

Supplementary Information

**Development of an *in situ* high-temperature
X-ray diffraction technique for lithium-ion battery
materials**

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Experimental

Electrochemical measurements

A slurry consisting of 90 wt% graphite powder and 10 wt% PVdF in an *N*-methyl-2-pyrrolidone (NMP, Nacalai Tesque) solution was cast onto Cu foil with a thickness of 10 μm . The electrode was dried in vacuum at 120 °C for 12 h, and then, cut into a disk with a diameter of 16 mm. Each electrode contained approximately 12 mg of graphite. A lithium metal sheet (Honjo Metal), which was pressed onto a stainless steel (SUS) plate with a diameter of 19 mm, was used as the counter electrode. After fabricating lithium cells in an Ar-filled glovebox, the cells were conditioned by cycling them three times at 0.02–3.0 V. The applied current was 0.3 mA, which corresponds to $\simeq 0.15 \text{ mA}\cdot\text{cm}^{-2}$ based on the electrode surface area.

DSC measurements

Each lithium cell was discharged to a desired Li composition after conditioning. The C_6Li_x samples were removed from the lithium cells in the Ar-filled glovebox, and then, inserted into an SUS pan that was 6 mm in diameter and 5 mm in height. We used two types of notation, i.e., C_6Li_x and C_6Li (C_{12}Li , C_{18}Li , etc.). The former represents the x composition for the DSC and XRD samples, while the latter represents the structure of the stage of graphite. For instance, $x = 0.5$ means that the sample does not consist of 100 % of the C_{12}Li phase. DSC measurements were performed at $\beta = 5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ up to 450 °C (Thermo plus EVO2, DSC8230L, Rigaku). The amount of the $\text{LiPF}_6/(\text{EC}+\text{DEC})$ electrolyte was fixed at 0.52 μL per 1 mg of graphite powder, which was selected based on the amount in typical commercial LIBs.² The temperature and heat generation (ΔH) in the DSC system were calibrated using the fusion temperature (T_f) and specific enthalpy (ΔH_f) of three different metals: $T_f = 156.6 \text{ }^\circ\text{C}$ and $\Delta H_f = 28.5 \text{ J}\cdot\text{g}^{-1}$ for In, $T_f = 232.0 \text{ }^\circ\text{C}$ and $\Delta H_f = 59.6 \text{ J}\cdot\text{g}^{-1}$ for Sn, and $T_f = 372.5 \text{ }^\circ\text{C}$ and $\Delta H_f = 23.2 \text{ J}\cdot\text{g}^{-1}$ for Pb. In this study, a positive or negative ΔH value

implies that the reaction proceeds exothermically or endothermically, respectively. The SUS was weighed before and after the measurements to ensure that no leakage occurred. This procedure is the same as that for our previous DSC analyses.¹⁻³

Only for the $x = 0.89$ sample, the DSC measurements were performed at $\beta = 2, 4, 6,$ and $8 \text{ } ^\circ\text{C}\cdot\text{min}^{-1}$ to determine the activation energy (E_a) of each exothermic reaction peak at $\sim 140 (= T_1), 270 (= T_2),$ and $300 (= T_3) \text{ } ^\circ\text{C}$ using the Kissinger method.⁴ The curves of the discharge process for preparing the DSC sample, including conditioning discharge and charge curves, are shown in Fig. S4f. The obtained DSC profiles and a plot of $10^3 T_p^{-1}$ vs. $\ln(\beta T_p^{-2})$ are shown in Figs. 6a and 6b, respectively.

In situ HT-XRD measurements

The C_6Li_x sample with $x = 0.77$ was prepared by the same electrochemical reaction as that for the DSC measurements; however, we employed a Cu foil with a thickness of $5 \text{ } \mu\text{m}$ to minimize signals from the Cu foil. The electrode contained 10.26 mg of graphite. The lithium cell was discharged to 0.02 V at a current of 0.3 mA at $25 \text{ } ^\circ\text{C}$, followed by conditioning for three cycles at 0.02–3.0 V. The electrode was removed from the lithium cell before the *in situ* XRD measurements, and then, packed into double Kapton bag B in the Ar-filled glovebox.

Synchrotron X-rays were monochromatized by a Si(111) channel-cut crystal, while diffracted X-rays were detected by a 2D detector (PILATUS 300K, Dectris). The energy of X-rays for XRD was fixed at 8.5 keV, which corresponds to a wavelength of $1.4588(2) \text{ } \text{Å}$. The temperature and air flow ($12 \text{ L}\cdot\text{min}^{-1}$) were controlled by two independent digital flow controllers (DFC-10, Inflinge Industrial). The duration of one XRD measurement was 1 min, but we merged five independent XRD patterns into a single pattern. Fig. S1 shows a photograph of the experimental setup for the *in situ* HT-XRD measurements.

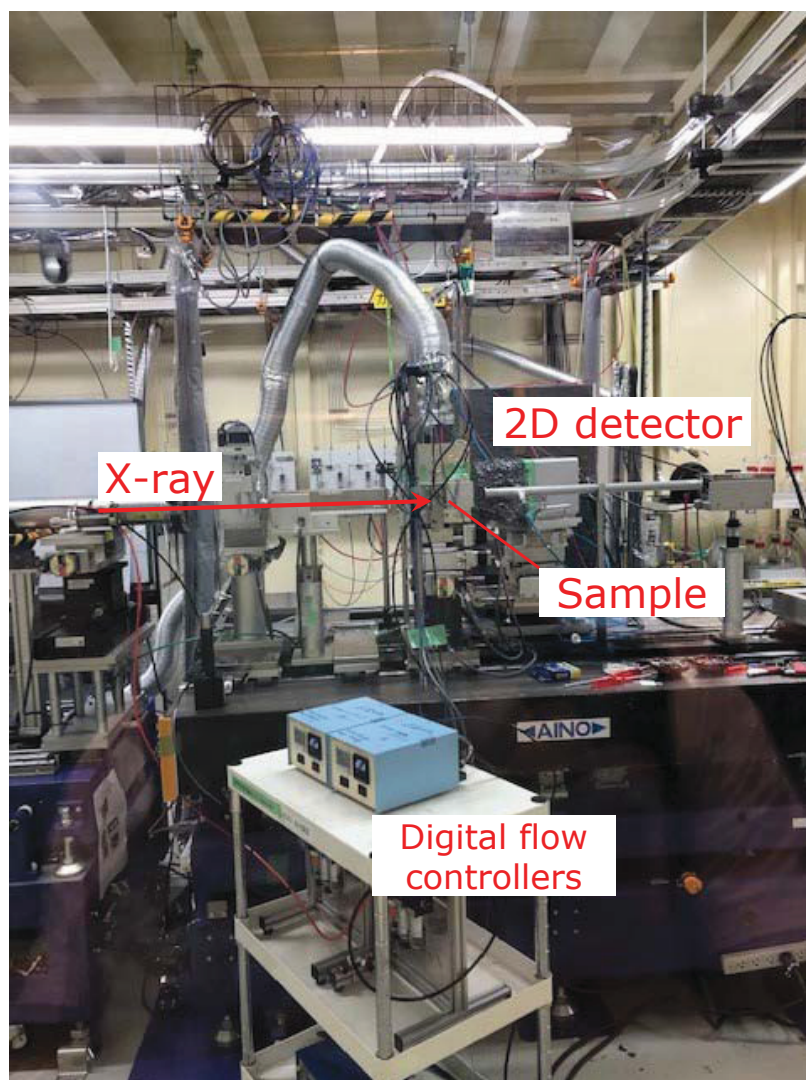


Fig. S1 Photograph of the experimental setup for the *in situ* HT-XRD measurements.

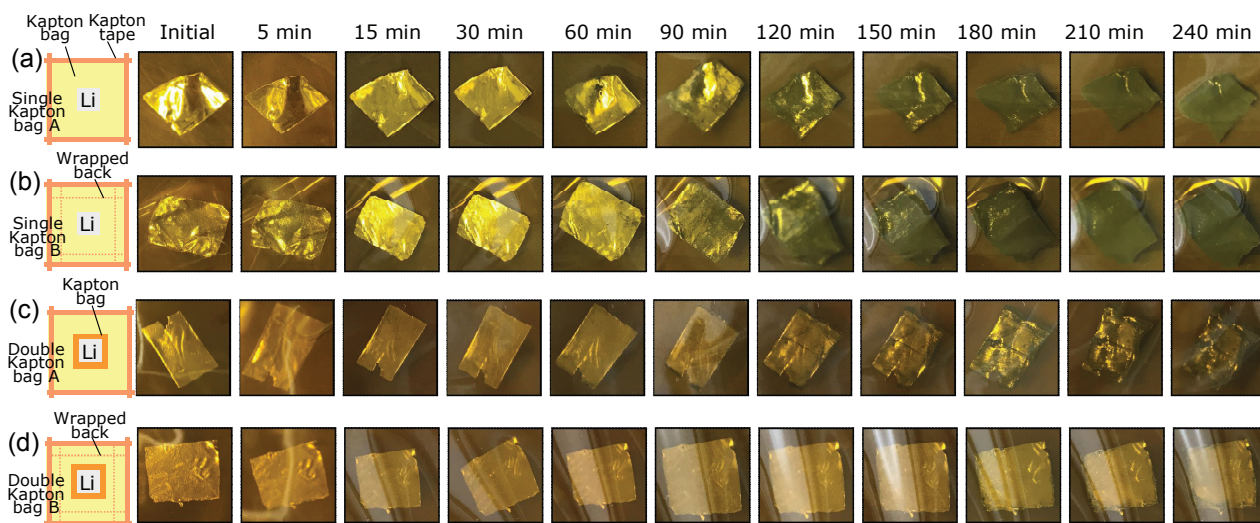


Fig. S2 Photographs of the Li metal during the atmospheric exposure experiments, wherein Li was inserted into (a) single Kapton bag A, (b) single Kapton bag B, (c) double Kapton bag A, and (d) double Kapton bag B.

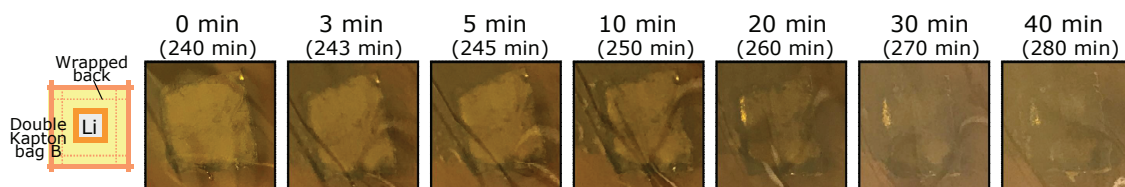


Fig. S3 Photographs of the Li metal in double Kapton bag B during the exposure experiment under steam. This experiment was performed after the atmospheric experiments that are shown in Fig. 1(d). The value in parentheses (bottom line) is the total exposure time.

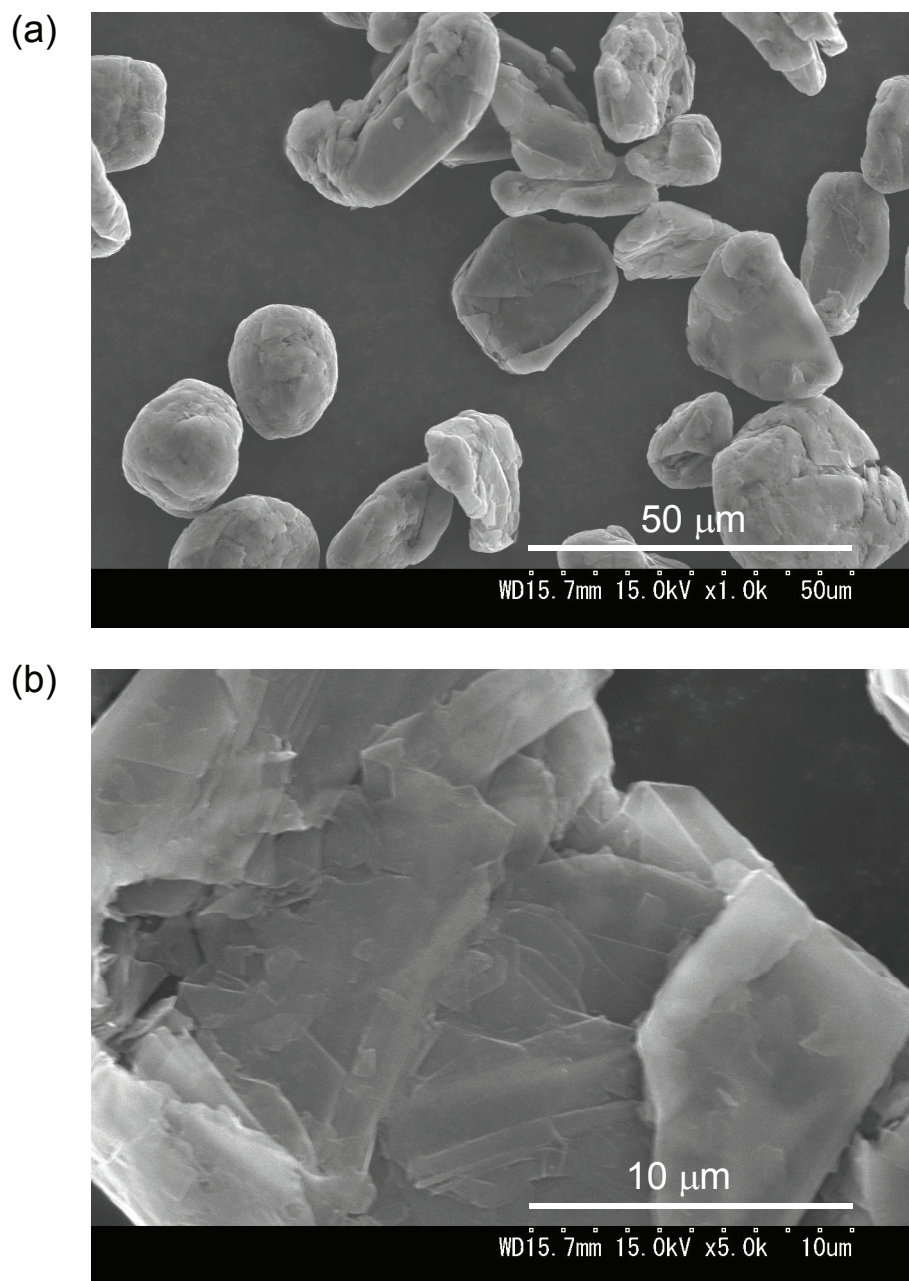


Fig. S4 SEM images of the graphite powder at (a) 50 μm and (b) 10 μm scales.

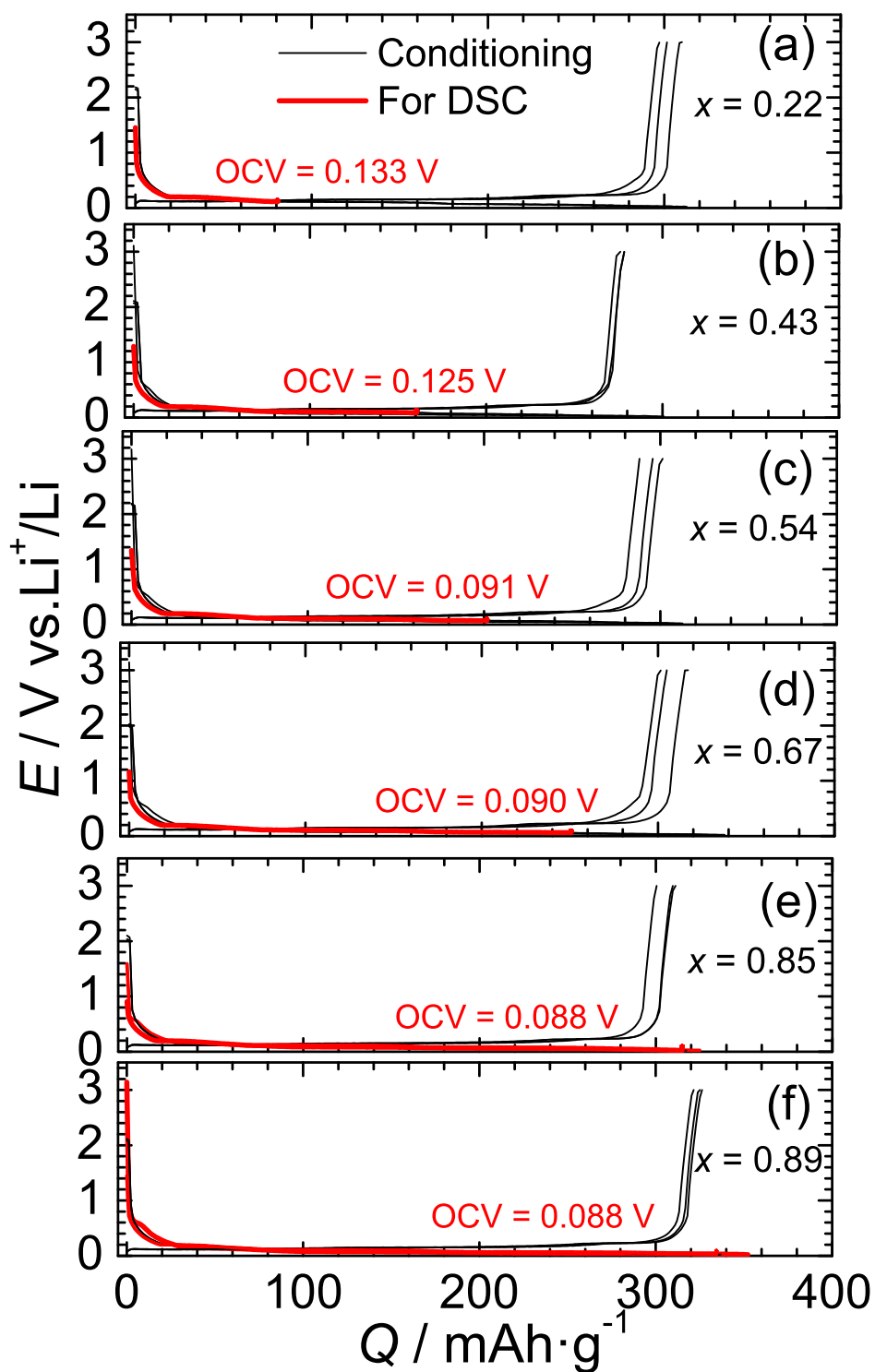


Fig. S5 Discharge curves (red line) for preparing the DSC samples with (a) $x = 0.22$, (b) $x = 0.43$, (c) $x = 0.54$, (d) $x = 0.67$, (e) $x = 0.85$, and (f) $x = 0.89$. The black lines represent the conditioning discharge and charge curves. The open circuit voltages (OCVs) before the DSC measurements are also provided.

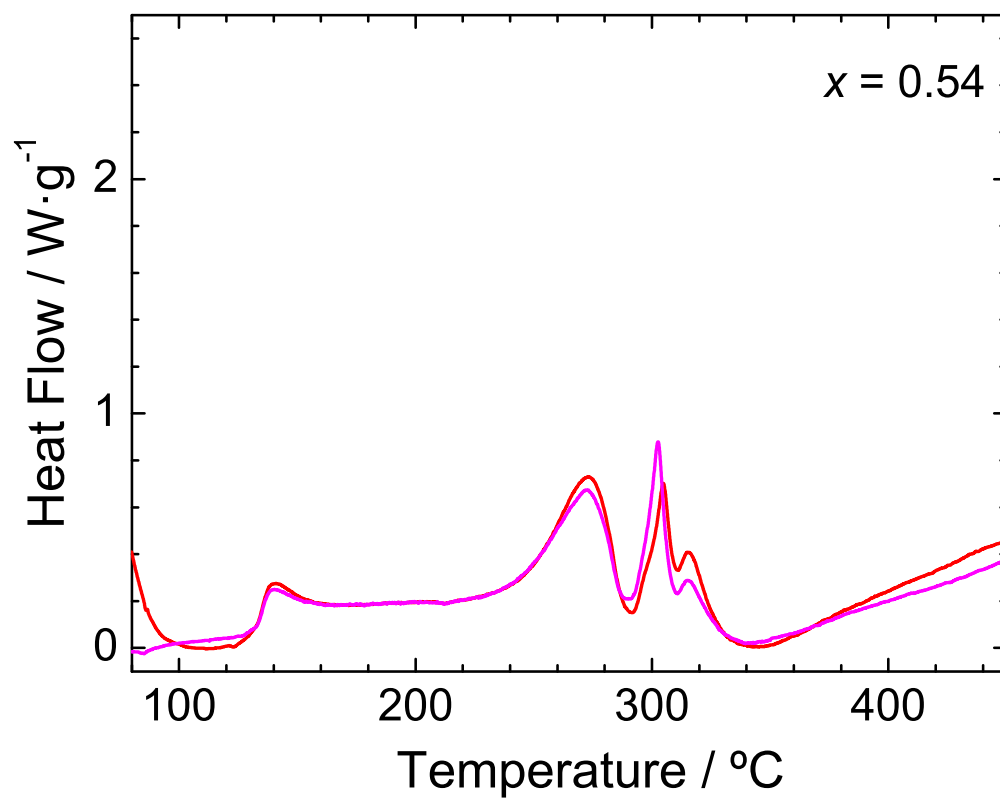


Fig. S6 DSC profiles of the $x = 0.54$ sample at $\beta = 5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

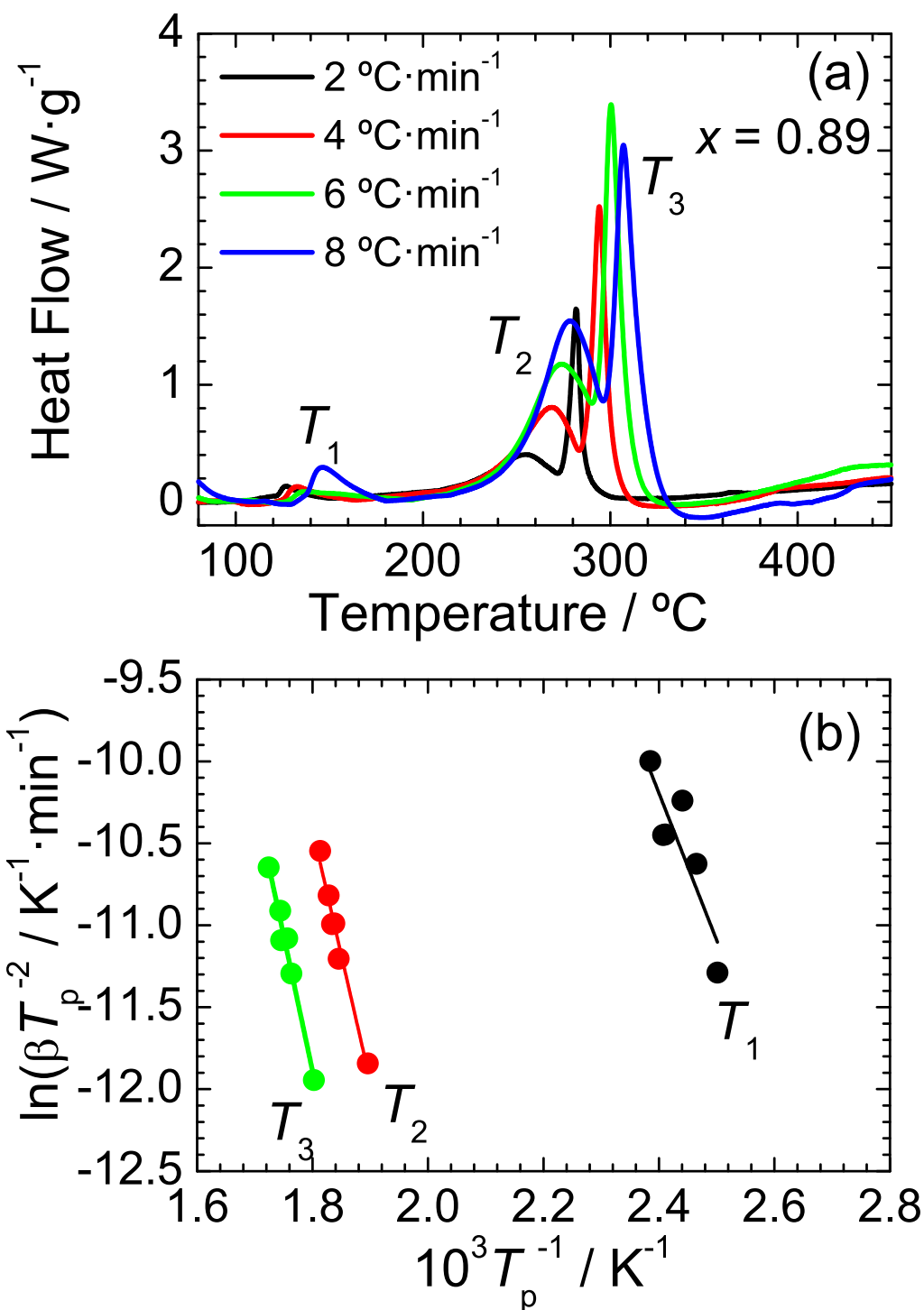


Fig. S7 (a) DSC profiles of the $x = 0.89$ sample at $\beta = 2, 4, 6,$ and $8 \text{ °C}\cdot\text{min}^{-1}$ and (b) $10^3 T_p^{-1}$ vs. $\ln(\beta T_p^{-2})$ plot, where T_p represents the exothermic reaction peaks at $T_1, T_2,$ and T_3 . We included the DSC data for the $x = 0.85$ sample at $\beta = 5 \text{ °C}\cdot\text{min}^{-1}$ in the $10^3 T_p^{-1}$ vs. $\ln(\beta T_p^{-2})$ plot.

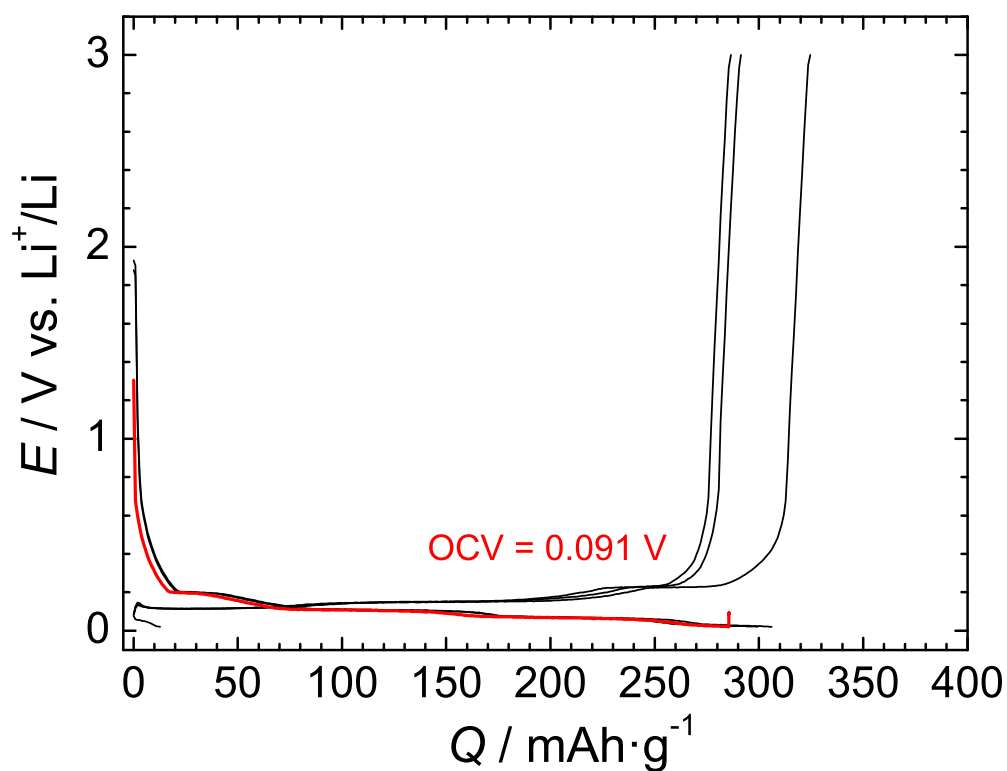


Fig. S8 Discharge curves (red line) for preparing the *in situ* HT-XRD measurement sample. The black lines represent the conditioning discharge and charge curves. The OCV before the XRD measurements is also provided.

References

- [1] K. Mukai, T. Inoue and M. Hasegawa, *J. Power Sources*, 2017, **366**, 185.
- [2] T. Inoue and K. Mukai, *ACS Appl. Mater. Interfaces*, 2017, **9**, 1507.
- [3] T. Inoue and K. Mukai, *Electrochem. Commun.*, 2017, **77**, 28.
- [4] H. E. Kissinger, *Anal. Chem.*, 1957, **29**, 1702.