Oxygen- and Sulfur-functionalized Ionic Liquids as electrolyte components in Lithium batteries

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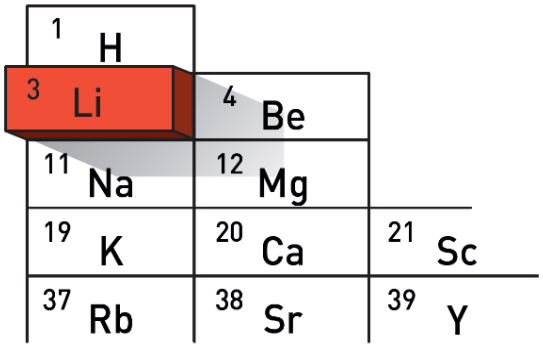
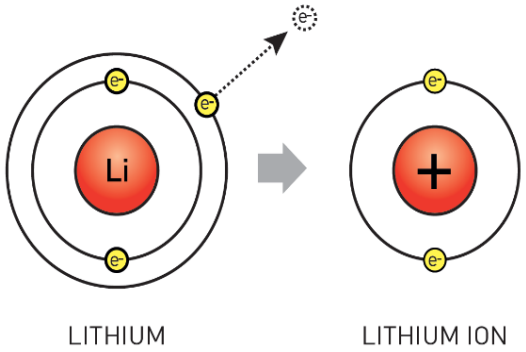
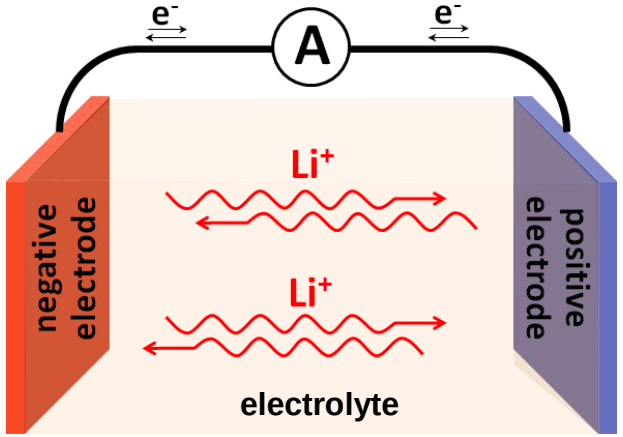
https://www.nobelprize.org/prizes/chemistry/2019/summary/

The NOBEL PRIZE in Chemistry 2019
was awarded for the
development of lithium-ion batteries.

Why Lithium?







It is the lightest metal: 0,53 g cm^{-3}

It has the the lowest redox potential: E° = -3,05 V vs SHE

CAN THE PRESENT LITHIUM ION BATTERY TECHNOLOGY BE SCALED-UP FOR **EV** and **STATIONARY** APPLICATIONS?

Barriers of various nature, and particularly **safety** concern, still prevent this step. New, more energetic, lower cost and safer electrode-electrolyte combinations must be exploited.

Breakthroughs in lithium battery technology can only be obtained by moving to innovative chemistries, this including electrode and electrolyte, high performance components.

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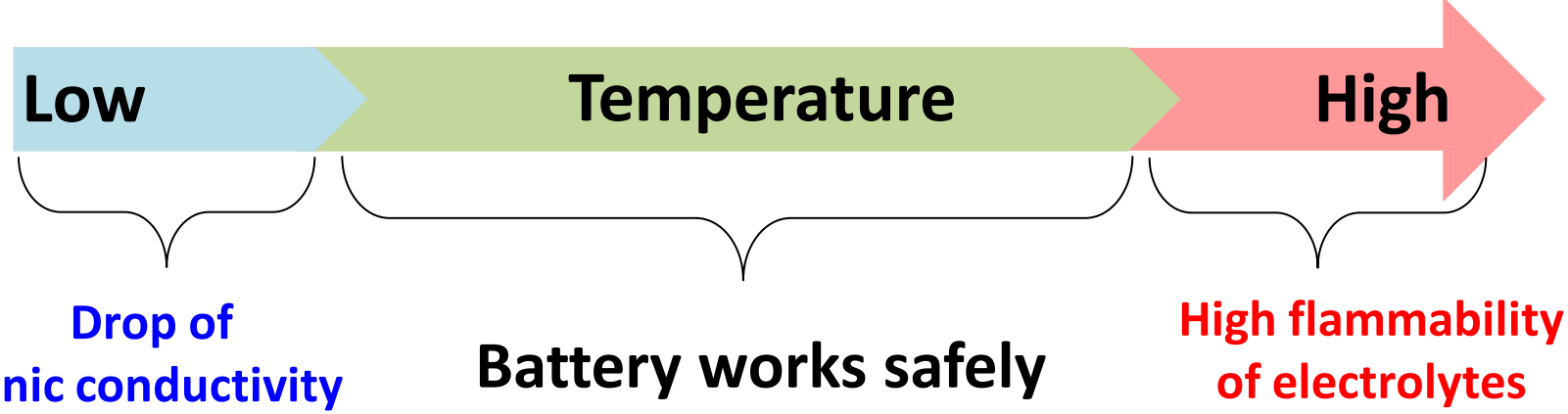
IMPROVEMENTS IN SAFETY AND RELIABILITY

Replacement of $LiPF_6$-alkyl carbonate electrolytes, due to:

- high vapor pressure and flammability
- incompatibility with the environment and human health (manipulation hazards)
- relatively narrow electrochemical stability domain (no with high voltage cathodes)

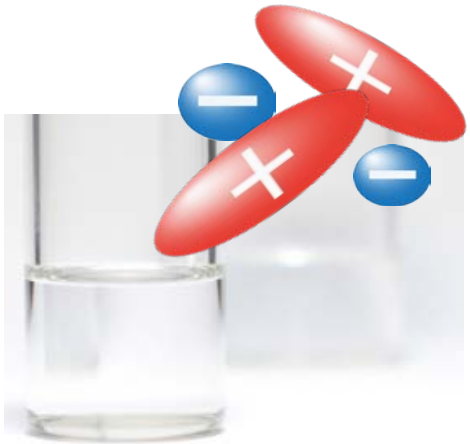
A Dell computer went on fire in a conference in Osaka in June 2006. Sony and Dell announced recall of Sony's lithium ion batteries packs (more than 4.5 million).

Byd e6 EV - May 26th, 2012, China



BY USING IONIC LIQUIDS (ILs) as ELECTROLYTE COMPONENTS:

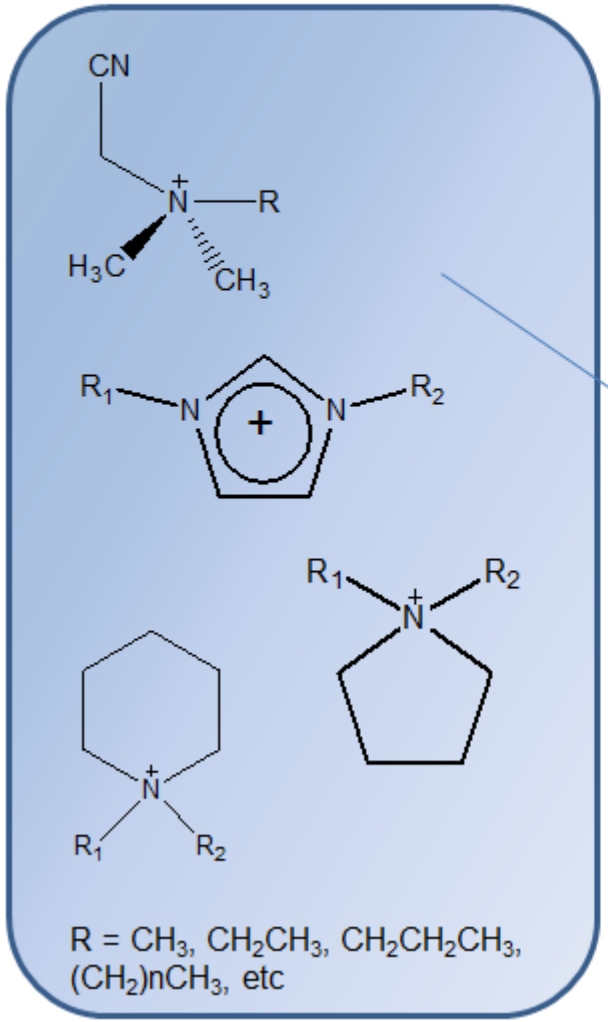
- Flammability can be controlled;
- Crystallization of electrolytes, which causes the poor ionic conductivity at low temperature, can be delayed;
- Lithium surface can be stabilized and dendrites formation can be controlled.

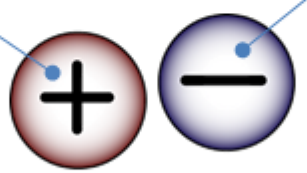


The aim of this work:

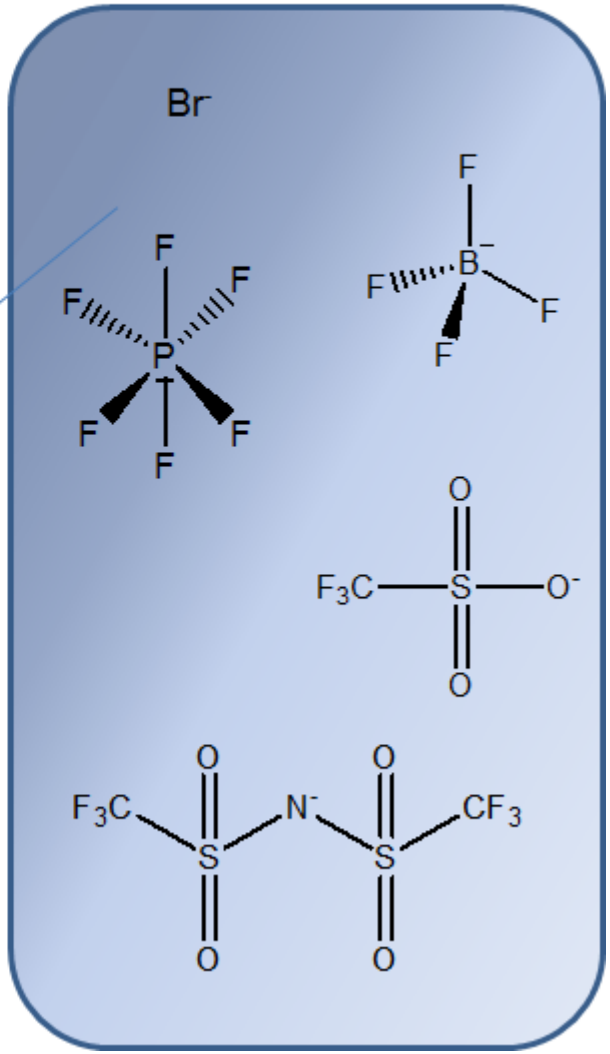
design new ILs, by playing with ions structure and composition, as effective and safe electrolytes over an extended T-range.

Possible combinations to form an IL





To be used as electrolyte components in lithium batteries, ILs must be added by a Li-salt!



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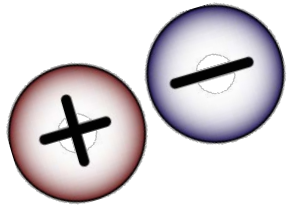
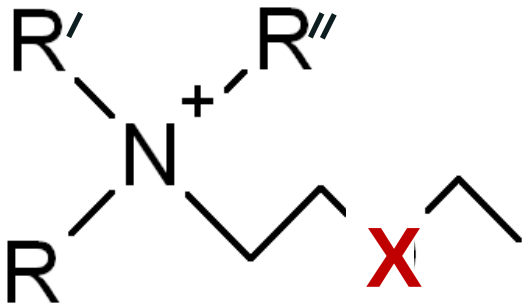
IL cations with functionalized side chains

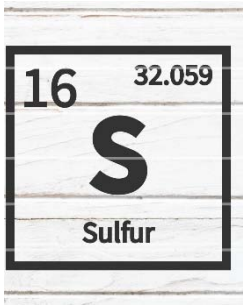




Why?

A flexible chain is expected to increase the conformational degrees of freedom of the cation moiety.

OXYGEN and **SULFUR** atoms in the cation core might dissociate Li salt, interact with Li^+ ions, inhibit self-aggregation between cation and neighbouring anions, improve polarity and salt solubility.



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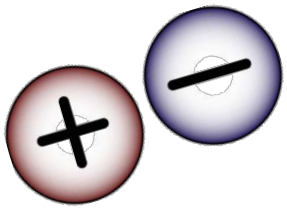
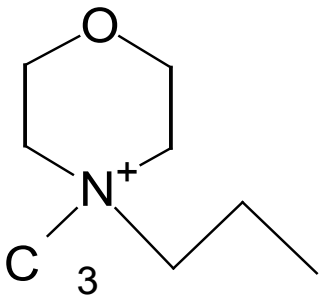
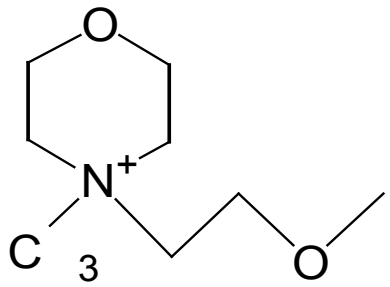
Our studies on new IL cations:

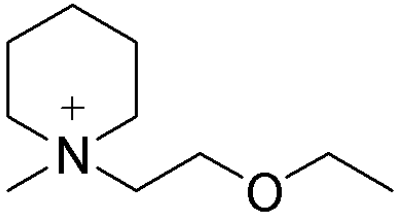




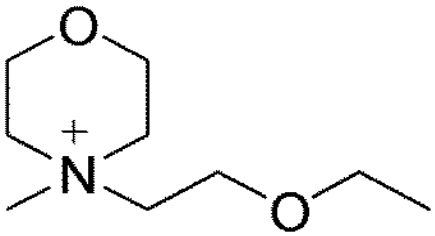
$M_{1,3}$: *N*-methyl-*N*-propylmorpholinium



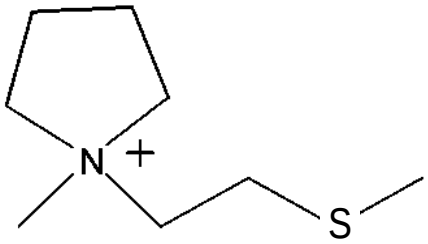
$M_{1,2O1}$: *N*-methoxyethyl-*N*-methylmorpholinium



$P_{1,2O2}$: *N*-ethoxyethyl-*N*-methylpiperidinium



$M_{1,2O2}$: *N*-ethoxyethyl-*N*-methylmorpholinium



$Py_{1,2S1}$: *N*-methyl-*N*-methylthioethylpyrrolidinium

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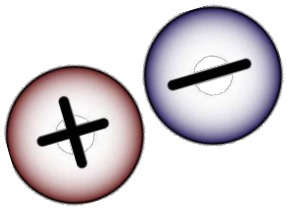
The effect of different IL anions:



TFSI*:* bis(trifluoromethanesulfonyl)imide

FSI*:* bis(fluorosulfonyl)imide

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Thermal properties - DSC

$M_{1,3}TFSI$

T_m = 40.8 °C

$M_{1,2O1}TFSI$

T_m was not observed

Ether modification on **cation** side-chain

$P_{1,2O2}TFSI$

T_m was not observed

$P_{1,2O2}FSI$

T_m = -12.0 °C

Anion substitution

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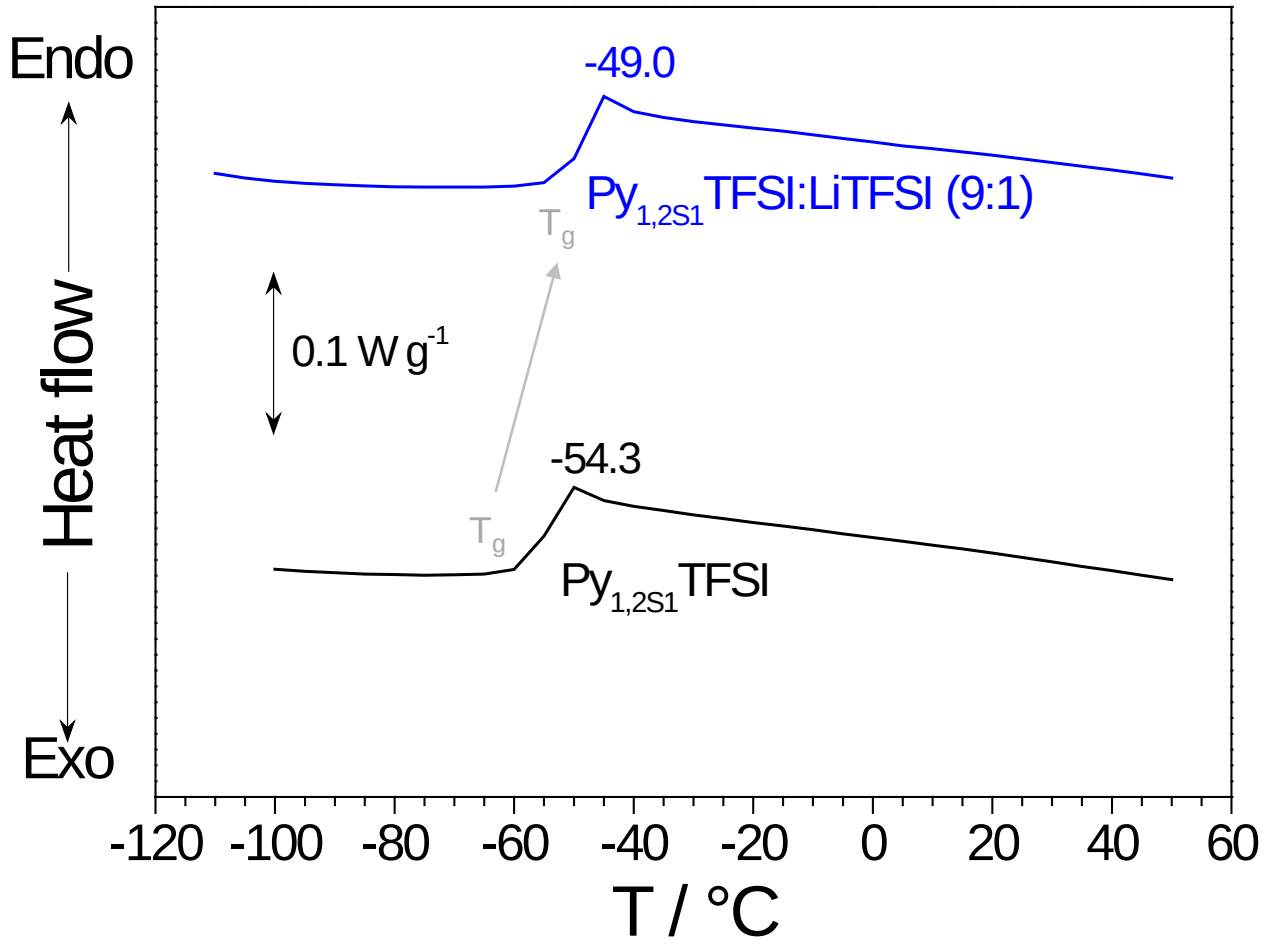
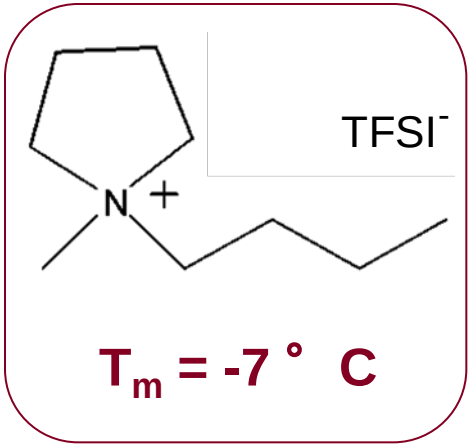
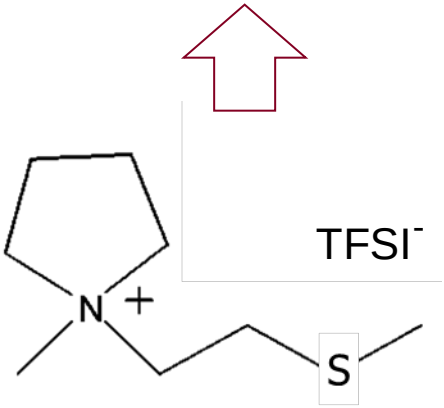
Thermal properties - DSC

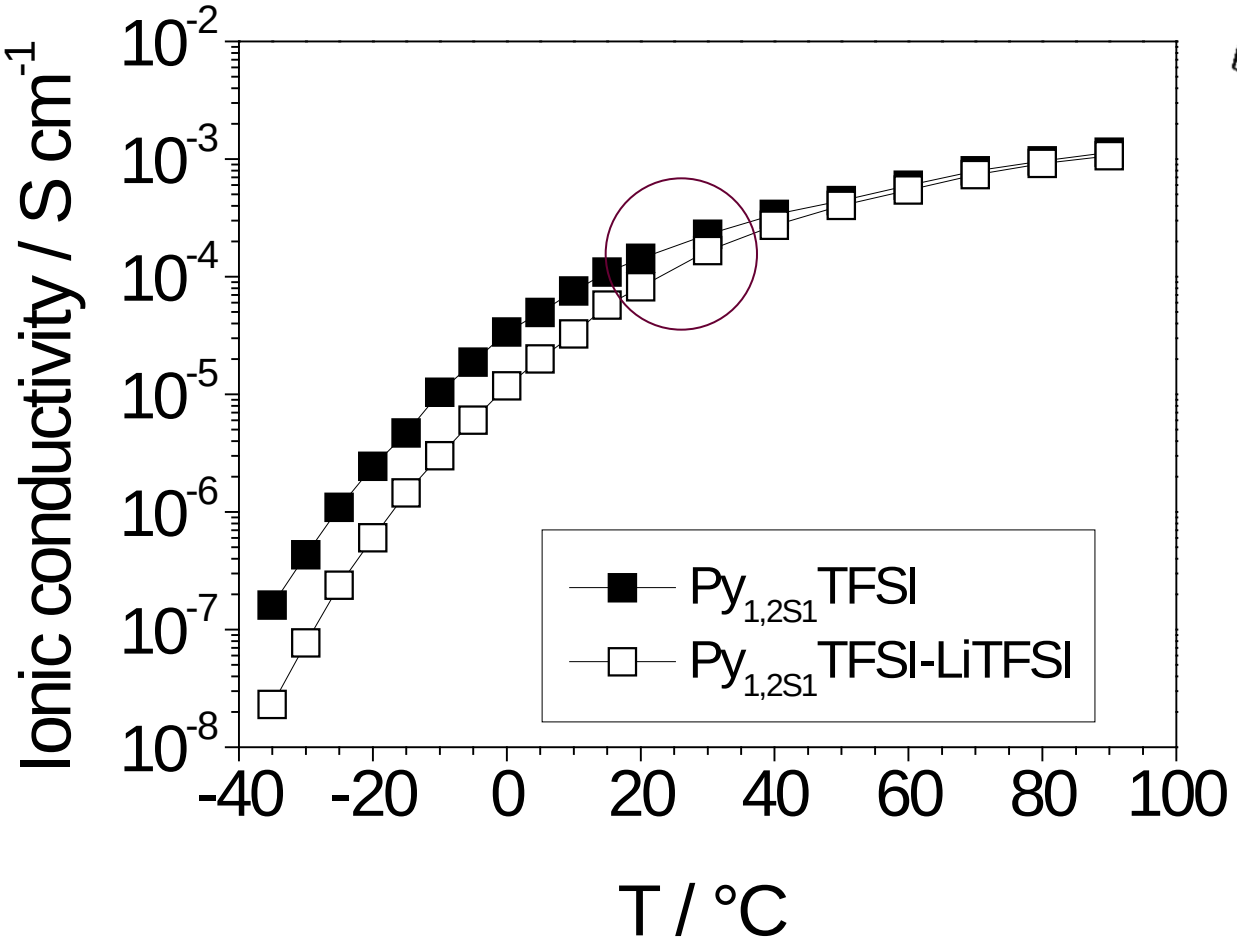


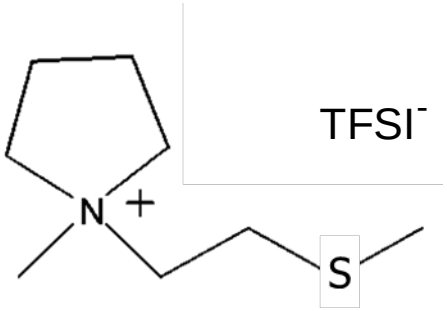




G.B. Appetecchi, A. D'Annibale, C. Santilli, E. Genova, L. Lombardo, M.A. Navarra, S. Panero, *Electrochemistry Communications*, 63 (**2016**) 26

Conducting properties





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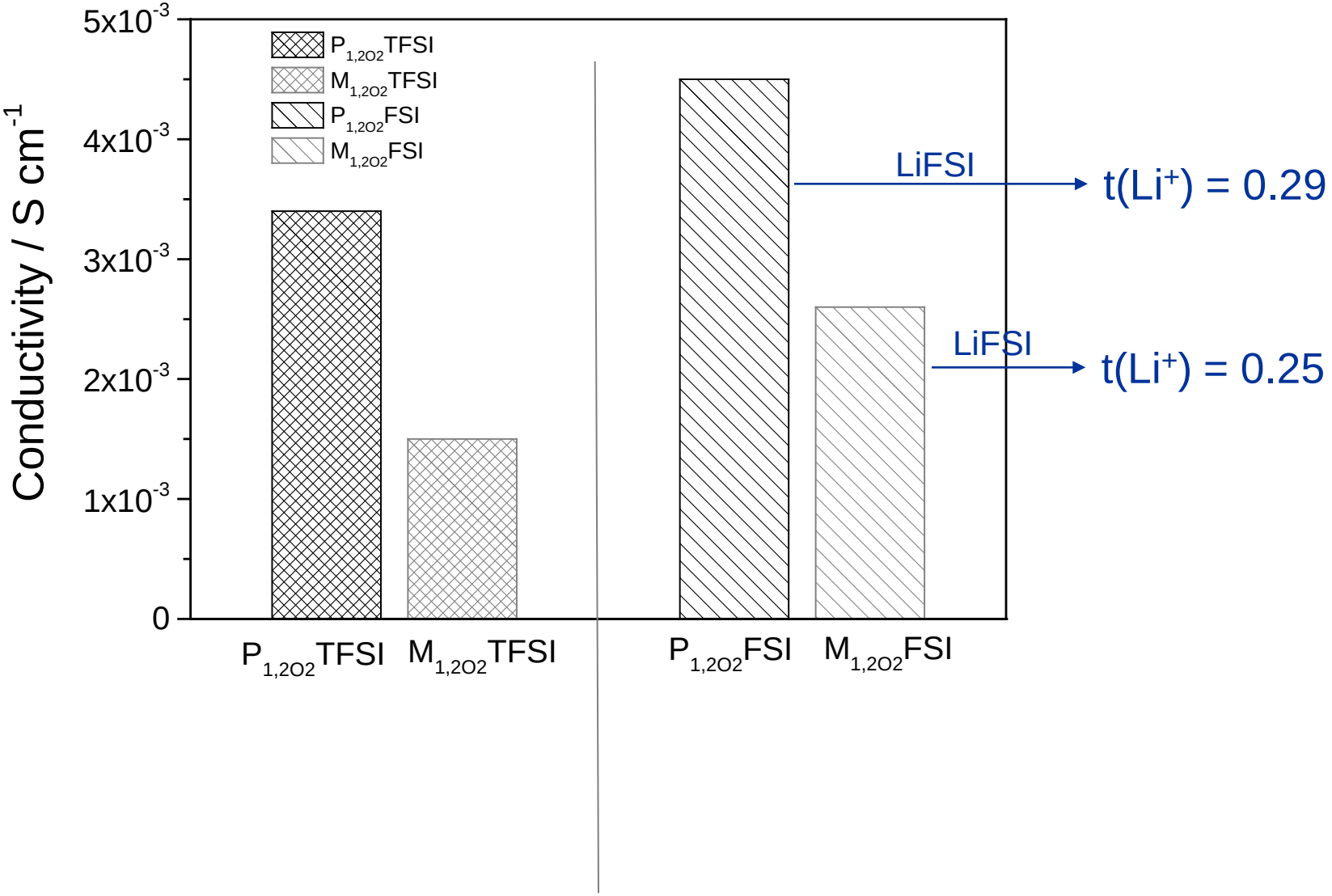
Ionic conductivity at 40 °C



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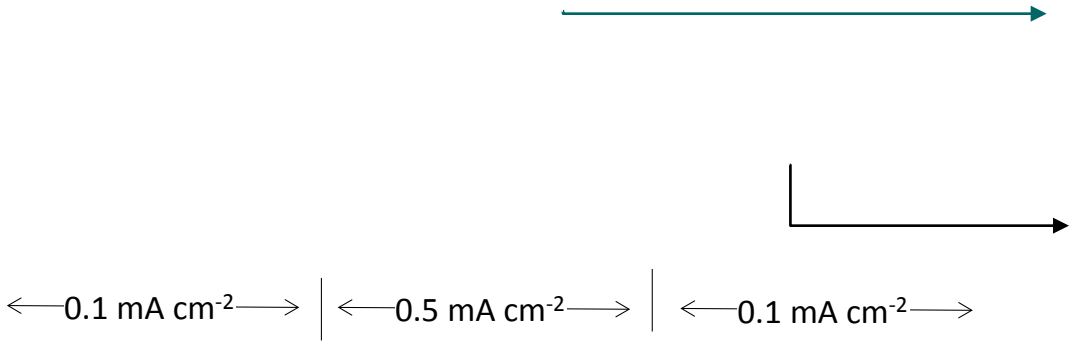
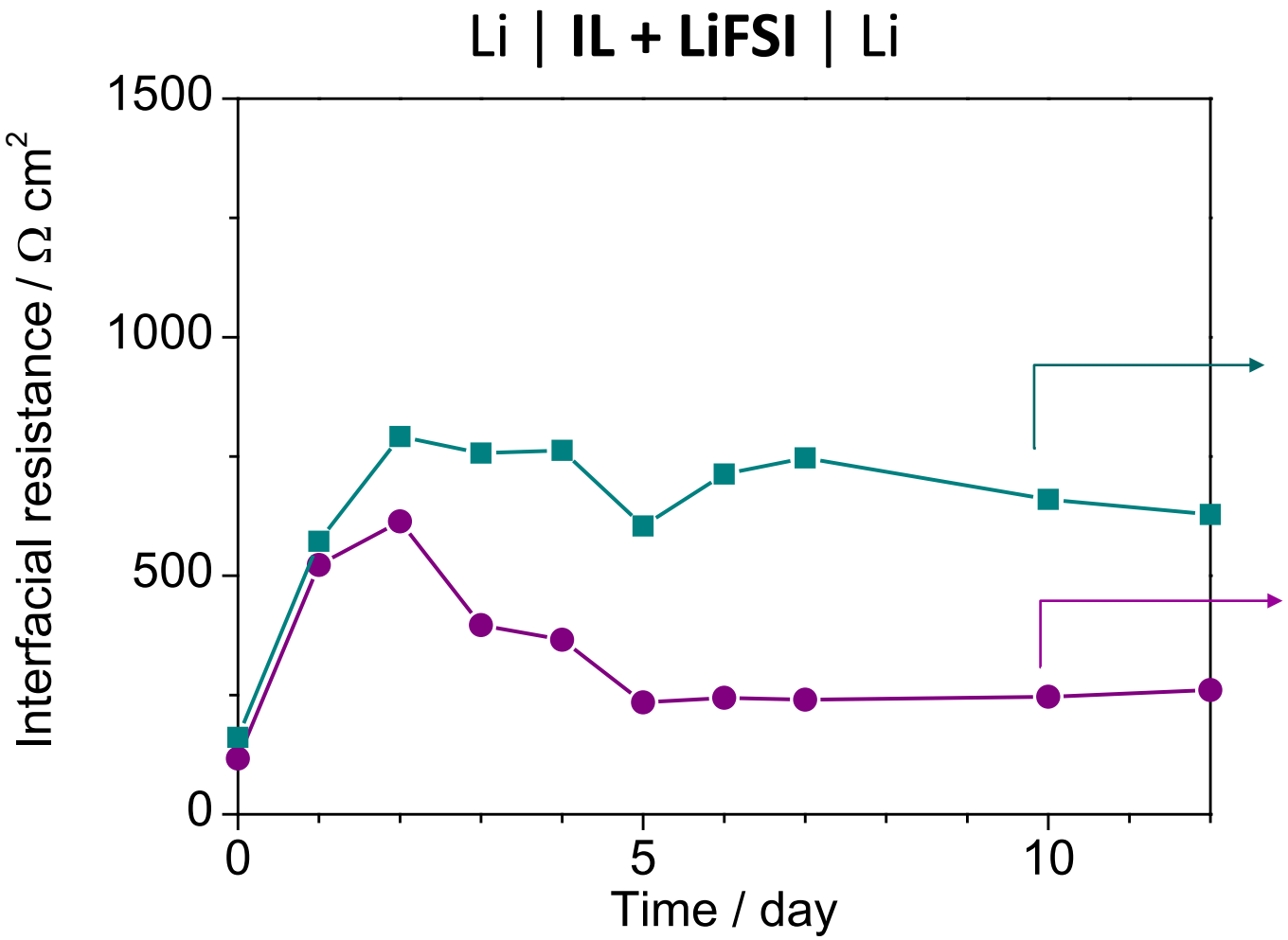
Stability vs Lithium

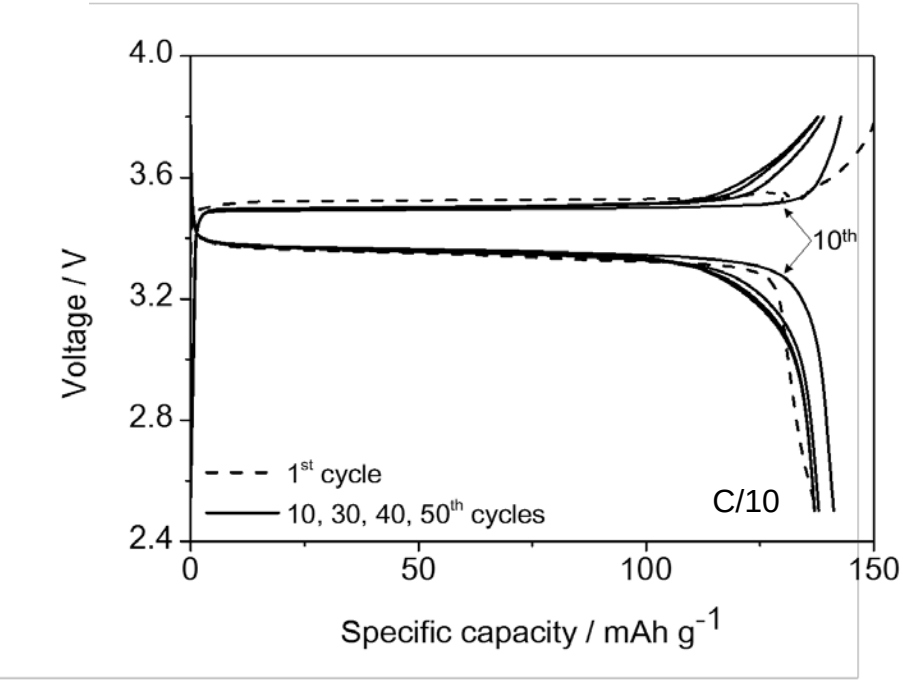
Li | **IL + LiFSI** | Li



Stability vs Lithium



Cycling performance: Li | $P_{1,2O2}FSI$ - LiFSI | $LiFePO_4$ (LFP)



1C = 0.847 mA cm^{-2}

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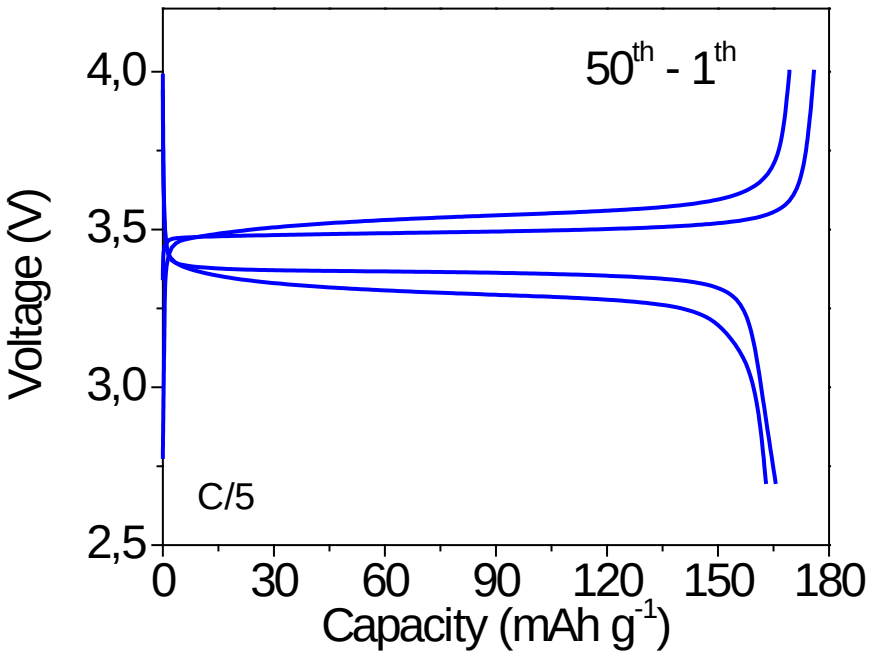
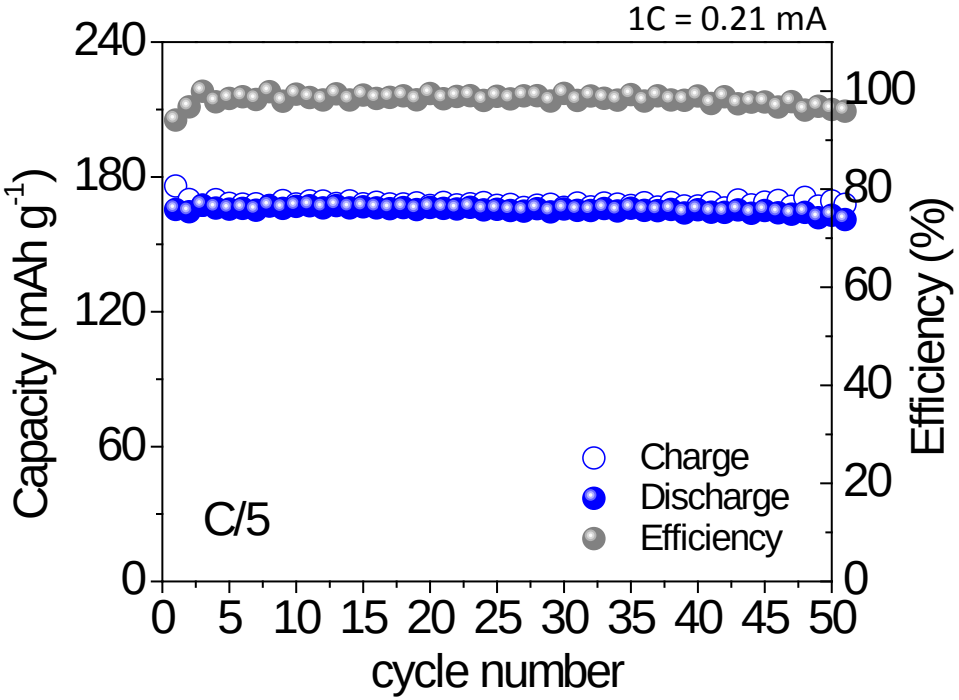
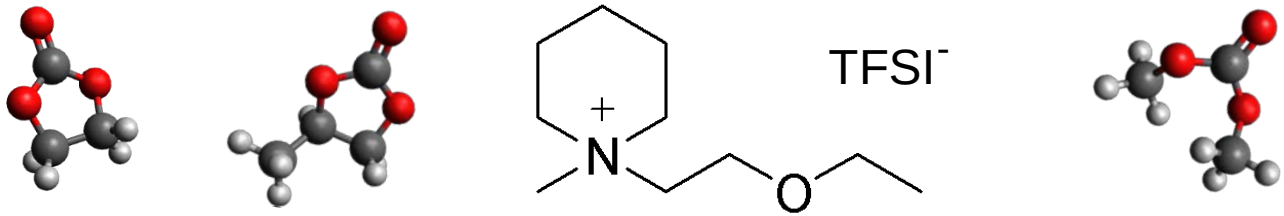
How to improve the cycling performance?

Li | $P_{1,2O2}$TFSI - LiTFSI - EC:PC:DMC | LFP







M.A. Navarra, K. Fujimura, M. Sgambetterra, S. Panero, A. Tsurumaki, N. Nakamura, H. Ohno, B. Scrosati, *ChemSusChem,* 10 (**2017**) 2496

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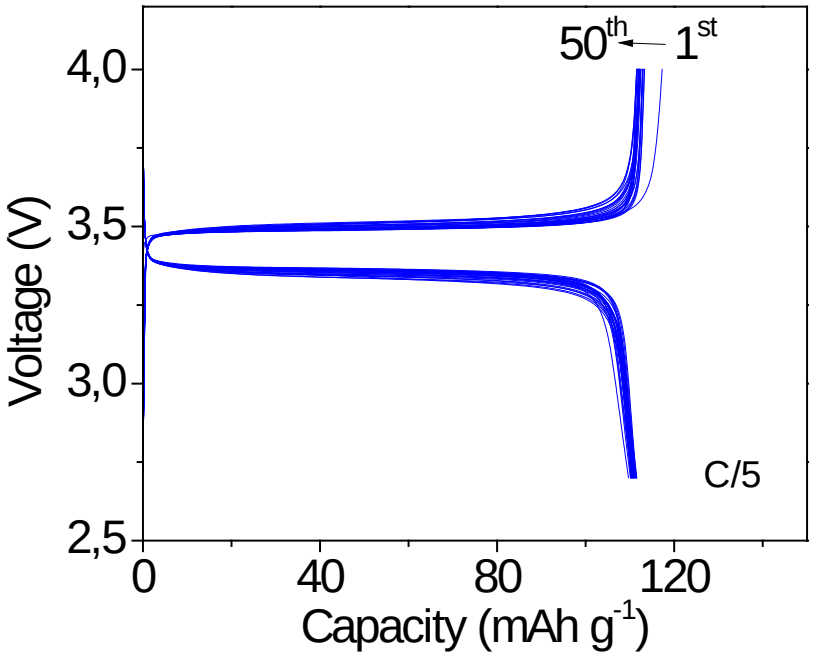
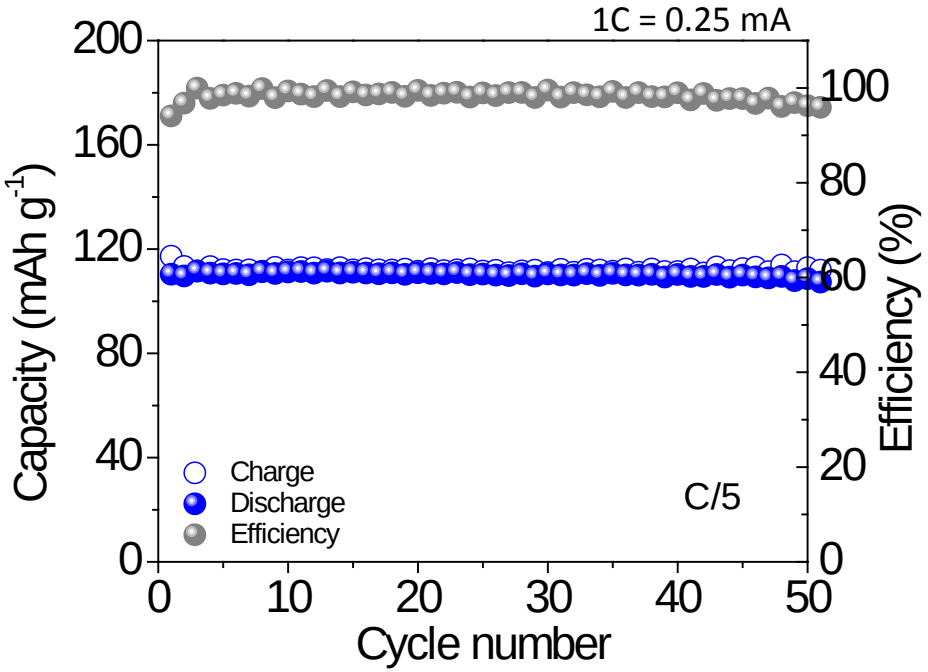
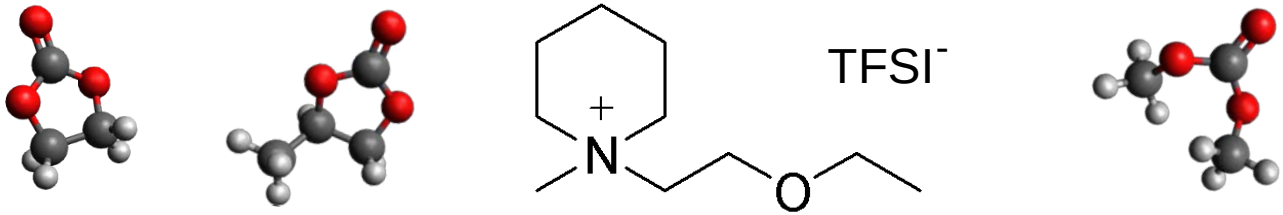
Cycling performance of a full Li-ion cell

Sn-C | $P_{1,2O2}$TFSI - LiTFSI - EC:PC:DMC | LFP







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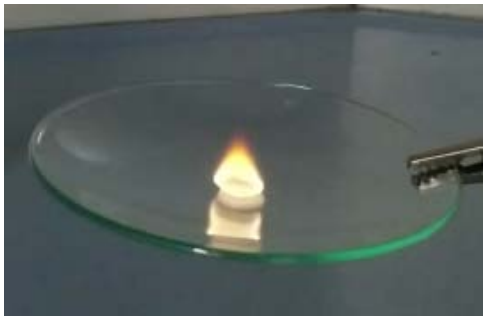
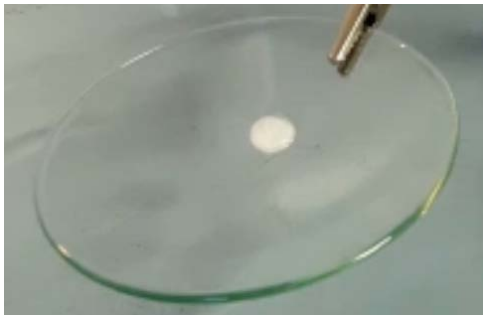
Flammability test

Commercial electrolyte

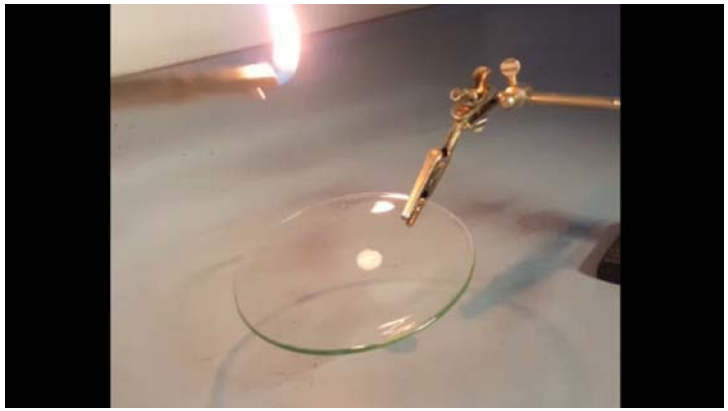


@ 1 s after ignition

IL-based electrolyte



@ 1 s after ignition



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Conclusions

The presence of ethero-atoms in the cation moiety strongly affects the IL properties.

- Both O- and S-functionalized side chains guarantee no melting/crystallization features in the whole range of T for practical battery applications.
- Higher conformational degrees of freedom and conductivity are associated to the ether group respect to the sulfur one.
- The best electrochemical performances were found by combining Piperidinium-based cations with FSI anion.
- Applicability of safe IL-based electrolytes in Li-metal and Li-ion batteries was demonstrated.

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Grazie per l'attenzione!

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