

# Extending the Low Temperature Operating Range of Sodium Metal Batteries with Acyclic/Cyclic Ether-Based Electrolytes

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## Article

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# Abstract

Despite the promise of sodium electrochemistry at ambient temperature, the performance of sodium metal batteries in frigid environments is hindered by high internal resistance and unstable solid electrolyte interphase (SEI), which strongly depends on the electrolyte composition. Here we present an electrolyte formulation consisting of acyclic/cyclic ethers as binary solvents and a compatible sodium salt, which is thermally stable down to  $-150^{\circ}\text{C}$ . This electrolyte not only provides low resistance but enables a protective SEI in cold environments. Long-term sodium-metal cycling is demonstrated at the gelid temperature of  $-80^{\circ}\text{C}$ , showing small overpotentials of  $\sim 150$  mV for over 750 hours. Both X-ray photoelectron spectroscopy and cryogenic transmission electron microscopy are performed to elucidate the temperature-dependent chemistry of the interphase. Full cells are further demonstrated, exhibiting a low decay rate ( $< 0.089\%$  per cycle) and a high average Coulombic efficiency ( $> 99.5\%$ ) at temperatures as low as  $-60^{\circ}\text{C}$ .

# Main

Lithium-ion batteries (LIBs) have been extensively employed in portable electronics and electric vehicles because of their high energy/power density and long cycle life<sup>1-3</sup>. Nevertheless, they inevitably suffer from severe energy/power losses in cold environments, especially when the temperature drops below  $-20^{\circ}\text{C}$ . For example, a commercial 18650 LIB only delivers  $\sim 5\%$  of energy density and  $\sim 1\%$  of power density at  $-40^{\circ}\text{C}$  compared to those achieved at room temperature ( $+20^{\circ}\text{C}$ )<sup>4,5</sup>. Such poor low-temperature performance limits their applications for aeronautics/space missions, polar expeditions and many military and civil facilities in cold regions, in which a battery operating temperature below  $-40^{\circ}\text{C}$  is required<sup>4,6</sup>.

Searching for a system with high electrochemical reactivity beyond the Li technologies would be promising to address the challenges associated with low temperature operation. As an alkali metal, sodium (Na) stands out given that it shares many chemical and physical properties with Li, while being more reactive and substantially more naturally abundant<sup>7-9</sup>. With a lower first ionization energy than Li ( $495.8$  vs.  $520.2$   $\text{kJ mol}^{-1}$ )<sup>10</sup>, Na chemistry can contribute to improved chemical/electrochemical reactivity and thus may facilitate electrochemical reactions in cold environments. Just like Li metal in Li-based batteries, Na metal plays a crucial role in Na batteries because of its low electrode potential ( $-2.714$  V vs. standard hydrogen electrode) and high theoretical specific capacity ( $1166$   $\text{mAh g}^{-1}$ )<sup>7-9</sup>. Nevertheless, investigation of Na batteries at low temperatures has been limited, and in particular understanding of the behavior of Na metal as an electrode is largely missing<sup>11-14</sup>.

Enabling low-temperature battery operation is furthermore highly dependent on the nature of the electrolyte<sup>17-19</sup>. The electrolyte resistance increases rapidly as temperature drops because of the relatively high freezing/melting points of traditional carbonate solvents and the reduced solubility of conducting salts<sup>5,17</sup>. Moreover, the structural and compositional evolution of the solid electrolyte interphase (SEI)

formed on Na metal is unclear at low temperatures. Differences of the SEI are likely due to the change of the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energies of electrolytes as a function of temperature<sup>6</sup>. Hence, the SEI-friendly electrolytes at ambient temperature might not be able to maintain the same protective capabilities to enable efficient cycling under cold conditions.

One viable solution to solve these problems is the formulation of electrolytes targeted for low-temperature operation using ether solvents with low melting points and SEI-benign salts. Using this strategy, we find here that a unary-solvent electrolyte using an acyclic ether is able to extend the Na metal operating temperature towards  $-40^{\circ}\text{C}$ . Furthermore, adding a cyclic ether as a reconcilable anti-freeze agent in a binary-solvent electrolyte can expand the temperature threshold of thermostability down to  $-150^{\circ}\text{C}$ . To achieve this superior performance, the trifluoromethanesulfonate (OTf) salt is found to play a critical role in stabilizing the SEI at low temperatures, as confirmed by X-ray photoelectron spectroscopy (XPS) and cryogenic transmission electron microscopy (cryo-TEM). We demonstrate stable Na plating/stripping in symmetric cells at an extreme temperature of  $-80^{\circ}\text{C}$ , exhibiting low overpotentials of  $\sim 150$  mV for over 750 hours. The achieved performance outperforms the state-of-the-art results of Na and Li metal anodes cycling at low temperatures ( $\leq -40^{\circ}\text{C}$ ) shown in **Supplementary Fig. 1** and **Supplementary Table 1**<sup>15-18</sup>. We further illustrate a full cell with a capacity decay of less than 0.089% per cycle and a high average Coulombic efficiency (CE) over 99.5% for over 100 cycles at temperatures as low as  $-60^{\circ}\text{C}$ .

### Screening of unary-solvent electrolytes at low temperatures

While 1M sodium hexafluorophosphate in diethylene glycol dimethyl ether ( $\text{NaPF}_6$ -DEGDME) has been shown to be a suitable electrolyte for the Na metal anode at ambient conditions<sup>20</sup>, it is impractical for low-temperature operation, mainly due to the precipitation of salt as temperature drops (**Supplementary Fig. 2**). Therefore, we screened the electrolytes using a variety of salt-solvent combinations. Low melting point ethers, including DEGDME, 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) were chosen as candidate solvents (**Supplementary Table 2**). A variety of conducting salts, including  $\text{NaPF}_6$ , sodium trifluoromethanesulfonate ( $\text{NaOTf}$ ), sodium perchlorate ( $\text{NaClO}_4$ ), sodium bis(trifluoromethanesulfonyl)imide ( $\text{NaTFSI}$ ) and sodium bis(fluorosulfonyl)imide ( $\text{NaFSI}$ ) were investigated as the candidate salts. The concentration of salt in the solvent was kept as 1M for the homogeneity screening of these unary-solvent electrolytes at low temperatures. The results (**Supplementary Table 3**) suggest that the solubility of  $\text{NaPF}_6$  cannot reach 1M concentration in all three solvents, while the other four salts present good solubility in DEGDME. Moreover, DOL cannot easily solvate Na salts except for  $\text{NaTFSI}$ . In sum, eight out of the fifteen unary-solvent electrolytes are thermally stable at  $-35^{\circ}\text{C}$  at 1M concentration, and these were subjected to further electrochemical evaluation with metallic Na.

### Electrochemical behavior of unary-solvent electrolytes

Galvanostatic cycling measurements were performed in symmetric Na/Na cells at a current density of 0.5 mA cm<sup>-2</sup> with a cycling capacity of 0.5 mAh cm<sup>-2</sup> at -20°C (**Fig. 1**) and at +20°C (**Supplementary Fig. 3**). At +20°C, 1M NaOTf-DEGDME presents the most stable cycling with the smallest average overpotential (< 10 mV) for 600 hours (300 cycles). In contrast, 1M NaTFSI-DOL shows increasing overpotential which rapidly reaches 1 V, and the 1M NaTFSI-DEGDME and NaTFSI-DME exhibit early failure, reaching the protection voltage (5 V) at 32 hours (16 cycles) and at 44 hours (22 cycles), respectively. The rest of the electrolytes exhibit asymmetric voltage profiles over cycling (**Supplementary Fig. 4**).

In contrast to the behavior at +20°C, no systems exhibit early failure at -20°C (**Fig. 1a**), likely owing to the reduced reactivity of the electrolyte with Na. Among the eight electrolytes, the 1M NaOTf-DEGDME displays the highest stability with smooth and steady voltage plateaus as well as the lowest overpotential of ~16 mV (**Fig. 1b**). In comparison, unstable and fluctuating voltage spikes are observed for the rest of the electrolyte recipes (**Fig. 1b** and **1c**). The overpotentials and voltage spike magnitudes of different electrolyte systems are compared in **Supplementary Table 4**. Because of the superior performance of the NaOTf-DEGDME at both +20°C and -20°C, it was selected for further testing in symmetric cells at -40°C (**Fig. 2a**). Remarkably, the initial overpotential of 40 mV rises to only 50 mV even after 500 hours of cycling at 0.5 mA cm<sup>-2</sup> (capacity: 1 mAh cm<sup>-2</sup>), corresponding to less than 0.2% increase per cycle. Even at a higher current density of 1 mA cm<sup>-2</sup>, an average overpotential of 100 mV can be maintained for over 300 hours. As for CE evaluation (**Fig. 2b**), the fluctuating profile at -40°C compared to +20°C suggests that the formation of stable SEI is difficult at lower temperatures.

### Characterization of unary-solvent electrolytes

To further understand the effects of temperature on cycling, the morphology of the SEI was characterized using scanning electron microscopy (SEM) (**Supplementary Figs. 5 to 8**). It is noted that both NaTFSI and NaFSI salts result in damaged surfaces (pores and/or cracks) of the deposited Na<sup>21-25</sup>. In contrast, the NaOTf-DEGDME enables relatively smooth surfaces at both +20°C and -20°C, where leaf-vein-like texture could be observed on the surface and within the cross-section. Such microstructure becomes more distinct at -40°C (**Fig. 2c**).

The chemical composition of the SEI formed in NaOTf-DEGDME was revealed using X-ray photoelectron spectroscopy (XPS), as shown in **Fig. 2c**. The binding energies of all elements were calibrated with respect to C<sub>1s</sub> at 284.8 eV. In the C<sub>1s</sub> XPS profile, the peak with binding energy at 293.4 eV is assigned to -CF<sub>3</sub>, and the ones at 288.7 eV and 286.6 eV are ascribed to O-C=O and C-O-C, respectively<sup>26-31</sup>. In the O<sub>1s</sub> spectrum, the peaks at 533.3 eV and 531.2 eV correspond to polyether-like compounds and C-O-Na (e.g. RCH<sub>2</sub>ONa)<sup>32</sup>, respectively, and the one at 536.3 eV is assigned to Na KLL. For S<sub>2p</sub>, the doublets at 169.6 eV and 167.2 eV (based on the 2p<sub>3/2</sub>) are assigned to SO<sub>4</sub><sup>2-</sup> and SO<sub>3</sub><sup>2-</sup>, respectively. As to F<sub>1s</sub>, the peaks at 689.3 eV and 684.1 eV are assigned to C-F and NaF, respectively<sup>26-31</sup>. These XPS spectra at different temperatures reveal similar composition on the SEI surface (**Fig. 2c**), suggesting the existence of -CF<sub>3</sub> containing compounds, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaF, C-O-Na and organic debris. It is noteworthy that

Na<sub>2</sub>SO<sub>3</sub> can only be detected on the surface at +20°C. Besides, Na<sub>2</sub>S (S<sup>2-</sup>: 161.1 eV) cannot be detected in the inner SEI at -20°C and -40°C (**Supplementary Fig. 9 to 11**). The presence of the species with lower oxidation states at lower temperatures suggests that the reaction kinetics between the electrolyte and Na is suppressed. Moreover, the XPS peak intensities at -40°C are significantly lower than those at +20°C and -20°C, indicating more limited SEI formation with decreasing temperature, which is in accord with the CE measurements. Importantly, the high consistency in SEI composition formed in NaOTf-DEGDME across these temperatures cannot be achieved in the other electrolyte systems (**Supplementary Figs. 12 to 23**). Note that the discussion of morphology and chemical composition of the SEIs in the other systems is detailed in the **Supplementary Information**.

### **Design of binary-solvent electrolytes for extreme low temperatures**

Motivated by the analysis of the nature of the SEI (**Supplementary Tables 5 and 6**)<sup>26-34</sup>, the NaOTf-DEGDME combination was selected as a launching point for further formulation of electrolytes that can operate below -40°C. A different solvent, DOL, which is a cyclic ether with a low melting point of -95°C, was introduced into DEGDME to produce binary-solvent electrolytes (**Fig. 3a**) to further improve the low-temperature properties of the electrolyte. However, the Na<sup>+</sup> solvation ability of DOL is lower than that of DEGDME<sup>35</sup>. Therefore, the solvent volume ratios (DEGDME:DOL=8:2, 5:5 or 2:8 volume fraction) and salt concentration (0.5M or 1M) were evaluated in the screening of binary-solvent electrolytes (**Supplementary Table 7**).

It can be observed that the introduction of DOL drastically extends the low temperature operating range of the NaOTf-DEGDME system, where a higher DOL volume leads to better Na cycling stability in symmetric cells (**Fig. 3b** and **Supplementary Fig. 24**). Additionally, a lower salt concentration (0.5M) could accommodate an increased DOL proportion, further enhancing the performance (**Fig. 3b**). At -80°C, the symmetric cell overpotential (~35 mV) in 0.5M NaOTf-DEGDME/DOL (2:8) is less than half of that (~75 mV) in 0.5M NaOTf-DEGDME/DOL (5:5) and six times less than that (>200 mV) in 1M NaOTf-DEGDME/DOL (5:5). We found that both the NaOTf salt and the DEGDME solvent are critical for enabling this superior low-temperature performance. Replacing DEGDME with DME leads to increased overpotentials and/or an asymmetric voltage profile (**Supplementary Fig. 25**), which also occurs with the substitution of NaOTf by NaClO<sub>4</sub> (**Supplementary Fig. 26**).

### **Evaluation of binary-solvent electrolytes**

To understand the mechanisms for the enhanced performance at low temperatures, the electrolyte resistance was investigated at different temperatures (**Fig. 3c**). Remarkably, the resistance of 0.5M NaOTf-DEGDME/DOL (2:8) at -80°C is only 3.4 times higher than that at +20°C. This difference is less than half of that of 0.5M NaOTf-DEGDME/DOL (5:5) and ten times smaller than that of 1M NaOTf-DEGDME. The lower electrolyte resistance change is possibly attributed to the lower dynamic viscosity of DEGDME/DOL (2:8) and good homogeneity/uniformity of this electrolyte (**Supplementary Figs. 27 and 28**). Differential scanning calorimetry (DSC) further confirms the high thermal stability of 0.5M NaOTf-

DEGDME/DOL (2:8), revealing no obvious phase transition even down to  $-150^{\circ}\text{C}$  (**Fig. 3d**)<sup>36</sup>. Similarly, no phase transition is detected until  $-140^{\circ}\text{C}$  for 0.5M NaOTf-DEGDME/DOL (5:5). In comparison, 1M NaOTf-DEGDME displays a second-order phase transition at  $-126^{\circ}\text{C}$  during cooling and a first-order phase transition at  $-64^{\circ}\text{C}$  (melting point of DEGDME) during the subsequent heating.

Given the low resistance and good thermal behavior, long-term Na/Na symmetric cells cycling at  $-80^{\circ}\text{C}$  were compared in **Supplementary Figs. 29** and **Fig. 3e**. The cells using 0.5M NaOTf-DEGDME/DOL (2:8) display small overpotentials of  $\sim 50$  mV without increasing for over 2,000 hours at  $0.2\text{ mA cm}^{-2}$  with  $0.1\text{ mAh cm}^{-2}$  cycled (**Supplementary Figs. 29**). Even at a higher current of  $0.5\text{ mA cm}^{-2}$  with a higher capacity of  $0.25\text{ mAh cm}^{-2}$ , a stable operation over 750 hours can still be achieved (**Fig. 3e**). Enlarged voltage profile (**Fig. 3f**) further suggests that the overpotential at  $0.5\text{ mA cm}^{-2}$  starts at 147 mV (after stabilization process) and slightly increases to 150 mV after 500 hours, revealing a smooth voltage profile without spikes. In comparison, the 0.5M NaOTf-DEGDME/DOL (5:5) electrolyte contributes to large spikes ( $> 4,000$  mV) and asymmetric voltage profile over cycling.

### Characterization of SEI in binary-solvent electrolyte

On top of the improvements in electrolyte properties, the binary-solvent system can alter the features of the SEI in comparison to the unary-solvent one (**Fig. 4a**). Specifically, the gradual increase of the volume fraction of DOL results in the vanishing of leaf-vein-like texture that was observed in NaOTf-DEGDME at low temperatures (**Supplementary Fig. 30** and **Fig. 4b**). As to the composition, XPS profiles of the NaOTf-DEGDME/DOL electrolyte at  $-80^{\circ}\text{C}$  (**Fig. 4c** and **Supplementary Figs. 31 to 34**) suggest similar SEI components detected in its unary-solvent counterpart. Cryo-TEM (**Fig. 4d** and **Supplementary Figs. 35 and 36**) further indicates the crystalline nature of the SEI (likely containing  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$ ) via identification of lattice fringes and analysis of electron diffraction patterns.

The uniformity/homogeneity of SEI achieved at  $-80^{\circ}\text{C}$  using the binary-solvent electrolyte supports the long-term stability observed in Na/Na symmetric cells (**Fig. 3e**). The high integrity of the SEI also contributes to a significantly improved CE behavior at  $-40^{\circ}\text{C}$  compared to that at  $+20^{\circ}\text{C}$ , showing an average value of  $\sim 97.6\%$  (**Supplementary Fig. 37**).

### Demonstration of full cells working at low temperatures

Full cells comprising  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  as the cathode<sup>8</sup> and Na metal as the anode in the 0.5M NaOTf-DEGDME/DOL (2:8) electrolyte were demonstrated at 0.2C ( $1\text{C}=110\text{ mA g}^{-1}$ ) at low temperatures down to  $-80^{\circ}\text{C}$  (**Fig. 5**). Galvanostatic cycling (**Fig. 5a**) reveals that the discharge capacity decreases with the cell being sequentially cooled. At  $-60^{\circ}\text{C}$ ,  $\sim 42\%$  of the specific capacity obtained at  $-20^{\circ}\text{C}$  can be retained. The capacity loss from the temperature stepping is reversible, which is fully recovered as the temperature rises. The charge-discharge voltage profiles from  $0^{\circ}\text{C}$  to  $-80^{\circ}\text{C}$  (**Fig. 5b**) suggest that the hysteresis is also temperature sensitive. At  $-60^{\circ}\text{C}$ , the hysteresis is about four times than that of at  $-40^{\circ}\text{C}$  and five times than that at  $-20^{\circ}\text{C}$ . For long-term cycling (**Fig. 5c**), a full cell at  $-20^{\circ}\text{C}$  exhibits an initial

discharge capacity of 91.8 mAh g<sup>-1</sup> (~83.5% of the theoretical value) with a low decay rate (< 0.055% per cycle) and a high average CE value (> 98.1%) for over 100 cycles. At -40°C, the initial capacity decreases to 67.5 mAh g<sup>-1</sup> while a higher CE value (> 99.6%) can be achieved. Even at -60°C, a similarly high CE (> 99.5%) can still be maintained with a high capacity retention of 91.1% (a decay rate < 0.089% per cycle) after 100 cycles. At -40°C and -60°C, C-rate performance up to 1C (**Fig. 5d**) further confirms the superiority of Na metal batteries using the designed electrolyte at extremely cold conditions.

## Conclusions

We have formulated low-temperature electrolytes comprising acyclic/cyclic ethers (DEGDME/DOL) and NaOTf salt, drastically extending the operating temperature limit for Na metal batteries. In particular, a unary-solvent electrolyte of 1M NaOTf-DEGDME readily enables stable Na metal cycling down to -40°C, showing low overpotentials of 100 mV at 1 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup> for over 300 hours. To further decrease the temperature threshold, DOL was introduced in binary-solvent electrolytes. An optimized electrolyte of 0.5M NaOTf-DEGDME/DOL (2:8) exhibits a resistance increase of only a factor of 3.4 from +20°C to -80°C and high thermal stability with no phase transition down to -150°C. We further demonstrate stable Na cycling with small overpotentials of 50 mV for over 2,000 hours at -80°C. The superiority is ascribed to the formation of a compact and passivating SEI. As a proof of concept, full cells comprising Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> as the cathode and Na metal as the anode present low capacity decay rates and high CE values over cycling down to -60°C.

## Methods

**Materials.** Metallic sodium (Na) chips were made from Na metal cubes (Sigma-Aldrich). Sodium hexafluorophosphate (NaPF<sub>6</sub>, Sigma-Aldrich), sodium trifluoromethanesulfonate (NaOTf, Beantown Chemical), sodium perchlorate (NaClO<sub>4</sub>, Sigma-Aldrich), sodium bis(trifluoromethanesulfonyl)imide (NaTFSI, Solvionic) and sodium bis(fluorosulfonyl)imide (NaFSI, Solvionic) were dried in an argon (Ar)-filled glove box (O<sub>2</sub> < 0.6 PPM, H<sub>2</sub>O < 0.1 PPM, Mbraun) before being used. Diethylene glycol dimethyl ether (anhydrous, Sigma-Aldrich), 1,2-dimethoxyethane (anhydrous, Sigma-Aldrich) and 1,3-dioxolane (anhydrous, Sigma-Aldrich) were directly used as solvents for the electrolytes.

**Characterization.** A temperature chamber (MC-812, ESPEC) was employed to ensure stable temperature environments between -80°C and +20°C. Tested coin cells were maintained at a specified temperature point for at least an hour for thermal equilibrium. Dynamic viscosity (or absolute viscosity) measurements were conducted using a viscometer (*microVISC*<sup>™</sup>, RheoSense), which was specifically calibrated for low temperature measurement (down to -40°C). Before testing, each sample (100 μl) was isothermally stored at target temperatures for over 10 hours. Scanning electron microscope (SEM) images were carried out using a field emission gun environmental SEM (XL 300 ESEM-FEG). Cryogenic transmission electron microscopy (cryo-TEM) analysis was conducted using an FEI Tecnai F30 TEM operating at 300 kV. The TEM sample was prepared by carrying out a single Na plating/stripping cycle

(0.25 mA cm<sup>-2</sup> for 2 hours) using a Cu TEM grid as the working electrode. The coin cell containing the grid was disassembled in an Ar-filled glove box, and the grid was washed with 0.5 mL of DEGDME and vacuum dried inside the glove box. Next, the grid was then loaded into a Gatan cryo specimen holder inside the glove box. The Cu TEM grid was quickly transferred (~ 10 s air exposure) from the argon environment into the TEM load lock, where it was brought to vacuum. Next, the temperature of the sample was decreased using liquid nitrogen and maintained at - 175°C during imaging. All images were recorded at a low dose rate between 1 and 2 · 10<sup>2</sup> electrons·Å<sup>-2</sup>·s<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) analysis was performed via PHI Versaprobe II scanning XPS microprobe with 0.47 eV system resolution using a monochromatic 1486.7 X-ray source. Notably, the samples were transferred into the XPS chamber via a sealed Ar-filled vessel to avoid exposure to air. Differential scanning calorimetry (DSC) was performed using a Netzsch DSC 204 F1 Phoenix. Both samples and reference were tested between - 150°C and + 20°C at a controlled rate of 10°C min<sup>-1</sup>.

**Electrochemical measurement.** 1M and 0.5M electrolytes were prepared in the Ar-filled glove box. The galvanostatic Na/Na symmetric cycling was conducted in 2032-type coin cells, which were assembled with two identical Na chips and a separator (Celgard 2400) filled with 40 µl of 1M/0.5M electrolytes. For Coulombic efficiency (CE) measurements, coin cells were assembled with stainless steel foil as the working electrode and freshly cut Na as the counter electrode with 40 µl of electrolyte. CE measurements were performed by plating and stripping with a current density of 0.5 mA cm<sup>-2</sup> over 1 h (0.5 mAh cm<sup>-2</sup> depositing or stripped per half cycle). Full cells were assembled with Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> cathodes and bare Na anodes with tested electrolytes. The synthesis and processing procedures of Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> along with the cathode preparation were detailed in our previous study<sup>8</sup>. Active material loadings were up to 2 mg cm<sup>-2</sup>. Both symmetric cells and full cells were performed using a standard battery tester (CT2001A, Wuhan LANHE Electronics Co., Ltd). Electrochemical impedance spectroscopy (EIS) was conducted using an electrochemical workstation (VMP3, Bio-Logic Science Instruments) at a scanning frequency from 1 MHz to 0.1 Hz with an AC amplitude of 5 mV. An electrolyte-soaked glass fiber membrane was sandwiched between two stainless-steel electrodes in coin cells for the testing.

**Statistics section.** For the change of electrolyte resistance (Fig. 3c), the averages and deviations are based on three consecutive measurements of electrochemical impedance spectroscopy results.

## Declarations

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## Author contributions

C.W. and W.L. conceived the idea. C.W. conducted the electrolyte formulation, materials characterization and electrochemical evaluation. A.T. and P.S. carried out the cryogenic transmission electron microscopy and corresponding analysis. C.W., A.T., M.T.M. and W.L. cowrote the paper. All the authors discussed the results and commented on the manuscript.

## Competing interests

The authors declare no competing interests.

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