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SUPPLEMENTARY INFORMATION

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Molecular crowding electrolytes for high-voltage aqueous batteries

Jing Xie, Zhuojian Liang and Yi-Chun Lu ✉

Electrochemical Energy and Interfaces Laboratory, Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong, Hong Kong Special Administrative Region, China. ✉e-mail: yichunlu@mae.cuhk.edu.hk

Supplementary Materials for

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Jing Xie, Zhuojian Liang and Yi-Chun Lu*

Electrochemical Energy and Interfaces Laboratory, Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong, Hong Kong SAR 999077, China
*E-mail: yichunlu@mae.cuhk.edu.hk

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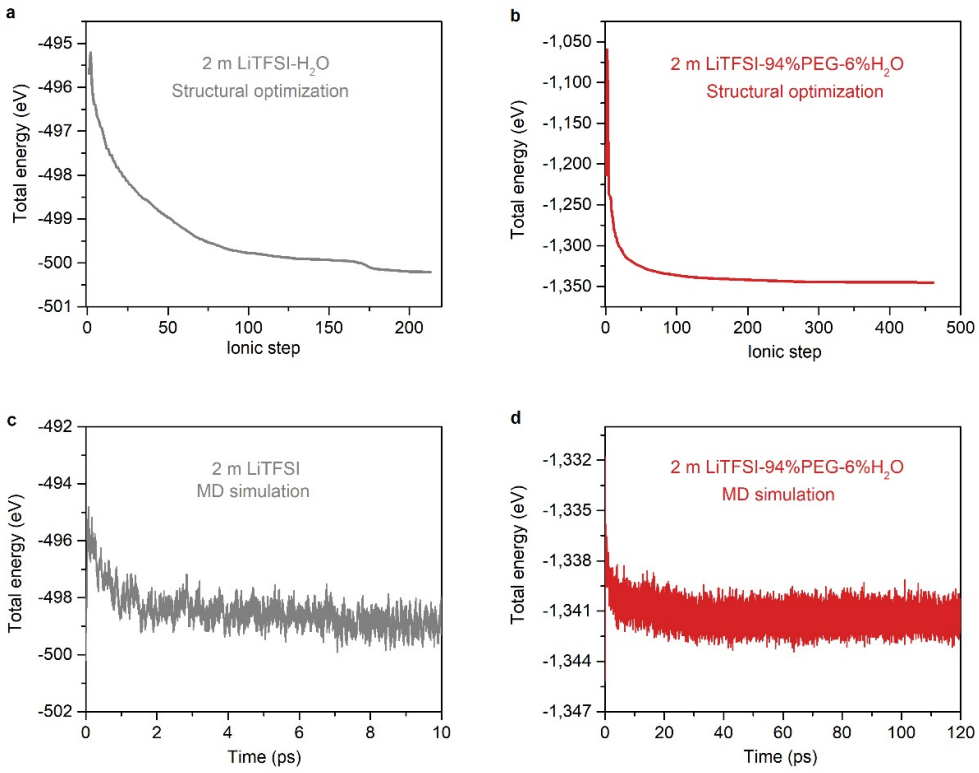
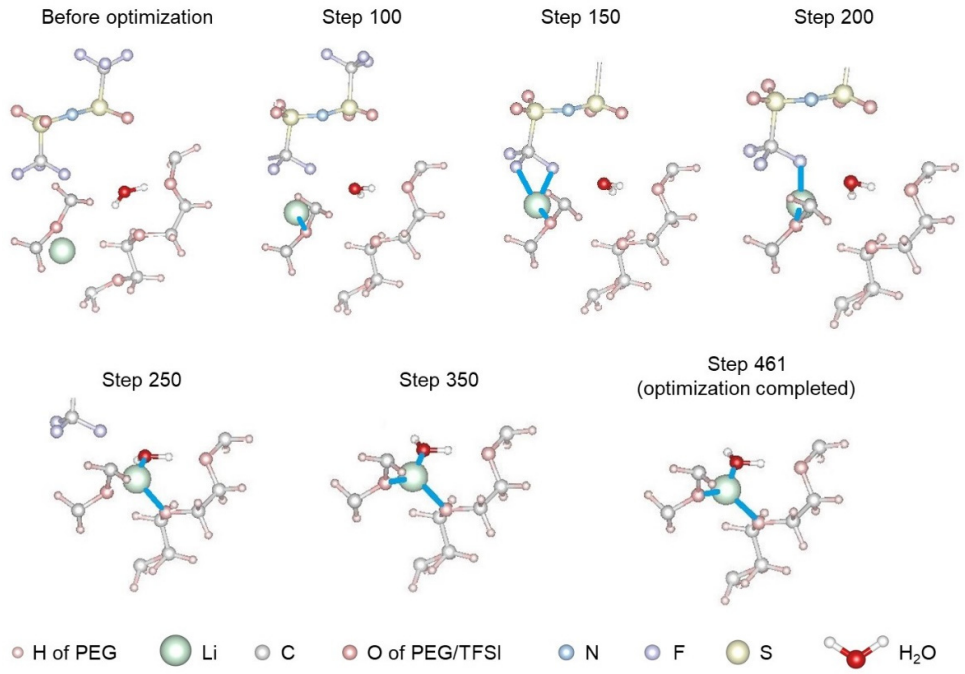
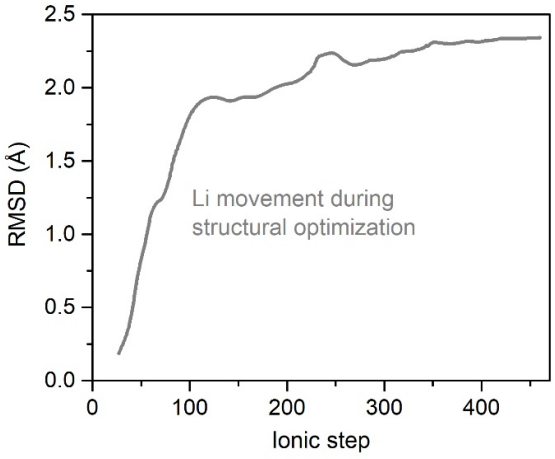


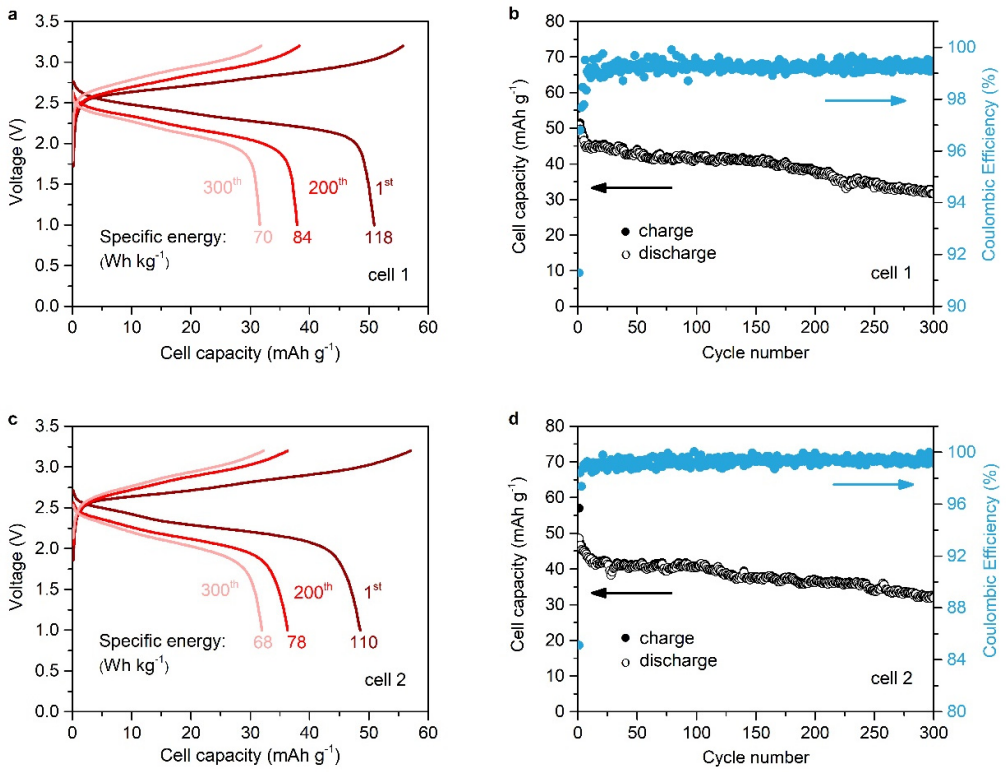
Supplementary Figure 1 | Illustration of the evolution of the total energy during the structural optimization and molecular simulation for the 2 m LiTFSI-H_2O and 2 m LiTFSI-94%PEG-6%H_2O systems. a-b, the evolution of the total energy of 2 m LiTFSI-H_2O and 2 m LiTFSI-94%PEG-6%H_2O during structural optimization with ionic and electronic self-consistent convergence of 10^{-3} and 10^{-4} eV, respectively. **c-d,** the evolution of the total energy of 2 m LiTFSI-H_2O and 2 m LiTFSI-94%PEG-6%H_2O during MD simulation at 300 K.



Supplementary Figure 2 | Snapshots of Li movement in the 2 m LiTFSI-94%PEG-6%H_2O system during structural optimization. The snapshots of Li coordination environment during structural optimization indicates that after energy calculation and lattice geometry adjustment, the structure of Li coordination has been stabilized as the energy converges (e.g. the structures after step 350 are similar). The blue line represents coordinate bonding.



Supplementary Figure 3 | Root-mean-square deviation (RMSD) of Li in 2 m LiTFSI-94%PEG-6%H_2O system during structural optimization. It reveals that the movement of Li tends to be steady after 350 ionic steps, which is consistent with the Li coordination environment snapshots (Supplementary Figure 2) showing stable structures with the total energy converged.



Supplementary Figure 4 | Cycling performance of two more repeated LTO/LMO cells in 2 m LiTFSI-94%PEG-6%H_2O at 1 C. a-b, The voltage profiles of 1st, 200th and 300th cycle and cycling stability of L-LTO/LMO cell 1 in 2 m LiTFSI-94%PEG-6% H_2O at 1 C. **c-d**, The voltage profiles of 1st, 200th and 300th cycle and cycling stability of L-LTO/LMO cell 2 in 2 m LiTFSI-94%PEG-6%H_2O at 1 C. The cell capacity was calculated on the basis of the total weight of positive and negative active materials.

Supplementary Table 1 | Composition and conductivity of fluorine-rich "water-in-salt" electrolytes for Li-ion batteries

Electrolyte	Composition(wt%)	Ionic conductivity ($mS\ cm^{-1}$)	Ref.
"Water-in-Salt" **21 m** LiTFSI	**LiTFSI: 85.8** H_2O: 14.2	8.21 (25 ºC)	1
"Water-in-Bisalt" **21 m** LiTFSI-**7 m** LiOTf	**LiTFSI: 74.2** **LiOTf: 13.5** H_2O: 12.3	6.5 (25 ºC)	2
"Water-in-Bisalt" gel **21 m** LiTFSI-**7 m** LiOTf-PVA	**LiTFSI: 66.6** **LiOTf: 12.6** PVA: 10.0 H_2O: 10.8	N	3,4
"Hydrate Melt" $Li(TFSI)_{0.7}(BETI)_{0.3}\cdot 2H_2O$ (**19.4 m** LiTFSI-**8.3 m** LiBETI)	**LiTFSI:56.9** **LiBETI:32.9** H_2O:10.2	3.0 (30 ºC)	5
"Hybrid Aqueous/Nonaqueous" **21 m** LiTFSI in H_2O-**9.25 m** LiTFSI in DMC(wt%=1:1)	**LiTFSI: 81.2** DMC: 9.4 H_2O: 9.4	5.0 (30 ºC)	6
"Monohydrate Melt" $Li(PTFSI)_{0.6}(TFSI)_{0.4}\cdot 1H_2O$ (**22.2 m** LiTFSI-**33.3 m** LiPTFSI)	**LiTFSI: 34.2** **LiPTFSI: 60.4** H_2O: 5.4	0.1(30 ºC)	7
$Li(TFSI)_{0.8}(MM3411)_{0.2}\cdot 1.4H_2O$ **31.4 m** LiTFSI-**7.9 m** LiMM3411	**LiTFSI:72.4** LiMM3411:19.6 H_2O:8.0	0.33(25 ºC)	8

Supplementary Table 2 | Comparison of price of PEG and commonly used fluorinated Li salts in "water-in-salt" electrolytes for Li-ion batteries

Chemical	Sigma (USD/g)	TCI (USD/g)
LiTFSI	4.2[9]	1.8[10]
LiOTf	5.0[11]	2.5[12]
LiBETI	N	43.6[13]
PEG 400	0.04[14]	0.06[15]

*the price is calculated based on the largest pack size

Supplementary Table 3 | Composition of 2 m LiTFSI-xPEG-(1-x)H_2O electrolytes

Electrolytes	Solvent (wt%)	
	PEG 400	H_2O
2 m LiTFSI-71P	71	29
2 m LiTFSI-80P	80	20
2 m LiTFSI-90P	90	10
2 m LiTFSI-94P	94	6
2 m LiTFSI-100P	100	0

Supplementary Discussion I

The total loss of charge based on the CE of each cycle after 300 cycles is:

$$\sum_{n=1}^{300}\left(\text{the charge capacity of } n^{\text{th}} \text{ cycle} * (1 - \text{CE of } n^{\text{th}} \text{ cycle})\right) = 0.56 \text{ mAh}$$

The loss of Li capacity after 300 cycles is:

The discharge capacity of 1st cycle – the discharge capacity of 300th cycle = 0.09 mAh

The capacity associated with electrolyte decomposition is estimated to be:

0.56 (mAh) – 0.09 (mAh) =0.47 mAh

Even if all of the electrolyte decomposition charge (0.47 mAh) comes from water splitting (which is unlikely considering potential salt TFSI decomposition[1]), the mass fraction of water decomposed per cycle is 0.02 wt%. The detail estimation is shown below.

The specific capacity of consumed water is:

$$\frac{2 * 96485(\frac{\text{C}}{\text{mol}})}{3.6\left(\frac{\text{C}}{\text{mAh}}\right) * 18(\frac{\text{g}}{\text{mol}})} = 2978 \text{ mAh/g}$$

The mass of decomposed water after 300 cycles is:

$$\frac{0.47 \text{ (mAh)}}{2978(\frac{\text{mAh}}{\text{g}})} = 1.6 * 10^{-4} \text{ g} = 0.16 \text{ mg}$$

The mass of water decomposed per cycle is:

$$\frac{0.16 \text{ (mg)}}{300 \text{ (cycles)}} = 5.3 * 10^{-4} \text{ mg}$$

Since the mass of water in electrolyte before cycling is 2.64 mg,

The mass fraction of water decomposed per cycle is:

$$\frac{5.3 * 10^{-4}(\text{mg})}{2.64 \text{ (mg)}} = 0.02 \text{ wt\%}$$

Supplementary movie captions

Supplementary movie 1. Flammability testing of 2 m LiTFSI-94%PEG-6%H_2O electrolyte. The fire of ignited cotton swab was extinguished after being immersed in the 2 m LiTFSI-94%PEG-6%H_2O electrolyte, suggesting the electrolyte is non-flammable and safe.

Supplementary movie 2. Flammability testing of commercial $LiPF_6$ in EC/DEC electrolyte. The commercial $LiPF_6$ in EC/DEC electrolyte started to burn after an ignited cotton swab was immersed in the electrolyte, indicating the electrolyte is flammable.

Supplementary movie 3. The comparison of the flammability of 2 m LiTFSI-94%PEG-6%H_2O, 2 m LiTFSI-PEG and 2 m LiTFSI-PEO. 2 m LiTFSI-94%PEG-6%H_2O soaked glass fiber was not ignited, while 2 m LiTFSI-PEG and polymer electrolyte 2 m LiTFSI-PEO(EO/Li^+=11) were both ignited, indicating the that 2 m LiTFSI-94%PEG-6%H_2O exhibits superior safety compared to 2 m LiTFSI-PEG and solid PEO polymer electrolyte.

Reference

1. Suo, L. et al. “Water-in-salt” electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science* **350**, 938-943 (2015).
2. Suo, L. et al. Advanced high-voltage aqueous lithium-ion battery enabled by “water-in-bisalt” electrolyte. *Angew. Chem. Int. Ed.* **55**, 7136-7141 (2016).
3. Yang, C. et al. 4.0 V aqueous Li-ion batteries. *Joule* **1**, 122-132 (2017).
4. Yang, C. et al. Aqueous Li-ion battery enabled by halogen conversion–intercalation chemistry in graphite. *Nature* **569**, 245-250 (2019).
5. Yamada, Y. et al. Hydrate-melt electrolytes for high-energy-density aqueous batteries. *Nat. Energy* **1**, 16129 (2016).
6. Wang, F. et al. Hybrid aqueous/non-aqueous electrolyte for safe and high-energy Li-ion batteries. *Joule* **2**, 927-937 (2018).
7. Ko, S. et al. Lithium-salt monohydrate melt: A stable electrolyte for aqueous lithium-ion batteries. *Electrochem. Commun.* **104**, 106488 (2019).
8. Forero-Saboya, J., Hosseini-Bab-Anari, E., Abdelhamid, M. E., Moth-Poulsen, K. & Johansson, P. Water-in-bisalt electrolyte with record salt concentration and widened electrochemical stability window. *J. Phys. Chem. Lett.* **10**, 4942-4946 (2019).
9. Bis(trifluoromethane)sulfonimide lithium salt. Sigma Aldrich https://www.sigmaaldrich.com/catalog/product/aldrich/15224?lang=en&region=HK. (Accessed: 13th September 2019)
10. Bis(trifluoromethane)sulfonimide lithium salt. TCI America https://www.tcichemicals.com/eshop/en/us/catalog/list/search?searchWord=LiTFSI&client=default_frontend&output=xml_no_dtd&proxystylesheet=default_frontend&sort=date:D:L:d1&oe=UTF-8&ie=UTF-8&ud=1&exclude_apps=1&site=en_us&mode=0. (Accessed: 13th September 2019)
11. Lithium trifluoromethanesulfonate. Sigma Aldrich https://www.sigmaaldrich.com/catalog/product/aldrich/481548?lang=en&region=HK&gclid=Cj0KCQjwt5zsBRD8ARIsAJfI4BipzCzk46aCb6D6zEFR4iLqAjIa3JXPzl0vzU0oSiGUEJO-5bpKs8IaAsjHEALw_wcB. (Accessed: 13th September 2019)
12. Lithium trifluoromethanesulfonate TCI America https://www.tcichemicals.com/eshop/en/us/catalog/list/search?searchWord=Lithium+trifluoromethanesulfonate&client=default_frontend&output=xml_no_dtd&proxystylesheet=default_frontend&sort=date:D:L:d1&oe=UTF-8&ie=UTF-8&ud=1&exclude_apps=1&site=en_us&pageSize=20&alignmentSequence=18&mode=0. (Accessed: 13th September 2019)
13. Lithium bis(pentafluoroethanesulfonyl)imide TCI America https://www.tcichemicals.com/eshop/en/us/catalog/list/search?searchWord=LiBETI&client=default_frontend&output=xml_no_dtd&proxystylesheet=default_frontend&sort=date:D:L:d1&oe=UTF-8&ie=UTF-8&ud=1&exclude_apps=1&site=en_us&pageSize=20&alignmentSequence=18&mode=0. (Accessed: 13th September 2019)

14. Poly(ethylene glycol) 400. Sigma Aldrich https://www.sigmaaldrich.com/catalog/product/aldrich/202398?lang=en&region=HK. (Accessed: 13th September 2019)
15. Poly(ethylene glycol) 400 TCI America https://www.tcichemicals.com/eshop/en/us/catalog/list/search?searchWord=PEG+400&client=default_frontend&output=xml_no_dtd&proxystylesheet=default_frontend&sort=date:D:L:d1&oe=UTF-8&ie=UTF-8&ud=1&exclude_apps=1&site=en_us&mode=0. (Accessed: 13th September 2019)