

Lithium chromium phosphate $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3$ as a cathode material for Li-ion batteries

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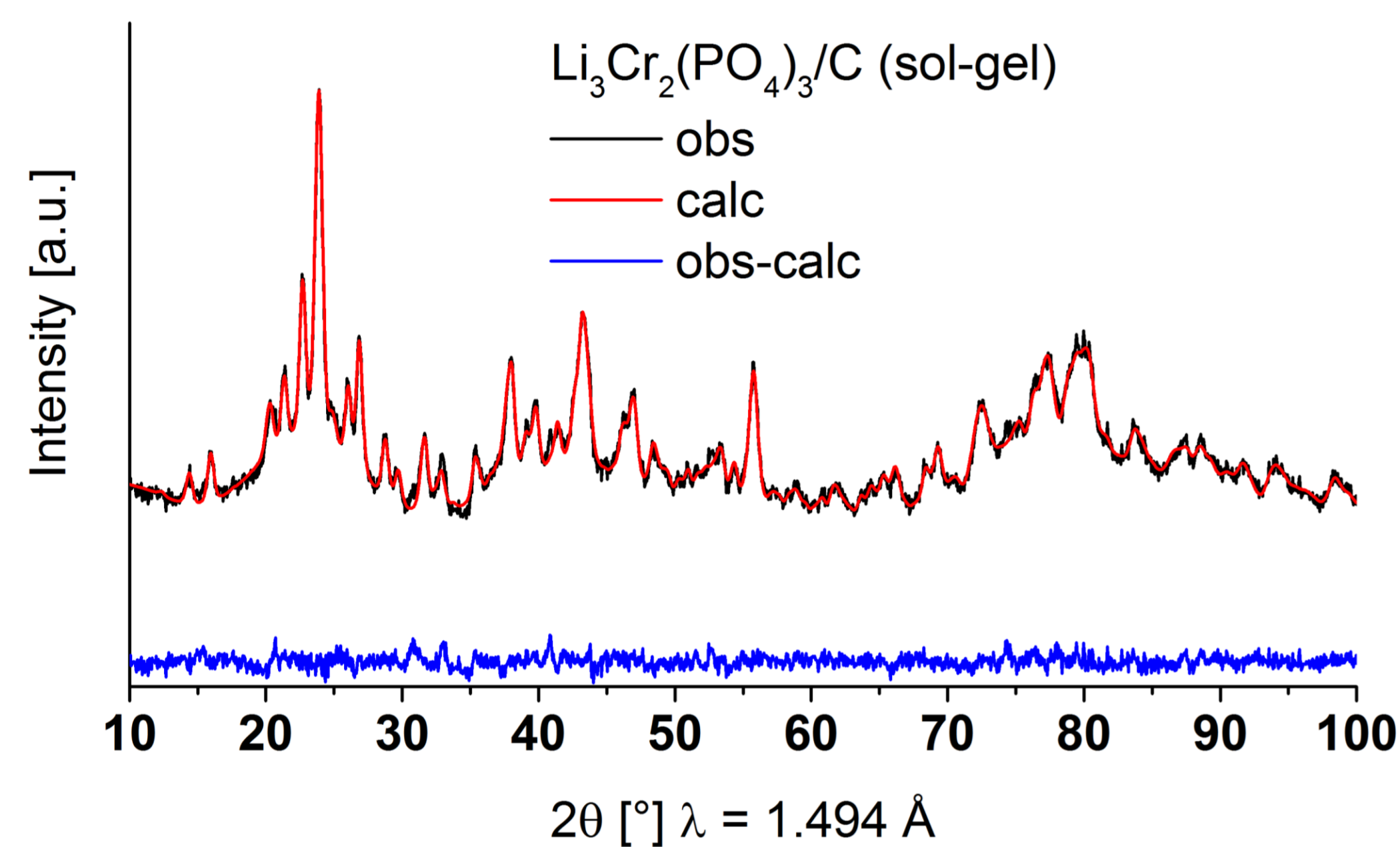
Motivation

- Possibility of multiple redox reactions of phosphate based chromium polyanions^{1,2}
- Theoretical specific charge: 261.6 mAh/g ($\text{Cr}^{4+/3+/2+}$)

Change of chromium oxidation state



Neutron powder diffraction (NPD)



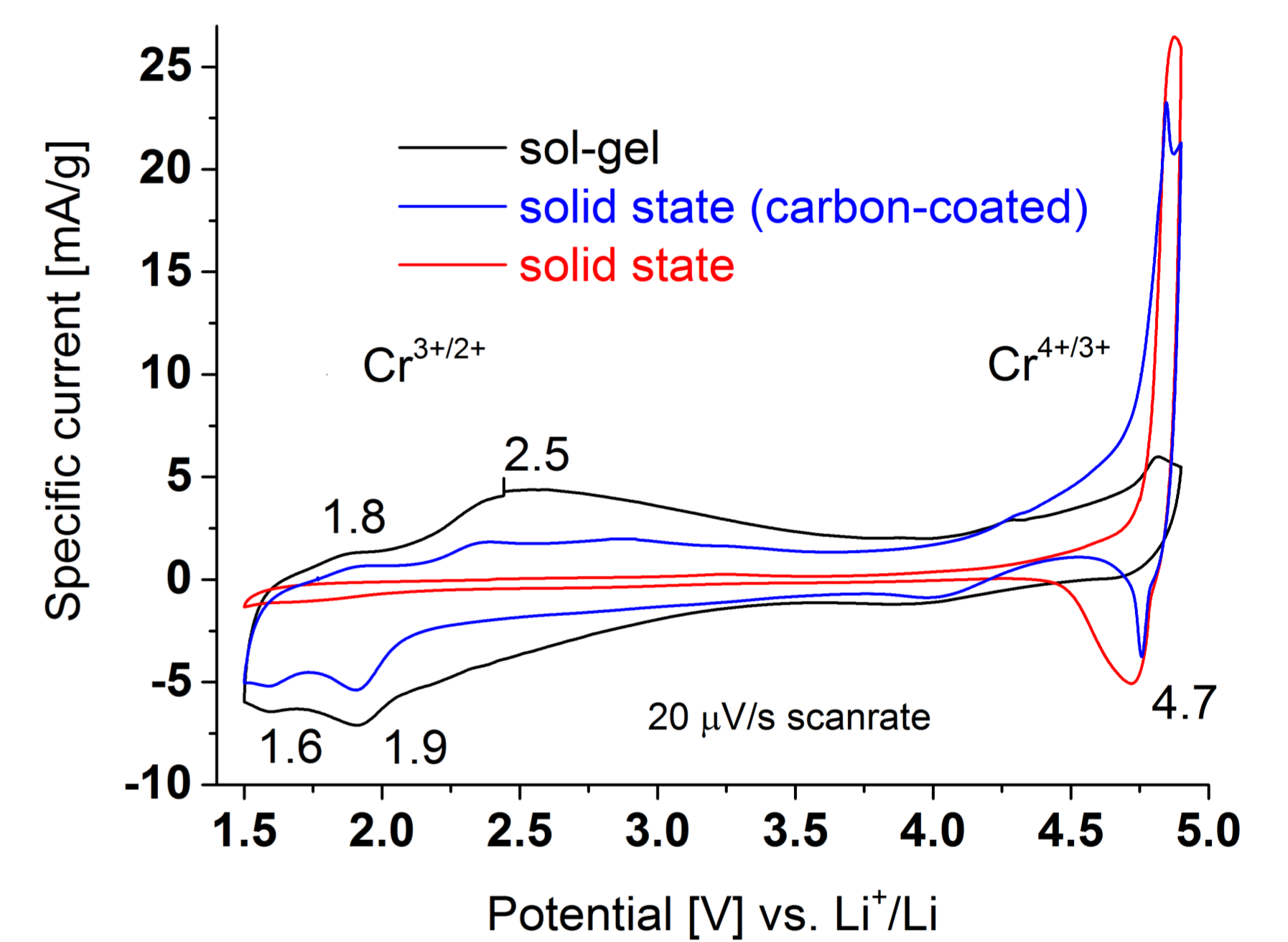
- Successful refinement of $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3/\text{C}$ ($\text{P2}_1/\text{c}$)

Conductivity

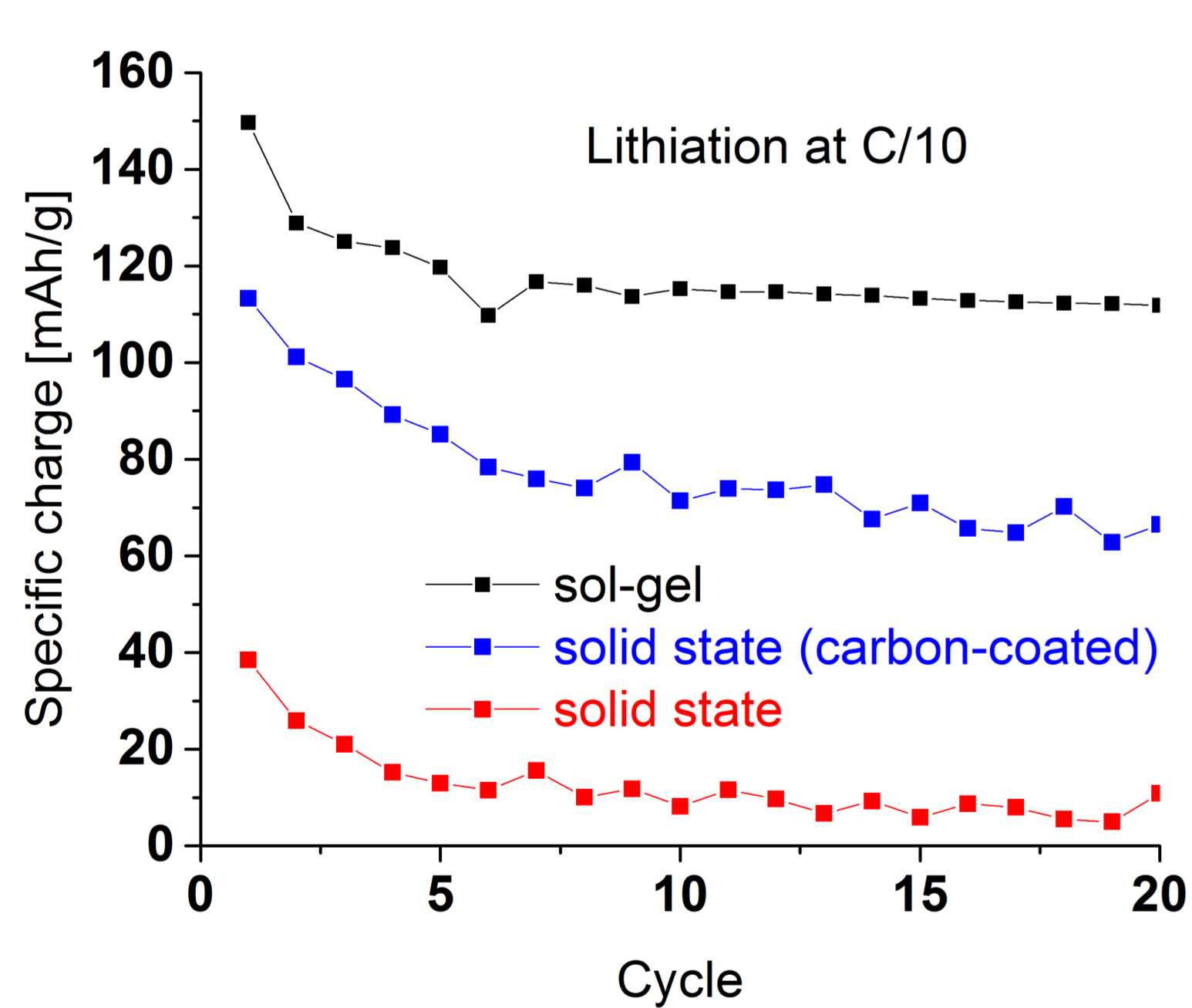
Material	Conductivity [S/cm]	Standard deviation σ
$\text{Li}_3\text{Cr}_2(\text{PO}_4)_3$ (solid state)	$2 \pm 0.5 \cdot 10^{-8}$	$2 \cdot 10^{-9}$
$\text{Li}_3\text{Cr}_2(\text{PO}_4)_3/\text{C}$ (sol-gel)	$4 \pm 4 \cdot 10^{-7}$	$2 \cdot 10^{-7}$

- Carbon coated material is ~10 times more conductive

Cyclic voltammetry

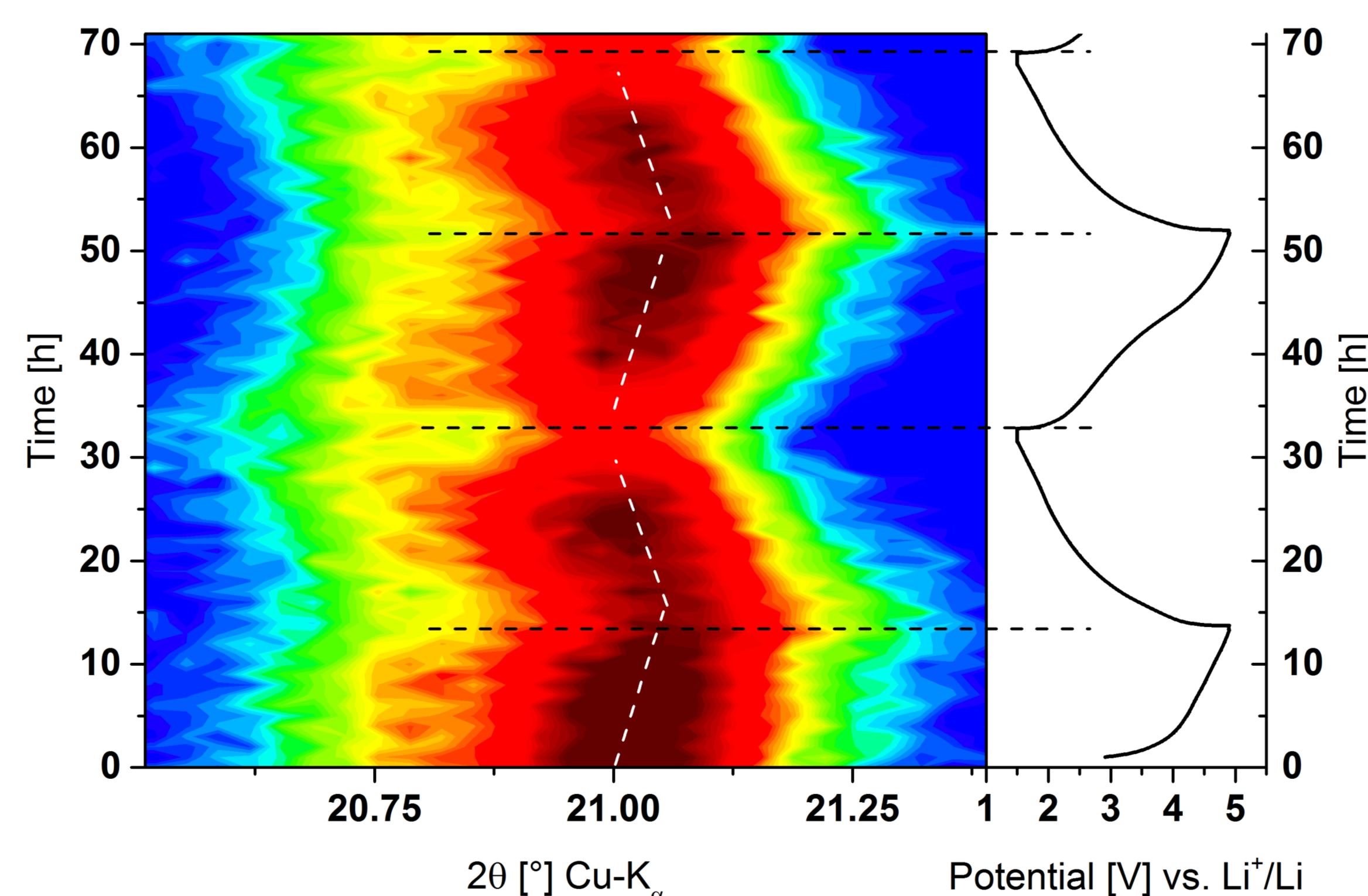


Specific charge evolution



- 120 mAh/g stable specific charge for $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3/\text{C}$ (sol-gel)
- Cycling conditions: C/10, 1.5 – 4.9 V vs. Li^+/Li ; 1M LiPF_6 in EC:DMC 1:1 wt

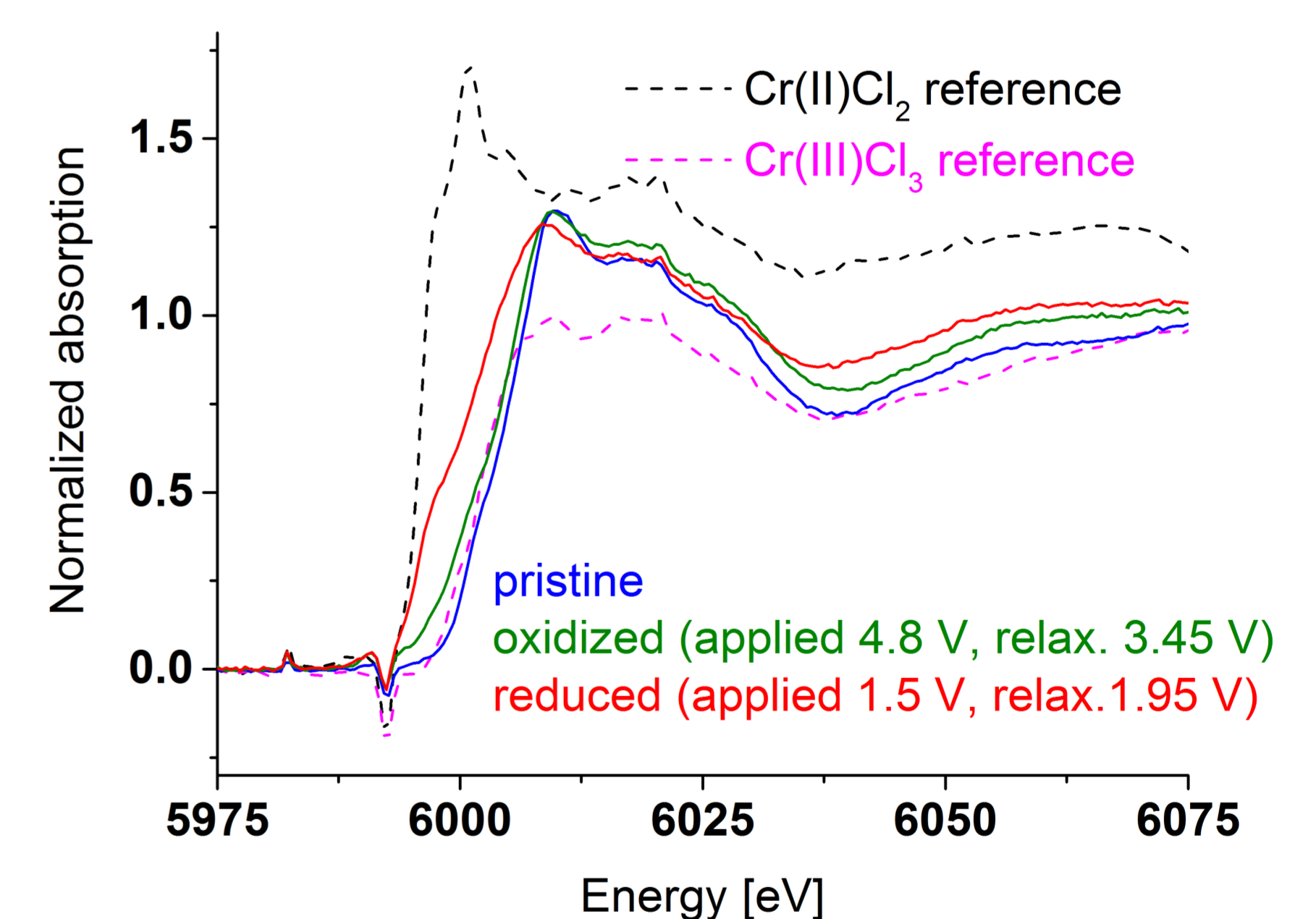
X-Ray diffraction



Operando XRD:

- Continuous shift of the peak ($2\theta = \sim 21^\circ$) upon cycling \rightarrow insertion reaction mechanism
- Conditions: C/20, 1.5 – 4.9 V vs. Li^+/Li ; 1M LiPF_6 in EC:DMC 1:1 wt, $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3/\text{C}$ (sol-gel).

Ex situ XANES



- Cycled material: $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3/\text{C}$ (sol-gel)
- Change in oxidation state of chromium for reduced electrode
- Oxidized and pristine electrode have similar white line (relaxation effect)

Conclusion / Outlook

Conclusion:

- Reversible electrochemical activity between 1.6 V and 2.5 V vs. Li^+/Li attributed to $\text{Cr}^{3+}/\text{Cr}^{2+}$ redox couple
- Specific charge stable at approximately 120 mAh/g
- $\text{Cr}^{4+/3+}$ redox couple expected at 4.7 V vs. Li^+/Li

Outlook:

- Operando XAS of $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3/\text{C}$ to investigate the Cr oxidation state(s) in the bulk
- Operando NPD to study insertion mechanism

