The role of an elastic interphase in suppressing gas evolution and promoting uniform electroplating in sodium metal anodes

Chen Gong^{1†}, *Shengda D. Pu*^{1†}, *Shengming Zhang*^{1†}, *Yi Yuan*^{1†}, *Ziyang Ning*¹, *Sixie Yang*¹, *Xiangwen*

Gao¹, Chloe Chau,¹ Zixuan Li,¹ Junliang Liu¹, Liquan Pi¹, Boyang Liu¹, Isaac Capone¹, Bingkun

Hu¹, Dominic L. R. Melvin¹, Mauro Pasta¹, Peter G. Bruce^{1,2*}, Alex W. Robertson^{3*}

¹ Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, United Kingdom

² Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QZ, United

Kingdom

³ Department of Physics, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, United

Kingdom

[†] These authors contributed equally to the manuscript.

* alex.w.robertson@warwick.ac.uk peter.bruce@materials.ox.ac.uk

	Li	Na	DME	EC	DMC	CO2	H ₂
Density (g/cm ³)	0.53	0.97	0.87	1.32	1.07	0.002	0.0009

Table S1. Densities of metals, gases and electrolyte solvents relevant to the reported liquid-cell TEM experiments.



Figure S1. Cycling performance of Na/Cu coin cell using DME electrolyte. (a) Coulombic efficiency and (b) voltage over 50 cycles. Deposition capacity at 0.5 mA cm⁻² for 0.5 mAh cm⁻², discharge to 1 V vs. Na⁺/Na.



Figure S2. Cycling performance of Na/Cu coin cells using DME electrolyte at different cycling rates. (a,c,e,g) Cell voltage with time and (b,d,f,h) representative capacity plots for 1, 3, 4, and 5 mA cm⁻² cycling rates, respectively. Deposition capacity of 0.5 mAh cm⁻², discharge to 1 V vs. Na⁺/Na, for all cells.



Figure S3. Cycling performance of $Na_3V_2(PO_4)_3/Na$ coin cells in ether and carbonate electrolyte. Capacity evolution over repeated charge/discharge cycling at a rate of 1C for (a) 1 M NaPF₆ in DME and (b) 1 M NaPF₆ in EC:DMC electrolyte. The active mass loading of cathode material is around 3.0 mg cm⁻² and C-rate was calculated by assuming a theoretical capacity of 118 mAh g⁻¹. (c,d) Charge and discharge capacity evolution and per cycle coulombic efficiency for DME and EC:DMC solvent electrolyte cells at 5C, respectively.



Figure S4. F 1s XPS depth profiles of the Na metal electrode in DME and EC:DMC electrolytes for 60s and 660s, respectively. After etching time of 60s, both the deposited Na in DME and EC:DMC electrolytes show significant Na-F peaks, while EC:DMC has stronger signal. After etching time 660s, the EC:DMC still has an obvious Na-F peak, while the Na-F signal in DME almost disappears, indicating that the SEI in EC:DMC is much thicker than DME.



Figure S5. Quantitative online-MS measurements of (a) dead Na, (b) NaH, and (c) CO₂ signature of organic carbonate SEI components such as $(CH_2OCO_2Na)_2$ and NaOCO₂R. All the cells are plated at 0.5 mA cm⁻² to 0.5 mAh cm⁻², and stripped to 1 V for 3 cycles. Concentration of 1 M NaPF₆ salt for all electrolytes.



Figure S6. SEM images of the plated Na in carbonate cell and ether coin cells. Surface morphology images were imaged following plating at 0.5 mA cm⁻² for 0.5 mAh cm⁻². Cross-sectional images were performed by plasma FIB, following plating at 0.5 mA cm⁻² for 3 mAh cm⁻². Scale bars are 20 μ m for the low magnification images, 2 μ m for the high magnification images, and 10 μ m for cross section images.



Figure S7. Photograph of the electroplated carbonate (top) and ether (bottom) electrolyte electrodes after being removed from their coin cells in a glove box.



Figure S8. A control experiment testing for beam damage in TEM mode. This is performed under the same imaging conditions as the cycling experiments, except with no external bias applied to the working electrode. TEM imaging an area of plated Na in NaPF₆ EC:DMC electrolyte for 0s (a), 45s (b), 90s (c), 150s (d). There is no bubble formation within the 150s, suggesting bubble formation and other side-reactions are not caused by beam damage. Scale bars are 1 μ m.



Figure S9. Large bubble observed growing beside the working electrode. The gas bubble forms once CV starts, and continually grows during cycling. Scale bars are 2 µm.



Figure S10. Measured mechanical properties of the SEIs formed on electroplated Na metal after ten cycles. (a,b) Representative force-displacement curves of the electrode surface after electroplating from ether and carbonate solvent electrolytes on to Cu current collectors (plating at 0.5 mA cm⁻² for 0.5 mAh cm⁻²). A low PeakForce setpoint (20 nN) was first used to avoid permanent damage to the SEI film and to measure the Young's modulus of the SEI in the elastic region. Subsequently, a higher PeakForce setpoint (350 nN) was deliberately used to break the SEI and record the force-response curves from nanoindentation. As the AFM probe tip approaches the sample surface, the started lower gradient line represents the force response from the SEI film generally followed by higher gradient line from Cu substrate. The percentage of elastic region for the SEI film is defined as the ratio of thickness of elastic region to the total thickness of the SEI film which also includes the plastic region. (c) Young's modulus and (d) elastic region distributions of the SEI layer on the electroplated electrodes from ~100 measurements.



Figure S11. Measured mechanical properties of the SEIs formed on electroplated Na metal after ten cycles (EC:DMC w/ 10% FEC) and 100 cycles (DME). (a,d) Representative force-displacement curves of the electrode surface after electroplating from EC:DMC solvent with 10% FEC additive, and DME at high current density (3 mA cm⁻²) and for 100 cycles, respectively. (b,e) Young's modulus and (c,f) elastic region of the SEI layer on the electroplated electrodes for the EC:DMC with FEC additive and high rate DME,

respectively.



Roughness: 12.4 \pm 2.1 nm

Roughness: 11.9 \pm 2.9 nm

Figure S12. AFM Images of pure Cu in air and electrolyte. The roughness of Cu in air is 12.4 ± 2.1 nm, and roughness of Cu in electrolyte is 11.9 ± 2.9 nm. The pristine Cu foil morphology is characterized under an identical scan performed in the air and electrolyte, verifying the morphology and capture resolution excluding any side effect from liquid electrolyte.



Figure S13. Cycling performance of Na/hard carbon coin cells. (a,b) Capacity evolution over repeated charge/discharge cycling at a rate of C/3 using 1 M NaPF₆ dissolved in either DME solvent (ether), and EC:DMC solvent for the electrolyte, respectively. (c-e) First cycle performance for DME and EC:DMC electrolytes at different rates. The active mass loading of hard carbon is around 3 mg cm⁻² and C-rate was

calculated by assuming a theoretical specific capacity of 150 mAh g⁻¹.



Figure S14. Schematic of the differential electrochemical mass spectrometry (DEMS) setup.



Figure S15. The in-situ liquid-cell AFM configuration used.