

ARTICLE

## Elucidating Cation Hydration Ratio in Water-in-Salt Electrolyte for Carbon-based Supercapacitor

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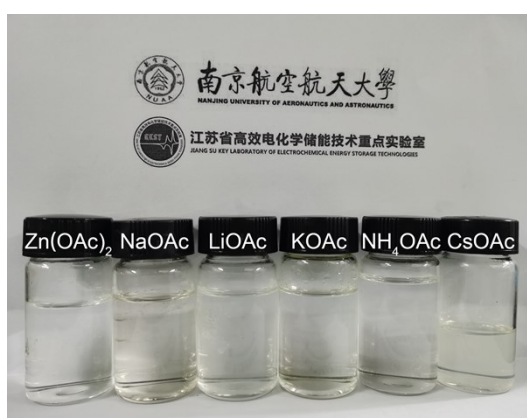


Fig. S1 Photo of completed dissolved saturated acetate-based electrolytes with different cations.

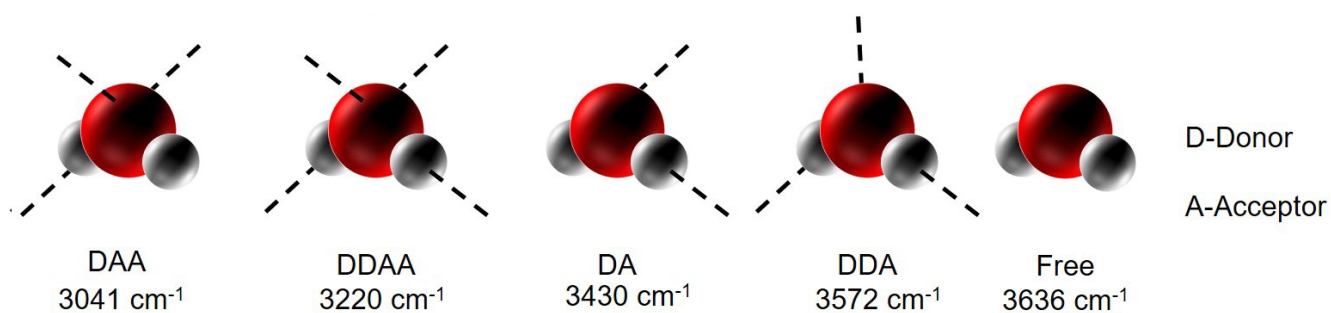
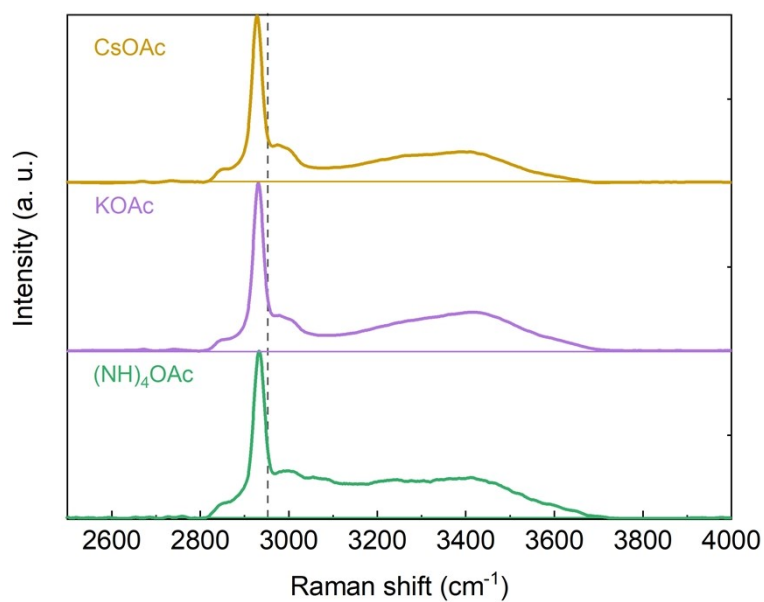


Fig. S2 Schematic diagram of water molecules in different vibrational states.



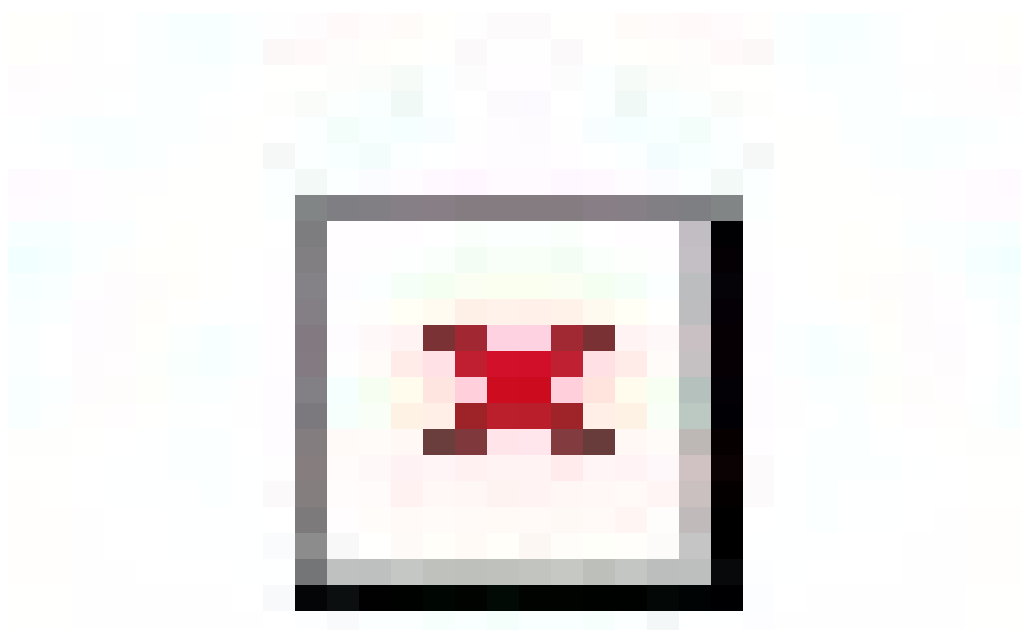
**Fig. S3** The Raman spectra of saturated aqueous acetate electrolytes with different cations range from 2500  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$ .

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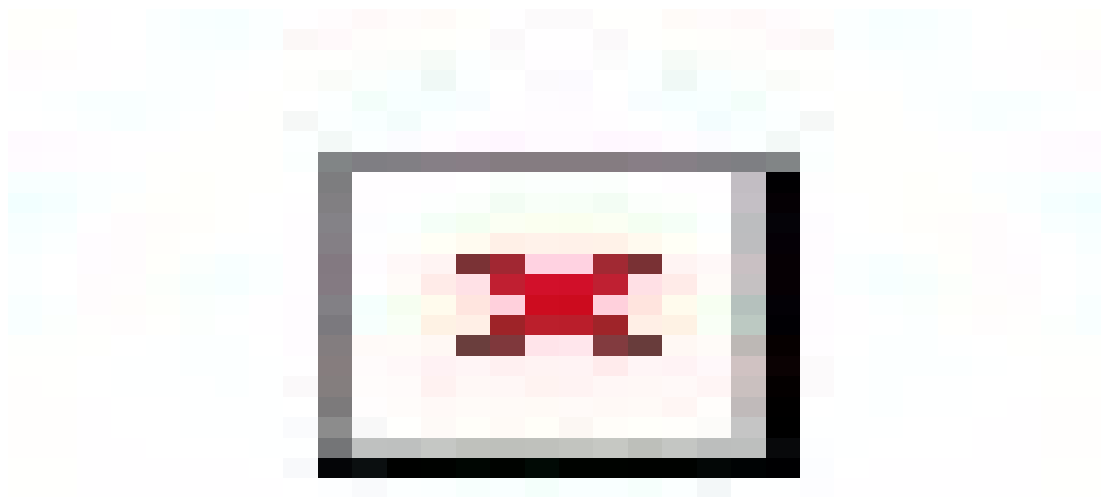
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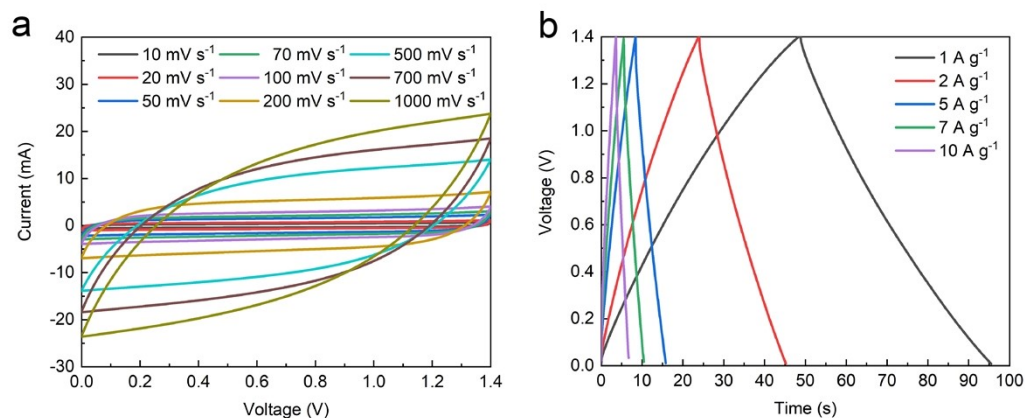
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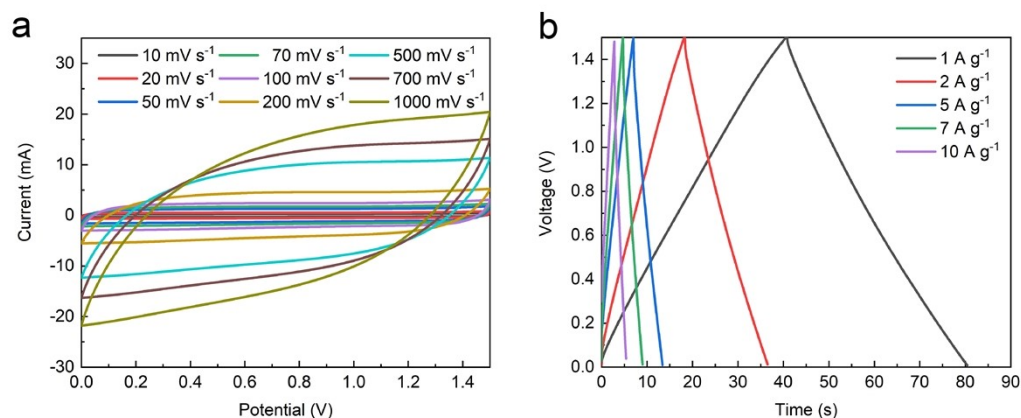
**Fig. S4** The annealing as a function of (a) temperature-time and (b) density-time. The equilibration processes as a function of (c) temperature-time and (d) density-time.



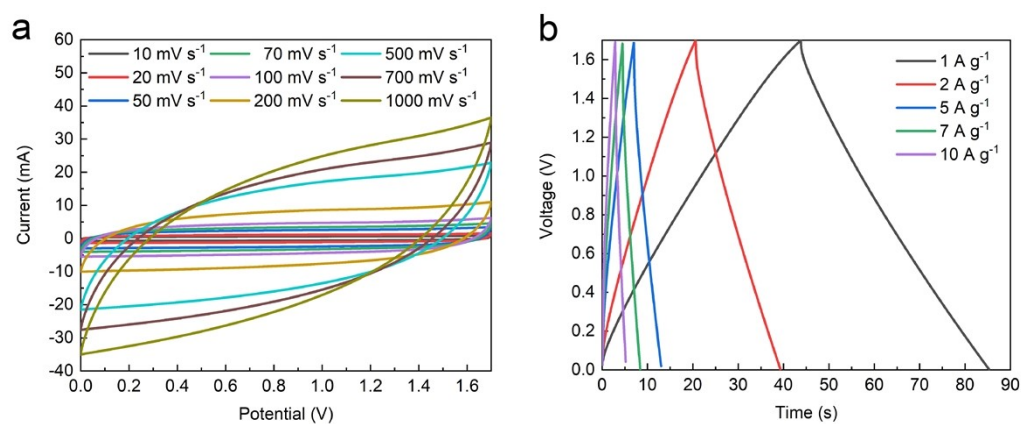
**Fig. S5** (a) Cyclic voltammograms potential window opening experiments. CVs were performed in three-electrode systems at  $10 \text{ mV s}^{-1}$ . (b) S-value of maximum operating potential for AC electrode in different WIS electrolytes.



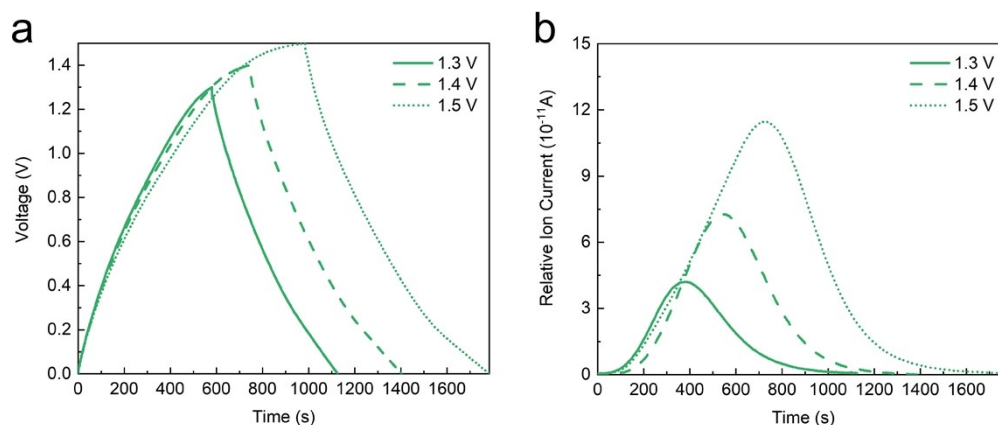
**Fig. S6** Rate performance of NH<sub>4</sub>-based SC. (a) CV curves at 10 mV s<sup>-1</sup> to 1000 mV s<sup>-1</sup>. (b) GCD curves at 1 A g<sup>-1</sup> to 10 A g<sup>-1</sup>.



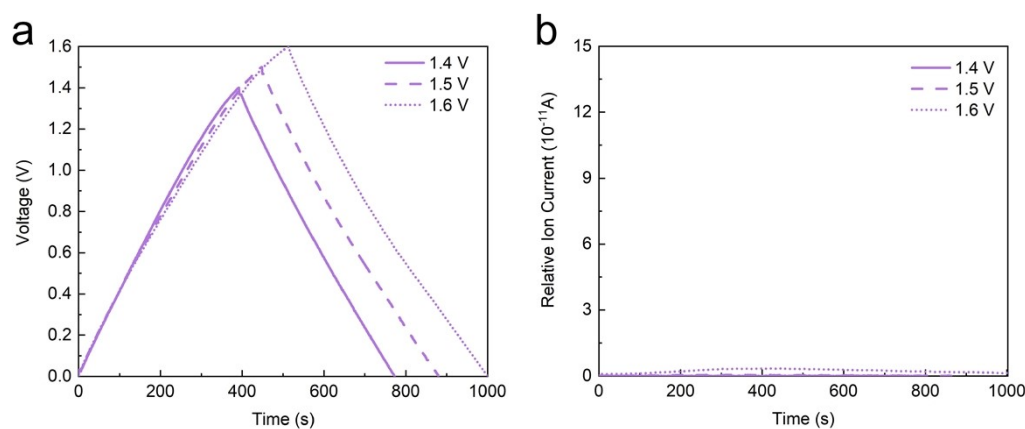
**Fig. S7** Rate performance of K-based SC. (a) CV curves at 10 mV s<sup>-1</sup> to 1000 mV s<sup>-1</sup>. (b) GCD curves at 1 A g<sup>-1</sup> to 10 A g<sup>-1</sup>.



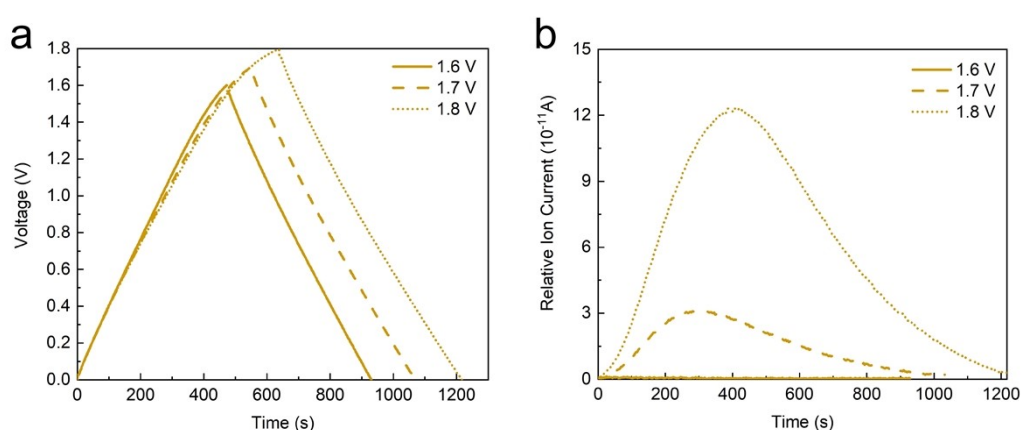
**Fig. S8** Rate performance of Cs-based SC. (a) CV curves at 10 mV s<sup>-1</sup> to 1000 mV s<sup>-1</sup>. (b) GCD curves at 1 A g<sup>-1</sup> to 10 A g<sup>-1</sup>.



**Fig. S9** The gas production analysis of  $\text{NH}_4$ -based SC at 1.3~1.5 V. (a) Galvanostatic charge-discharge curves at  $0.1 \text{ A g}^{-1}$ . (b) DEMS signals about  $\text{H}_2$ .



**Fig. S10** The gas production analysis of K-based SC at 1.4~1.6 V. (a) Galvanostatic charge-discharge curves at  $0.1 \text{ A g}^{-1}$ . (b) DEMS signals about  $\text{H}_2$ .



**Fig. S11** The gas production analysis of Cs-based SC at 1.6~1.8 V. (a) Galvanostatic charge-discharge curves at  $0.1 \text{ A g}^{-1}$ . (b) DEMS signals about  $\text{H}_2$ .

**Table S1** The ionic size and solvation structure of different cations<sup>1</sup>

Ion	BR (nm)	HR (nm)
K <sup>+</sup>	0.133	0.331
Cs <sup>+</sup>	0.186	0.329
NH <sub>4</sub> <sup>+</sup>	0.148	0.331

**Table S2** The number of simulated molecules in different WIS electrolytes systems

Electrolyte	Cations	Anions	H <sub>2</sub> O molecules
KOAc	200	200	420
CsOAc	300	300	330
NH <sub>4</sub> OAc	100	100	290

**Table S3** The density of SCs with different cations at room temperature.

	NH <sub>4</sub> OAc	KOAc	CsOAc
Density (g cm <sup>-3</sup> )	1.0974	1.3661	2.1152

**Table S4** The self-discharge of SCs with different cations.

	NH <sub>4</sub> OAc	KOAc	CsOAc
Voltage of SCs self-discharge (V)	0.61	0.70	0.92
Voltage retention rate of SCs self-discharge after 12 h (%)	43.6	46.6	54.1

## Notes and references

1. A. G. Volkov, S. Paula and D. W. Deamer, *Bioelectrochem. Bioenerg.*, 1997, **42**, 153-160.