SUPPORTING INFORMATION

Plating and Stripping of Calcium in an Alkyl Carbonate Electrolyte at Room Temperature

Saeid Biria,[1] Shreyas Pathreeker,[1] Hansheng Li,[1] Ian D. Hosein[1*]

1. Syracuse University, Department of Biomedical and Chemical Engineering, Syracuse, NY, 13244

*Corresponding Author: idhosein@syr.edu

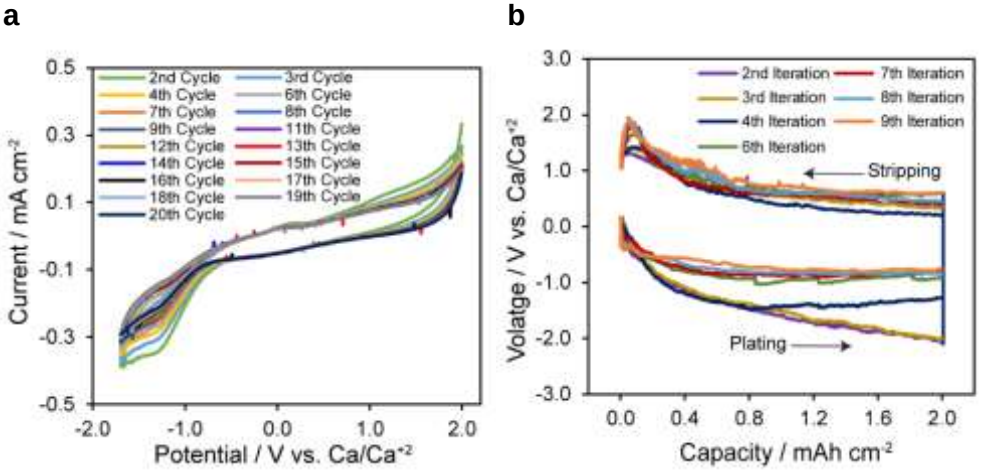

Figure S1. Electrochemical results of calcium plating and stripping in 1 M $Ca(BF_4)_2$ in EC-PC solvent. (a) Cyclic voltammograms of at room temperature (~23° C) shown for other iterations as well as cycles 11-20. (b) Galvanostatic calcium plating and stripping at a rate of 0.55 mA cm^{-2} shown for other iterations.

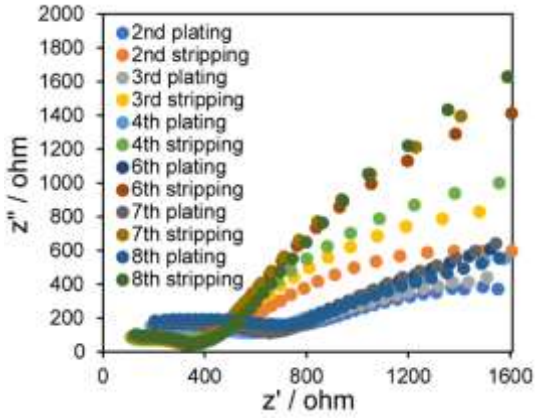

Figure S2. Nyquist plots after different plating and stripping cycles.

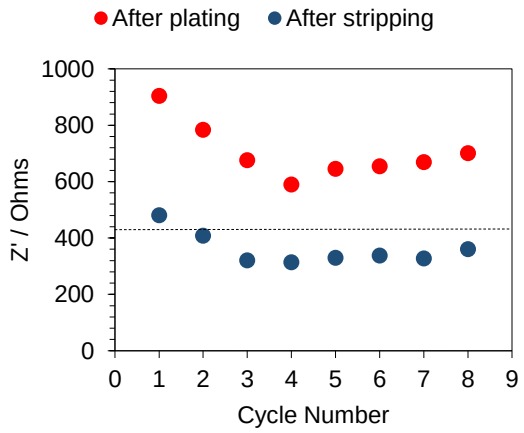

Figure S3. Plots of the real resistance associated to R_{SEI} as a function of cycle number for both plating and stripping steps. Dashed line shows the value before plating and stripping.

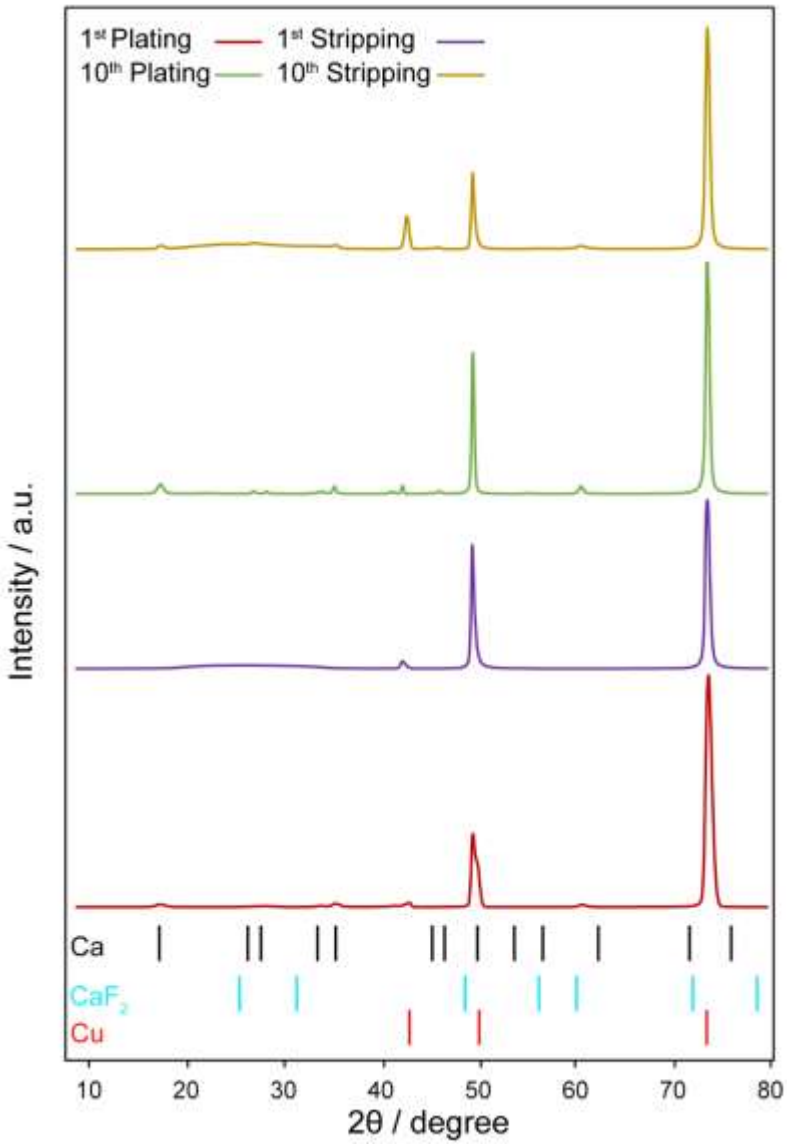

Figure S4. XRD of the substrate for different cycles, as well as the positons of reference peaks for calcium and copper metal, from the deposits and substrate, respectively.

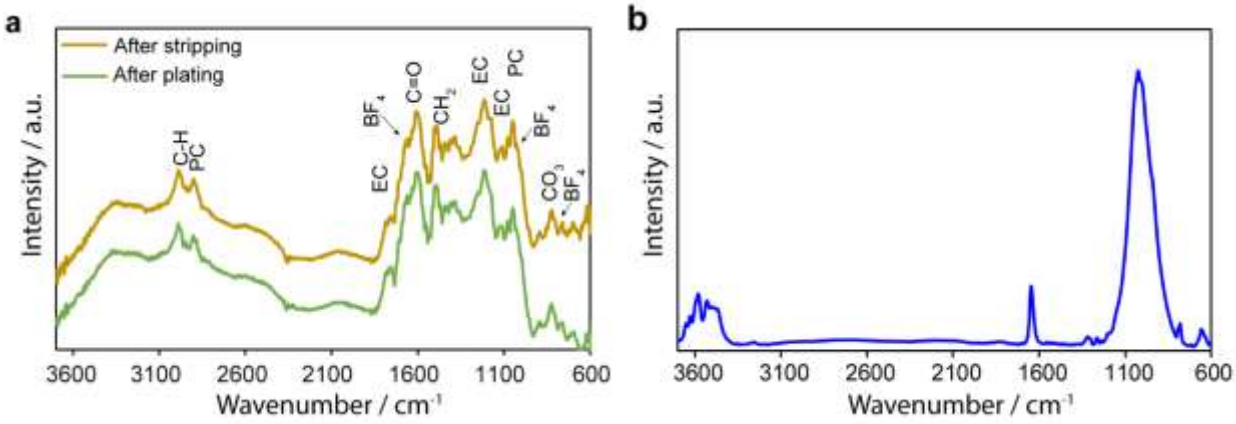

Figure S5. (a) FTIR spectra of the Cu substrate after the 10th plating and stripping steps. (b) Reference FTIR spectra for the $Ca(BF_4)_2$ salt.

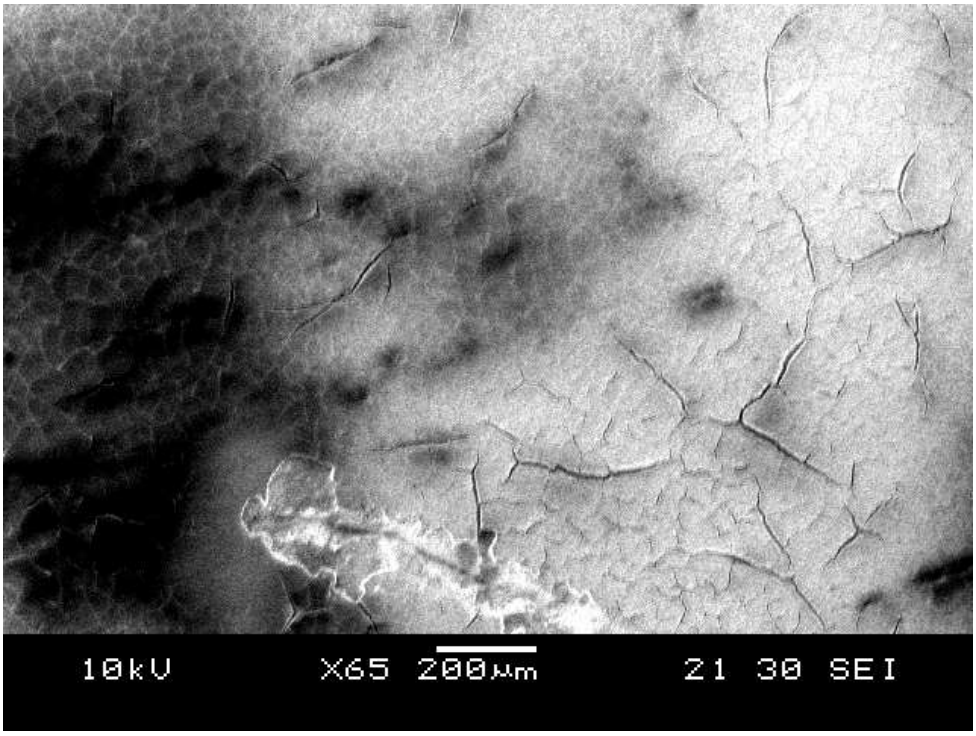

Figure S6. SEM image showing the large-scale morphology of the SEI layer after the 10th stripping.

Table S1. Nucleation overpotentials extracted from the galvanostatic cycling data for the first 10 cycles.

Cycle Number	Nucleation Overpotential (mV)
1	-340
2	-60
3	-30
4	-10
5	-30
6	-20
7	-10
8	-30
9	-60
10	-120

Table S2. Summary of measured R_{SEI} values after each plating and stripping cycle.

Cycle Number	R_{SEI} after plating (Ω)	R_{SEI} after stripping (Ω)
1	904	481.2
2	783.9	408.4
3	676.3	321.2
4	590	313.5
5	645	330.3
6	654.3	338.1
7	668.9	327.9
8	701.5	360.8

Table S3. Summary of wavenumber assignment ranges corresponding to the peaks identified in FTIR analysis.

Functional group assigned	FTIR (cm^{-1})	References
C-H	2974	Ref. 1
PC	1041 2912	NIST Chemistry WebBook, SRD 69 https://webbook.nist.gov/cgi/cbook.cgi?ID=C108327&Type=IR-SPEC&Index=1
EC	1124 1203 1791	Ref. 2 Ref. 3
C=O (asym. stretching)	1598	Ref. 3
C=O (sym. stretching)	1300	Ref. 3
CH_2 (bending)	1420	Ref. 3
CO_3 (bending)	808	Ref. 3
BF_4^-	1197, 1014	NIST Chemistry WebBook, SRD 69 https://webbook.nist.gov/cgi/cbook.cgi?ID=C14874705&Mask=800

REFERENCES

1. Misra, A.; Tyagi, P. K.; Singh, M. K.; Misra, D. S., FTIR studies of nitrogen doped carbon nanotubes. *Diamond and Related Materials* **2006,** *15*, 385-388.
2. Gatehouse, B. M.; Livingstone, S. E.; Nyholm, R. S., 636. The infrared spectra of some simple and complex carbonates. *Journal of the Chemical Society (Resumed)* **1958**, 3137-3142.
3. Ponrouch, A.; Frontera, C.; Barde, F.; Palacin, M. R., Towards a calcium-based rechargeable battery. *Nat. Mater.* **2016,** *15*, 169-173.