Supporting information for:

Operando Tracking of Solution-Phase Concentration Profiles in Liion Battery Positive Electrodes using X-Ray Fluorescence

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ABSTRACT: The trade-off between energy density and power capabilities is a challenge for Li-ion battery design as it highly depends on the complex porous structures that holds the liquid electrolyte. Specifically, mass-transport limitations lead to large concentration gradients in the solution-phase and subsequently to crippling overpotentials. The direct study of these solution-phase concentration profiles in Li-ion battery positive electrodes has been elusive, in part because they are shielded by an opaque and paramagnetic matrix. Herein we present a new methodology employing synchrotron hard X-ray fluorescence to observe the concentration gradient formation within Li-ion battery electrodes in *operando*. This methodology is substantiated with data collected on a model LiFePO₄/Li cell using a 1M LiAsF₆ in 1:1 EC:DMC electrolyte under galvanostatic and intermittent charge profiles. As such, the technique holds great promise for optimization of new composite electrodes and for numerical model validation.

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Experimental Procedures

Electrode fabrication

The electrodes were made free-standing (without a current collector support). The composition of each film consisted of 80% wt LiFePO₄ (Phostech Lithium Inc., P2 grade), 10% wt Carbon black (Alfa Aesar), and 10% wt Polytetrafluoroethylene (60% dispersion in H_2O) (Millipore Sigma, ON, Canada). The components were mixed using a pestle and mortar. Once firm, the solid mixture was rolled with a metallic rod until a uniform film without cracks was obtained. Disks were punched from the film using a custommade hammer-driven punch with a 1/2" inner diameter (Canadian Light Source, Canada) before being completely dried *in vacuo* at 100°C for at least 5 hours. The thickness of the electrode was measured using a thickness gauge and the results presented in this work were obtain with a 325 μ m thick electrode with a porosity of 50%.

Electrode transport properties

The scanning electrochemical cell measurements (SECM) were performed using 2mM anthracene as the irreversible analyte in 1:1 EC:DMC with 1M LiPF₆ supporting electrolyte. Each film was measured 3 or more times at a distance of 1-2 μ m with a Pt microelectrode. The mean of the measured bulk (I_{ss}^b) and steady-state currents (I_{ss}^*) was used to calculate the effective diffusion coefficient ($D_{Li^+}^*$).

	Porosity (%)	Thickness (µm)	$I_{ss}^{b}(nA)$	$I_{ss}^{*}(nA)$	$D^*_{Li^+}$ (cm/s ²)
Film 1	52	165	15.5	8.56	9.4x10 ⁻⁷
Film 2	50	167	14.7	7.67	8.9x10 ⁻⁷
Film 3	47	165	15.3	8.3	9.2x10 ⁻⁷
Mean	50	166	15.2	8.18	9.2x10 ⁻⁷

Table S1: Film properties and transport parameters through free-standing LiFePO₄ electrodes.

 I^{b}_{ss} is the measured bulk steady-state current before measurement, I^{*}_{ss} is the steady-state current through the film and $D^{*}_{Li^{+}}$ is the calculate diffusion coefficient through the film. The transport properties were calculated by relating the steady-state current ratio of the bulk and of the film to the ratio of the diffusion coefficients:

$$I_{ss}^{b}/I_{ss}^{*} = D_{ss}^{b}/D_{ss}^{*}$$
 (1)

The bulk diffusion coefficient was taken to be 1.7×10^{-6} cm/s² for a similar solvent system of 4:6 EC/DEC.¹

XRF Cell Design



Figure S1: Disassembled cell: 1) Swagelok 1/2" nut 2) stainless steel current collector 3) back ferrule 4) front ferrule 5) stainless steel spring 6) stainless steel spacer 7) active components 8) threaded cell joint 9) analysis area with 250-300 µm thick wall

XRF linescans at OCV



Figure S2: Normalized K_{α} counts as a function of depth for Fe (blue), As (orange) and Cr (red) while at open circuit voltage at 4 different times. Bottom inset shows measured potential as a function of time. Vertical dashed lines in inset indicate the time for the corresponding colored line in the linescan plot.

(Dis)charge curves



Figure S3: Potential vs. capacity for the cell imaged in Fig. 2 and Fig. 3. The cell was (dis)charged galvanostatically at a rate of 0.4C (purple) and 1C (yellow).

Charge concentration profile

Charge concentration profile at 0.4C for the same cell used in Fig. 2 and Fig. 3 of this work.



Figure S4: Li⁺ concentration profile in the cell during charge at a current of 0.4C. The cartoon at the top displays the various cell components as a function of depth. The bottom inset shows the potential response as a function of time where the vertical dashed lines indicate the time for the corresponding colored line in the gradient plot.

Intermittent (dis)charge

An intermittent (dis)charge profile is applied to the electrode seen in Fig. 2 and Fig. 3.



Figure S5: Data collected during an intermittent (dis)charge at various currents. a) heatmap of As K α as a function of depth within the electrode and time with bottom insets showing the measured potential and applied current as a function of time. The cartoon on the right displays the various cell components as a function of depth. b) As/Li⁺ concentration as a function of the depth within the electrode and time. c) Li⁺ concentration as a function of depth within the positive electrode with bottom inset showing the measured potential versus time. Vertical dashed lines in inset indicate the time for the corresponding colored line in the gradient plot.

Li⁺ concentration heatmap



Figure S6: Data collected during a (dis)charge at 0.4C and 1C. Heatmap of $[Li^+]$ as a function of depth within the electrode and time with bottom insets showing the measured potential and applied current as a function of time. The cartoon on the right displays the various cell components as a function of depth.

Li⁺ concentration vs. time at set depths



Figure S7: Data collected during a (dis)charge at 0.4C and 1C. [Li⁺] as a function of time for 3 separate depths: near current collector (pink), middle of electrode (blue) and near separator (red). The cartoon on the right displays the various cell components with the approximate depth of each curve indicated by a band of the same color.

(Dis)charge at rate of C

Showing the a) maximum and b) minimum Li^+ concentration observed in the cell observed in Fig. 2 and Fig. 3.



Figure S8: Li^+ concentration profile in the cell during a) discharge at a current of 1C and b) charge at a current of 1C. The cartoon at the top displays the various cell components as a function of depth. The bottom inset shows the potential response as a function of time where the vertical dashed lines indicate the time for the corresponding colored line in the gradient plot.

References

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