Supporting Information

Enabling Highly Reversible Sodium Metal Cycling Across a Wide Temperature Range with Dual-Salt Electrolytes

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SUPPLEMENTARY FIGURES

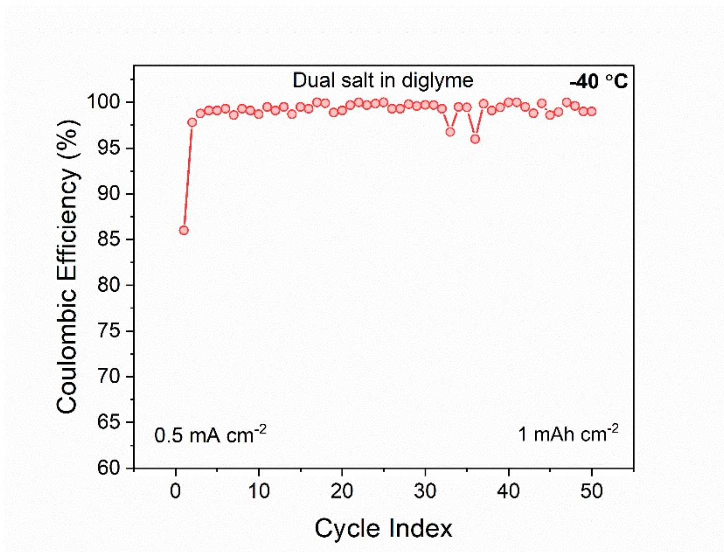

Figure S1. Coulombic efficiency measurements at -40 °C using the dual-salt electrolyte. The experiment used a current density of 0.5 mA cm^{-2} with 2-h half-cycles, for a deposited capacity of 1 mAh cm^{-2}. The average CE value over the 50 cycles is 98.98 %.

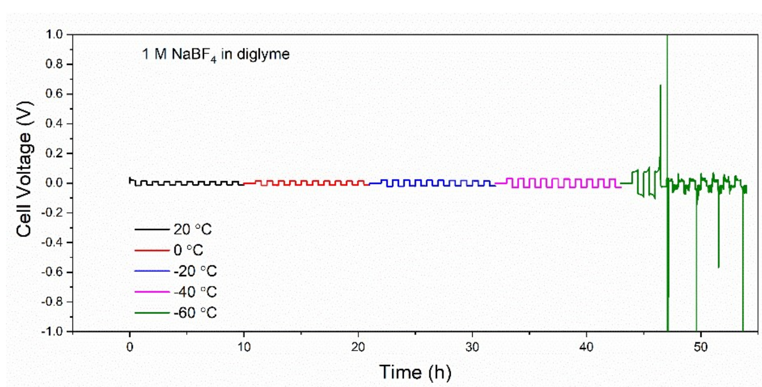

Figure S2. Temperature-dependent galvanostatic cycling of Na/Na symmetric cells using an electrolyte consisting of 1.0 M $NaBF_4$ in diglyme. The experiment used a current density of 0.5 mA cm^{-2} with 30-min half-cycles.

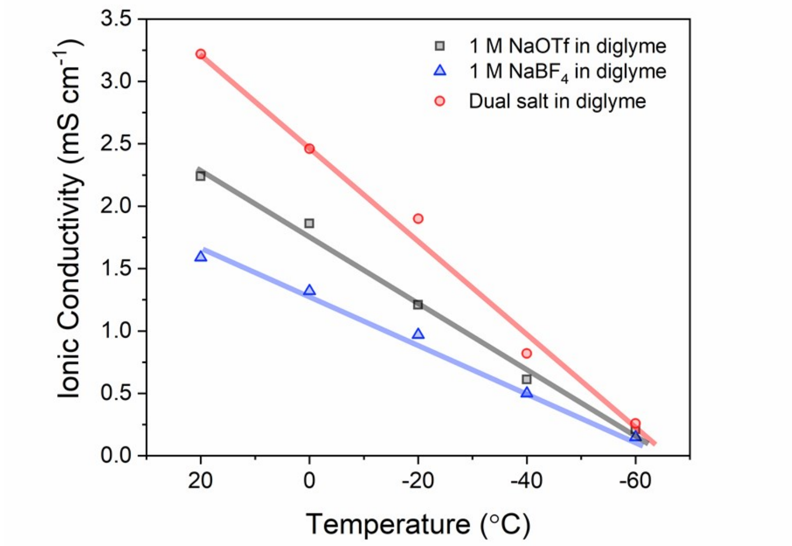

Figure S3. Temperature-dependent ionic conductivity of the following electrolytes: 1.0 M NaOTf in diglyme (black), 1.0 M $NaBF_4$ in diglyme (blue) and dual salts in diglyme (red).

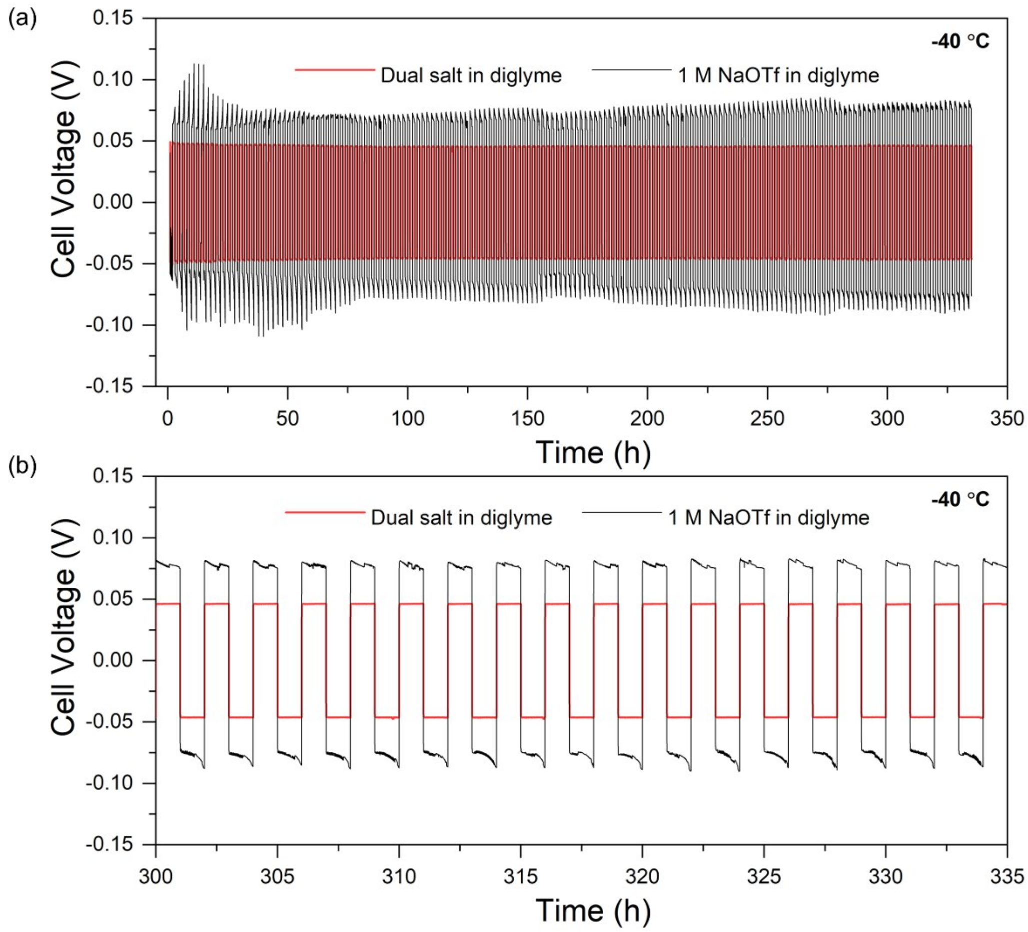

Figure S4. (a) Long-term cycling of Na/Na symmetric cells at -40 °C using a current density of 1 mA cm^{-2} with 1 mAh cm^{-2} plated per half-cycle. (b) This plot shows an enlarged view of the final 18 cycles of (a).

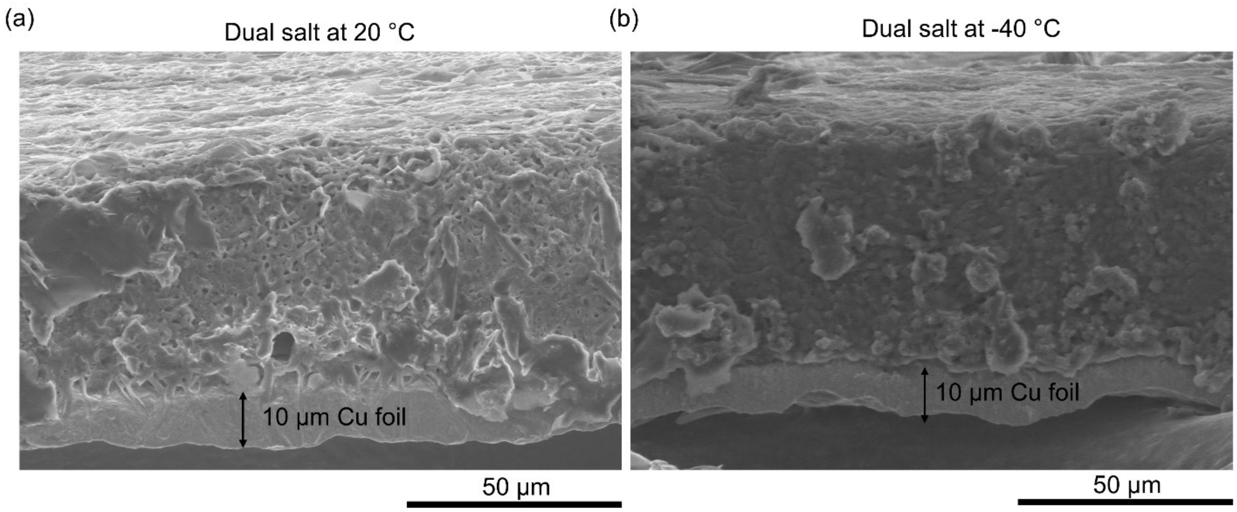

Figure S5. Cross-sectional SEM images after electrodeposition of 4 mAh cm^{-2} of sodium on Cu foil using the dual salt electrolyte. (a) Deposition at 20 °C, (b) deposition at -40 °C. The electrodeposition was carried out using a current density of 0.5 mA cm^{-2}.

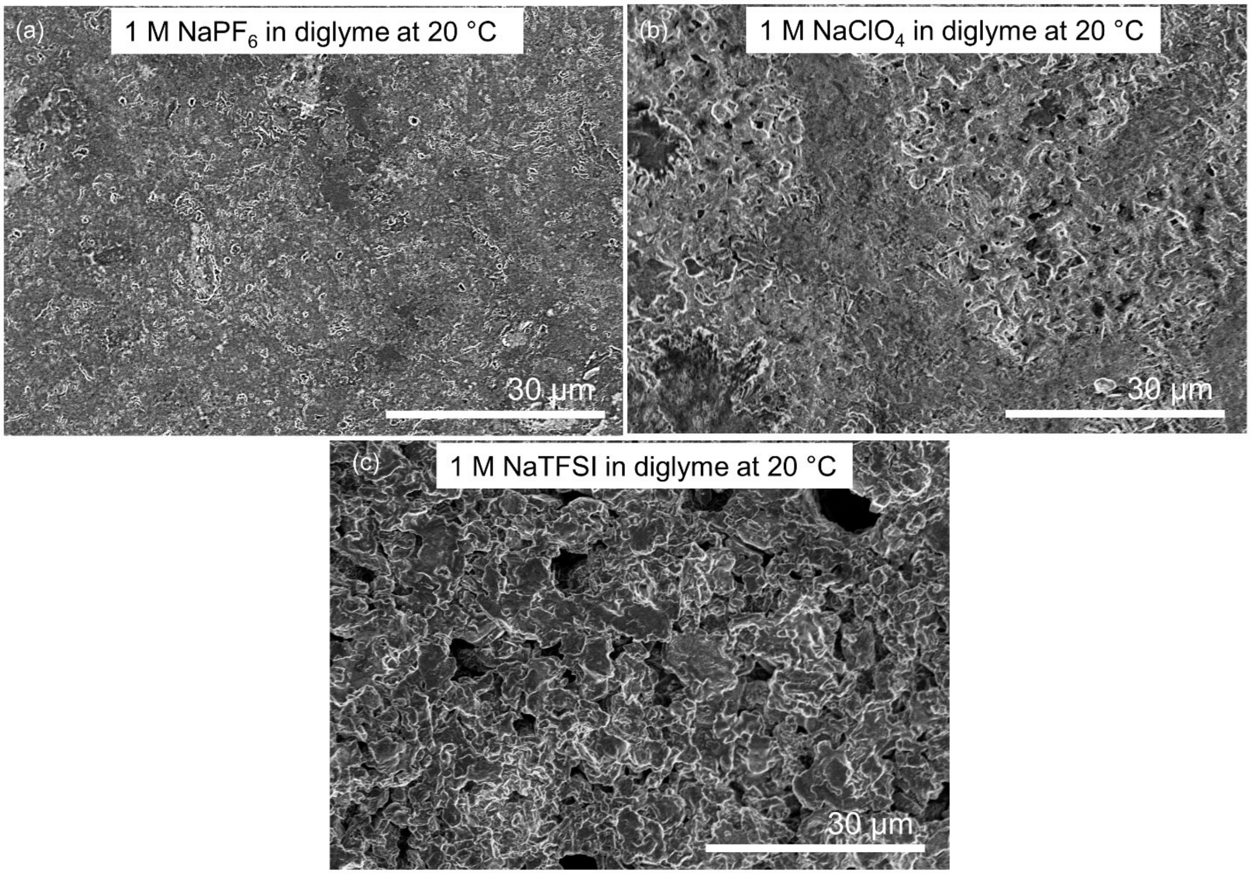

Figure S6. Morphology of electrodeposited sodium on stainless steel foils using a current density of 0.5 mA cm^{-2} for 30 min with various electrolytes at 20 °C. The electrolytes are (a) 1.0 M $NaPF_6$ in diglyme, (b) 1.0 M $NaClO_4$ in diglyme, and (c) 1.0 M NaTFSI in diglyme.

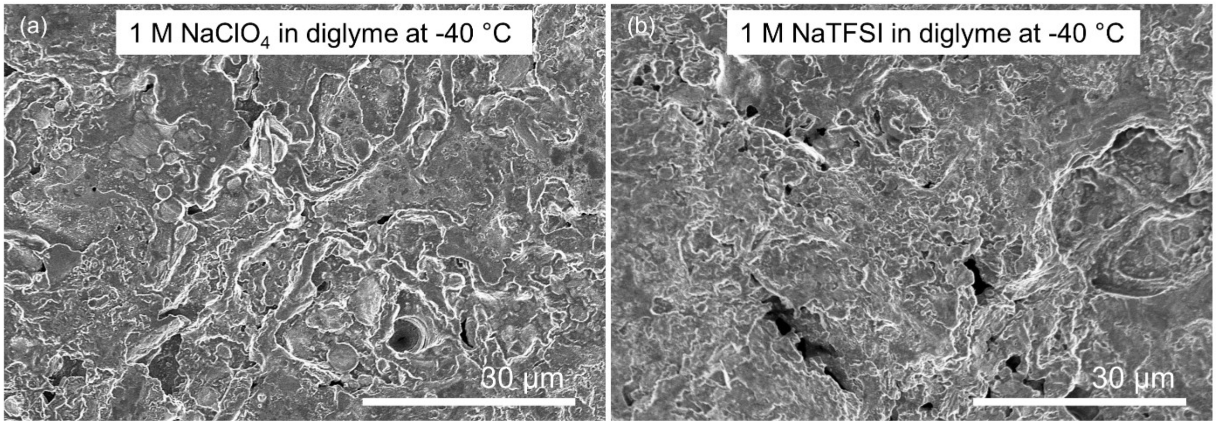

Figure S7. Morphology of electrodeposited sodium on stainless steel foils using a current density of 0.5 mA cm^{-2} for 30 min with various electrolytes at -40 °C. (a) 1.0 M $NaClO_4$ in diglyme; (b) 1.0 M NaTFSI in diglyme electrolyte. Nucleation of sodium was not possible for the electrolyte with 1.0 M $NaPF_6$ at -40 °C, which is why it is not shown.

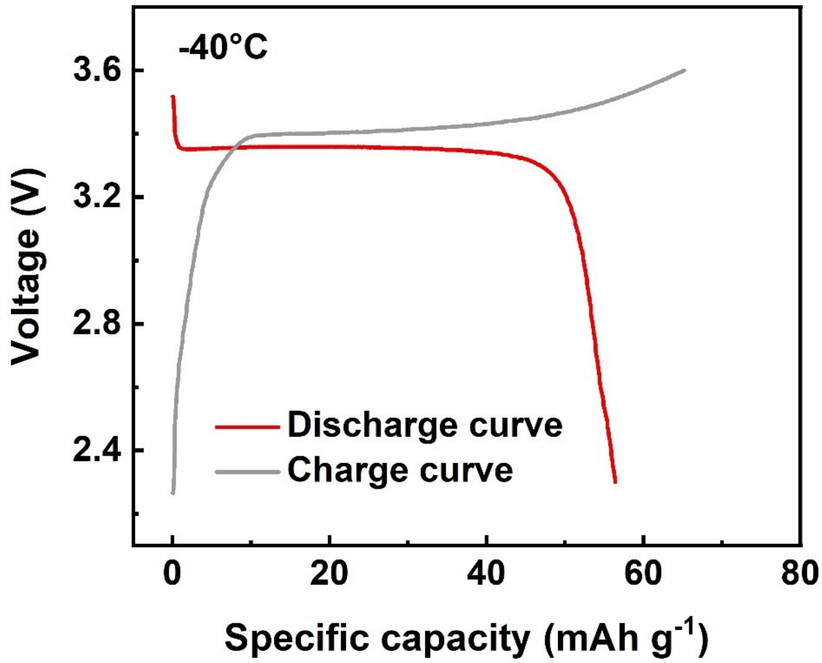

Figure S8. The charge-discharge profile of the first cycle of a $Na/Na_3V_2(PO_4)_3$ cell operating at -
-40 °C.

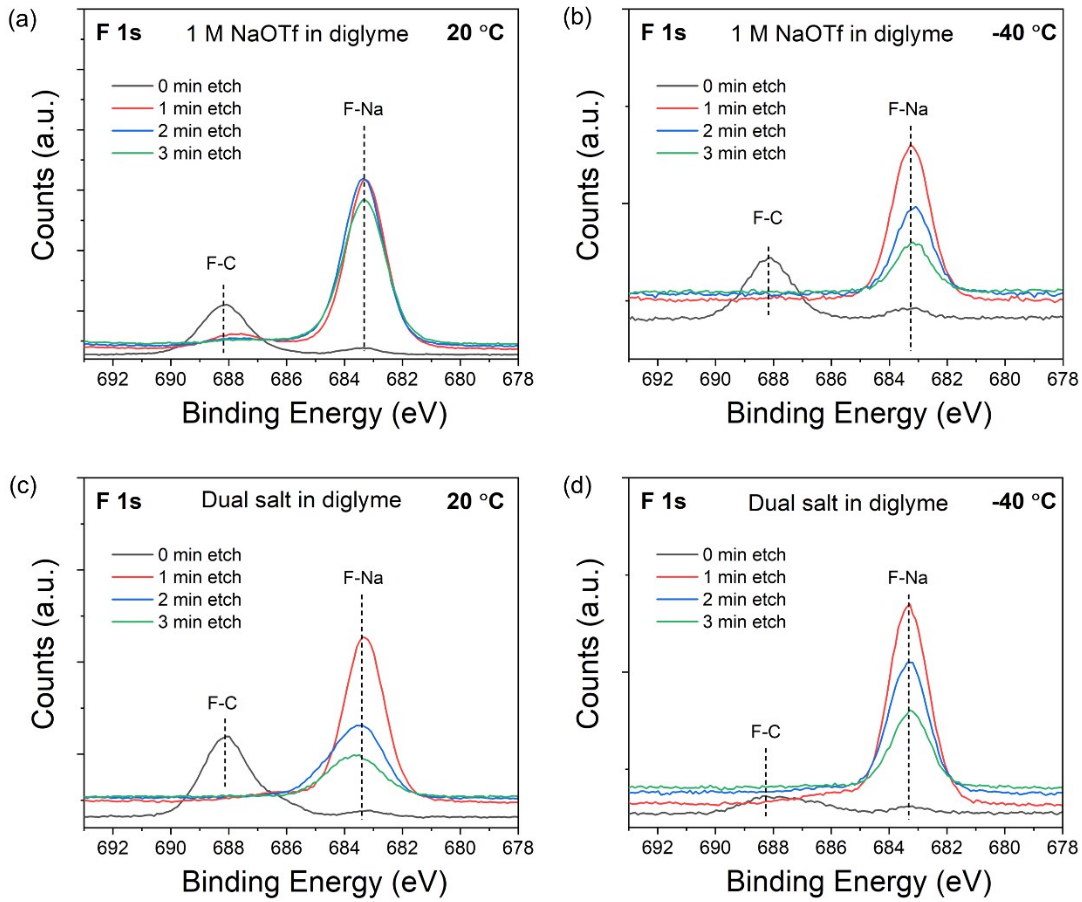

Figure S9. Depth profile F 1s core level XPS spectra of SEI formed with various electrolytes. (a) 1.0 M NaOTf in diglyme at 20 °C, (b) 1.0 M NaOTf in diglyme at -40 °C, (c) dual salt in diglyme at 20 °C, and (d) dual salt in diglyme at -40 °C.

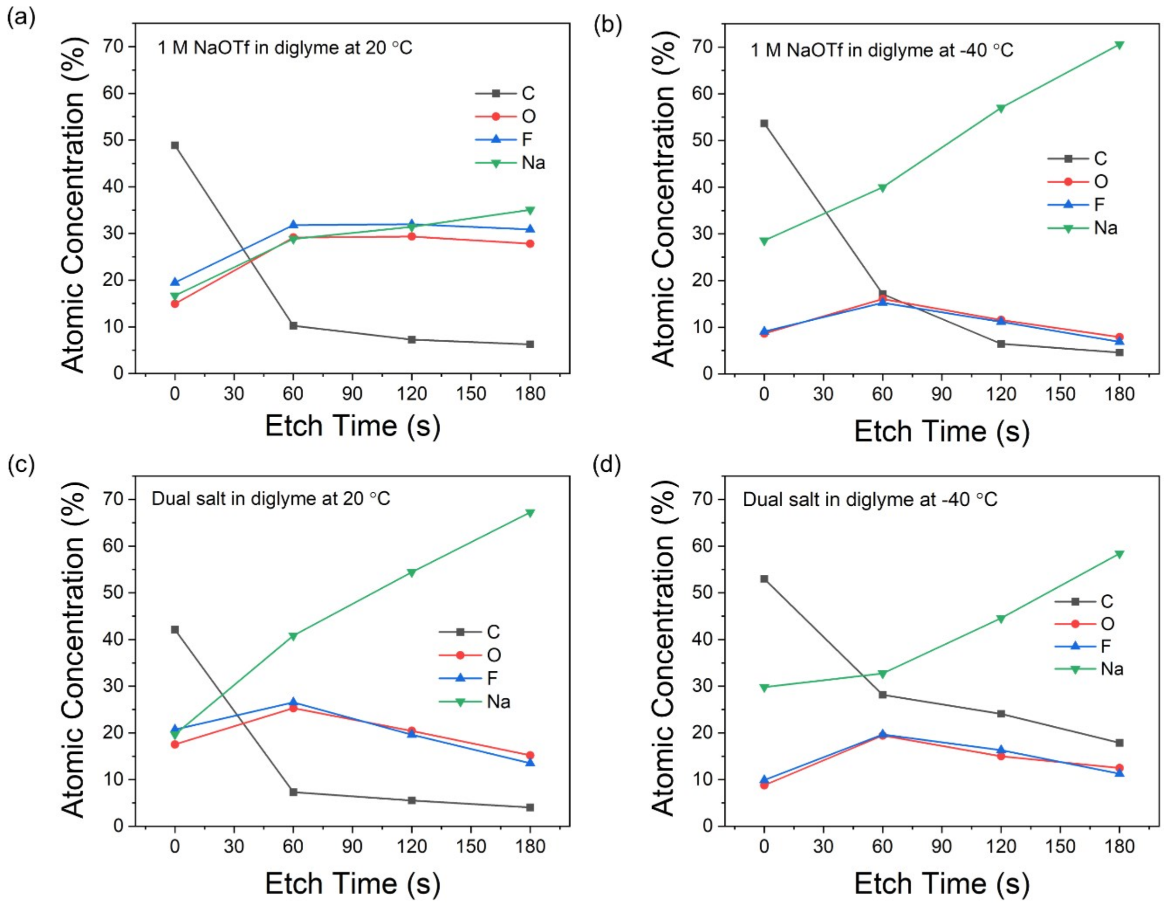

Figure S10. Atomic concentration of C, O, F and Na from depth profile XPS measurements collected from SEI films grown in various electrolytes at different temperatures. (a) 1.0 M NaOTf in diglyme at 20 °C. (b) 1.0 M NaOTf in diglyme at -40 °C. (c) Dual salt in diglyme at 20 °C. (d) Dual salt in diglyme at -40 °C.

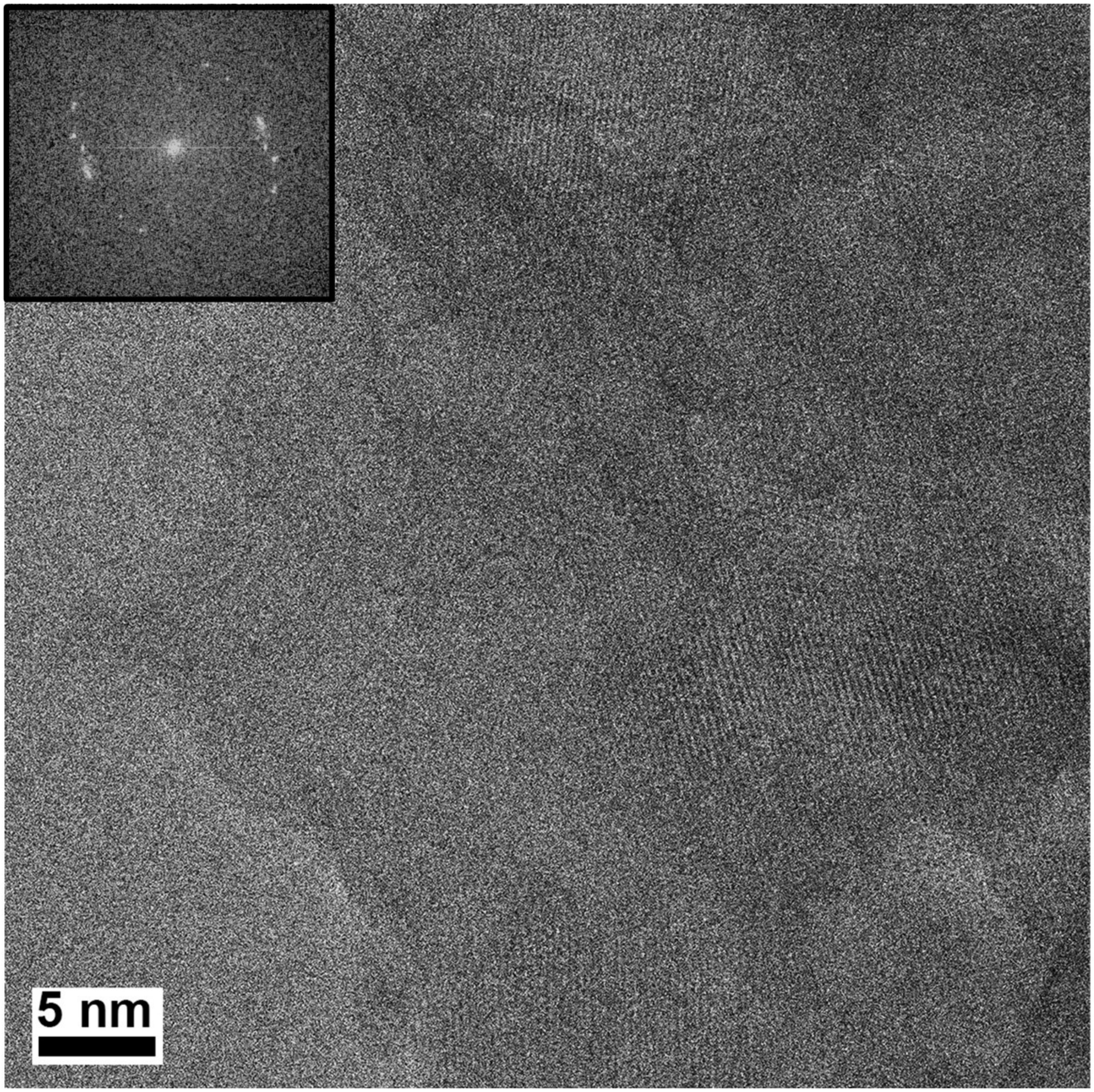

Figure S11. High resolution cryo-TEM image of the SEI formed at -40 °C using the dual-salt electrolyte, with the FFT inset. This is the same image as shown in Fig. 6a, but without the colored overlays.

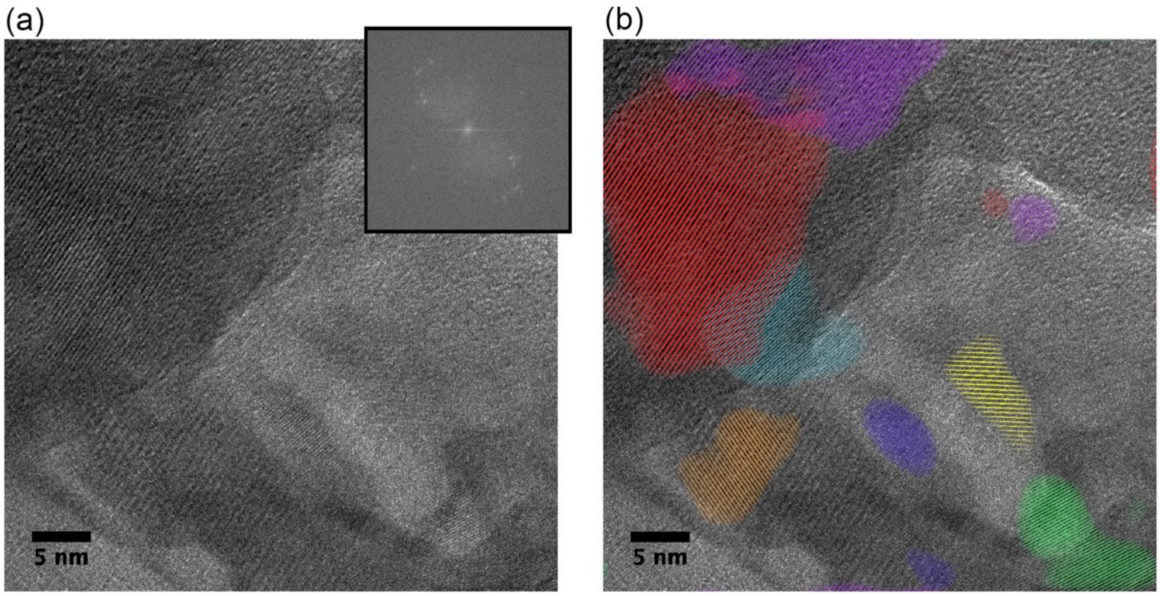

Figure S12. Cryo-TEM image of the SEI formed at 20 °C using the dual-salt electrolyte. (a) High resolution cryo-TEM micrograph with the FFT inset. (b) The same image with sets of lattice fringes from individual crystallites highlighted in different colors. The lattice fringes are generally consistent with the dominant lattice spacings found in Na_2SO_4, Na_2CO_3, and Na_2O.

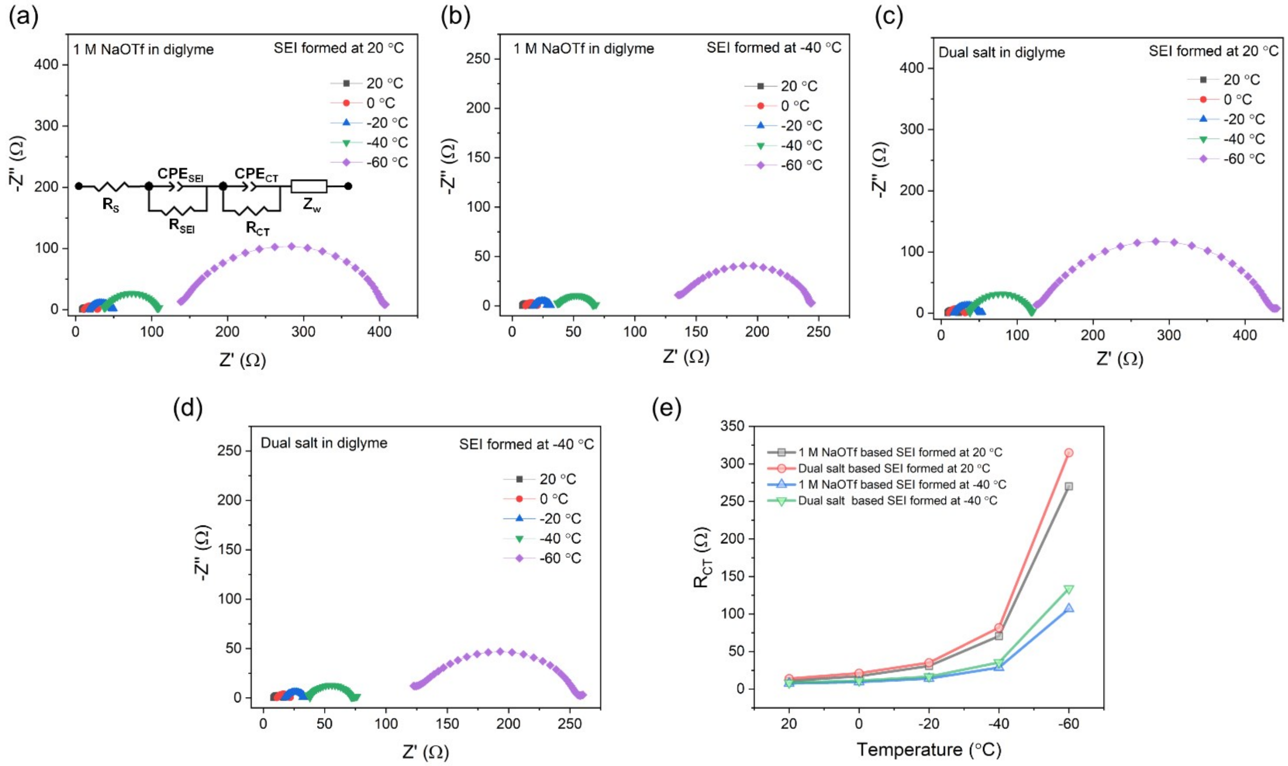

Figure S13. (a) Nyquist plot from a symmetric Na/Na cell with 1.0 M NaOTf electrolyte that was galvanostatically cycled once at 20 °C, followed by collecting EIS measurements at the various temperatures shown. The inset shows the equivalent circuit diagram used to interpret the impedance spectra. (b) Nyquist plot of a symmetric Na/Na cell with 1.0 M NaOTf electrolyte that was cycled once at -40 °C, followed by collecting EIS measurements at the various temperatures shown. (c) Nyquist plot of a symmetric Na/Na cell with the dual-salt electrolyte that was galvanostatically cycled once at 20 °C, followed by collecting EIS measurements at the various temperatures shown. (d) Nyquist plot of a symmetric Na/Na cell with the dual-salt electrolyte that was cycled once at -40 °C, followed by collecting EIS measurements at the various temperatures shown. (e) Extracted charge transfer resistance at various temperatures from the Nyquist plots.

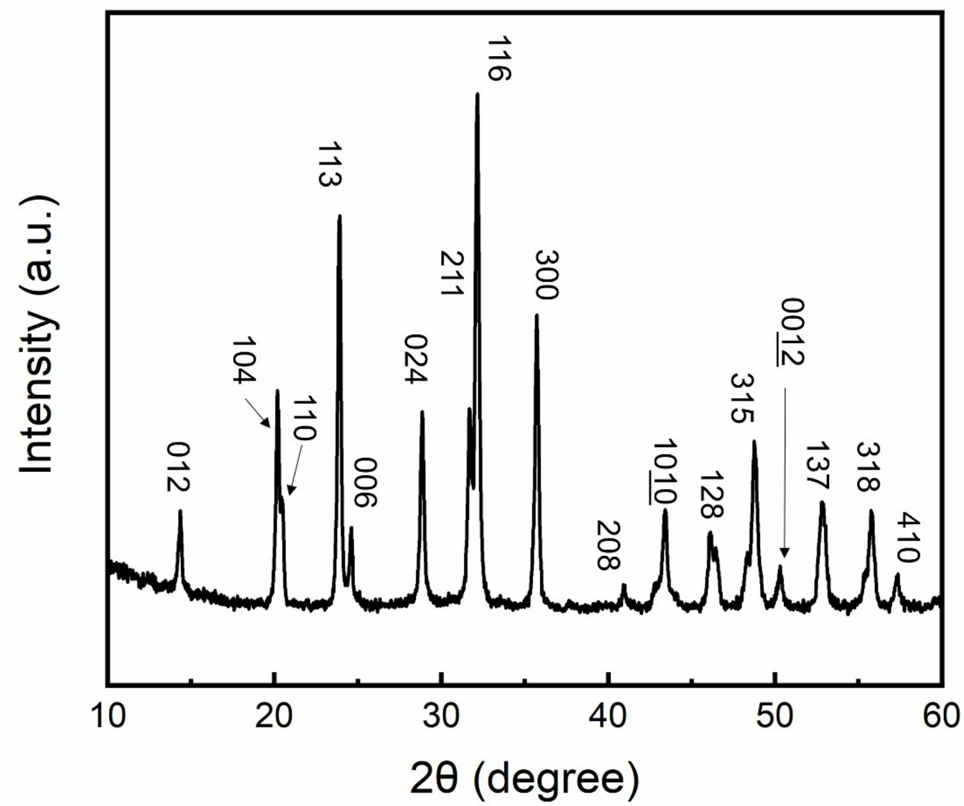

Figure S14. XRD pattern of the synthesized $Na_3V_2(PO_4)_3$ sample. All the diffraction peaks are indexed to the R-3c space group, corresponding to the previously reported data in the literature.[1, 2]

References

1. Q. An, F. Xiong, Q. Wei, J. Sheng, L. He, D. Ma, Y. Yao and L. Mai, *Adv. Energy Mater.*, 2015, **5**, 1401963.
2. Z. Jian, W. Han, X. Lu, H. Yang, Y.-S. Hu, J. Zhou, Z. Zhou, J. Li, W. Chen, D. Chen and L. Chen, *Adv. Energy Mater.*, 2013, **3**, 156-160.