

报告标题: Tetrahydropyran-Assisted Solvation Structure Modulation
in Glyme Ether Electrolytes for Highly Stable Anode-Free Sodium Metal
Batteries

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Tetrahydropyran-Assisted Solvation Structure Modulation in Glyme
Ether Electrolytes for Highly Stable Anode-Free Sodium Metal Batteries

Table of Contents

Abstract.....	1
Keywords	1
Introduction.....	2
Experimental Section.....	4
Results and discussion	7
Conclusion	19
Acknowledgments	19
References.....	21

Abstract

Anode-free sodium metal batteries (AFSMBs) have the potential to achieve a higher energy density by eliminating traditional anode materials. However, the performance is greatly dependent on the electrolyte, particularly on how it changes the solvation structure of Na^+ and interfacial desolvation. In this study, tetrahydropyran (THP) was introduced to reduce the strong coordinating effect between diglyme (G2) and Na^+ , enabling the PF_6^- anions to enter the first solvation shell and form a solvation structure rich in contact ion pairs (CIPs). This structure lowered the activation energy of Na^+ by 69% and demonstrated excellent performance in ion transfer. The GT2 electrolyte (1 M NaPF_6 in G2/THP (1/2, v/v)) has an ionic conductivity of 6.83 mS cm^{-1} and a Na^+ transference number of 0.798 at 20°C . In the $\text{Al}@\text{C}||\text{Na}$ half-cell, the GT2 electrolyte exhibits a Coulombic efficiency of 99.96% and a smooth morphology of deposited sodium metal. In the $\text{NFPP}||\text{Na}$ half-cell, the GT2 electrolyte supports 1000 cycles at 1 C and retains 75% capacity at 30 C. It also forms an inorganic-rich SEI/CEI on the electrode surface. The $\text{NFPP}||\text{Al}@\text{C}$ anode-free pouch cell delivers a capacity of 1400 mAh at 1C, and its energy density reaches 168.6 Wh kg^{-1} , indicating excellent practicality.

Keywords

Electrolytes, Anode-Free Sodium Metal Batteries, Ether

Introduction

Sodium ion batteries (SIBs) are considered a competitor in the field of large-scale energy storage systems, because of the abundance of sodium resources, low cost, and the fact that they share similar electrochemical mechanisms with lithium ion batteries.^{1,2} Nevertheless, the path to commercialization for SIBs still encounters difficulties, one of which concerns the selection of anode material.^{3,4} The traditional sodium metal anode has a high theoretical capacity (1166 mAh g⁻¹) and the lowest redox potential, but during cycling it forms an unstable solid electrolyte interphase (SEI) and dendrites, causing a low CE, a short cycle life, and even safety problems.⁵ To overcome these issues, Anode-Free Sodium Metal Batteries (AFSMBs) have been developed.^{6,7} These batteries raise the energy density by depositing and stripping sodium metal directly onto the current collectors and thus omitting the need for anode materials.⁸ However, AFSMBs' performance relies significantly on the electrolyte. The electrolyte must enable the rapid transfer of sodium ions and form a stable and uniform SEI on the electrode to inhibit dendrite growth, prevent electrolyte decomposition, and maintain a high efficiency of plating and stripping.^{9,10} Therefore, the development of an electrolyte is of the utmost importance to achieve the commercialization of AFSMBs.

In SIBs, the solvation structure of electrolytes has a decisive influence on the electrochemical performance of batteries.^{11,12} Ether-based electrolytes, especially diglyme (G2),^{13,14} have received wide attention because of their good compatibility and high ionic conductivity.¹⁵ However, the strong coordination between G2 solvents and Na⁺ leads to a tight solvation structure, resulting in a high desolvation energy barrier for Na⁺ at the electrode/electrolyte interface, which limits ion transfer and prevents uniform deposition.¹⁶ The strong solvation effect excludes the PF₆⁻ anions from the first solvation shell, so that the solvent decomposition products form the SEI. These organic components are not dense or stable and are less effective in dendrite suppression.¹⁷ To overcome the limitations of the G2 solvent, researchers have focused on improving electrolyte performance by changing the solvation structure. The usual approaches include adding weak solvation additives¹⁸, using highly concentrated electrolytes¹⁹, and developing new electrolytes.²⁰ These methods seek to diminish the strong coordination between solvents and Na⁺, encourage the anions to participate in solvation, and lead to the formation of inorganic-rich stable SEIs. Hence, the desolvation energy is lowered, and ion transfer is accelerated.

The objective of this study is to control the solvation structure of the 1 M NaPF₆-G2 electrolyte by introducing tetrahydropyran (THP) to enhance the electrochemical performance of the AFSIBs. It was discovered that the weak solvation properties of THP allow it to form a weak C-H...O hydrogen bond with the G2 solvent and enable it to reduce the strong coordination between G2 and Na⁺. The results of molecular dynamics (MD) and nuclear magnetic resonance (NMR) show that as the amount of THP increases in the electrolyte, the coordination number of G2 and Na⁺ gradually

decreases, yet more PF_6^- anions enter the first solvation shell, forming more contact ion pairs (CIPs). The Raman spectroscopy proves the transition in solvation structure from solvent-separated ion pairs (SSIPs) to CIPs. This anion-rich solvation structure lowers the desolvation activation energy, increases the speed of ion transfer, and promotes the formation of an inorganic-rich SEI containing F and P elements, thus suppressing sodium dendrite formation and leading to smooth, uniform deposition of sodium metal. Electrochemical tests indicate that the GT2 electrolyte presents a high ionic conductivity, increased Na^+ transference number, lower desolvation energy, and advanced cycling stability and rate performance. Eventually, AFSMB coin cells and pouch cells were assembled and their practicality was demonstrated. These observations offer new insights into the commercialization of AFSMBs.

Experimental Section

Materials

The cathode current collectors, including carbon-coated aluminum (Al/C), the conductive agent Super P, and the polymer binder Poly(vinylidene Fluoride) (PVDF), were purchased from Guangdong Canrd New Energy Technology Company. The cathode material, $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ (NFPP), was purchased from Jiangsu Hid Func Technology. The supporting salt, sodium hexafluorophosphate (NaPF_6), was purchased from Duoduo Chemical Reagent Co., Ltd. Diglyme (G2) and tetrahydropyran (THP) were purchased from TCI (Shanghai) Chemical Industry Development Co., Ltd. Al@C||NFPP pouch cells were purchased from Jiangsu Jufeng New Energy Technology Co., Ltd.

Material Synthesis: Electrode and Electrolyte Preparation

The cathode electrode was obtained by mixing NFPP powder, Super P, and PVDF at a mass ratio of 8:1:1. It was uniformly spread onto Al foil and dried at 80 °C in a vacuum oven for 12 hrs. The areal mass loading of the electrode was controlled to 1- 2 mg cm⁻². The anode electrode was obtained from Al@C foil and was cleaned in ethanol. All solvents were dehydrated with a 4 Å molecular sieve to avoid trace water. The PG electrolyte was prepared by dissolving 1 M NaPF_6 in G2. The GT1 electrolyte was prepared by dissolving 1 M NaPF_6 in G2 and THP in a 1:1 ratio. The GT2 electrolyte was prepared by dissolving 1 M NaPF_6 in G2 and THP in a 1:2 ratio. The GT3 electrolyte was prepared by dissolving 1 M NaPF_6 in G2 and THP in a 1:3 ratio. The GT4 electrolyte was prepared by dissolving 1 M NaPF_6 in G2 and THP in a 1:4 ratio. The solutions were stirred at room temperature inside a glove box for over 12 hours for homogenization. All electrolyte preparations were required to be carried out in an argon-filled glove box (MBRAUN, Shanghai, China) with $\text{O}_2 < 0.1$ ppm and $\text{H}_2\text{O} < 0.1$ ppm.

Electrochemical Measurements

The CR2032 coin cells and pouch cells were assembled in an argon-filled glove box. The half-cells were assembled using Na metal foil and cathode materials as the electrode and separated by a separator with prepared electrolytes. Al@C||Na cells were assembled using Al@C foil (with a diameter of 16 mm) and Na metal foil (with a diameter of 12 mm) and a separator injected with the corresponding electrolytes. Na||Na cells were assembled using two Na metal foils on each side of the separators. The Land test system (CT3002A, Wuhan, China) was used to perform electrochemical cycling tests and rate performance tests at 25 °C. The Aurbach method of Al||Na was carried out at 25 °C. The Al@C||Na full cells and half cells were cycled between 2.0 and 3.6 V. Electrochemical impedance spectroscopy (EIS) was tested on the Energylab XM electrochemical workstation (Solartron Analytical, Princeton, U.S.) with the frequency range from 10⁻² to 10⁵ Hz and a 2 mV AC amplitude. The ionic conductivity (σ) of the

electrolytes was obtained by assembling a symmetric stainless cell and calculated based on the following equation:

$$\sigma = \frac{L}{R \times S}$$

Where R is the bulk resistance, L is the thickness of the separator, and S is the contact area between the stainless steel and the separator. The Na⁺ transference number (t_{Na^+}) of the electrolytes was obtained by assembling symmetric Na||Na cells and calculated based on the following equation:

$$t_{Na^+} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})}$$

Where ΔV is the constant voltage applied across the cell, R_0 is the initial resistance tested before polarization, I_0 is the initial current, I_{ss} is the steady-state current, and R_{ss} is the resistance after polarization.

Characterizations

X-ray photoelectron spectroscopy (XPS) was used to collect XPS data and find the binding energy values, with the C 1s peak (284.8 eV) as the reference point. Nuclear Magnetic Resonance (NMR) was used to characterize the chemical environment of sodium ions and H, F, and C in electrolytes. 2D ¹H-¹H and ¹H-¹³C COSY spectra of the GT2 electrolyte were measured at 25 °C. A transmission electron microscope (TEM, JEOL JEM-2100Plus) was used to observe the SEI and CEI. A scanning electron microscope (SEM, Nova Nano SEM 450) was used to observe the surface morphology of Na metal deposition. Before characterization, the electrodes were rinsed with the solvent for over 30 seconds and further dried under vacuum. Raman Spectroscopy (HORIBA LabRAM HR Evolution, Japan) was used to analyze solvation structures of electrolytes and distinguish the percentages of AGG, CIP, and SSIP. The time-of-flight secondary ion mass spectrometry (ToF-SIMS, IONTOF M5 Instrument (IONTOF GmbH)) was used to test the components of the interface layer on the electrode surface. The measurements were carried out over a sputtered area of 50 × 50 μm².

Computations and Calculations

All molecular dynamics simulations were performed using the GROMACS software package at 298.15K with the General Amber Force Field (GAFF) employed to describe all molecular interactions. Atomic partial charges were derived from restrained electrostatic potential (RESP) fitting based on quantum chemical calculations performed at the B3LYP/6-311G** level of theory with Grimme's D3 empirical dispersion correction (GD3BJ) using Gaussian software, followed by RESP charge analysis using the Multiwfn program. The systems were first energy-minimized using the steepest descent algorithm for 10,000 steps with a convergence criterion of 100 kJ mol⁻¹ nm⁻¹, followed by a multi-stage equilibration protocol: an initial 0.5 ns NVT equilibration with simulated annealing from 10 K to the target temperature using a thermostat coupling constant of 0.1 ps, 1 ns NVT equilibration at the target temperature, and subsequently 4 ns NPT equilibration. The production MD simulations were carried out in the NVT ensemble for 10 ns with a time step of 1 fs. Temperature was maintained

at the respective target temperature throughout the equilibration and production phases using the velocity-rescale thermostat with a coupling constant of 0.2 ps. Periodic boundary conditions were applied in all three dimensions using the Verlet cutoff scheme. Electrostatic interactions were calculated using the particle mesh Ewald (PME) method with a real-space cutoff of 1.2 nm, while van der Waals interactions were truncated at 1.2 nm with long-range dispersion corrections applied. All bonds involving hydrogen atoms were constrained using the LINCS algorithm. Trajectory frames were saved every 10 ps during the production run for subsequent analysis.

Results and discussion

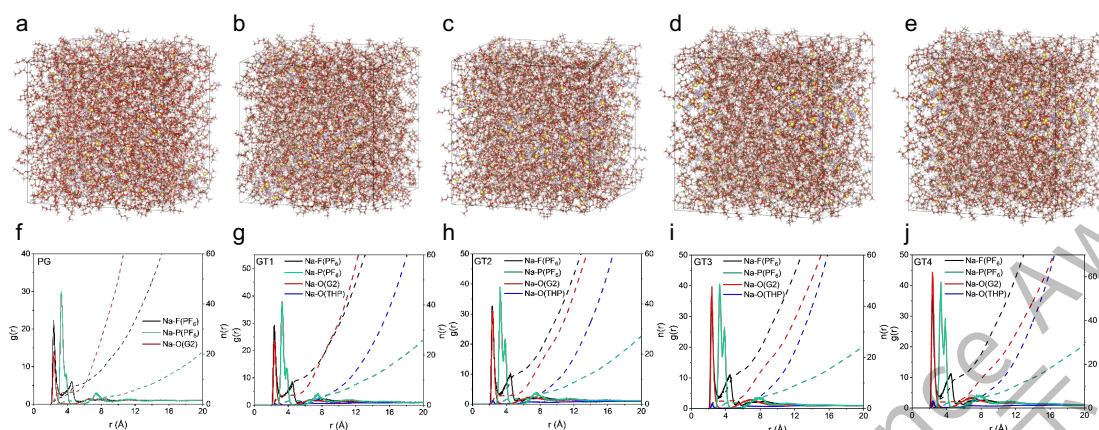


Figure 1. Simulations of electrolyte solvation structures. Snapshots obtained by MD simulations at 298.15 K of (a) PG, (b) GT1, (c) GT2, (d) GT3, and (e) GT4 electrolytes. The calculated radial distribution functions [RDF, $g(r)$, solid lines] and coordination numbers [$n(r)$, dashed lines] of Na^+ in (f) PG, (g) GT1, (h) GT2, (i) GT3, and (j) GT4 electrolytes.

A classical molecular dynamics (MD) simulation was performed to examine the interaction between the solvents and sodium salt. **Fig. 1a-e** present snapshots from the MD simulations of the five electrolytes. The following table shows the details of the modelling. **Table 1** demonstrates the wide distribution of Na^+ ions, suggesting that sodium salts dissolve extensively in the solvents.

Table 1. Constructed modelling systems and detailed system compositions.

Electrolytes	Number of NaPF_6	Number of G2 Molecules	Number of THP Molecules
PG	100	704	0
GT1	100	352	511
GT2	100	234	682
GT3	100	176	767
GT4	100	141	818

The radial distribution functions and the coordination numbers of the five electrolytes are given in **Fig. 1f-j**. The peak positions in the RDFs reveal the coordinating relationship between solvents, anions, and sodium ions. The peaks for Na and O atoms in G2, Na and O atoms in THP, and Na and F atoms in the anion PF_6^- are all located at approximately 2.4 Å, corresponding to the first solvation shell around the sodium ions. This proves that sodium ions can coordinate with both the O atoms of the solvents and F atoms of the anions. Meanwhile, the peak of Na and P atoms of PF_6^- at approximately 3.27 Å suggests that the P atoms of the anion are situated outside the first solvation shell.

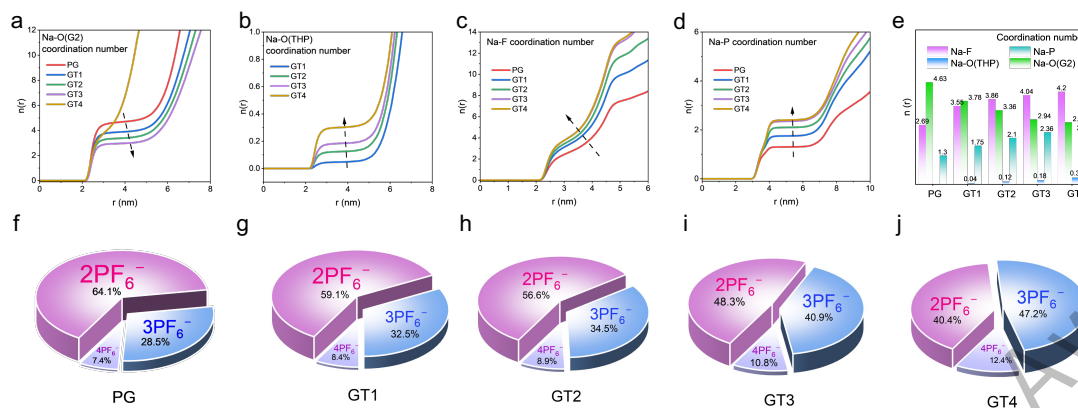


Figure 2. The analysis of coordination number analysis. Coordination number distribution curves in different electrolytes of (a) Na-O(G2), (b) Na-O(THP), (c) Na-F, and (d) Na-P. (e) Coordination number at the position of the minimum value of the radial distribution function. The proportion of different numbers of anions in the solvation structures of (f) PG, (g) GT1, (h) GT2, (i) GT3, and (j) GT4 electrolytes.

In **Fig. 2a and 2b**, as the ratio of THP in the electrolyte increases, the coordination number of Na and O atoms in G2 gradually decreases, while the coordination number of Na and O atoms in THP increases correspondingly. **Fig. 2c and 2d** present the coordinating relationship between Na and the anions. Both the Na-F and Na-P coordination numbers increase with THP content. This demonstrates that increasing the ratio of THP weakens the strong coordination between G2 and the sodium ions, loosens the solvation structure, and enables the anions to enter its solvation structure and form the SEI. **Fig. 2e** summarizes the coordination numbers of Na with different coordinating atoms in each electrolyte; the values are taken at the minimum of the RDF for each atom and represent a complete solvation structure. The coordination numbers of Na and O atoms in G2 for the PG, GT1, GT2, GT3, and GT4 electrolytes are 4.63, 3.78, 3.36, 2.94, and 2.81, respectively. The coordination numbers of Na and P atoms in the anions in the PG, GT1, GT2, GT3, and GT4 electrolytes are 1.30, 1.75, 2.10, 2.36, and 2.4, respectively. The coordination numbers of Na and F atoms in the anions in the PG, GT1, GT2, GT3, and GT4 electrolytes are 2.69, 3.55, 3.86, 4.04, and 4.2, respectively. Consequently, as the ratio of THP in the electrolyte increases, the involvement of the G2 solvent in the solvation structure gradually decreases, while the participation of PF_6^- anions gradually increases, resulting in an anion-rich solvation structure.

To further investigate the role of PF_6^- anions in solvation structures, the distribution of the number of anions was analyzed. As shown in **Fig. 2f-j**, the solvation structures contain 2-4 anions, with two and three PF_6^- anions having a very high ratio, but the percentages vary among electrolytes. The percentages of solvation structures containing two PF_6^- anions in PG, GT1, GT2, GT3, and GT4 are 64.1%, 59.1%, 56.6%, 48.3%, and 40.4%, respectively. The percentages of containing three PF_6^- anions in PG, GT1, GT2, GT3, and GT4 are 28.5%, 32.5%, 34.5%, 40.9%, and 47.2%, respectively. The percentages of containing four PF_6^- anions in PG, GT1, GT2, GT3, and GT4 are

7.4%, 8.4%, 8.9%, 10.8%, and 12.4%, respectively. Using weighted statistics, the number of PF_6^- anions in the solvation structures of the PG, GT1, GT2, GT3, and GT4 electrolytes is 2.433, 2.493, 2.523, 2.625, and 2.72, respectively. As the proportion of THP in electrolytes increases, the percentages of solvation structures with 2 PF_6^- anions gradually decrease. This indicates that more PF_6^- anions are incorporated into the solvation structures; these anion-rich solvation structures are transported to the electrode and thus contribute to the formation of SEI.

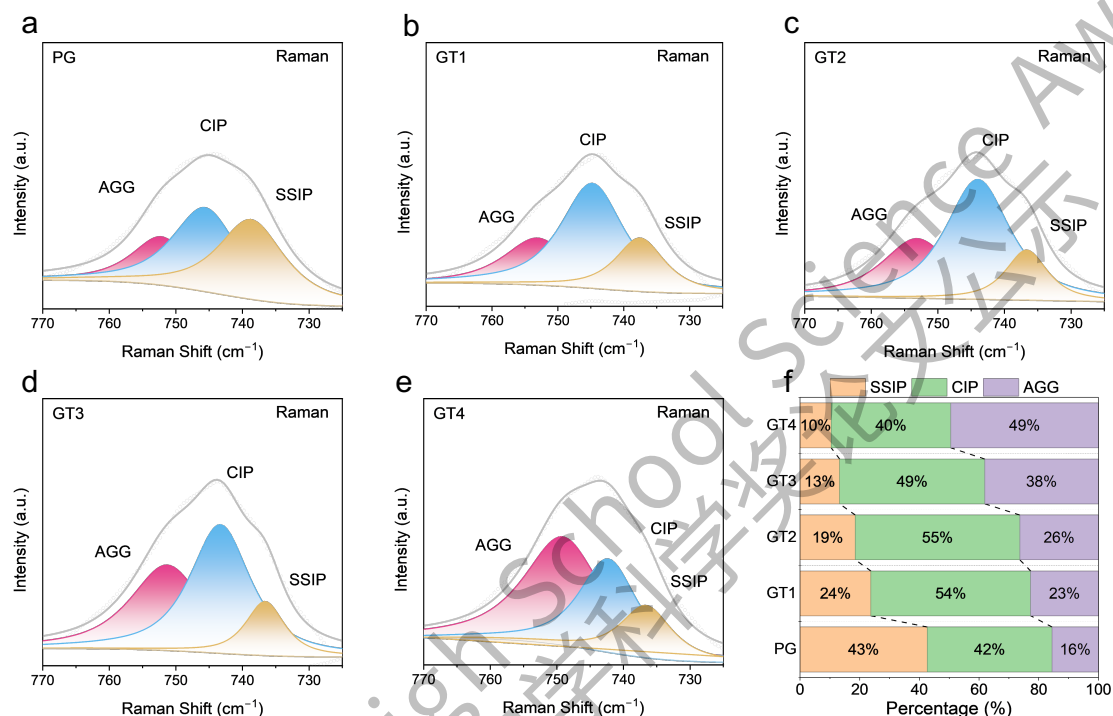


Figure 3. Peaks of SSIPs, CIPs, and AGGs from Raman peak deconvolution in (a) PG, (b) GT1, (c) GT2, (d) GT3, and (e) GT4 electrolytes. (f) Proportion of SSIPs, CIPs, and AGGs.

Changes in the chemical environment of ions directly affect the symmetry and electron-cloud distribution in PF_6^- . This is displayed in the Raman spectroscopy by shifts in position, intensity, and full width at half maximum (FWHM). Raman spectroscopy was employed to monitor the vibrations of PF_6^- , thereby revealing the microstructural differences in ionic association states in the electrolytes (**Fig. 3a-3e**). The PF_6^- peaks can be deconvoluted into solvent-separated ion pairs (SSIPs), contact ion pairs (CIPs), and aggregates (AGGs), with peaks at 736.7, 744.1, and 753.1 cm^{-1} , respectively. The percentages of SSIPs, CIPs, and AGGs can be determined from the peak areas (**Fig. 3f**). As the proportion of THP increases, the percentages of SSIPs in the solvation structures drop considerably, while the ratios of CIPs increase markedly. This proves that in the PG electrolyte, the strong coordination ability of G2 results in a closely bonded solvation structure with Na^+ , pushing PF_6^- away from the first solvation shell. Upon addition of THP, the solvation structure shifts toward CIPs, and the strong coordination of G2 is reduced, so PF_6^- enters the first solvation shell.¹⁷ This promotes the desolvation of Na^+ and the formation of an inorganic-rich SEI. As the content of THP increases,

the ratio of AGGs rises, and the coordination of G2 is further weakened. However, excessive AGGs cause a reduction in ionic conductivity and have a negative effect on the rate performance of the battery. Therefore, considering the balance between ionic conductivity and desolvation behavior, the GT2 electrolyte exhibits an advantage due to its relatively high proportion of CIPs and lower levels of AGGs and SSIPs.

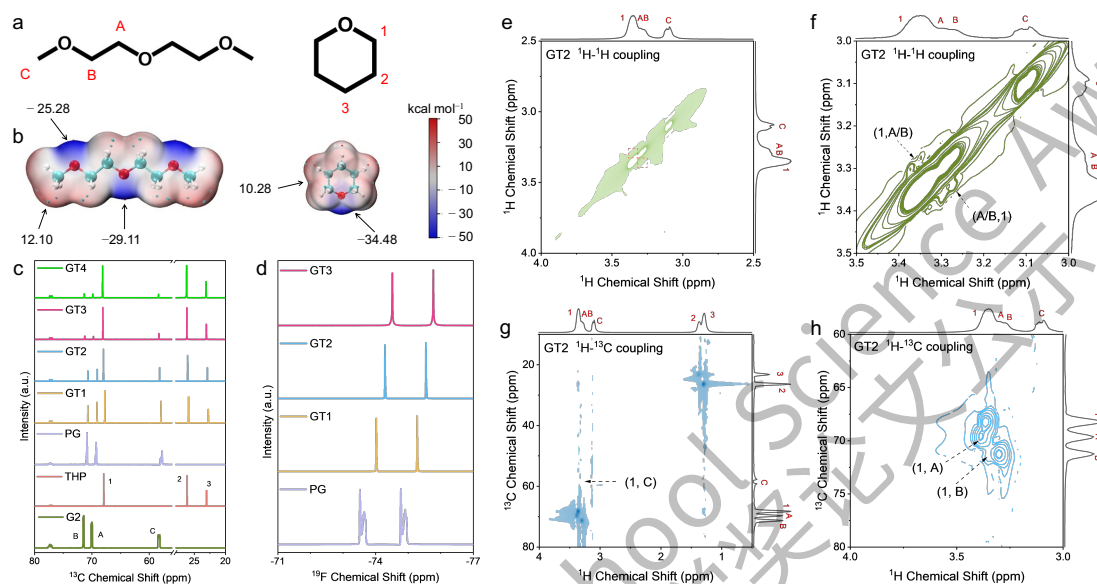


Figure 4. Characterization of electrolyte solvation structures. (a) Chemical structures and (b) the ESP energy of G2 and THP solvents. (c) ^{13}C and (d) ^{19}F NMR spectra of solvents and electrolytes. (e) ^1H - ^1H NOESY spectra and (f) partially enlarged detail. (g) ^1H - ^{13}C HSQC spectra and (h) partially enlarged detail.

To examine the mechanism by which THP affects solvation structures, NMR spectroscopy was employed to analyze the changes in these structures. In **Fig. 4a-4b**, the electrostatic potentials (ESP) of the G2 and THP molecules were calculated, and the minimum and maximum ESP values were determined. By calculation, the most negative ESP value for G2 was located near the central O atom with a value of $-29.11 \text{ kcal mol}^{-1}$; the ESP values of the other two O atoms were $-25.28 \text{ kcal mol}^{-1}$. In THP, the most electronegative O atom increased the ESP of the adjacent α -H atom to $10.28 \text{ kcal mol}^{-1}$. The oxygen atom in THP exerts a strong electron-withdrawing effect on the adjacent α -carbon atoms through bond polarization and inductive effects, resulting in deshielded and partially acidic α -protons. These α -protons can participate in $\text{C}-\text{H}\cdots\text{O}$ weak hydrogen bonding with the O atoms of the G2 solvents. This phenomenon can be investigated by 1D and 2D NMR.

Fig. 4c demonstrates the ^{13}C NMR spectrum. The peaks of C atoms in the A, B, and C positions of the G2 molecule are located at 70.04, 71.50, and 58.35 ppm; the peaks of C atoms in the A, B, and C positions of the THP molecule are located at 67.95, 26.14, and 23.03 ppm. In the PG electrolyte, the ^{13}C peaks shift downfield due to the deshielding effect caused by Na^+ , indicating the coordinating interaction between Na^+ and the G2 solvent. After including THP in the electrolyte, the $\text{C}-\text{H}\cdots\text{O}$ weak

hydrogen-bonding effect removes some of the electron density from the α -C in G2, thus enhancing the deshielding effect. Consequently, the ^{13}C NMR peaks shift further downfield in the GT1 and GT2 electrolytes, highlighting the effect of THP on Na^+ -G2 coordination. However, as the THP content continues to increase, THP acts as a diluent and enters the inner solvation shell; Na^+ then coordinates with THP, weakening the Na^+ -G2 coordination. As a result, the ^{13}C peaks in GT3 and GT4 slightly shift upfield as compared to GT2.

Furthermore, the ^{19}F NMR spectrum clearly presents the changes in the anion environment (**Fig. 4d**). The ^{19}F peaks in the PG electrolyte are located at -73.52 and -74.78 ppm. The ^{19}F peaks in the GT1 electrolyte are located at -74.02 and -75.28 ppm. The ^{19}F peaks in the GT2 electrolyte are located at -74.2 and -75.55 ppm. The ^{19}F peaks in the GT3 electrolyte are located at -74.51 and -75.77 ppm. When THP is included in the electrolyte, the ^{19}F peaks shift gradually upfield. This demonstrates that more PF_6^- anions enter the solvation structure. The results are consistent with the MD simulations and Raman spectroscopy.

To investigate the non-covalent interactions involving weak hydrogen bonding $\text{C}-\text{H}\cdots\text{O}$ among solvents in the GT2 electrolyte, $^1\text{H}-^1\text{H}$ (Nuclear Overhauser Effect Spectroscopy) NOESY and $^1\text{H}-^{13}\text{C}$ (Heteronuclear Single Quantum Coherence) HSQC were employed. In **Fig. 4e**, both the horizontal and vertical axes display the ^1H NMR spectrum of the electrolyte. Apart from the strong diagonal signals of intramolecular $^1\text{H}-^1\text{H}$ interactions, certain off-diagonal cross peaks are presented in the NOESY spectrum. The two cross peaks (1, A/B) and (A/B, 1) (**Fig. 4f**) correspond to the α -H of position 1 in THP and H of position A and B in G2. This phenomenon is also observed in the $^1\text{H}-^{13}\text{C}$ HSQC spectrum. In **Fig. 4g-4h**, the $\text{C}-\text{H}\cdots\text{O}$ weak hydrogen bonds can interact with all three O atoms in G2. This demonstrates that THP has a modulating effect on the solvation structure.

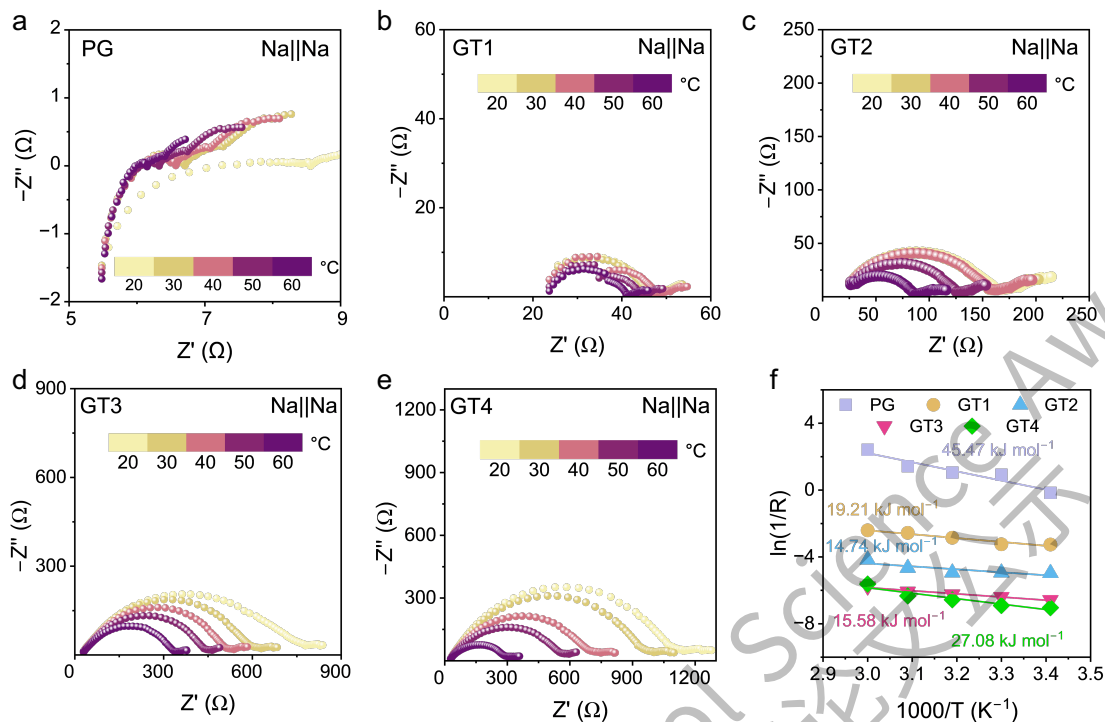


Figure 5. Nyquist plots at various temperatures obtained from Na||Na symmetric cells in (a) PG, (b) GT1, (c) GT2, (d) GT3, and (e) GT4 electrolytes. (f) Activation energies obtained from Nyquist plots.

The presence of THP improves the solvation structure of G2 and resolves the issue of difficult desolvation caused by the strong solvation ability of G2. This conclusion is supported by experimenting with varying temperatures in electrochemical impedance spectroscopy (EIS) measurements (Fig. 5a-5e).

According to the Arrhenius relationship, the equation can be derived:

$$1/R_{SEI} = A \exp(-E_a/RT)$$

Where R is the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$), R_{SEI} is the resistance of the SEI, and E_a is the activation energy for desolvation, which can be determined through the Nyquist plot. E_a can be obtained by carrying out a linear regression of $\ln(1/R)$ against $1/T$. In Fig. 5f, the values of E_a for the PG, GT1, GT2, GT3, and GT4 electrolytes are 45.47, 19.21, 14.74, 15.58, and 27.08 kJ mol^{-1} , respectively. The GT2 electrolyte has the smallest activation energy for desolvation, which proves that GT2 has the lowest energy barrier for Na^+ and thus promotes desolvation at the interface. This confirms that the inclusion of THP improves the GT2 electrolyte regarding interfacial kinetics.

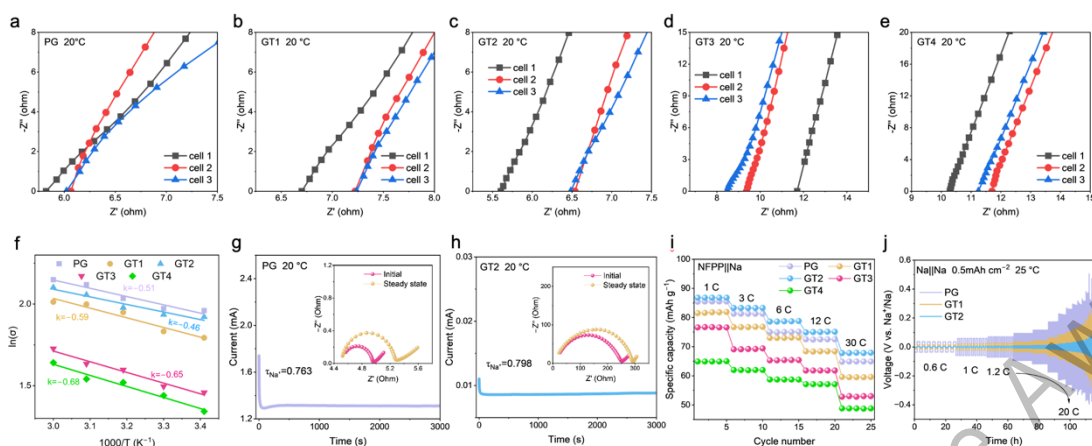


Figure 6. Nyquist plot measuring electrical conductivity of (a) PG, (b) GT1, (c) GT2, (d) GT3, and (e) GT4 electrolytes. (f) Ionic conductivities of five electrolytes between 20 to 60 °C. Nyquist plots and chronoamperograms of Na||Na symmetric cells and t_{Na+} for g) PG and h) GT2 at 25 °C. (i) Rate performance of NFPP cathode in different electrolytes. (j) Rate performance at 0.5 mAh cm⁻² of Na||Na symmetric cells.

By performing EIS on symmetric stainless steel cells and averaging three cells for each electrolyte, the ionic conductivities of PG, GT1, GT2, GT3, and GT4 electrolytes at 20 °C, determined by performing EIS on symmetric stainless steel cells and averaging the results for three cells per electrolyte, are 7.4, 6.01, 6.83, 4.3, and 3.83 mS cm⁻¹, respectively (**Fig. 6a-6e**). Although the ionic conductivity of GT2 is less than that of the PG electrolyte, it still has the highest value of all the electrolytes containing THP. This result is consistent throughout all temperatures from 20 °C to 60 °C (**Fig. 6f**). When the $\ln(\sigma)$ values are linearly fitted against $1000/T$ data, the slopes of PG, GT1, GT2, GT3, and GT4 electrolytes are -0.51 , -0.59 , -0.46 , -0.65 , and -0.68 , respectively. The slopes correspond to the activation energies in the solvation structures. The smaller slope observed in GT2 indicates that there is a lower diffusion energy barrier, resulting in a greater ability of ion transfer.

The conclusion is supported by the transference number. In **Fig. 6g-6h**, PG has a transference number of 0.763, whereas GT2 has a transference number of 0.798.^{21, 22} This is because the G2 solvation structure in the PG electrolyte primarily undergoes transport by a vehicular mechanism, whereas GT2 contains more CIPs in the THP solvent, and the dynamic, compact solvation structure improves the ion's hopping ability.

The GT2 electrolyte displays better rate performance among the electrolytes. In the NFPP||Na half -cells, the PG, GT1, GT2, GT3, and GT4 electrolytes give discharge capacities of 81.3, 76.7, 83.3, 69.1, and 62 mAh g⁻¹ at 3 C, respectively (**Fig. 6i**), with the GT2 electrolyte exhibiting the highest capacity. At a high rate of 30 C, the GT2 electrolyte still manages to provide a discharge capacity of 67.9 mAh g⁻¹. In the rate performance tests of Na||Na symmetric cells (**Fig. 6j**), the PG and GT1 electrolytes

show serious voltage fluctuations at high rates, while the GT2 electrolyte maintains stable cycling even at a high rate of 20 C.

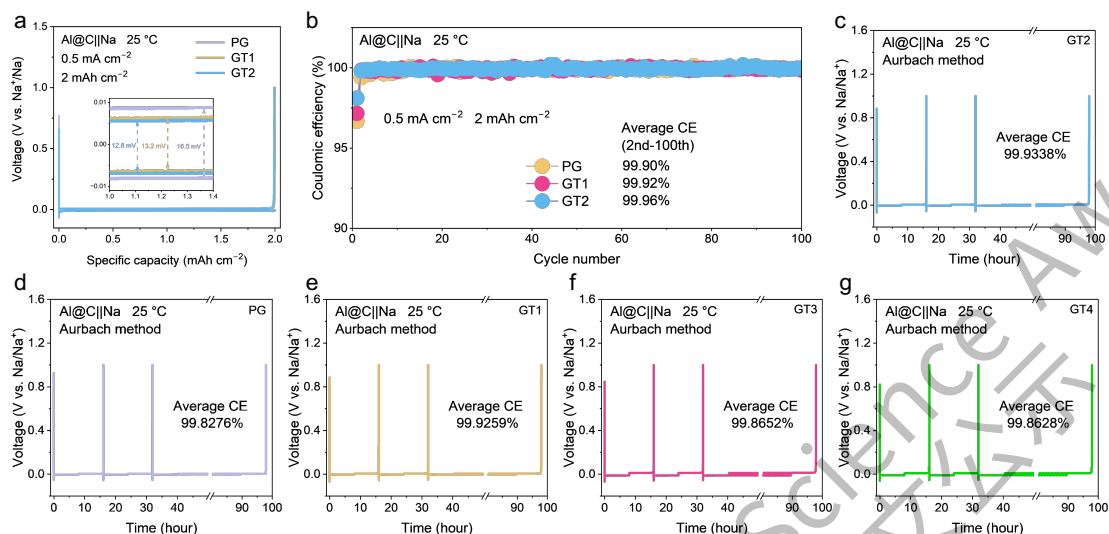


Figure 7. Electrochemical performance of Al@C||Na half cells. (a) Voltage profiles in different electrolytes during Na plating/stripping on the Al@C at 0.5 mA cm⁻² and 2.0 mAh cm⁻² and the comparison of polarization. (b) The CEs of Na plating/stripping on the Al@C at 0.5 mA cm⁻² and 2.0 mAh cm⁻². CE of Na plating/stripping on the Al@C using the Aurbach method in (c) GT2, (d) PG, (e) GT1, (f) GT3, and (g) GT4 electrolytes.

Improvements in the deposition process have enabled the GT2 electrolyte to achieve superior electrochemical performance. In **Fig. 7a**, the polarization value of the GT2 electrolyte during charge and discharge is 12.8 mV, which is notably lower than 16.5 mV for the PG electrolyte and 13.2 mV for the GT1 electrolyte. This result indicates a small interfacial polarization and a rapid desolvation in the GT2 electrolyte compared to the other electrolytes. **Fig. 7b** displays the stable cycling performance of Al@C||Na half-cells. At 0.5 mA cm⁻² and 2.0 mAh cm⁻², the initial Coulombic efficiencies (ICE) of the PG, GT1, and GT2 electrolytes are 96.67%, 97.26%, and 98.11%, respectively. From the second to the hundredth cycle, the average CEs for the PG, GT1, and GT2 electrolytes are 99.90%, 99.92%, and 99.96%, respectively, demonstrating that the GT2 electrolyte achieves high plating and stripping CEs. The average CE measured by the Aurbach method directly reflects irreversible negative effects, such as electrolyte decomposition and the formation of dead sodium, on sodium-metal plating and stripping stability. In **Fig. 7c-7g**, the average CEs determined by the Aurbach method for the GT2, PG, GT1, GT3, and GT4 electrolytes are 99.9338%, 99.8276%, 99.9259%, 99.8652%, and 99.8628%, respectively. The GT2 electrolyte exhibits the highest CE, indicating superior anode cycling stability. Rapid desolvation and efficient solvation structure transport further enhance the stability of plating and stripping of sodium metal on Al@C, thereby improving the battery cycling performance.

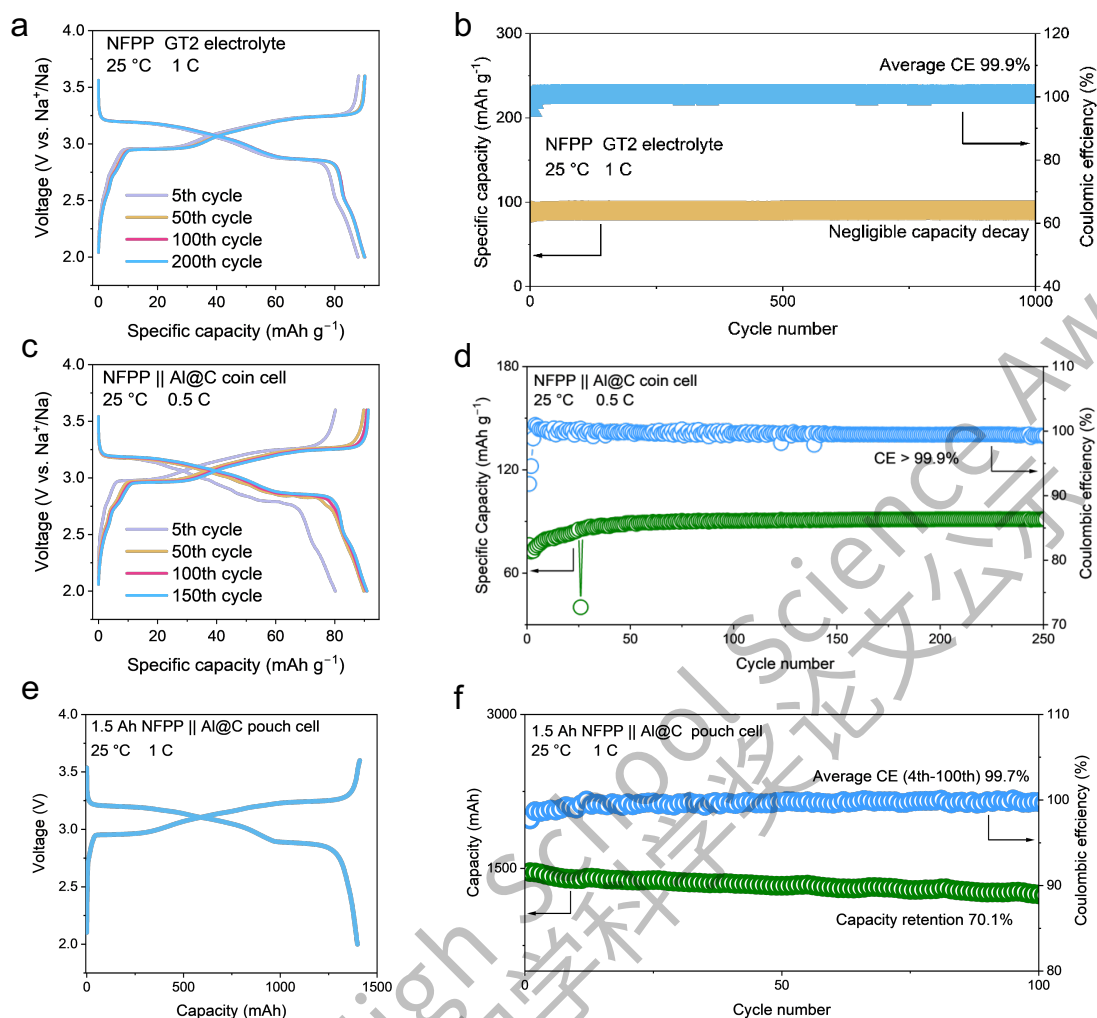


Figure 8. Electrochemical performance of NFPP||Na half-cells and AFSBs using the GT2 electrolyte. (a) Voltage profiles, (b) Cycling performance at 1 C of NFPP cathode. (c) Voltage profile, (d) Cycling performance at 0.5 C of NFPP||Al@C anode-free coin cell. (e) Voltage profile, (f) Cycling performance at 1 C of NFPP||Al@C anode-free pouch cell.

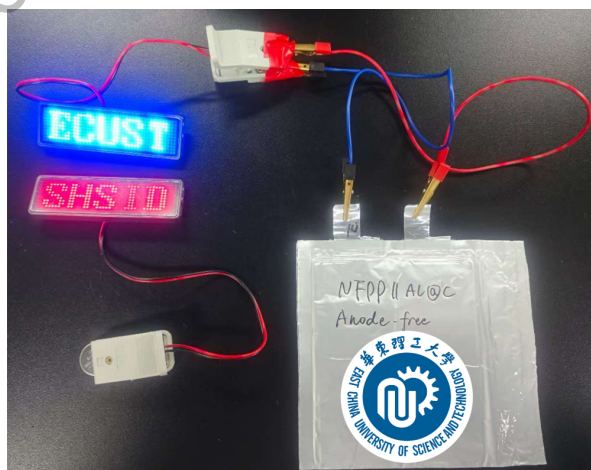


Figure 9. Actual performance in use of anode-free sodium coin and pouch cells.

The GT2 electrolyte also demonstrates strong electrochemical performance at the cathode. In **Fig. 8a-8b**, the GT2 electrolyte delivers a capacity of 91 mAh g⁻¹ at 1C at the NFPP cathode and maintains this capacity with no significant loss after 1000 cycles, indicating excellent cathode stability. In addition, an NFPP||Al@C coin-type anode-free full-cell was assembled (**Fig. 8c-8d**). With a stable interface, the specific capacity of the full-cell (based on the cathode) gradually increases during the first 20 cycles and stabilizes at 90.9 mAh g⁻¹ at 0.5C. Moreover, the capacity remains stable after 250 cycles at 0.5C, with a CE exceeding 99.9%.

To verify the application performance of the GT2 electrolyte, an NFPP||Al@C anode-free pouch cell with a capacity of 1.5 Ah was purchased and tested after electrolyte injection, sealing, and three low-rate cycles. In **Fig. 8e**, the pouch cell delivers a capacity of 1400 mAh at 1C. Based on the total cell weight, the energy density is 168.6 Wh kg⁻¹. The GT2 electrolyte also displays cycling stability. In **Fig. 8f**, the pouch cell retains 70.1% capacity after 100 cycles, and the average CE from the 4th to the 100th cycle is greater than 99.7%. This demonstrates that the GT2 electrolyte is highly compatible with the NFPP cathode and has significant application value. For instance, both the coin-cell and pouch-cell can power LED displays reading “SHSID” and “ECUST” (**Fig. 9**).

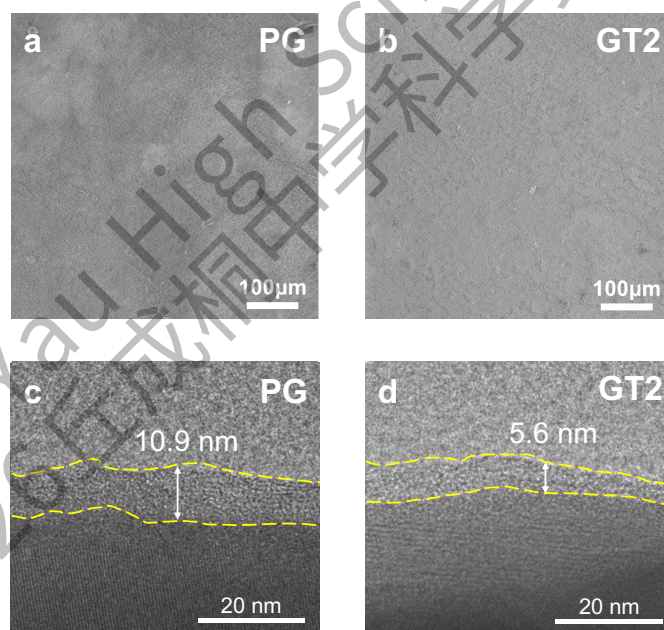


Figure 10. SEM images of deposited Na metal using (a) PG and (b) GT2 electrolytes. TEM image of the CEI layers on the NFPP cathode in (c) PG and (d) GT2 electrolytes.

Rapid desolvation and ion transfer increase the efficiency of plating and stripping of sodium metal on the anode because Na⁺ is able to deposit uniformly and stably on the anode current collector. In **Fig. 10a-10b**, the morphology of Na metal deposited on the anode current collector was examined using scanning electron microscopy (SEM). The

sodium metal deposited in the PG electrolytes shows pits and striations, whereas the deposited metal in the GT2 electrolyte is smooth and flat. Uniform Na deposition is the foundation of the high plating and stripping efficiency of the GT2 electrolyte.

When transmission electron microscopy (TEM) is used to investigate the morphology of the cathode, the CEI layer on the NFPP surface can be observed. In **Fig. 10c-10d**, the CEI layer formed with the PG electrolyte (10.9 nm) is thicker than the CEI layer formed with the GT2 electrolyte (5.6 nm), which indicates that the PG electrolyte tends to be oxidized at the cathode, leading to a thicker CEI layer, a greater interfacial resistance, and worse rate performance. On the other hand, the GT2 electrolyte can form a thinner and smoother CEI layer on the surface of the NFPP cathode, thus has an advantage in cathode rate performance.

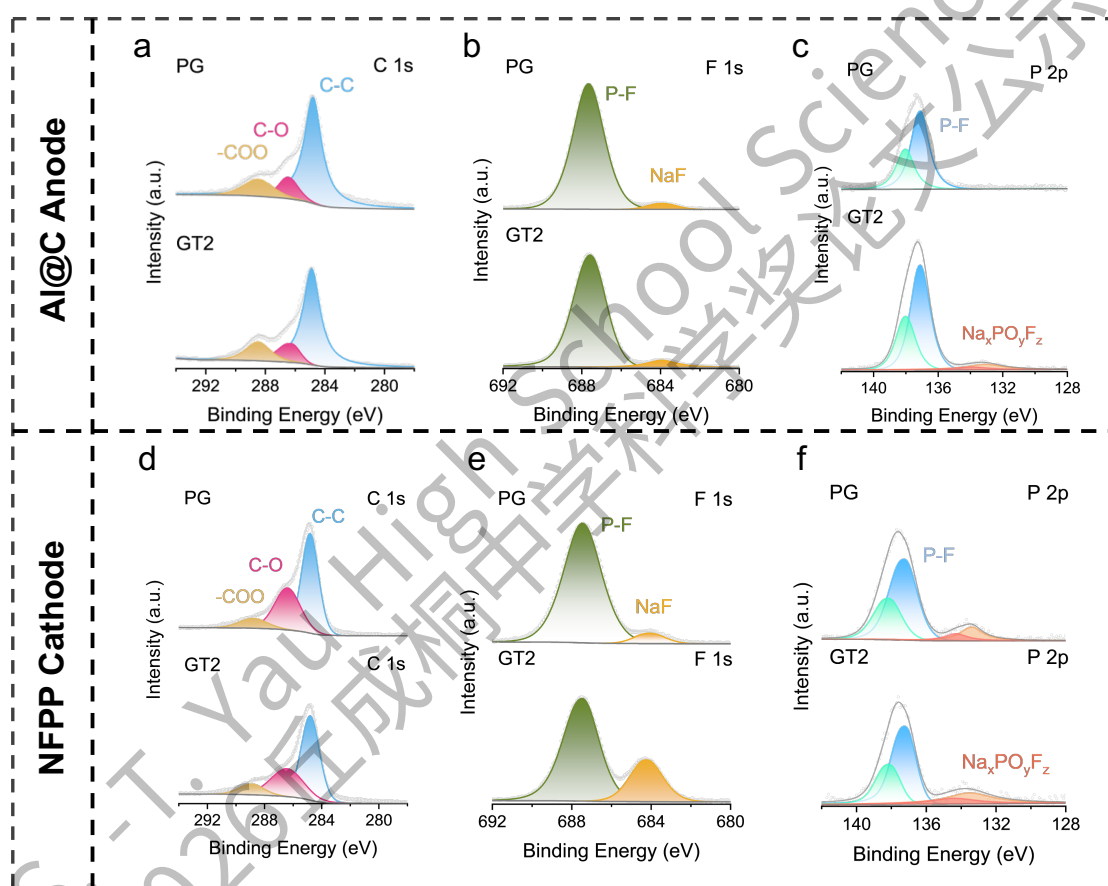


Figure 11. XPS spectra of electrodes using PG and GT2 electrolytes. (a) C 1s, (b) F 1s, and (c) P 2p XPS spectra of the Al@C anode. (d) C 1s, (e) F 1s, and (f) P 2p XPS spectra of the NFPP cathode.

The performance of the electrode-electrolyte interface (SEI) was examined using X-ray photoelectron spectroscopy (XPS) to analyze the composition of the interface. In **Fig. 11a**, the C 1s was mainly composed of organic components. The C 1s spectrum was deconvoluted into C—C (284.8 eV), C—O (286.4 eV), and —COO (289.0 eV).²³ This demonstrates that at the anode interface, G2 and other ether solvents produce long-chain polyether $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$, which are the primary source of organic

compounds at the interface. In **Fig. 11b-11c**, the F 1s and P 2p spectra were deconvolved to give F 1s as NaF (683.9 eV) and P—F (687.6 eV). ¹⁷**Fig. 11c** reveals that the P 2p spectra exhibit two P 2p spin-orbit doublets corresponding to P-F (136.3 eV) and Na_xPO_yF_z (134.5 eV). From these results, the GT2 electrolyte leads to the formation of more inorganic compounds, such as NaF and Na_xPO_yF_z. This indicates that the presence of THP allows more PF₆⁻ to enter the first solvation shell, resulting in an SEI that contains a higher proportion of inorganic elements of F and P. The SEI that is rich in inorganic compounds is more stable and denser and has a higher ionic conductivity, which improves both cycling stability and the plating and stripping efficiency at the anode.

The GT2 electrolyte can also establish a stable CEI interface on the NFPP cathode. In **Fig. 11d-11f**, the GT2 electrolyte produces a greater amount of inorganic components in the CEI when compared to the PG electrolyte, specifically more NaF and Na_xPO_yF_z. The inorganic-rich CEI composition ensures the stable cycling of the GT2 electrolyte on the NFPP cathode.

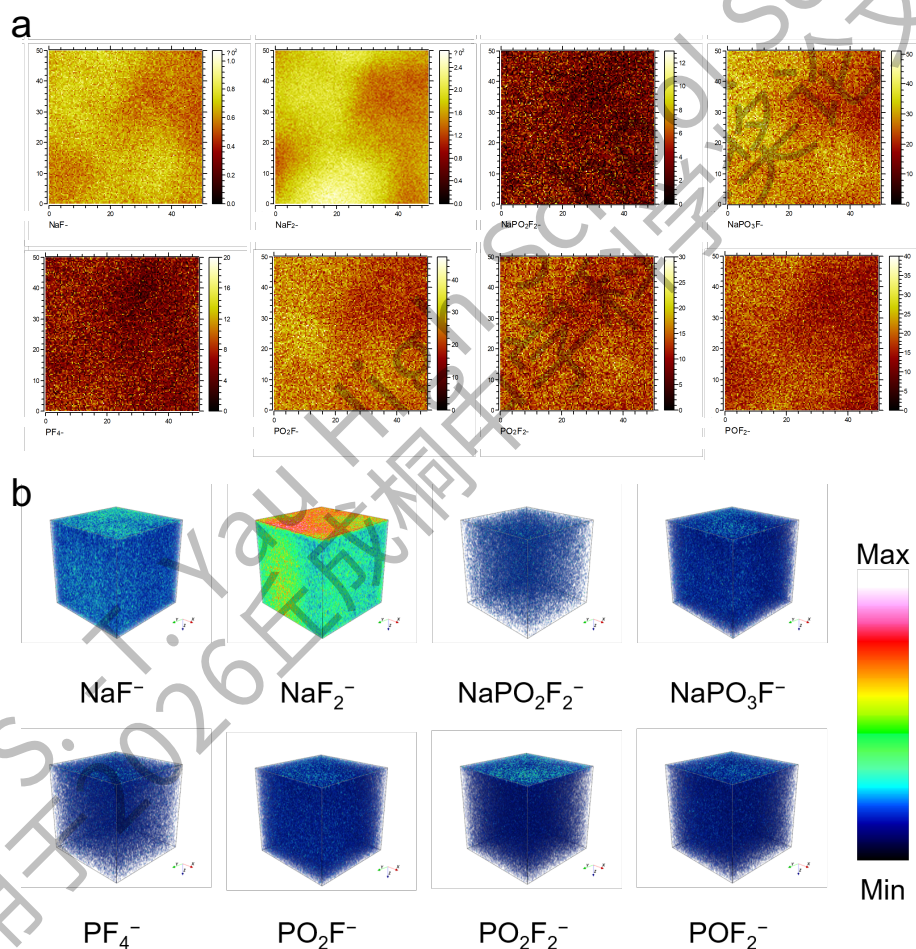


Figure 12. (a) ToF-SIMS 2D views of inorganic components by secondary ion species sputtered from the cycled NFPP cathode. (b) ToF-SIMS 3D views of inorganic components by secondary ion species sputtered from the cycled NFPP cathode.

To characterize the spatial distribution of inorganic components on the cathode, time-of-flight secondary ion mass spectrometry (ToF-SIMS) was employed. An area of $50 \times 50 \mu\text{m}^2$ was chosen on the NFPP cathode for the analysis. **Fig. 12a** presents the 2D distribution of the inorganic components on the surface of the electrode. The 3D view given in **Fig. 12b** reveals the distribution of inorganic compounds at various depths. The result demonstrates that a considerable amount of NaF^- and NaF_2^- is present in the CEI and is found at various depths. Additionally, species containing P were detected; most form compounds with F, including $\text{NaPO}_2\text{F}_2^-$, NaPO_3F^- , PF_4^- , PO_2F^- , PO_2F_2^- , and POF_2^- , and these are mainly concentrated near the surface. These components are the products of film formation from the PF_6^- anions. This indicates that the solvation structure of the GT2 electrolyte contains a large amount of PF_6^- , thus leading to the formation of an inorganic-rich CEI, which enhances the cathode stability of the GT2 electrolyte and ensures the stable operation of the NFPP cathode during cycling.

Conclusion

This research has successfully introduced THP into G2 solvent electrolyte, effectively regulated the Na^+ solvation structure, and improved the electrochemical performance of AFSMBs. Various types of characterizations reveal how THP weakens the strong coordination of G2 and Na^+ , fosters the formation of $\text{C}-\text{H} \cdots \text{O}$ weak hydrogen bonds, which enables the PF_6^- anions to be included in the first solvation shell, resulting in a CIP-rich solvation structure that supports ion transfer and provides a stable interface. The solvation structure reduces the desolvation energy barrier of Na^+ , speeds up interfacial dynamics, and forms an inorganic-rich SEI/CEI, which stops dendrite formation and electrolyte decomposition. The GT2 electrolyte that was discovered exhibits outstanding performance in ion transfer, electrode interface stability, and cycling life, especially at high rates and in an anode-free full cell. This study thus provides important theoretical guidance and experimental evidence for the design of high-performance electrolytes for AFSMBs.

Acknowledgments

Prof. Chen Long and Ms. Zhou Dandan supervised this research project. Prof. Chen provided guidance on research topic selection, experimental design, data analysis, methodology, and manuscript revision. The guidance was paid. Ms. Zhou provided guidance on the selection of the research topic, experimental design, data analysis, methodology, and manuscript revision. The guidance was unpaid. The experiments were conducted at the Chemical Engineering Department, East China University of Science and Technology.

The topic originated from the demand for high-energy-density energy storage technologies. Prof. Chen proposed the research topic, which was finalized through online research and discussions among the supervisors and the student. Electrolyte preparation, cell assembly, and electrochemical testing were performed by Lian Leyi, with assistance and supervision from Prof. Chen and Ms. Zhou to ensure safety. Lian Leyi also conducted the Molecular Dynamics simulations, Raman spectroscopy, X-ray Photoelectron Spectroscopy, Electrochemical Impedance Spectroscopy, Nuclear Magnetic Resonance, and battery cycling, while Prof. Chen and Ms. Zhou provided methodological guidance and contributed to result interpretation. The experimental protocol was designed collaboratively by Prof. Chen and Lian Leyi. The first draft of the manuscript was written by Lian Leyi and revised by Prof. Chen and Ms. Zhou.

During the Electrochemical Impedance Spectroscopy measurement, we encountered difficulties assembling Na||Na symmetric cells. Unlike conventional half-cells, these cells use two Na metal discs as the electrodes, so the experimental result is influenced only by the electrolyte, not the electrode. However, Na metal is much thicker and softer than traditional electrodes. If we use the PP/PE separator ($\sim 25\ \mu\text{m}$ thick), an internal void forms between the Na metals, leading to an abnormally high bulk resistance in the measurement. If we use the Glass Microfiber Filter Grade A (GF/A) separator ($\sim 0.26\ \text{mm}$), which is much thicker than PP/PE, there is a risk that the Na metal might deform or even penetrate the separator during assembly, causing direct contact between the electrodes (Na metals) and resulting in internal short circuits. To address this, we tested multiple separator combinations, including 2 PP/PE, 3 PP/PE, 1 GF/A, 2 GF/A, 1 GF/A with 1 PP/PE, and 1 GF/A with 2 PP/PE. We tested all of them with EIS and discovered that the combination of 1 GF/A and 2 PP/PE had the best performance. We also controlled the crimping pressure to ensure sufficient contact while avoiding excessive force that could break the separator.

This project was the result of collaborative work in which the student was given consistent guidance from both supervisors. The challenges encountered during the EIS measurement reflect the practical problems in battery research and highlight the significance of problem-solving skills. This study resolved a possible issue in the field of anode-free sodium metal batteries by proposing a new electrolyte, established an experimental basis for the assessment of solvation structures and interfacial performance, and thus pushed the development of sodium-ion batteries a step further. I would like to express my gratitude to my supervisors, Prof. Chen and Ms. Zhou, for their guidance during the research, and also to the East China University of Science and Technology for providing the laboratory and experimental facilities.

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