# Supplementary Materials for

## Ultrahigh-voltage aqueous electrolyte for wide-temperature supercapacitors

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#### Discussion of electrolyte and electrochemical performance

Discussion of high operating voltage. From the point of view of practical application, the leakage current of a device is crucial, but it is rarely reported. As shown in Supplementary Figure 1a, the GCD curve of 3.2 V exhibited a deformation when charging and discharging. This may be attributed to two reasons. The first is that the aqueous electrolyte may decompose under higher voltage and produce side reactions<sup>1</sup>. The second is due to the presence of leakage current, which is often ignored by researchers. Therefore, the study of leakage current is shown in Supplementary Figure 1b, c. As shown in Supplementary Figure 1b, the leakage current at 3.2 V operating voltage dropped obviously at the beginning and then gradually became smaller and more stable (0.7 mA). The initial current is called the "absorption current". This is due to the fact that SCs are charged/discharged through the absorption and release of ions, and the current is high when ions try to reach the inside of hole in carbon materials<sup>2</sup>. In addition, we also researched the relationship between leakage current and potential. The leakage current increases gradually with the change of working voltages (Supplementary Figure 1c). What's more, the ratio (d) of the amount of electricity generated by leakage current to the total amount of electricity is calculated by the following formula to further illustrate the change of Coulombic efficiency:

$$Q_1 = C * U \tag{1}$$
$$C = C_1 * m \tag{2}$$

$$Q_2 = \vec{l} * t \tag{3}$$

$$d = Q_1 / Q_2 \tag{4}$$

where  $Q_1$  is the total amount of electricity,  $Q_2$  represents the amount of electricity generated by leakage current. U is the operating voltage.  $C_1$  and m is the specific capacitance and the mass of active material, respectively. I and t refer to the leakage current and discharge time. According to the above formula, the ratio of the electricity generated by leakage current to the total electricity is 6% when the operating voltage is 3.2 V, which may well explain why the Coulombic efficiency of the device is 94.8% at 3.2 V.

Therefore, the leakage current should be taken into full consideration when the device is used at high voltage.

**Discussion of electrolyte Price.** In our work, the prices of the corresponding pack size of chemical reagent were chosen to calculate the cost of different electrolytes. Pure aqueous electrolytes ignore the cost of water, while other electrolytes need to calculate the cost of additives. Supplementary Table 1 shows the price of different chemical reagent and the corresponding cost of hybrid electrolytes is shown in Supplementary Table 2. The cost of different electrolytes is calculated using the following formula:

$$A = P_1 * \mathbf{m}_1 + P_2 * \mathbf{m}_2 \tag{5}$$

$$P_{1,2} = \frac{a}{b} \tag{6}$$

$$m_1 = \frac{n * M}{1000}$$
(7)

$$m_2 = P_{1,2} * B \tag{8}$$

where A is refers to the price per unit mass of electrolyte,  $P_1$  and  $P_2$  represent the cost per unit mass of salt and additive, a and b, can be calculated based on the data in Supplementary Table 1,2.  $m_1$  and  $m_2$  are the mass of salt and additive, respectively. n is the molar mass of salt. M refers to the molecular weight of the salt. B represents the mass fraction of additive. Discussion of electrolyte additive. To select a better additive, three types of organic solvents: ethylene glycol (EG), acetonitrile (ACN) and ethanol (ET) were added to the 1 m Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. Supplementary Table 3 demonstrates the physical properties of these organic additive<sup>3</sup>. The physical performance of the hybrid electrolyte formed by the organic additive and 1m Na<sub>2</sub>SO<sub>4</sub> (marked as 1m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/(organic additive)) are shown in Supplementary Table 4. Obviously, the conductivity and viscosity of 1m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/EG hybrid electrolyte is superior to that of others. The addition of high conductivity EG to aqueous electrolyte is beneficial to improve ion transport in the electrolytes<sup>4</sup>. Supplementary Figure 4 shows the contact angles test of different hybrid electrolytes. The contact angle of 1m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O, 1m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/EG, 1m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/ACN, 1m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/ET hybrid electrolytes on commercial active carbon (AC) electrode is 154.58°, 67.88°, 74.22° and 111.51°, respectively. The low contact angle demonstrated that the 1m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/EG aqueous electrolyte possesses superior wettability. Supplementary Figure 5a shows the device diagram for the linear sweep voltammogram (LSV) with the commercial active carbon (AC) as a working electrode, Ag/AgCl as a reference electrode and Pt as a counter electrode. As shown in Supplementary Figure 5b, 1 m Na<sub>2</sub>SO<sub>4</sub>/EG hybrid electrolyte demonstrated a wider electrochemical stability window of  $\approx 3.88$  V (versus Ag/AgCl). This result demonstrates that the activity of free water molecules is inhibited and water decomposition is reduced. Supplementary Figure 5c-e show the CV curves of 1m Na<sub>2</sub>SO<sub>4</sub>/EG, 1m Na<sub>2</sub>SO<sub>4</sub>/ACN and 1m Na<sub>2</sub>SO<sub>4</sub>/ET electrolytes under different voltage windows. The CV curve of 1m Na<sub>2</sub>SO<sub>4</sub>/EG hybrid electrolyte displayed a quasi-rectangle even at 3.2 V, indicating that water composition is well inhibited in 1m Na<sub>2</sub>SO<sub>4</sub>/EG electrolyte. Supplementary Figure 5f shows the electrochemical impedance spectrum (EIS) of different hybrid electrolytes. The equivalent series resistance of SCs in 1m Na<sub>2</sub>SO<sub>4</sub>/EG, 1m Na<sub>2</sub>SO<sub>4</sub>/ACN and 1m Na<sub>2</sub>SO<sub>4</sub>/ET electrolytes is 1.0  $\Omega$ , 4.1  $\Omega$  and 10.0  $\Omega$ , respectively. Therefore, the EG as the organic additive of aqueous electrolyte shows the outstanding physical and chemical performance.

**Discussion of the theoretical calculation.** All the simulation conducted in this work were performed using DFT model. The adsorption energy calculation formula of the water molecules and EG on the surface of carbon electrode is as follows:

$$\Delta G_{ads} = G_{m^*} - G^* - G_m \tag{9}$$

where  $\Delta G_{ads}$  represents the adsorption energy.  $G_{m^*}$  and  $G^*$  refer to the total energy after and before adsorption on the carbon electrode, respectively. In addition, the  $G_m$  is the energy of carbon electrode. For the pure aqueous electrolyte without EG,  $G_{m^*}$ ,  $G^*$  and  $G_m$  is -612.104 eV, -14.613 eV and -597.951 eV, respectively. After the introduction of EG,  $G_{m^*}$  and  $G^*$  is -649.832 eV and -52.36 eV, respectively. Based on the above data, the adsorption energy of water molecule and EG molecule can be calculated. Moreover, we study the oxygen evolution reaction (OER) process and the elementary steps are as follows<sup>5</sup>:

$$H_2O(1) + * \to HO^* + H^+ + e^-$$
 (10)

$$HO^* \to O^* + H^+ + e^- \tag{11}$$

$$O^* + H_2 O (1) \to HOO^* + H^+ + e^-$$
 (12)

$$HOO^* \to O_2^* + H^+ + e^-$$
 (13)

$$O_2^* \to O_2(\mathbf{g}) + * \tag{14}$$

The model structure of OER is shown in Supplementary Figure 9, which is consistent with the above process.

**Discussion of AC-based SC Specific Capacitance.** The specific capacitance of electrode was calculated from the GCD curves using the following equation<sup>6</sup>:

$$C = \frac{I * \Delta t}{m * \Delta V} * 2 \tag{15}$$

where C (F g<sup>-1</sup>) refers to the specific capacitance, I (A) is current,  $\Delta t$  (s) is discharge time, m (g) represents the mass of active materials,  $\Delta V$  refers to the working voltage.

**Discussion of the AC-based SC performance at different temperature.** The high-and-low temperature property of electrolytes is a critical parameter for the energy storage device in practical applications. In general, the cycling stability of the device is one of the criteria to measure the aqueous electrolytes. Supplementary Figure 13 shows the Coulombic efficiency and capacity retention at different operating temperatures and working voltage is 2.4 V. An average capacitance retention of 96.9% is achieved at -20 °C after 10,000 cycles. Moreover, the SC using 1 m Na<sub>2</sub>SO<sub>4</sub>/50%EG electrolyte cycles with a high capacitance retention of 98% at 100 °C operating temperature after 20,000 cycles, demonstrating an improved electrochemical stability. Supplementary Figure 14, 15 show the cycling stability at higher operating voltage (2.8 V and 3.0 V). A comparison of the cycling performance at different temperatures and those reported literatures is shown in Supplementary Table 5.

## **Supplementary Figures**



**Fig. S1. The electrochemical performance of high operating voltage. a**, GCD curves at 3.2 V operating voltage. **b**, leakage current curves of AC-based SC. **c**, the leakage current at different potential (2.8 V-3.2 V).



**Fig. S2. The electrochemical performance of AC-based supercapacitor. a**, CV curves under different voltage windows. **b-f**, CV curves at different scan rate and operating voltage. **g**, Coulombic efficiency of AC-based SC using different content EG additives at different operating voltages. **h**, GCD curves at different current density.



Fig. S3. The electrochemical performance of AC-based supercapacitor. a-e, cycling stability test range from 2.0 V to 3.0 V and the current density is 3.5 A g<sup>-1</sup>. f, the electrochemical stability window of the 1m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/0%EG, 1m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/20%EG, 1m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/20%EG, 1m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/30%EG and 1m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/50%EG aqueous electrolytes at a scanning rate of 5 mV s<sup>-1</sup>.



**Fig. S4.** Contact angle test of different organic additives hybrid electrolytes on commercial AC electrode.



**Fig. S5. The electrochemical performance of the supercapacitor using commercial AC electrodes and 1 m Na<sub>2</sub>SO<sub>4</sub>/ (organic additive) hybrid electrolyte. a**, Diagram of three electrode test device. **b**, The ESW of 1m Na<sub>2</sub>SO<sub>4</sub>/ (organic additive) hybrid electrolytes. Blue: 1 m Na<sub>2</sub>SO<sub>4</sub>/ ET; Green: 1 m Na<sub>2</sub>SO<sub>4</sub>/ ACN; Red: 1 m Na<sub>2</sub>SO<sub>4</sub>/ EG. **c-e**, CV curves of 1 m Na<sub>2</sub>SO<sub>4</sub>/ ET hybrid electrolyte (**c**) 1 m Na<sub>2</sub>SO<sub>4</sub>/ ACN hybrid electrolyte (**d**) and 1 m Na<sub>2</sub>SO<sub>4</sub>/ EG hybrid electrolyte (**e**). **f**, EIS curves of the different hybrid electrolytes. Blue: 1 m Na<sub>2</sub>SO<sub>4</sub>/ET; Green: 1 m Na<sub>2</sub>SO<sub>4</sub>/ACN; Red: 1 m Na<sub>2</sub>SO<sub>4</sub>/EG



**Fig. S6. a,** Contact angle test of hybrid electrolytes with different amount of EG on commercial AC electrode. **b,** Conductivity and viscosity curves of different hybrid electrolytes. **c,** EIS plots of SCs using the 0% EG, 20% EG, 30% EG and 50% EG/H<sub>2</sub>O/1 m Na<sub>2</sub>SO<sub>4</sub> hybrid electrolyte. **d,** a comparison of conductivity and viscosity at different aqueous electrolytes.



Fig. S7. The electrochemical performance of AC-based supercapacitor with different EG content. a-d, CV curves at  $1m Na_2SO_4/H_2O/0\%EG$  (a),  $1m Na_2SO_4/H_2O/20\%EG$  (b),  $1m Na_2SO_4/H_2O/30\%EG$  (c) and  $1m Na_2SO_4/H_2O/50\%EG$  (d) and the operating voltage range from 1.8 V to 3.0 V.



Fig. S8. a, b <sup>1</sup>H NMR spectra in different electrolytes.



Fig. S9. Process structure diagram of the OER.



Fig. S10. The electrochemical performance of a supercapacitor based on the 1 m  $Na_2SO_4/H_2O/50\%EG$  electrolyte. a, electrochemical stability window of 3D graphite electrode. b, GCD curves at 2.8 V operating voltage and the current density is 3 A g<sup>-1</sup>. c-f, the CV curves of the 3D graphite-based supercapacitor in 1 m  $Na_2SO_4/H_2O/50\%EG$  electrolyte at 3 A g<sup>-1</sup> and the operating voltage is 2 V, 2.4 V, 2.6 V and 2.8 V, respectively.



Fig. S11. The electrochemical performance of a supercapacitor based on the 1 m  $Na_2SO_4/H_2O/50\%EG$  electrolyte and graphene measured. a, electrochemical stability window of graphene electrode. b, GCD curves at 2.4 V operating voltage windows and the current density is 3 A g<sup>-1</sup>. c, EIS test result. d-f, the CV curves of the graphene supercapacitor in 1 m  $Na_2SO_4/H_2O/50\%EG$  electrolyte at 3 A g<sup>-1</sup> and the operating voltage is 2 V (d), 2.6 V (e) and 3 V (f) operating voltage, respectively.



Fig. S12. The performance of electrolytes. EIS curves at different temperature.



Fig. S13. The cycling stability of AC-based SC using 1 m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/50%EG electrolyte under wide temperatures. a-f, the cycling stability of the AC-based supercapacitor at 2.4 V and the operating temperature is -40 °C (a), -20 °C (b), 60 °C (c), 90 °C (d), 100 °C (e) and 105 °C (f).



Fig. S14. The cycling stability of AC-based SC using 1 m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/50%EG electrolyte under wide temperatures. a-f, the cycling stability of the AC-based supercapacitor at 2.8 V operating voltage and the operating temperature is -40 °C (a), -20 °C (b), 3 °C (c), 60 °C (d), 90 °C (e) and 105 °C (f).



Fig. S15. The cycling stability of AC-based SC using 1 m Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/50%EG electrolyte at high operating voltage and different temperatures. a-d, the cycling stability of the AC-based supercapacitor at 3.0 V working voltage and the operating temperature is -40 °C (a), -20 °C (b), 60 °C (c) and 90 °C (d).

### **Supplementary Tables**

**Table. S1.** The prices of different chemical reagent from the Sigma Aldrich company (In dollar terms, URL: https://www.sigmaaldrich.cn/CN/en/campaigns/sf-rvn-platform, Date: 3rd August, 2022)

Chemical Reagent	CAS No.	Pack Size	Price (\$)	Price(\$/g)
LiTFSI	90076-65-6	250 g	1881.65	7.53
PEG	25322-68-3	20,000 g	1713.09	0.09
$Na_2SO_4$	1157-82-6	50,000 g	3028.72	0.06
NaClO <sub>4</sub>	7601-89-0	2500 g	677.13	0.27
ACN	75-05-8	16 L	616.95	0.048
EG	107-21-1	10 L	545.87	0.049

**Table. S2.** The prices of different hybrid electrolytes, which were calculated based on the above the price data.

Electrolytes	Price (\$ g <sup>-1</sup> )
$1 \text{ m Na}_2 \text{SO}_4/\text{H}_2\text{O}$	0.01
2 m LiTFSI/H <sub>2</sub> O/50%PEG	4.53
21 m LiTFSI/H <sub>2</sub> O	45.36
1 m NaClO <sub>4</sub> /H <sub>2</sub> O/95%ACN	0.08
1 m NaClO <sub>4</sub> /H <sub>2</sub> O/95%EG	0.08
17 m NaClO <sub>4</sub> /H <sub>2</sub> O	0.64
1 m Na <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> O/50%EG	0.03

**Table S3.** The physical properties of different organic solvents. All tests were obtained at room temperature.

Organic	Dielectric	Viscosity	Conductivity
Additive	$Constant(\varepsilon)$	(mPa s <sup>-1</sup> )	( µ S m <sup>-1</sup> )
ET	24.3	1.07	1.35*10-13
ACN	36.6	0.37	6*10-4
EG	37	2.2	0.2

Viscosity (mPa s <sup>-1</sup> )	Conductivity (mS cm <sup>-1</sup> )
1.16	18.6
2.41	13.2
2.35	6.2
3.16	13.2
	Viscosity (mPa s <sup>-1</sup> ) 1.16 2.41 2.35 3.16

**Table S4.** The physical properties of different hybrid electrolyte.

Electrolyte	Operating voltage	Operating temperature	Capacitance Retention	Ref	
5 m NaClO <sub>4</sub> /H <sub>2</sub> O	1.2 V	-30°C	99.3% after 1350 cycles	7	
NaClO <sub>4</sub> /NaOH/H <sub>2</sub> O	1.4 V	-30°C	96.5% after 500 cycles	8	
6 M KOH/H <sub>2</sub> O	1.5 V	-18°C	94% after 1000 cycles	9	
20 m LiTFSI/H <sub>2</sub> O	2.4 V	-20°C	70% after 5000 cycles	10	
8.1 m NaClO <sub>4</sub> /H <sub>2</sub> O	2.3 V	-50°C	91% after 7000 cycles	11	
	2.4 V	-40°C	97.7% after 20,000 cycles	_	
		-20°C	96.9% after 10,000 cycles		
		0°C	94.4% after 10,000 cycles		
		3°C	95.1% after 10,000 cycles		
		60°C	98.9% after 20,000 cycles		
		90°C	94.8% after 30,000 cycles		
		100°C	98% after 20,000 cycles		
		105°C	97.7% after 10,000 cycles		
	2.8 V	-40°C	96.7% after 6700 cycles	T1.1.	
1 m Na <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> O/EG		-20°C	97.7% after 10,000 cycles	Inis	
		3°C	97.9% after 10,000 cycles	WOLK	
		60°C	97.6% after 10,000 cycles		
		90°C	96.8% after 20,000 cycles		
		105°C	94.4% after 6700 cycles		
	3.0 V	-40°C	95% after 5000 cycles		
		-20°C	68% after 2700 cycles	_	
		60°C	89% after 10,000 cycles		
		90°C	93% after 10,000 cycles		
		105°C	98% after 5000 cycles		

Table S5. Electrochemical performance comparison of AC-based aqueous SC at different temperatures

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