Electrochemical potential window of molecular crowded electrolyte with various Li salt

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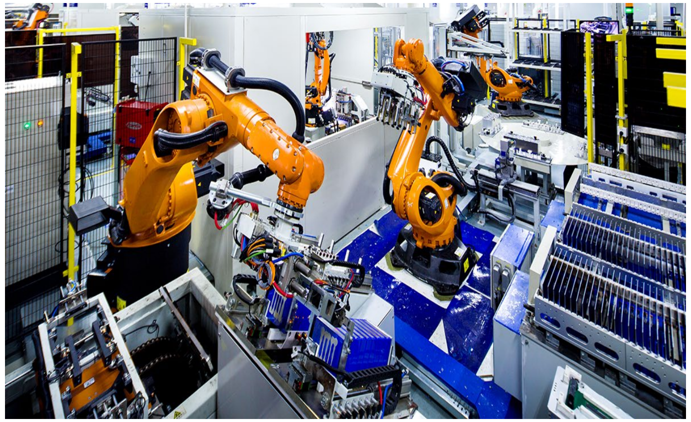
Aqueous Battery

Non-aqueous Battery has…



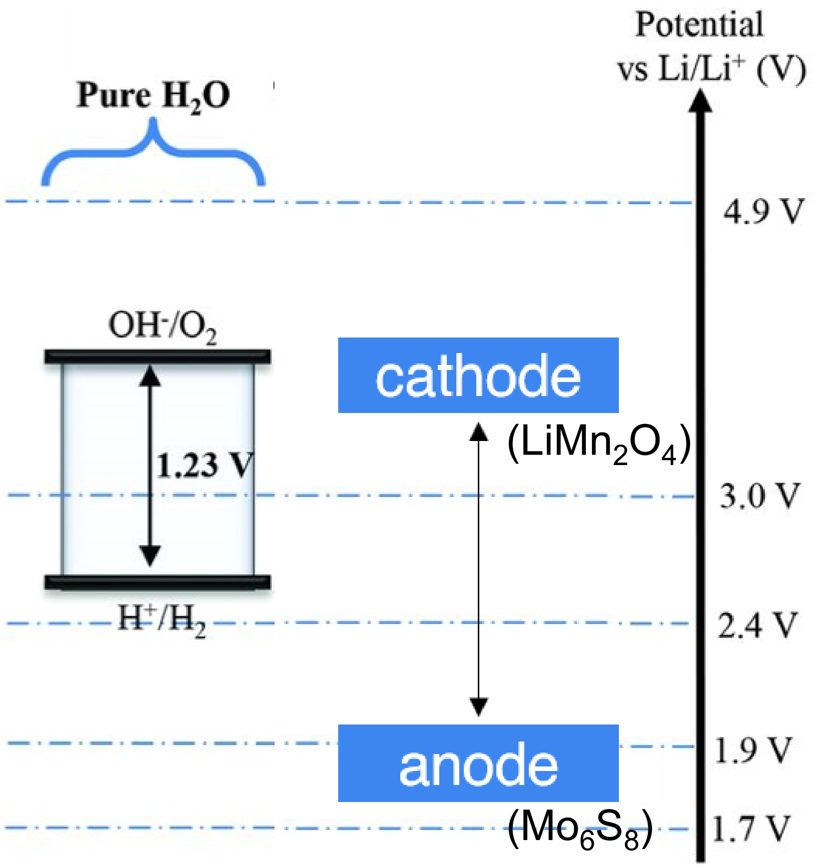
Safety Issue	Cost Issue	Environmental Issue
- Flammability - Toxicity	- Material - Production	- Wastes

→ Aqueous Battery can solve this!

Aqueous Battery

Major Limitation

: Electrochemical potential window (EW)



Narrow EW of H_2O

→ Hard to use aqueous electrolyte

Science 2015, **350**, 938-943

Aqueous Battery

- Electrochemical potential window?

TABLE 18-1

Standard Electrode Potentials*

Reaction	E^0 at 25°C, V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.359
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.087
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.065
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+ 0.799
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+ 0.771
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+ 0.536
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+ 0.337
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$	+ 0.334
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	+ 0.268
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+ 0.222
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+ 0.017
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	**0.000**
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	− 0.151
$PbSO_4 + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	− 0.350
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	− 0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	− 0.763

*See Appendix 5 for a more extensive list.

H_2O Electrolysis : $H_2O \rightarrow H_2 + \frac{1}{2} O_2$

1.23V !!!

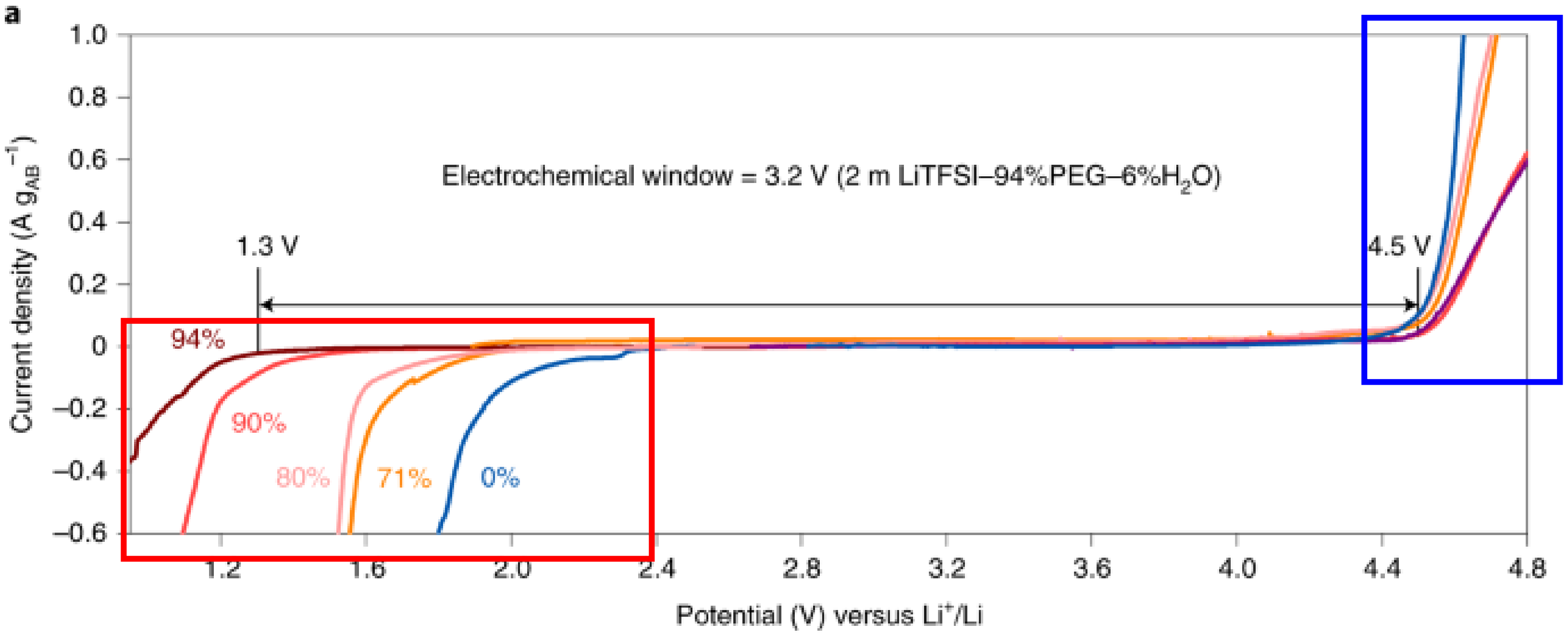
Charging the aq. battery
with the voltage higher than 1.23V

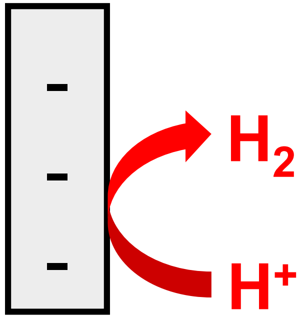
➡ ~~Charging battery~~!

H$_2$, O$_2$ Evolution (=water electrolysis)

Aqueous Battery

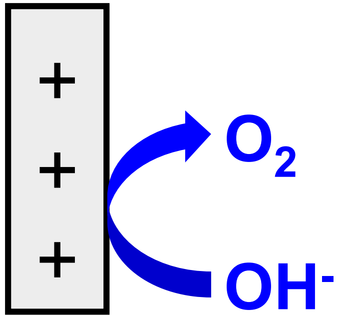
- Electrochemical potential window?





Hydrogen (H_2)
Evolution
Reaction

Oxygen (O_2)
Evolution
Reaction

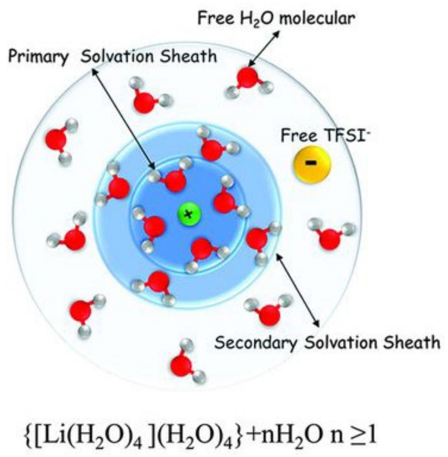


Water-in-salt electrolyte

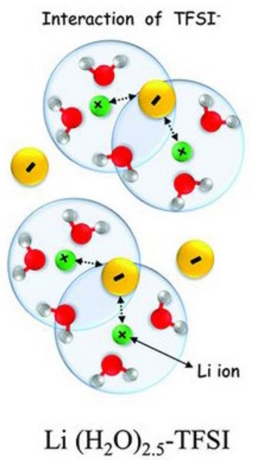
"Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries

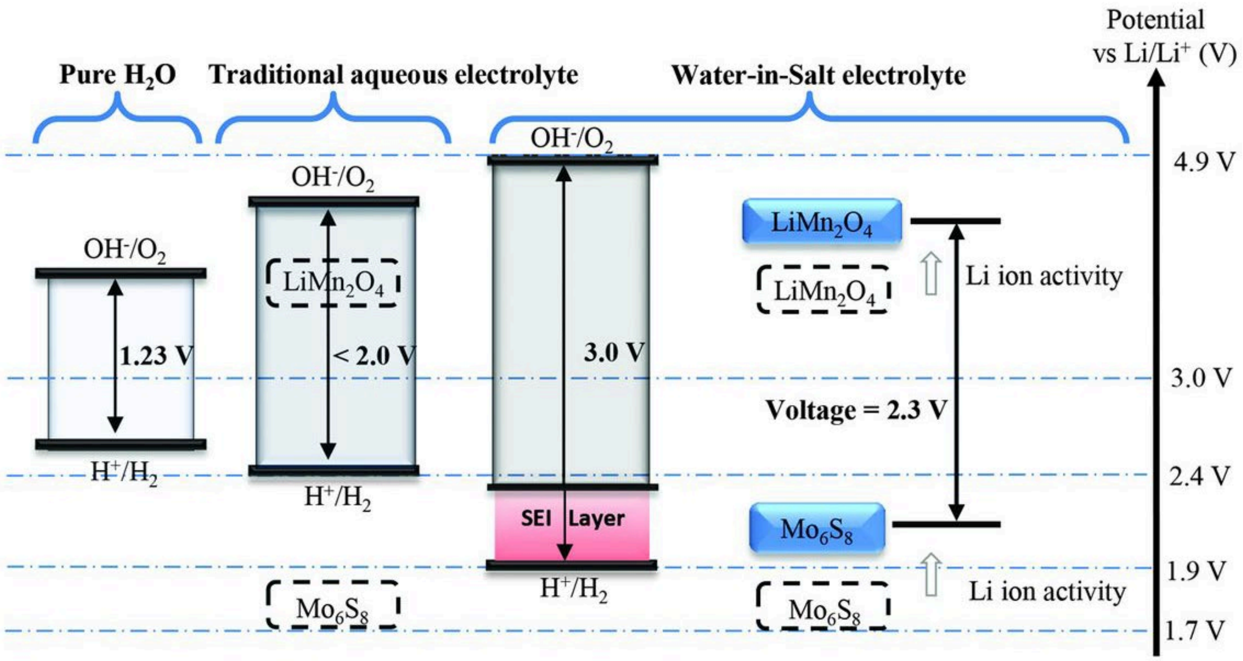
Science 2015, **350**, 938-943

Salt-in-Water
(Low concentration)



Water-in-Salt
(High concentration)





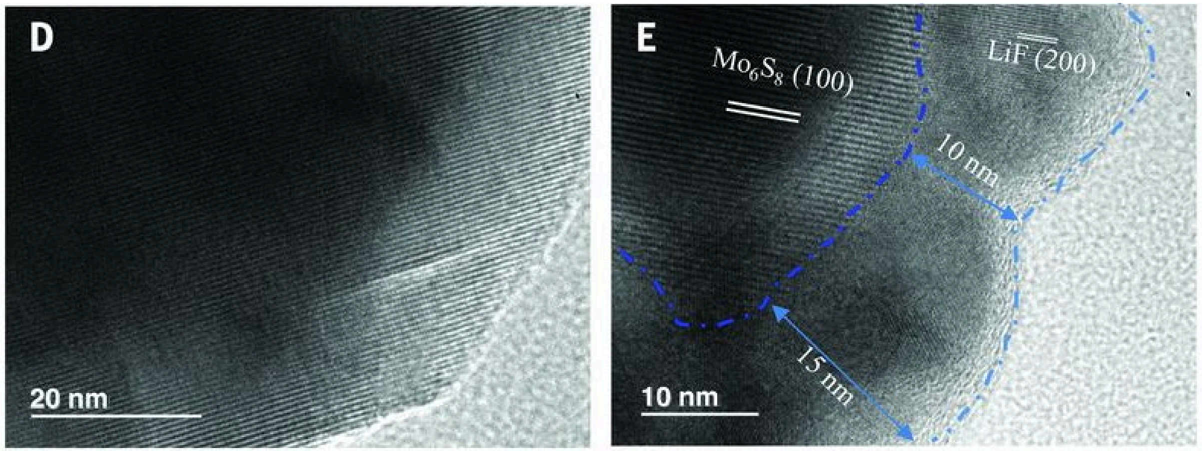
"Water-in-salt(WiS)" electrolyte
➔ <u>**High-voltage**</u> aqueous lithium-ion chemistries

Water-in-salt electrolyte

Water-in-Salt(WiS) & Water-in-Bisalt(WiBS) electrolyte

- Expansion the EW

- Formation of a stable solid electrolyte interphase (SEI)



Science 2015, **350**, 938-943

- But still,

  High cost, Toxicity, …

Widening the window by molecular crowding electrolytes

Molecular crowding electrolytes for high-voltage aqueous batteries

Nat. Mater. 2020, **19,** 1006-1011

ARTICLES
https://doi.org/10.1038/s41563-020-0667-y
nature materials
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Molecular crowding electrolytes for high-voltage aqueous batteries

Jing Xie, Zhuojian Liang and Yi-Chun Lu

Developing low-cost and eco-friendly aqueous electrolytes with a wide voltage window is critical to achieve safe, high-energy and sustainable Li-ion batteries. Emerging approaches using highly concentrated salts (21–55 m (mol kg⁻¹)) create artificial solid–electrode interfaces and improve water stability; however, these approaches raise concerns about cost and toxicity. Molecular crowding is a common phenomenon in living cells where water activity is substantially suppressed by molecular crowding agents through altering the hydrogen-bonding structure. Here we demonstrate a 'molecular crowding' electrolyte using the water-miscible polymer poly(ethylene glycol) as the crowding agent to decrease water activity, thereby achieving a wide electrolyte operation window (3.2 V) with low salt concentration (2 m). Aqueous $Li_4Ti_5O_{12}/LiMn_2O_4$ full cells with stable specific energies between 75 and 110 W h kg^{-1} were demonstrated over 300 cycles. Online electrochemical mass spectroscopy revealed that common side reactions in aqueous Li-ion batteries (hydrogen/oxygen evolution reactions) are virtually eliminated. This work provides a path for designing high-voltage aqueous electrolytes for low-cost and sustainable energy storage.

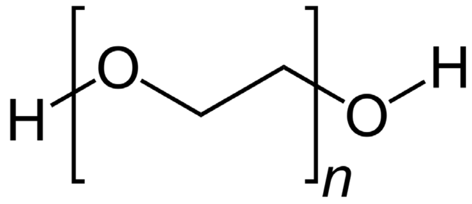
Molecular Crowding

Phenomenon that
crowding agents reach
a concentration of more than 80 mg/ml

→ Hydrogen-bonding structure of water changed

→ Properties of solution can be modified!

➡ Water-miscible polymer Poly(ethylene glycol) (PEG) can act as a crowding agent.

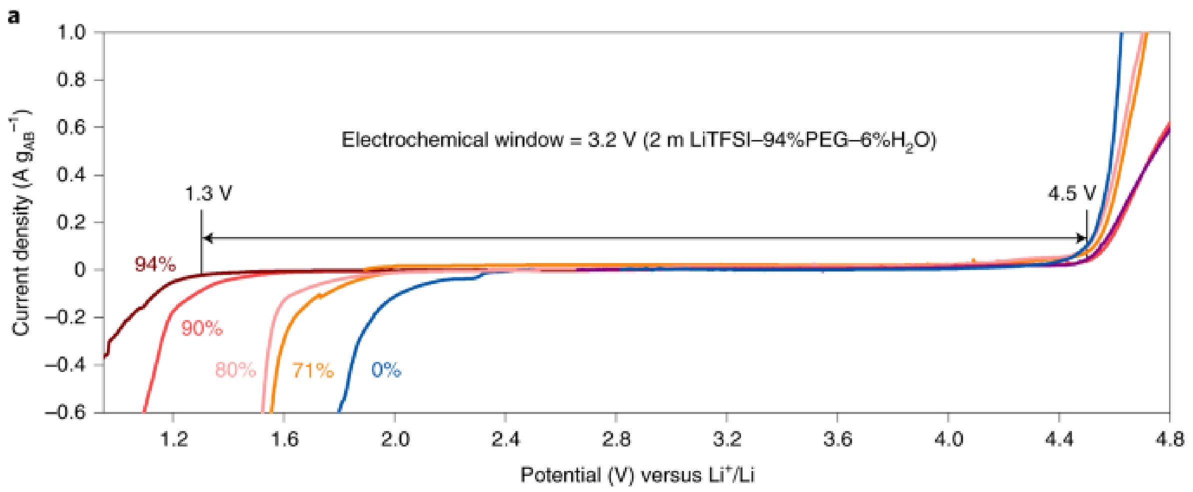


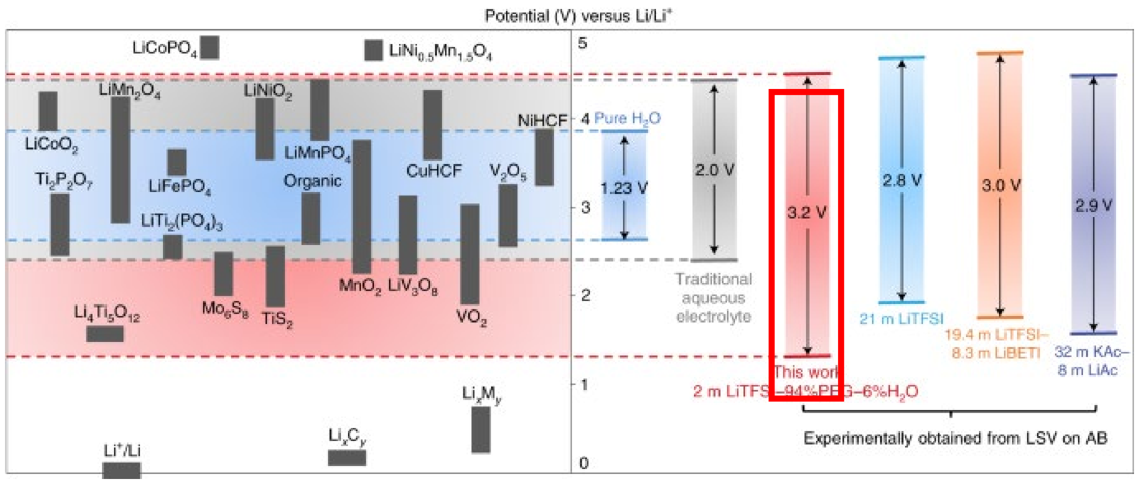
Widening the window by molecular crowding electrolytes

Molecular crowding electrolytes for high-voltage aqueous batteries

Nat. Mater. 2020, **19,** 1006-1011

Aqueous Electrolyte : 2 m LiTFSI-94%PEG-6%H_2O





Higher PEG concentration

→ Wider the EW

Widen the EW up to **3.2V**

Widening the window by molecular crowding electrolytes

Molecular crowding electrolytes for high-voltage aqueous batteries

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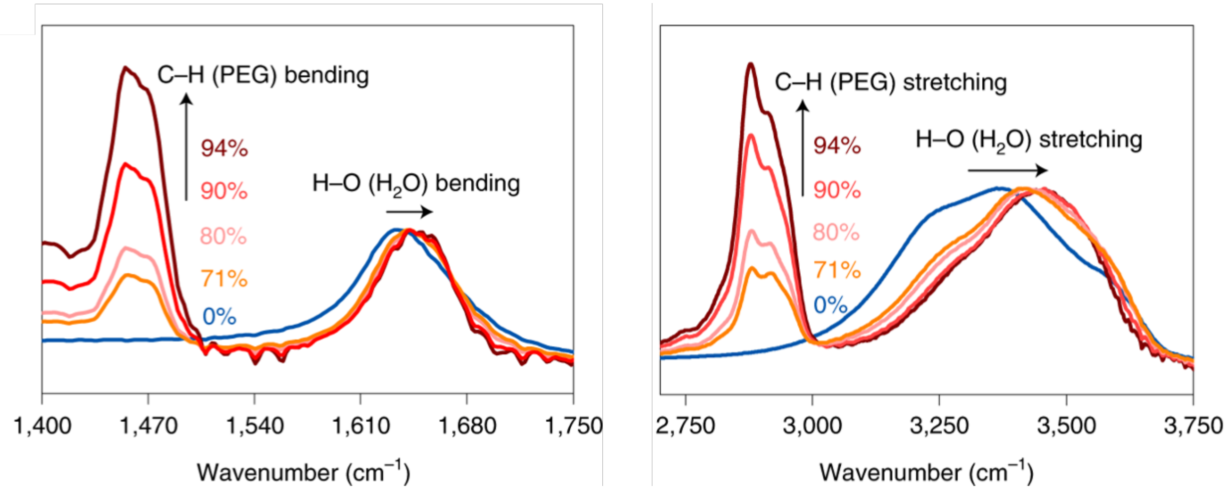
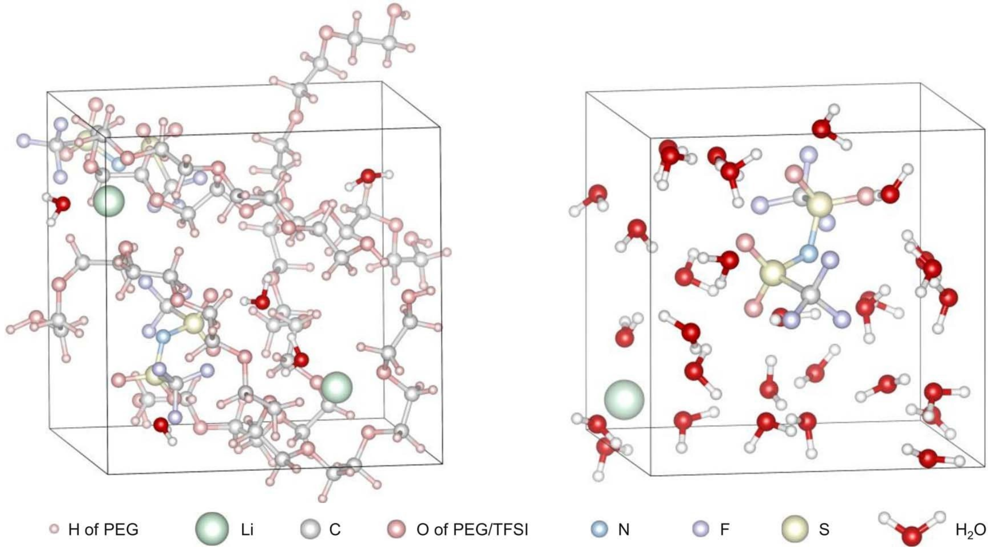


Higher PEG concentration

→ Strengthened H-O bond in H_2O

→ Weaker hydrogen-bond between PEG-H_2O



Visualized hydrogen-bond network by MD simulation

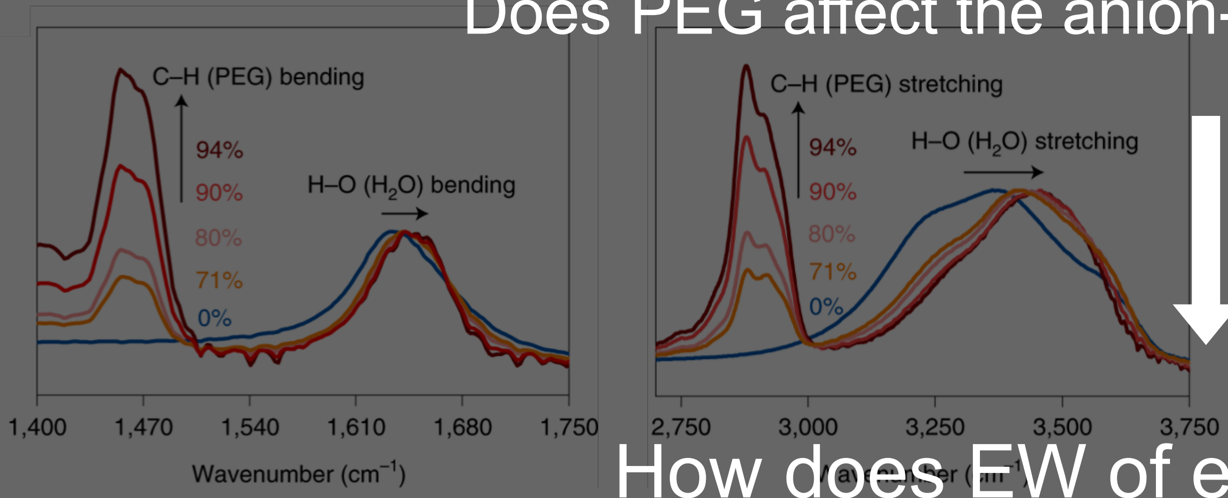
➡ PEG **affects the interaction** among the solvent molecules in the electrolyte

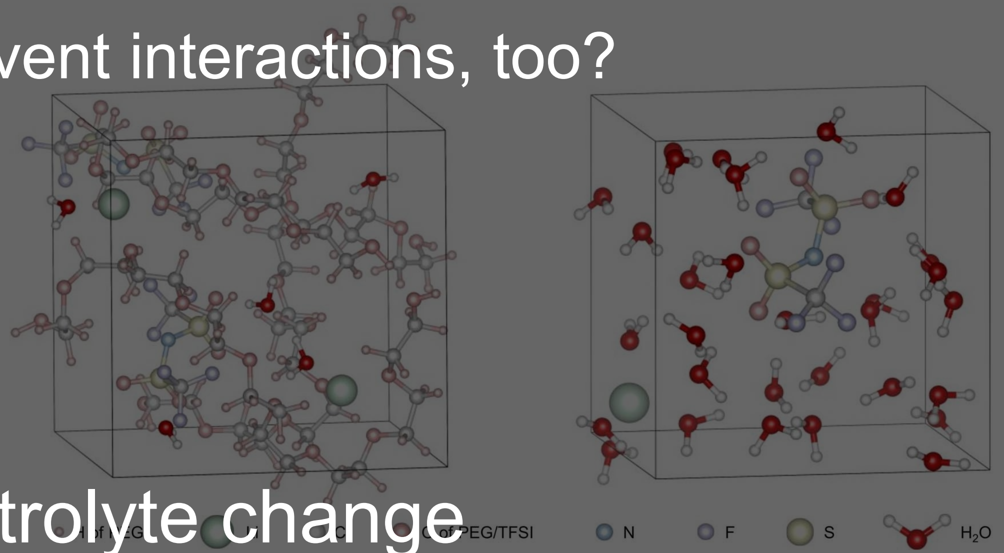
Widening the window by molecular crowding electrolytes

Molecular crowding electrolytes for high-voltage aqueous batteries

Nat. Mater. 2020, **19,** 1006-1011

Does PEG affect the anion-solvent interactions, too?





How does EW of electrolyte change with PEG and various anions?

Higher PEG concentration

→ Strengthened H-O bond in H_2O

→ Weaker hydrogen-bond between PEG-H_2O

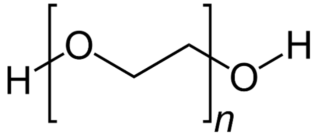
Visualized hydrogen-bond network by MD simulation

PEG **affects the interaction** among the solvent molecules in the electrolyte

Nat. Mater. 2020, **19,** 1006-1011

Effect of PEG on electrochemical window

In the previous article (*Nat. Mater.* 2020, **19,** 1006-1011),

- Crowding agent: Liquid PEG, M_n = 400 

- Linear Sweep Voltammetry

    - Three electrode system

        - Working Electrode: Acetylene black (AB) coated Al foil

        - Counter Electrode: Activated Carbon (AC)

        - Reference Electrode: Ag/AgCl

→

- Working Electrode: Glassy Carbon (GC, 3φ)

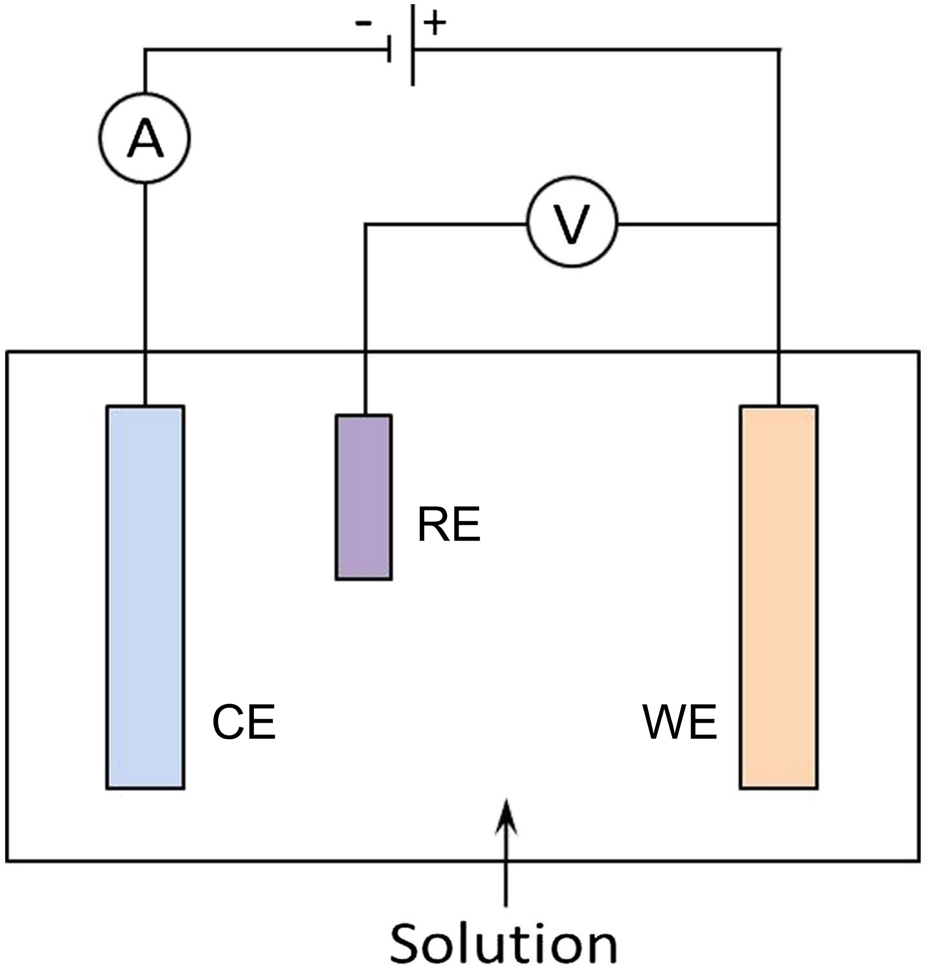
- Counter Electrode: Pt coil

- Reference Electrode: Ag/AgCl (3 M NaCl)

- Scan rate: 0.2 mV/s

Effect of PEG on electrochemical window

* Three Electrode System



Working Electrode : **Main Reaction**

Counter Electrode : Current Related

Reference Electrode : Voltage Related

Goal of the research

1. Anions used in this research

- Interaction between anion and H_2O → **Hofmeister series**

'salting out' of anionic proteins　　　　'salting in' of anionic proteins

CO_3^{2-} **SO_4^{2-}** HPO_4^{2-} **OAc^-** Cl^- Br^- I^- **NO_3^-** **ClO_4^-** SCN^- **$TFSI^-$** →

Kosmotropes
:Strongly hydrated anion : structure-making

Chaotropes
: Weakly hydrated anion : structure-breaking

→ Choose five water-soluble Li salts : **Li_2SO_4**, **LiOAc**, **$LiNO_3$**, **$LiClO_4$**, **LiTFSI**
(Others are water-insoluble)

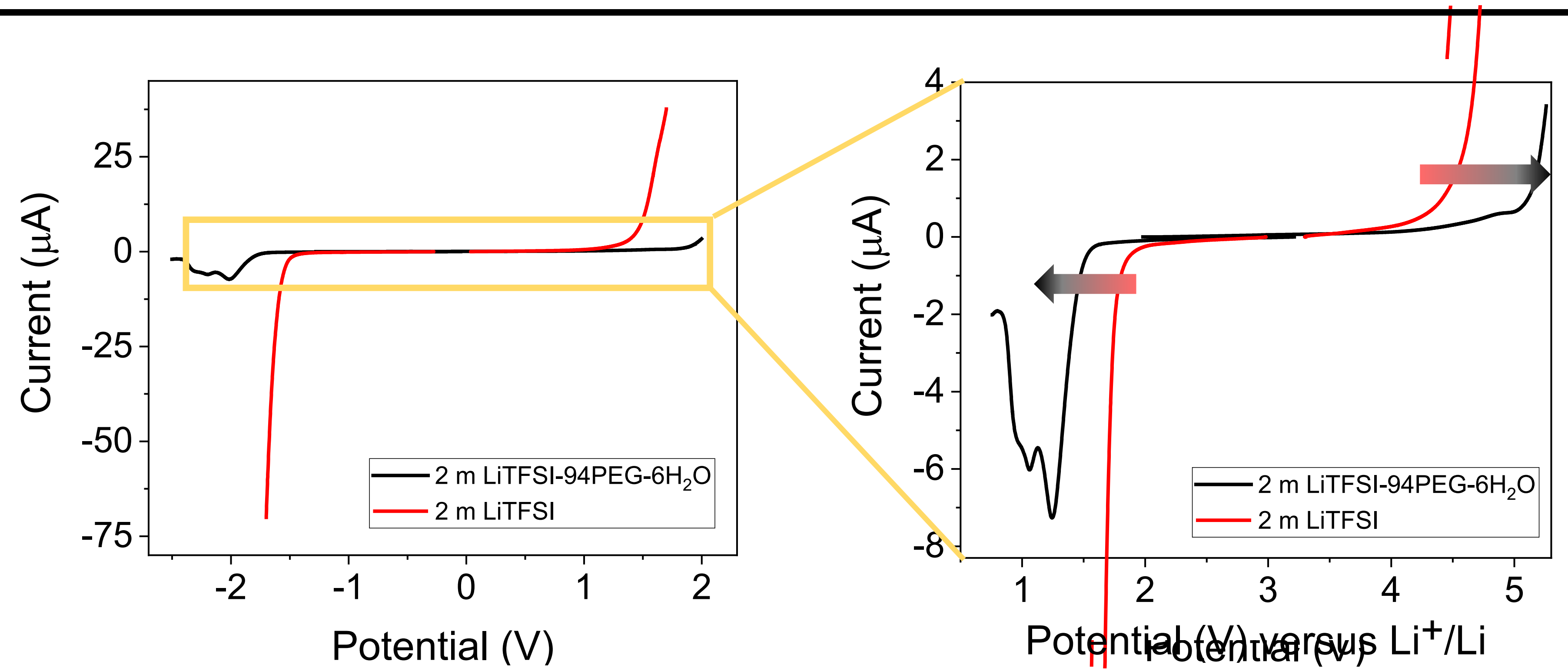
2. Expected Result

- Different onset potential will be shown from different anions.

- **OER potential** will show significant difference than HER potential

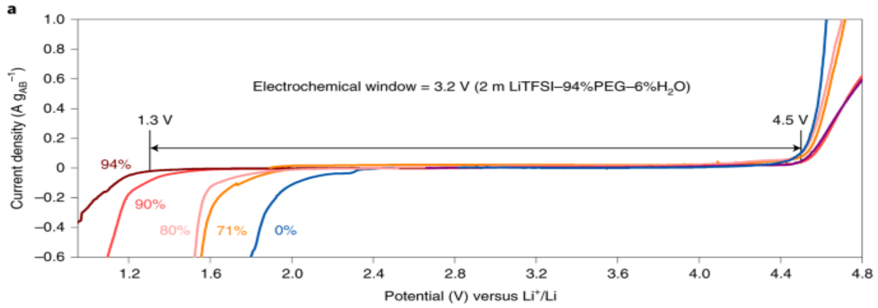
∵ Anions are expected to show differences at **positively charged electrode**.

Effect of PEG on electrochemical window



→ Crowding agent PEG expands the EW in both HER & OER

→ Similar results compared to the previous report (*Nat. Mater.* 2020, **19,** 1006-1011)



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WE: Glassy carbon (GC, 3φ), RE: Ag/AgCl (3 M NaCl), CE: Pt coil, 10 min Ar bubbling before experiment, Scan rate: 0.2 mV/s

Molecular crowding electrolyte with Li_2SO_4

Because of the low solubility of Li_2SO_4,

2 m Li_2SO_4
- 94%PEG - 6%H_2O

0.2 m Li_2SO_4
- 94%PEG - 6%H_2O

Li_2SO_4 is **insoluble** in solvent, 94%PEG-6%H_2O

1. Reduce the PEG

   : **2 m Li_2SO_4–13%PEG–87%H_2O**

2. Reduce the Li_2SO_4

   : **0.5 m Li_2SO_4–45%PEG–55%H_2O**

Molecular crowding electrolyte with Li_2SO_4

Because of the low solubility of Li_2SO_4,

Li_2SO_4 is **insoluble** in solvent, 94%PEG-6%H_2O

1. Reduce the PEG

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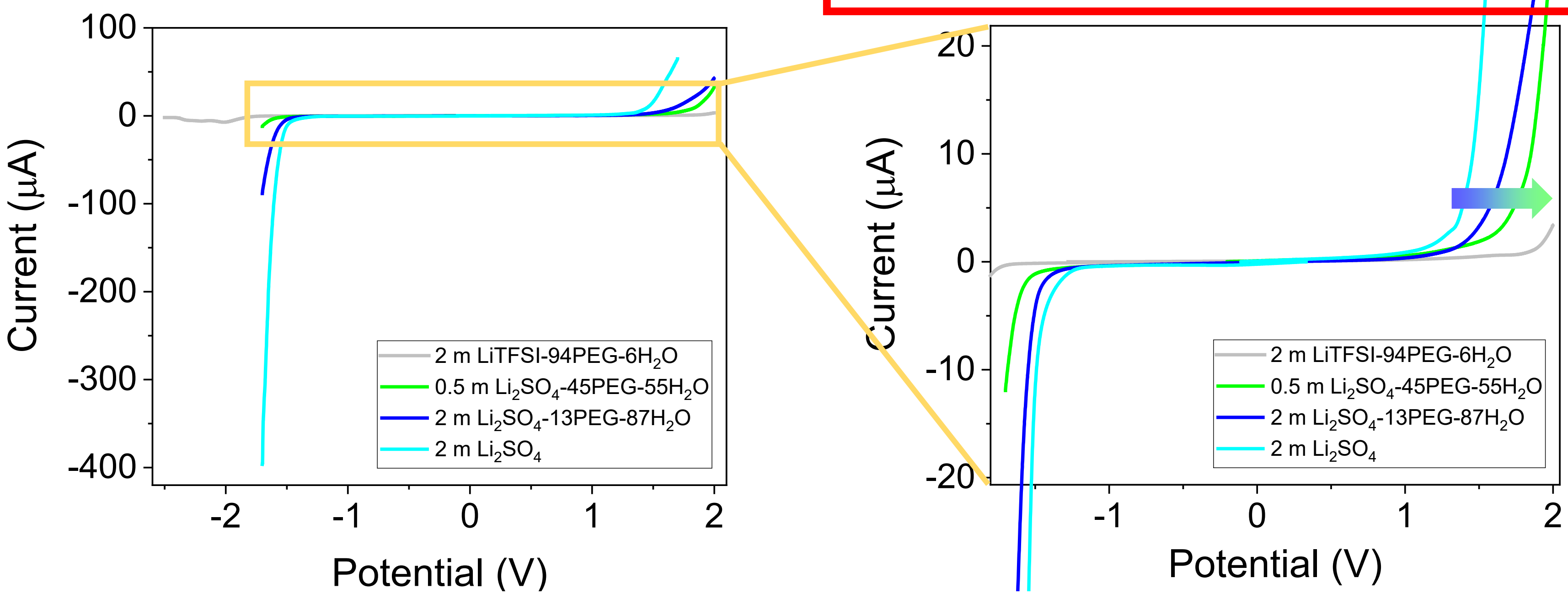


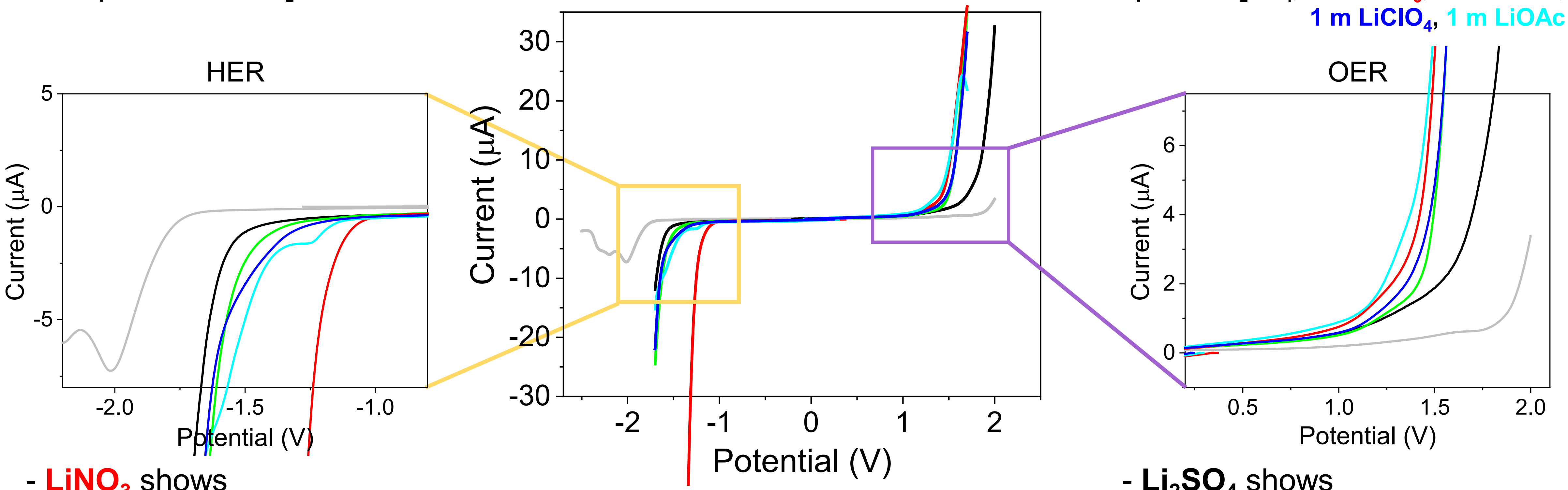
→ Select **45%PEG-55%H_2O** as solvent / **1 m of Li^+ cation**

WE: Glassy carbon (GC, 3φ), RE: Ag/AgCl (3 M NaCl), CE: Pt coil, 10 min Ar bubbling before experiment, Scan rate: 0.2 mV/s

Molecular crowding electrolyte with various anions

Solvent | 45%PEG-55%H_2O

Solute | 0.5 m Li_2SO_4, 1 m $LiNO_3$, 1 m LiTFSI, 1 m $LiClO_4$, 1 m LiOAc



- **$LiNO_3$** shows the lowest HER overpotential
- **Li_2SO_4, LiTFSI, $LiClO_4$, LiOAc** → Similar potential

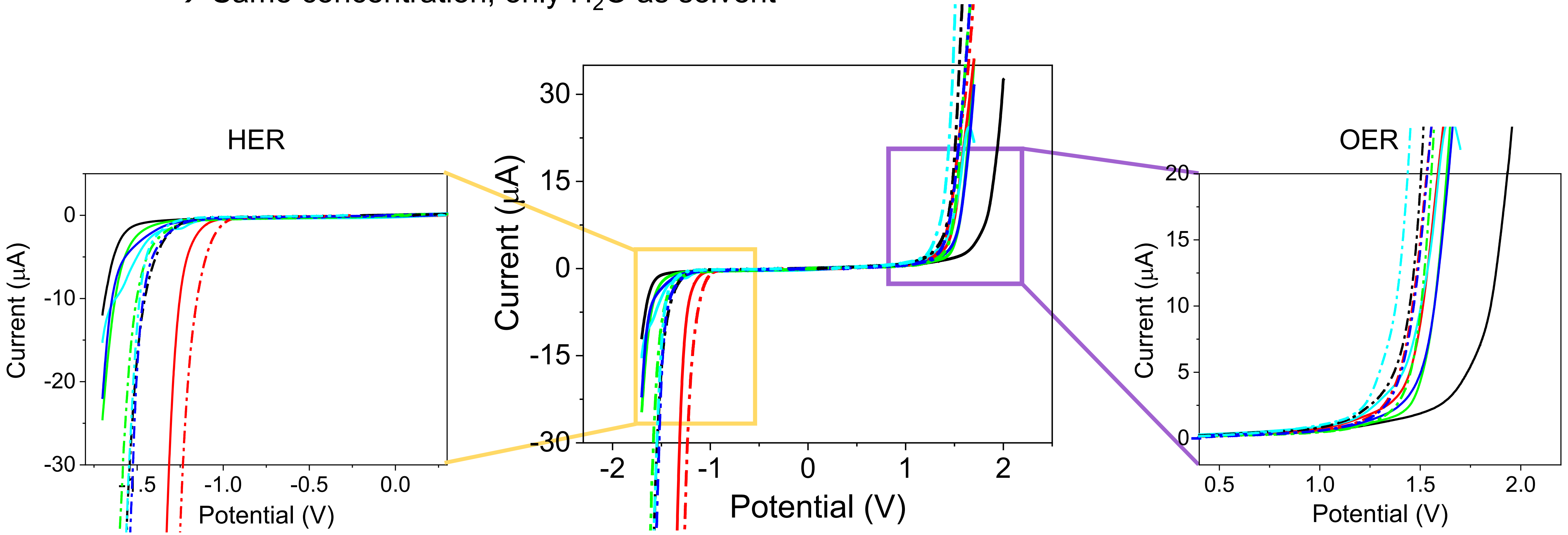
- **Li_2SO_4** shows the highest OER overpotential
- **LiOAc, $LiNO_3$, $LiClO_4$, LiTFSI** → Similar potential

WE: Glassy carbon (GC, 3φ), RE: Ag/AgCl (3 M NaCl), CE: Pt coil, 10 min Ar bubbling before experiment, Scan rate: 0.2 mV/s

Molecular crowding electrolyte with various anions

With Controls

→ Same concentration, only H_2O as solvent



* Solid line : 45%PEG-55%H_2O as solvent
Dash-dot line : only H_2O as solvent

Solute | 0.5 m Li_2SO_4, 1 m $LiNO_3$, 1 m LiTFSI, 1 m $LiClO_4$, 1 m LiOAc

WE: Glassy carbon (GC, 3φ), RE: Ag/AgCl (3 M NaCl), CE: Pt coil, 10 min Ar bubbling before experiment, Scan rate: 0.2 mV/s

Molecular crowding electrolyte with various anions

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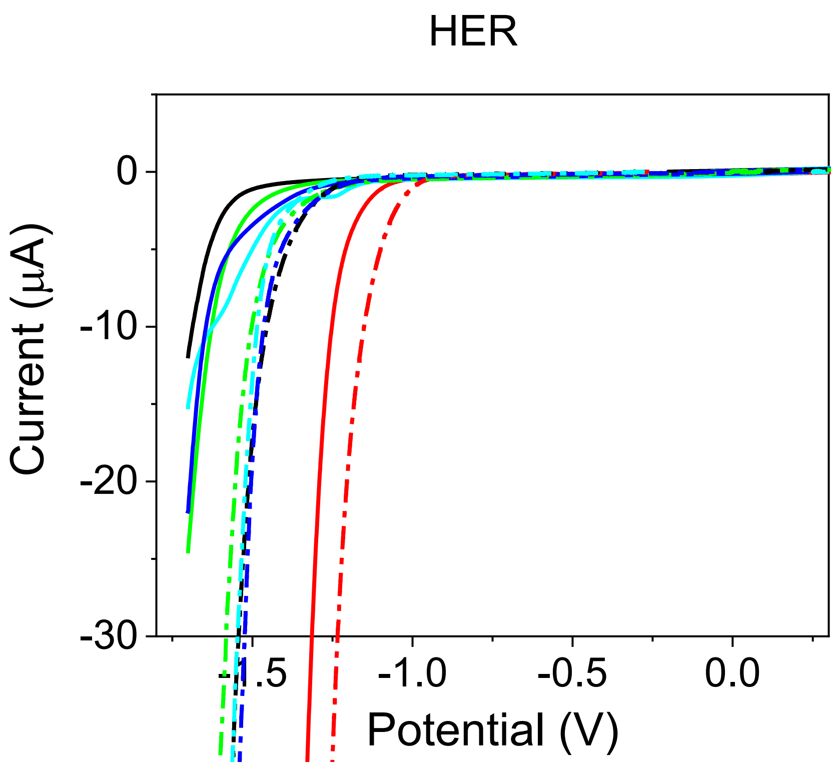
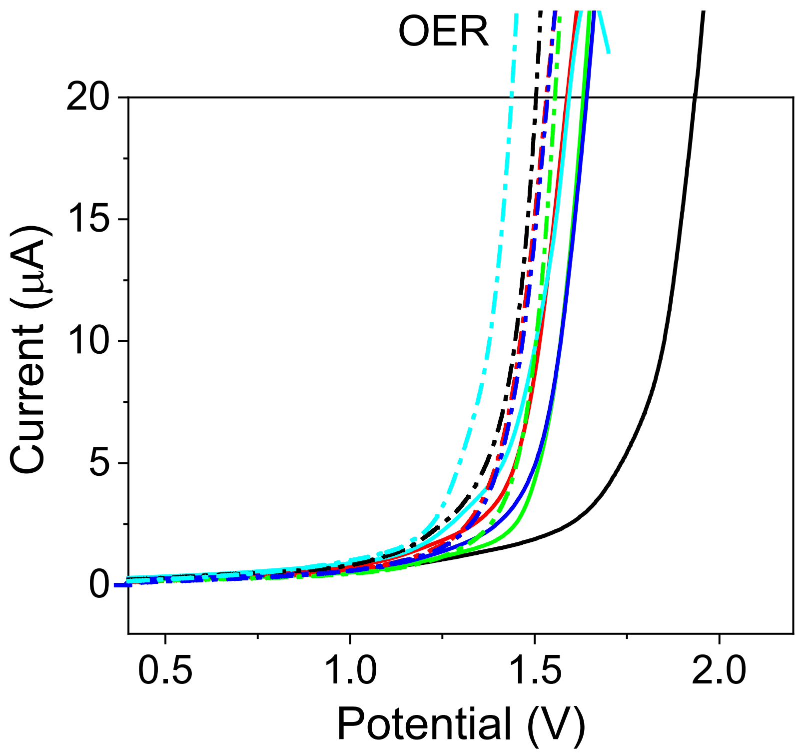


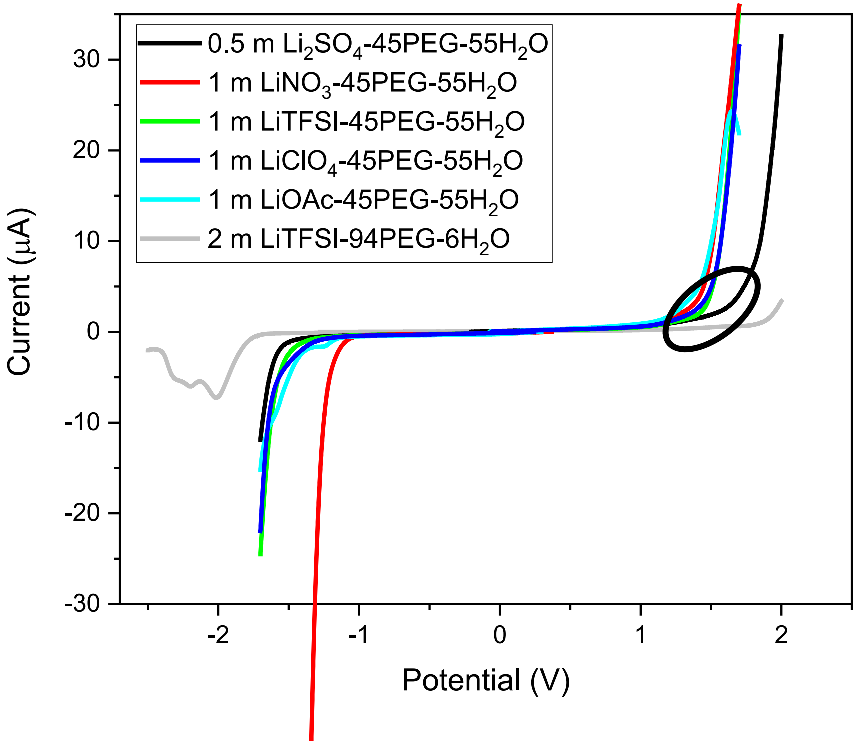


- PEG Widen EW (HER potential ⬇, OER potential ⬆)

- Change of the potential differs from anion to anion

WE: Glassy carbon (GC, 3φ), RE: Ag/AgCl (3 M NaCl), CE: Pt coil, 10 min Ar bubbling before experiment, Scan rate: 0.2 mV/s

Research Summary



→ OER of $\mathbf{SO_4^{2-}}$ only shows significant change

Interaction between anion and H_2O → **Hofmeister series**

'salting out' of anionic proteins — 'salting in' of anionic proteins

CO_3^{2-} SO_4^{2-} HPO_4^{2-} OAc^- Cl^- Br^- I^- NO_3^- ClO_4^- SCN^- $TFSI^-$

Kosmotropes
:Strongly hydrated anion
& structure-making

Chaotropes
: Weakly hydrated anion
& structure-breaking

Charge of the anions

OER : OAc^- ~ NO_3^- ~ ClO_4^- ~ $TFSI^-$ < SO_4^{2-}

Similar potential
→ Charge : '-1'

Charge : '-2'

Future Work

1. Cyclability of the positive electrode for molecular crowding electrolytes

Electrochemical Window → Cyclability Test

→ Important factor for battery

2. 'Concentration' – 'Max. solubility' ratio

	Concentration	Solubility (25˚C)	Conc. / Solubility
Li_2SO_4	0.5 m	3.11 m	16.1 %
LiTFSI	1 m	> 20 m	< 5 %
$LiClO_4$	1 m	5.62 m	17.8 %
$LiNO_3$	1 m	13.1 m*	7.63 %
LiOAc	1 m	6.82 m	14.7 %

(* Solubility at 28˚C)

In this experiment,
ratio was different for each electrolyte

→ Changing the concentration
to equalize this ratio…

Thank You!