Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Phase transition kinetics of $LiNi_{0.5}Mn_{1.5}O_4$ analyzed by temperature-controlled operando X-ray absorption spectroscopy

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**Equations used for obtaining rate constants**

Charging process:

$$[Li1] \xrightarrow{k_1} [Li0.5] \xrightarrow{k_2} [Li0]$$

$$-\frac{d}{dt}[Li1] = k_1[Li1]$$

$$\frac{d}{dt}[Li0.5] = k_1[Li1] - k_2[Li0.5]$$

$$\frac{d}{dt}[Li0] = k_2[Li0.5]$$

These equations can be solved and the concentration of [Li1], [Li0.5] and [Li0] at time t can be obtained as follows, where $[Li1]_0$ is the initial concentration of Li1.

$$[Li1] = [Li1]_0 e^{-k_1 t}$$

$$[Li0.5] = [Li1]_0 \left(\frac{k_1}{k_2 - k_1}\right)\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$[Li0] = [Li1]_0 \left\{1 - \frac{1}{k_2 - k_1}\left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right)\right\}$$

Discharging process:

$$[Li0] \xrightarrow{k_3} [Li0.5] \xrightarrow{k_4} [Li1]$$

$$-\frac{d}{dt}[Li0] = k_3[Li0]$$

$$\frac{d}{dt}[Li0.5] = k_3[Li0] - k_4[Li0.5]$$

$$\frac{d}{dt}[Li0] = k_4[Li0.5]$$

They can be solved similarly and the concentration of [Li0], [Li0.5] and [Li1] can be obtained as follows with the initial concentration of Li0 $[Li0]_0$.

$$[Li0] = [Li0]_0 e^{-k_3 t}$$

$$[Li0.5] = [Li0]_0 \left(\frac{k_3}{k_4 - k_3}\right)\left(e^{-k_3 t} - e^{-k_4 t}\right)$$

$$[Li1] = [Li0]_0 \left\{1 - \frac{1}{k_4 - k_3}\left(k_4 e^{-k_3 t} - k_3 e^{-k_4 t}\right)\right\}$$

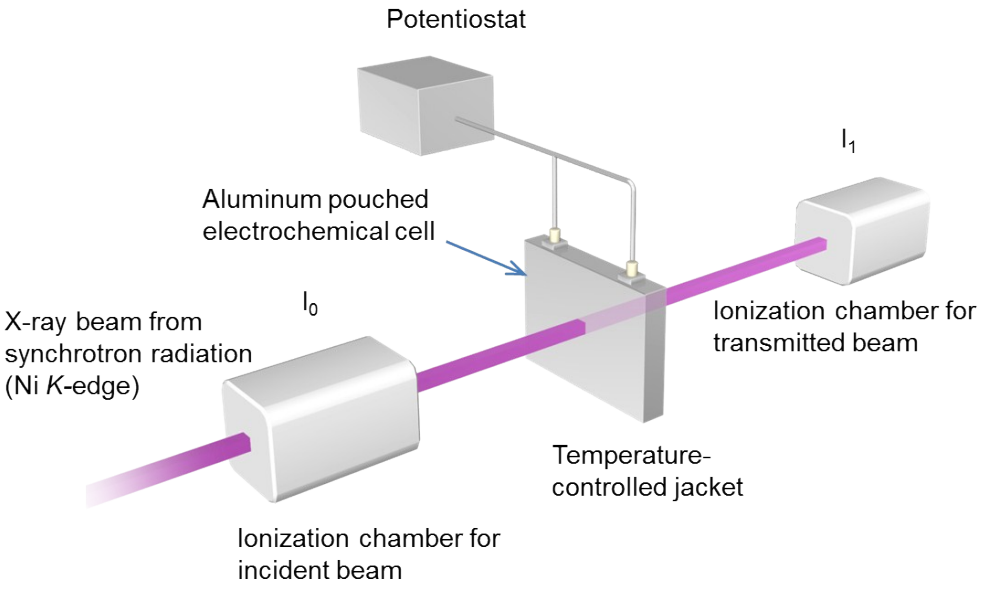



Figure S1 Temperature-controlled *operando* XAS measurement system.

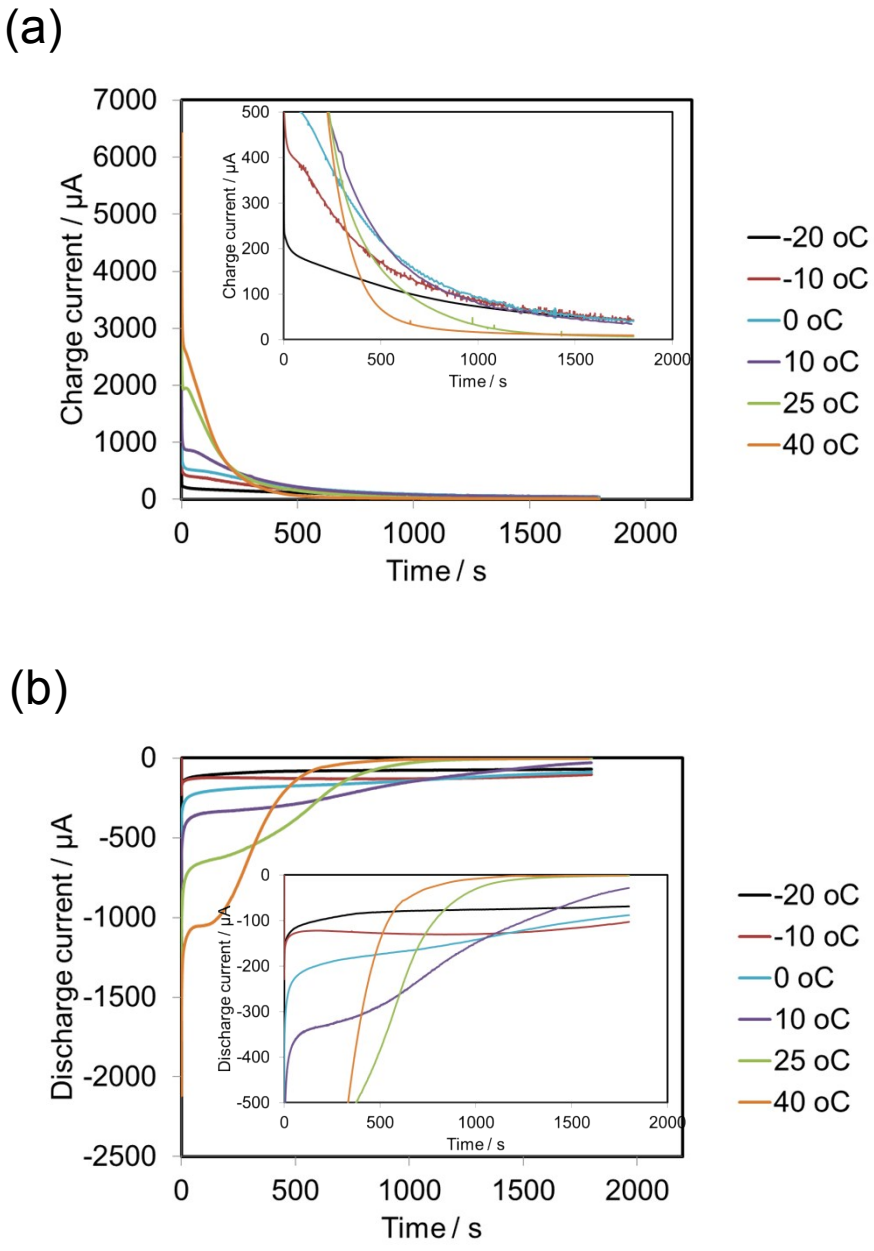
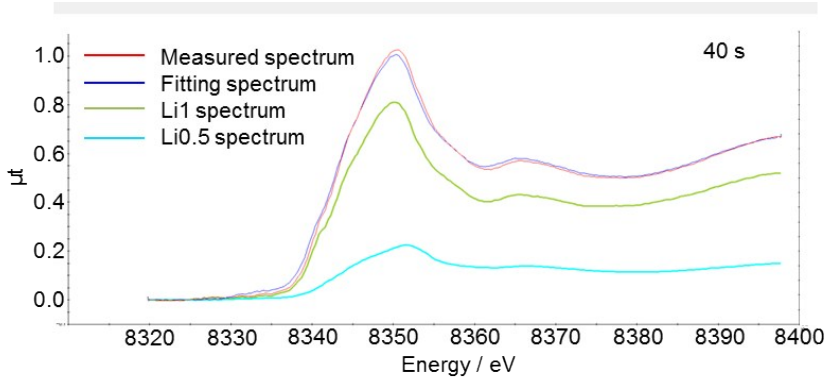
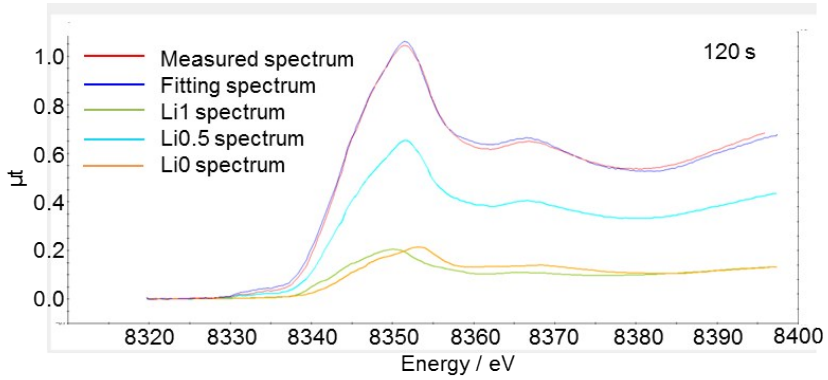



Figure S2 Current-time curves in potential step (a) charging and (b) discharging experiments.



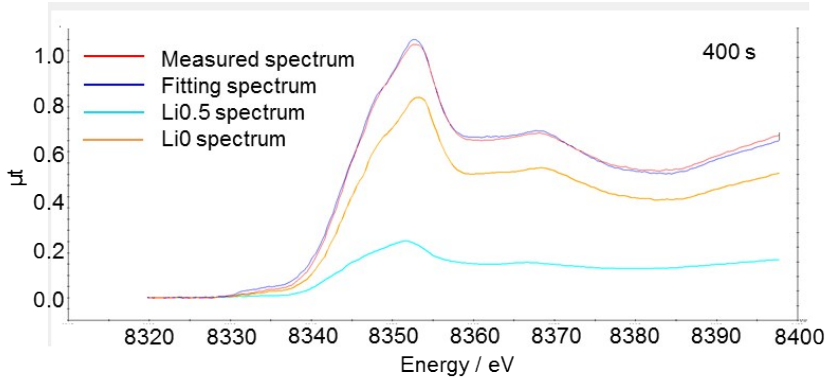




Figure S3 Examples of XANES spectra obtained at 40 s, 120 s and 400 s after potential step charging at 40 °C.