Supporting information

Electron transfer phase transition and reduction process in $Na_xCo_{0.44}Mn_{0.56}[Fe(CN)_6]_{0.90}$ ($0.00 < x < 1.60$)

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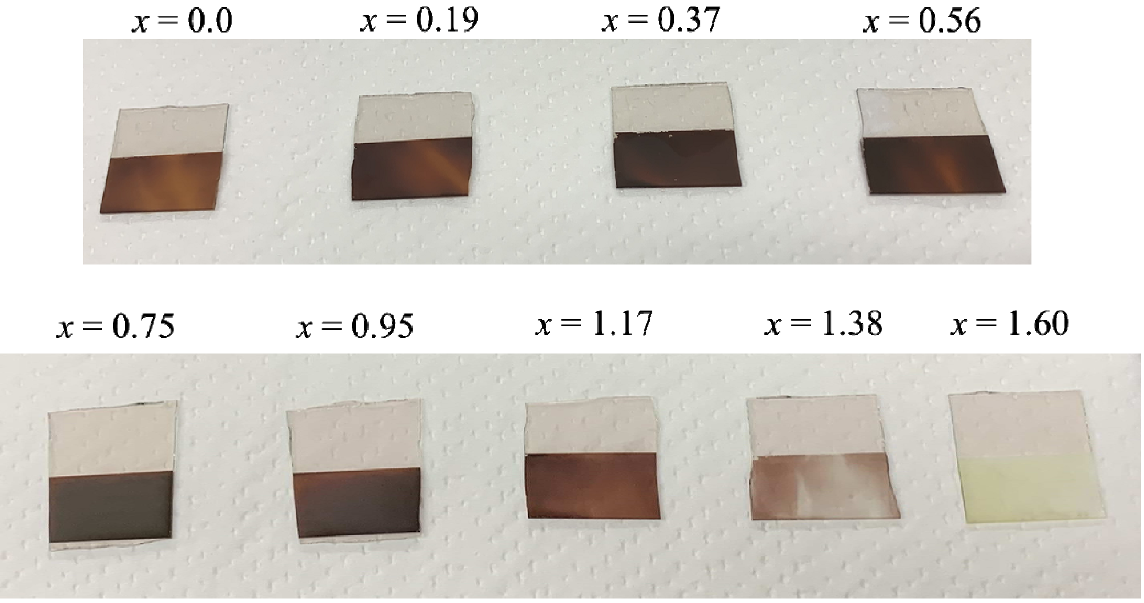


Fig. S1: Pictures of the x-controlled $Na_xCo_{0.44}Mn_{0.56}[Fe(CN)_6]_{0.90}$ films. x of the film was electrochemically controlled in a three-pole beaker-type cell, whose working, referential, and counter electrodes were the CoMn-PBA film, a standard Ag/AgCl electrode, and Pt, respectively. The electrolyte was aqueous solution containing 17 mol/kg $NaClO_4$. The charge and discharge rate was ~ 0.5 C (240mA/g). x was evaluated from the total current under the assumption that $x = 0.0$ in the fully oxidized state.

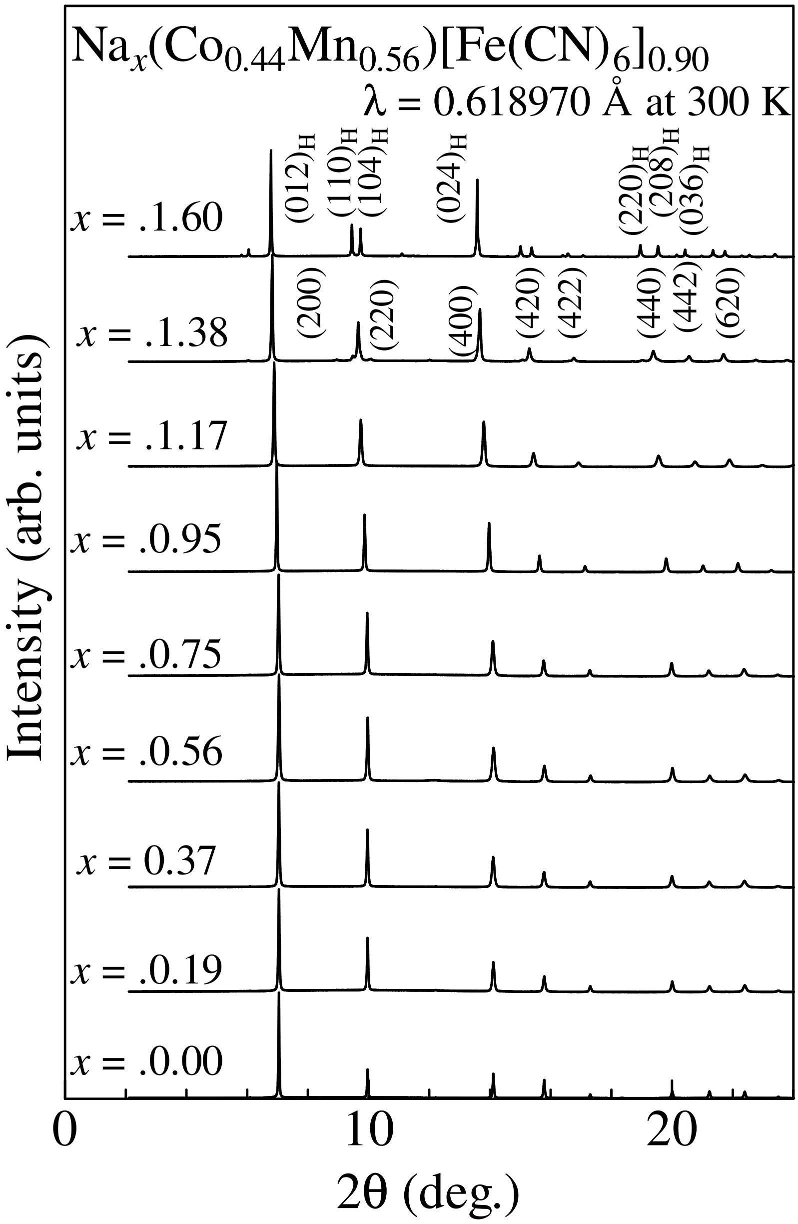
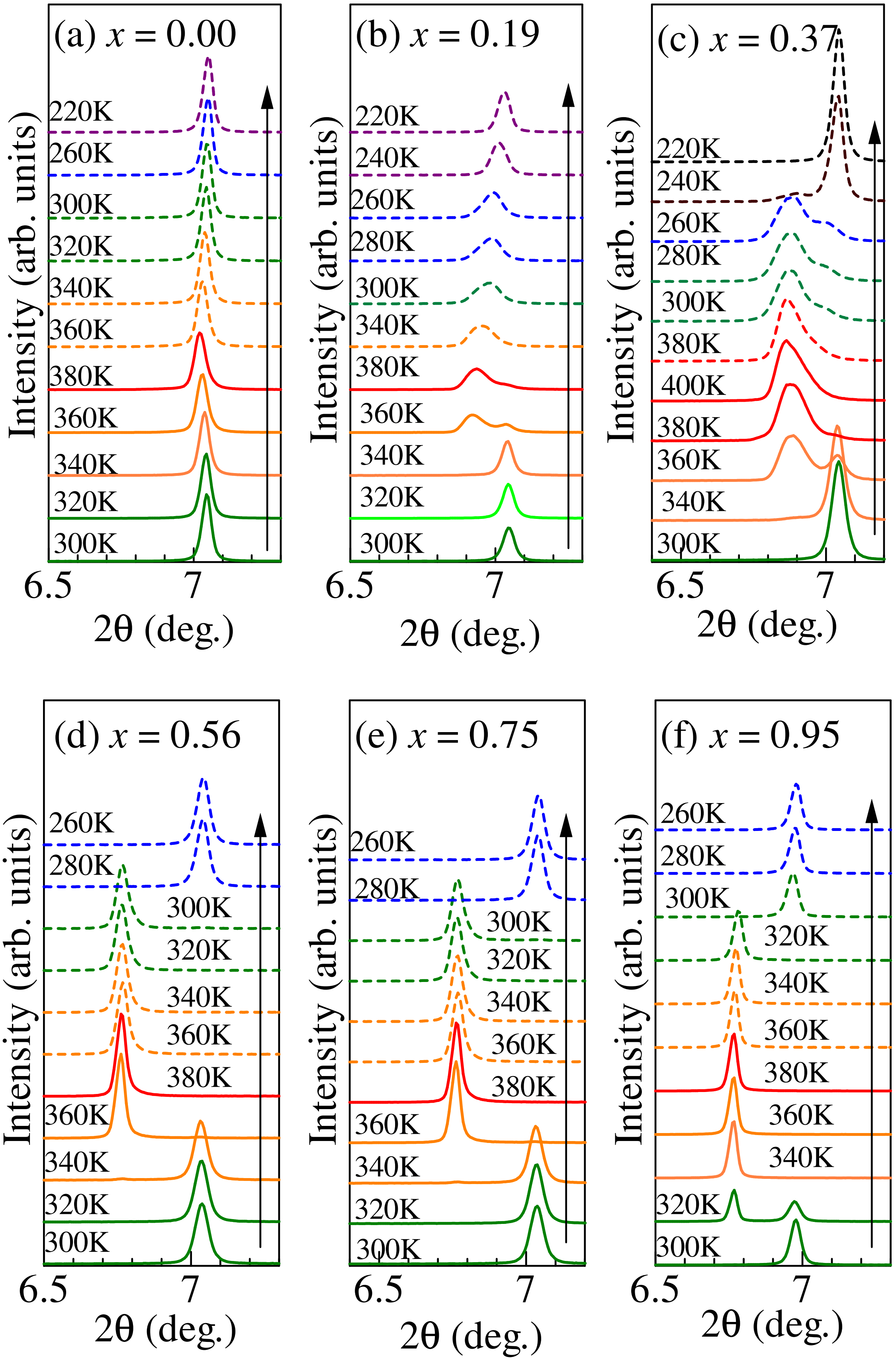


Fig. S2: X-ray powder diffraction (XRD) patterns of $Na_xCo_{0.44}Mn_{0.56}[Fe(CN)_6]_{0.90}$ at 300K. Values in parentheses represent indexes in the face-centered cubic (fcc) structure. Subscript H represents indexes in the trigonal (hexagonal setting) structures. The X-ray wavelength was 0.618970 Å. The films were removed from the ITO glass and were filled in 500 μmϕ glass capillaries. The capillary was placed at the Debye-Scherrer camera. The XRD patterns were monitored using a Si microstrip solid-state detector (MYTHEN, Dectries Ltd.). Typical exposure time was 1 min.


(a) $x = 0.00$
220K
260K
300K
320K
340K
360K
380K
360K
340K
320K
300K
Intensity (arb. units)
6.5
7
2θ (deg.)
(b) $x = 0.19$
220K
240K
260K
280K
300K
340K
380K
360K
340K
320K
300K
Intensity (arb. units)
6.5
7
2θ (deg.)
(c) $x = 0.37$
220K
240K
260K
280K
300K
380K
400K
380K
360K
340K
300K
Intensity (arb. units)
6.5
7
2θ (deg.)
(d) $x = 0.56$
260K
280K
300K
320K
340K
360K
380K
360K
340K
320K
300K
Intensity (arb. units)
6.5
7
2θ (deg.)
(e) $x = 0.75$
260K
280K
300K
320K
340K
360K
380K
360K
340K
320K
300K
Intensity (arb. units)
6.5
7
2θ (deg.)
(f) $x = 0.95$
260K
280K
300K
320K
340K
360K
380K
360K
340K
320K
300K
Intensity (arb. units)
6.5
7
2θ (deg.)

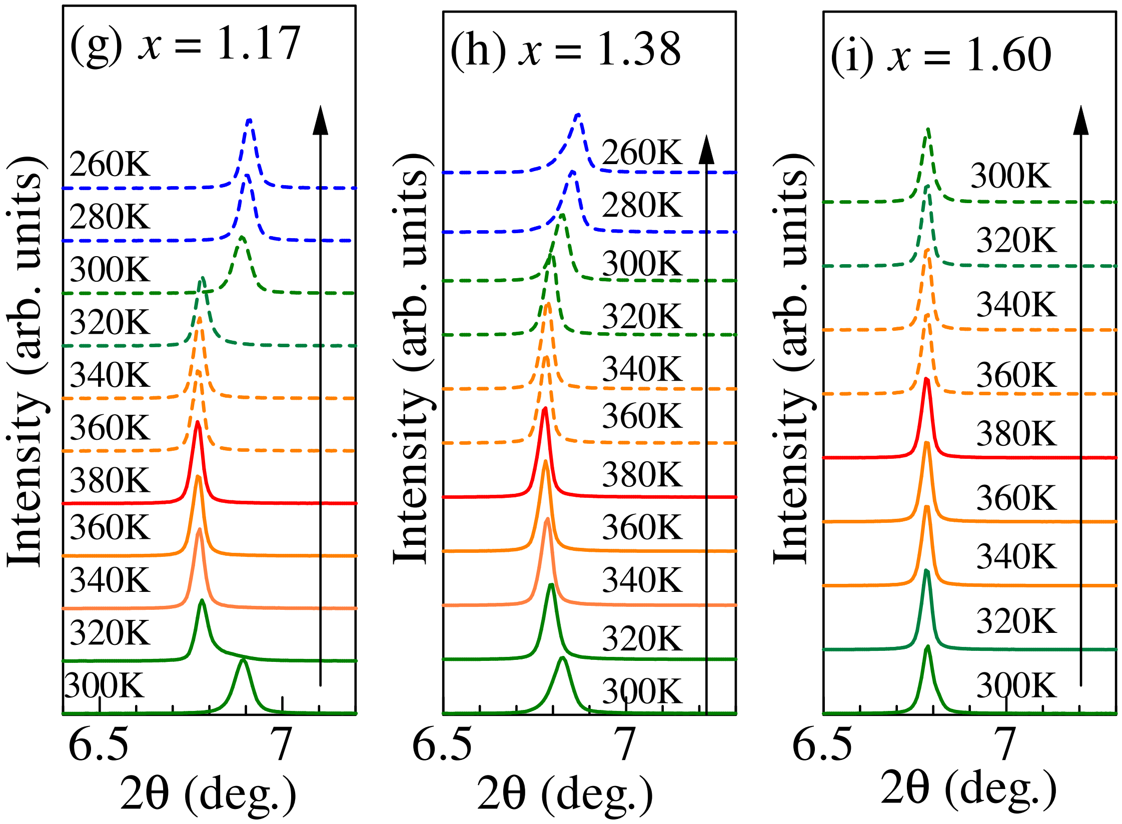


Fig. S3: Magnified XRD patterns of the CoMn-PBA against temperature (*T*): (a) $x = 0.00$, (b) 0.19, (c) 0.37, (d) 0.56, (e) 0.75, (f) 0.95, (g) 1.17, (h) 1.38, and (i) 1.60. Solid and broken patterns indicated that the patterns were obtained in the warming and cooling runs, respectively. *T* was increased from 300 K to 380 K, and then decreased from 380 K to 220 – 300 K. Vertical arrows indicated the measurement order. The X-ray wavelength was 0.618970 Å.

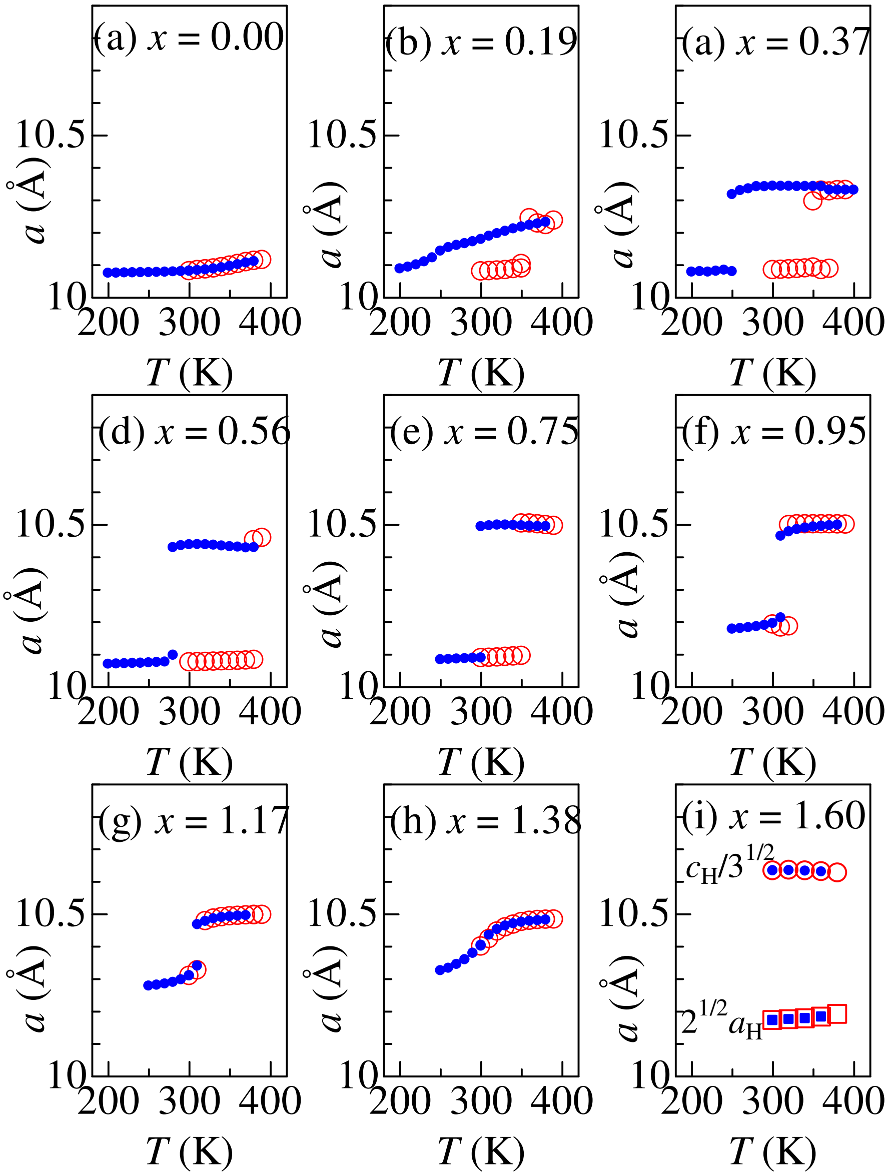


Fig. S4: Lattice constant (a) of CoMn-PBA against temperature (T): (a) $x = 0.00$, (b) 0.19, (c) 0.37, (d) 0.56, (e) 0.75, (f) 0.95, (g) 1.17, (h) 1.38, and (i) 1.60. a_H and c_H in (i) are the lattice constant in the trigonal (hexagonal setting) structure. Open and filled circles represents that the data were obtained in the heating and cooling runs, respectively. The cell parameters were refined with use of Rietan-FP program. Trigonal (hexagonal setting) structure ($R\bar{3}m$; $Z = 3$) was used at $x = 1.60$, while fcc structure ($Fm\bar{3}m$; $Z = 4$) structure was used for $x > 1.38$. a value returns to the initial value after the waring and cooling experiments, suggesting that variation of the H_2O concentration is negligible.

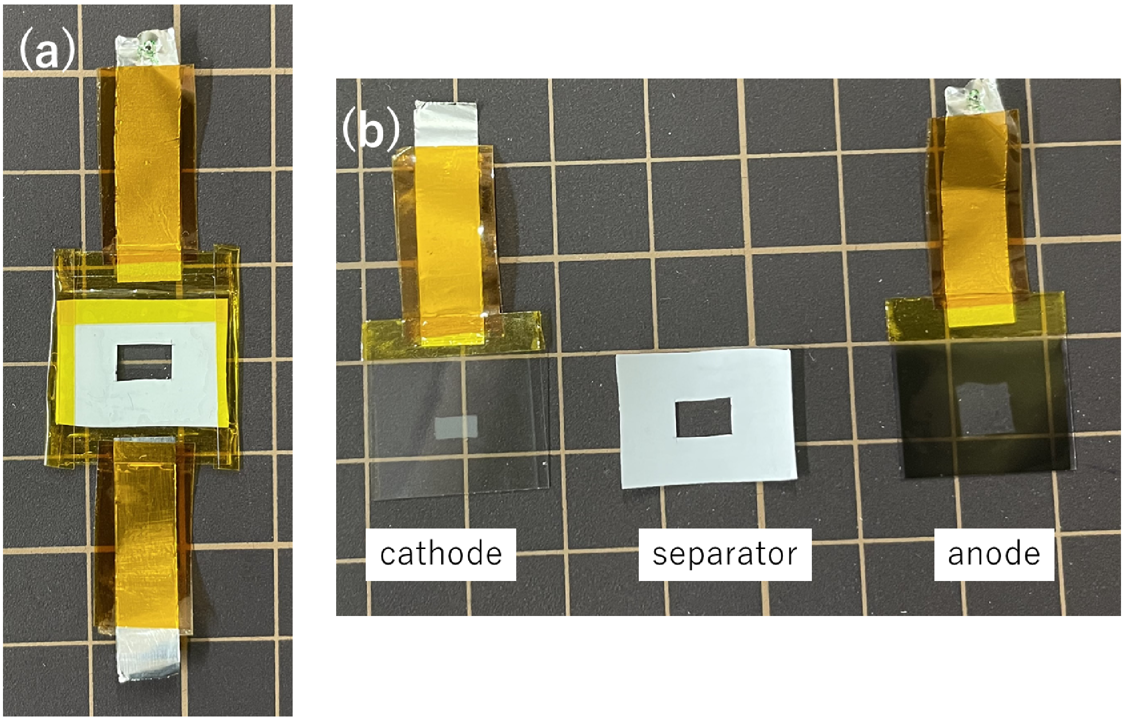


Fig. S5: Picture of the optical two-pole cell used for the *in situ* visible-UV absorption spectroscopy; (a) overall view and (b) parts. Cathode was the CoMn-PBA film (2mm in length, 4mm in width, and 0.6μm in thickness). Anode was a $Na_{0.22}Ni[Fe(CN)_6]_{0.68}$ film (13.5mm in length and 18mm in width). The anode film has 5mm square window at the central position. The redox potential of anode is considered constant against charge/discharge process, since its area (= 218mm^2) is much larger than that (= 8mm^2) of cathode. The electrolyte was an aqueous solution of 17kg/mol $NaClO_4$. The separator (25 μm in thickness) also has window at the central position. These windows prevent extra absorption and scattering in the in situ UV-visible absorption measurements. An Al mask (1.7mm in length and 3.7mm in width), which prevent light leakage, was used in the measurement.

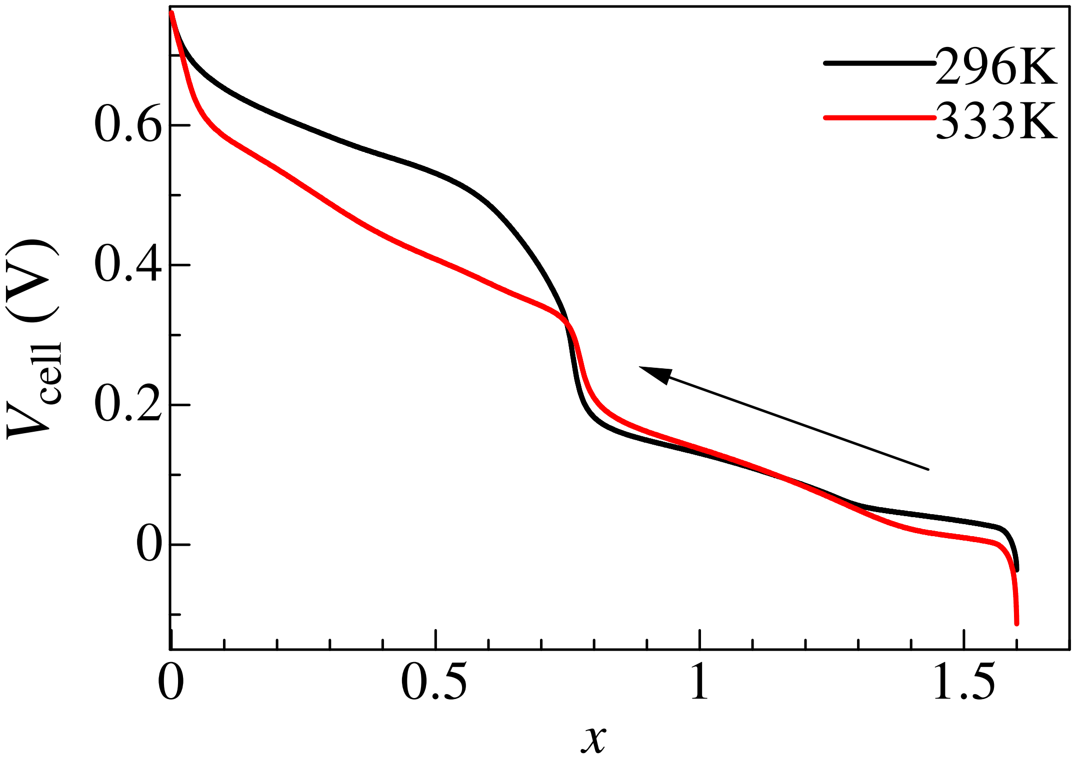


Fig. S6: Charge curve of the optical two-pole cell used for the *in situ* visible-UV absorption spectroscopy at 269K and 333K. Cathode, anode, and electrolyte were the CoMn-PBA film, a $Na_{0.22}Ni[Fe(CN)_6]_{0.68}$ film, and an aqueous solution of 17kg/mol $NaClO_4$. The redox potential of anode is considered constant against charge/discharge process, since its area (= 218mm^2) is much larger than that (= 8mm^2) of cathode. The charge rate was 1.4 C (90 mA/g).