Supporting information

Na^+ diffusion kinetics in nanoporous metal-hexacyanoferrates

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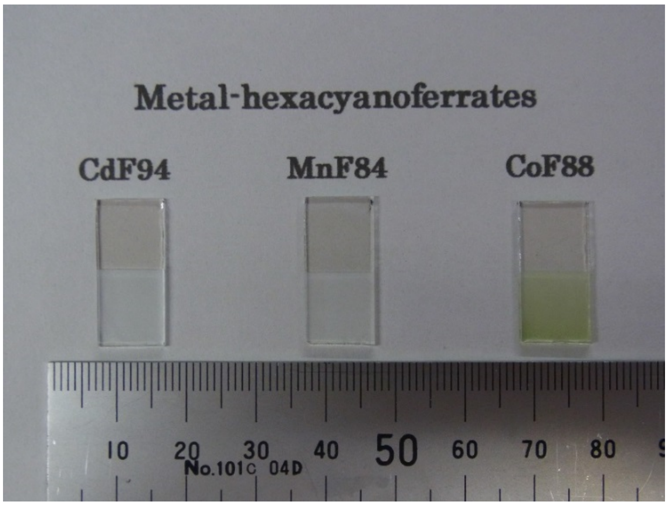

Fig. S1: Pictures of CoF88, MnF84, and CdF94 films on ITO transparent electrodes.

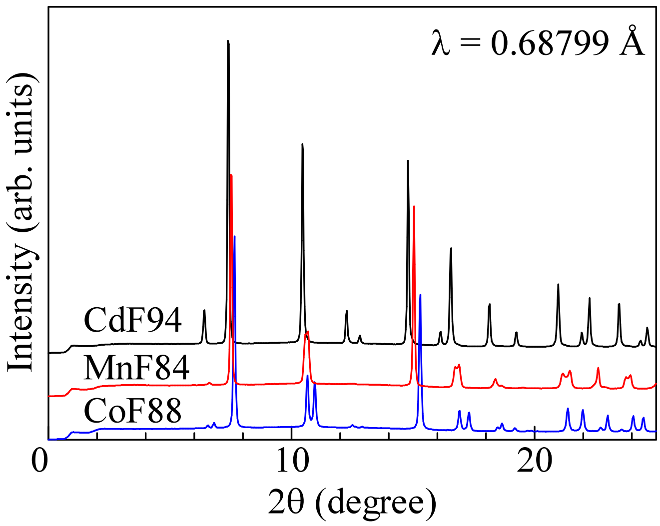

Fig. S2: X-ray powder diffraction patterns of as-grown CoF88, MnF84, and CdF94 films. The films were carefully removed from the ITO glass substrate with a microspatula, and then fine powders were used to fill 300μmϕ glass capillaries. X-ray wavelength was 0.68799 Å. Experiments were performed at BL8B of Photon Factory. In MnF84 and CoF88, all the reflections can be indexed in the hexagonal ($R\underline{3}m$; Z=12) setting. In CdF94, all the reflections can be indexed in the face-centered cubic ($Fm\underline{3}m$; Z= 4) setting. The lattice constants were determined by Rietveld analysis: $a_H/\sqrt{2}$=10.515(1) Å and $c_H/\sqrt{3}$=10.085(1) Å for CoF88 (x= 1.52), $a_H/\sqrt{2}$=10.603(1) Å and $c_H/\sqrt{3}$=10.429(2) Å for MnF84 (x= 1.36), and a=10.7068(9) Å for CdF94 (x= 1.76).

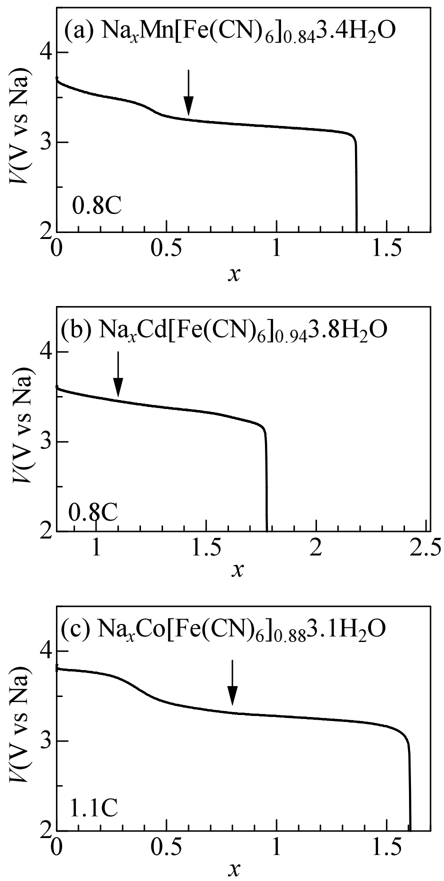

Fig. S3: Discharge curves of (a) MnF84, (b) CdF94, and (c) CoF88 films in propylene carbonate (PC) containing 1M $NaClO_4$ against Na metal. The redox reactions are as follows: (a) $1.36Na^+ + Mn^{II}_{0.52}Mn^{II}_{0.48}[Fe^{III}(CN)_6]_{0.84} \rightarrow Na^+ + Na_{0.36}Mn^{II}[Fe^{III}(CN)_6]_{0.84} \rightarrow Na_{1.36}Mn^{II}[Fe^{II}(CN)_6]_{0.84}$, (b) $0.94Na^+ + Na_{0.82}Cd^{II}[Fe^{III}(CN)_6]_{0.94} \rightarrow Na_{1.76}Cd^{II}[Fe^{II}(CN)_6]_{0.94}$, (c) $1.52Na^+ + Co^{III}[Fe^{III}(CN)_6]_{0.52}[Fe^{III}(CN)_6]_{0.48} \rightarrow Na^+ + Na_{0.52}Co^{III}[Fe^{II}(CN)_6]_{0.88} \rightarrow Na_{1.52}Co^{II}[Fe^{II}(CN)_6]_{0.88}$. Arrows indicated the position where electrochemical impedance spectra were measured.

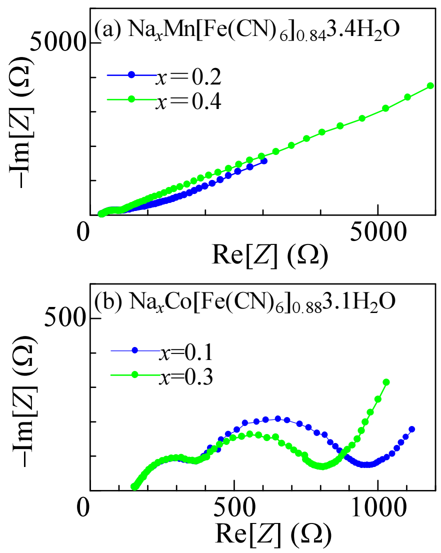

Fig. S4: Electrochemical impedance spectra (EIS) of (a) MnF84 and (b) CdF94 films in propylene carbonate (PC) containing 1M $NaClO_4$ against Na metal.

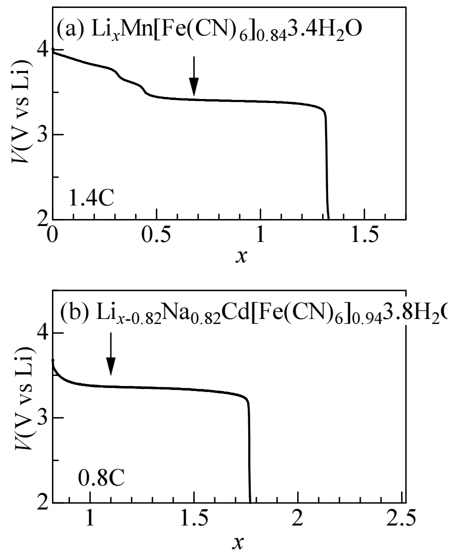

Fig. S5: Discharge curves of (a) MnF84 and (b) CdF94 films in ethylene carbonate (EC) / diethyl carbonate (DEC) containing 1M $LiClO_4$ against Na metal. The redox reactions are as follows: (a) $1.36Li^+ + Mn^{II}_{0.52}Mn^{II}_{0.48}[Fe^{III}(CN)_6]_{0.84}$ ➔ $Li^+ + Li_{0.36}Mn^{II}[Fe^{III}(CN)_6]_{0.84}$ ➔ $Li_{1.36}Mn^{II}[Fe^{II}(CN)_6]_{0.84}$, (b) $0.94Li^+ + Na_{0.82}Cd^{II}[Fe^{III}(CN)_6]_{0.94}$ ➔ $Li_{0.94}$ $Na_{0.82}Cd^{II}[Fe^{II}(CN)_6]_{0.94}$. Arrows indicated the position where electrochemical impedance spectra were measured.

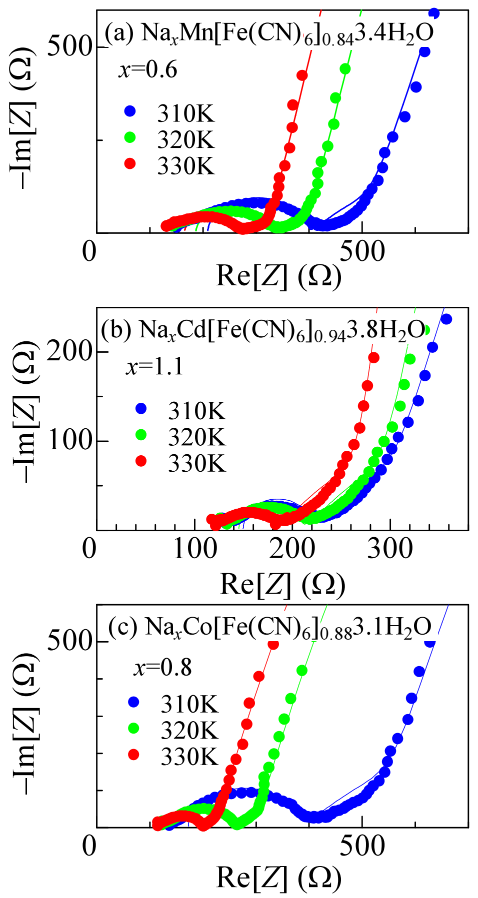

Fig. S6: Temperature dependence of the EIS curves of (a) MnF84, (b) CdF94 and (c) CoF88 films in PC containing 1M $NaClO_4$ against Na metal. Solid curves are results of the least-squares fittings with the Randles equivalent circuit model.

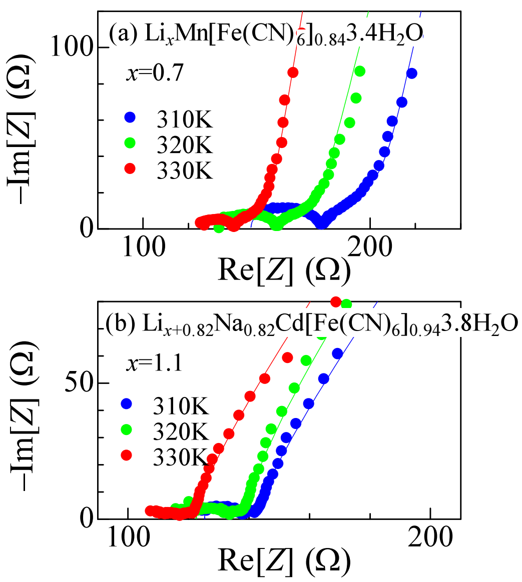

Fig. S7 Temperature dependence of the EIS curves of (a) MnF84 and (b) CdF94 films in ethylene carbonate (EC) / diethyl carbonate (DEC) containing 1M $LiClO_4$ against Li metal. Solid curves are results of the least-squares fittings with the Randles equivalent circuit model.

film	x	f_c (s^{-1})	D (cm^2/s)	E_a (eV)
MnF84	0.6	0.10	2.3×10^{-10}	0.22
CdF94	1.1	0.19	7.7×10^{-10}	0.12
CoF88	0.8	0.05	0.5×10^{-10}	0.86

Table. S1 Critical frequency (f_c) at 305 K, Na^+ diffusion constant (D) at 305 K, and activation energy (E_a) of D of MnF84, CdF94, and CoF88. Note that D was determined by the lease-squares fitting of the EISs, not from f_c. x is the Na concentration.

film	x	f_c (s^{-1})	D (cm^2/s)	E_a (eV)
MnF84	0.7	0.19	4.6×10^{-10}	0.48
CdF94	1.1	1.16	3.5×10^{-9}	0.25

Table. S2 Critical frequency (f_c) at 305 K, Li^+ diffusion constant (D) at 305 K, and activation energy (E_a) of D of MnF84 and CdF94. Note that D was determined by the lease-squares fitting of the EISs, not from f_c. x is the Li concentration.