

## Batteries

ACME Faculty, EHVE course  
B.Sc. Studies, III year, V semester

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## Electrolytes for Lithium-ion cells

## Electrolytes for Li-ion cells

- Electrolyte role is to transport lithium cations from anode to cathode and back and it cannot conduct electrons.
- In a total cell components cost, depending on the cell size, electrolyte share is between 5 and 15%. About 2/3 of that is a salt cost.
- Li-ion cell market size is around \$60 billion (2019) and it is assumed that it will reach ca. \$110 billion in 2024, most of it in consumer electronics.

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## Electrolytes for Li-ion cells

Cell parameters depending on electrolyte parameters (exclusively, among other or indirectly) :

- Current density (conductivity);
- Storage and operation temperature (thermal stability);
- Charge-discharge cycle efficiency (cation transference number, conductivity);
- Energy density (electrochemical stability and compatibility enabling using better anodes and/or cathodes);
- Safety and environmental friendliness (safety, toxicity);
- Cost (cost).

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## Electrolytes for Li-ion cells

Properties that electrolyte for Li-ion cells should have:

- Good ionic conductivity ( $>1 \text{ mS cm}^{-1}$ );
- No electronic conductivity;
- High lithium cation transference number ( $>0.3$ );
- Thermal stability ( $-20 - +150^\circ\text{C}$  range);
- Electrochemical stability (2-4.5 V vs Li);
- Compatibility with other cell components (in temperature and potential ranges that can occur in cell);
- Non-toxicity;
- Low cost.

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## Electrolyte types

- Liquid ← used in all standard commercial cells
- Gel ← used in some cells for special applications
- Liquid polymer (oligomer)
- Solid polymer (SPE) ← used in narrow range of high-temperature cells but considered the future of Li-ion cells
- Ceramic
- Composite (e.g. gel with ceramic additive)
- Polyanions
- Ionic liquids
- other...

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## Solvents/matrices

- Carbonates (PC, EC, DMC, DEC, EMC, VC, FEC)
- Oligomers (predominantly PEG)
- Legacy: AN, GBL, THF, 2-MeTHF, EA.
  
- Polymer matrices: PEO (for SPE), PVdF (for gel)
- Legacy (in reality): PAN, PMMA, etc.

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## Which solvents are preferred (wish list)

- Low viscosity;
- Low melting point;
- High boiling/decomposition point;
- High dielectric constant;
- Acceptor number-donor number;
- Low vapor pressure (or lack thereof);
- Lack of bonds that are easy to break in oxidative or reductive conditions (broad electrochemical stability);
- Low cost;
- Non-toxic;

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## Why mixtures?

Solvent	Advantages ( $\eta$ / mPa s, $T$ / °C)	Disadvantages
EC	high $\epsilon$ , high b.p. (+248), cheap	high m.p. (+36), high $\eta$ (1.9)
PC	high $\epsilon$ , high b.p. (+242), cheap	graphite exfoliation, high $\eta$ (2.5)
DME	very low $\eta$ (0.45), low m.p. (-58)	unstable SEI
DMC	low $\eta$ (0.58), cheap	low $\epsilon$ (3.1), low b.p. (+91), high m.p. (+4.6)
DEC	low $\eta$ (0.75), low m.p. (-74)	low $\epsilon$ (2.8), expensive
EMC	low $\eta$ (0.64), low m.p. (-53)	low $\epsilon$ (2.9), expensive

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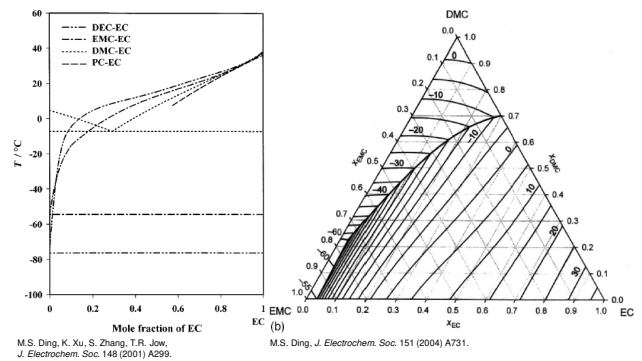
## Why mixtures?

Commonly (commercially) used solvent mixtures from the more to the less common (typical ratios in brackets):

- **EC:DMC** (1:1, 3:7, 1:2)
- **EC:DEC** (3:7, 1:2)
- **EC:DEC:DMC** (1:1:1)
- **EC:EMC** (more expensive devices, 1:2)
- **EC:DMC:EMC** (low temperature applications, 1:1:1)
- **EC:DEC:DMC:EMC** (low temperature applications, 1:1:1:2)
- **EC:PC** (PC can be used in the presence of large amount of more polar EC, which then forms the lithium cation solvation layer)
- **EC:PC:DMC** (1:1:2, 1:1:1)
- **EC:DMC:DME** (1:2:0.125), etc.

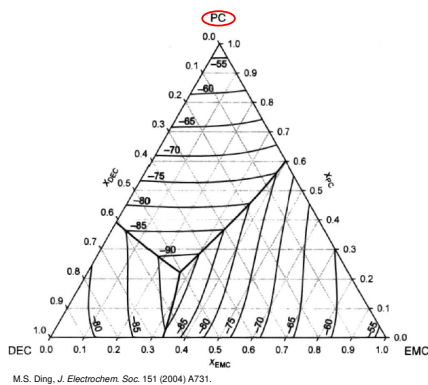
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## Why mixtures?



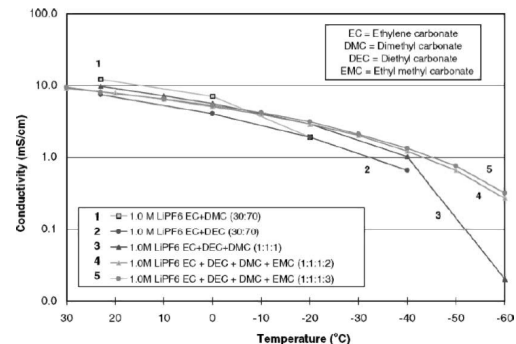
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## Why mixtures?



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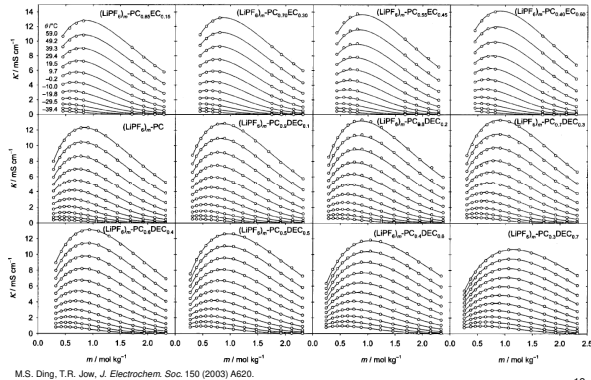
## Why mixtures? Salt effect



M.C. Smart, B.V. Ratnakumar, L.D. Whitcanack, K.B. Chin, S. Surampudi, H. Croft, D. Tice, R. Staniewicz, *J. Power Sources* 119-121 (2003) 349.

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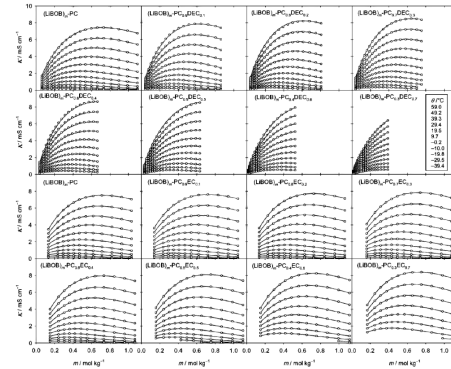
## Salt effect - concentration



M.S. Ding, T.R. Jow, *J. Electrochem. Soc.* 150 (2003) A620.

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## Salt effect - concentration



M.S. Ding, K. Xu, T.R. Jow, *J. Electrochem. Soc.* 152 (2005) A132.

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## Additives – used as needed

- Increasing conductivity (e.g. DME <10%, ceramic ones – in the form of suspension; rarely used);
- Increasing the lithium cation transference number (e.g. calixarenes – anion traps; not used in practice);
- Increasing electrochemical or chemical stability or stabilizing the SEI layer (VC 1-3%, FEC 5-15%);
- Flame retardants (TFP >10%);
- Moisture scavengers (sorbents);
- Gas scavengers, mostly for CO<sub>2</sub> (sorbents).
- **The presence of any additive affects all other electrolyte parameters!**

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## Salts

Most important salts proposed over the years:

- LiClO<sub>4</sub> – explosive at increased temperature;
- LiBF<sub>4</sub> (LiF formation, unstable and growing SEI);
- LiPF<sub>6</sub>, LiAsF<sub>6</sub>, LiSbF<sub>6</sub> – toxic, unstable;
- LiTf, LiFSI, LiTFSI, LiBETI – aluminum corrosion, expensive;
- LiBOB, LiDFOB, LiPF<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>) – form unstable SEI;
- LiTFSM, LiTFAB – expensive manufacturing;
- Imidazole-BF<sub>3</sub> family – low conductivity;
- Aluminum salts family – low conductivity and unstable at required potential range;
- Azole salts family (e.g. LiTDI).

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## But not these salts...



- ClO<sub>4</sub><sup>-</sup> – explosive, particularly when in contact with transition metals;
- AsF<sub>6</sub><sup>-</sup> and SbF<sub>6</sub><sup>-</sup> are toxic;
- PF<sub>6</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup> – easily decompose:  
 $\text{BF}_4^- \rightarrow \text{BF}_3 + \text{F}^-$      $\text{PF}_6^- \rightarrow \text{PF}_5 + \text{F}^-$   
 PF<sub>6</sub><sup>-</sup> decompose in a presence of even traces (1/1 000 000) of water or acid;  
 $\text{PF}_5 + \text{H}_2\text{O} \rightarrow \text{POF}_3 + 2\text{HF}$  (both toxic)
- TFSI and BETI – corrode aluminum (that makes current collectors in cell);

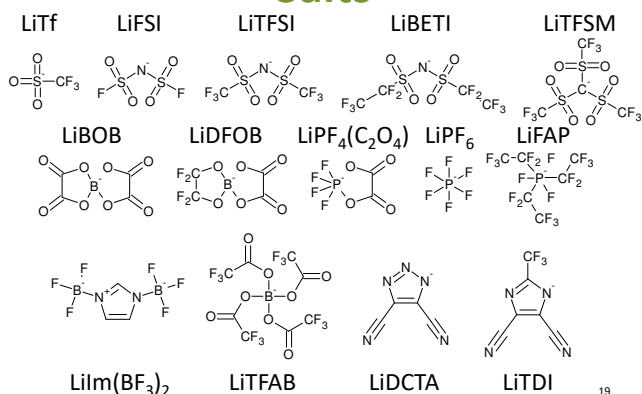
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## But not this salts...

LiPF<sub>6</sub> is so far the dominant salt in the battery market despite its known disadvantages (that is why so many substitutes were proposed over the past 30 years):

- Decomposition to toxic, caustic and carcinogenic compounds (e.g. HF, POF<sub>3</sub>) upon contact with even traces of water (as low as 1 ppm, so with every solvent used, which usually contain up to 30 ppm) – that is why Li-ion cells should not be opened;
- Thermal decomposition starting from 70°C on (that is why there are warning labels on batteries against putting them into the direct sunlight, close to heat sources and heating above 60°C);
- Incompatibility with new electrode generations (both anodes – e.g. silicon, and cathodes – e.g. silicates);
- Low cycle efficiency (one of the reasons is low T<sub>Li+</sub> ≈ 0.3);

## Salts



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## Salts in practice

- LiPF<sub>6</sub> is used in almost all commercially available cells (in all electronic devices available on consumer market);
- Since 2018 in many cells for high-end mobile electronics and electric vehicles there is a second salt in the history of lithium-ion cells used – LiTDI – as a main salt or as a second salt to support LiPF<sub>6</sub> (20-66% of LiPF<sub>6</sub> content);
- LiBF<sub>4</sub> is often used in primary lithium cells, but in acetonitrile, PC or GBL as a solvent due to its low price, lack of safety requirements (like in case of Li-ion cells) and no presence of transition metals in a cell;

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## Anion design

Unification of charge distribution over anion through:

- the use of aromatic/heteroaromatic rings;
- symmetrical design
- flat shape, or shape that have multiple symmetry planes;
- multiple tautomeric forms;
- presence of electron withdrawing groups (e.g. -CF<sub>3</sub>, -CN);
- presence of groups containing fluorine, but not fluorine itself (-CF<sub>3</sub> group keeps fluorine strongly at carbon).

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## What should not be done when designing anions

- The use of highly electronegative elements in the anion (those to the right on periodic table);
- The use of functional groups or atoms with high electron density/free electron pairs.

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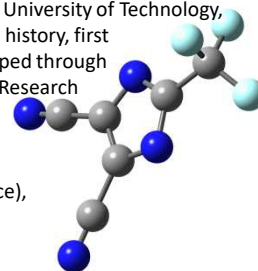
## What also should not be done when designing anions

- Too big structure (viscosity increases);
- Too long atomic chains (spatial effects and chain movements, a large number of degrees of freedom);
- Slowing down the anion at all cost (through increasing the size of the anion or use of additives inhibiting movement/trapping anion) – there is always some anion-cation interaction, so slowing down the anion indirectly results in slowing down the cation;
- The use of groups that react with water or oxygen (it makes dealing with such salts and electrolytes much harder).

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## LiTDI salt – Polish product

Salt designed and developed at Warsaw University of Technology, second salt in the 30 years of Li-ion cells history, first European salt. Patented in 2008, developed through cooperation within ALISTORE European Research Institute. Wide cooperation just like any other large modern invention: Warsaw University of Technology, Universite de Picardie Jules Verne (France), Sapienza Universita di Roma (Italy), Uppsala University (Sweden).

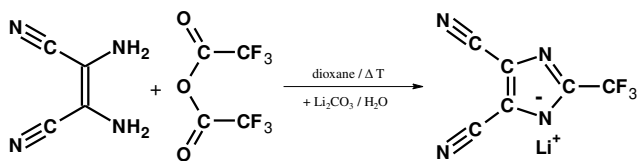


Commercialization in 2010-2018 by French company Arkema.

- Siemens Award
- Prime Minister of Poland Award
- WUT President Award
- Ignacy Mościcki Science Award

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## LiTDI salt



- Low cost (cheap substrates), on-step and one-pot synthesis with high efficiency and no special requirements towards substrates purity, particular impurities level or atmosphere – contrary to  $\text{LiPF}_6$ .

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## LiTDI salt

LiTDI:

- is stable up to  $256^\circ\text{C}$ ; up to 4.7 V vs lithium and does not corrode aluminum; is stable against/in water;
  - does not require stabilizing additives or acid/water sorbents (like  $\text{LiPF}_6$ );
  - has higher  $\text{Li}^+$  cation transference number (over 0.5) and the same effective conductivity (of  $\text{Li}^+$  cations);
  - is compatible with new electrode materials;
  - is not as toxic as  $\text{LiPF}_6$  and is not decomposing to the toxic compounds (but keep protecting your eyes);
- It is the first salt that fulfills all industrial requirements toward lithium salts since the beginning of Li-ion cell industry (30 years).

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## LiTDI salt

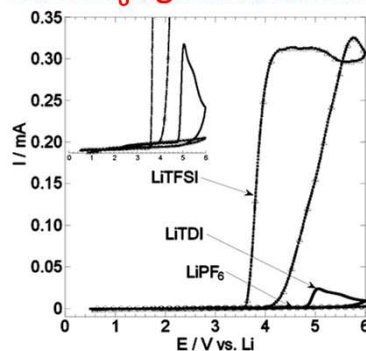
Additionally, LiTDI salt thanks to its property of stable water complexing (without a loss of salt functional parameters) is effective water scavenger – drying up the rest of the cell and extending its life that way, e.g. by hindering the cathode material corrosion.

Thanks to that LiTDI is used also as an additive for standard electrolytes, which extends cell life by the factor of 2-3.

It particularly well extends cell life at higher temperatures, at which standard electrolytes based on  $\text{LiPF}_6$  very quickly cease to work. For instance, at  $45^\circ\text{C}$  (temperature of smartphone during quick charge or when playing 3D game) cell with  $\text{LiPF}_6$  works up to 200 cycles, but with LiTDI it easily work over 1000 cycles, or if LiTDI is an additive for  $\text{LiPF}_6$ , then up to 700 cycles.

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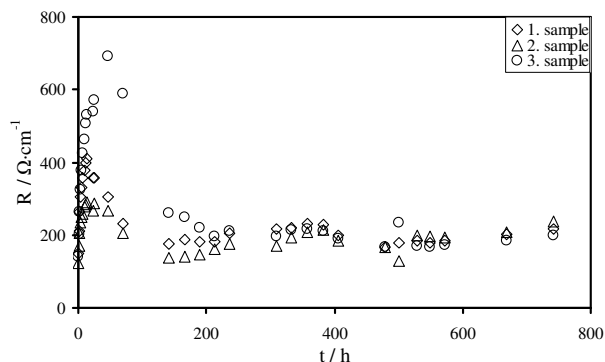
## Electrochemical stability of LiTDI and $\text{LiPF}_6$ against aluminum



L. Niedzicki, G.Z. Zukowska, M. Bukowska, P. Szczecinski, S. Grugeon, S. Laruelle, M. Armand, S. Panero, B. Scrosati, M. Marciniek, W. Wieczorek, *Electrochim. Acta* 55 (2010) 1450.

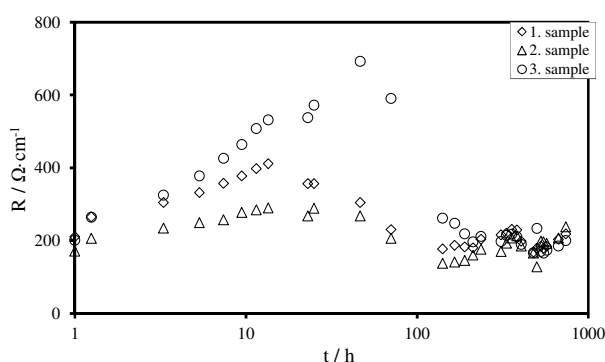
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## Chemical stability of LiTDI (storage time)

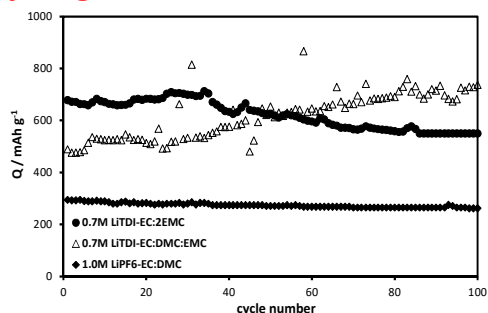


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## Chemical stability of LiTDI (storage time)



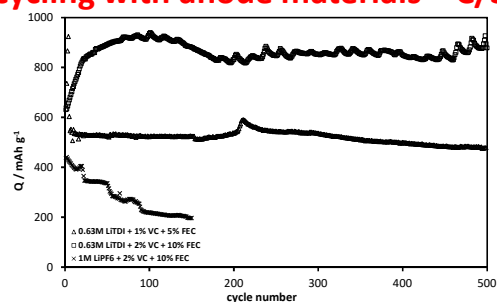
## Stability of LiTDI and LiPF<sub>6</sub> during cycling with anode materials – C/Si



L. Niedzicki, B. Brzozowski, P. Wleczorek, *Electrochim. Acta* 174 (2015) 625.

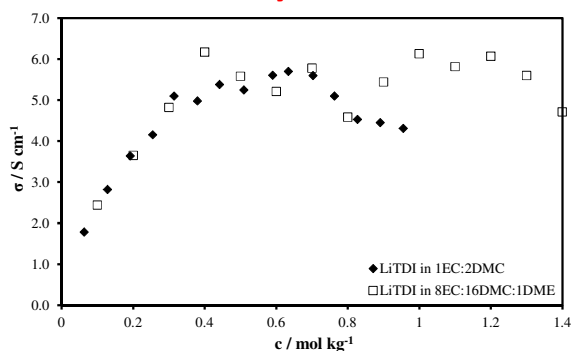
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## Stability of LiTDI and LiPF<sub>6</sub> during cycling with anode materials – C/Si



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## LiTDI in battery solvent mixtures



L. Niedzicki, E. Karpierz, A. Bitner, M. Kasprzyk, G.Z. Zukowska, M. Marcinek, W. Wleczorek, *Electrochim. Acta* 117 (2014) 224.

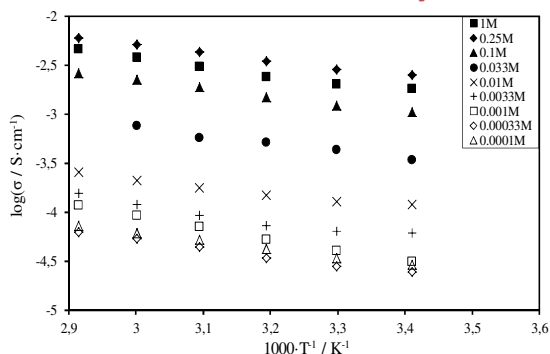
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## LiTDI in battery solvent mixtures

mixture	$\sigma / \text{mS cm}^{-1}$	$T_{\text{Li}^+}$	$\sigma_{\text{Li}^+} / \text{mS cm}^{-1}$
0.3 mol/kg LiTDI in EC:DEC:DMC (1:1:1)	5.52	0.333	1.84
0.7 mol/kg LiTDI in EC:DEC:DMC (1:1:1)	4.96	0.497	2.47
0.4 mol/kg LiTDI in EC:DEC (1:2)	3.24	0.601	1.95
0.7 mol/kg LiTDI in EC:DEC (1:2)	3.51	0.563	1.98
0.31 mol/kg LiTDI in EC:DMC (1:2)	5.09	0.622	3.17
0.63 mol/kg LiTDI in EC:DMC (1:2)	5.70	0.553	3.15
0.3 mol/kg LiTDI in EC:DEC:DME (8:16:1)	4.07	0.614	2.50
0.5 mol/kg LiTDI in EC:DEC:DME (8:16:1)	4.35	0.850	3.69
1.2 mol/kg LiTDI in EC:DEC:DME (8:16:1)	3.74	0.666	2.49
0.4 mol/kg LiTDI in EC:DMC:DME (8:16:1)	6.17	0.648	4.00
1 mol/kg LiTDI in EC:DMC:DME (8:16:1)	6.13	0.731	4.48
1 mol/kg LiPF <sub>6</sub> in EC:DEC:DMC (1:1:1)	10.08	0.244	2.46
1 mol/kg LiPF <sub>6</sub> in EC:DMC (1:2)	10.15	0.350	3.55

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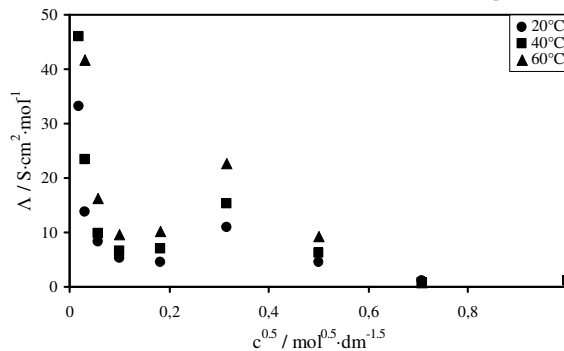
## TDI-PC conductivity



L. Niedzicki, M. Kasprzyk, K. Kuziak, G.Z. Zukowska, M. Marcinek, W. Wleczorek, M. Armand, *J. Power Sources* 196 (2011) 1386.

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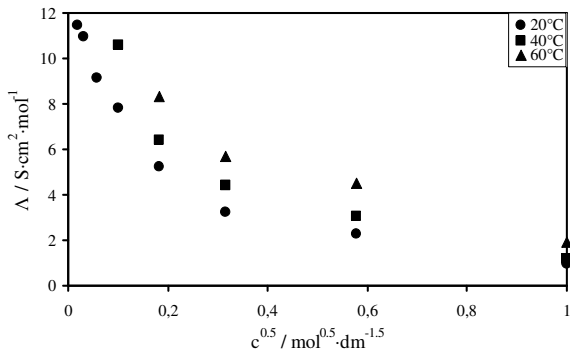
## TDI-PC molar conductivity



L. Niedzicki, M. Kasprzyk, K. Kuziak, G.Z. Zukowska, M. Marcinek, W. Wleczorek, M. Armand, *J. Power Sources* 196 (2011) 1386.

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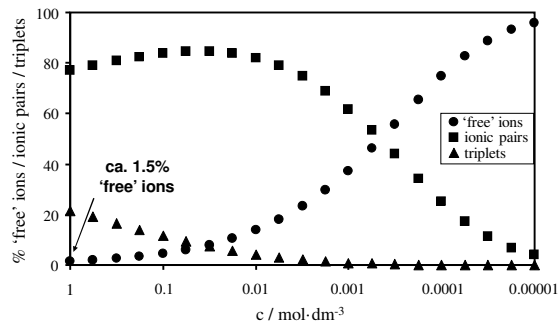
## HDI-PC molar conductivity



L. Niedzicki, M. Kasprzyk, K. Kuziak, G.Z. Zukowska, M. Marcinek, W. Wiecek, M. Armand, J. Power Sources 196 (2011) 1386.

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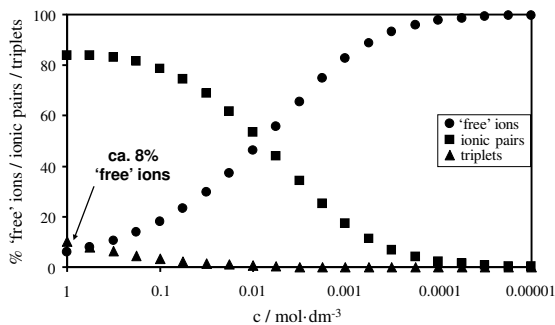
## TDI-PC association



L. Niedzicki, M. Kasprzyk, K. Kuziak, G.Z. Zukowska, M. Marcinek, W. Wiecek, M. Armand, J. Power Sources 196 (2011) 1386.

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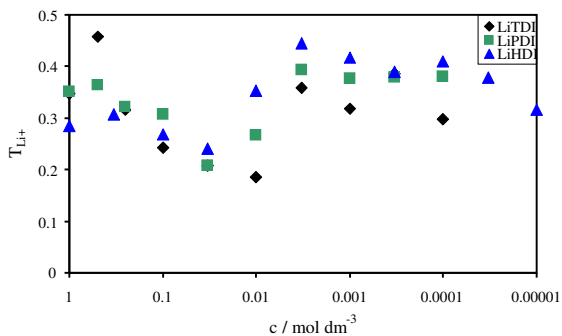
## HDI-PC association



L. Niedzicki, M. Kasprzyk, K. Kuziak, G.Z. Zukowska, M. Marcinek, W. Wiecek, M. Armand, J. Power Sources 196 (2011) 1386.

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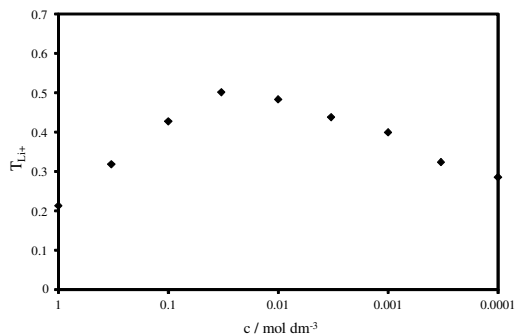
## Lithium cation transference numbers in imidazoles in PC



L. Niedzicki, M. Kasprzyk, K. Kuziak, G.Z. Zukowska, M. Marcinek, W. Wiecek, M. Armand, J. Power Sources 196 (2011) 1386.

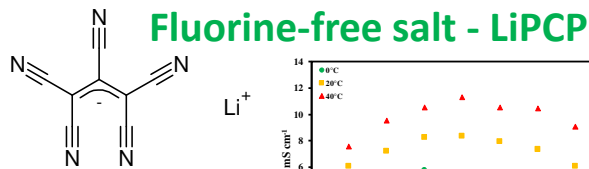
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## Lithium cation transference numbers in imidazoles in PEG

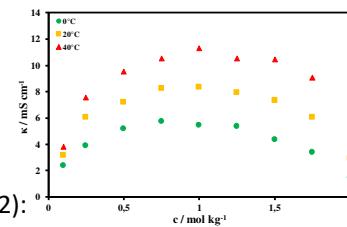


L. Niedzicki, M. Kasprzyk, K. Kuziak, G.Z. Zukowska, M. Armand, M. Bukowska, M. Marcinek, P. Szczepinski, W. Wiecek, J. Power Sources 192 (2009) 612.

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- Fluorine-free (first in history)
- LiPCP in EC:DMC (1:2):
  - high conductivity -  $\sigma > 8 \text{ mS cm}^{-1}$
  - high  $t_{Li^+} > 0.5$
  - electrochemical stability up to 4.4 V vs Li (does not corrode aluminum)
  - thermal stability up to **280°C**



L. Niedzicki et al., patent PL 232856

## Electrolyte types

- Liquid
- Gel
- Liquid polymer (oligomer)
- Solid polymer (SPE)
- Polyanions
- Ceramic
- Ionic liquids
- Composite (e.g. gel with ceramic additive)

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## Solid electrolytes

Solid electrolytes, more precisely Solid Polymer Electrolytes (SPE) are materials conducting ions designed in such a way that they could replace liquid electrolytes. SPE (based on PEO) have following advantages compared to liquid electrolytes:

- are non-flammable (they are not volatile);
- buffer electrode density (volume) change (are flexible);
- cannot leak in case of cell damage.

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## Solid electrolytes

SPEs (based on PEO) have unfortunately some disadvantages as well, comparing to liquid electrolytes (and that is why they are not used yet in commercially available cells apart from high-temperatures, but they are still considered the future of the battery industry thanks to their high safety properties):

- very poor conductivity (usually  $<0.1 \text{ mS cm}^{-1}$  at  $20^\circ\text{C}$ );
- poor parameters at low temperatures (which means  $<40^\circ\text{C}$ , the lower, the worse);
- poor contact with electrodes (points of contact);
- low lithium cation transference numbers (usually  $<0.2$ );
- stability of PEO (without costly modifications) only up to 4 V vs Li;
- some can react with metallic lithium.

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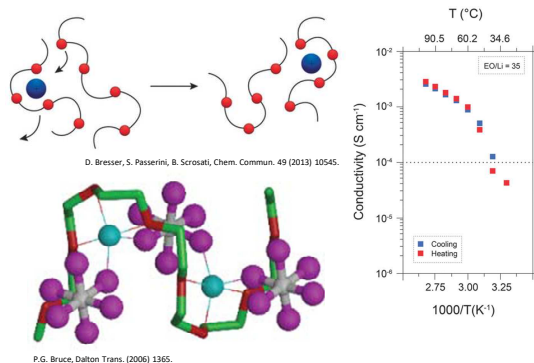
## Solid electrolytes

SPE are usually based on PEO (poly(ethylene oxide)  $(-\text{CH}_2\text{CH}_2\text{O}-)_n$ ), but it still gives a large room for maneuver. First of all, polymer can be copolymerized (during polymerization, structural units (mers) of other polymers can be added), chains can be branched (including hyperbranching), plasticizers can be added that make SPE to have better properties at low temperatures and higher conductivity. Ceramic additives can be added to decrease polymer crystallinity degree.

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## Solid electrolytes

Lithium cation movement mechanism in PEO:



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## Solid electrolytes

PEO conducts mostly in its amorphous form. Li-PEO complex forms in amorphous phase in ratio that allows lithium cations to easily move along the polymer chain and between them as well as allows for some chain movement (increases their degree of freedom). Unfortunately, PEO below  $65^\circ\text{C}$  crystallizes to a large extent. Ionic conductivity occurs also in a crystalline phase (in crystallites with a Li:EO ratio of 1:6, but not 1:3, as there is no 'free' sites on the chain for jump between them). However, conductivity in crystalline phase suffers much when temperature is below  $60^\circ\text{C}$ .

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## Solid electrolytes

Use of additives that decrease crystallinity degree and/or disable crystallites formation as well as salt choice and salt-to-polymer ratio allows to bring down the temperature at which SPE have large spike of conductivity. Unfortunately, all attempts to bring down this temperature clearly below 40°C failed so far. Such achievement would enable manufacturing of cells that would operate properly at room temperatures or even lower (otherwise big losses of energy and energy density are required for heating and due to thermal insulation use).

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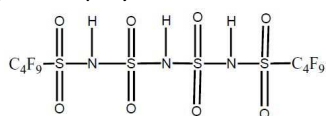
## Polyanionic electrolytes

Polyanions are subtype of SPEs. Polyanions are polymers that possess at least one functional group per structural unit (mer) that can dissociate (carboxylic group, for instance) and form stable anion group (negatively charged). The common groups are  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$  and also some polymers containing amide group ( $-\text{C}(\text{O})\text{NH}-$ ). Separate type of polyanions are polyacids, e.g. polyphosphoric or recently synthesized TFSI-based oligomers, of the  $\text{CF}_3-(\text{SO}_2-\text{NH})_n-\text{SO}_2-\text{CF}_3$  type or polymer containing  $(-\text{SO}_2-\text{NH}-\text{SO}_2-\text{CF}_3)$  group.

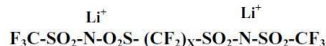
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## Polyanionic electrolytes

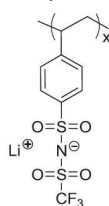
Polyanions conduct similarly to SPEs, i.e. conductivity does not exceed  $0.1 \text{ mS cm}^{-1}$  at room temperature. Some have very high lithium cation transference numbers ( $T_+ > 0.9$ ), but at the cost of conductivity. Oligomeric polyanions have low  $T_+$  ( $< 0.2$ ).



J. Nie, X. Li, D. Liu, R. Luo, L. Wang, J. Fluor. Chem. 125 (2004) 27.



O.E. Geiculescu, Y. Xie, R. Rajagopal, S.E. Creager, D.D. DesMarceau, J. Fluor. Chem. 125 (2004) 1179.



S. Feng, D. Shi, F. Liu, L. Zheng, J. Nie, W. Feng, X. Huang, M. Armand, Z. Zhou, Electrochim. Acta 93 (2013) 254.

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## Gel electrolytes

Gel electrolytes are a concept combining SPEs and liquid electrolytes, thanks to which they have advantages of both types while minimizing their disadvantages. Among the advantages are:

- high conductivity (close to the liquid, when compared to the actual conductivity of liquid electrolytes after taking into account the separator);
- good mechanical properties, close to that of SPE;
- electrochemical stability closer to that of liquid (e.g.  $>4.5 \text{ V}$  vs Li);
- damaged cells won't leak (capillary forces keep liquid electrolyte in pores even under high underpressure);

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## Gel electrolytes

Gel electrolytes disadvantages are:

- high manufacturing cost;
- issues with contact with the electrodes (like SPEs);
- PVdF-HFP can decompose in the presence of metallic lithium;
- mechanical properties are worse than those of SPE.

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## Gel electrolytes

Gel electrolytes idea consists in keeping the liquid electrolyte in pores of the material, which can be made of SPE. PVdF-HFP contains crystalline phase, which has a role of keeping mechanical properties of the electrolyte (forms a skeleton of a structure). Amorphous phase with liquid electrolyte forms kind of a solid electrolyte at the interphase layer. Its conductivity is close to that of a liquid electrolyte (due to its large share of a material).

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## Gel electrolytes

Gel electrolyte is usually produced by the Bellcore method (from the name of the first company to use it commercially). Polymer (PVdF-HFP) is dissolved in the mixture of volatile solvent (acetone, sometimes AN or NMP) and low volatile solvent (DBF – dibutyl phthalate; or other solvent that does not mix with the volatile one, like cyclohexane). Subsequently, the volatile solvent is evaporated and from the resulting membrane the low volatile solvent is extracted (by means of diethyl ether for instance, or evaporated in very harsh conditions – T,p). The pores formed upon extraction of the low volatile solvent are filled with liquid electrolyte (by soaking membrane in it). Such electrolyte is almost impossible to remove from those pores. Pores diameter is typically much lower than 500 nm.

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## Gel electrolytes

Other, now-legacy method consists in impregnation of SPE with a solvent (plasticizer). Such method was abandoned due to the poor mechanical parameters of resulting electrolyte.

Modification that links old and new methods bases on the same process as Bellcore method, but salt is dissolved along with the polymer and after evaporation and extraction of supporting solvents, then resulting membrane is soaked in the electrolyte solvent.

Battery industry predominantly uses Bellcore method.

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## Ceramic electrolytes

Ceramic electrolytes are not based on dissociated salts conductivity like all the previous ones. Instead, they base on defects movement in crystalline/amorphous structure that has ionic-like character. Such movement requires energy (activation energy, like any process), so the higher temperature, the better conductivity. Thus, ceramic electrolytes find use in high-temperature cells (Na-S, ZEBRA). However, in the recent years some electrolytes appeared on the market that have room temperature conductivity close to the liquid electrolytes ( $10^{-5}$ - $10^{-4}$ , or even closer to  $10^{-3}$  S  $\text{cm}^{-1}$ ).

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## Ceramic electrolytes

Ceramic electrolytes are mainly mixed glass-crystal materials. While lithium is a mandatory component of such materials, other dominating components are sulfur and/or phosphorous, e.g.:  $(1-x)\text{Li}_2\text{S}-x\text{P}_2\text{S}_5$  (at  $x=0.3$  it is reference material for most ceramic materials classes). Moreover, conductivity is enhanced by a presence of atoms of elements from IV group (14) e.g.:  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_2\text{S}-\text{SiS}_2(+\text{Li}_3\text{PO}_4)$ ,  $\text{Li}_2\text{S}-\text{Ga}_2\text{S}_3-\text{GeS}_2-\text{LiI}$ . Recently, nonstoichiometric doped materials became popular, for instance:  $\text{Li}_{3+x}\text{Ge}_x\text{P}_{1-x}\text{S}_4$  (e.g.  $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ ). Also popular are perovskite-like structured materials, for instance:  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$  (e.g.  $\text{Li}_{0.36}\text{La}_{0.54}\text{TiO}_3$ ).

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## Thin film cells

Thin film cells are cells that consist of thin layers of (usually) solid electrolytes (ceramic or SPEs for flexible applications) and electrodes. They are usually manufactured using CVD technology (Chemical Vapor Deposition), ALD (Atomic Layer Deposition), sometimes even linked with epitaxial techniques (depending on electrodes composition). Whole cell has usually thickness of 0.1 mm order of magnitude (from ca. 50  $\mu\text{m}$  up to about 1 mm). Capacity of such cells is from 100  $\mu\text{Ah cm}^{-1}$  up to ca. 3  $\text{mAh cm}^{-1}$ . thin film cells are used in small remote sensors (particularly passive ones), RFID tags or to power chips on credit or ID cards, etc.

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## Thin film cells

Electrode materials in thin film cells are the same as those in typical cells (with more fine grains maybe). Due to the solid state of components, there can be large savings in container (both cost and volume). One can also immerse whole cell in a final product (e.g. credit card).



Infinite Power Systems Technical White Paper - May 2012.  
„Organic-free, all-solid-state thin-film batteries for cell phones, tablets, and future devices“

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## Ionic liquids

Ionic liquids (IL) consist of ions only and are actually salts that have melting points below 100°C. For practical reasons, group of ILs that are liquid from or below room temperature (RT) is treated separately and is called RTIL. For battery applications electrolyte melting point should be below 0°C, obviously. ILs have very diverse compositions, as multiple organic and inorganic structures can be used for anions and cations for ILs. So far there are at least few hundred cations and few dozens anions identified that can be used to form ILS (although not every cation with every anion combination of those can form IL).

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## Ionic liquids

For application in Li-ion cells (due to requirements of oxidation and reduction resistance in broad range of potentials) there are few dozens cations and about a dozen anions identified so far:

Typical anions used in ILs are the same as those used to form salts for Li-ion cells liquid electrolytes:

$\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{B}(\text{C}_2\text{O}_4)_2^-$ ,  $\text{BF}_2(\text{C}_2\text{O}_4)^-$ ,  $\text{B}(\text{OC}(\text{O})\text{CF}_3)_4^-$ ,  $\text{B}(\text{CN})_4^-$ ,  $\text{SO}_3\text{CF}_3^-$ ,  $\text{N}(\text{SO}_2\text{F})_2^-$ ,  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ ,  $\text{N}(\text{SO}_2\text{CF}_2\text{CF}_3)_2^-$ ,  $\text{C}(\text{SO}_2\text{CF}_3)_3^-$ ,  $\text{PF}_3(\text{CF}_2\text{CF}_3)_3^-$ , as well as experimental ones, for instance DCTA and TDI.

Most popular are  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{SO}_3\text{CF}_3^-$  (Tf),  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$  (TFSI) i  $\text{PF}_3(\text{CF}_2\text{CF}_3)_3^-$  (FAP).

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## Ionic liquids

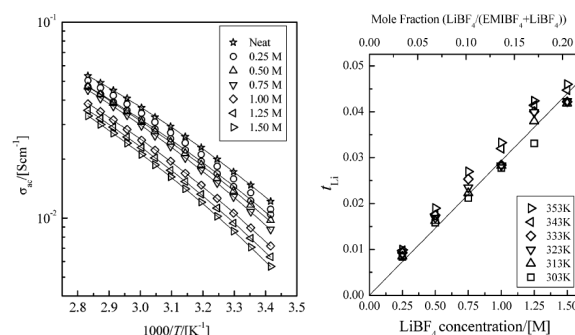
Cations with potential for ILs application in Li-ion cell electrolytes are:

- imidazolide (typically 1-alkyl-3-methylimidazole or 1-alkyl-2,3-dimethylimidazole, where alkyl has 2-8 carbons, usually even number);
- pyrrolidine (e.g. 1-methyl-1-alkylpyrrolidine, where alkyl can be simple or branched chain);
- ammonium (asymmetric tetraalkylammonium or trialkylaloxammonium);
- piperidine (N-alkyl-N-methylpiperidine);
- pyridine (N-alkylpyridine, where alkyl can be simple or branched chain);
- phosphonium (asymmetric tetraalkylphosphonium where alkyls are at least four carbon simple chains).

In applications imidazoles are predominant, pyrrolidine and piperidine are used to a lesser extent.

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## Traditional ionic liquids



K. Hayamizu, Y. Aihara, H. Nakagawa, T. Nukuda, W.S. Price, *J. Phys. Chem. B* 108 (2004) 19527.

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## Composite electrolytes

Composite electrolytes are electrolytes with mixed composition, linking two or more materials from different class, e.g. SPE with ceramic, liquid with ceramic, SPE with liquid, SPE with ILs. In laboratory scale almost all combinations were at least approached (3 and 4 component combinations as well) with various results. In practice, it is rare to obtain significantly better parameters (synergy) compared to single materials. This class formally includes electrolytes containing ceramic additives. One of the only successful composite materials is gel electrolyte class (liquid+SPE). Presently, extensive studies are conducted around the world on composite electrolytes containing ILs.

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