

Improved performance of liquid- and gel-state electrolytes by using borate-based salts and ionic liquids

Akiko Tsurumaki*, Mario Branchi, Stefania Panero, and Maria Assunta Navarra

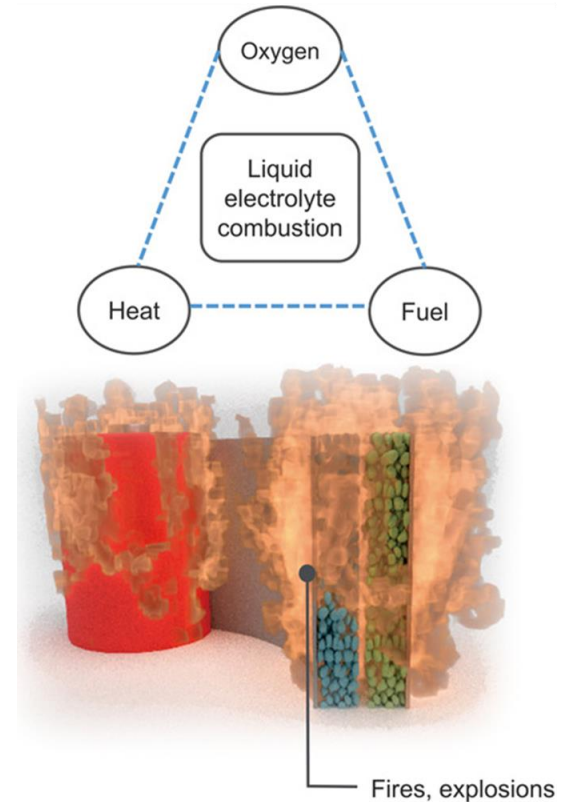
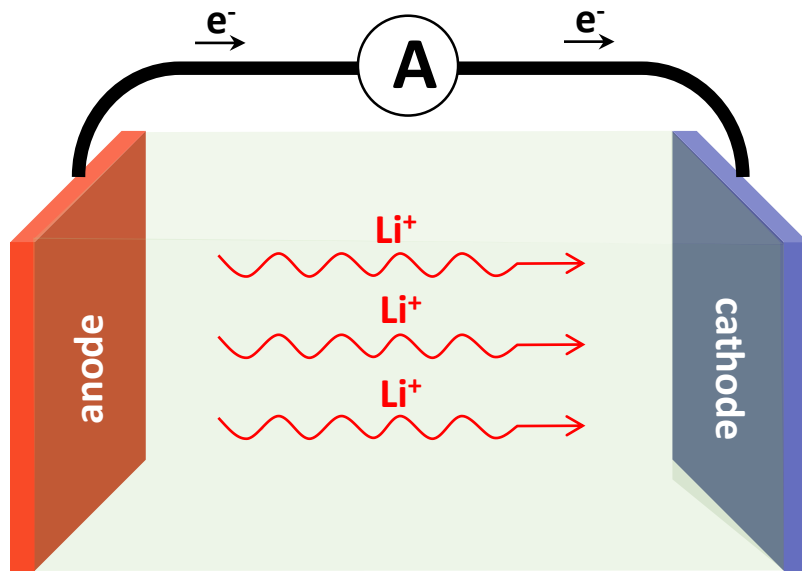
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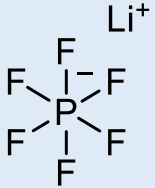
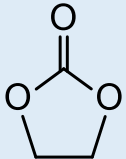
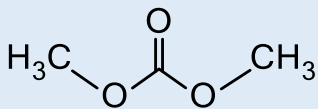
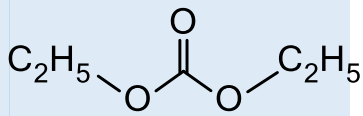
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Functions required for the electrolytes

- **Performance:** High ionic conductivity to realize theoretical capacity
- **Safety:** High stability under any conditions (high voltage, low and high temperatures etc.)

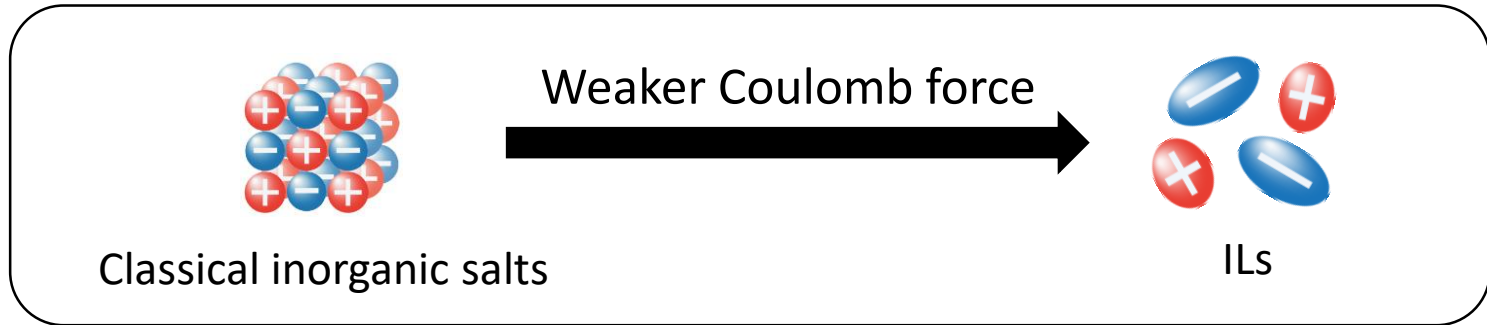


LP71: a conventional electrolyte

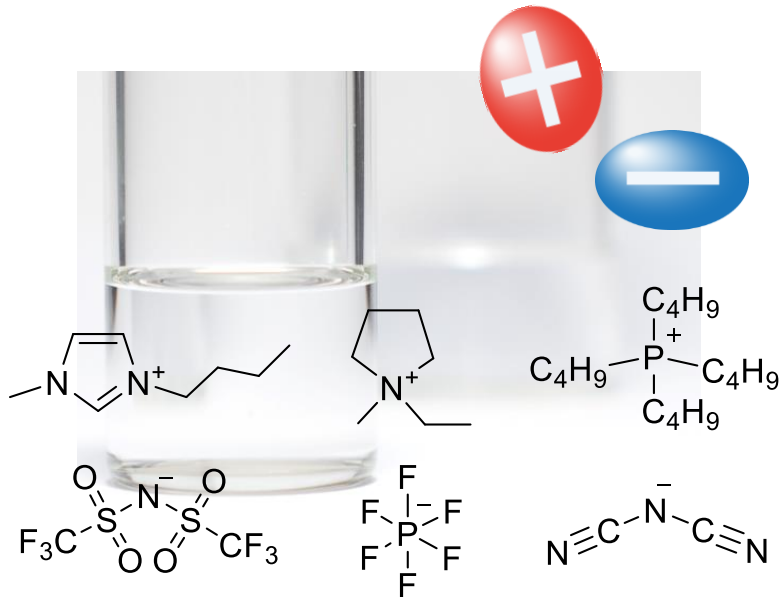
	LiPF ₆ (1M)	EC	DMC	DEC
Structure				
T _{boil} / °C	-	238	90	127
T _{melt} / °C	200 (dec)	38	3	-43
T _{flash} / °C	-	143	17	25
Dielectric const.	-	90	3.1	2.8
Viscosity / cP	-	1.9@40°C	0.59	0.75

- ✓ Sufficient ionic conductivity
- ✓ High stability with many kinds of electrode
(ability to form a solid electrolyte interface (SEI))
- ✗ Temperature limitation

Ionic liquids (ILs) as electrolytes and additives



- ❑ Composed of only ions (alike NaCl, LiPF_6)
- ❑ Most ions are organic, relatively large, and asymmetric

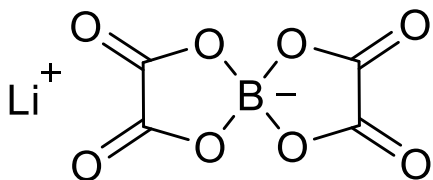


- ✓ Lower melting point ($T_m < \text{r.t.}$)
- ✓ High ionic conductivity
- ✓ Huge variety of ion structures

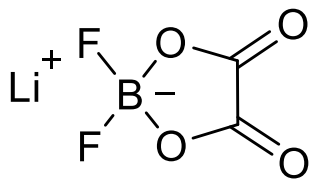
“Designable electrolytes”
(10^{18} possibilities)

How to design ILs?

1) Select lithium salts with suitable anion structures



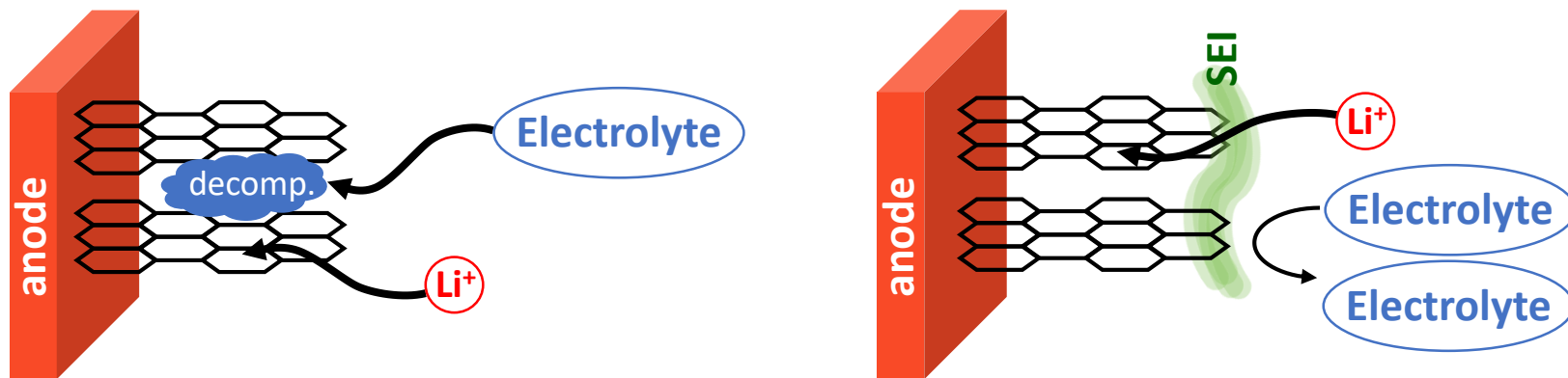
LiBOB



LiDFOB

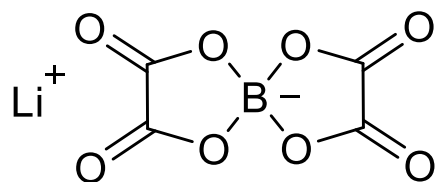
- ✓ Formation of SEI
(both on anode and cathode)
- ✗ High melting point ($\sim 300^{\circ}\text{C}$)
- ✗ Low solubility ($\approx 0.1\text{M}$)

SEI (Solid Electrolyte Interface) protects electrolyte from the decomposition at the interface of electrodes

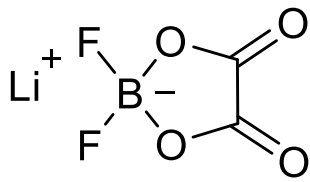


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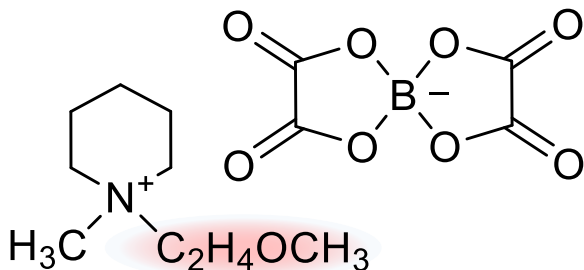
LiBOB



LiDFOB

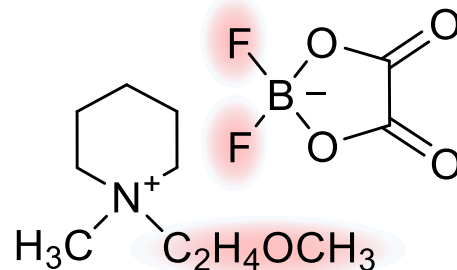
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2) Design suitable cation structure



BOB-IL

N-methoxyethyl-*N*-methyl-
piperidinium bis(oxalato)borate

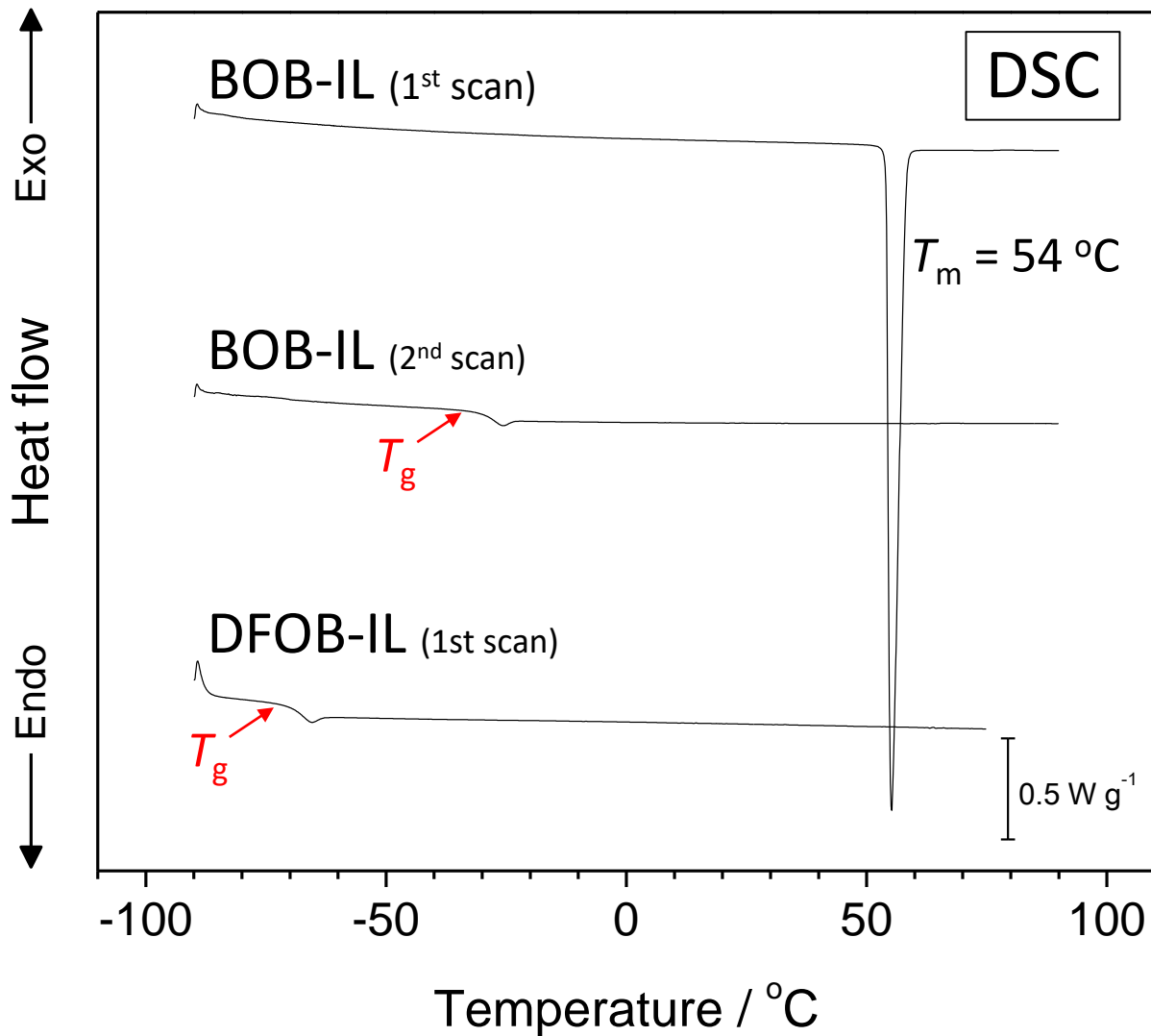


DFOB-IL

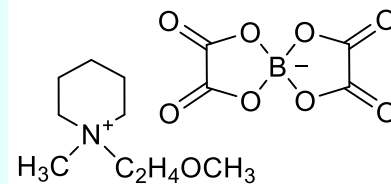
N-methoxyethyl-*N*-methyl-
piperidinium difluoro(oxalato)borate

3) Assess the combination of anion and cation

Fundamental properties of the pure ILs



BOB-IL

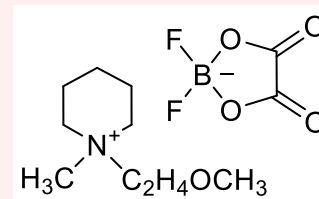


T_{melt} : 54.5 °C, T_{glass} : -29.8 °C

$T_{\text{decomp.}}$: 272.1 °C

$\sigma_{60\text{°C}}$: $0.6 \times 10^{-3}\text{ S cm}^{-1}$

DFOB-IL

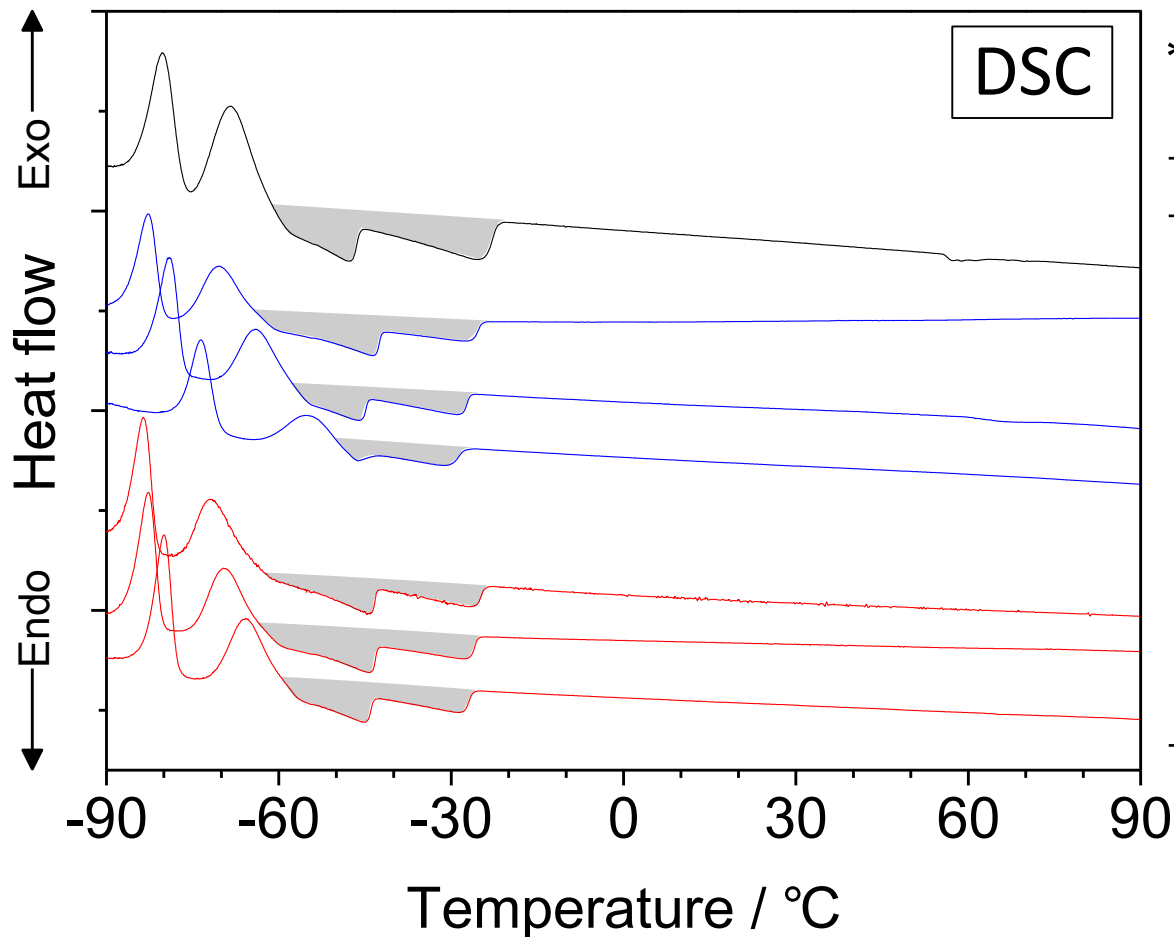


T_{melt} : n.d., T_{glass} : -68.0 °C

$T_{\text{decomp.}}$: 284.4 °C

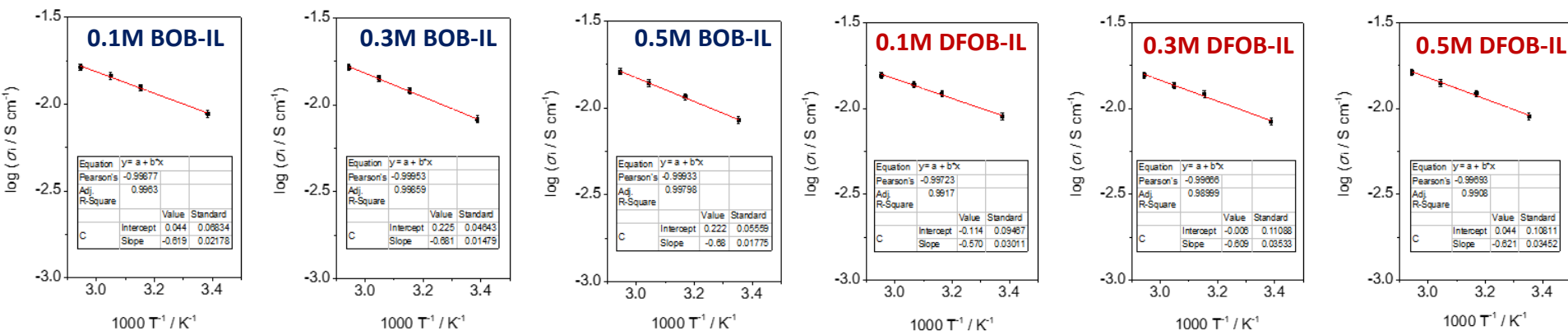
$\sigma_{60\text{°C}}$: $4.0 \times 10^{-3}\text{ S cm}^{-1}$

Differential scanning calorimetry of LP71*-IL mixtures



**Suppression in the crystallinity of LP71
was more pronounced when BOB-IL was used.**

Ionic conductivity of LP71-IL mixtures



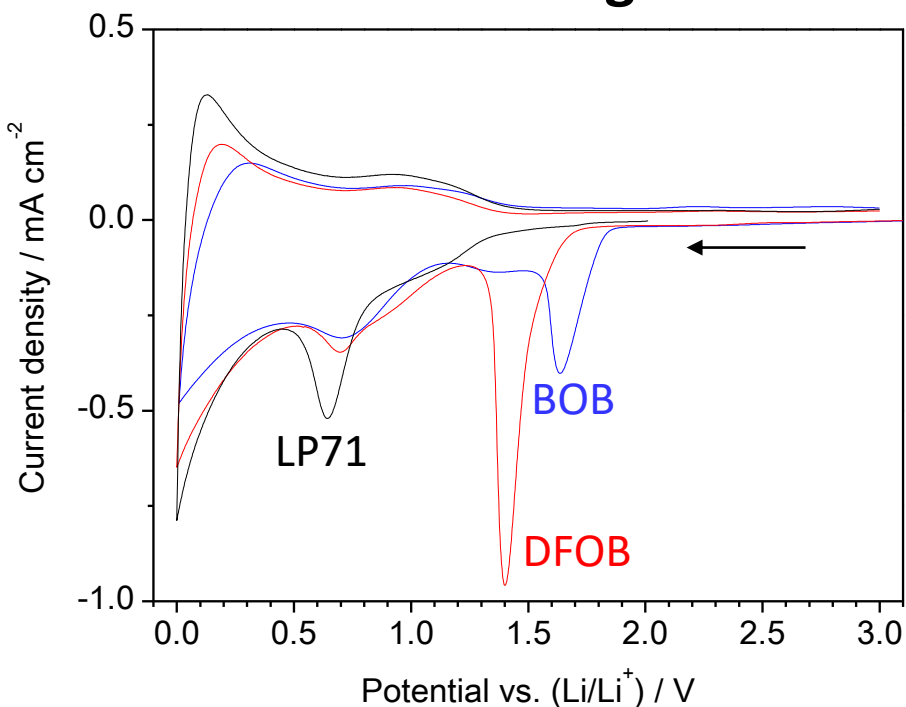
Mixtures	$\sigma_{\text{room } T} / \text{mS cm}^{-1}$	$E_a / \text{kJ mol}^{-1}$
LP71	9.10	11.09
BOB-IL 0.1M	9.19	11.85
0.3M	8.66	13.04
0.5M	8.31	13.08
DFOB-IL 0.1M	9.32	10.91
0.3M	8.81	11.66
0.5M	8.86	12.10

All the solution exhibited $\sigma > 10^{-3} \text{ S cm}^{-1}$ at room T.

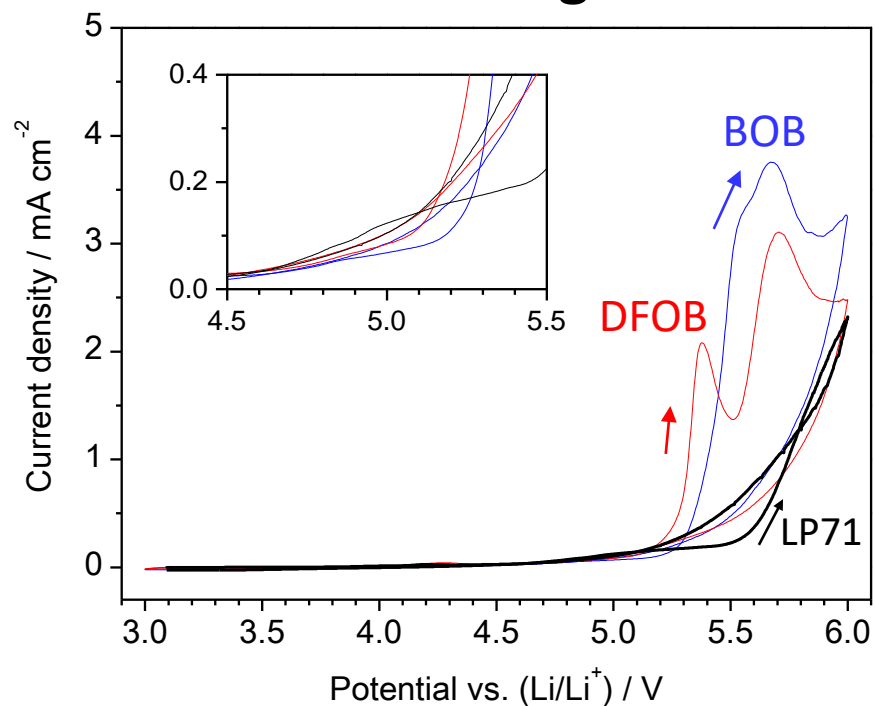
Cyclic voltammetry of LP71-IL mixtures

Cell composition: Super P (WE) | electrolyte | Li (CE/RE)

Cathodic region



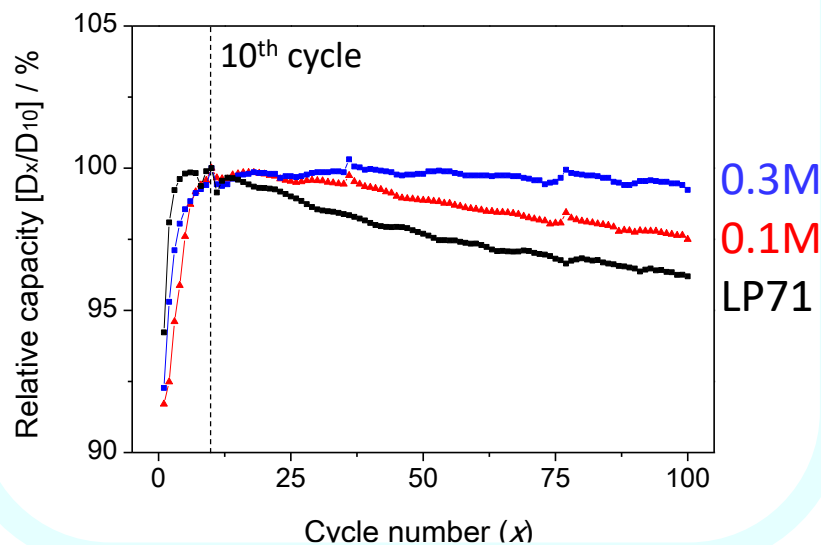
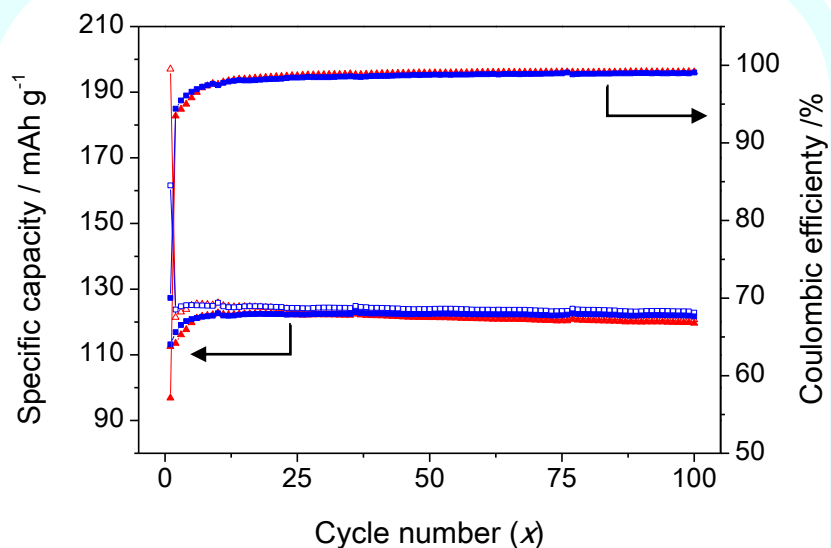
Anodic region



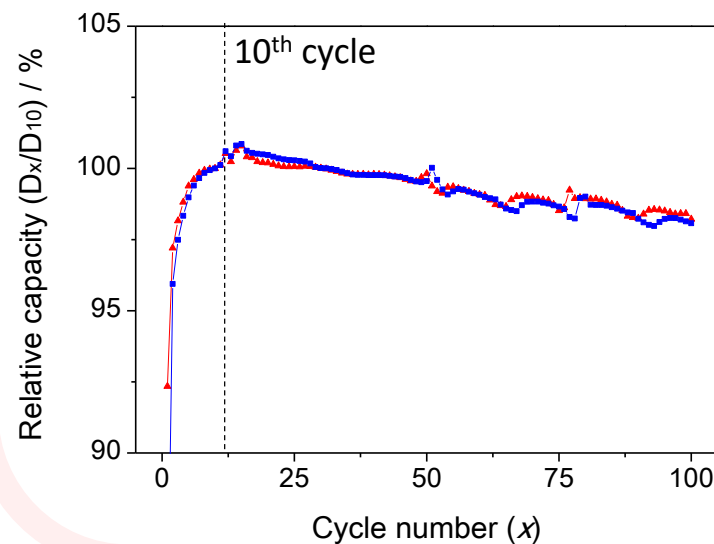
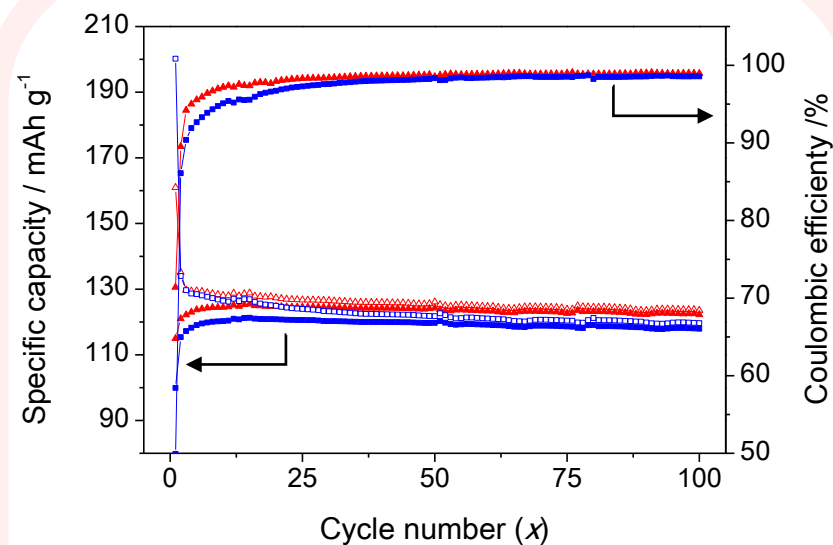
Formation of SEI was confirmed in the both scans.

Cell capacity of Li | LP71-IL | LNMO

BOB-IL



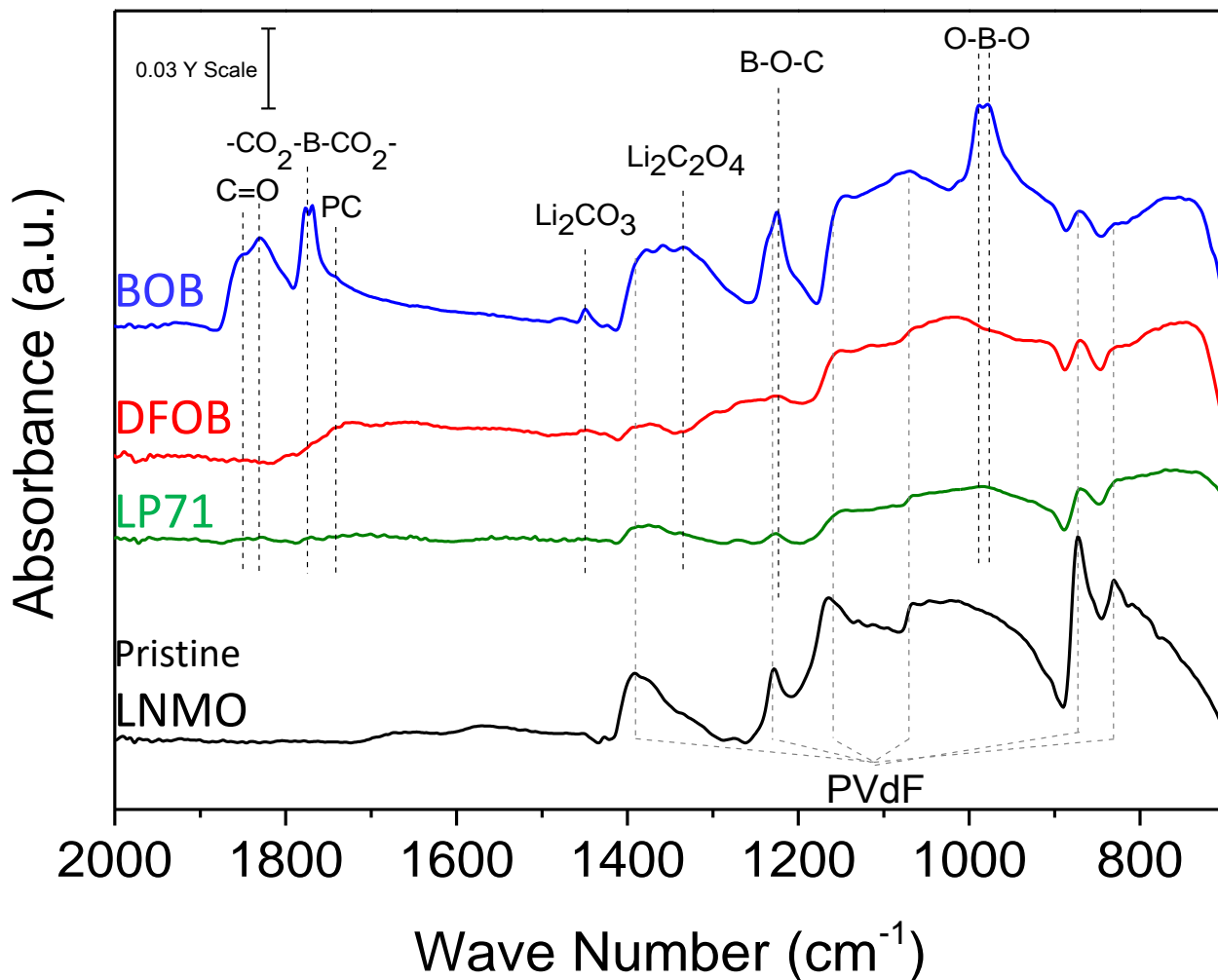
DFOB-IL



The cells exhibited the capacity higher than 120 mAh g^{-1} .

FTIR-ATR spectra of SEI deposited on LNMO*

*after 100 galvanostatic cycling



When BOB-IL was additive, SEI layers contained boron compounds and polycarbonate species.

Conclusion

- ✓ **Two novel ILs were synthesized**
- ✓ **Used as additives in conventional electrolytes, the ILs:**
 - **formed SEI at both anodic and cathodic voltages;**
 - **improved the capacity retention in Li|LNMO cells.**
- ✓ **BOB-IL 0.3M has the strongest impact:**
 - **SEI layers, based on boron compounds and polycarbonate species on the LNMO cathode.**
- ✓ **Prepared gel electrolyte based on the electrolyte mixture containing BOB anion**