A Sustainable NH$_4^+$ Ion Battery by Electrolyte Engineering

Zhengnan Tian$^{1*}$, Jun Yin$^{2*}$, Tianchao Guo$^1$, Zhiming Zhao$^1$, Yunpei Zhu$^1$, Yizhou Wang$^1$, Jian Yin$^1$, Yeguo Zou$^3$, Yongjiu Lei$^1$, Jun Ming$^3$, Osman Bakr$^1$, Omar F. Mohammed$^{1,3}$, Husam N. Alshareef$^{1,*}$

$^1$Materials Science and Engineering, Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

$^2$Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon 999077, Hong Kong, P. R. China

$^3$Advanced Membranes and Porous Materials Center, KAUST Catalysis Center, Physical Science and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

$^4$State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

*Corresponding author. E-mail: husam.alshareef@kaust.edu.sa

†These authors contributed equally to this work.
Methods

**Synthesis of CuHCF, PTCDI and PTCDI@MXene**

The CuHCF cathode material was prepared as previously reported in the literature[1]. 40 ml CuSO$_4$ solution (0.2 M) was added dropwise into 40 ml of K$_3$[Fe(CN)$_6$] solution (0.1 M) under magnetic stirring. After 6 h of reaction, the olive-green precipitate was rinsed with deionized water and centrifuged multiple times, and then dried in an oven at 60 °C overnight. The pure PTCDI was purchased from Sigma Aldrich and used without any purification. Ti$_3$C$_2$T$_x$ was prepared by the following steps. Firstly, one gram of Ti$_3$AlC$_2$ MAX powder was slowly added into a mixture solution of 1 ml of HF (49%), 6 ml of HCl (12 M), and 3 ml of DI water and stirred at 42 °C for 15 hours. Subsequently, the mixture was taken out and rinsed with deionized (DI) water repeatedly until the pH value is 6. Then, 20 ml aqueous LiCl solution (0.75 M) was added in the sediment and stirred for 30 mins at room temperature. Next, four additional centrifuge cycles were utilized to washed the Li$^+$ intercalated multilayer MXene sediment. Finally, the MXene suspension was collected by centrifugation at 500 rpm for 10 mins. The PTCDI@MXene is prepared by mixing Ti$_3$C$_2$T$_x$ water solution (3 mg ml$^{-1}$) and PTCDI powder. After stirring for 6 hours under nitrogen protection, the obtained mixture is freeze-dried.

**Preparation of the sucrose added electrolytes**

The lithium triflate, sodium triflate, potassium triflate, ammonium triflate and sucrose powder was purchased from Sigma Aldrich and used without any purification. For the preparation of MOTf@S and NH$_4$OTf@S electrolytes, 17.1 g sucrose powder (5.0 m) is dissolved in 10 ml water under constant stirring at 90 °C for 2 hours. After that, 2 m salts are added into the above sucrose solution. The electrochemical window, ionic conductivity and electrochemical performance in electrolytes with different sucrose concentrations are shown in Figure S9.

**Materials characterization**

Powder X-Ray Diffraction (PXRD) patterns were performed on a D8 Advance X-ray diffractometer (Bruker, Germany) with a Cu K$\alpha$ radiation ($\lambda$=1.5406 Å). DSC measurements were tested from room temperature to −70 °C and then to room
temperature at 5 °C min⁻¹ (DSC-TA Discovery 250) in a nitrogen atmosphere. The morphology of the samples was characterized by a scanning electron microscope (SEM, Quattro). Liquid nuclear magnetic resonance (NMR) analysis of the electrolytes was performed using a coaxial insert with DMSO as the reference (Bruker AV-III 600 MHz Liquid NMR). The coaxial insert was used to preserve the electrolyte environment from interaction with the reference solution. The viscosity of the solution was obtained via electro magnetically spinning viscometer (EMS-1000, KYOTO ELECTRONICS MANUFACTURING CO., LTD.) Transmission Fourier transform infrared spectroscopy (FTIR) spectra were carried out using FIIR-Nicolet iS spectrometer. Raman spectroscopy spectra were carried out using a Witec Apyron spectrometer.

**Electrochemical measurements.**

Ionic conductivities of different separators are achieved by conducting EIS tests on symmetrical steel plate coin cells, where the steel plates served as both the cathode and the anode. Their values are calculated using the equation as follows:

$$\sigma = \frac{l}{R_b A}$$

Where $\sigma$ represents the ionic conductivity, $l$ represents the thickness of the membrane, $A$ represents the area of the steel plate electrode, and $R_b$ represents the bulk resistance$^{[2]}$. The electrolyte conductivity in figure 1d is tested in totally same condition, including the temperature, pressure and electrolyte volume. The HER and OER are tested by LSV in three-electrode system, where Pt plate is employed as the work electrode, saturated calomel electrode (SCE) is used as the reference electrode and graphite rod is employed as the counter electrode.

All the three-electrode tests (CV and GCD) are using Bio-Logic VMP-3 electrochemical workstation, where graphite rod was employed as the counter electrode and saturated calomel electrode (SCE) was used as the reference electrode. For the PTCDI anode, the electrode was prepared by mixing 70% of PTCDI, 20% of conductive carbon black and 10% of polytetrafluoroethylene (PTFE) binder. Then, the mixed paste was pressed on the stainless steel mesh. The mass loading was 5 mg cm⁻². For the PTCDI@MXene anode, the electrode is prepared by mixing 80% of PTCDI@MXene
powder, 10% conductive carbon and 10% PTFE binder. For the CuHCF cathode, the electrode was prepared by mixing 80% of Prussian blue, 10% of conductive carbon black and 10% of polytetrafluoroethylene (PTFE) binder. The mass loading was 5 mg cm⁻². The full battery was assembled by 2032-type coin cell with mass ratio of PTCDI@MXene and CuHCF (1: 2, the CV and GCD curves of different mass ratio are shown in Figure S8c-d). The amount of the electrolyte is 80 µL. Before assembling the full cell, the CuHCF cathode needs to be pre-intercalated with ammonium ions (undergone a full discharge process to -0.4 V vs. SCE in a three-electrode system. The full battery CV and GCD curves are obtained by Bio-Logic VMP-3 electrochemical workstation. The full battery cycling stability is obtained by the Neware battery tester system (BTS4008-5V-20mA, China). The current density of full battery GCD is calculated by the total mass of PTCDI@MXene anode. The energy density of full battery is calculated by the total mass of PTCDI and CuHCF. The pouch battery was assembled by commercial aluminum plastic film with mass ratio of PTCDI@MXene 220 mg and CuHCF 450 mg. The current density of GCD curves is calculated based on the PTCDI@MXene anode mass.

**Theoretical simulation**

We performed ab-initio molecular dynamics (MD) simulations by using generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, together with the projector-augmented wave (PAW) method, as implemented in the VASP code. We built electrolyte structures based on the aqueous electrolytes with 2 m NaOTf. The dimension of simulation box was 18.8 Å × 18.8 Å × 18.8 Å for NaOTf@S (contained 15 NaOTf, 8 sucrose, and 96 H₂O) and for NH₄OTf@S (contained 15 NH₄OTf, 8 sucrose, and 96 H₂O). The plane-wave basis set cutoffs of the wavefunctions were set at 400 eV. The atomic positions of the initial structures were fully relaxed until the forces on each atom less were less than 0.02 eV/Å. After optimizing the electrolyte structures, the ab-initio MD simulations were performed with a time step of 1 fs and the NVT ensemble was used to control the temperature at 300 K. After carrying out 2000 fs equilibration run, another 2000 fs production run were used for the analysis.
**Supplementary Figures**

Figure S1. (a) Molecular structure of water, ammonium, triflate and sucrose molecules. (b) LSV curves of Pt plate in different cation based dilute electrolytes. The concentration of LiOTf, NaOTf and NH4OTf electrolytes is 2 m in water solution. The C-NH4OTf represents 25 m NH4OTf in water solution. (c) LSV curves of Pt plate in sucrose added electrolytes, where the concentration of salts is 2 m and of sucrose is 5 m.
Figure S2. (a) Raman spectra of different electrolytes. (b) $^1$H NMR spectrum of DMSO as the reference. (c) $^1$H NMR spectrum of NH$_4^+$ ions. (d) $^{17}$O NMR spectrum of DMSO as the reference.
Figure S3. (a) DSC data of 2 m NH₄OTf and 2 m NH₄OTf@S. (b) DSC data of 2 m NaOTf and 2 m NaOTf@S. (c) DSC data of 2 m LiOTf and 2 m LiOTf@S. (d) Viscosity of the sucrose added electrolytes at different temperatures. (e) Viscosity of the dilute electrolytes at different temperatures. (f) Digital photos of the electrolytes before freezing and after freezing.
Figure S4. (a) SEM image of the PTCDI anode. (b) XRD pattern of the PTCDI anode. (c) FTIR of the PTCDI anode. (d) SEM image of the CuHCF cathode. (e) XRD pattern of the CuHCF cathode. (f) FTIR of the CuHCF cathode.
Figure S5. (a) Ultraviolet–visible spectroscopy of the electrolytes after PTCDI dissolution. (b) CV curves of PTCDI in 2 m NH$_4$OTf@S electrolyte at different scan rates. (c) CV curves of PTCDI in 2 m NH$_4$OTf electrolyte at different scan rates. (d) Corresponding specific storage charge calculated according to a and b. (e) Rate performance of PTCDI in 2 m NH$_4$OTf@S electrolyte at different current densities. (f) GCD curves of PTCDI in 2 m NH$_4$OTf electrolyte at different current densities.
Figure S6. (a) CV curves of CuHCF in 2 m NH$_4$OTf electrolyte at different scan rates. (b) CV curves of CuHCF in 2 m NH$_4$OTf@S electrolyte at different scan rates. (c) Corresponding specific storage charge calculated by a and b. (d) GCD curves of CuHCF in 2 m NH$_4$OTf electrolyte at different current densities. (e) Rate performance of CuHCF in different electrolytes. (f) The magnified coulombic efficiency of PTCDI in 2 m NH$_4$OTf@S electrolyte. (g) The magnified coulombic efficiency of PTCDI in 2 m NH$_4$OTf electrolyte.
Figure S7. (a-b) SEM images of PTCDI@MXene anode. (c) XRD of the PTCDI@MXene electrode. (d) FTIR of the PTCDI@MXene electrode. (e) CV curves of bare MXene and PTCDI@MXene in 2 m NH$_4$OTf@S electrolyte (the scan rate is 1 mV s$^{-1}$). The bare MXene is contributed around 19% of the total capacity. (f) Cycling stability of bare MXene and PTCDI@MXene in 2 m NH$_4$OTf@S electrolyte. The capacity retention ratio to 500 cycles of bare PTCDI and PTCDI@MXene is 82.7% and 91.2% respectively.
Figure S8. (a) GCD curves of the full battery under different current densities at -20 °C. (b) GCD curves of the full battery under different current densities at 60 °C. Noting that the charge voltage is up to 1.9 V because of the electrolyte decomposition at high temperature. (c-d) CV and GCD curves of different mass ratio for balancing the anode and cathode capacity. 1: 1 means making the practical discharge capacity of anode and cathode same. 1: 1.2 means making the practical discharge capacity of cathode is 1.2 times than anode capacity (cathode excess). 1.2: 1 means making the practical discharge capacity of anode is 1.2 times than anode capacity (anode excess).
**Figure S9.** (a) Electrochemical window of various electrolytes with different sucrose concentration (the work electrode is Pt wire and scan rate is 10 mV s$^{-1}$). (b) Ionic conductivity summary of the electrolytes at room temperature. (c) Discharge curves at the first cycle of PTCDI in different electrolytes. (d) Charge and discharge curves of PTCDI in 3.0 m sucrose and 5.0 m sucrose electrolytes.
### Table S1

<table>
<thead>
<tr>
<th>Anode</th>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Energy density</th>
<th>Cycle (A g⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTCDI@MXene</td>
<td>CuHCF</td>
<td>2 m NH₄OTf@S</td>
<td>41.5</td>
<td>2000 (77%)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5 A g⁻¹ at 20 °C</td>
<td></td>
</tr>
<tr>
<td>PTCDI@MXene</td>
<td>CuHCF</td>
<td>2 m NH₄OTf@S</td>
<td>10000 (80%)</td>
<td>0.2 A g⁻¹ at −20 °C</td>
<td>[2]</td>
</tr>
<tr>
<td>PTCDI</td>
<td>N-CuHCF</td>
<td>5.8 m (NH₄)₂SO₄</td>
<td>31</td>
<td>1000 (72%)</td>
<td>[3]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.6 A g⁻¹</td>
<td></td>
</tr>
<tr>
<td>PANI</td>
<td>NH₄V₄O₁₀</td>
<td>1.0 M (NH₄)₂SO₄</td>
<td>NA</td>
<td>1000 (34%)</td>
<td>[4]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0 A g⁻¹</td>
<td></td>
</tr>
<tr>
<td>PTCDI</td>
<td>Ni-APW</td>
<td>1.0 M (NH₄)₂SO₄</td>
<td>43</td>
<td>1000 (67%)</td>
<td>[5]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.12 A g⁻¹</td>
<td></td>
</tr>
<tr>
<td>NaTi₃(PO₄)₃</td>
<td>Berlin green</td>
<td>0.5 M (NH₄)₂SO₄</td>
<td>38</td>
<td>600 (53%)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5 A g⁻¹</td>
<td></td>
</tr>
<tr>
<td>h-MoO₃</td>
<td>CuFePAB</td>
<td>1.0 M NH₄Cl@PAM</td>
<td>21.3</td>
<td>2000 (87%)</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0 A g⁻¹</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>CuHCF</td>
<td>1.0 M (NH₄)₂SO₄</td>
<td>NA</td>
<td>1000 (76.5%)</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+0.1 M ZnSO₄</td>
<td></td>
<td>1.8 A g⁻¹</td>
<td></td>
</tr>
</tbody>
</table>


