

Supporting Information

**Depth-Resolved X-Ray Absorption Spectroscopic Study on Nanoscale Observation
of Electrode / Solid Electrolyte Interface for All Solid State Lithium Ion Battery**

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Table S1. Working functions of LATP-GC substrate, LiCoO₂ film, and interlayer films observed from a photoelectron spectroscopy.

		Work function / eV
LiCoO ₂		5.33
Li _{1-x} CoO ₂ (deintercalated at 3.92 V)		5.39
LATP-GC		5.00
Interfacial layer	MoO ₂	5.00
	NbO ₂	5.31
	ZrO ₂	5.50

Table S2. Calculated parameters from Co K-edge EXAFS of LiCoO₂/ L ATP-GC electrolyte and LiCoO₂/ NbO₂/ L ATP-GC electrolyte before charged at various channel of PILATUS detector.

before deintercalation	Co-O			Co-Co			Residue(%)
	CN	R/Å	σ/Å	CN	R/Å	σ/Å	
LiCoO ₂ /L ATP-GC							
150	6	1.904	0.080	6	2.818	0.074	2.196
151	6	1.905	0.071	6	2.816	0.068	0.937
152	6	1.908	0.069	6	2.816	0.066	1.153
153	6	1.908	0.070	6	2.815	0.064	1.829
154	6	1.907	0.064	6	2.814	0.066	1.902
LiCoO ₂ /NbO ₂ /L ATP-GC							
150	6	1.903	0.072	6	2.820	0.071	0.930
151	6	1.903	0.071	6	2.818	0.068	0.900
152	6	1.904	0.070	6	2.815	0.066	0.860
153	6	1.905	0.067	6	2.814	0.067	0.795
154	6	1.907	0.066	6	2.814	0.064	0.933

Table S3. Calculated parameters from Co K-edge EXAFS of LiCoO₂/LATP-GC electrolyte and LiCoO₂/NbO₂/LATP-GC electrolyte after charged to 3.92 V measured at various channel of PILATUS detector.

after deintercalation	Co-O			Co-Co			Residue(%)	
	CN	R/Å	σ/Å	CN	R/Å	σ/Å		
LiCoO ₂ /LATP-GC								
	150	6	1.891	0.075	6	2.824	0.075	2.204
	151	6	1.889	0.075	6	2.822	0.072	1.709
	152	6	1.889	0.076	6	2.822	0.072	1.394
	153	6	1.888	0.073	6	2.819	0.072	1.684
	154	6	1.890	0.075	6	2.821	0.073	1.308
LiCoO ₂ /NbO ₂ /LATP-GC								
	150	6	1.899	0.076	6	2.827	0.077	1.320
	151	6	1.897	0.071	6	2.827	0.073	1.029
	152	6	1.894	0.071	6	2.824	0.073	1.296
	153	6	1.892	0.068	6	2.824	0.071	1.888
	154	6	1.891	0.070	6	2.821	0.072	1.224

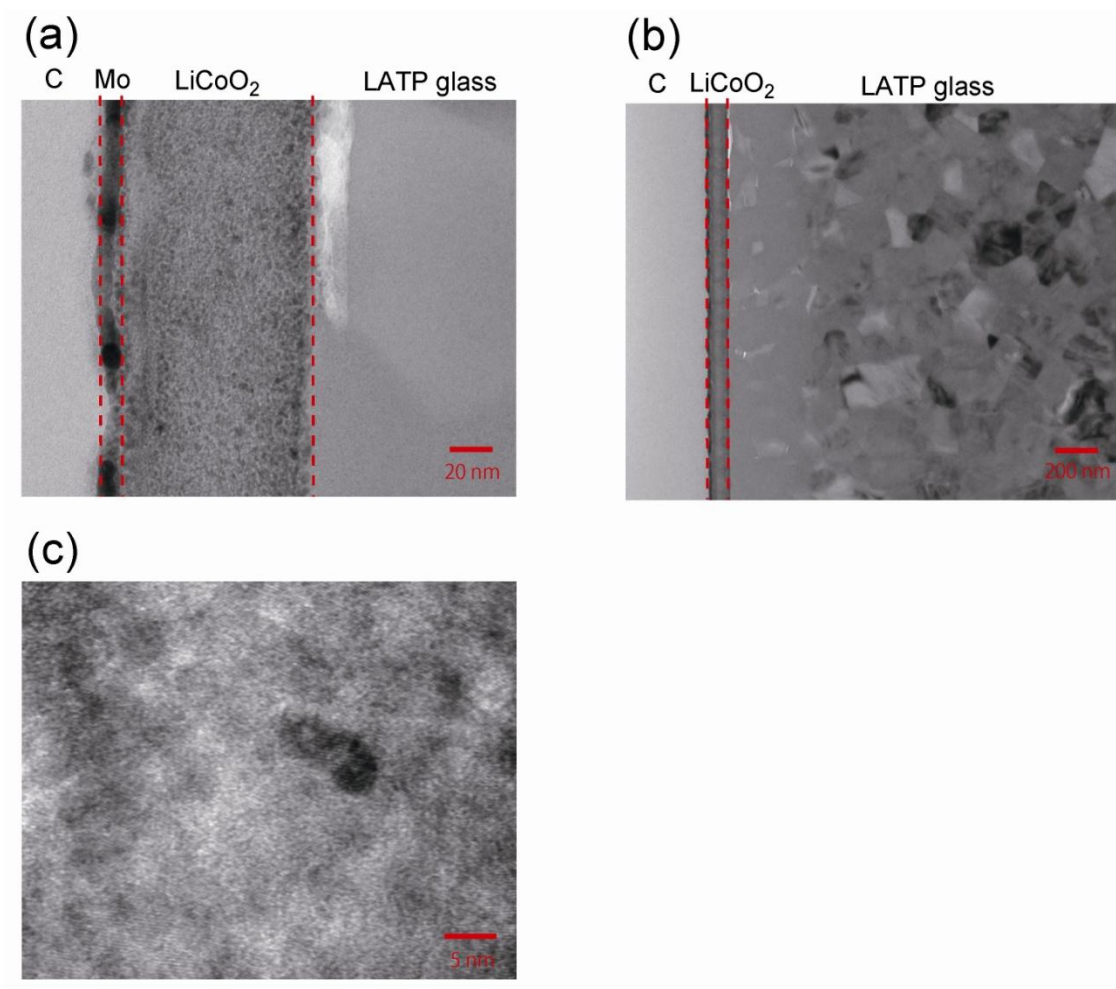


Figure S1. TEM images of the LiCoO₂ film /LATP glass electrolyte assemble.

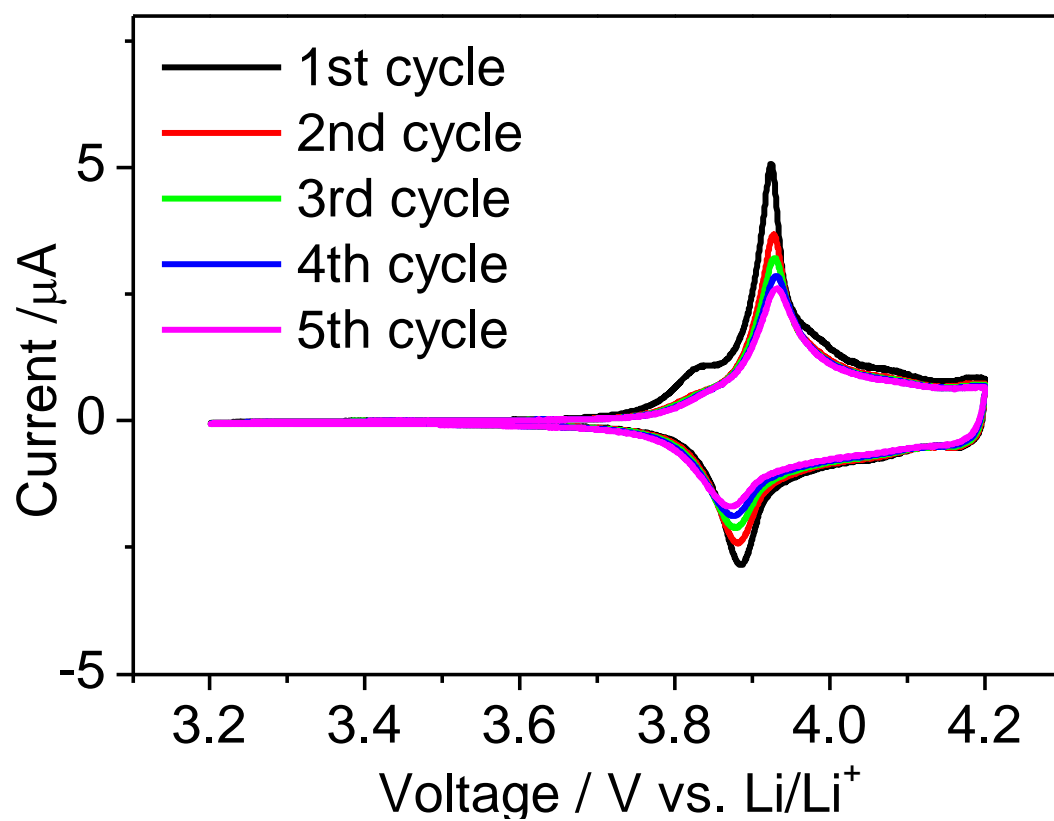


Figure S2. Cyclic voltammograms of the LiCoO₂ film /LATP glass electrolyte assemble; $\nu = 0.1 \text{ mV s}^{-1}$.

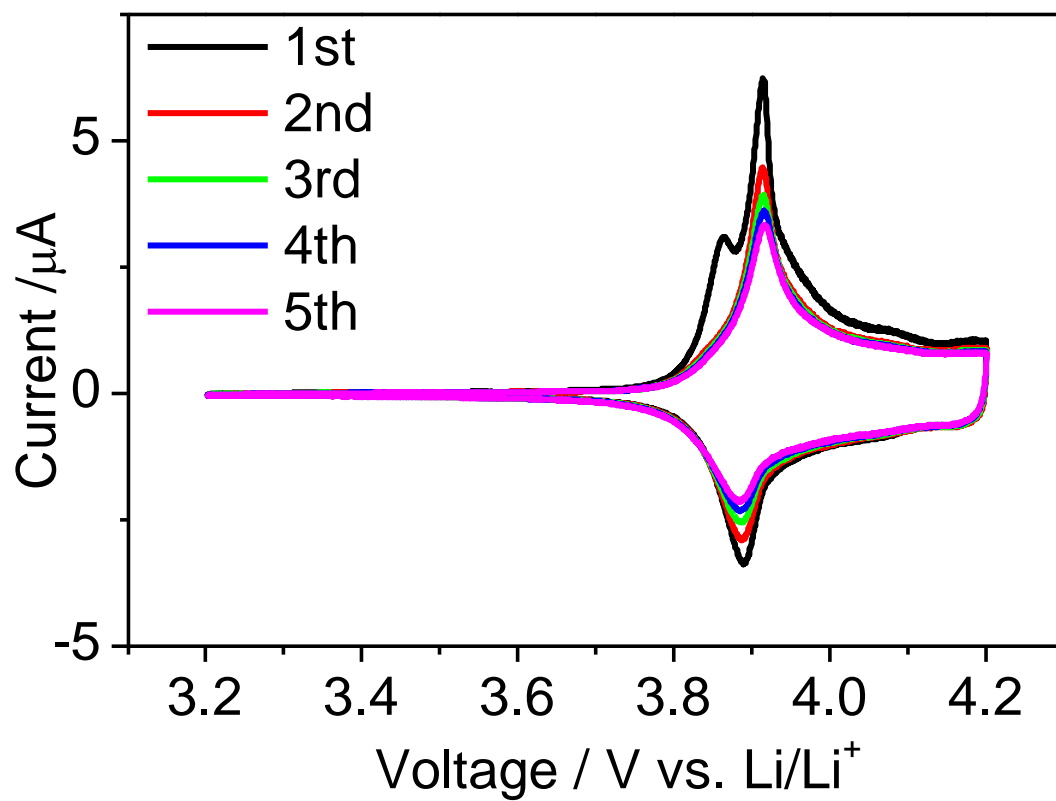


Figure S3. Cyclic voltammograms of the LiCoO₂ film/NbO₂ film/LATP glass electrolyte assemble; $\nu = 0.1 \text{ mV s}^{-1}$.

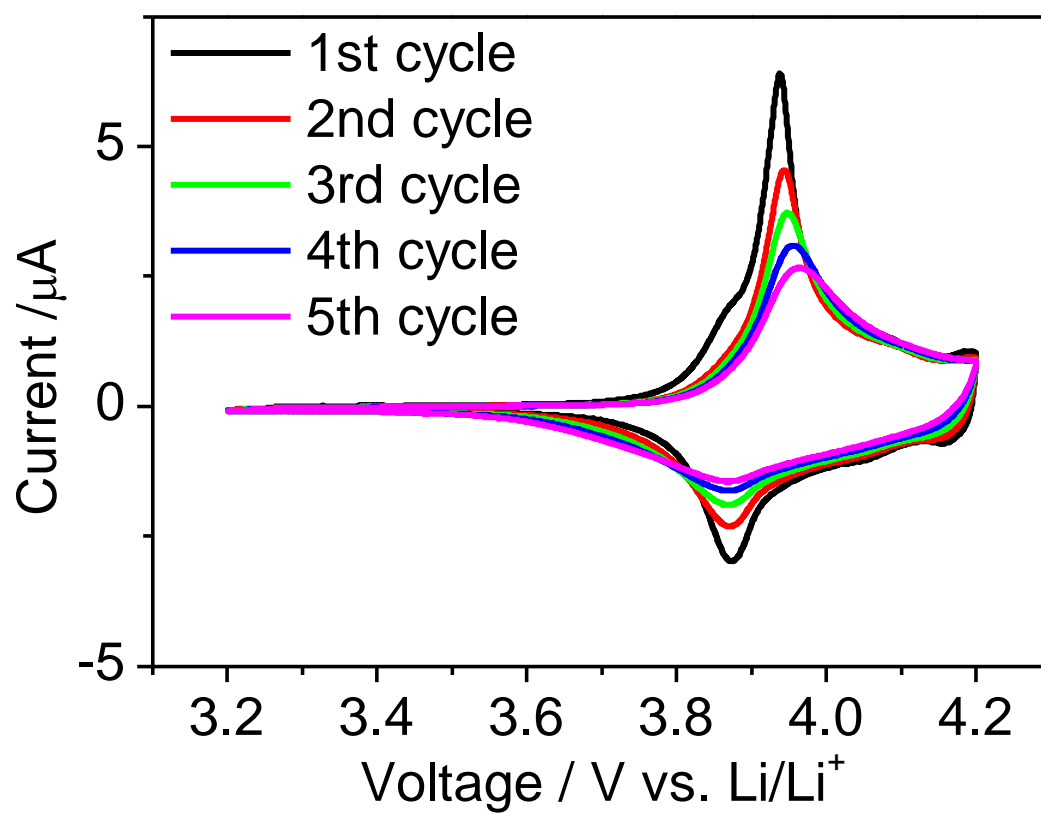


Figure S4. Cyclic voltammograms of the LiCoO_2 film/ ZrO_2 film/LATP glass electrolyte assemble; $\nu = 0.1 \text{ mV s}^{-1}$.

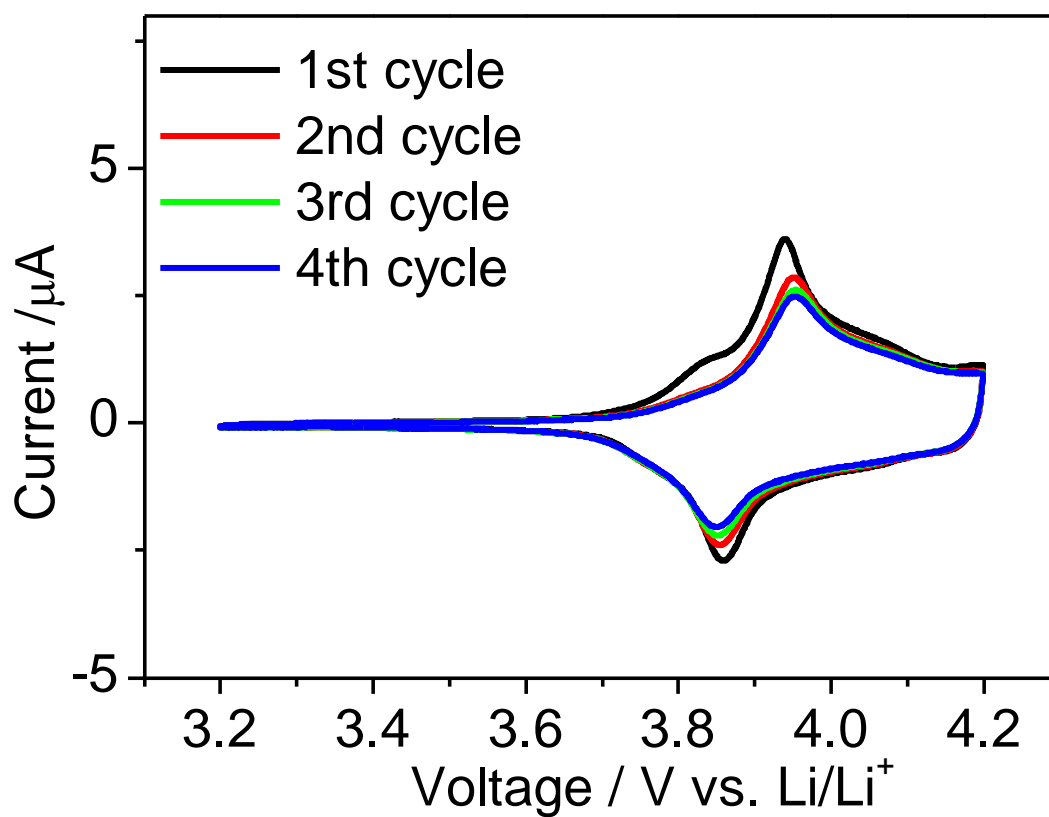


Figure S5. Cyclic voltammograms of the LiCoO_2 film/ MoO_2 film/LATP glass electrolyte assemble; $\nu = 0.1 \text{ mV s}^{-1}$.

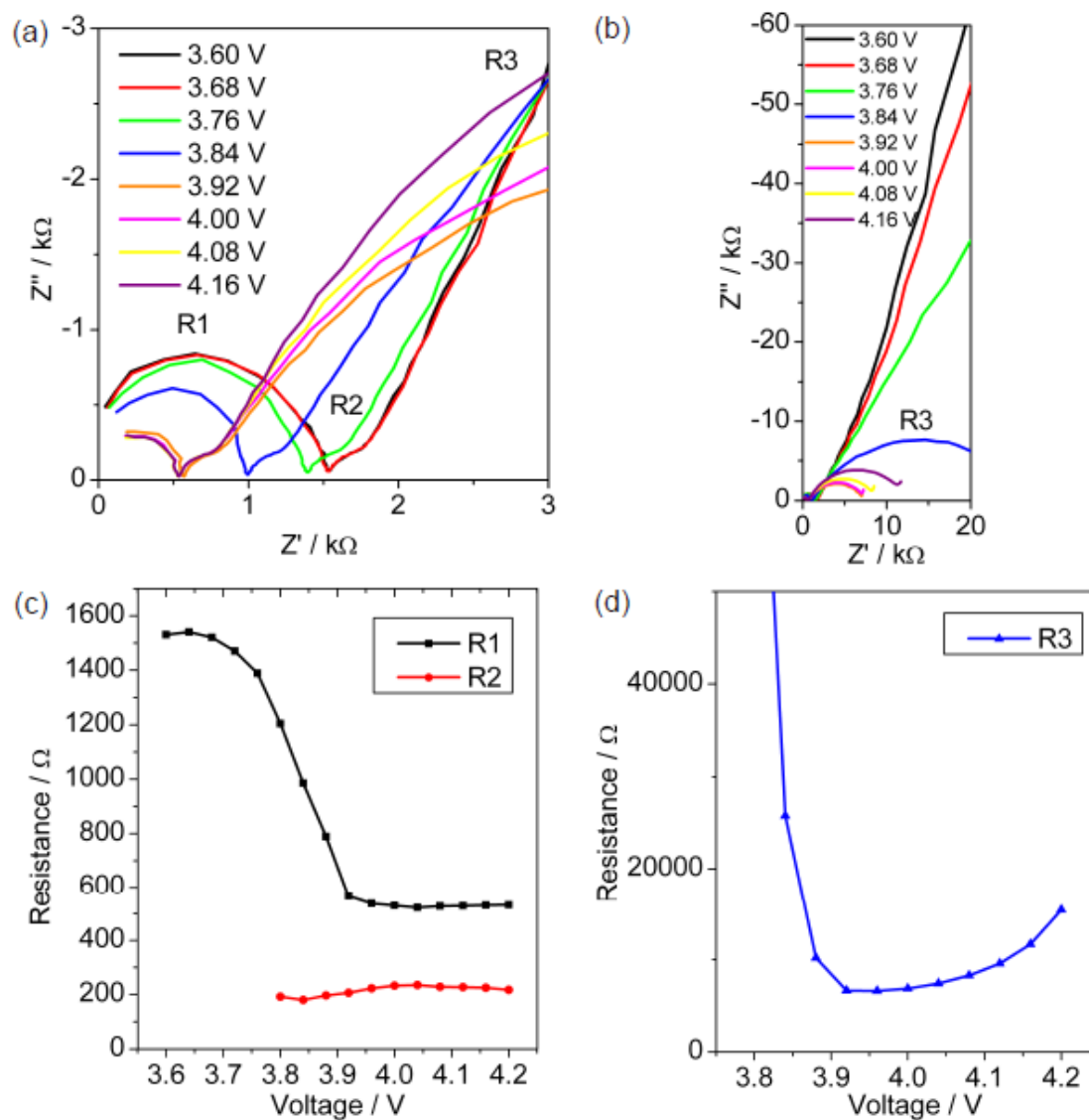


Figure S6. (a) and (b) The results from the electric impedance spectroscopy for LiCoO₂ film /LATP glass measured at various voltages. (c) and (d) Calculated resistance by using the equivalent circuit shown in Fig.4(a) as a function of voltages.

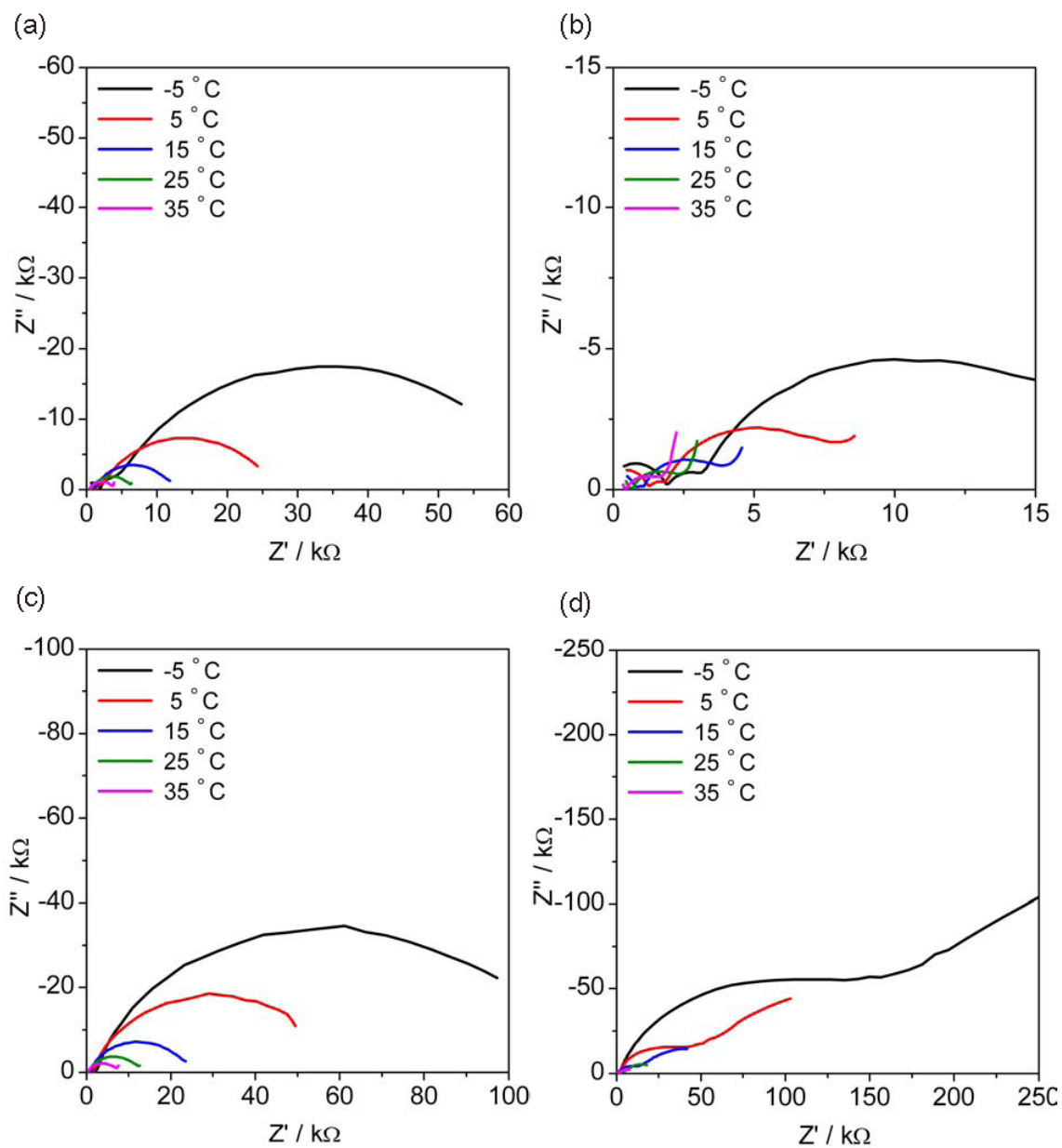


Figure S7. The results from the electric impedance spectroscopy for (a) LiCoO₂ film /LATP glass, (b) LiCoO₂ film/NbO₂ film/LATP glass, (c) LiCoO₂ film/ZrO₂ film/LATP glass, and (d) LiCoO₂ film/MoO₂ film/LATP glass measured at various temperatures (from -5 °C to 35 °C).

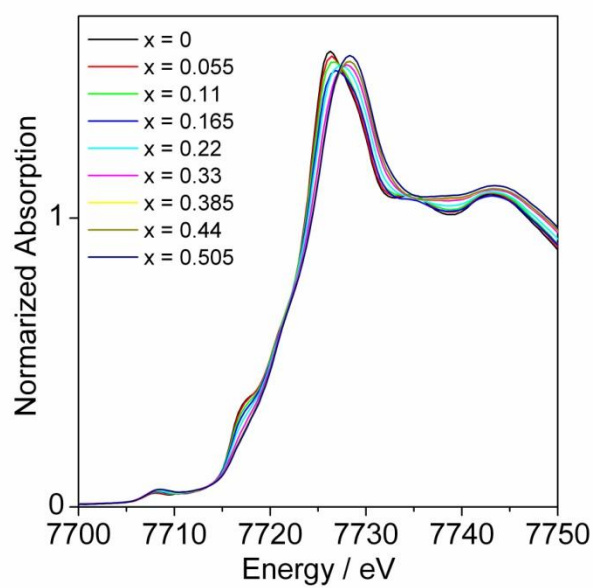


Figure S8. Co K-edge XANES spectra of Li_xCoO_2 .

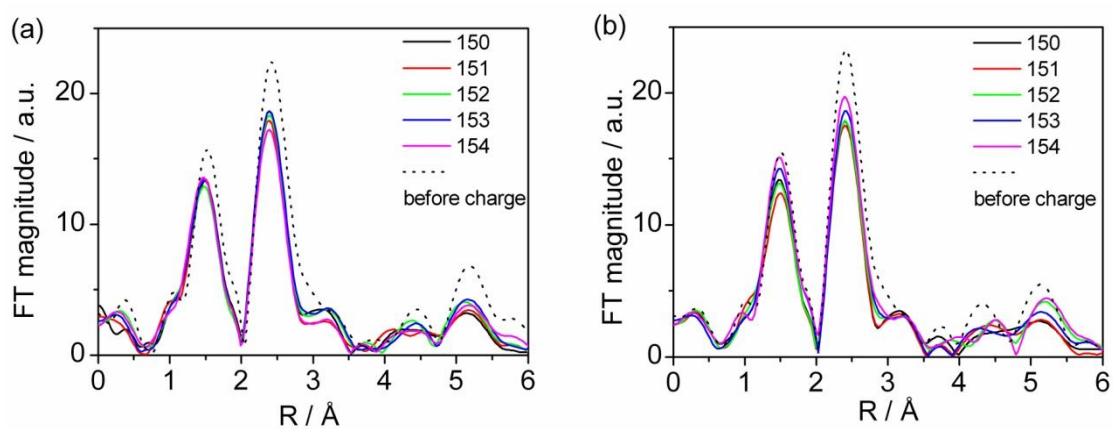


Figure S9. Fourier transforms (FTs) of the Co K-edge EXAFS oscillations for (a) $\text{LiCoO}_2 / \text{LATP-GC}$ electrolyte and (b) $\text{LiCoO}_2 / \text{NbO}_2 / \text{LATP-GC}$ electrolyte after charged at 3.92 V with each channel of PILATUS detector detecting around the interface. Dot line shows FT of same sample before charge.

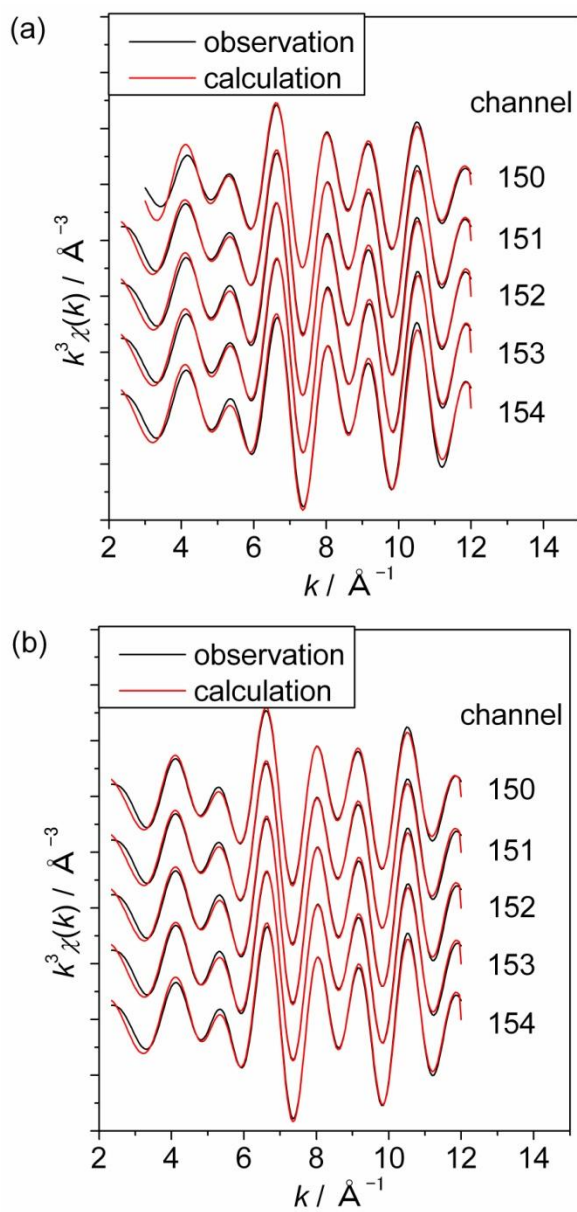


Figure S10. Experimental (black line) and calculated (red line) Fourier-filtered k^3 -weighted Co K-edge EXAFS oscillations for various PILATUS channel of (a) LiCoO_2 /LATP-GC electrolyte and (b) LiCoO_2 / NbO_2 /LATP-GC electrolyte.

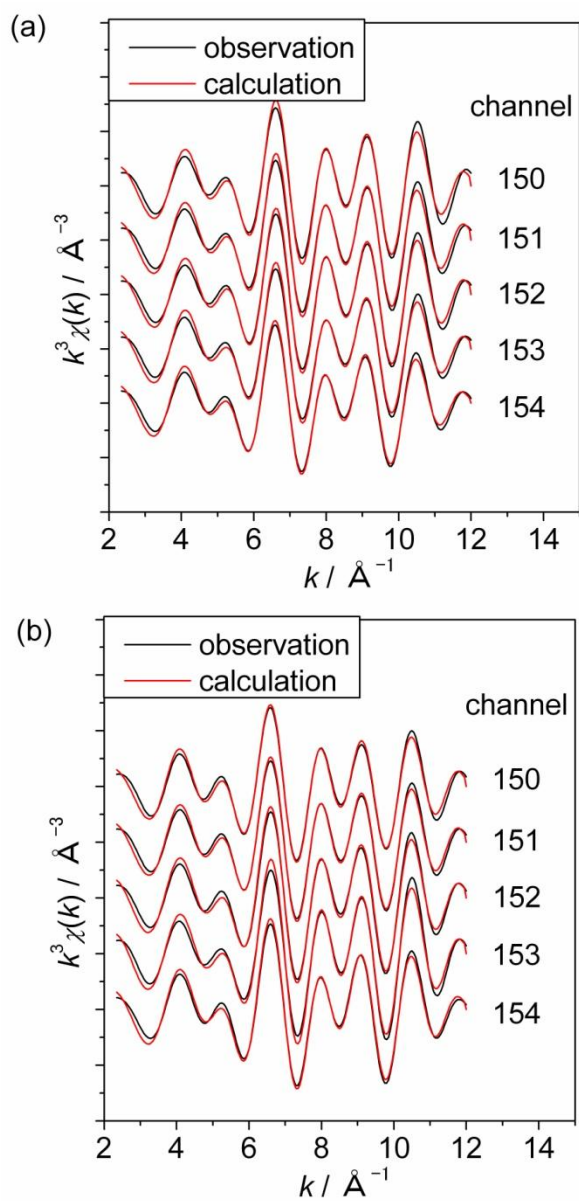


Figure S11. Experimental (black line) and calculated (red line) Fourier-filtered k^3 -weighted Co K-edge EXAFS oscillations for various PILATUS channel of (a) LiCoO_2 /LATP-GC electrolyte and (b) LiCoO_2 / NbO_2 /LATP-GC electrolyte after charged at 3.92 V.

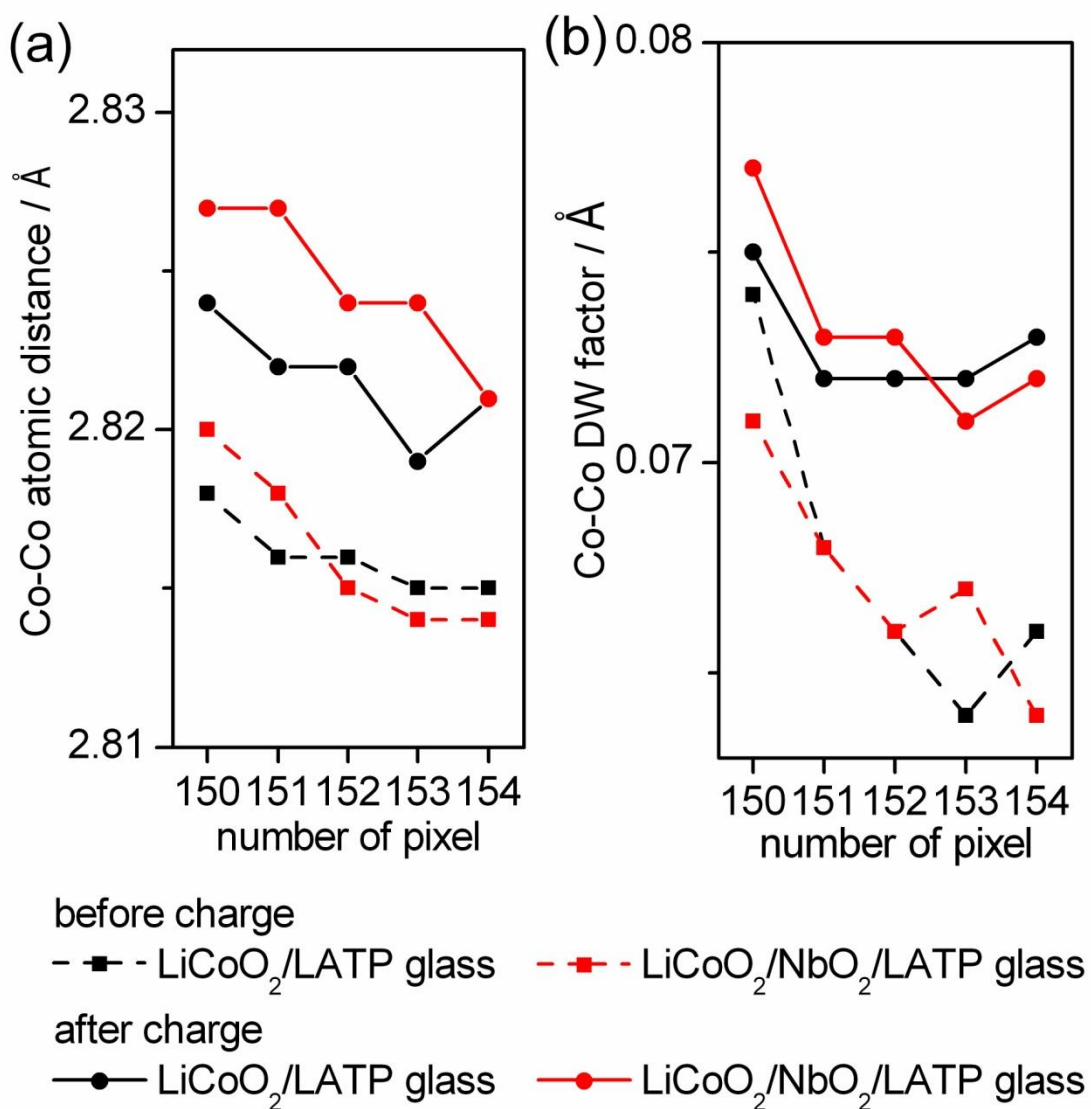


Figure S12. (a) Co-Co interatomic distance and (b) CoCo Debye-Waller factor for LiCoO₂/LATP-GC electrolyte and LiCoO₂/NbO₂/LATP-GC electrolyte observed at various PILATUS channels. Solid and dot lines show the parameters for after and before charge, respectively.