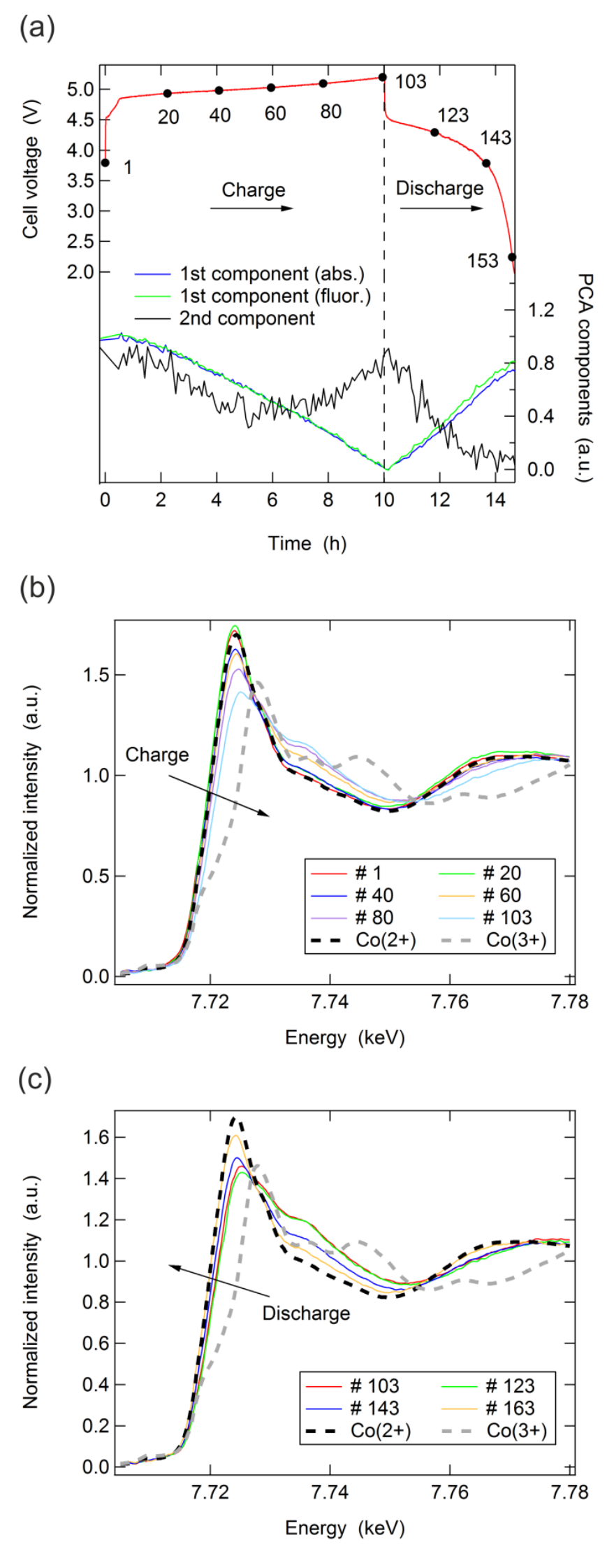






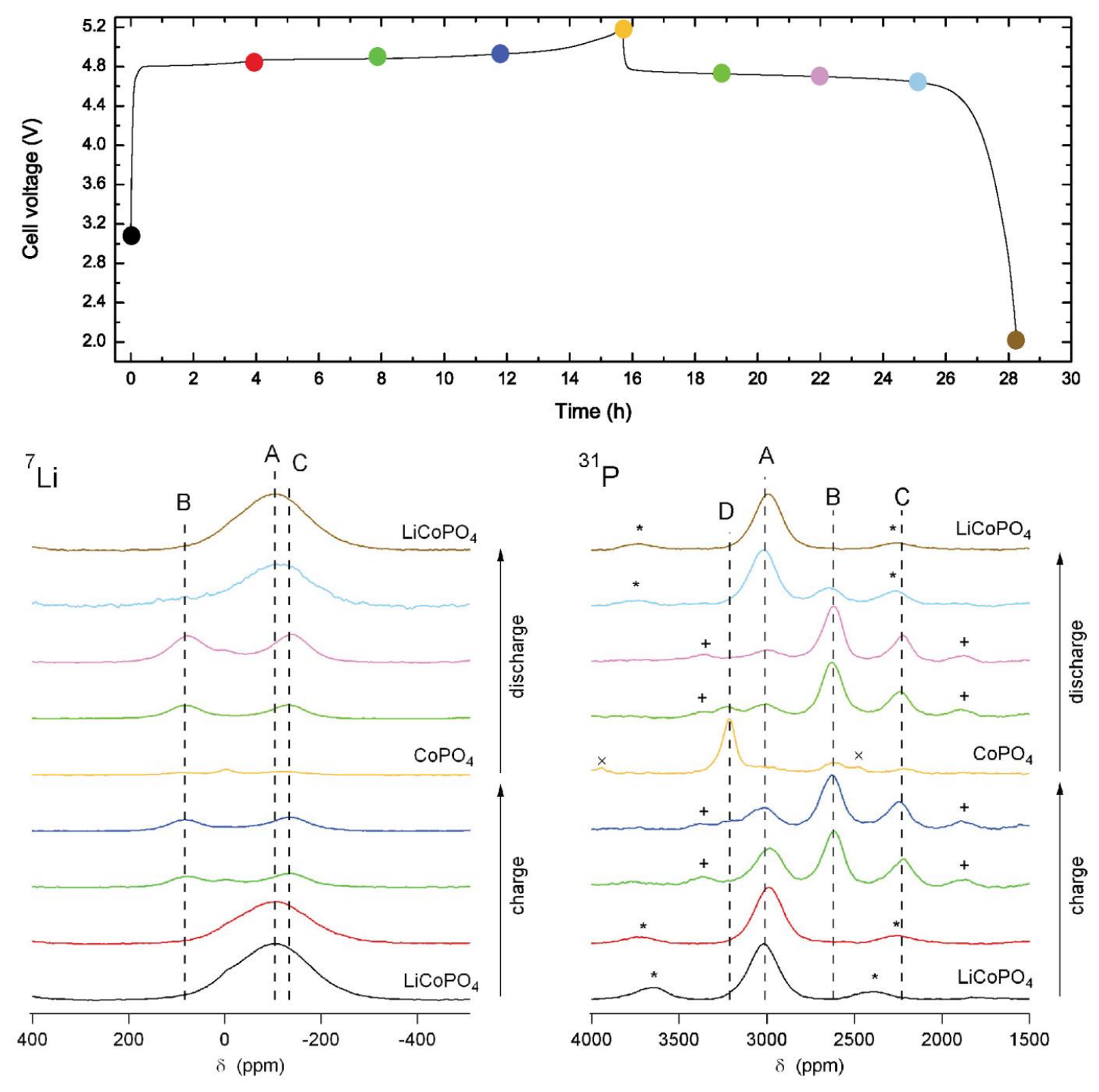
From the lattice constants, a composition of about $Li_{\approx 0.7}CoPO_4$ ist estimated for the intermediate phase.

In Situ XAS



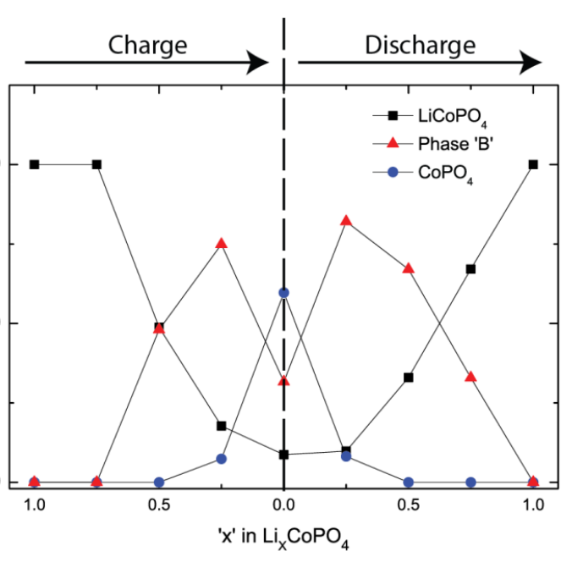
In situ XAS reveals a good reversibility of the Co^{2+}/Co^{3+} oxidation/reduction. Pricincipal component analysis hints at a two-step reaction.

Ex Situ ^7Li and ^{31}P NMR

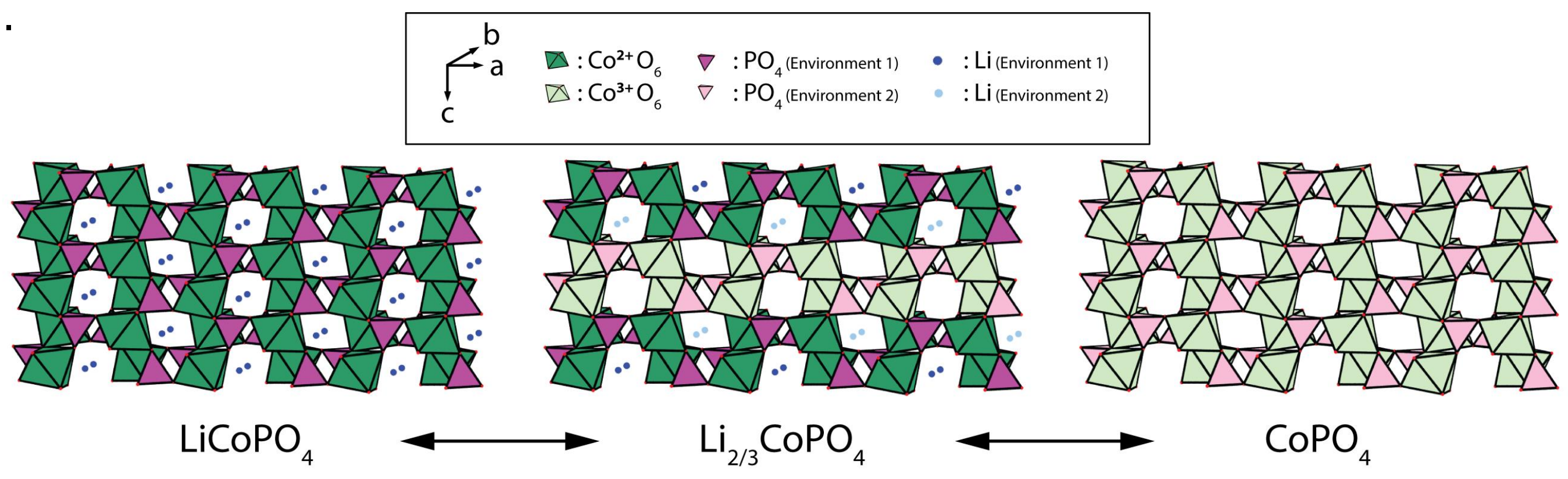


^7Li and ^{31}P Mas NMR reveal an intermediate phase with two Li environments (relative intensity of 1:1) and two P environments (2:1)

The presence of two different Li environments and two different P environments in the intermediate phase can be explained by the different Co^{2+}/Co^{3+} environments.



phase evolution



Summary

In situ XRD, *ex situ* $^7Li/^{31}P$ NMR spectroscopy, and to some extent *in situ* XAS all reveal the existence of two two-phase redox reaction steps upon the (de)lithiation process of $LiCoPO_4$. For the first time the lithiation state of the intermediate phase is determined by *ex situ* ^7Li and ^{31}P NMR spectroscopy to be $Li_{2/3}CoPO_4$ which is in good agreement with our and previous XRD and neutron diffraction measurements. The reversibility of the delithiation/relithiation, as observed by XRD, XAS, and NMR, is high. The poor cycling stability has to be ascribed to side reactions of the electrolyte.

References [1] N. N. Bramnik, K. Nikolowski, C. Baehtz, K. G. Bramnik, H. Ehrenberg, *Chem. Mater.* **19** (2007), 908.