

## **Supporting Information**

# **Quasi-Solid-State Lithium Metal Batteries Using the $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2-\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ Composite Positive Electrode**

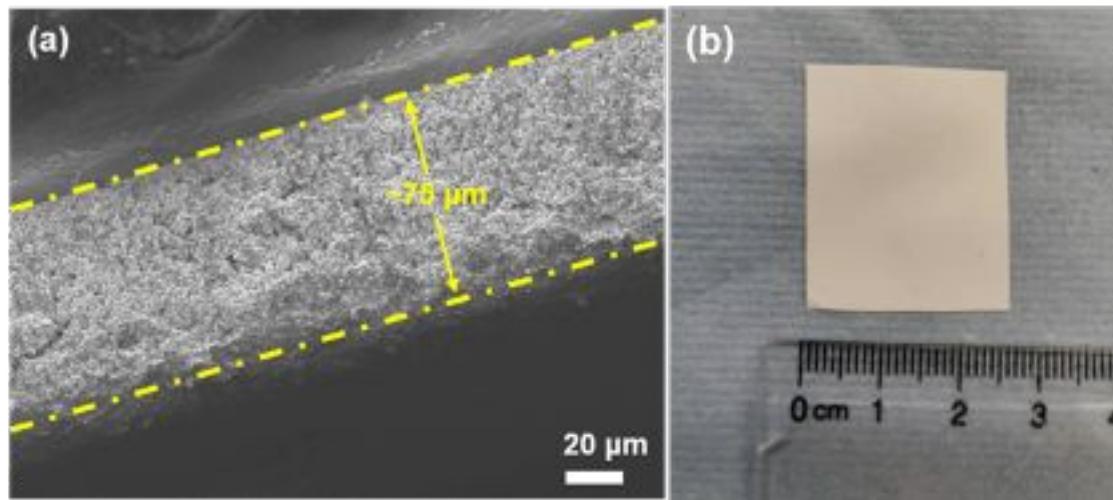
*Zhen Chen,<sup>#,§</sup> Xinpei Gao,<sup>#,§</sup> Jae-Kwang Kim,<sup>‡</sup> Guk-Tae Kim,<sup>#,§,\*</sup> Stefano Passerini,<sup>#,§,\*</sup>*

*<sup>#</sup> Helmholtz Institute Ulm (HIU), 89081 Ulm, Germany.*

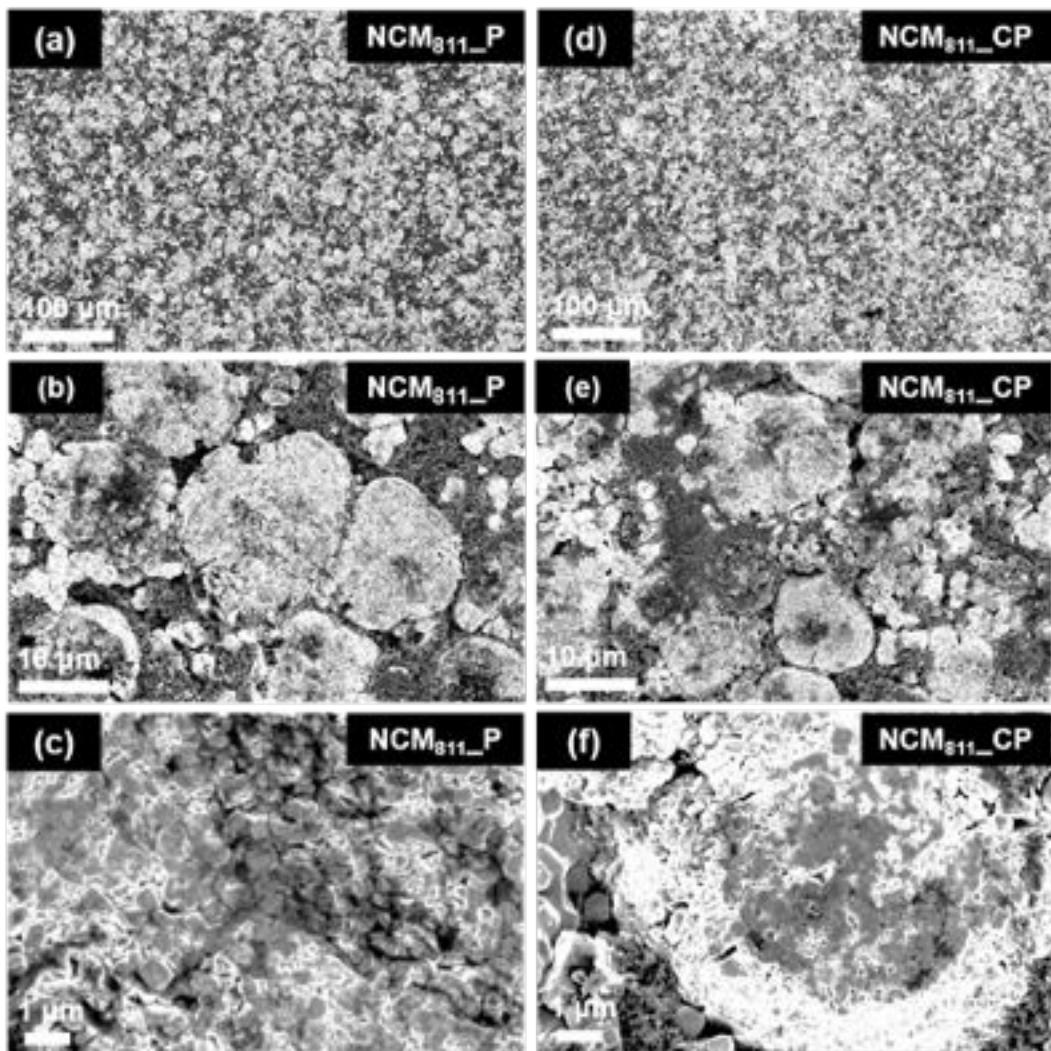
*<sup>§</sup> Karlsruhe Institute of Technology (KIT), 76021 Karlsruhe, Germany.*

*<sup>‡</sup> Department of Energy Convergence Engineering, Cheongju University, Cheongju, Chungbuk 28503, Republic of Korea*

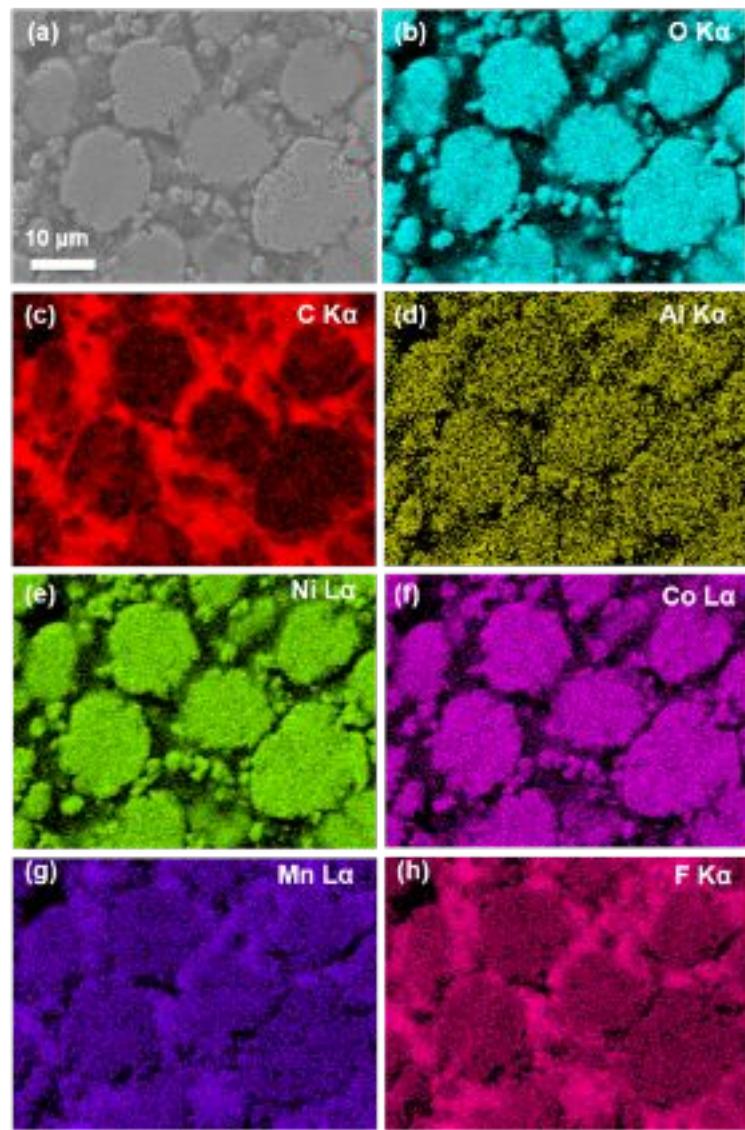
***Corresponding authors:** guk-tae.kim@kit.edu; stefano.passerini@kit.edu*



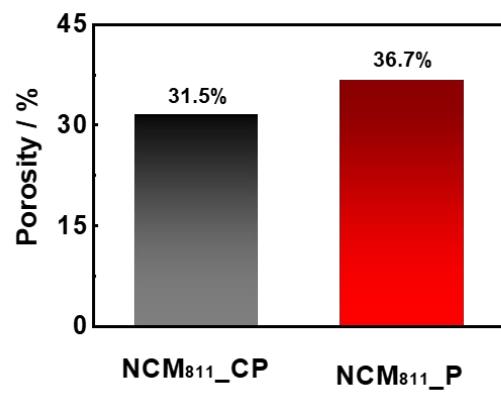
**Figure S1.** (a) The cross-sectional view and (b) a digital photo of a piece of LATP/PVDF-TrFE/ILE hybrid electrolyte.



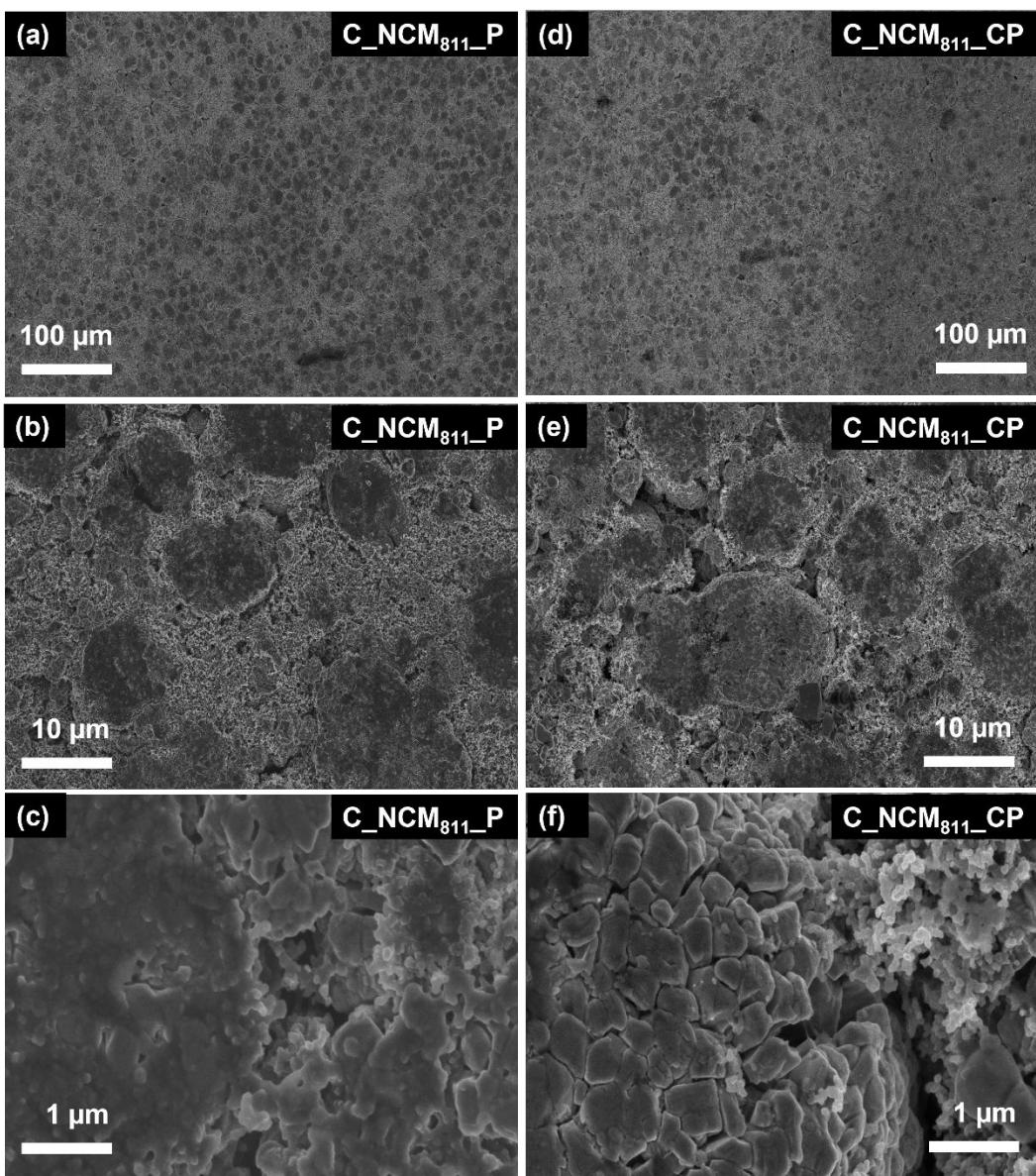
**Figure S2.** SEM images of pristine (a–c) NCM<sub>811</sub>\_P and (d–f) NCM<sub>811</sub>\_CP electrodes.



**Figure S3.** (a) SEM image and corresponding elemental EDS mapping of a pristine NCM<sub>811</sub>\_P electrode: (b) O K $\alpha$ , (c) C K $\alpha$ , (d) Al K $\alpha$ , (e) Ni L $\alpha$ , (f) Co L $\alpha$ , (g) Mn L $\alpha$  and (h) F K $\alpha$ .



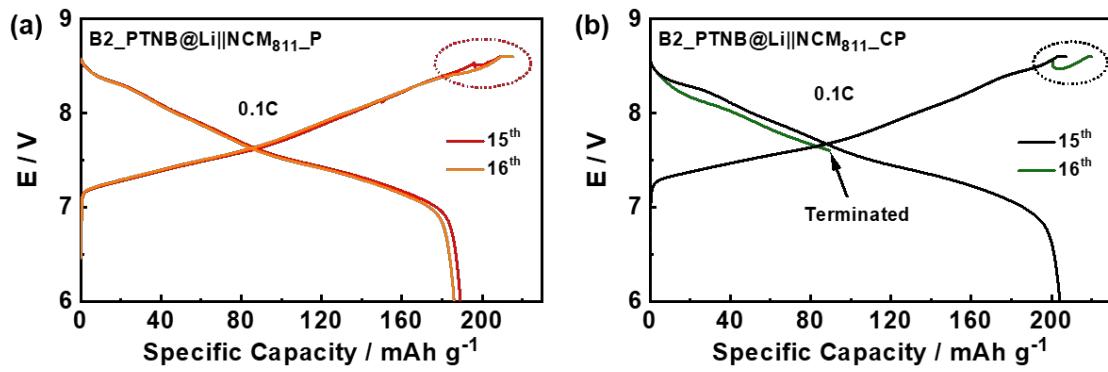
**Figure S4.** Comparison of electrode porosity of pristine NCM<sub>811</sub>\_CP and NCM<sub>811</sub>\_P electrodes.



**Figure S5.** Ex situ electrode morphology investigation of (a–c) cycled  $\text{NCM}_{811}\text{-P}$  (denoted as  $\text{C}_\text{-}\text{NCM}_{811}\text{-P}$ ) and (d–f) cycled  $\text{NCM}_{811}\text{-CP}$  (denoted as  $\text{C}_\text{-}\text{NCM}_{811}\text{-CP}$ ) electrodes recovered from  $\text{PTNB@Li}||\text{NCM}_{811}\text{-P}$  and  $\text{PTNB@Li}||\text{NCM}_{811}\text{-CP}$  cells after 200 cycles at 0.5C, respectively.



**Figure S6.** A digital photo showing the open circuit voltage of a fresh 2-layer bipolar stacked cell.



**Figure S7.** Dis-/charge voltage profiles of 15<sup>th</sup> and 16<sup>th</sup> cycles of (a) B2\_PTNB@Li||NCM<sub>811</sub>\_P and (b) B2\_PTNB@Li||NCM<sub>811</sub>\_CP bipolar cells.

**Table S1.** The ILE volume percentage within the NCM<sub>811</sub>\_P and NCM<sub>811</sub>\_CP composite electrodes.

Sample	Electrode weight (mg)	Electrode thickness (μm)	Electrode volume <sup>a</sup> (excl. Al, cm <sup>3</sup> )	Electrode weight with ILE (mg)	ILE volume <sup>b</sup> (cm <sup>3</sup> )	ILE volume (vol.%)
NCM <sub>811</sub> P	7.44	24	0.000904	7.81	0.000246	27.2
NCM <sub>811</sub> CP	7.71	25	0.001017	8.13	0.000279	27.5

<sup>a</sup> the thickness of Al current collector is 16 μm; <sup>b</sup> the molecular density of ILE is 1.504 g/cm<sup>3</sup>

**Table S2.** Detailed information for the calculation of the NCM<sub>811</sub>\_P electrode porosity.

	Mass fraction (wt.%)	Mass (g)	Theoretical density (g cm <sup>-3</sup> )	Practical volume (cm <sup>3</sup> )	Theoretical volume (cm <sup>3</sup> )	Porosity (%)
NCM <sub>811</sub>	92	0.002462	4.70			
Super C65	4	0.000107	1.60	0.001029	0.000651	36.7
PVDF	4	0.000107	1.78			

**Table S3.** The detailed information for the calculation of the NCM<sub>811</sub>\_CP electrode porosity.

	Mass fraction (wt.%)	Mass (g)	Theoretical density (g cm <sup>-3</sup> )	Practical volume (cm <sup>3</sup> )	Theoretical volume (cm <sup>3</sup> )	Porosity (%)
NCM <sub>811</sub>	82	0.002476	4.70			
Super C65	4	0.000121	1.60			
PVDF	4	0.000121	1.78	0.001130	0.000774	31.5
LATP	10	0.000302	2.92			

**Table S4.** The Z' values collected at 60.9 kHz, 226.2 Hz and 2.7 Hz upon various cycling numbers.

Cycle number	PTNB@Li  NCM <sub>811</sub> _P			PTNB@Li  NCM <sub>811</sub> _CP		
	Z' (60.9 kHz) / Ω	Z' (226.2 Hz) / Ω	Z' (2.7 Hz) / Ω	Z' (60.9 kHz) / Ω	Z' (226.2 Hz) / Ω	Z' (2.7 Hz) / Ω
20 <sup>th</sup>	14.6	30.7	42.1	14.2	27.2	39.7
40 <sup>th</sup>	14.3	28.8	39.3	14.0	25.1	36.1
60 <sup>th</sup>	14.2	28.0	38.4	14.1	24.4	35.0
80 <sup>th</sup>	14.2	27.5	38.0	13.7	23.6	33.8
100 <sup>th</sup>	14.3	27.4	38.2	14.0	23.4	33.8
120 <sup>th</sup>	14.5	27.5	38.6	14.0	23.1	33.5
140 <sup>th</sup>	14.5	27.6	39.2	14.1	22.9	33.7
160 <sup>th</sup>	14.7	28.1	40.3	14.1	22.8	34.0
180 <sup>th</sup>	14.9	28.5	41.5	14.2	22.8	34.4
200 <sup>th</sup>	15.2	29.2	42.9	14.4	22.8	34.9