

## Supporting Information

### **Synergistic Effects of $\text{Li}_3\text{InCl}_6$ /VGCF Composite Coating on the Electrochemical Performance of Single-Crystalline $\text{LiNi}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.3}\text{O}_2$ Cathodes for All-Solid-State Lithium Batteries**

Yu-Han Tsai,<sup>a</sup> Celastin Bebina Thairiyarayar,<sup>a</sup> Cheng-Wei Kao,<sup>b</sup> Jeng-Kuei Chang,<sup>c</sup> Soorathep

Kheawhom,<sup>d</sup> Qunjie Xu<sup>e,f</sup> and Wei-Ren Liu<sup>a,d,\*</sup>

<sup>a</sup> Department of Chemical Engineering, R&D Center for Membrane Technology, Chung Yuan

Christian University, Taoyuan City, 320314, Taiwan

<sup>b</sup> National Synchrotron Radiation Research Center, Hsinchu, 30076, Taiwan

<sup>c</sup> Department of Materials Science and Engineering, National Yang Ming Chiao Tung

University, Hsinchu 30010, Taiwan

<sup>d</sup> Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University,

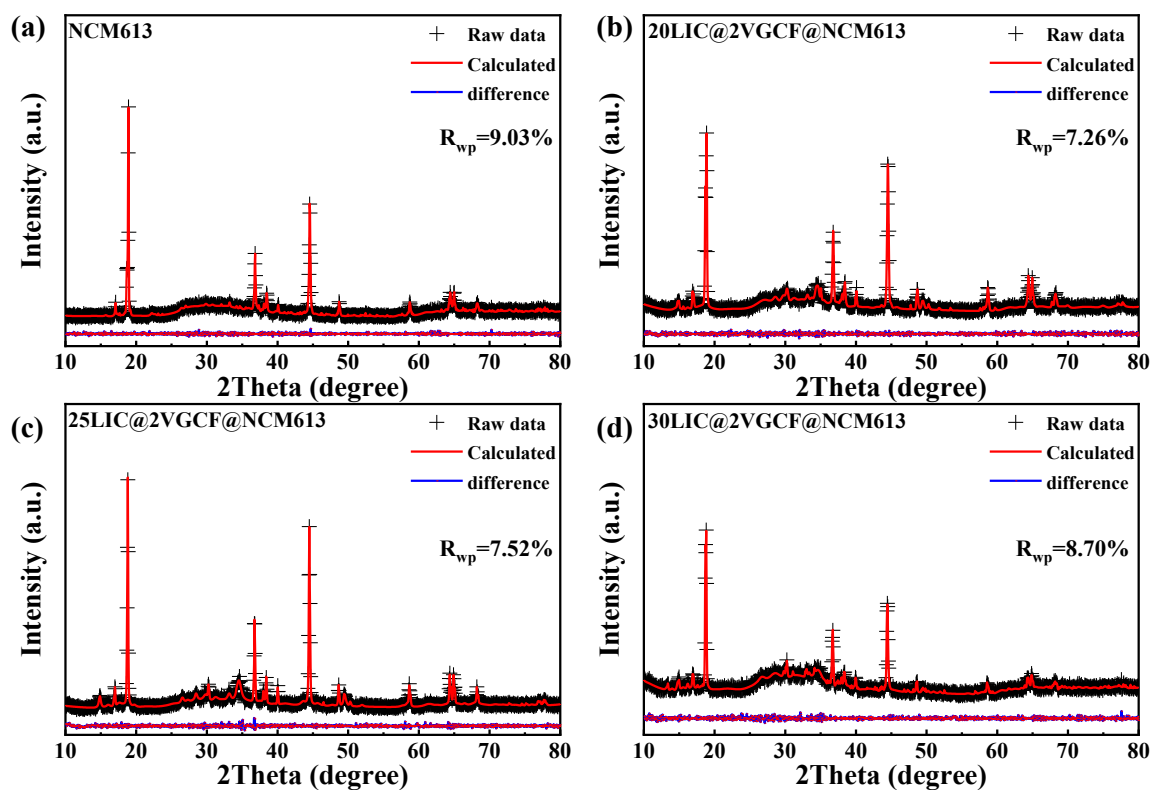
Bangkok, 10330, Thailand

<sup>e</sup> Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric

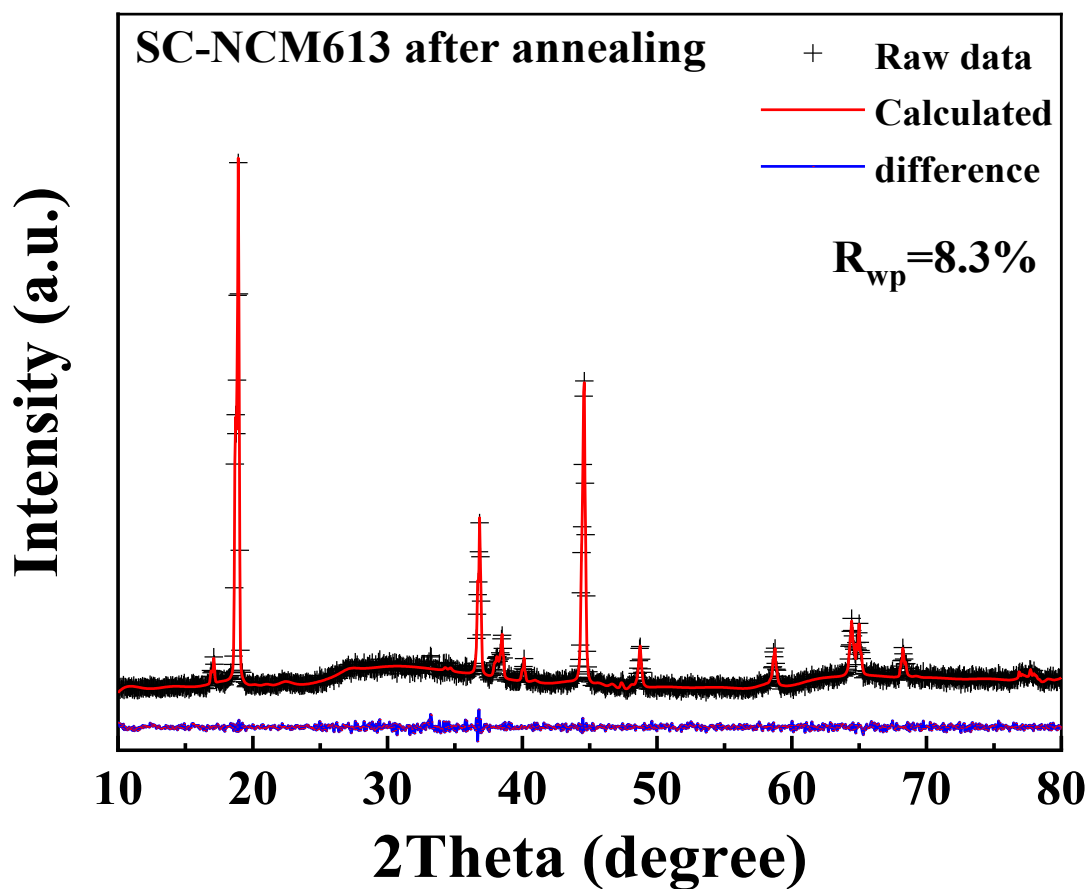
Power, Shanghai Engineering Research Center of Energy-Saving in Heat Exchange Systems,

Shanghai University of Electric Power, Shanghai 200090, China

<sup>f</sup> Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China



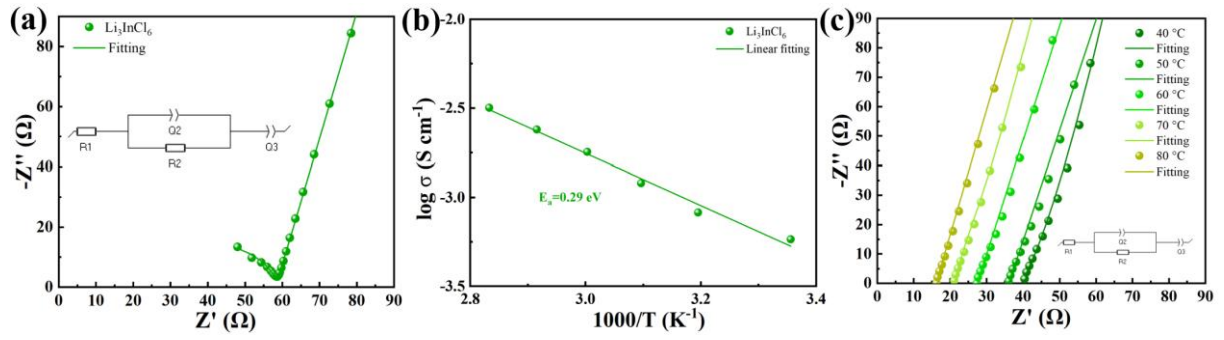
**Figure S1.** XRD Rietveld refinement profiles of SC-NCM613 cathode materials with varying  $\text{Li}_3\text{InCl}_6$  coating ratios using TOPAS software: (a) SC-NCM613; (b) 20LIC@2VGCF@NCM613; (c) 25LIC@2VGCF@NCM613; (d) 30LIC@2VGCF@NCM613.



**Figure S2.** XRD Rietveld refinement profiles of heat-treated SC-NCM613 cathode material using TOPAS software.

**Table S1.** Lattice parameters of heat-treated single-crystalline NCM613 determined by Rietveld refinement.

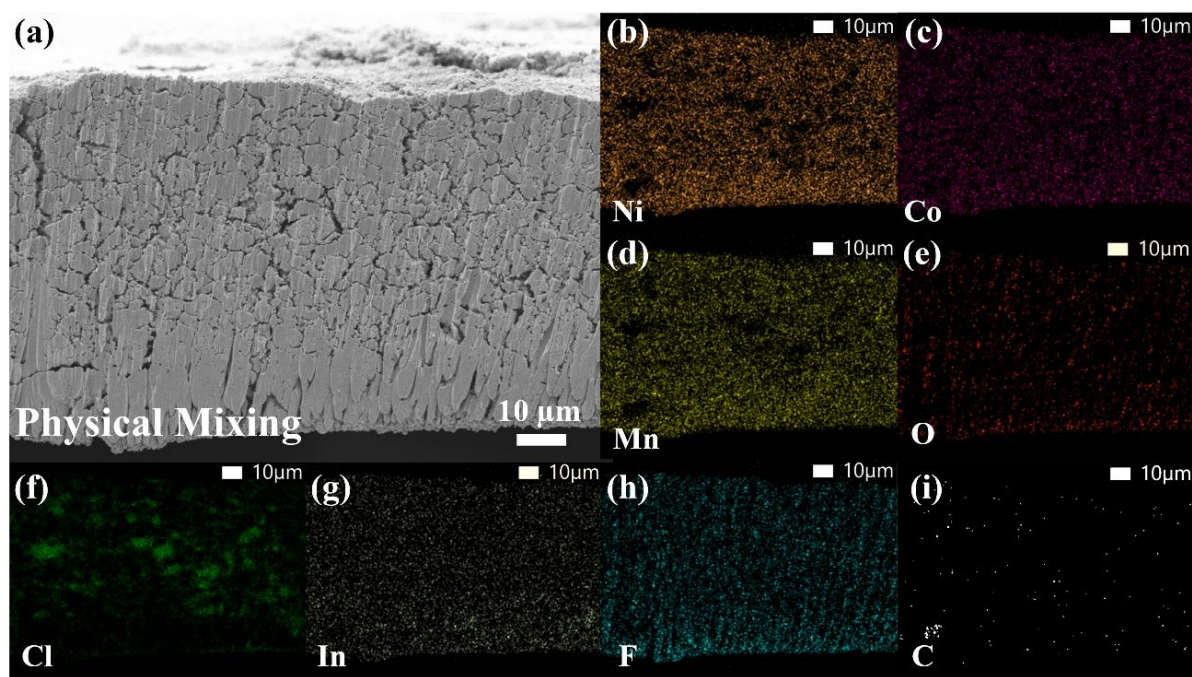
Samples	$a$ (Å)	$c$ (Å)	$c/a$	Cell Volume(Å <sup>3</sup> )	$R_{wp}$ (%)	$I_{(003)}/I_{(104)}$
NCM613 After annealing	2.868(7)	14.2070(6)	4.952	101.25(6)	8.302	1.6746



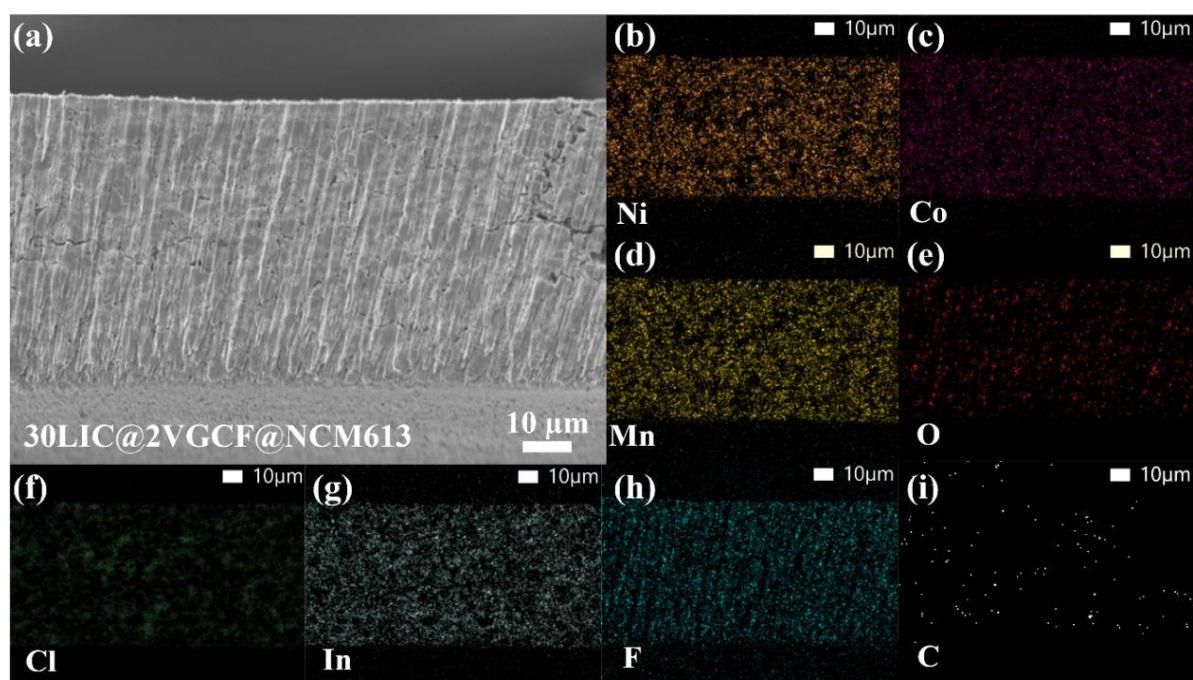
**Figure S3.** (a) Nyquist plots at RT, (b) Arrhenius plot and their corresponding Nyquist plot (c) at different temperatures of  $\text{Li}_3\text{InCl}_6$  (Inset: Equivalent circuit).

**Table S2.** Ionic conductivities and their resistance values of  $\text{Li}_3\text{InCl}_6$ .

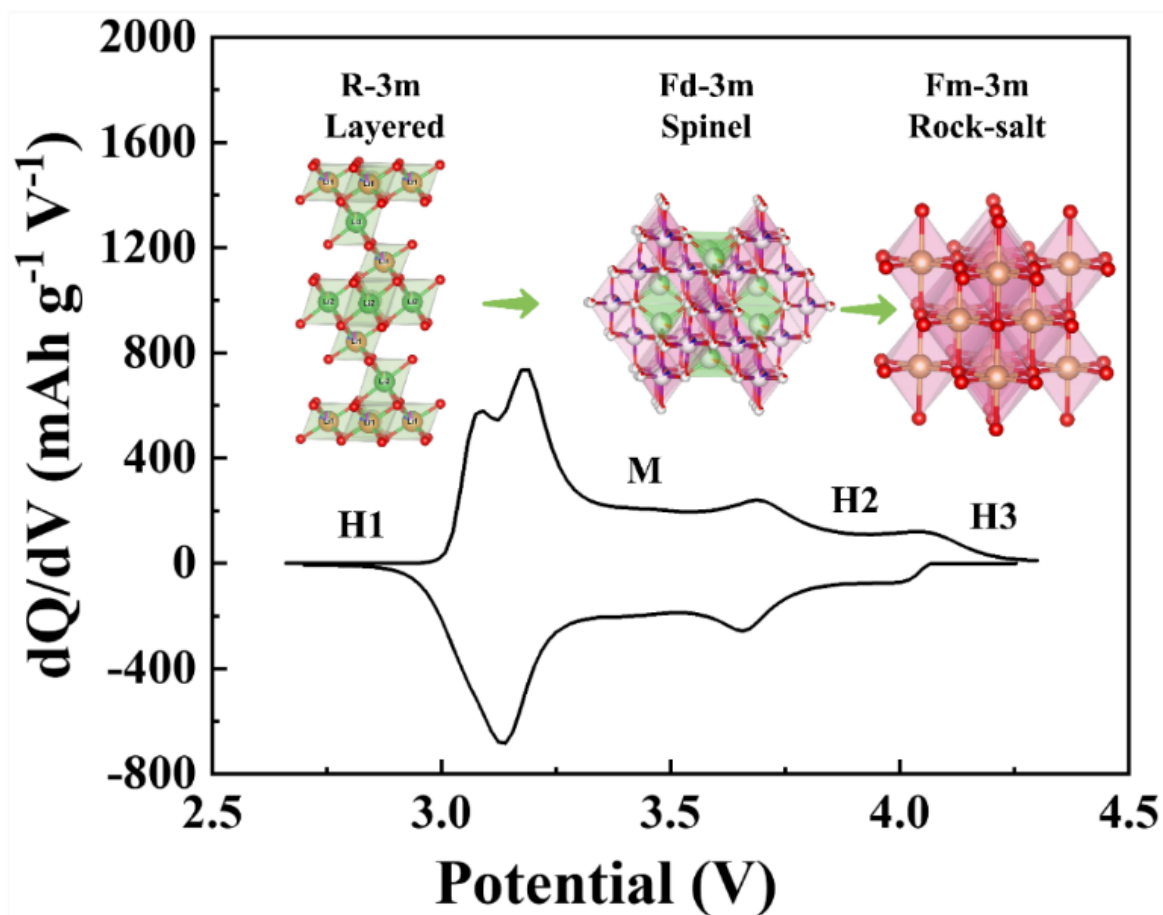
$\text{Li}_3\text{InCl}_6$	$R_1$ ( $\Omega$ )	$R_2$ ( $\Omega$ )	$R_{\text{tot}}=(R_1+R_2)$ ( $\Omega$ )	$L$ (cm)	Ionic conductivity ( $\times 10^{-3} \text{ S cm}^{-1}$ )
25 °C	25.76	32.51	58.27	0.062	1.355
40 °C	37.57	2.742	40.312	0.062	1.958
50 °C	30.12	5.793	35.913	0.062	2.198
60 °C	25.69	1.871	27.561	0.062	2.864
70 °C	21.15	2.986	24.136	0.062	3.271
80 °C	15.53	0.63	16.16	0.062	4.885



**Figure S4.** Composite cathode prepared by physical mixing: (a) scanning electron microscopy (SEM) image; (b–i) energy-dispersive X-ray spectroscopy (EDS) elemental maps for (b) Ni, (c) Co, (d) Mn, (e) O, (f) Cl, (g) In, (h) F, and (i) C.

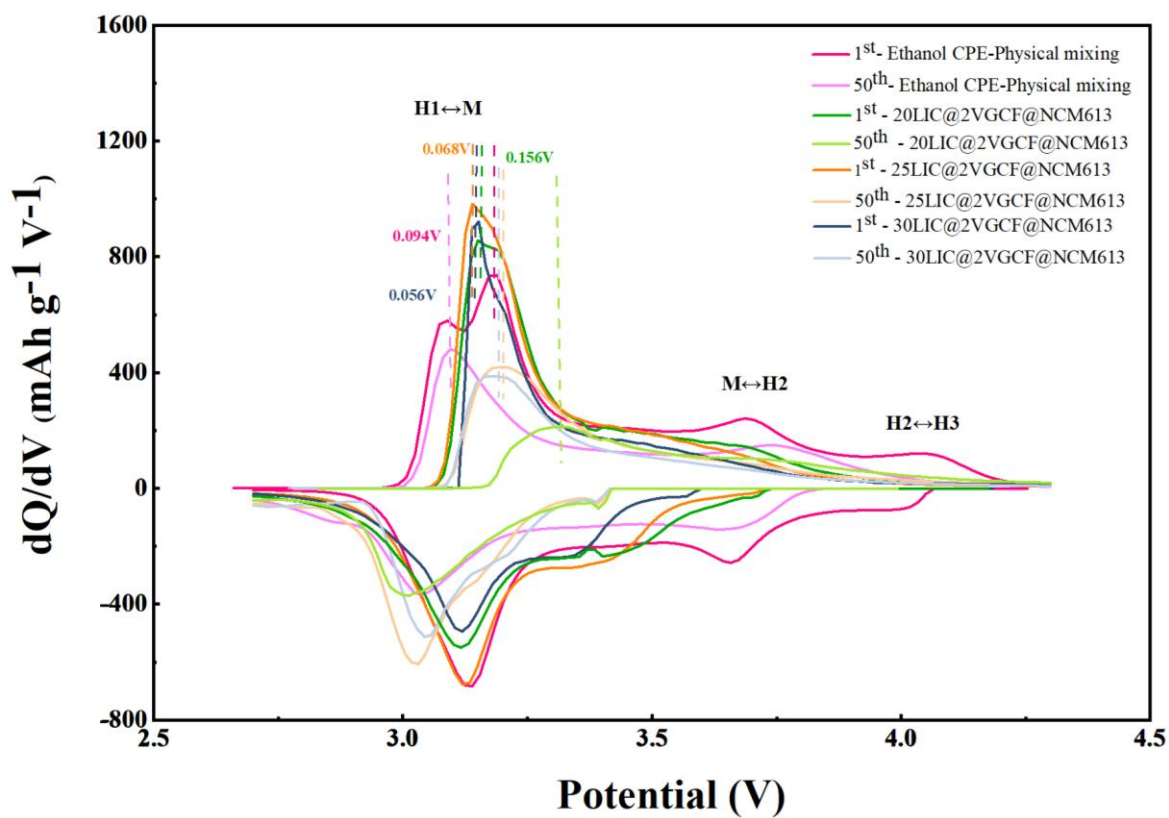


**Figure S5.** 30LIC@2VGCF@NCM613-prepared composite cathode: (a) scanning electron microscopy (SEM) image; (b–i) energy-dispersive X-ray spectroscopy (EDS) elemental maps of (b) Ni, (c) Co, (d) Mn, (e) O, (f) Cl, (g) In, (h) F, and (i) C.



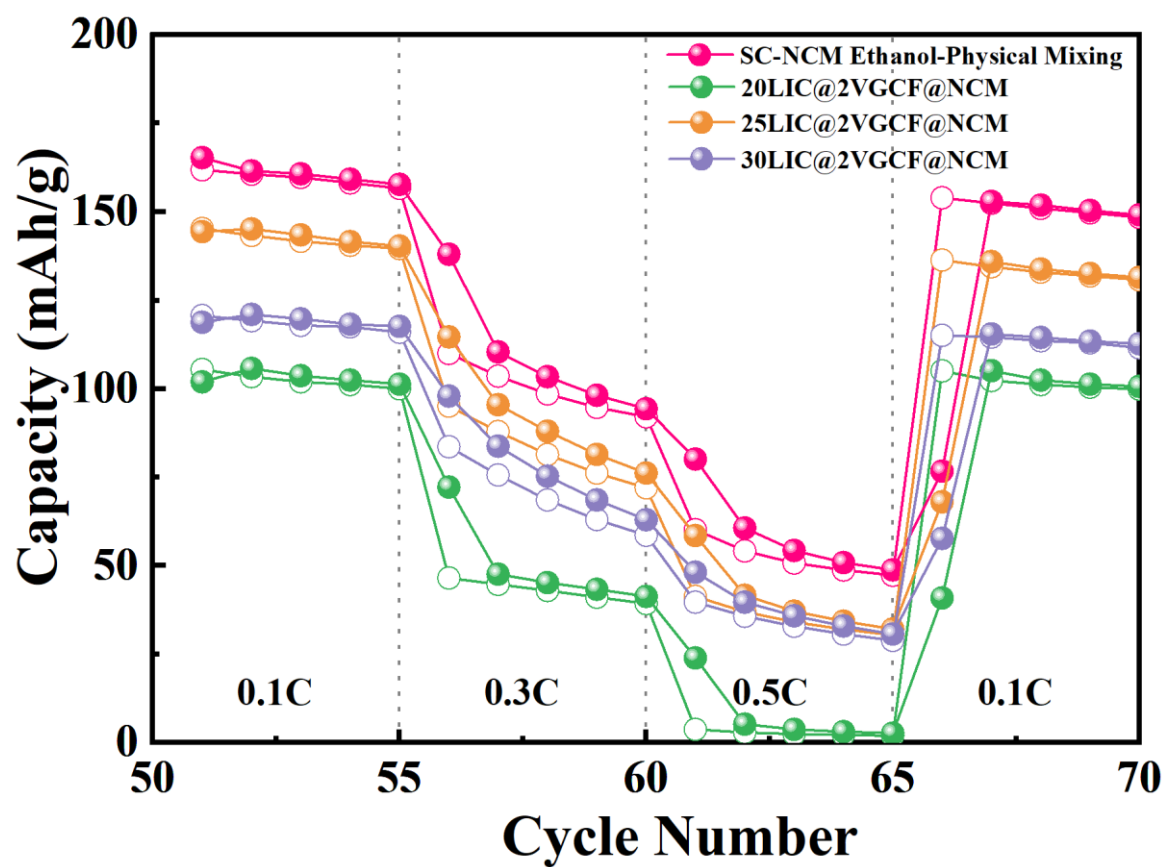
**Figure S6.** Schematic illustration of the phase-transition and corresponding microstructural evolution of the SC-NCM613 ( $\text{LiNi}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.3}\text{O}_2$ ) composite cathode during the first charge–discharge cycle.



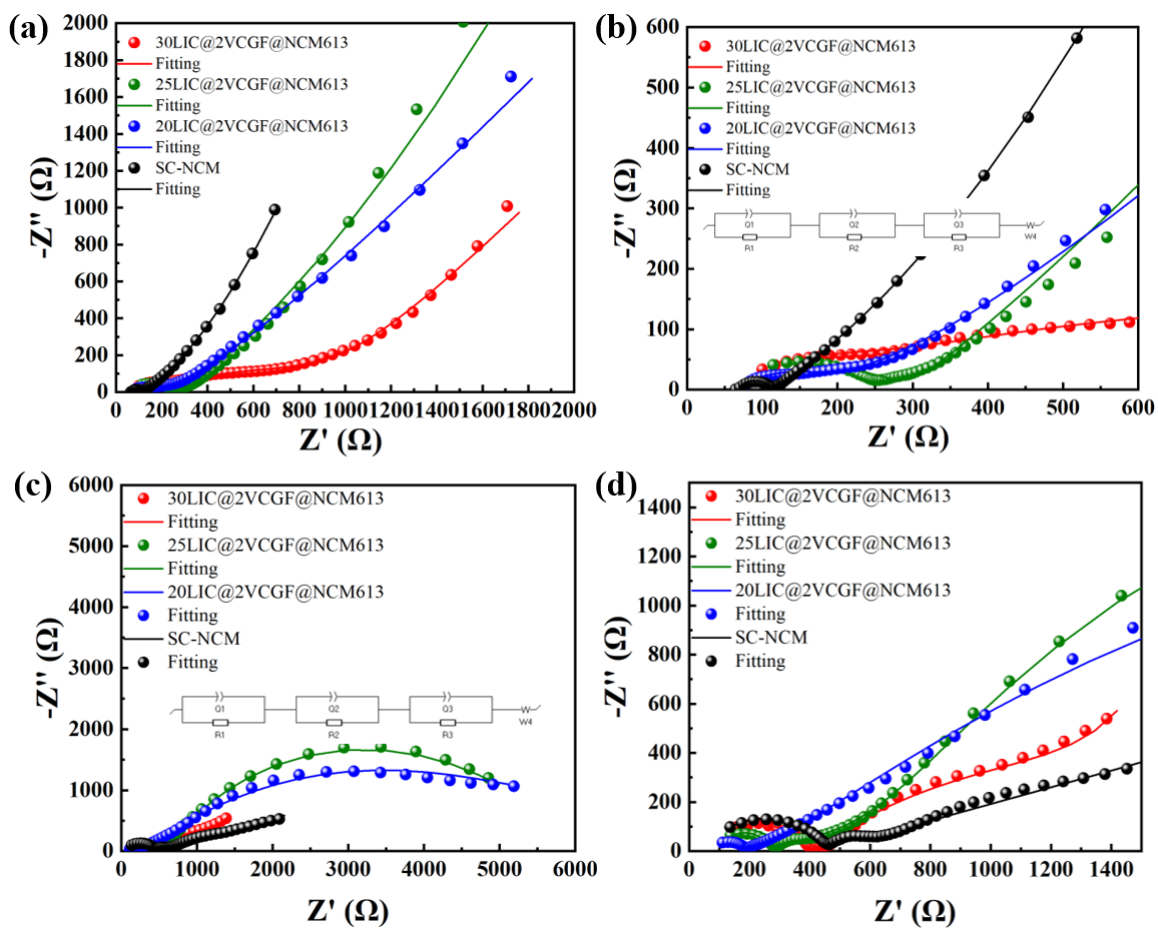


**Figure S7.** Comparison of derivative capacity ( $dQ/dV$ ) plots of SC-NCM613 (Ethanol CPE-Physical mixing) and coated with varying  $\text{Li}_3\text{InCl}_6$  ratios during 1<sup>st</sup> and 50<sup>th</sup> cycles.

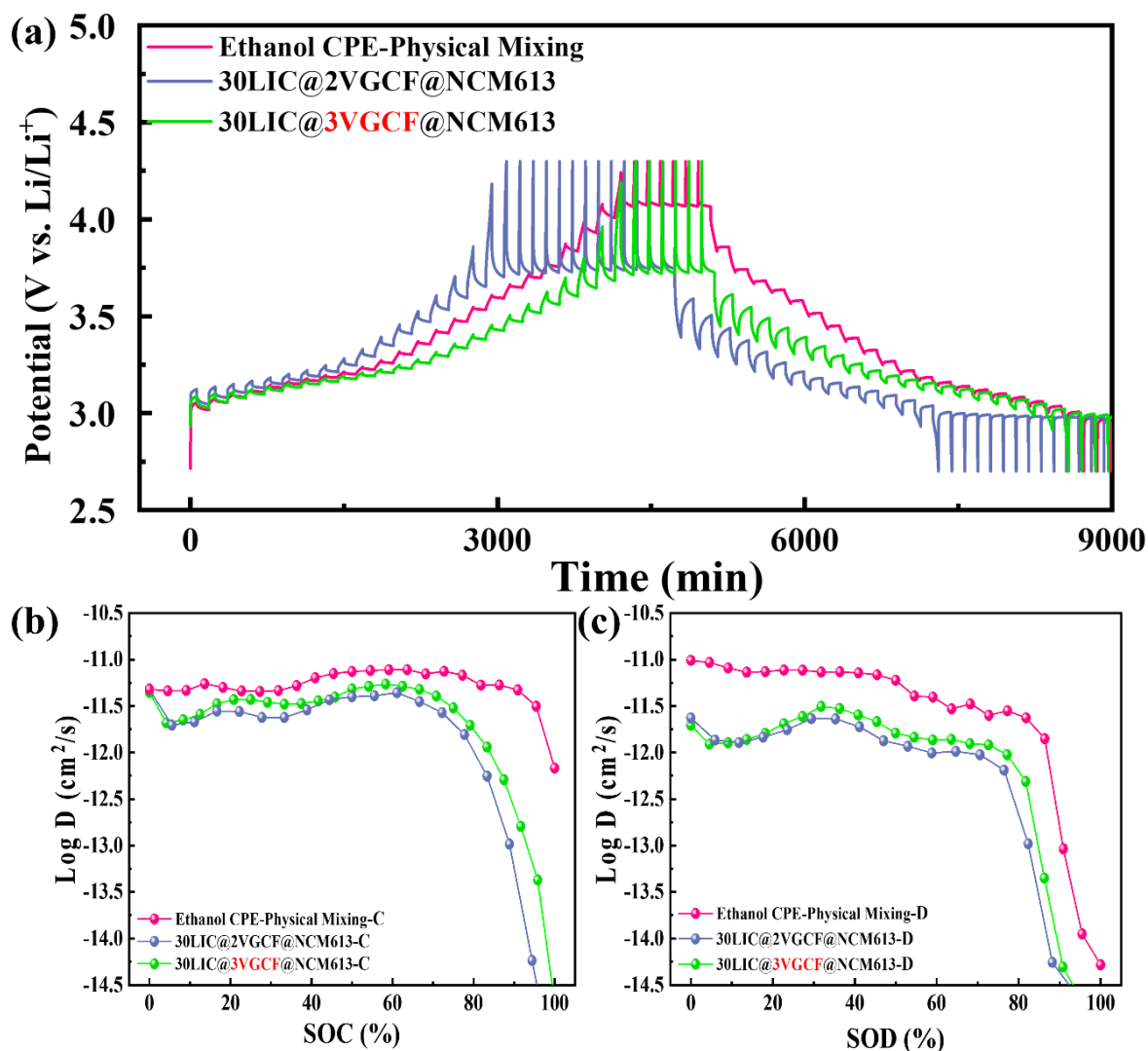




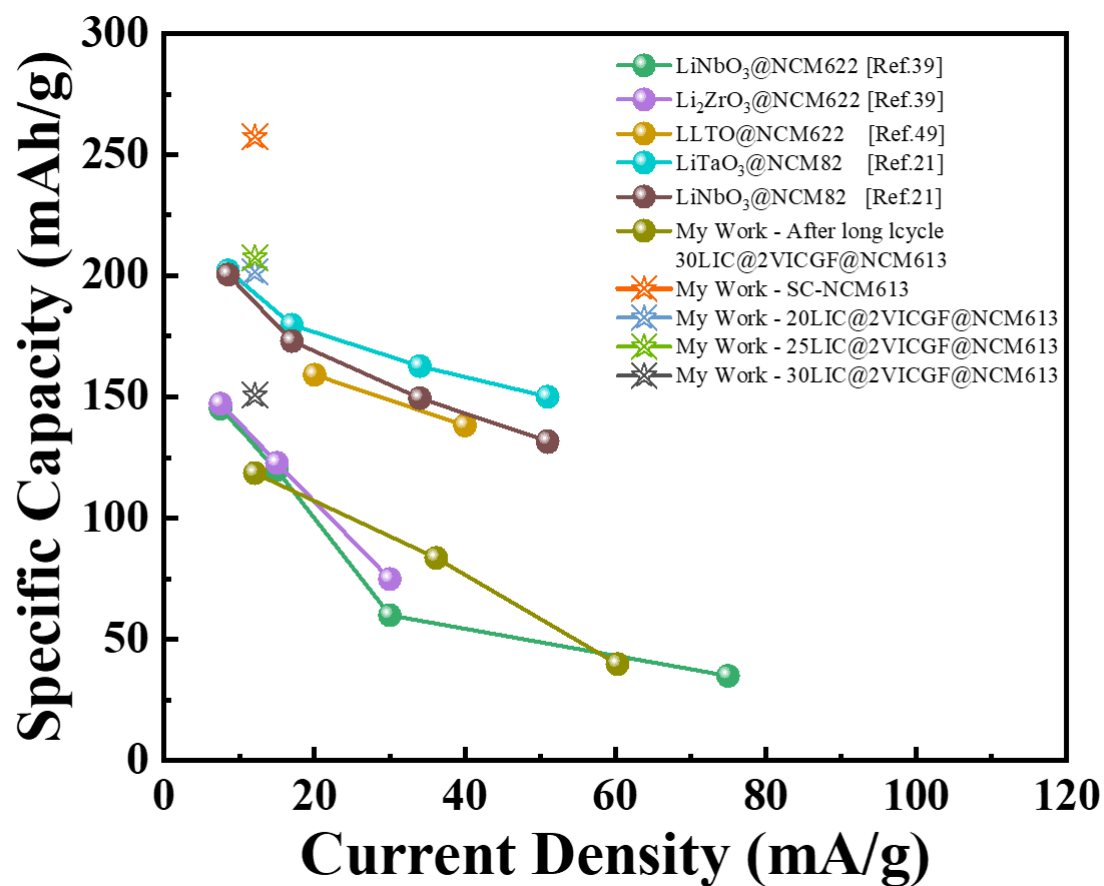
**Figure S8.** Rate capability tests of SC-NCM613 and coated with varying  $\text{Li}_3\text{InCl}_6$  ratios after 50 cycles.



**Figure S9.** Nyquist plots of before (a) - (b) enlarged view and after (c) - (d) enlarged view of SC-NCM613 coated with varying  $\text{Li}_3\text{InCl}_6$  ratios at 10 cycles (Inset: Equivalent circuit).



**Figure S10.** (a) GITT test results during the first cycle for the physically mixed SC-NCM613 composite cathode material, and the NCM@2VGCF@30LIC and NCM@3VGCF@30LIC cathode materials; (b) the corresponding lithium-ion diffusion coefficients ( $D_{Li^+}$ ) during the charging process; (c) the corresponding lithium-ion diffusion coefficients ( $D_{Li^+}$ ) during the discharging process.



**Figure S11.** Comparative study of specific capacities between literature reports and present results.