Supporting Information

Revealing the multi-functions of Li_3N in the suspension electrolyte for lithium metal batteries

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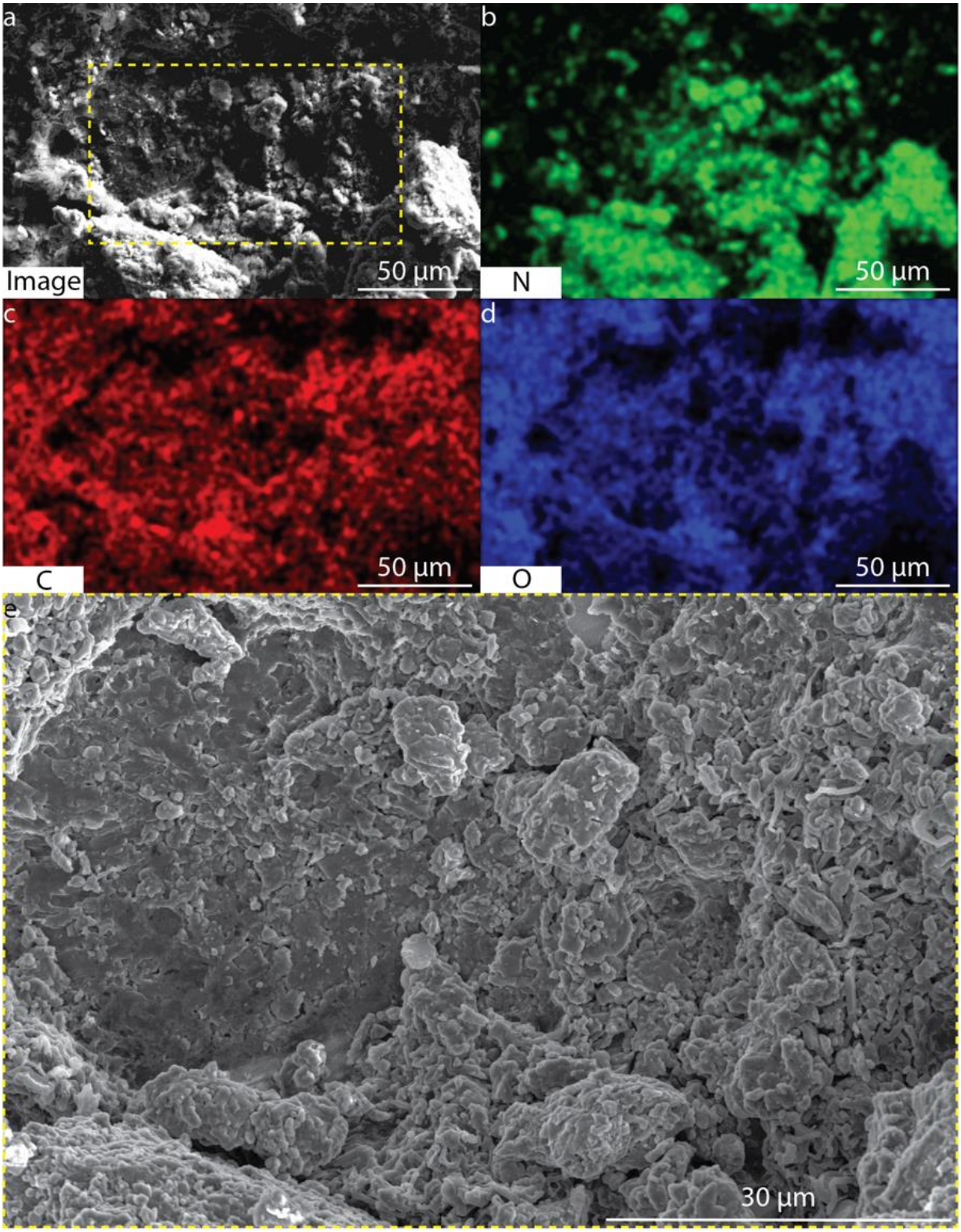

Figure S1. SEM image (a) of Li^0 electrodeposits on Cu from Li|Cu cell with Li_3N SE at 1 mA cm^{-2} and 1 mAh cm^{-2} with elemental mapping of nitrogen (b), carbon (c), and oxygen (d) obtained from energy-dispersive x-ray spectroscopy. (e) is the higher magnification SEM image of (a) demarcated by the dashed rectangle region.

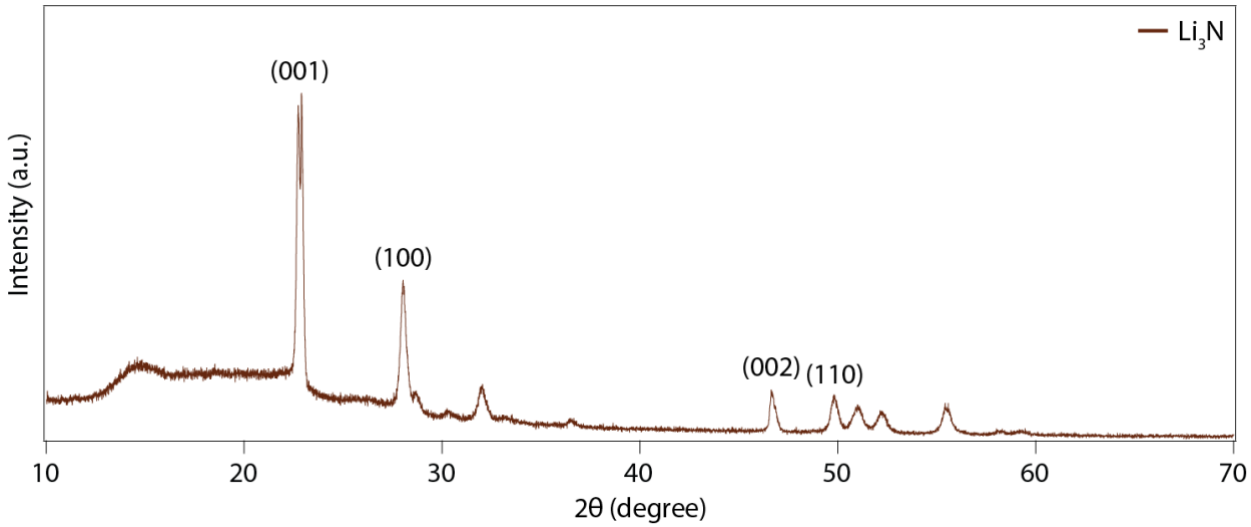

Figure S2. XRD measurement of Li_3N nanopowders. The observed surface structures were Li_3N (001), (100), (002), and (110) surfaces.

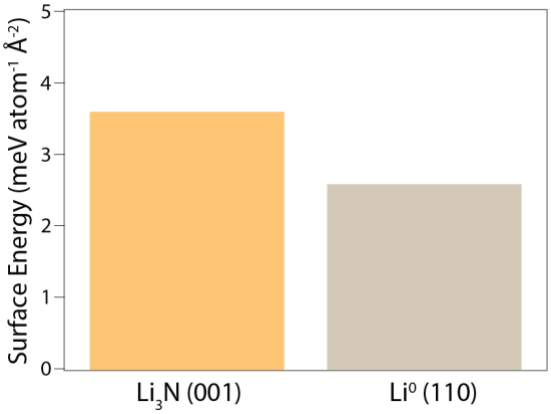

Figure S3. Computed surface energies of Li_3N (001) and Li^0 (110) *via* first-principles calculations.

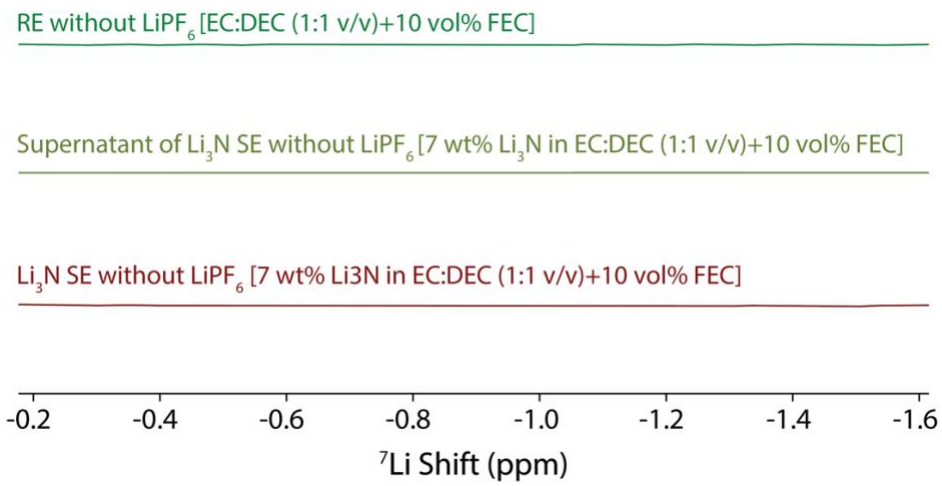

Figure S4. ^7Li NMR spectra of RE and Li_3N SE without $LiPF_6$.

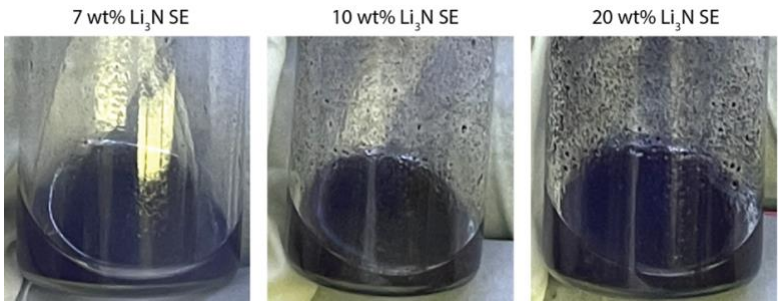

Figure S5. Physical images of 7 wt%, 10 wt%, and 20 wt% Li_3N SE.

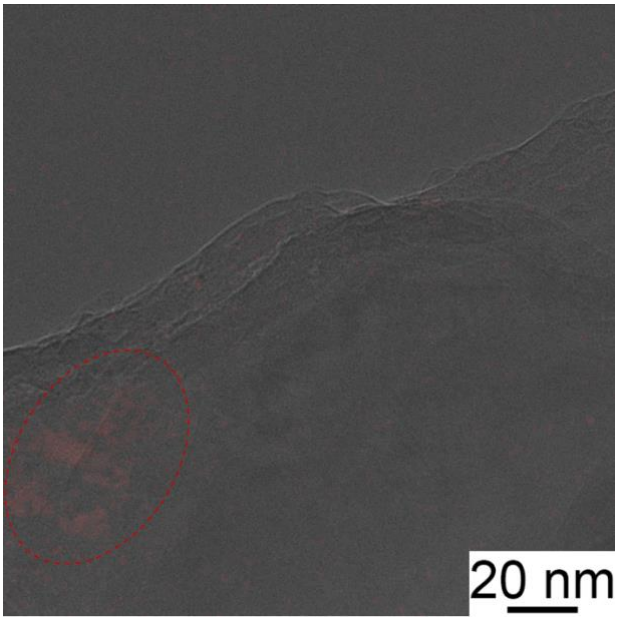

Figure S6. Overlayed inverse FFT of Figure 4d inset indicating the observed Li_3N lattice (marked by the red dashed circle) in the electrodeposited Li^0.

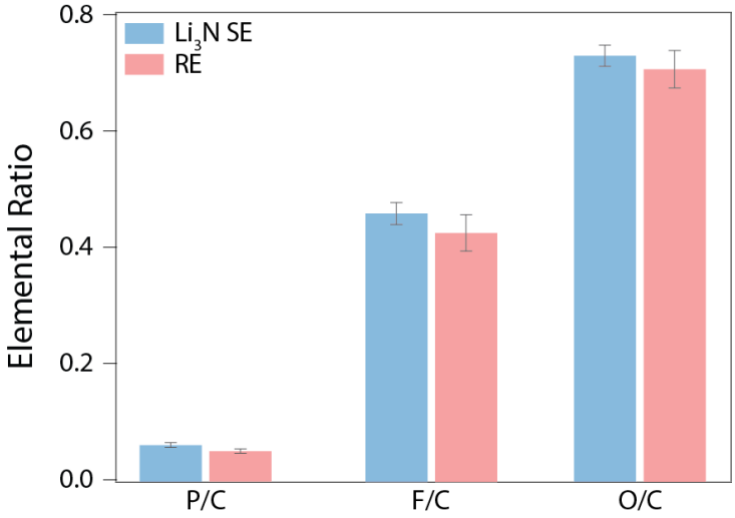

Figure S7. Calculated P/C, F/C, and O/C ratios from XPS survey scans for electrodeposited Li^0 with RE and Li_3N SE. Three measurements were taken at different sports from the sample to obtain the standard errors of the elemental ratios.

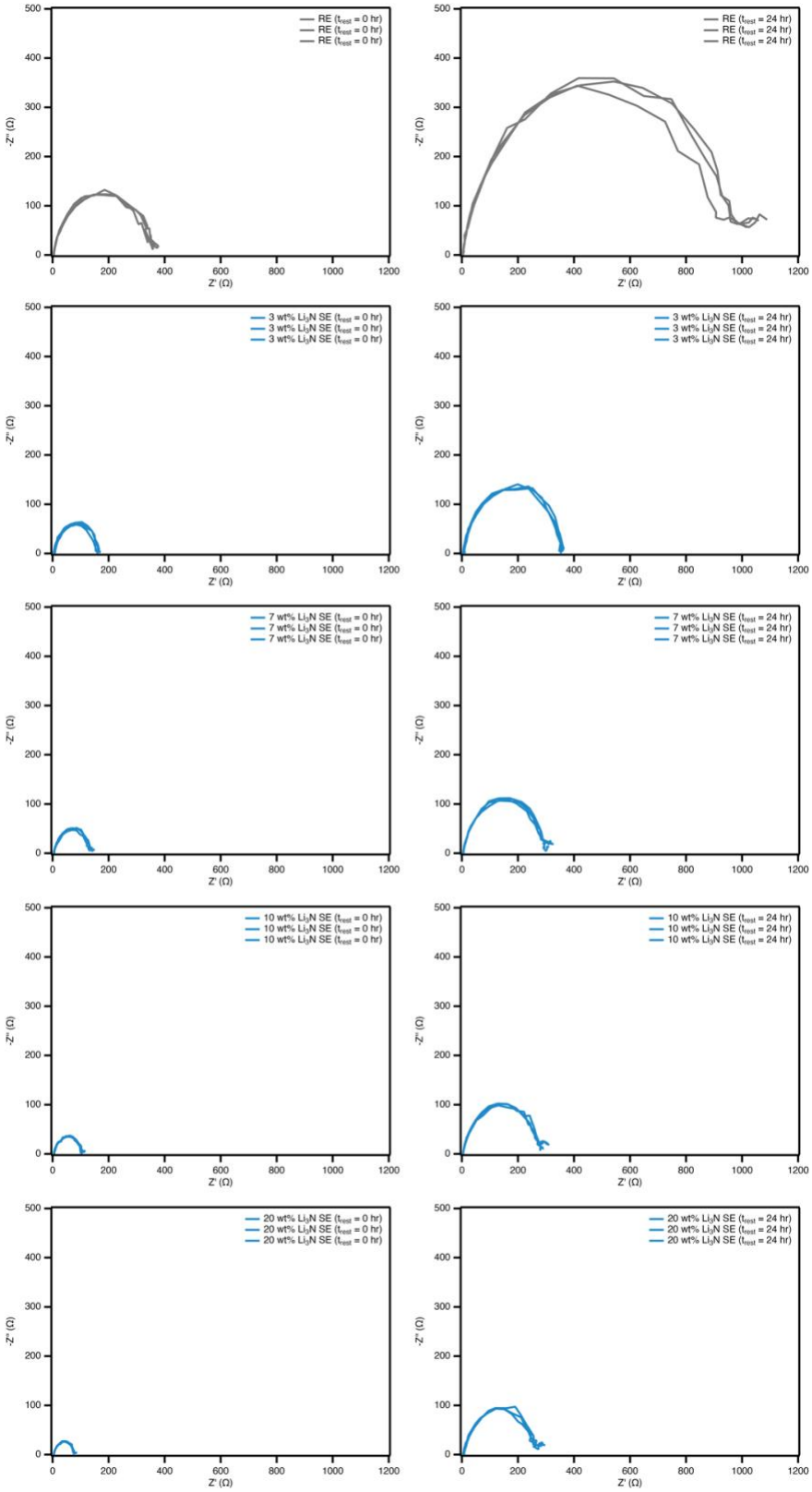

Figure S8. Nyquist plots of Li|Li cells with 0 wt% (RE) ~ 20 wt% Li_3N SE measured before (t_{rest} = 0 hr) and after ageing time (t_{rest} = 24 hrs).

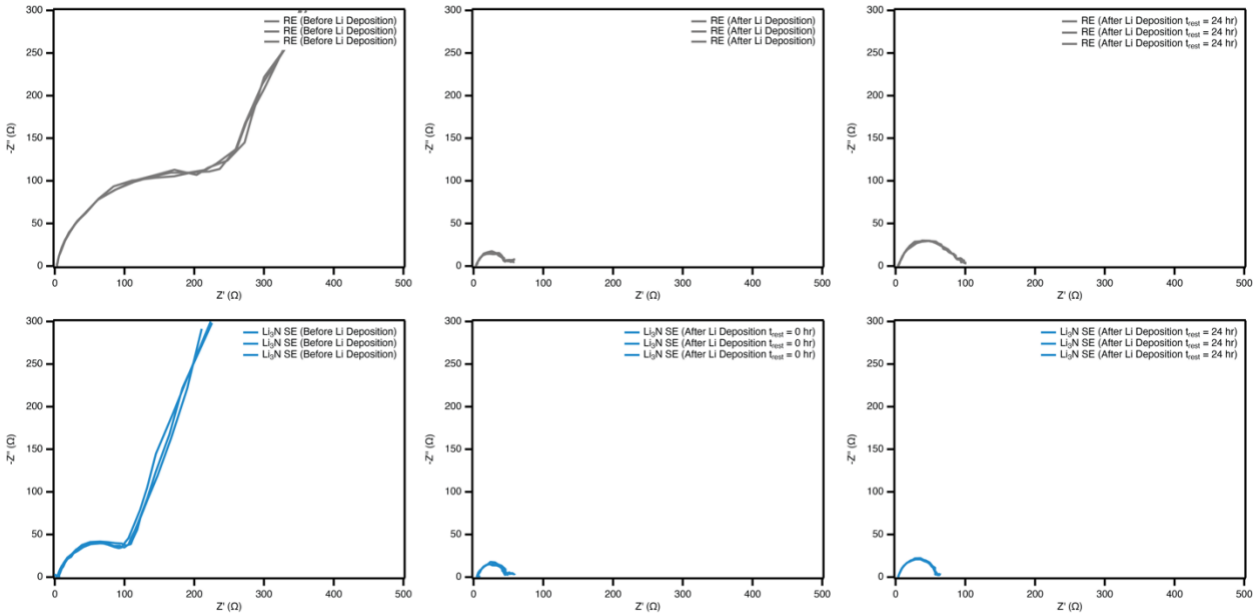

Figure S9. Nyquist plots of Li|Cu cells with RE and Li_3N SE measured before and after Li^0 electrodeposition (1 mAh cm^{-2} & 1 mA cm^{-2}) at t_{rest} = 0 hr and after ageing electrodeposited Li^0 at t_{rest} = 24 hrs.

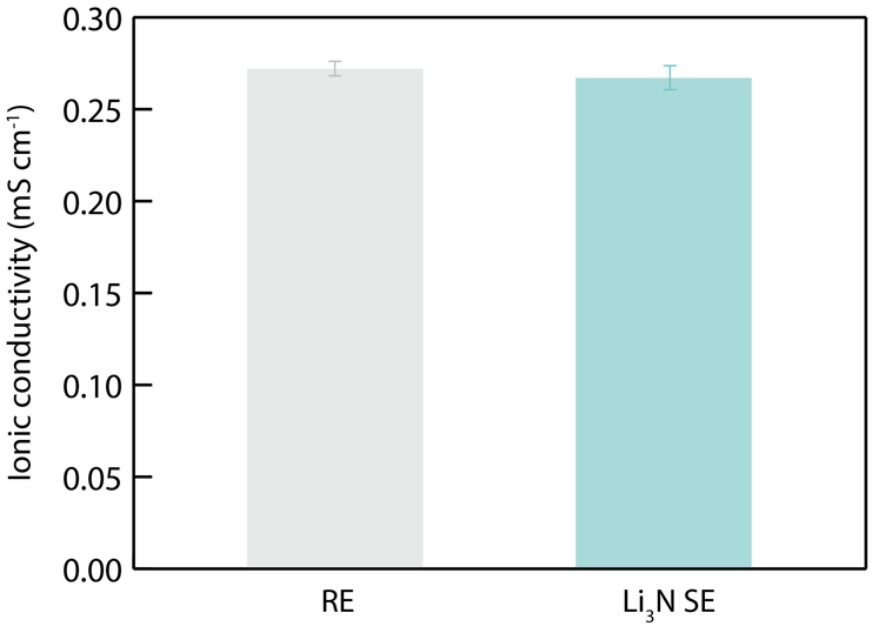

Figure S10. Ionic conductivity of RE (0.272 ± 0.008 mS cm^{-1}) and Li_3N SE (0.261 ± 0.013 mS cm^{-1}).

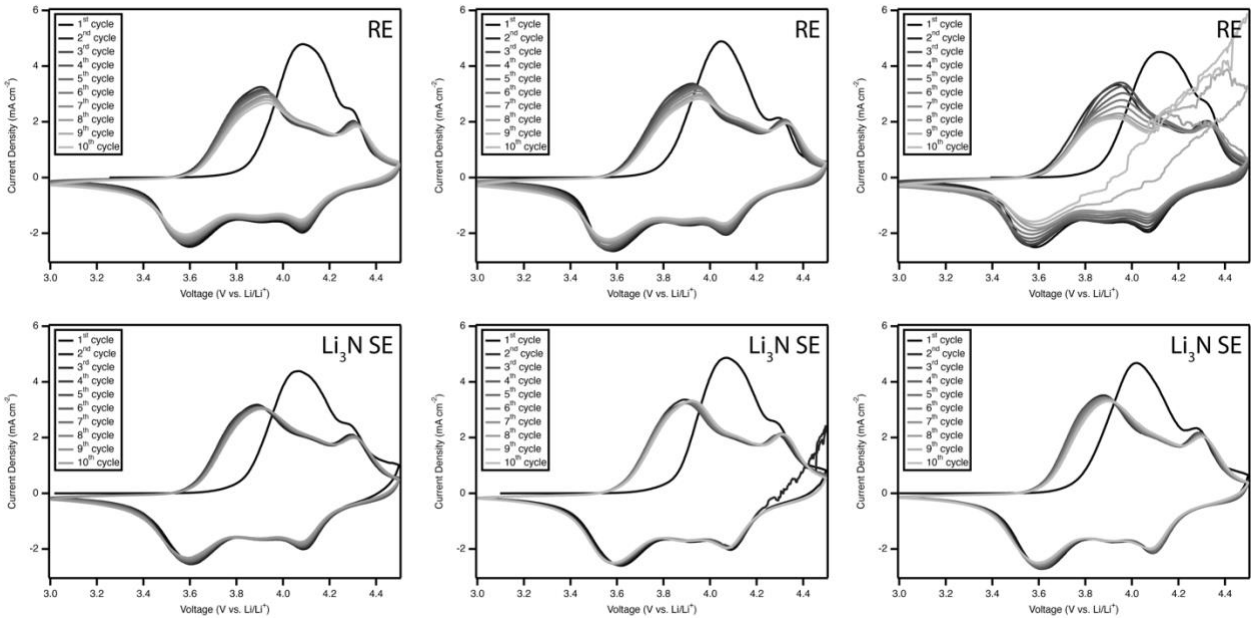

Figure S11. Cyclic voltammograms of first 10 cycles measured from Li|$Li_1Ni_{0.8}Co_{0.1}Mn_{0.1}$ cells with RE and Li_3N SE. Three identical Li|$Li_1Ni_{0.8}Co_{0.1}Mn_{0.1}$ cells were measured from each of the electrolytes. The voltage window and scan rate were 3.0 V – 4.5 V vs. Li/Li^+ and 0.1 mV s^{-1}.

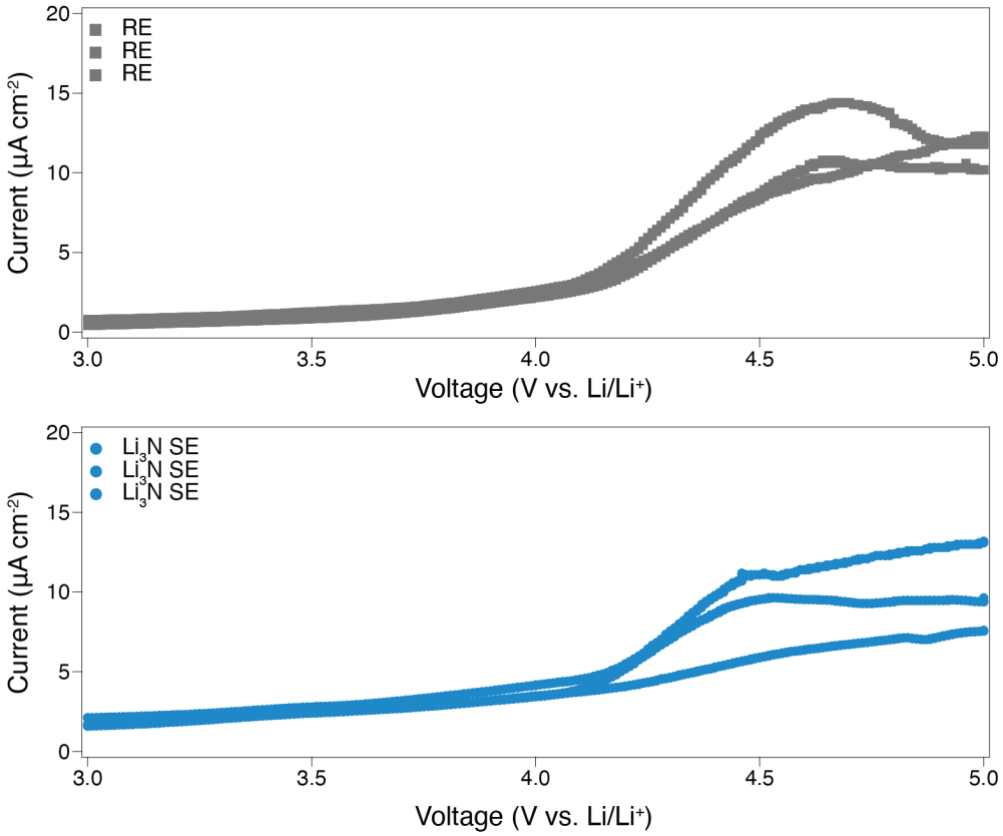

Figure S12. Linear sweep voltammetry measured from Li|Al cells with RE and Li_3N SE. Three identical Li|Al cells were measured from each of the electrolytes. The recorded voltage window and sweep rate were 3.0 V – 5.0 V vs. Li/Li^+ and 1 mV s^{-1}.

Li_3N	Li|Li t_{rest}=0 hr	Li|Li t_{rest}=24 hr
0%	335.521	930.457
0%	343.283	994.829
0%	332.233	1000.626
Mean	**337.012**	**975.304**
Error	**2.675**	**18.359**
3%	151.135	347.113
3%	159.592	354.027
3%	157.443	358.697
Mean	**156.057**	**353.279**
Error	**2.072**	**2.747**
7%	126.776	287.095
7%	130.094	293.361
7%	129.992	290.833
Mean	**128.954**	**290.429**
Error	**0.889**	**1.486**
10%	96.713	275.443
10%	101.022	276.895
10%	101.806	279.469
Mean	**99.847**	**277.269**
Error	**1.292**	**0.961**
20%	70.931	249.971
20%	73.978	250.341
20%	74.363	252.017
Mean	**73.091**	**250.776**
Error	**0.886**	**0.514**

Table S1. Averaged interfacial impedances of the Li|Li cells.

Electrolyte	Li|Cu t_{rest}=0hr	Li|Cu After Deposition t_{rest}=0hr	Li|Cu After Deposition t_{rest}=24hr
RE	258.238	42.449	90.862
RE	244.581	41.559	92.063
RE	229.291	39.908	95.637
Mean	**244.037**	**41.305**	**92.854**
Error	**6.826**	**0.608**	**1.171**
Li_3N SE	96.859	41.297	55.799
Li_3N SE	99.766	40.981	54.407
Li_3N SE	105.487	43.321	55.889
Mean	**100.704**	**41.866**	**55.365**
Error	**2.069**	**0.598**	**0.391**

Table S2. Averaged interfacial impedances of the Li|Cu cells.

Li_3N	ΔV	I_0	I_{ss}	R_0	R_{ss}	Transport Number
0%	10	0.0683715	0.046463	120.3	138	0.33615754
0%	10	0.0729	0.0523262	124.1	147.8	0.301883119
0%	10	0.0457438	0.0363654	191.95	187.91	0.306153907
Mean						**0.315**
Error						**0.0088**
3%	10	0.0672273	0.055105	123.8	120.5	0.409191147
3%	10	0.055	0.0416071	147.7	140.9	0.343090792
3%	11	0.04236	0.03335	235	262.4	0.365965926
Mean						**0.373**
Error						**0.0158**
7%	10	0.0835711	0.0691874	100.6	98.48	0.4138225
7%	10	0.0786024	0.06594	101.4	93.85	0.446734087
7%	10.7	0.08	0.05207	102.5	122.2	0.375183362
Mean						**0.412**
Error						**0.0169**
10%	10	0.066663	0.0544	113.9	100.7	0.434392653
10%	10.7	0.0552121	0.04287	145.5	150.3	0.486425907
10%	10.7	0.04947	0.0384356	190.3	220	0.445173945
Mean						**0.455**
Error						**0.0129**
20%	10	0.074	0.0651	110	93.22	0.416214696
20%	10.7	0.05226	0.038	153.9	167.6	0.446095568
20%	10.7	0.056376	0.04073	136.7	147.7	0.461691139
Mean						**0.441**
Error						**0.0109**

Table S3. Averaged Li^+ transport numbers measured from the Li|Li cells.