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## **Supporting Information**

#### For

# Smoothly migration of ions in carbon electrodes with bimodal pores at

# ultralow temperature of -100 °C

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#### **Modeling and Theoretical Calculations**

The geometry and the total energy of solvated ions were calculated using density functional theory (DFT), which was implemented in the Vienna *ab initio* simulation package (VASP)<sup>1</sup> by adopting the projector-augmented wave (PAW) method<sup>2</sup>. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) function<sup>3</sup> was used to describe the exchange correlation interactions. The cut-off energy was 450 eV, and the criteria of convergence for energy and force were 10<sup>-4</sup> eV and 10<sup>-2</sup> eV/Å, respectively. A cubic supercell with a size *L* of 30 Å was adopted to optimize the molecules. For charged ions with solvation shell, the leading errors from neutralizing background charge<sup>4</sup> was corrected by

$$\frac{e^2 q^2 \alpha}{L\varepsilon},\tag{1}$$

where *q* is the net charge of the supercell,  $\alpha$  is the Madelung constant of a point charge *q* in a homogeneous background charge *-q*, and  $\varepsilon$  (~20) is the dielectric constant of the solvent, which was estimated as the volumetric average of the ACN and DIOX dielectric constants (**Table S1**).

The solvation energy was calculated using the following formula:

$$\Delta E = E(A^+ nB) - E(A^+) - nE(B), \qquad (2)$$

where  $E(A^+nB)$ ,  $E(A^+)$  and E(B) denote the total energy calculated from DFT of the solvated ion, naked ion and solvent molecule, respectively and *n* is the solvation number.

The vibrational frequency (v) was calculated using the harmonic model as follows:

$$v = \frac{1}{2\pi} \sqrt{\frac{k_f}{m}} \,, \tag{3}$$

$$k_f = \frac{2\Delta E}{\Delta x^2},\tag{4}$$

where  $k_f$  is the spring constant,  $\Delta E$  is the calculated binding energy change when the solvent molecule deviates from the equilibrium binding distance by  $\Delta x$ , and *m* is the mass of a solvent molecule. In this work,  $k_f$  is about 9.5 N/m, and the frequency is estimated as  $10^{12}$  Hz.

Temperature-dependent ion desolvation model using Arrhenius equation is proposed to determine the desolvation rate *k*:

$$k = A \cdot e^{-\frac{E_a}{k_b T}}$$
(5)

where A is the pre-exponential factor, a frequency of attempt in desolvation, which can be estimated as the vibrational frequency v of the entire solvent molecule bound to the MeEt<sub>3</sub>N<sup>+</sup> ion (~10<sup>12</sup> Hz in this work),  $E_a$  is the activation energy for the desolvation process (binding energy between the solvent molecule and ion),  $k_b$  is the Boltzmann constant and T is the thermodynamic temperature in Kelvin.

Figures



**Figure S1** a) XRD patterns and b) Raman spectra of CDC-400 and CDC-1000, high-resolution TEM images of c) CDC-400 and d) CDC-1000.

These CDC samples are produced by the selective layer-by-layer removal of metal atoms from carbide lattices, which allowed atomic-level control during synthesis. The pores in the produced carbon can be well tuned and the pore size distribution of the sample is very narrow.



**Figure S2** a) Low-temperature  $N_2$  adsorption and desorption isotherms and b) pore size distributions of CDC-400 and CDC-1000, desolvation energy of c) ACN- and d) DIOX-solvated MeEt<sub>3</sub>N<sup>+</sup> ion. We calculated the solvation energy when the solvent number increases from 4 to 5. The values are positive and negligible in ACN and DIOX, respectively. So, 0,1,2,3,4 were determined in this work.

When a fully solvated MeEt<sub>3</sub>N<sup>+</sup> ion (1.03 nm) pass through the 0.8 nm slit-shaped pore opening in CDC-400, the solvation shell needs to decrease by removal of two solvent molecules (the solvated MeEt<sub>3</sub>N<sup>+</sup> ion size now is 0.72 nm) to match the size of the pore opening.



**Figure S3** Interfacial resistances ( $R_i$ ) and average desolvation time scales ( $\tau_0$ ) of CDC-400 and CDC-1000 at different temperatures.



Figure S4 CV curves of CDC-1000 measured at 20 and -100 °C with a scan rate of 2 mV s<sup>-1</sup>.

In CDC-1000, ions could smoothly pass through the pore opening. Low scan rate ensures longer ion diffusion time and more ions to be adsorbed by the internal surface. Consequently, the CDC-1000 reveal a sustained high capacitance.



Figure S5 Electrolyte conductivity vs. temperature for the electrolytes with different solvents.



**Figure S6** (a, b) CV curves of CMK-3 measured at -90 °C and -70 °C in ACN / MF and ACN / DIOX electrolytes, respectively, with different scan rates. (c, d) Specific capacitance vs. scan rate of EDLCs based on CMK-3 measured at different temperatures.



Figure S7 (a) TEM image of CMK-3, (b) SEM image of CNT.



 $P/P_0$ Figure S8 Low-temperature N<sub>2</sub> adsorption-desorption isotherm of *h*AC.



Figure S9 (a) SEM and (b) TEM images of hAC. The inset in (b) is XRD pattern of hAC.



**Figure S10** Nyquist plots of *h*AC measured at -100 °C in different electrolytes: (a) 0.3 M MeEt<sub>3</sub>NBF<sub>4</sub> in a 3:7 v/v mixture of ACN and MF. (b) 0.3 M MeEt<sub>3</sub>NBF<sub>4</sub> in a 3:7 v/v mixture of ACN and DIOX.

When  $MeEt_3N-BF_4$  is used as salt of the electrolyte, one solvent molecular should be removed from the solvated ion to pass through the pore opening duing charging, an additional resistance would exist and consequently affect the low-temperature performance of SC.



**Figure S11** CV curves of *h*AC measured at different temperatures with scan rate of 100 mV s<sup>-1</sup>. The electrolyte used here is 0.3 M SBP-BF<sub>4</sub> in a 3:7 v/v mixture of ACN and MF. The areal capacitance is about 270 mF cm<sup>-2</sup>.



**Figure S12** Galvanostatic charge/discharge curves of SCs based on soy protein AC (*h*AC) measured (a) at different temperatures using a current density of 1 A  $g^{-1}$  and (b) at -100 °C using different current densities. The electrolyte used here is 0.3 M SBP-BF<sub>4</sub> in a 3:7 v/v mixture of ACN and MF.



Figure S13 Cyclic stability of EDLCs based on *h*AC measured at 20 and -100 °C using a current density of 5 A g<sup>-1</sup> for 10,000 cycles.



**Figure S14** Nyquist plots of (a) *h*AC and (b) CNT measured at -100 °C. The electrolyte here is 0.3 M  $MeEt_3NBF_4$  in a 3:7 v/v mixture of ACN and MF.



Figure S15 CV curves of (a) hAC and (b) CNT measured at -100 °C with different scan rates.

# Tables

	8 5	5
Solvation number	*Geometry (Å)	Geometry (Å)
	ACN- solvated MeEt <sub>3</sub> N <sup>+</sup>	DIOX- solvated MeEt <sub>3</sub> N <sup>+</sup>
0	4.8×4.8×6.4	4.8×4.8×6.4
1	4.8×7.1×9.6	6.5×6.7×8.0
2	7.2×8.7×10.1	6.5×8.2×10.8
3	9.3×10.2×10.2	6.5×10.9×12.7
4	10.1×10.2×13.2	10.3×11.0×12.6

10.1×10.2×13.2

Table S1 Solvation geometry of ACN- and DIOX-solvated MeEt<sub>3</sub>N<sup>+</sup> ion

\*Geometry of solvated ion means the sizes of each axis.

Table S2 Volumetric capacitance and rate performance of different electrodes at -100 °C

10.3×11.0×12.6

Electrode materials	Areal capacitance (mF cm <sup>-2</sup> )	Thickness (µm)	Volumetric capacitance (F cm <sup>-3</sup> )	Rate performance
CNT	~120	~380	~3	
СМК-3	~120	~35	~34	Similar
hAC	~270	~40	~66	

#### References

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