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High-Energy Aqueous Sodium-Ion Batteries

Ting Jin, Xiao Ji, Peng-Fei Wang, Kunjie Zhu, Jiaxun Zhang, Longsheng Cao, Long Chen, Chunyu Cui, Tao Deng, Sufu Liu, Nan Piao, Yongchang Liu, Chao Shen, Keyu Xie, Lifang Jiao,* and Chunsheng Wang*

Abstract: Water-in-salt electrolytes (WISE) have largely widened the electrochemical stability window (ESW) of aqueous electrolytes by formation of passivating solid electrolyte interphase (SEI) on anode and also absorption of the hydrophobic anion-rich double layer on cathode. However, the cathodic limiting potential of WISE is still too high for most high-capacity anodes in aqueous sodium-ion batteries (ASIBs), and the cost of WISE is also too high for practical application. Herein, a low-cost 19 m (m: $molkg^{-1}$) bi-salts WISE with a wide ESW of 2.8 V was designed, where the lowcost 17 m NaClO₄ extends the anodic limiting potential to 4.4 V, while the fluorine-containing salt (2 m NaOTF) extends the cathodic limiting potential to 1.6 V by forming the NaF-Na₂O-NaOH SEI on anode. The 19 m NaClO₄-NaOTF-H₂O electrolyte enables a 1.75 V $Na_3V_2(PO_4)_3 \parallel Na_3V_2(PO_4)_3$ full cell to deliver an appreciable energy density of 70 $Whkg^{-1}$ at 1 C with a capacity retention of 87.5 % after 100 cycles.

Introduction

Lithium-ion batteries (LIBs) have been widely applied in portable electronic devices and are penetrating into electric vehicle owing to their high energy and power density.^[1] With the rapid-increased demand for limited lithium resource, it will be very challenged to further reduce the price of LIBs for large-scale energy storage. Owing to the low cost and high reliability, aqueous sodium ion batteries (ASIBs) are considered as promising alternatives for the large-scale energy storage.^[2] The key issue of ASIBs is their low energy density

College of Chemistry, Nankai University, Tianjin 300071 (China) E-mail: jiaolf@nankai.edu.cn

Dr. T. Jin, Dr. X. Ji, Dr. P.-F. Wang, J. Zhang, Dr. L. Cao, Dr. L. Chen, Dr. C. Cui, T. Deng, S. Liu, Dr. N. Piao, Prof. C. Wang Department of Chemical and Biomolecular Engineering University of Maryland, College Park, MD 20742 (USA) E-mail: cswang@umd.edu

Dr. T. Jin, Dr. C. Shen, Prof. K. Y. Xie

State Key Laboratory of Solidification Processing, Center for Nano Energy Materials, School of Materials Science and Engineering, Northwestern Polytechnical University and Shaanxi Joint Laboratory of Graphene (NPU) Xi'an 710072 (P. R. China)

 Supporting information and the ORCID identification number(s) for
 the author(s) of this article can be found under: https://doi.org/10.1002/anie.202017167. caused by the narrow electrochemical stability window (ESW) of water (1.23 V). Recently, various water-in-salt electrolytes (WISE) and their derivatives have significantly broadened the ESW of aqueous electrolytes by the formation of SEI on anodes and absorbing hydrophobic anions on cathodes, and have been applied for various alkali metal-ion batteries.^[3]

High concentration fluoride salts (9.26 m NaOTF,^[4] 37 m NaFSI^[5]) have been used for WISE, in which unsolvated OTF⁻ and FSI⁻ anions can expel water away from cathode, as well as the solvation sheath of Na⁺ involved OTF⁻/FSI⁻ can be reduced to NaF-based SEI on anode surface.^[6] Due to the low solubility of NaOTF in water, a large amount of remaining free water and unsatisfactory SEI stability in 9.26 m NaOTF make it can only support a 1.0 V $Na_{0.66}[Mn_{0.66}Ti_{0.34}]O_2 \parallel NaTi_2(PO_4)_3$ full cell.^[4] Although 37 m NaFSI WISE has a wide ESW of 2.6 V, the fragile S-F bond in FSI⁻ is very easy to hydrolyze in water and then to lower the pH value of electrolyte, leading to the reduced stability of anodes. Since NaClO₄ has a high solubility in water (17 m)and low price, 17 m NaClO₄ was also investigated as a WISE.^[7] According to the Hofmeister series, ClO₄⁻ anion has strong tendency to participate in Na⁺-solvation structure with ion aggregation, making it more likely to break the water network in electrolyte.^[8] However, due to the reduced products (such as NaCl) of NaClO₄ are easily soluble in aqueous electrolytes, effective SEI layer cannot be formed in 17 m NaClO₄ and thereby leading to the high cathodic limit.^[9] One method to further extend ESW of WISE is to add the secondary salt. Hu et al. recently reported a super high concentration water-inbisalt electrolyte (WIBSE) of 9 m NaOTF + 22 m TEAOTF.^[10] Introducing 22 m TEAOTF into 9 m NaOTF extended the ESW to 3.3 V. However, the low ionic conductivity $(11.2 \text{ mS cm}^{-1})$ and high viscosity (30.2 MPa s)reduced the power density of the cells. In addition, the ionic liquid of TEAOTF is extremely expensive and increases the cost of the WIBSE.^[10] Up to date, only a few anodes with potential beyond 2.0 V can be used in WISE or WIBSE SIBs (such as NaTi₂(PO₄)₃, prussian blue analogues, organic compounds, and vanadium oxides) due to the limitation of cathodic stability potential of electrolytes (>2.0 V). To improve the energy density and stability of ASIBs, cathodic limiting potential of WISE or WIBSE urgently needs to be further extended.

Herein, we designed a low-cost 19 m $NaClO_4$ -NaOTF (17 m $NaClO_4 + 2$ m NaOTF) electrolyte that possesses an ESW to 2.8 V with a low cathodic limiting potential of 1.6 V. Introducing 2 m NaOTF into 17 m $NaClO_4$ electrolyte is to form a NaF-based SEI on the anode surface since OTF⁻ in

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^[*] Dr. T. Jin, K. Zhu, Dr. Y. Liu, Prof. L. Jiao Key Laboratory of Advanced Energy Materials Chemistry (Ministry of

Education) Renewable Energy Conversion and Storage Center (ReCast)

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Na⁺-solvation structure can be reduced.^[4] The results of X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) characterization indicate that the SEI layer consisting NaF, Na₂O and NaOH was formed. The robust SEI can block water decomposition on the anode surface. Consequently, 19 m NaClO₄–NaOTF enables a 1.75 V symmetric full cell (Na₃V₂(PO₄)₃ || Na₃V₂-(PO₄)₃) to achieve a high energy density of 70 Wh kg⁻¹ (based on the total mass of cathode and anode), in which the potential of Na₃V₂(PO₄)₃ anode (1.70 V) is an extremely low value among the current anodes in ASIBs. The full cell delivers a capacity retention of 87.5% at 1 C after 100 cycles and lifespan up to 500 cycles at 5 C.

Results and Discussion

Figure 1 a presents the ESW of different aqueous electrolytes (1 m NaClO₄, 9 m NaClO₄, 17 m NaClO₄, 17 m NaClO₄ + 2 m NaOTF). The inset of Figure 1 a shows the magnified window regions near the cathodic and anodic limits. The ESW expands as the NaClO₄ concentration increases. More impressively, when 2 m NaOTF was introduced into the highly concentrated 17 m NaClO₄, the hydrogen and oxygen evolution potentials of the electrolyte were further broadened to ca. 1.6 V and ca. 4.4 V vs. Na⁺/Na, respectively.

Raman spectroscopy was applied to evaluate the bonding effects between water and salts (Figure 1b). In NaClO₄– NaOTF–H₂O electrolytes, the peaks at 464, 631, 934, 1116, and 1045 cm⁻¹ correspond to ClO₄⁻ symmetric and asymmetric stretching vibration modes (v₁, v₃), ClO₄⁻ bending vibration modes (v₂, v₄), and SO₃ stretching band (v_s), respectively.^[4,11] The O–H stretching vibration modes of water molecules in different electrolytes are also shown in



Figure 1. Solvation structure and property of $NaClO_4-NaOTF-H_2O$ electrolytes. a) The ESW of different electrolytes, namely 1 m $NaClO_4$, 9 m $NaClO_4$, 17 m $NaClO_4$ and 19 m $NaClO_4-NaOTF$. Inset in (a) are magnified window regions near the cathodic and anodic limits. b) Raman spectra of 19 m $NaClO_4-NaOTF$ compared with other aqueous electrolytes, namely 1 m $NaClO_4$, 9 m $NaClO_4$, 17 m $NaClO_4$, and 9 m $NaClO_4$, 9 m $NaClO_4$, 9 m $NaClO_4$, 17 m $NaClO_4$, and 9 m NaOTF. c) The FTIR spectra of 19 m $NaClO_4-NaOTF$ compared with other aqueous electrolytes, namely 1 m $NaClO_4$, 9 m $NaClO_4$.

Raman spectroscopy. In pure water, the O-H stretching vibration exhibits two broad Raman bands of symmetric (ca. 3200 cm^{-1}) and asymmetric (ca. 3400 cm^{-1}) vibration modes, which are ascribed to the diverse hydrogen-bonding environments in water clusters.^[12] With the concentration of NaClO₄ increased to 17 m, the O-H stretching vibration bands are altered from two broad bands to a sharp peak and accompanied by the blue-shift. When 2 m NaOTF was introduced into 17 m NaClO₄, the O-H stretching vibration band shows the most sharp peak near 3565 cm⁻¹, which is the characteristic of crystalline hydrates and indicates that most of the water molecular structure is broken.^[11,13] Fourier transform infrared (FTIR) spectroscopy was conducted to further understand the interaction among Na⁺, ClO₄⁻, OTF⁻ and water, as displayed in Figure 1c. The O-H stretch band around 3400 cm⁻¹ is broken down into a few Gaussian peaks that are corresponded to hydrogen-bonded water molecules with different donor (D) and acceptor (A) hydrogen bonds.^[14] As shown in Figure S1 (Supporting Information), O-H stretch band in pure H₂O can be deconvoluted into five subbands: 3043, 3225, 3432, 3575, and 3638 cm⁻¹, which are assigned to OH vibrations participated in DAA, DDAA, DA, DDA hydrogen-bonding, and free OH₂ vibrations, respectively.^[14a,15] 1 m NaClO₄ in Figure 1 c presents the similar spectrum as pure H₂O due to that most of water do not participate in Na⁺ ion solvation in this low concentration. The blue-shift of O-H stretching vibration in concentrated electrolyte is ascribed to the interaction between water hydrogen bond network and Na salts. In 19 m NaClO₄-NaOTF-H₂O electrolyte, three Gaussian peaks centered at 3354, 3480, and 3593 cm⁻¹ correspond to DDAA, DA, and DDA hydrogen bonds, respectively. The disappearance of DAA and free OH₂ vibrations indicates the reduced activity and mobility of water molecules. Moreover, the sub-bands in low frequency demise to high-frequency ones demonstrate the breakdown of water-rich clusters, leading to the reduced activity of water.[16]

An independent gradient model (IGM) was also performed to illustrate the intermolecular interactions in Na-ClO₄–NaOTF–H₂O electrolytes. The interactions of ClO₄⁻– H₂O, H₂O–H₂O, and OTF⁻–H₂O in Figure 2 a are attributed to hydrogen bonding in aqueous electrolytes. The binding energies decrease in the order of H₂O–H₂O (-0.25 eV) > ClO₄⁻–H₂O (-0.54 eV) > OTF⁻–H₂O (-0.55 eV). Since OTF⁻ and ClO₄⁻ anions have the more negative binding energy with H₂O, they are more easier to combine with H₂O than H₂O–H₂O, which inhibits the emergence of water-rich clusters.

The structure of 17 m NaClO₄ and 19 m NaClO₄–NaOTF were simulated by classic molecular dynamic (cMD). The simulated structure for 19 m NaClO₄–NaOTF is shown in Figure 2b. Figure 2c and d show the cMD simulated pair distribution function and coordination number of Na and O-atom in 17 m NaClO₄ and 19 m NaClO₄–NaOTF, respectively. As shown in Figure 2d, the first coordinated shell of Na⁺ ion is composed of 2.95 Ow (oxygen from water) and 3.01 OCl (oxygen from ClO₄⁻) in 17 m NaClO₄. For 19 m NaClO₄–NaOTF (Figure 2d), the average first coordinated shell is composed of 2.98 Ow, 2.79 OCl, and 0.22 OOTF (oxygen from



Figure 2. The intermolecular interactions, solvation structure and SEI character in NaClO₄–NaOTF–H₂O electrolytes. a) Binding energies of ClO_4^- –H₂O, H₂O–H₂O, and OTF⁻–H₂O dimers and their IGMs. Green responds Van der Waals interaction which includes hydrogen bond interaction. b) cMD simulated structure for 19 m NaClO₄–NaOTF. cMD simulated pair distribution function and coordination numbers of Na with O-atom from water (Ow), ClO_4^- (OCl), and OTF⁻ (OOTF) in the 17 m NaClO₄ (c) and 19 m NaClO₄–NaOTF (d); inset in (d) is OTF⁻ involved solvation structure extracted from cMD simulation; e) Density of states of NaF from first-principles calculation.

OTF⁻). Therefore, the addition of 2 m NaOTF leads to the OTF⁻ involved Na⁺-solvation structure. A represented structure for the solvation structure in the 19 m NaClO₄-NaOTF is shown in the inset of Figure 2d, in which the gray dashed lines represent the hydrogen bond between OTF- and water molecules. This result demonstrates that the introduction of OTF⁻ can further break the hydrogen bond network between H₂O and H₂O, in coincidence with the results of Raman and FTIR spectrums. According to the previous study,^[4] OTF⁻ can be electrochemically reduced to F- and further combine with Na⁺ to form NaF-based SEI on the anode. In Figure 2e, the large band gap of 6.09 eV shown in the density of state (DOS) indicates that NaF exhibits insulator character to block the further reaction between the anode and electrolyte. Ionic conductivity and viscosity of different electrolytes were evaluated. As shown in the Supporting Information, Figure S2, 17 m NaClO₄ has a higher ionic conductivity than that of 9 m NaOTF electrolyte. Introducing 2 m NaOTF into 17 m NaClO₄ slightly reduces the ionic conductivity from 113.86 mS cm⁻¹ for 17 m NaClO₄ to 95.25 mS cm⁻¹ for 19 m NaClO₄-NaOTF. The ionic conductivity of 19 m NaClO₄-NaOTF is much higher than those of the Li-ion and Na-ion WISEs (Supporting Information, Figure S3), even 10 times higher than that of conventional organic electrolytes.^[17] Although the concentration of 19 m NaClO₄-NaOTF electrolyte is relatively high, its viscosity is only 12.3 MPa S, which is much lower than previous WISE for aqueous batteries (Supporting Information, Figure S3). The higher ionic conductivity and low viscosity of 19 m NaClO₄-NaOTF electrolyte ensure the fast Na⁺ transport and easy to penetrating into porous electrodes.

 $Na_3V_2(PO_4)_3$ (NVP) has two sodiation/desodiation plateaus at about 1.7 V and 3.4 V based on the redox of V^{2+}/V^{3+} and V^{3+}/V^{4+} , respectively. And both of them are within the ESW of 19 m NaClO₄–NaOTF electrolyte (1.6–4.4 V). Therefore, the electrochemical behaviors of 19 m NaClO₄–NaOTF electrolyte were evaluated by using a symmetrical NVP ||

NVP full cell. Since NVP has a low electronic conductivity,^[18] herein, we prepared carbon coated NVP (NVP@C) via an electrospinning method. The synthesis and characterization of NVP@C are shown in the Supporting Information, Figures S4–S7.

The electrochemical properties of NVP@C as anode and cathode were evaluated in 19 m NaClO₄-NaOTF electrolyte. Figure 3a plots the typical charge/discharge profiles of NVP@C at 1 C (1 C = 117 mAg⁻¹). The NVP@C exhibits a capacity of 112.2 mAhg^{-1} at a high redox potential (ca. 3.45 V) and a capacity of 56.5 mAhg^{-1} at a low redox potential (ca. 1.70 V) with an ultra-low polarization, agreeing well with the redox peaks in CV curves (Supporting Information, Figure S8). It is noteworthy that the redox potentials of NVP@C in 19 m NaClO₄-NaOTF is about 0.2 V higher than that in organic electrolyte (1 M NaClO₄ in EC/ PC/5 vol% FEC) due to high salt concentration (according to Nernst equation) (Supporting Information, Figure S9). The symmetric NVP@C || NVP@C full-cell (Figure 3b) with positive-to-negative capacity ratio of 1.2 was assembled, where the excess cathode of about 20% was used to compensate the loss of Na during the formation of SEI on the anode. The CV curves of the full cell shown in Figure 3c present a pair of



Figure 3. The electrochemical performance of symmetric NVP@C || NVP@C full cell. a) The charge/discharge curves of NVP@C on both anode and cathode sides at 0.5 C. The potential has been converted to Na⁺/Na reference. b) The as-assembled symmetric NVP@C || NVP@C full cell. c) CV curve of full cell in 19 m NaClO₄– NaOTF at a scan rate of 0.1 mVs⁻¹. d) The cycling performance and CE of full cell in 17 m NaClO₄ and 19 m NaClO₄–NaOTF at 1 C. e) The relative intensity of the H₂ peak for the cells cycled in 19 m NaClO₄– NaOTF at different cycles, inset is the test processes. f) The comparison of energy density for NVP@C || NVP@C full cell with previously reported full cells in ASIBs.

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redox peaks (1.77/1.70 V) from the voltage difference between the V^{3+}/V^{4+} and V^{2+}/V^{3+} redox couples in NVP. Moreover, the redox peaks are highly overlapping with an ultra-small peak separation value (ΔE) of 0.07 V, indicating the fast kinetics and superior reversibility of Na⁺ extraction/ insertion. Additionally, there is a small peak near 1.74 V in first three cycles. However, it can be found that this peak gradually decreased in the following cycles and disappeared after 10 cycles (Supporting Information, Figure S10), which means that this peak may be ascribed to the formation of SEI. Figure S11 compares the initial Coulombic efficiency (CE) of full cell cycled in 19 m NaClO₄-NaOTF and 17 m NaClO₄ electrolytes. The initial CE of full cell cycled in 19 m NaClO₄-NaOTF is as high as 89.5%, while the initial CE in 17 m NaClO₄ is only 78.2%, suggesting the more serious side reactions in 17 m NaClO₄. As shown in Figure 3d, the CE increase to ca. 99.8% and ca. 98.2% for 19 m NaClO₄-NaOTF and 17 m NaClO₄ after 10 cycles, respectively. The higher CE facilitates excellent cycling performance of full cell in 19 m NaClO₄-NaOTF, with a high capacity retention of 87.5% after 100 cycles at 1 C. And the charge/discharge curves in 1st, 5th, 20th, and 50th cycles of full cell in 19 m NaClO₄-NaOTF at 1C are presented in the Supporting Information, Figure S12. While due to the limited Na source, the capacity decreased to ca. 66.5% after 200 cycles (Supporting Information, Figure S13). To confirm the inhibited H_2 evolution in 19 m NaClO₄-NaOTF, we in situ measured H₂ evolution from the cells with 19 m NaClO₄-NaOTF using gas chromatograph (GC). The test processes are shown in the inset of Figure 3e, in which N₂ was used as carrier gas to transport the cell gas to GC. Before testing, GC was calibrated using ultrapure H₂ gas and the peak at 1.75 min was identified to hydrogen. The GC spectrograms of released H₂ for the cells with 19 m NaClO₄-NaOTF electrolytes at different charge/discharge cycles are presented in the Supporting Information, Figure S14. The relative intensity of the H₂ peak for the cells cycled at different cycles are shown in Figure 3e. It can be found that the relative intensity of the H_2 peak gradually decreased with charge/discharge cycles and almost completely disappeared after 10 cycles. The undetectable H₂ peak after 10 cycles verified that the formed SEI in 19 m NaClO₄-NaOTF completely suppressed H₂ evolution within the GC resolution, which enhanced the CE to ca. 99.8%. Based on the total mass of cathode and anode, the full cell delivers a discharge capacity of ca. $40 \text{ mA} \text{ hg}^{-1}$ with an average voltage of 1.75 V, corresponding to the energy density of ca. 70 Whkg⁻¹, outperforming the full cells in previously reported ASIBs (Figure 3 f).^[4,7,19] Owing to the high ionic conductivity and low viscosity, the full cell also exhibits superb rate performance with 75.6% capacity retention at 5 C after 500 cycles and nearly 100% CE (Supporting Information, Figure S15). Additionally, the potential of NVP@C (1.7 V) is lower than almost all reported anodes in ASIBs (Supporting Information, Figure S16), which enable to fabricate ASIBs with high energy density. Using high potential cathode (>4.0 V) replace NVP (3.4 V) can further enhance the energy density of cells since the NVP does not fully use the high anodic limiting potential (4.4 V) of 19 m NaClO₄-NaOTF.

Ex situ XRD was conducted to validate the reaction mechanism of NVP@C electrodes. XRD patterns for cathode and anode during the charge/discharge processes in full cell are displayed in Figure 4. For the cathode (Figure 4b), during the charging process (A \rightarrow C), the peaks related to Na₃V₂- $(PO_4)_3$ (dash A) gradually decrease accompanied by the appearance of $NaV_2(PO_4)_3$ (dash C). During the discharging process $(C \rightarrow E)$, the peaks come back to their original positions, verifying the reversible two-phase reaction between $Na_3V_2(PO_4)_3$ and $NaV_2(PO_4)_3$.^[20] For the anode (Figure 4c), the characteristic peaks of $Na_3V_2(PO_4)_3$ slightly shift to lower 2θ angles during charging process and return to their original positions after discharging process $(A \rightarrow C \rightarrow E)$, which is presumably owing to the small expansion/shrinkage of lattice caused by the insertion/desertion of Na⁺. This phenomenon indicates that the electrochemical reaction for anode is a solid-solution reaction without phase transition. The change of V valence in NVP@C cathode and anode was investigated through XPS. The results indicate the reversible redox reaction of V^{2+}/V^{3+} and V^{3+}/V^{4+} for anode and cathode, respectively (Supporting Information, Figure S17). Both the results of ex-situ XRD and XPS demonstrate reversible electrode reaction in 19 m NaClO₄-NaOTF.

The SEI layer in 19 m NaClO₄–NaOTF was characterized using XPS with argon sputtering. The high-resolution Na1s and F1s spectra are presented in Figure 5a and b. It is noteworthy that the position of Na 1s signal shifts to high



Figure 4. Electrode reaction mechanism. a) Typical charge/discharge curves of full cell for the first cycle at 1 C. The points A–E marked the states where data were collected for XRD analysis. XRD patterns of (b) NVP@C cathode and (c) NVP@C anode at selected states.

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Figure 5. Solid electrolyte interphase (SEI) on an electrode. a)–c) XPS spectrum of pristine and cycled NVP@C anode at full sodiation state after Ar sputtering with different times, a) Na 1s, b) F 1s, c) P 2p. d) SEM image for the Ga⁺ ion beam sputtered crater for TOF-SIMS. e) TOF-SIMS depth profiles and f) chemical mapping of F^- , OH^- , O^{2-} species in SEI.

binding energy (1071.1→1071.5 eV) after cycling, corresponding to the appearance of NaF on the surface.^[21] The Na 1s signal became broad after the sputtering for 900 s owing to the appearance of NVP pristine electrode. For the F1s, the peak at 689.1 eV for pristine electrode is assigned to the -CF₂from PTFE binder.^[4,12d] The F 1s signal shifted to 678.8 eV after cycling, which is identified to -CF₃- species come from the residual salt on anode surface.^[3b,4] The peak at 684.3 eV appeared after sputtering, corresponding to NaF species.^[4] Moreover, with the sputtering time increasing, the signal of NaF still much strong, which means NaF-based SEI is dense and robust. P 2p signal is served as a reference due to it has no change in composition during electrochemical reaction (Figure 5c). It can be found that the signal of P 2p almost disappears after cycling and reappear after long-time sputtering, further confirming the robust SEI film successfully formed on anode surface.

To further probe the chemical composition and element depth distribution in SEI, TOF-SIMS was performed on anode after 10 cycles. The SEM image of Ga⁺ ion beam sputtered area displayed in Figure 5d presents that the depth of sputtered crater is 765.81 nm. The negative species were chosen to analyze the components of SEI interface, including F^- (m/e = 19), OH⁻ (m/e = 17) and O²⁻ (m/e = 16). Figure 5 e shows the depth profile of these negative modes. The chemical mappings are displayed in Figure 5 f. The intensity of F⁻ is most strong near the electrode surface and lasts to about 118 nm, which is the representative of NaF.^[22] During the process of SEI formation, trace H₂O in highly concentrated electrolyte can be reduced at the anode surface which leads to the formation of H₂ gas and OH⁻, thus leading to the precipitation of NaOH on the anode surface. OH- can chemically react with OTF- through a nucleophilic attack process, leading to the degradation of the -CF₃ group from OTF⁻ and catalyze the formation of fluorinated SEI (such as NaF), thereby inhibiting the H₂ evolution on the anode and thus protecting the anode.^[23] With the increase of sputtering depth, the amount of OH⁻ gradually decreased while F⁻ significantly increased and remained at a high value, which indicates that NaF is the main component in SEI. This may be due to the higher solubility of NaOH than NaF. Furthermore, O²⁻ species also has an obvious signal, representing the Na-O compounds (such as Na₂O) in SEI layer. The appearance of $\mathrm{Na_2O}$ may be ascribed to the reaction of $\mathrm{Na^+}$ and dissolved trace O_2 in the electrolyte $(4Na^+ + O_2 + 4e^- \rightarrow 2Na_2O)$.^[9] The robust SEI layer consisted of NaF-Na2O-NaOH as the good electronic insulator can effectively block the decomposition of H₂O and thus assisting to achieve superb stability of full cell in 19 m NaClO₄-NaOTF electrolyte.

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Conclusion

A low-cost 19 m (17 m NaClO₄ + 2 m NaOTF) WISE was developed for ASIBs, in which NaClO₄ was mainly used to reduce water activity as evidenced by Raman and FTIR characterization as well as DFT calculations, while a small amount of NaOTF was applied to assist formation of the robust SEI. Both XPS and TOF-SIMS demonstrate the formation of NaF-Na2O-NaOH SEI on anode surface during the first few cycles, which effectively inhibits the further decomposition of water. 19 m NaClO₄-NaOTF possesses a wide ESW of 1.6-4.4 V (vs. Na+/Na), a higher ionic conductivity of 95.25 mS cm⁻¹ and a lower viscosity of 12.28 MPas. Consequently, the electrolyte can enable a 1.75 V symmetric NVP@C || NVP@C full cell to deliver a high energy density of 70 Whkg⁻¹, a capacity retention of 87.5% for 100 cycles at 1 C as well as the superior rate capability at 5 C cycled up to 500 cycles. The strategy of combining inorganic salts and fluoride salts in electrolytes maybe provide a new avenue to develop the low-cost and high-energy aqueous alkali metal-ion batteries.

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Conflict of interest

The authors declare no conflict of interest.

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Research Articles



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High-Energy Aqueous Sodium-Ion Batteries



A NaClO₄/NaOTF electrolyte was designed for aqueous Na-ion batteries (ASIBs). The solid electrolyte interphase (SEI) containing NaF–Na₂O–NaOH forming on the anode extended the cathodic limiting potential of electrolyte to 1.6 V, and the hydrophobic anions extend the anodic to 4.4 V. A 1.75 V Na₃V₂(PO₄)₃ || Na₃V₂(PO₄)₃ cell achieved a high energy density of 70 Wh kg⁻¹ with 87.5% capacity retention after 100 cycles.