# SCI 2024

## *Chimica*
## ELEMENTI DI FUTURO

**XXVIII Congresso Nazionale della Società Chimica Italiana**

MILANO, 26 - 30 Agosto 2024

# Characterization of hybrid DMSO-aqueous electrolytes for non-flammable lithium-ion batteries

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Società Chimica Italiana
XXVIII National Congress
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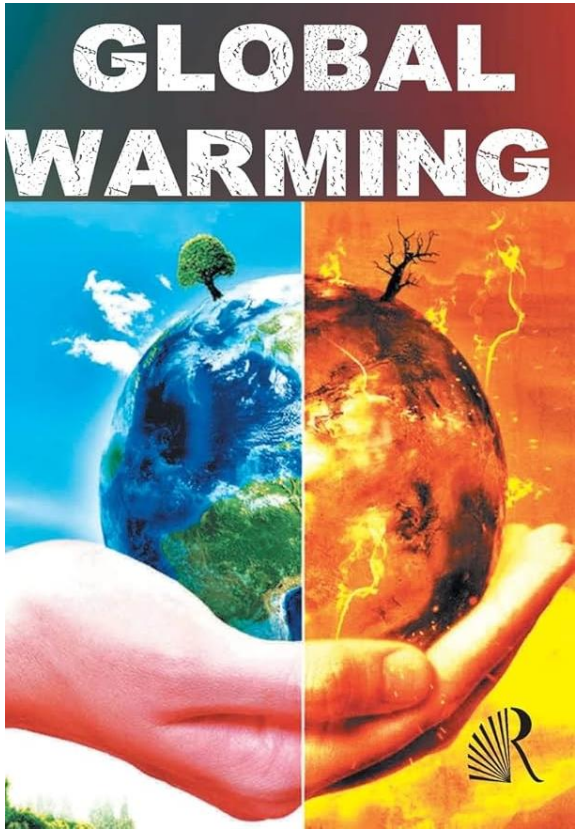
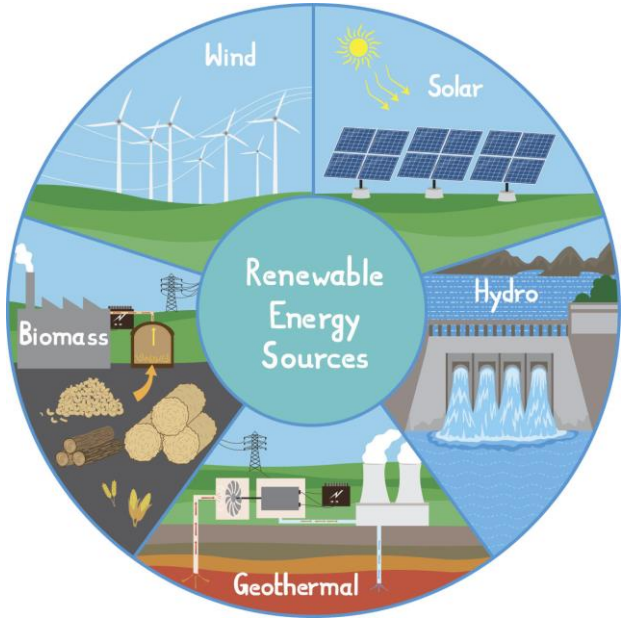
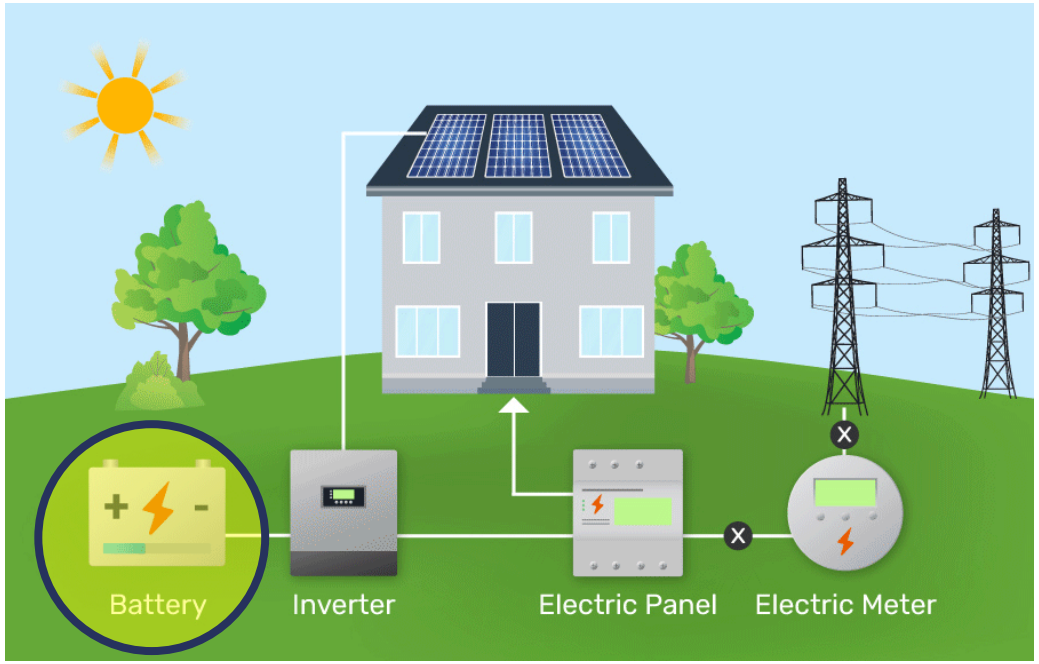
# Why batteries?

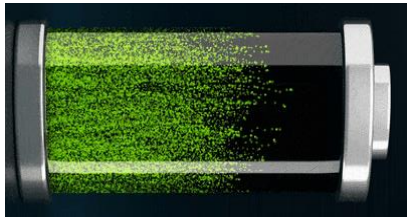



Renewable energies



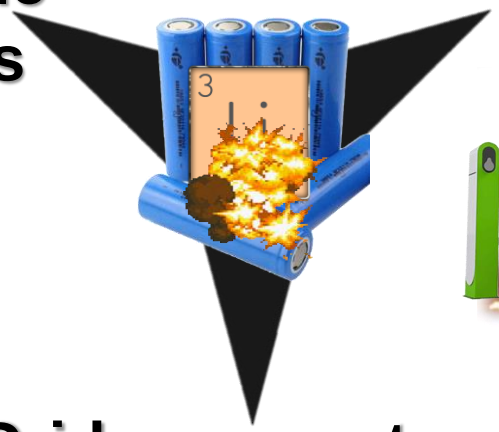




Batteries



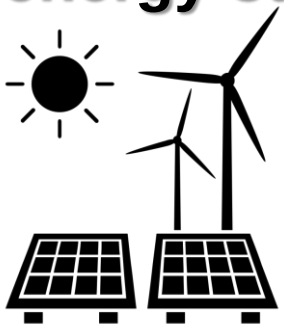
# Lithium-ion batteries' safety problem

**Portable devices**



**Vehicles**

**Grid energy storage**

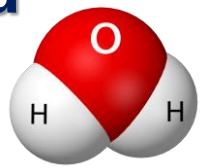


Why?

F mable carbo s

DM

**Water-based electrolytes**



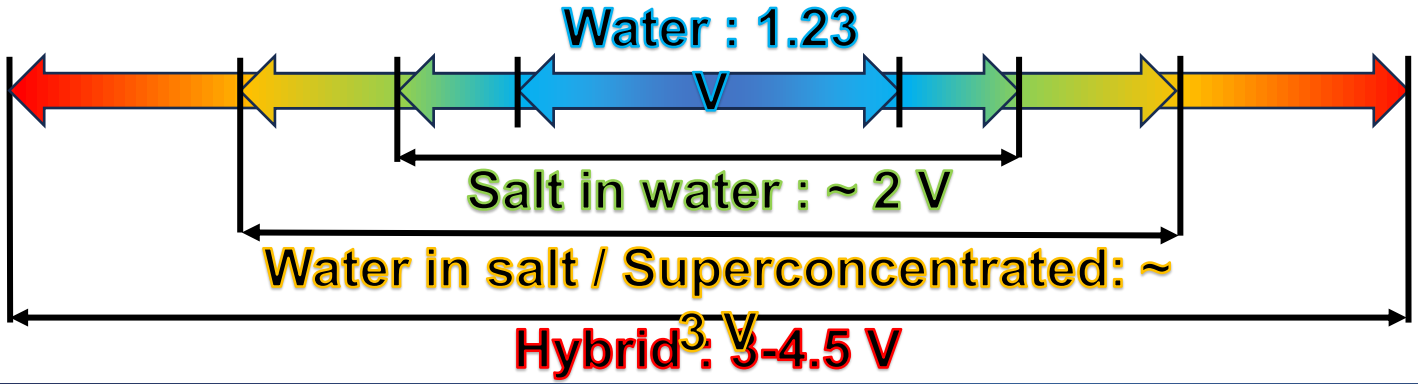
# Water-based electrolytes

- Non-flammable
- High ionic conductivity
- Low viscosity
- Natural and abundant
- Cheap


Narrow Electrochemical Stability Window


Low potential achievable in cells

Less electrodes available

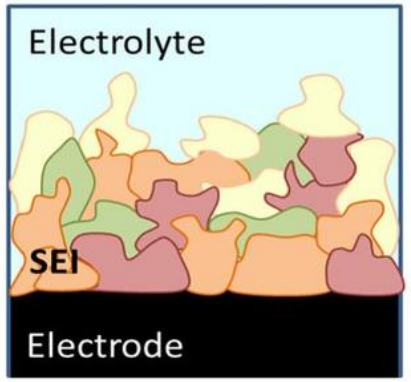



SEI layer composition:

- LiF
- $Li_2CO_3$
- $Li_2O$

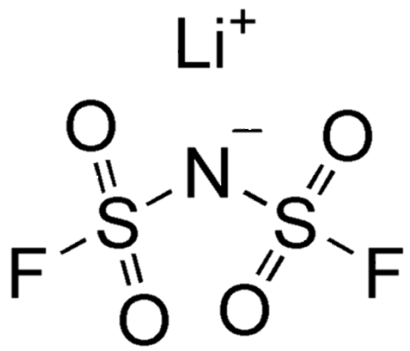
Additives:

- Fluorinated salts
- Organic solvents



# Electrolytes designed and studied

Salt: LiFSI




With fluorine atom

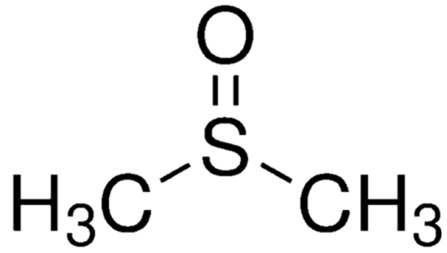
High soluble


3 electrolytes:

DMSO: water : LiFSI

2 : 2 : 1, 2 o 3

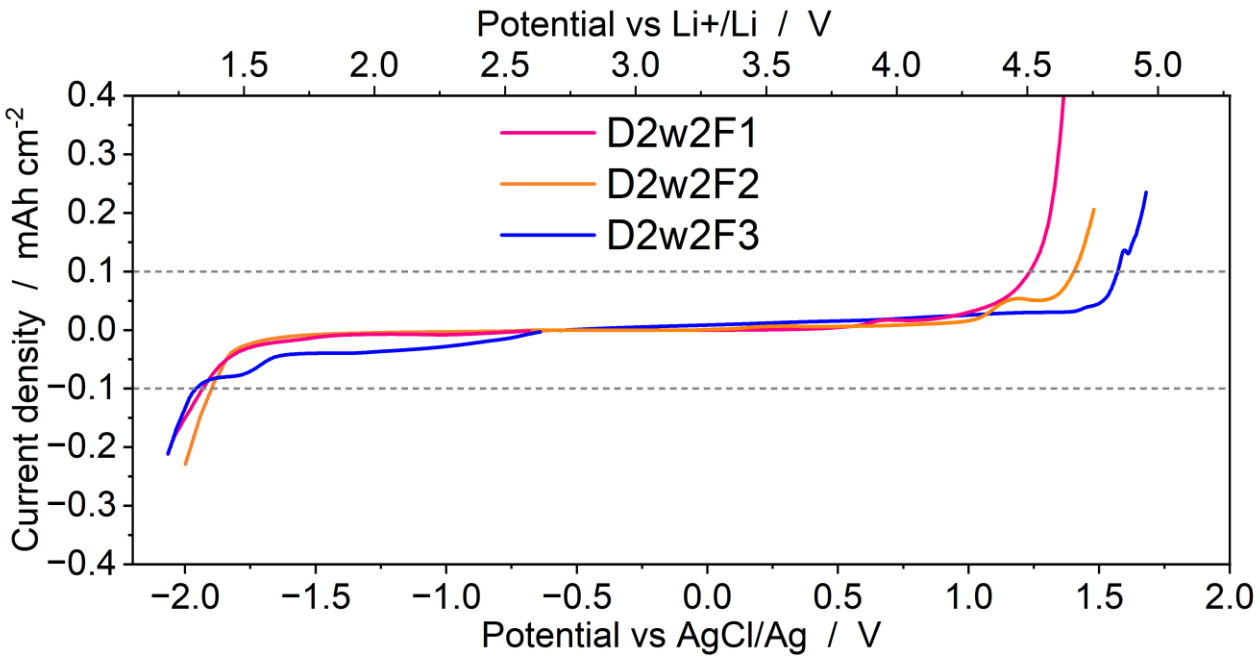
Cosolvent: DMSO




- Non-flammable
- Low toxicity
- Economic
- Safe to handle

**D2w2F1 (5.2 m)** **D2w2F2 (10.4 m)** **D2w2F3 (15.6 m)**

# Electrochemical Stability Windows




Linear Sweep Voltammetry measurement

3 Current collectors tested:

- Aluminum
- Carbon-coated aluminum
- Stainless steel

| Electrolyte | ESW |
|---|---|
| D2w2F1 | 3.16 V |
| D2w2F2 | 3.31 V |
| D2w2F3 | **3.52 V** |

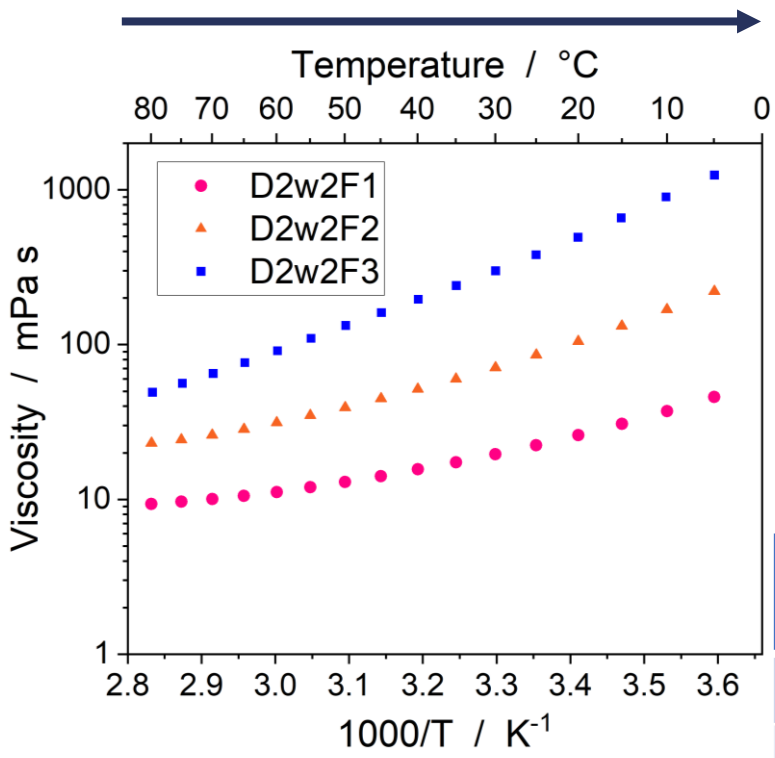
Best current collectors:

Al on negative

CC-Al on positive

# Viscosity and Conductivity

Temperature ↑ = Motion ↑ = Viscosity ↓

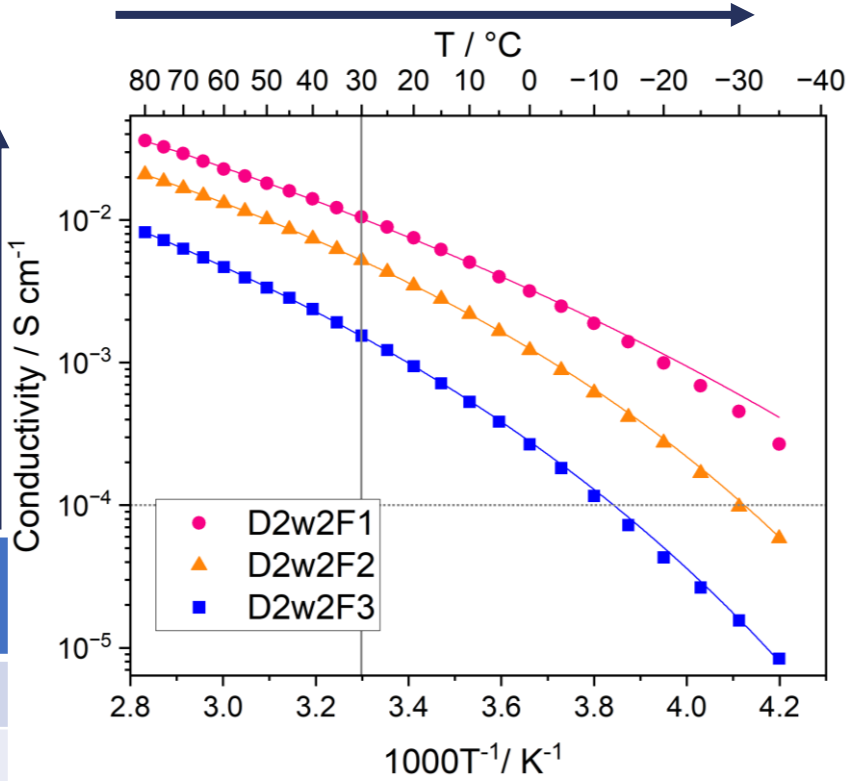



+ Salt
+ Ions
+ Viscosity

| Electrolyte | Viscosity at 25°C | Conductivity at 25°C |
|---|---|---|
| D2w2F1 | 22.3 cP | 8.92 mS cm$^{-1}$ |
| D2w2F2 | 85.8 cP | 4.33 mS cm$^{-1}$ |
| D2w2F3 | 380.8 cP | 1.22 mS cm$^{-1}$ |

+ Salt
+ Viscosity
- Conductivity

Temperature ↑ = Motion ↑ = Conductivity ↑



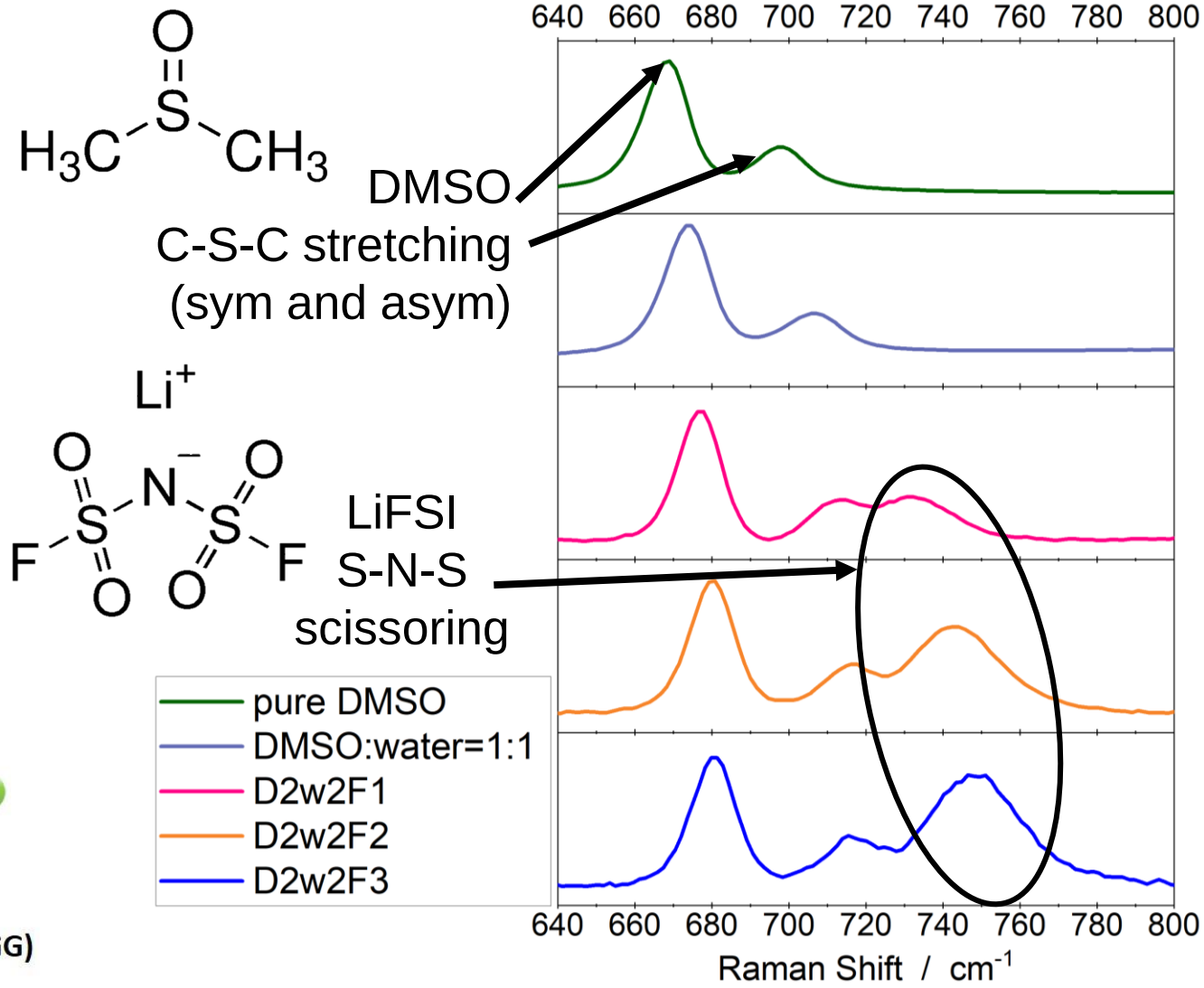
# Raman

Water addition to DMSO

- Blueshift in C-S-C stretching peak of DMSO
- Strong interaction between water and DMSO (H-bonds)

Salt concentration increase

- Big blueshift in S-N-S stretching peak of FSI
- Transition SSIP -> CIP -> AGG

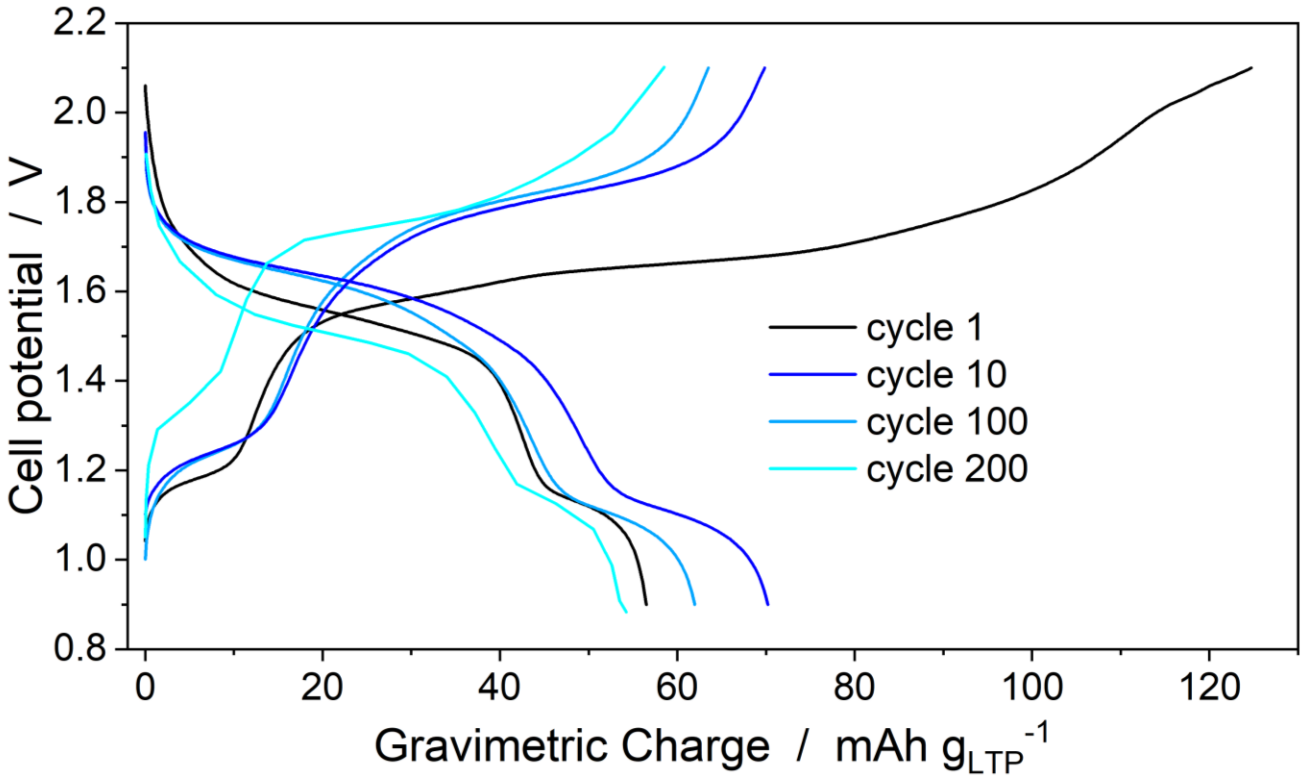
# Full cell performances

Electrodes

$LiTi_2(PO_4)_3$
Working potential : 2.3-2.7 V vs $Li^+/Li$
Theoretical capacity: 138 mAh $g^{-1}$

$LiMn_2O_4$
Working potential : 4.2-4.6 V vs $Li^+/Li$
Theoretical capacity: 148 mAh $g^{-1}$

D2w2F1 and D2w2F2 cells last only few cycles



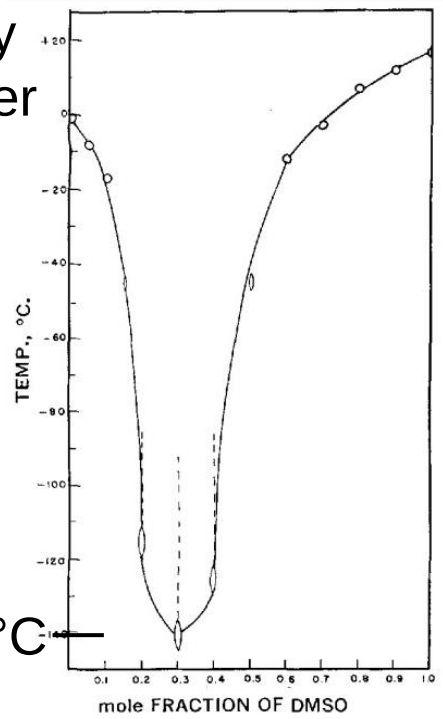

| C-rate | Mean capacity | Mean energy | Average potential | Mean efficiency | Capacity retention |
|---|---|---|---|---|---|
| 0.5 C | 62 mAh $g^{-1}$ | 40 mWh $g^{-1}$ | 1.5 V | 95.4% | 80.3% |

# Cold performances

## Water/DMSO phase diagram

Only water

Only DMSO




-140°C

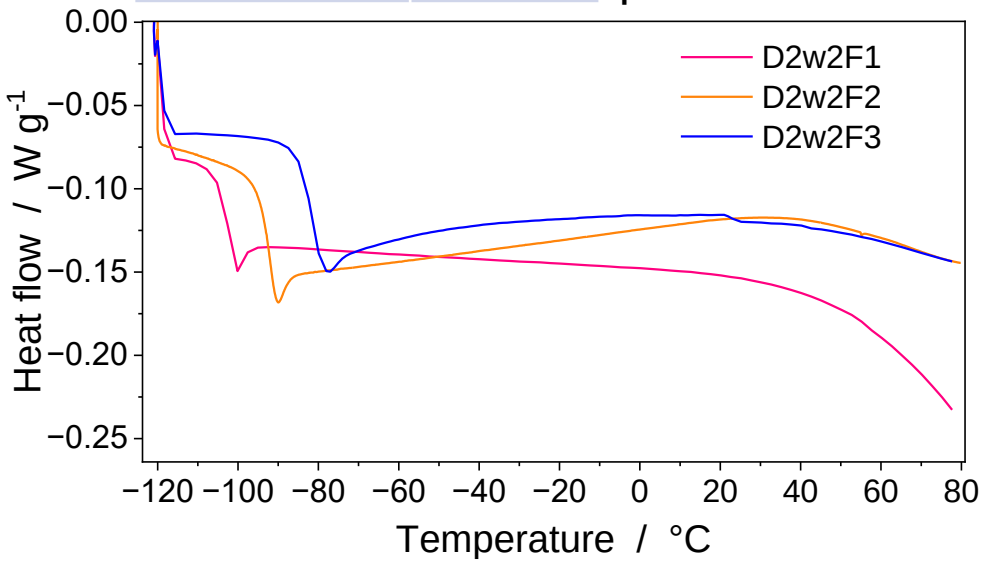
R.N. Havemeyer, Freezing point curve of dimethyl sulfoxide—water solutions, J Pharm Sci 55 (1966) 851–853. https://doi.org/10.1002/jps.2600550822

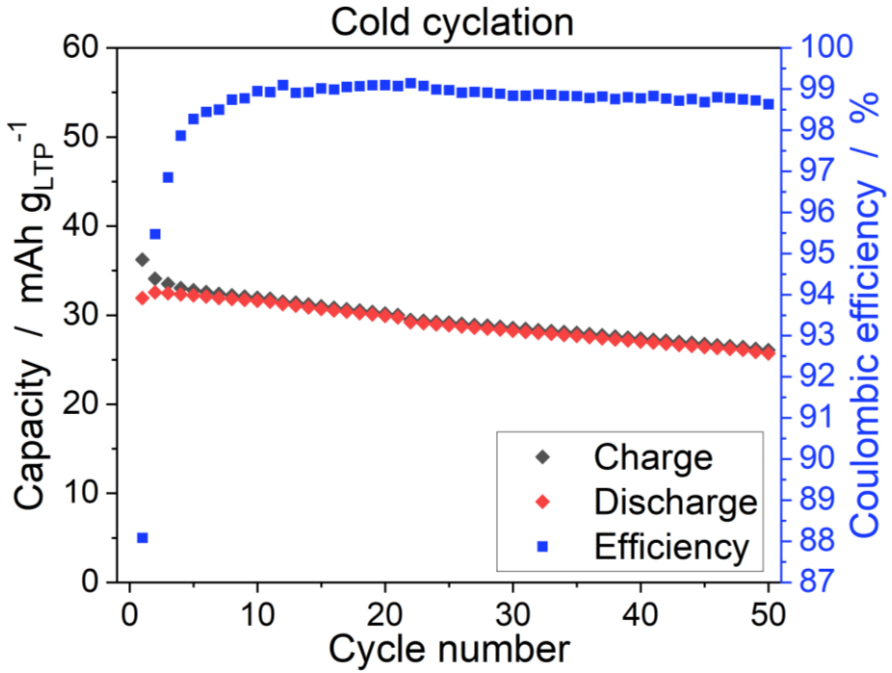
## DSC

| Electrolyte | Tg / °C |
|---|---|
| D2w2F1 | -106 |
| D2w2F2 | -97 |
| D2w2F3 | -87 |

Only glass transitions

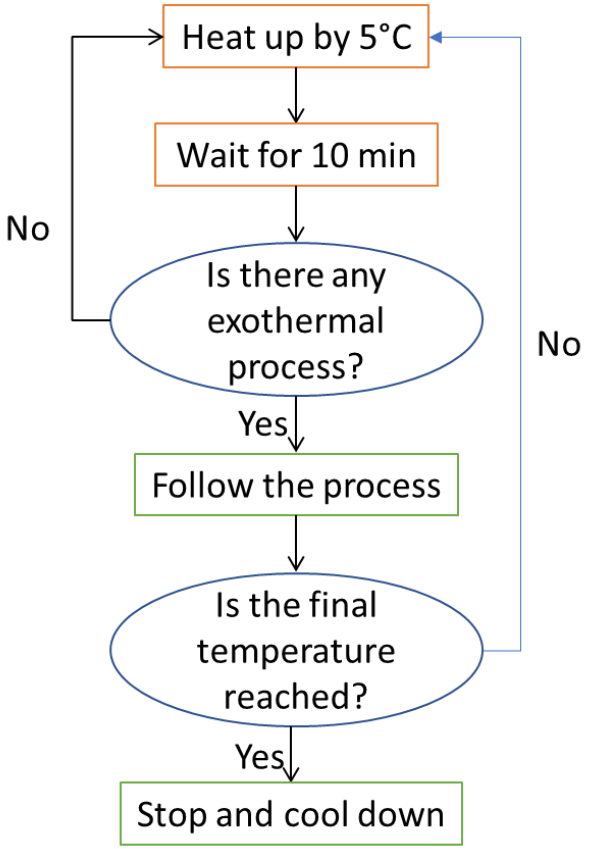
No other phenomena




-10°C cycling
50 cycles
Retention : 80.6%
Cell potential : 1.3 V.
Energy : 15 Wh $kg_{AM}^{-1}$

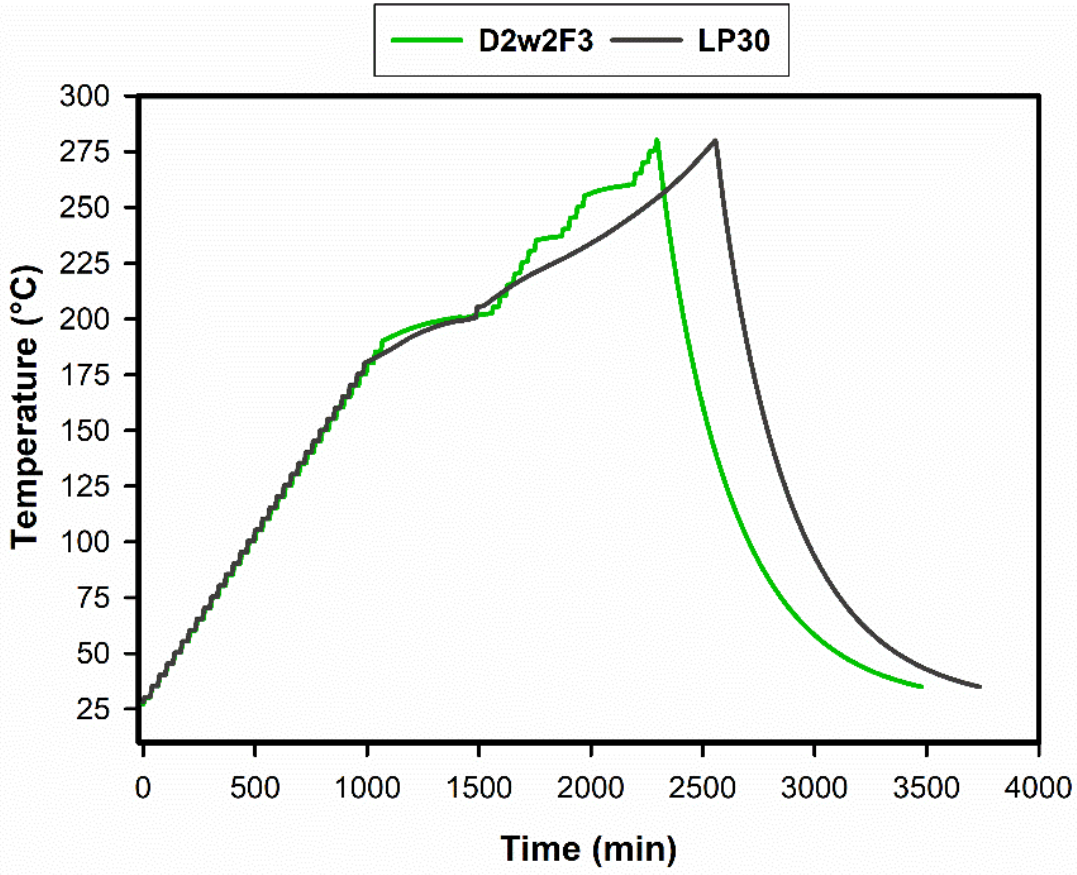
# Accelerated Rate Calorimetry




It's a basic safety test

**Commercial electrolyte (LP30)**:
1st thermal event: stopped
2nd thermal event: **go to thermal runaway**

**D2w2F3**:
1st thermal event: stopped
2nd thermal event: absent
Two more little events
**No thermal runaway**



# Conclusions

Designed novel aqueous electrolytes with DMSO (water+DMSO+LiFSI)

- ESW reaches 3.5 V (vs 1.23 V of pure water)
- Conductivity > 0.1 mS $cm^{-1}$ even at low temperatures
- Studied the intermolecular interactions water/DMSO and solvents/salt
- Tested in a full cell device (200 cycles)
- Thermal characterization: stable at low temperature and able to cycling
- Safety improved respect to commercial electrolyte

# Thanks for the attention!

## Any question?

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