Design and characterization of high-performance water-based electrolytes for lithium-ion batteries

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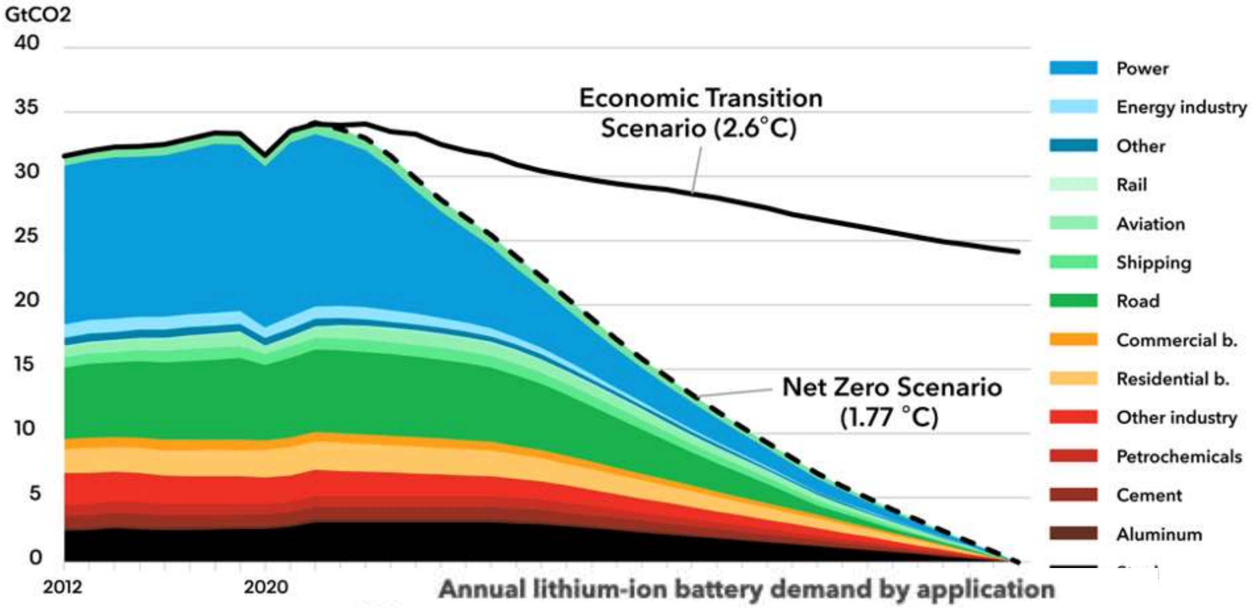
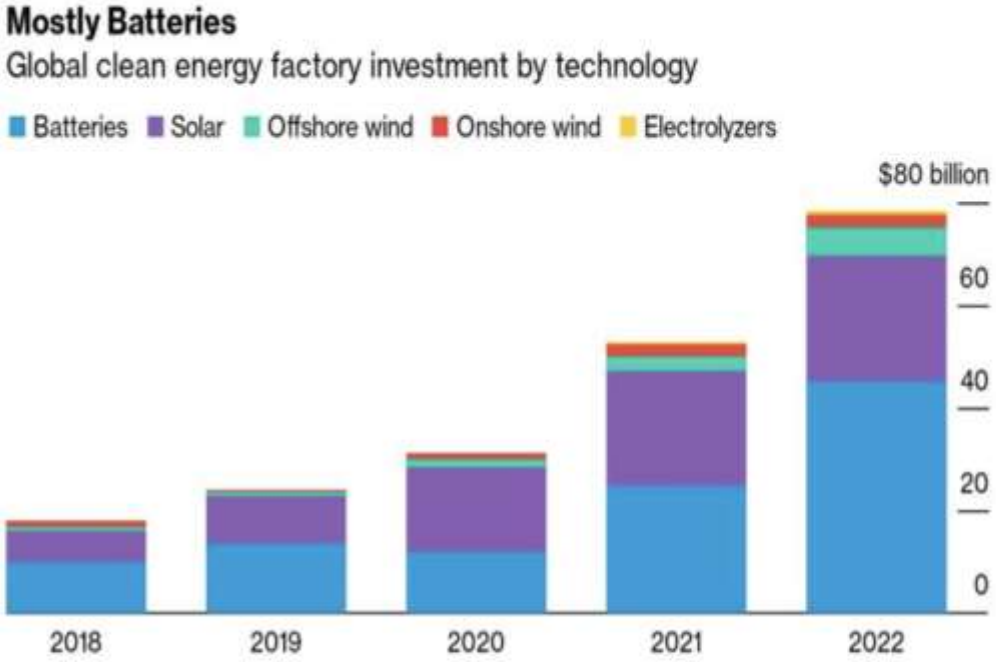
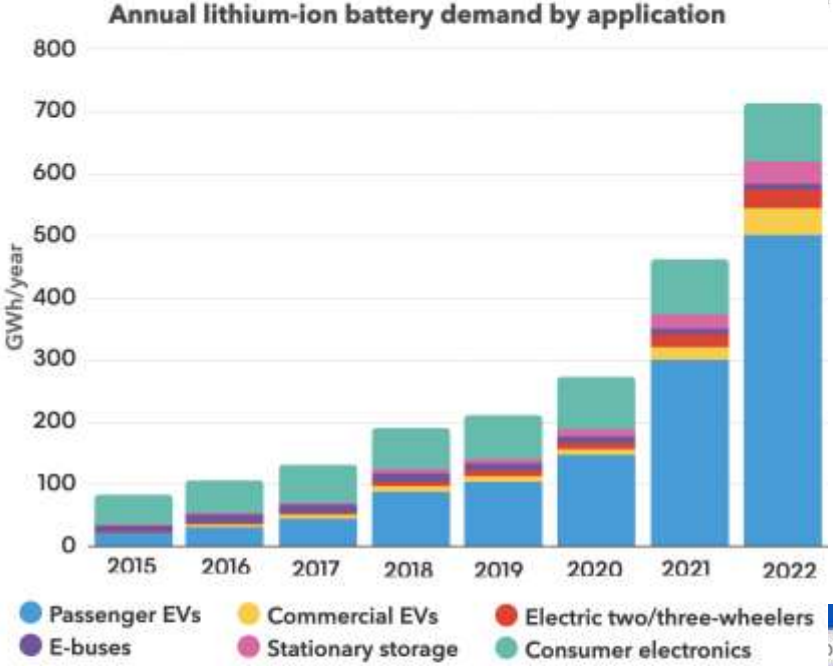
Brief introduction: from global warming to lithium ion batteries

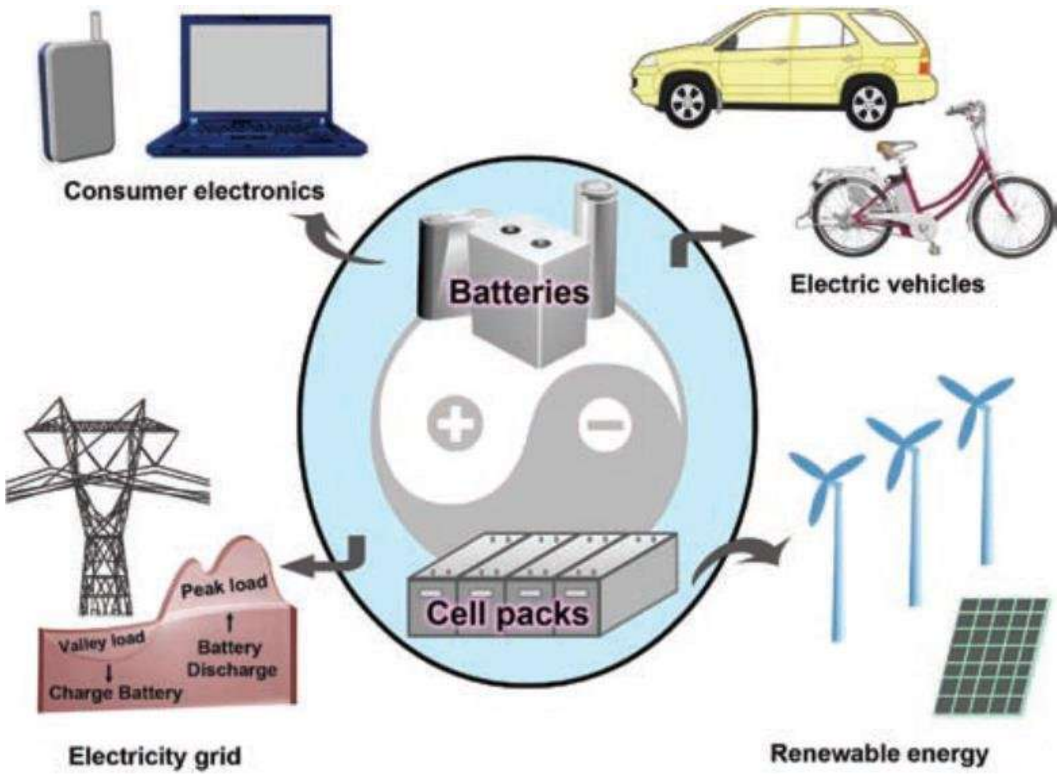






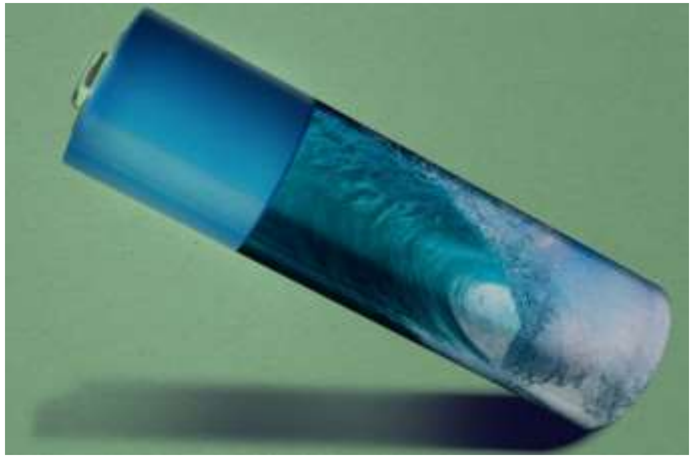
Lithium-ion batteries: pros and cons

Wide range of applications



Main safety problem:
Flammability of electrolytes

Possible solution: water-based electrolytes



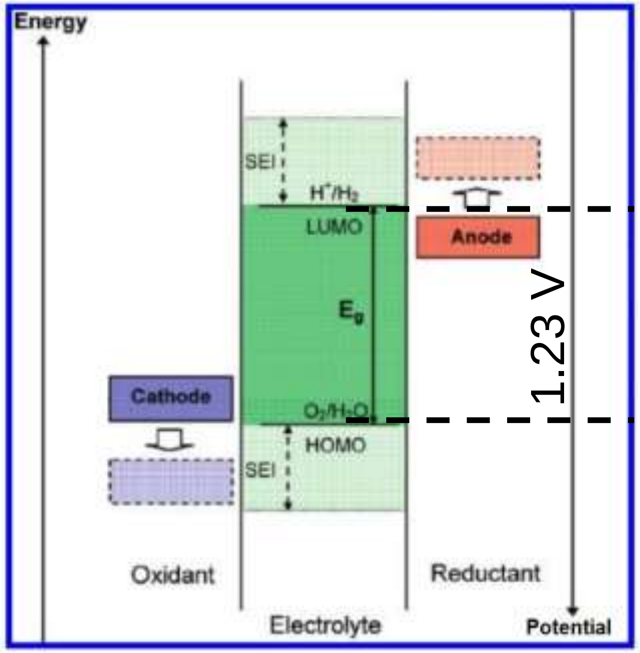
Water-based electrolytes: pros and cons

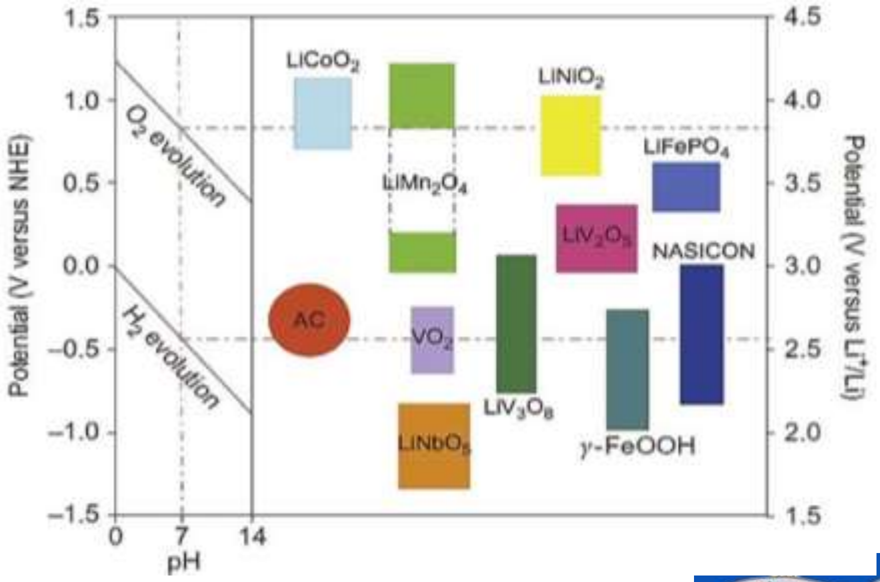
- Natural and abundant
- High dielectric constant (ε = 78 at 25°C)
- Good ionic conductivity
- Low viscosity
- Cheaper water-soluble salts

Narrow electrochemical stability window is a key obstacle

Low potential available for cells

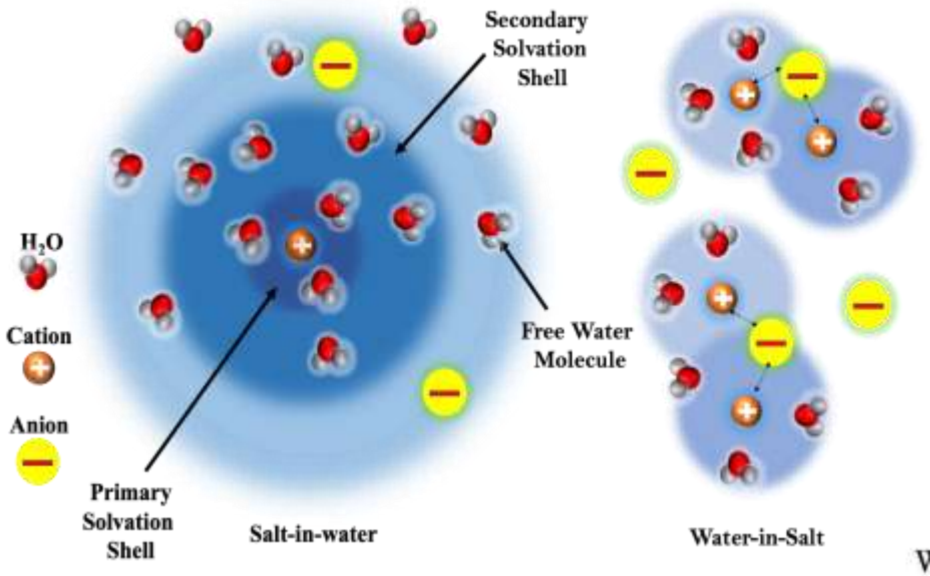
Most Li ion electrodes operate beyond these potentials

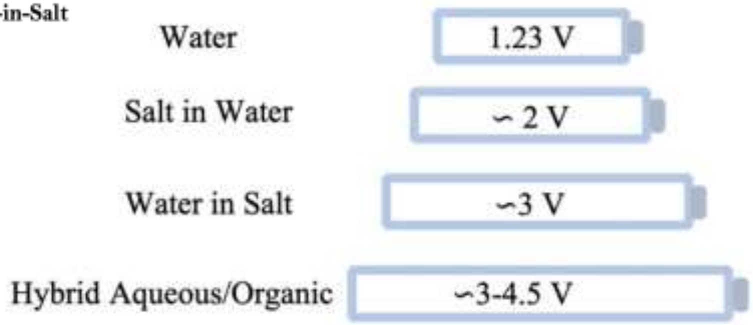




Concentrated Aqueous Electrolytes/Water-in-Salt Electrolyte

Increase salt concentration: superconcentration/Water-In-Salt





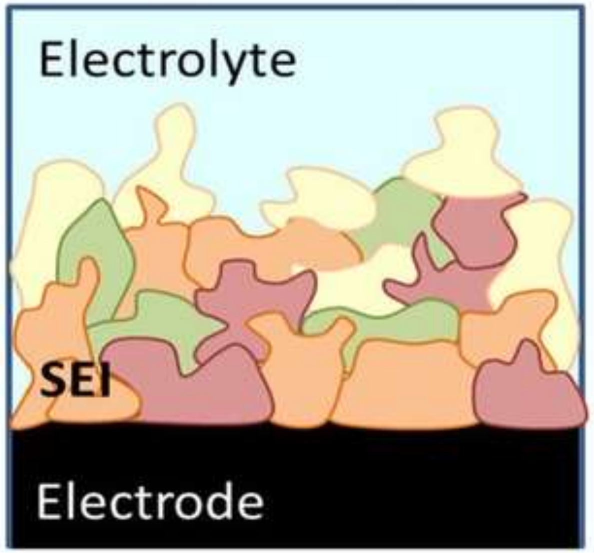
Narrow electrochemical stability window is a key obstacle

Add SEI additives

Solid Electrolyte Interphase (SEI) layer hinder undesired reactions and protect the interphase

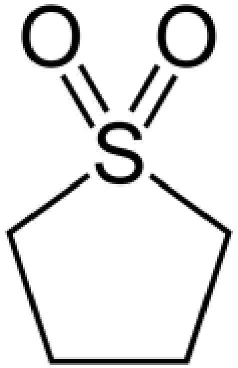
Main composition:
- LiF
- Li_2CO_3
- Li_2O

Addtives:
- Fluorinated salts
- Organic solvents

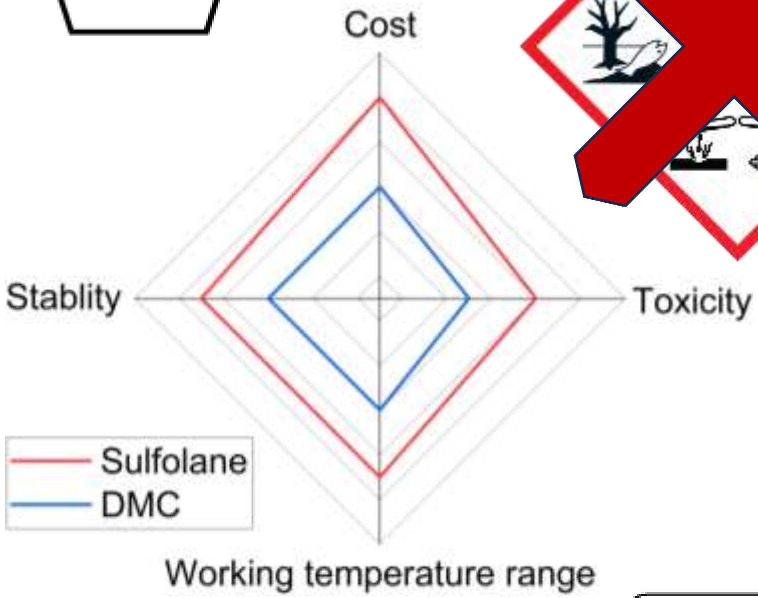


Aim: design new water-based electrolyte design

Co-solvent: sulfolane (SL)



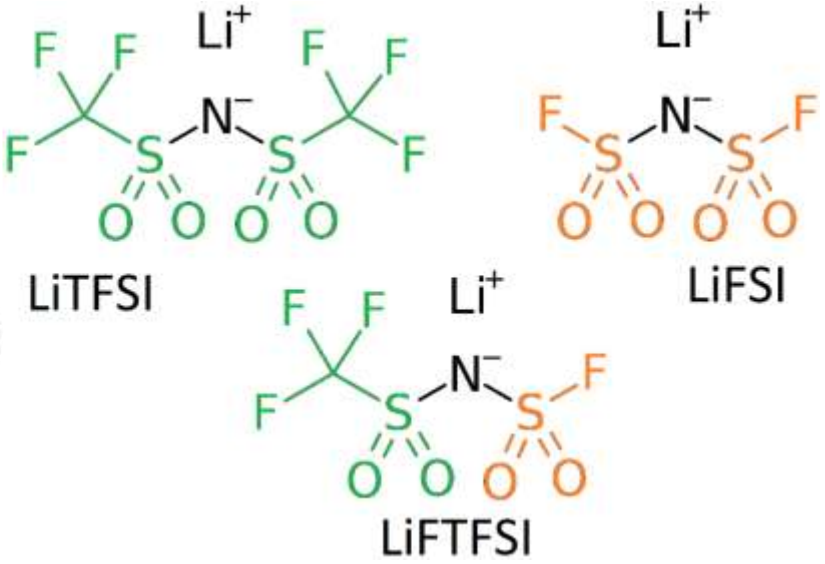
- Non-flammable
- Low toxicity
- Cheap



$SL+H_2O$
+
LiFTFSI

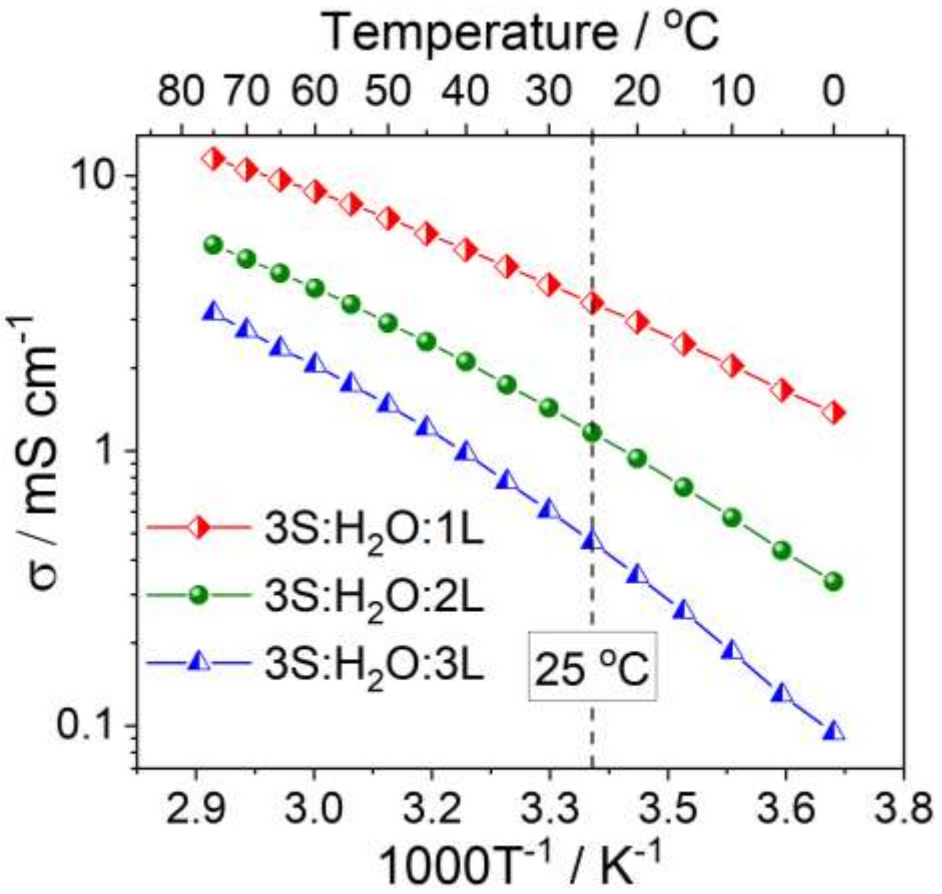
$1.3S:H_2O:1L$	$1.3S:H_2O:2L$	$3S:H_2O:3L$
2.(2.6 mol kg^{-1})	2.(5.2 mol kg^{-1})	(7.9 mol kg^{-1})

Salt: LiFTFSI



- High F content for SEI formation
- Asymmetry to hinder crystallization

Conductivity measurements



From EIS spectra:

- From 1 Hz to 400 kHz
- sine amplitude of 25 mV in
- dip-probe symmetric platinum electrode cell

The temperature dependence on conductivity follows a VTF behavior: $\sigma = \sigma_o \exp\left(\frac{-E_{pa}}{T-T_0}\right)$.

Electrolyte	σ at 25°C / mS cm^{-1}	T_g / °C	T_0 / °C	T_g-T_0 / °C	σ_0 / S cm^{-1}	E_{pa} / eV
3S:H_2O:1L	**3.45**	-98	-116	18	0.35	0.056
3S:H_2O:2L	**1.16**	-83	-100	17	0.33	0.060
3S:H_2O:3L	**0.47**	-76	-88	12	0.23	0.063

Electrochemical stability with different current collectors

LSV: employed to measure the working range and chose the best current collectros

Alluminum (Al):
- more stable on the cathodic side
- suffers from corrosive reactions on the anodic side

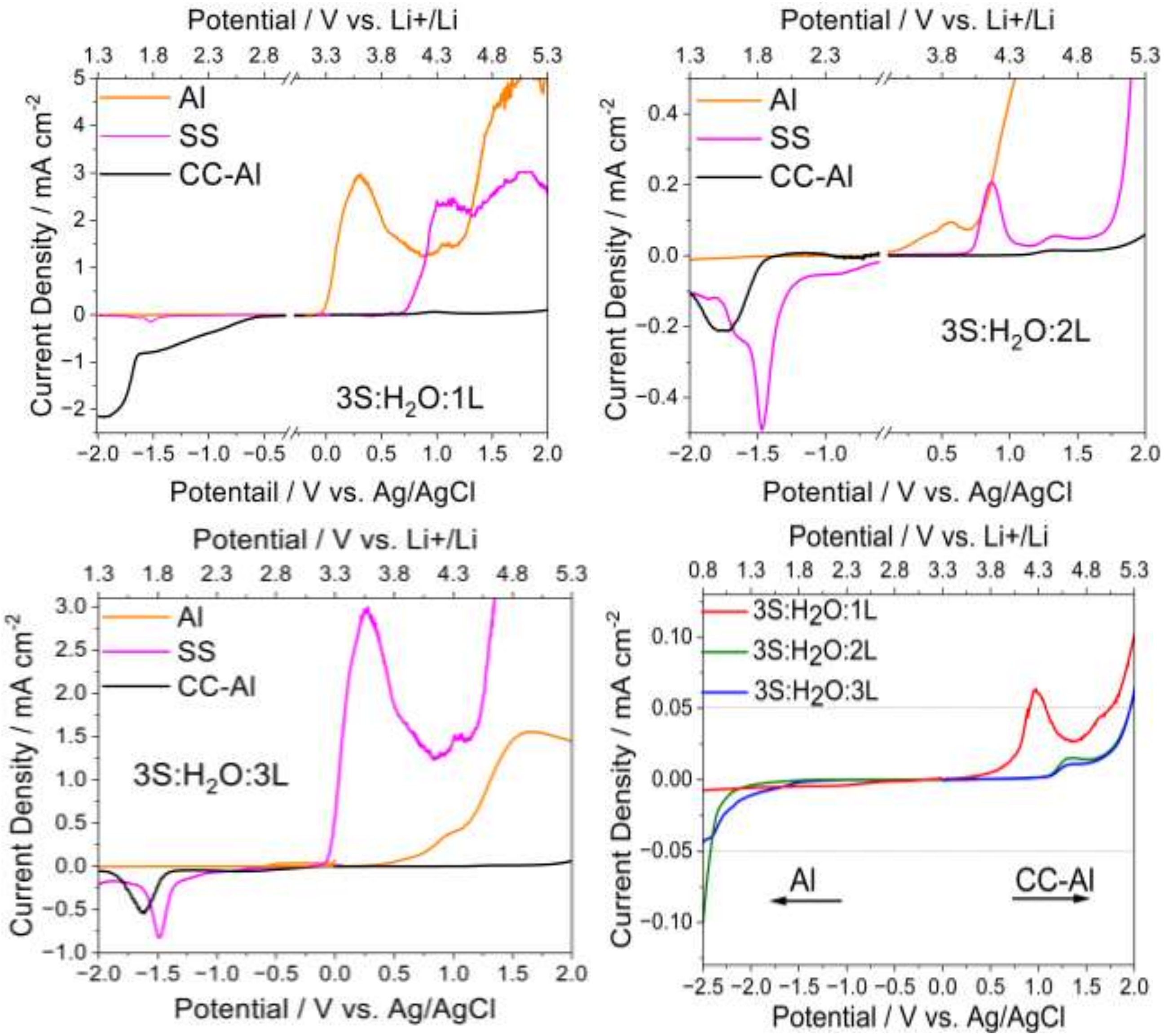
Stainless Steel (SS):
is never the best choice on both sides

Carbon Coated Alluminum (CC-Al):
shows very good stability on the anodic side

Best combination:
- Al for the negative side
- CC-Al for the positive side

=> ESW > 3.5 V

3S:H2O:1L is the worst electrolyte



Solvation structure of the hybrid electrolytes

Electrolytes Raman spectra exhibits a band around 735 cm^{-1} related to a vibrational movement involving contraction/expansion of the full anion.

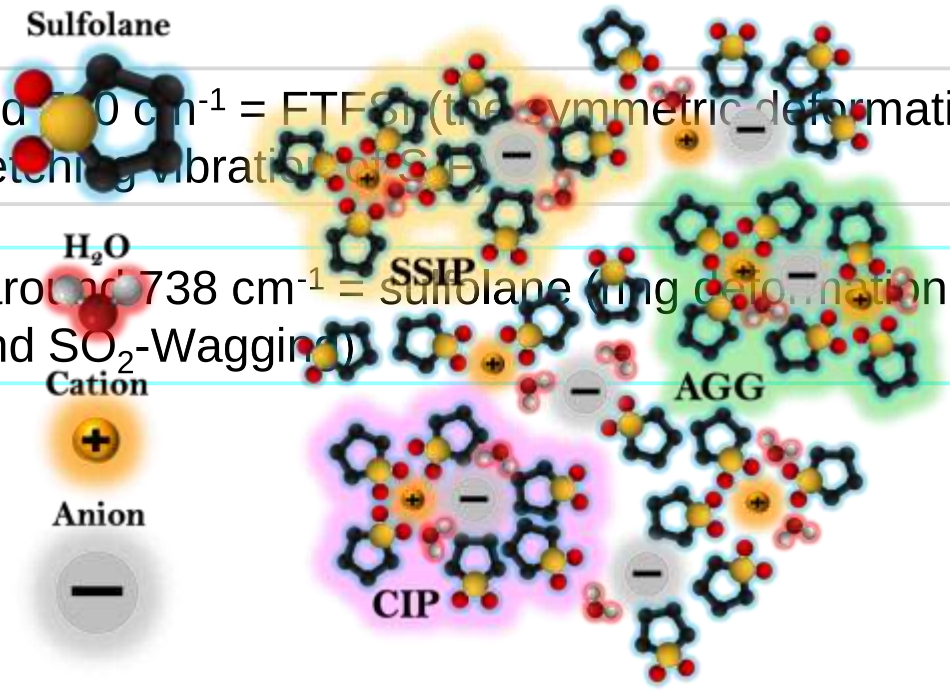
First sub-band around 730 cm^{-1} = Solvent-Separated Ion Pairs (SSIP)

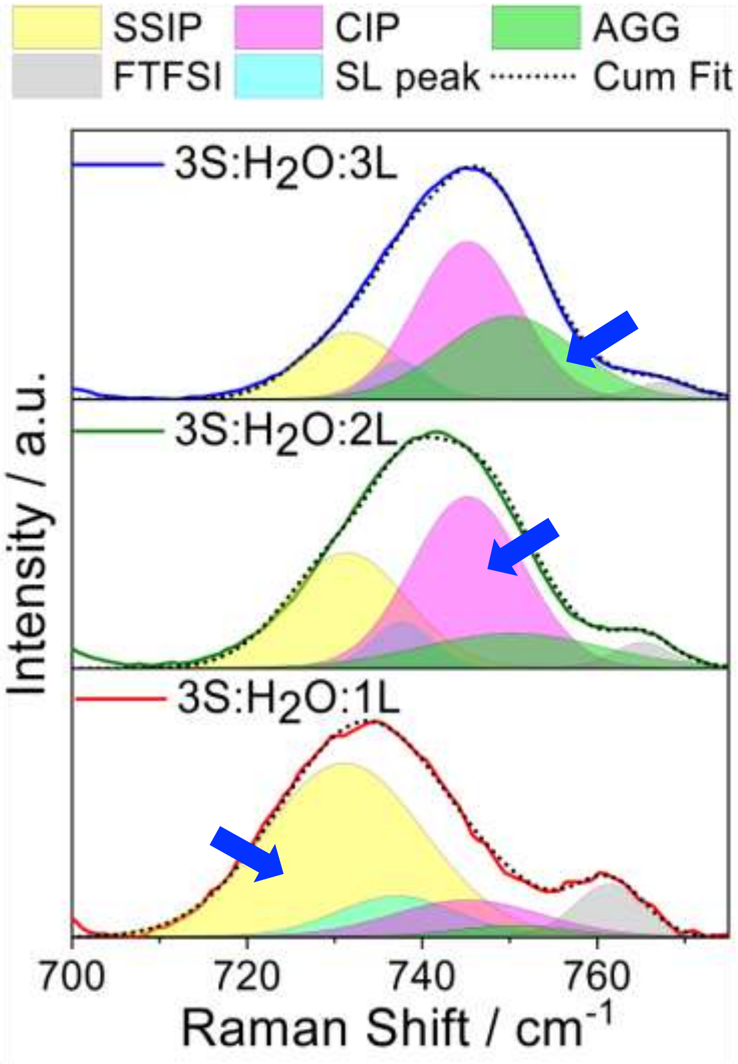
Second sub-band around 747 cm^{-1} = Contact Ion Pairs (CIP)

Third sub-band at 751 cm^{-1} = Aggregates (AGG)

Peak around 7[illegible]0 cm^{-1} = FTFSI (the symmetric deformation of CF_3 and the stretching vibration of S-F)

Sub-band around 738 cm^{-1} = sulfolane (ring deformation, CH_2-Rocking, and SO_2-Wagging)

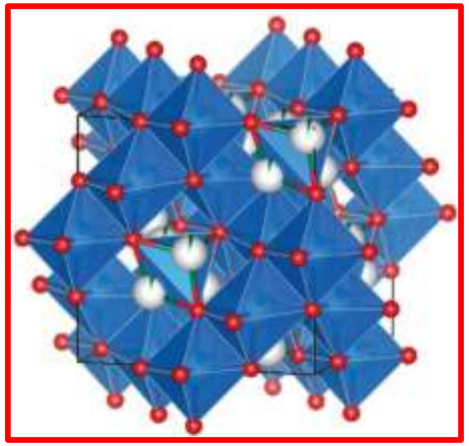


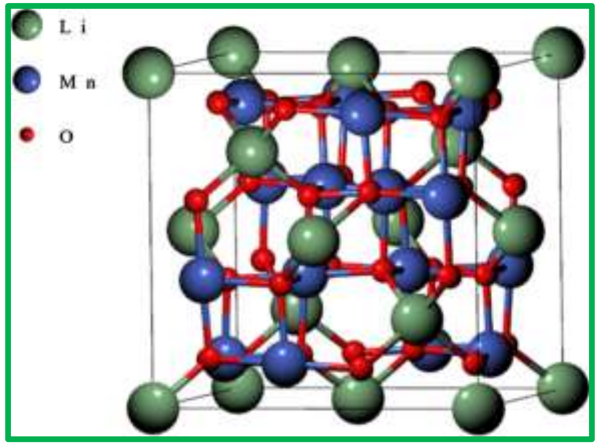


Electrodes for a full cell

Negative electrode:
Spinel $Li_4Ti_5O_{12}$ (LTO)

Positive electrode:
Spinel $LiMn_2O_4$ (LMO)





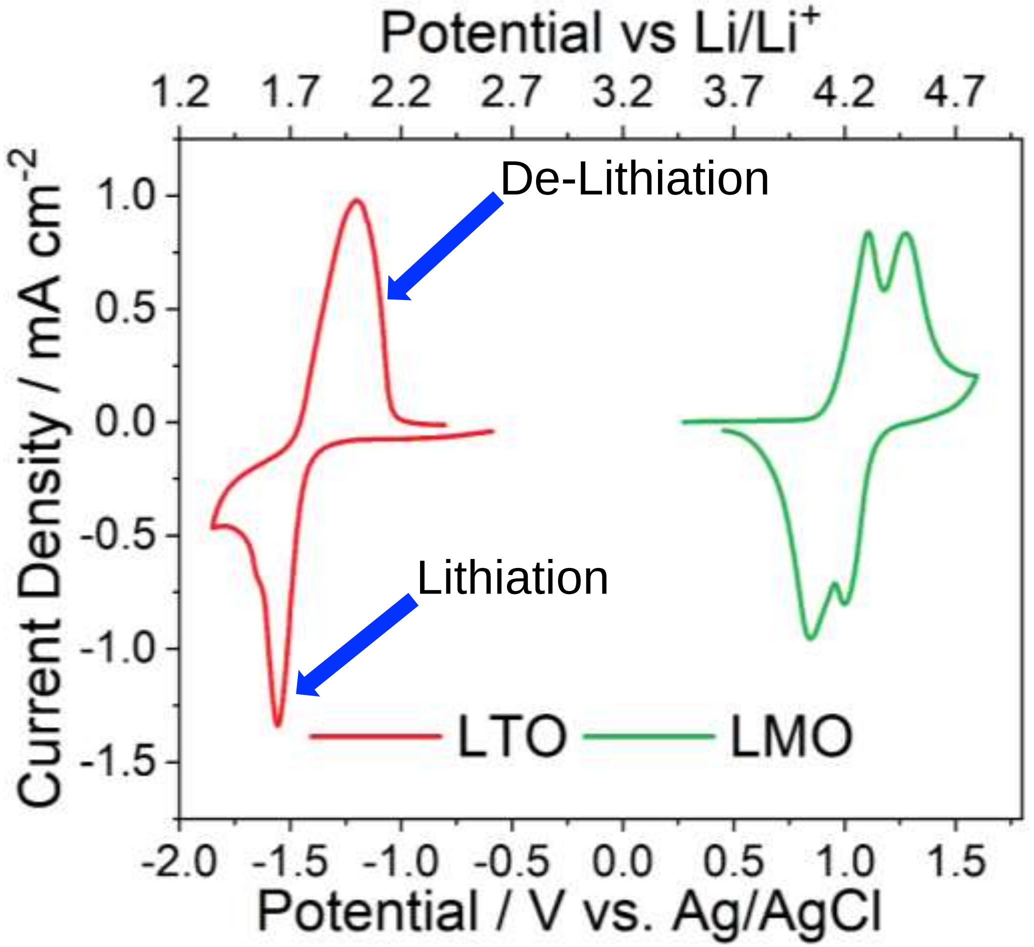
LTO displays a full reduction peak.

LMO has two insertion/exctraction processes.

Working potential:
1.65 V vs Li^+/Li
Theoretical capacity:
175 mAh g^{-1}

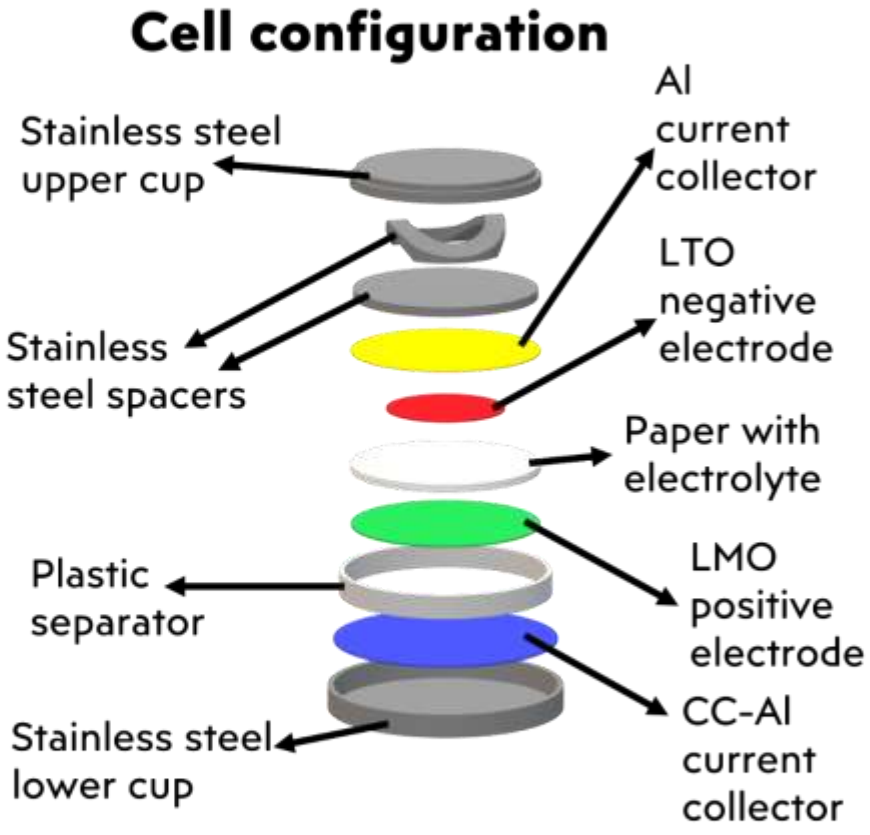
Working potential:
4.2-4.5 V vs Li^+/Li
Theoretical capacity:
148 mAh g^{-1}

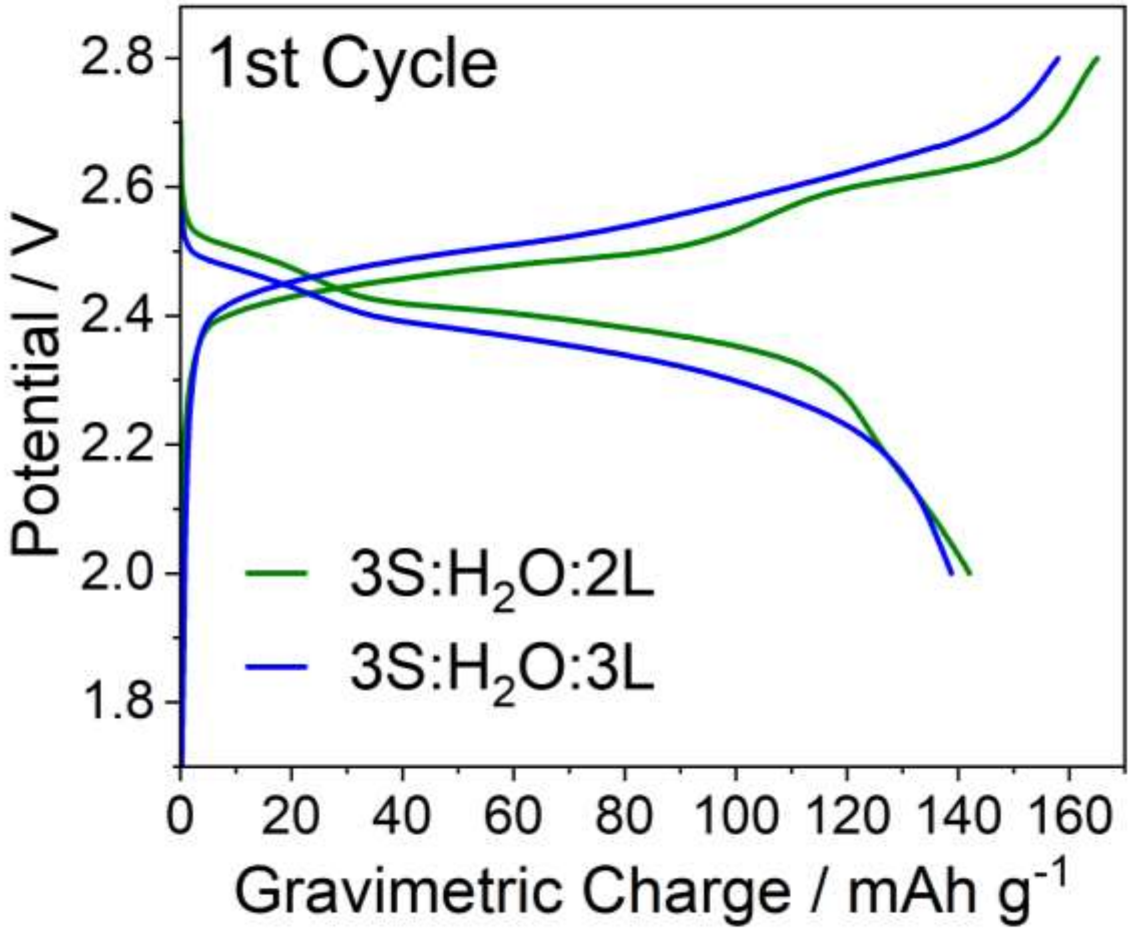
Lithiation/de-lithiation profiles of LMO and LTO were studied via CV



LTO/LMO full cells cycling: 3S:H_2O:2L and 3S:H_2O:3L

GCPL measurements were done in R2032 coin cells at room temperature (30°C)



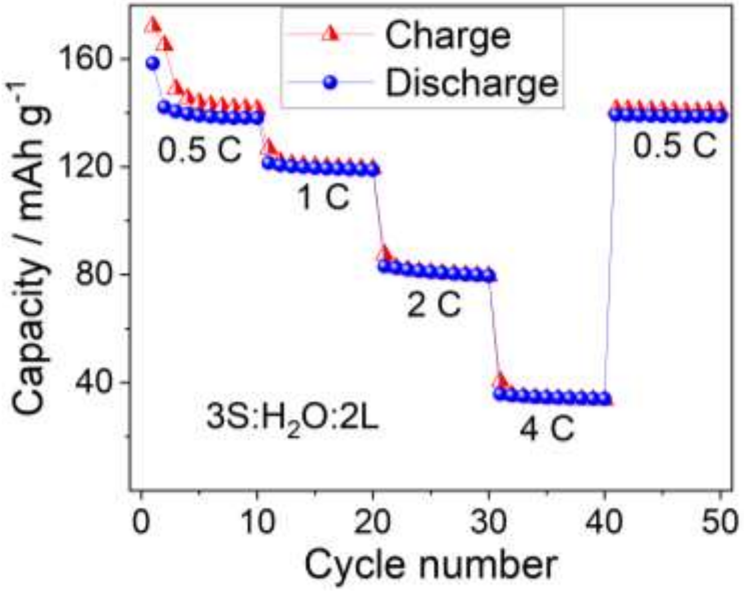


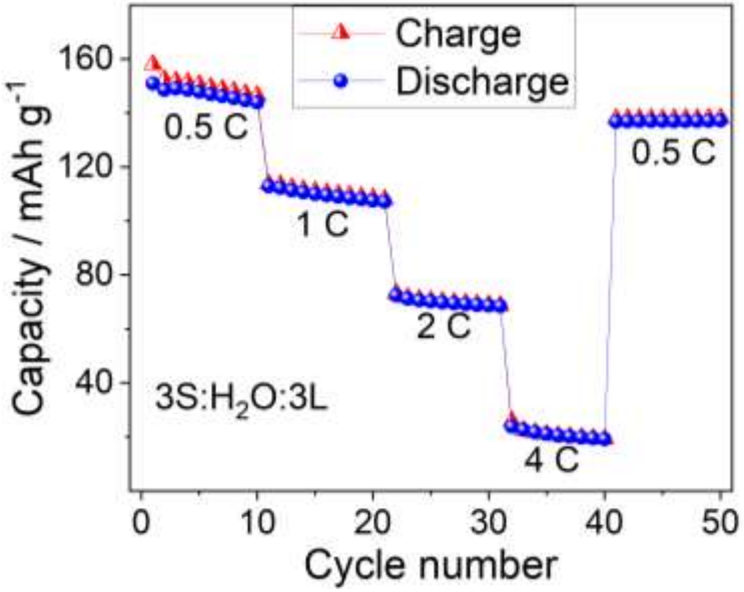
LTO and LMO electrode mas loading was 5.2 and 6.7 mg cm^{-2}

Coulombic efficiency of the first cycle:

- 86% for 3L:H_2O:2L
- 88% for 3L:H_2O:3L

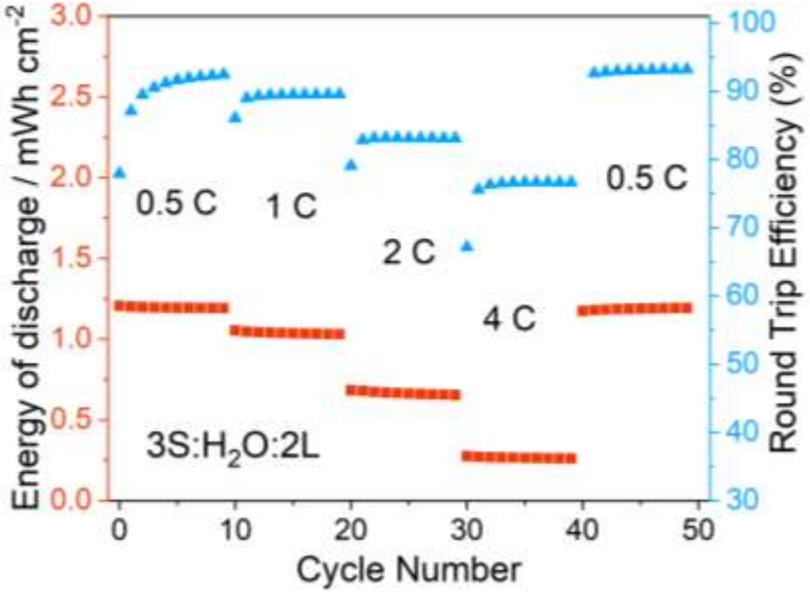
LTO/LMO full cells cycling: rate performance

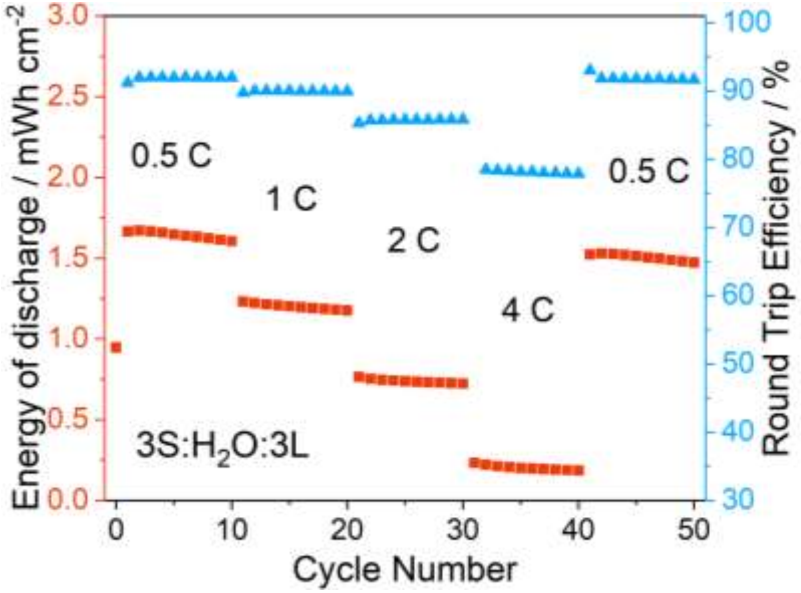




Normalizations over the limiting electrode (LTO)

$3S:H_2O:2L$ reach higher capacity than $3S:H_2O:3L$ at the higher currents. It is maybe due to the differences in conductivity.

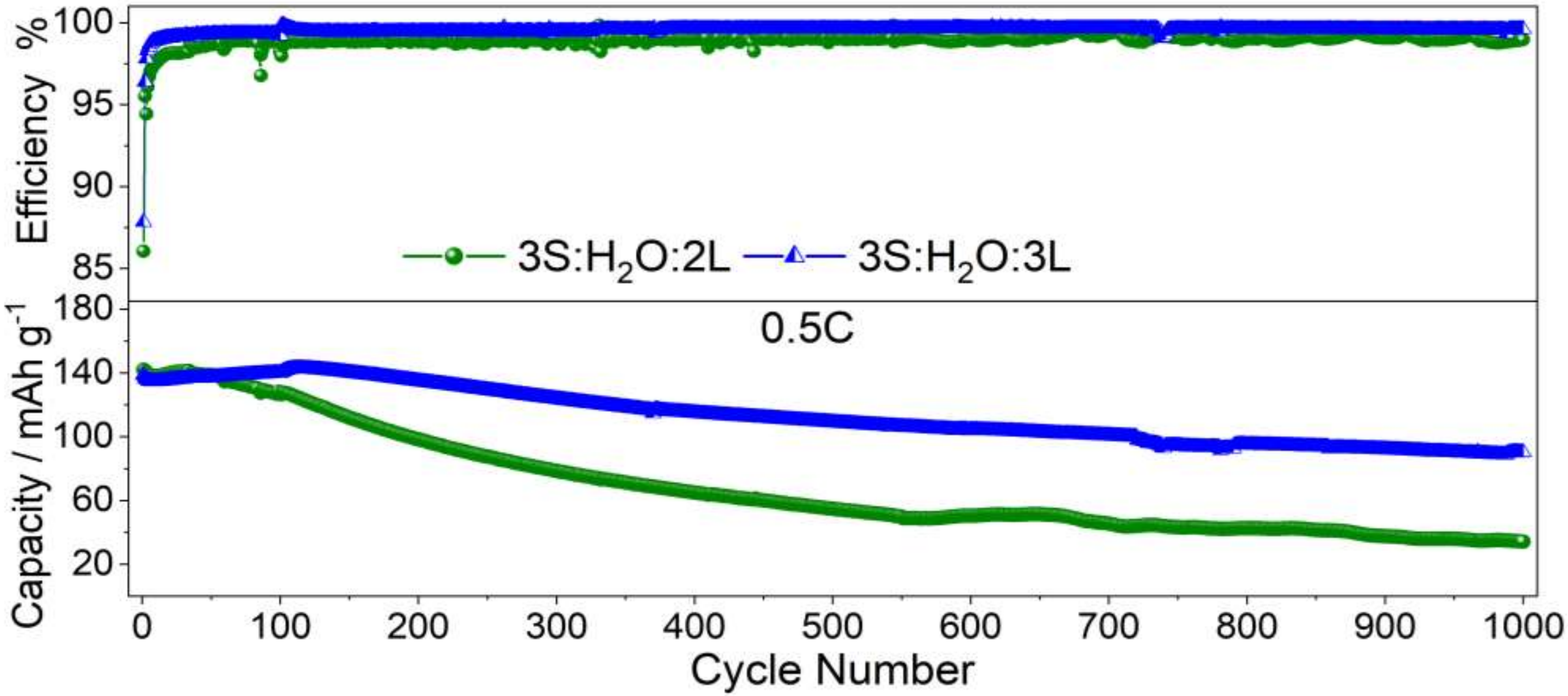




Performances are restored after high current cycling

Round trip energy efficiencies higher than 90% at 0.5C for the $3S:H_2O:2L$ and $3S:H_2O:3L$

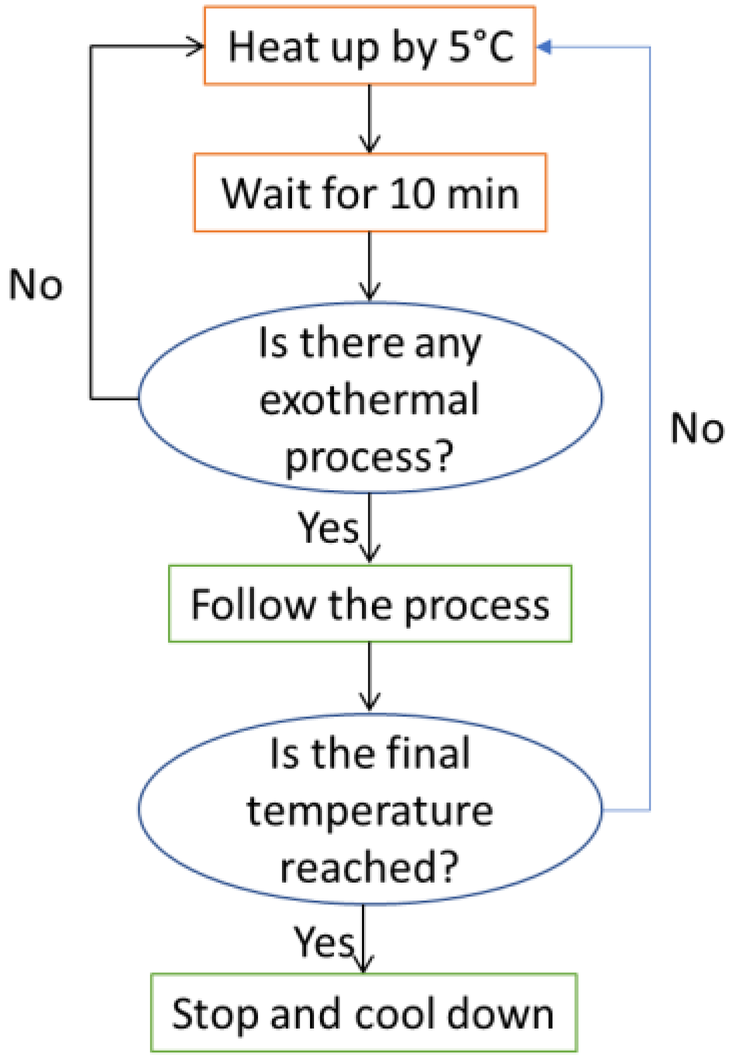
LTO/LMO full cells cycling: long-lasting performance

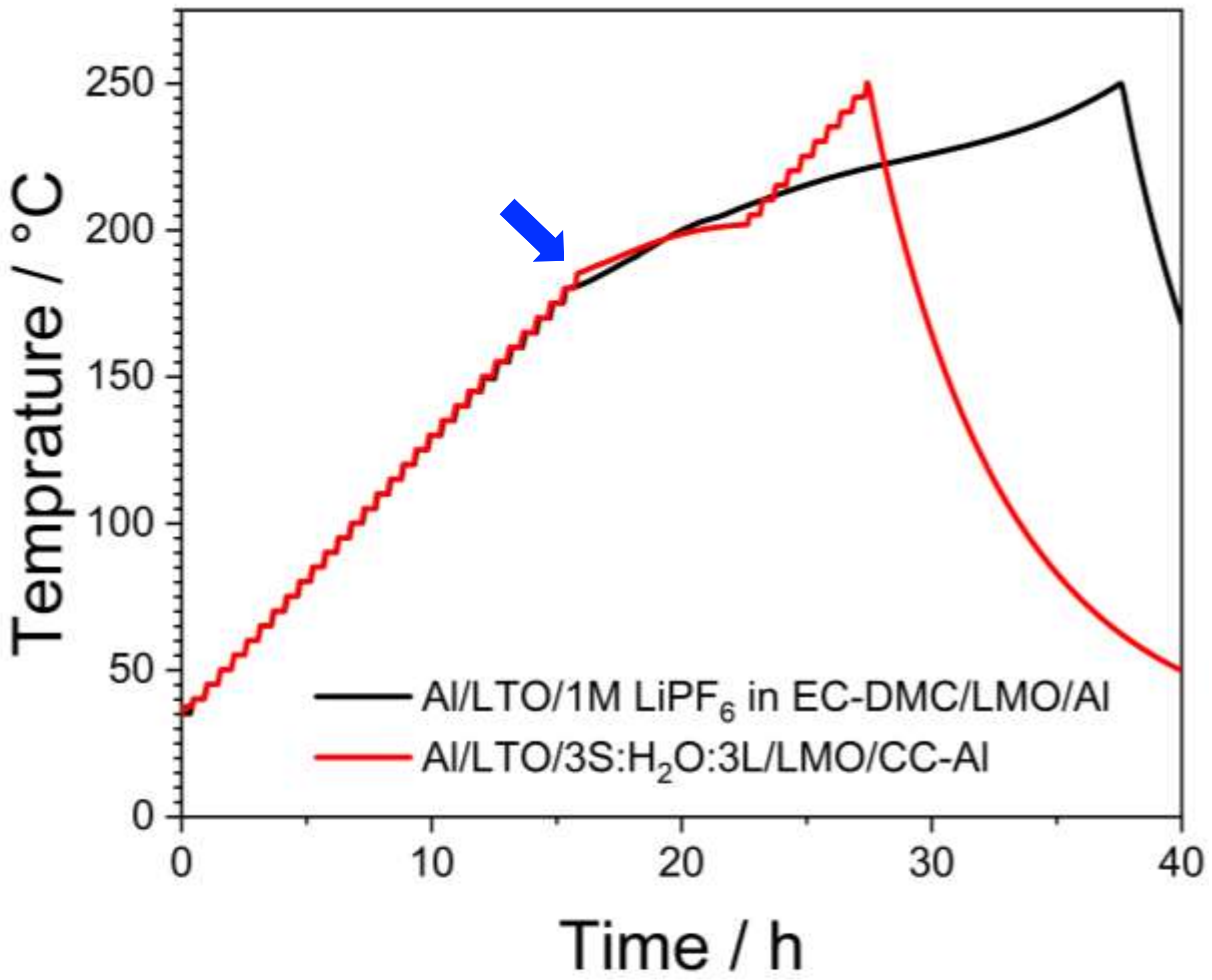


C rate	Electrolyte	Starting charge / mAh g^{-1}	Final charge / mAh g^{-1}	Mean efficiency	Charge ratention
0.5 C (1000 cycles)	**3S:H_2O:2L**	142	34	98.9%	23.9%
	3S:H_2O:3L	139	90	99.5%	**64.7%**

Accelerated Rate Calorimetry (ARC) tests

Procedure:





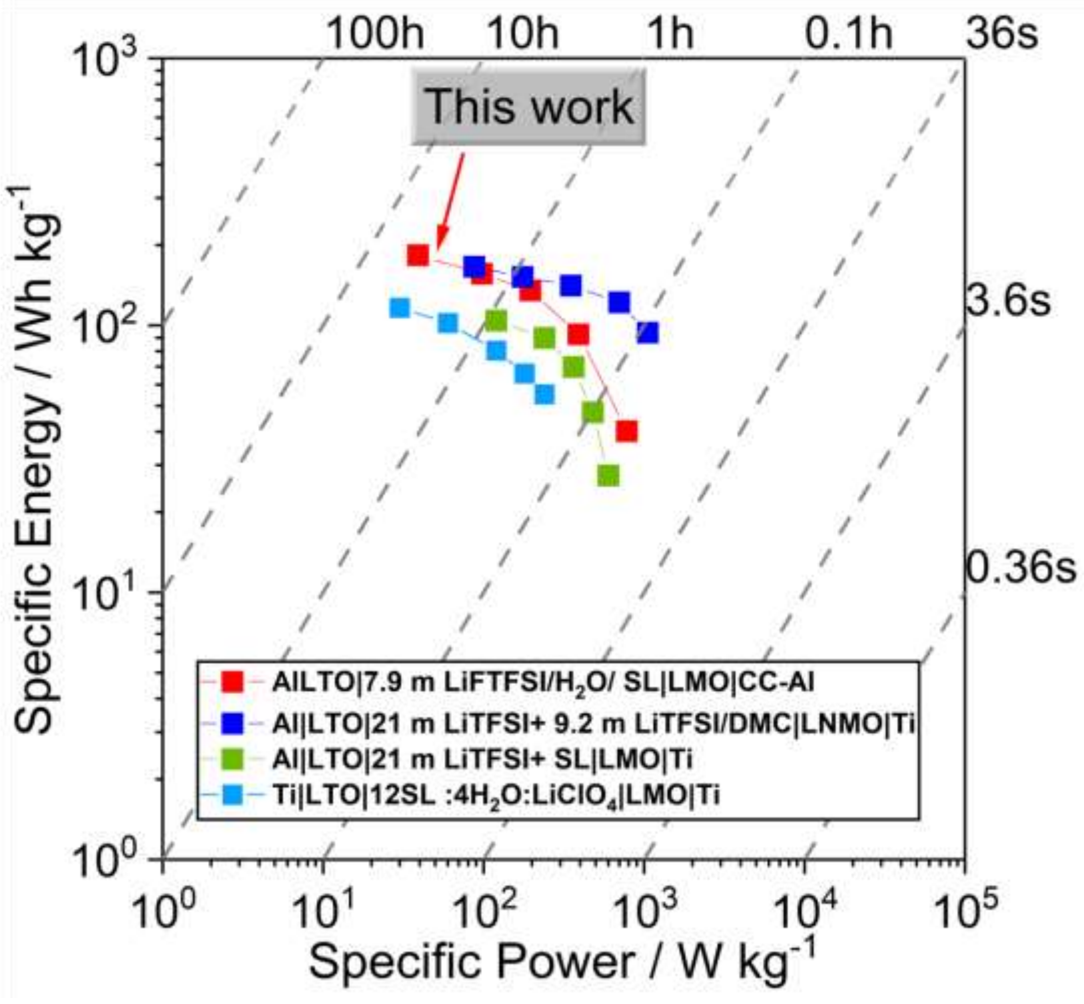
Commercial electrolyte: an exothermal process starts and never ends

3S:H_2O:3L : the same exothermal process ends spontaneously

Conclusions

- We have developed novel hybrid organic/aqueous electrolyte with ESW above 3 V using sulfolane as an organic co-solvent
- Physicochemical and electrochemical characterization was done
- The solvation structure with unique coordination structures such SSIPs, CIPs and AGGs was deeply studied via Raman spectroscopy
- The hybrid electrolyte enables a full aqueous LTO/LMO cell with an average voltage of 2.4 V and specific energy of 156 Wh kg^{-1}
- A viable choice for future generation non-flammable, eco-friendly, economic, and highly safe aqueous batteries

Ragone Plot



THANK YOU FOR YOUR ATTENTION

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