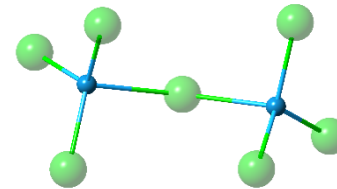
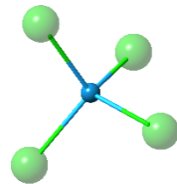




CHALMERS
UNIVERSITY OF TECHNOLOGY

A Challenge for Rechargeable Al Batteries: Departing from $AlCl_3$



Toshihiko Mandai and Patrik Johansson

Department of Applied Physics
Chalmers University of Technology
SE-412 96, Göteborg, Sweden

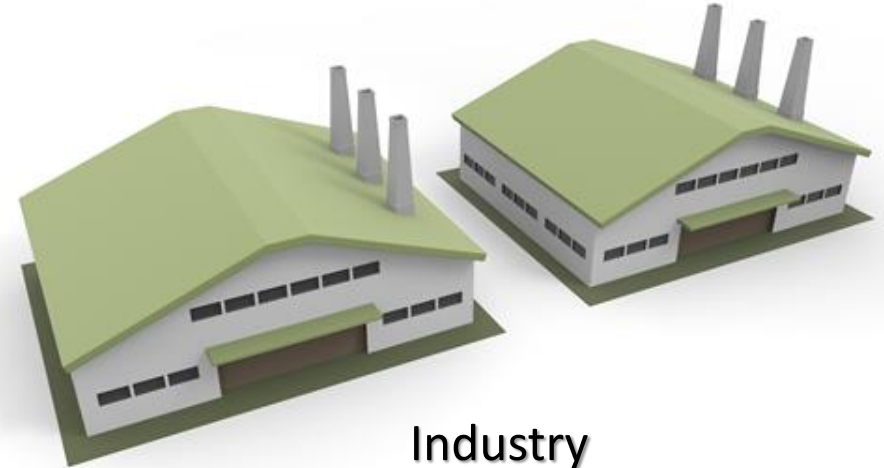
Growing Demands for Electric Power



Portable devices



Portable battery



Industry

Stationary energy storage

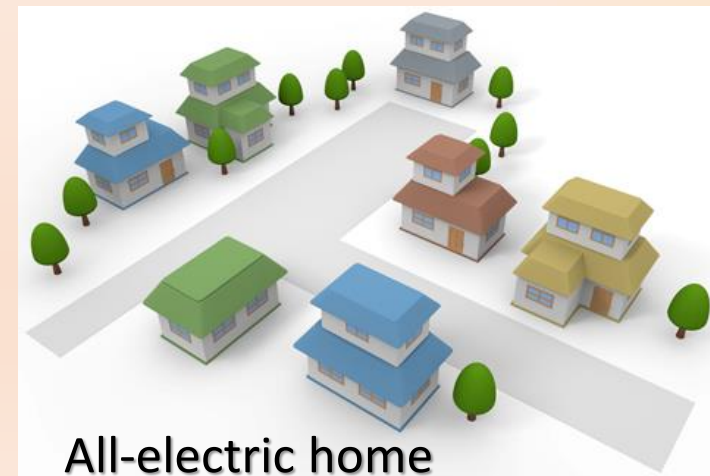


(Nissan Leaf)

Electric cars

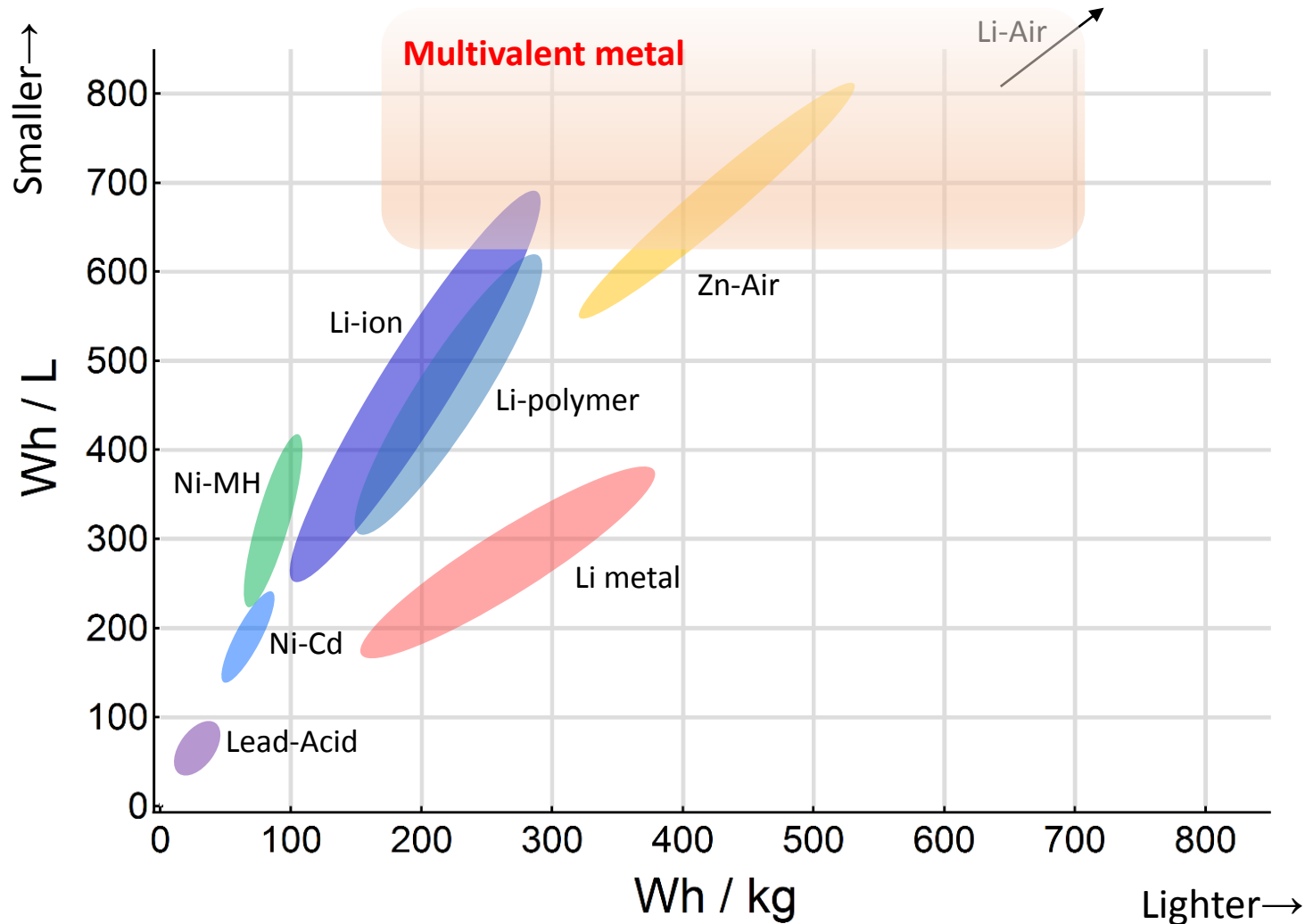


(Lindholmen Science Park)



All-electric home

Post Lithium-ion Battery Technologies



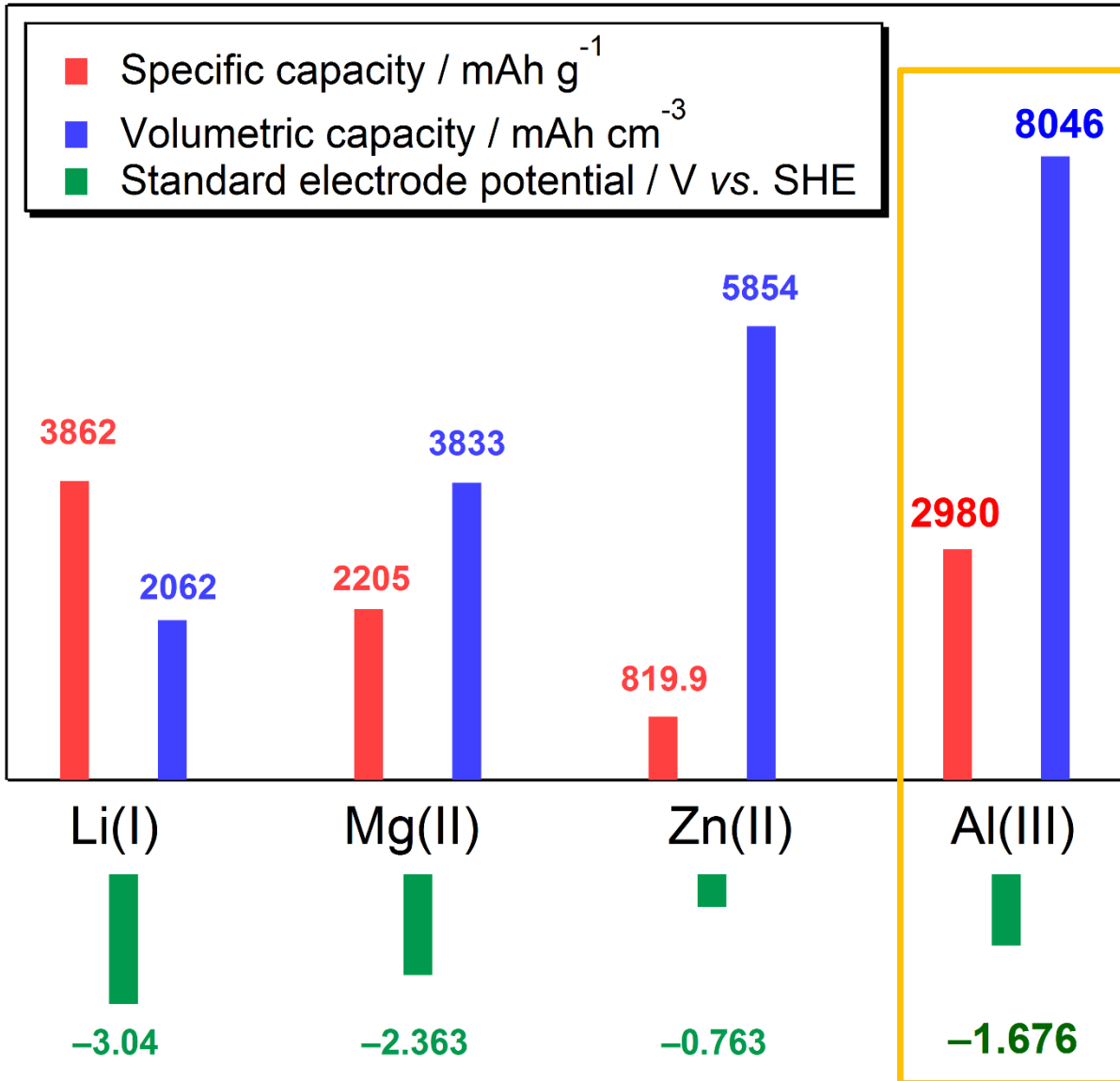
Multivalent metals

Magnesium (Mg^{2+})

Zinc (Zn^{2+})

Aluminium (Al^{3+})

Why Aluminium?



Price of various metals

Metals	Price / \$ kg ⁻¹
Li	6.6
Mg	4.7
Zn	2.4
Al	2.3

Mineral Commodity Summaries 2015

A rechargeable Al-battery is promising especially for large-scale storage

State of the Art: Al Rechargeable Battery

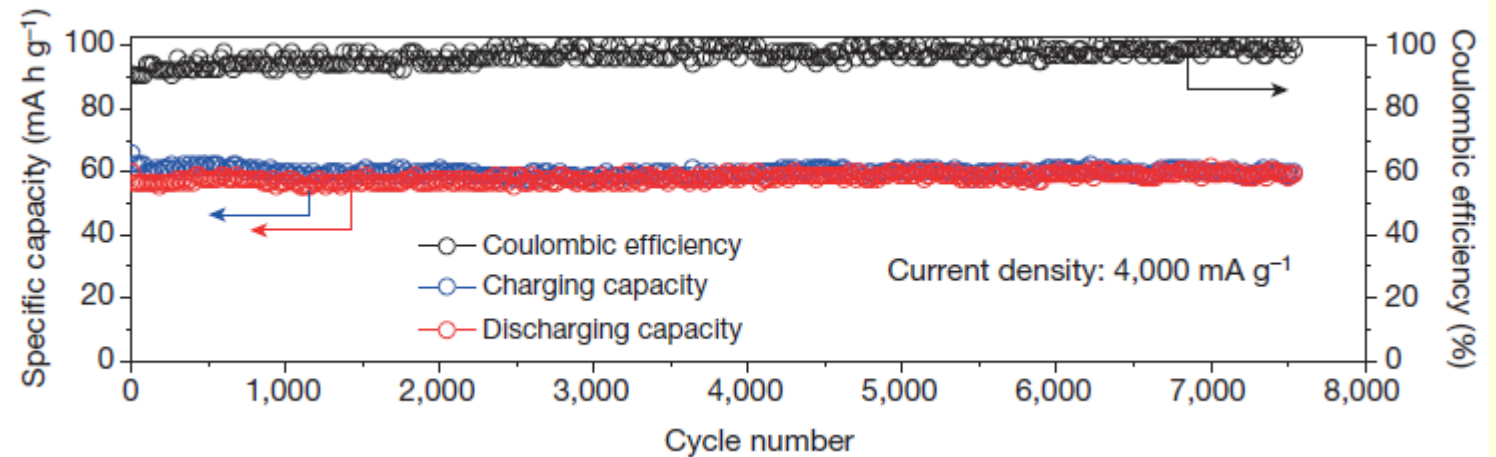
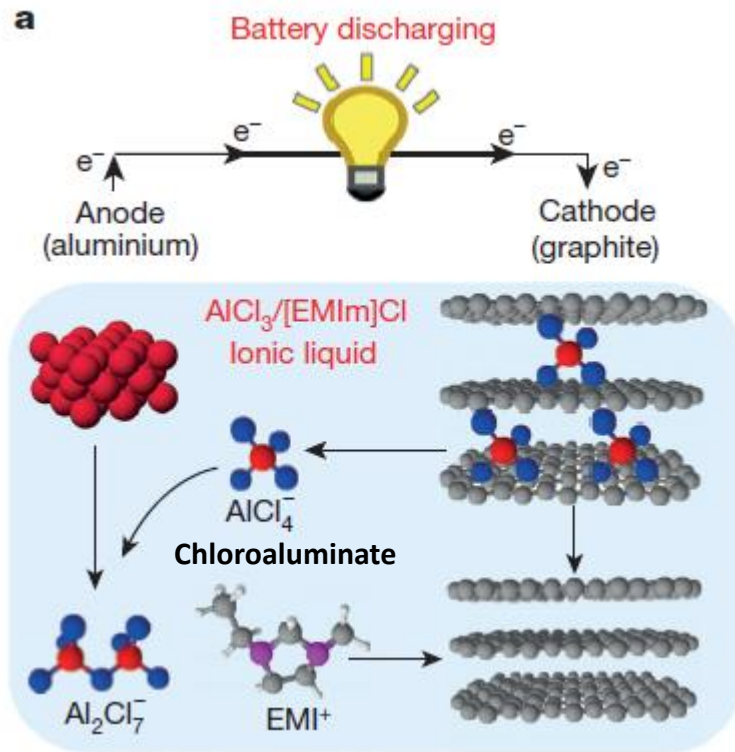
LETTER

doi:10.1038/nature14340

An ultrafast rechargeable aluminium-ion battery

Nature 2015, 520, 324.

Meng-Chang Lin^{1,2*}, Ming Gong^{1*}, Bingan Lu^{1,3*}, Yingpeng Wu^{1*}, Di-Yan Wang^{1,4,5}, Mingyun Guan¹, Michael Angell¹, Changxin Chen¹, Jiang Yang¹, Bing-Joe Hwang⁶ & Hongjie Dai¹



Ultrafast and super-long cycling achieved by:

- i) AlCl_3 -ionic liquid electrolyte,**
- ii) Al metal anode, and**
- iii) special graphite cathode.**

State of the Art: Electrolytes for Al Deposition

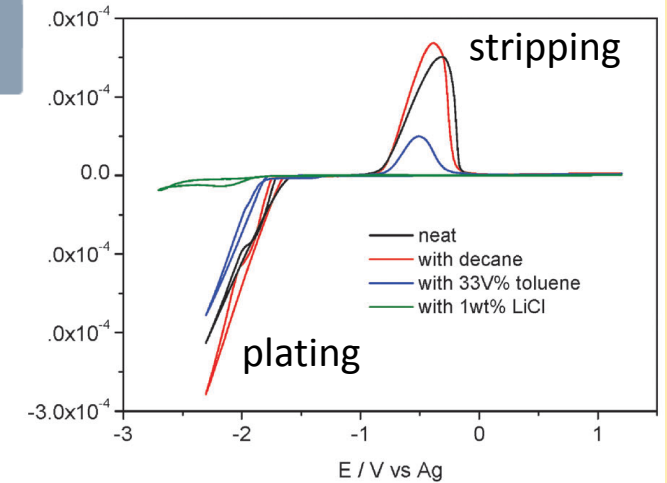
PAPER

[View Article Online](#)
[View Journal](#) | [View Issue](#)

Aluminium electrodeposition under ambient conditions

Cite this: *Phys. Chem. Chem. Phys.*,
2014, 16, 14675

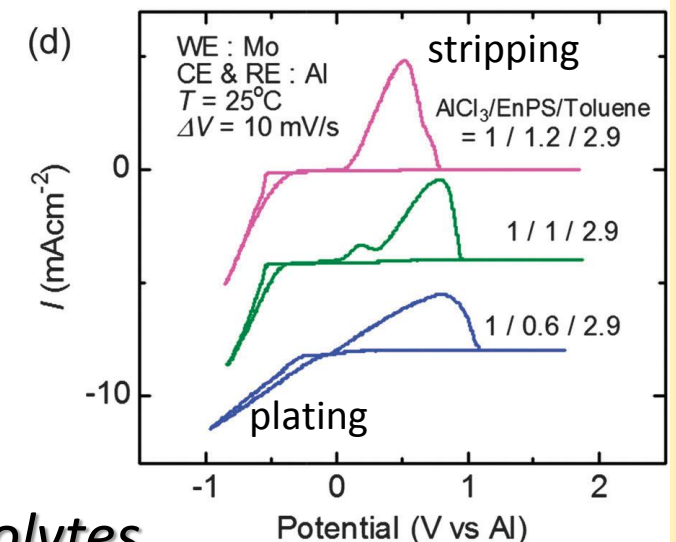
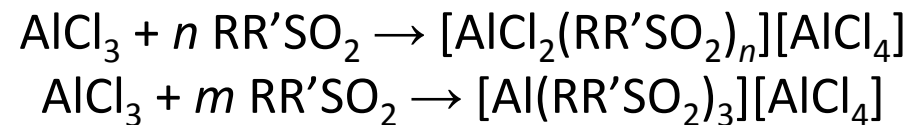
Andrew P. Abbott,^{*a} Robert C. Harris,^a Yi-Ting Hsieh,^{ab} Karl S. Ryder^a and I-Wen Sun^b



Cite this: *Phys. Chem. Chem. Phys.*,
2015, 17, 5758

Sulfone-based electrolytes for aluminium rechargeable batteries†

Yuri Nakayama,^{*a} Yui Senda,^b Hideki Kawasaki,^c Naoki Koshitani,^a Shizuka Hosoi,^a Yoshihiro Kudo,^a Hiroyuki Morioka^a and Masayuki Nagamine^a



Combining **AlCl₃** with appropriate bases result in good Al electrolytes

Problems of $AlCl_3$ -based Electrolytes

✓ Chemical nature of $AlCl_3$

Strong Lewis acid → Catalyst for Friedel-Crafts Reactions



Reactive with moisture and various bases exothermic!!



✓ $AlCl_3$ -based electrolytes



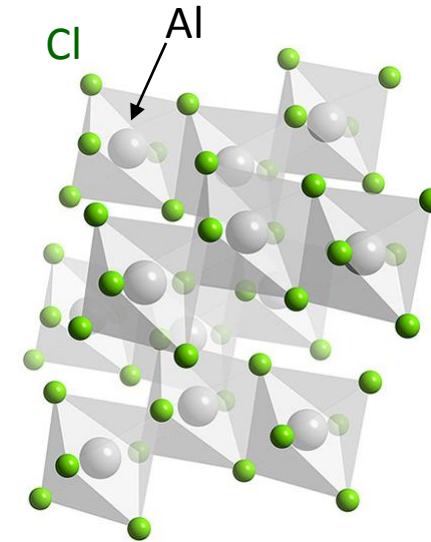
Pros

High ionic conductivity
Excellent electrochemical reactivity

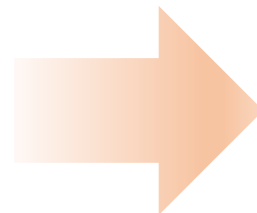


Cons

Thermal-degradation during preparation
Water sensitive
Corrodes various substrates



Polymer form in the solid state
(ChemTube3D, Univ. of Liverpool)



*We should **depart from** $AlCl_3$ -based electrolytes!*

Non-aqueous Al Electrolytes Tested



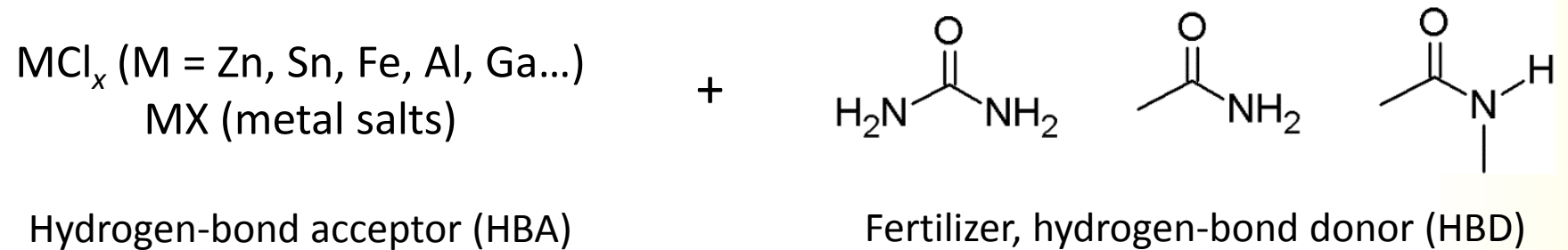
Salt	Solvent	Supporting Salt (with and without)	Salt/Solvent Ratio
Al[TfO] ₃	PC		
	EC		
	THF		
Al[TFSI] ₃	Glymes (G1–G4)	LiTFSI, LiFSI, LiTfO,	1:3-1:19
	Acetonitrile (ACN)		
	Succinonitrile (SN)	NaTFSI, NaFSI, NaTfO,	
Al(NO ₃) ₃	Sulfone series	ILs	
	Dimethyl sulfoxide		
	Ethylene-amine series		
Al(BF ₄) ₃	Conventional ILs		

No electrochemical activity at all → Look for different approach

Possible Candidates for Al-Electrolytes

➤ Deep Eutectic Solvents (DESs)

Fluids composed of mutually miscible several components to form eutectics



Metal-containing materials with low melting points → applicable to electrolytes?

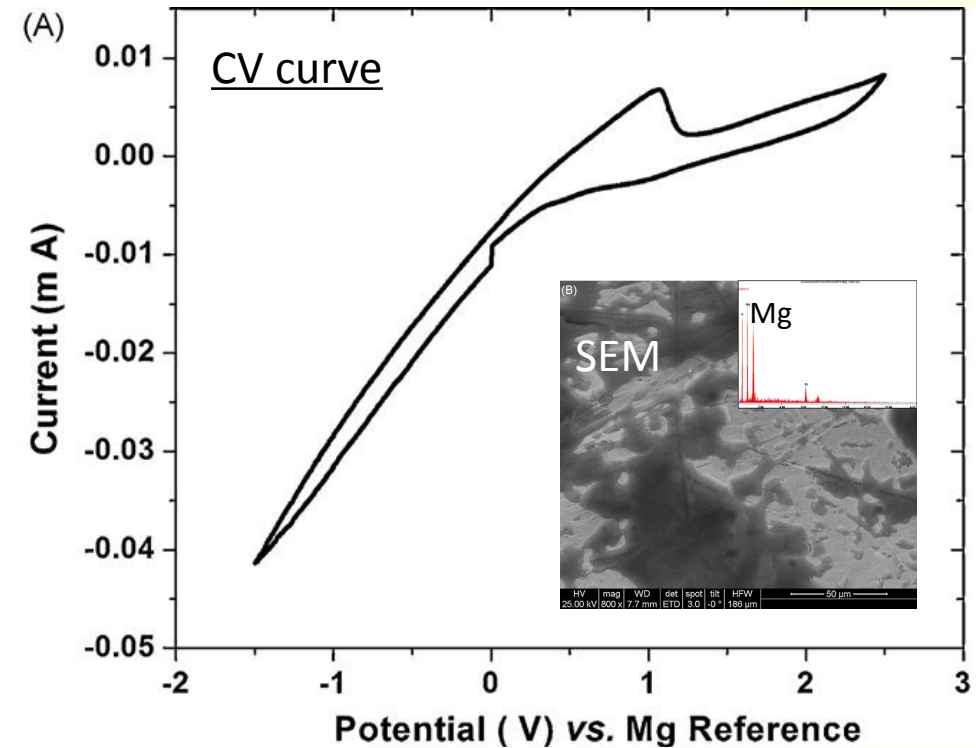
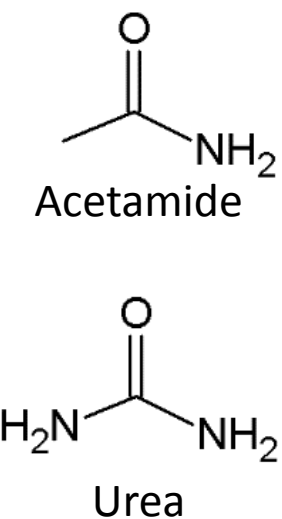
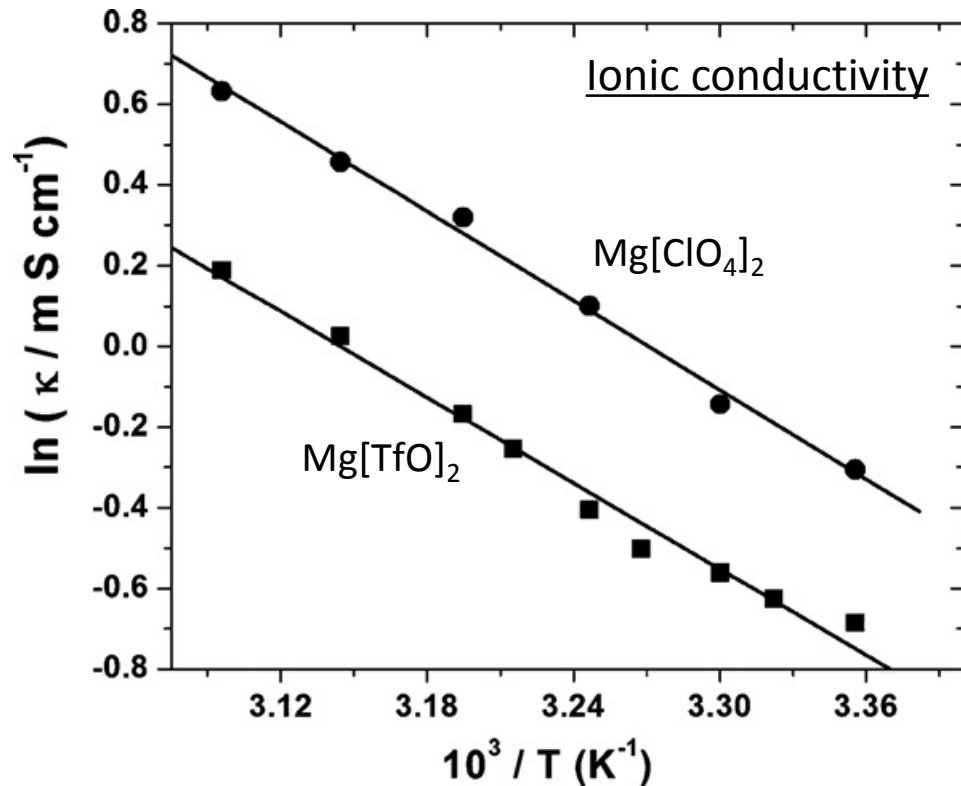
➤ Cationic solvates

=> the electrochemical activity being cationic rather than anionic

Mg-salt + Acylamino-compound Electrolytes

✓ Mg[TfO]₂ or Mg[ClO₄]₂/acetamide/urea (0.05/0.57/0.38) eutectics

N. S. V. Narayanan, et al.,
J. Power Sources **2010**, *195*, 4356.

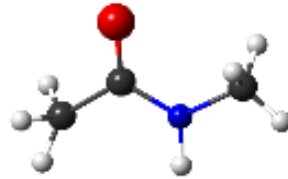
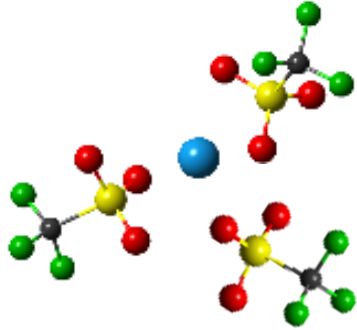


Mg metal can be electroplated from these ternary electrolytes
Approx. analogous electrochemistry of **Mg and Al?**



Apply to **Al electrolyte**

Design of AlCl_3 -free Electrolyte



$\text{Al}[\text{TfO}]_3$ /*N*-methylacetamide (NMA)/urea ternary electrolyte

$\mathbf{M}(x)$, based on the mole fraction of NMA x_{NMA} ($x_{\text{NMA}} = 0.475\text{--}0.832$)

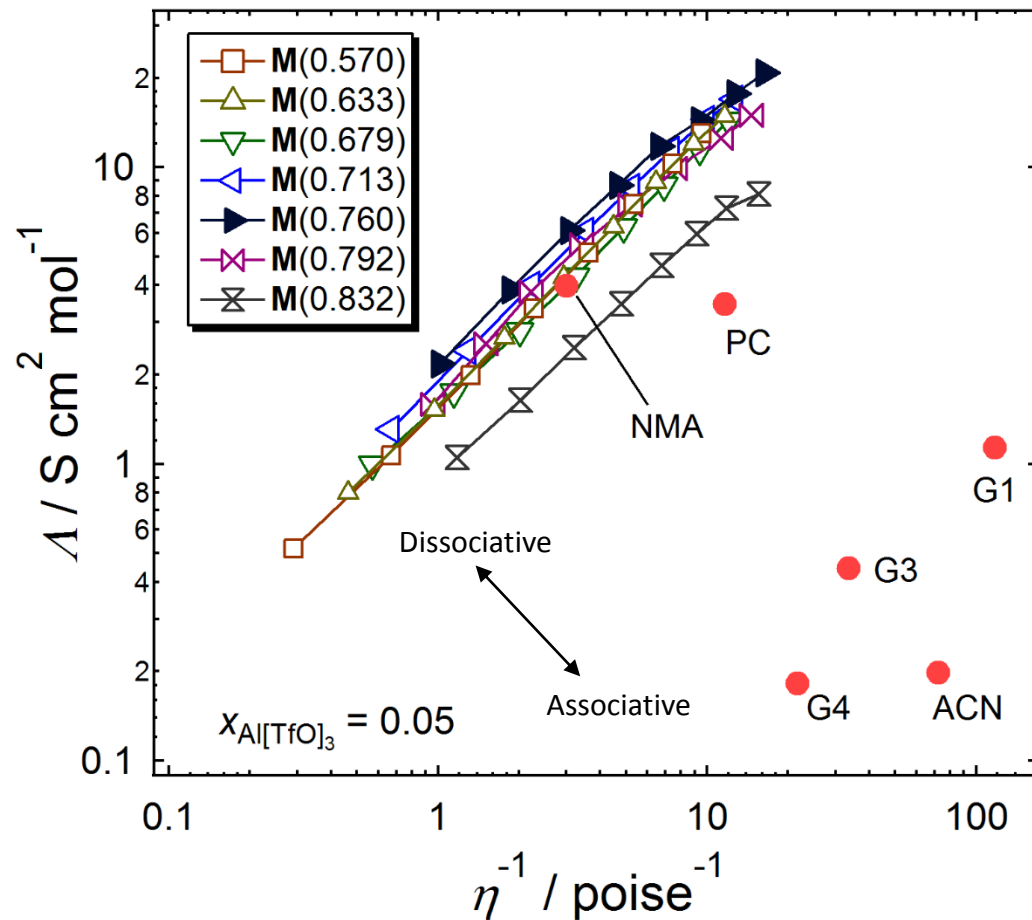
Transport properties

Species determination

Electrochemical properties

Remarkable Solvation Ability of NMA/Urea

✓ Walden plot: Salt dissociation



Physicochemical properties of different electrolytes

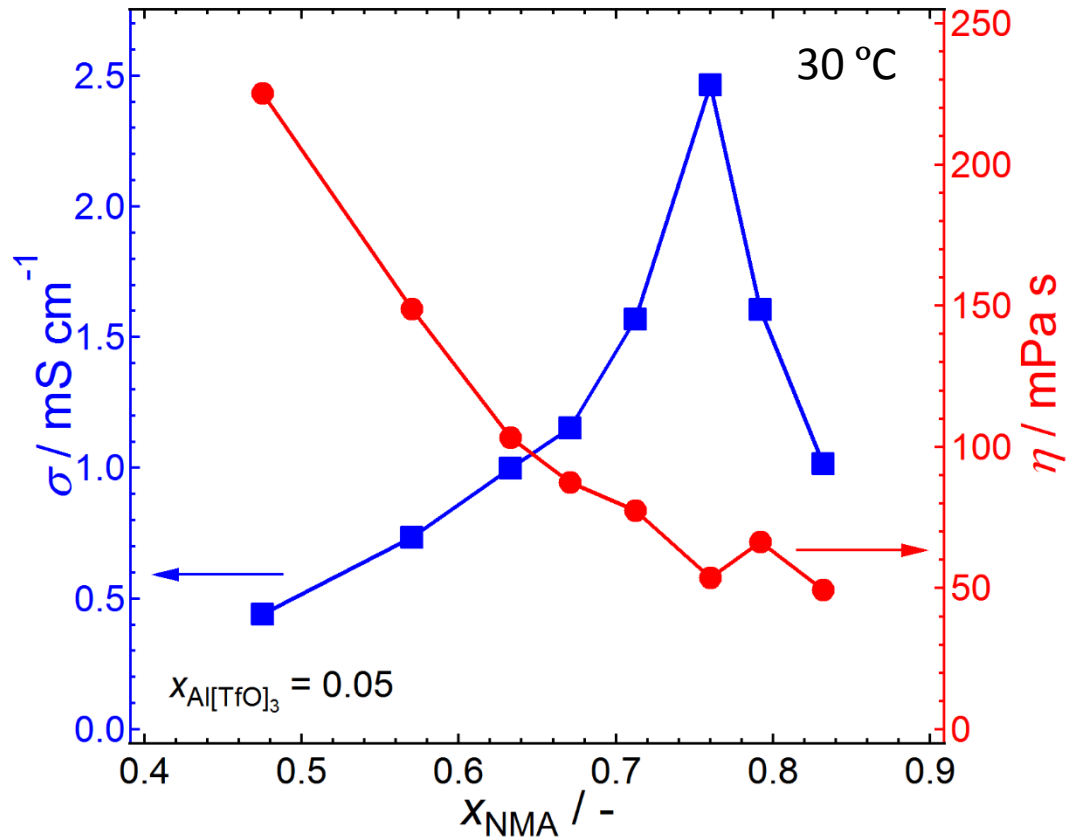
Electrolyte	$c / \text{mol dm}^{-3}$	η / cP	$\sigma / \text{mS cm}^{-1}$	$\epsilon_r / -$
G1	0.456	0.855	0.52	7.07
G3	0.271	2.99	0.12	7.63
G4	0.226	4.63	0.041	7.78
ACN	0.815	1.39	0.16	35.9
PC	0.540	8.63	1.9	62.9
NMA	0.597	33.4	2.4	178
M(0.760)	0.638	53.8	2.5	(81.3)

- Salt dissociation depends on solvent dielectric properties
- NMA/urea => remarkable solvation ability for Al^{3+} .

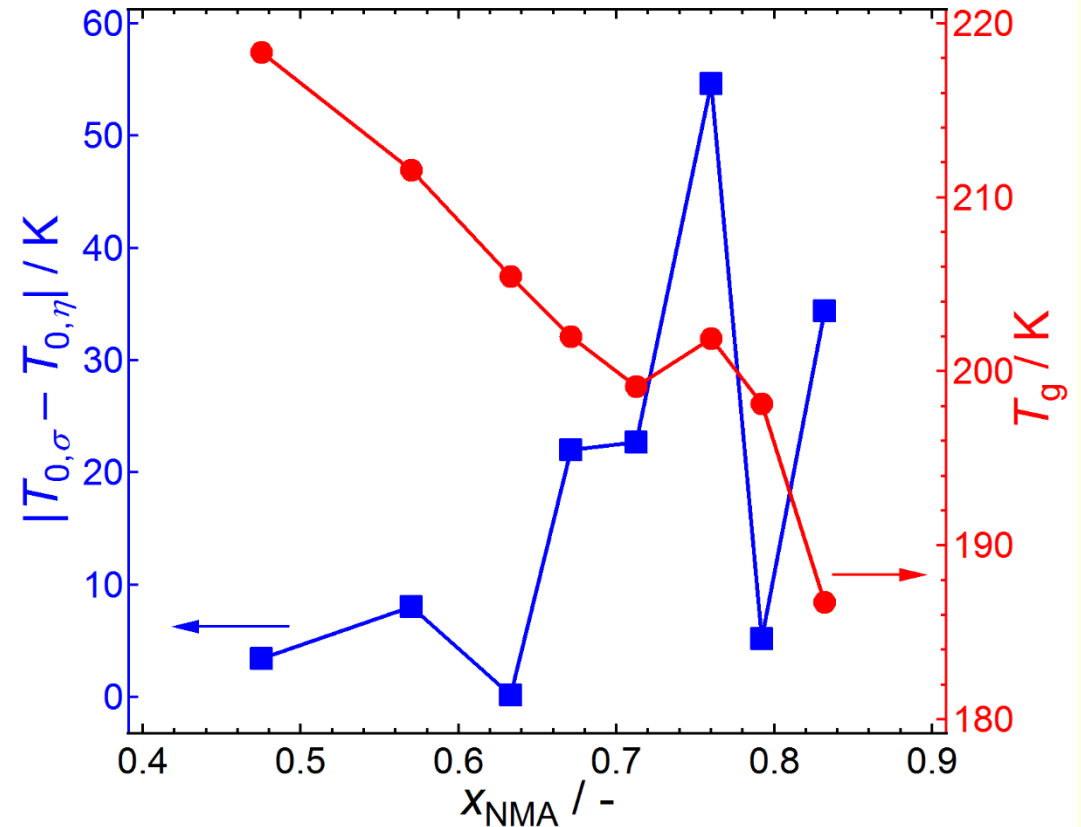
- A strong relationship between *composition and salt dissociation*

Electrolyte Optimization: Transport Mechanism

✓ Ionic conductivity and viscosity



✓ Glass transition temperature

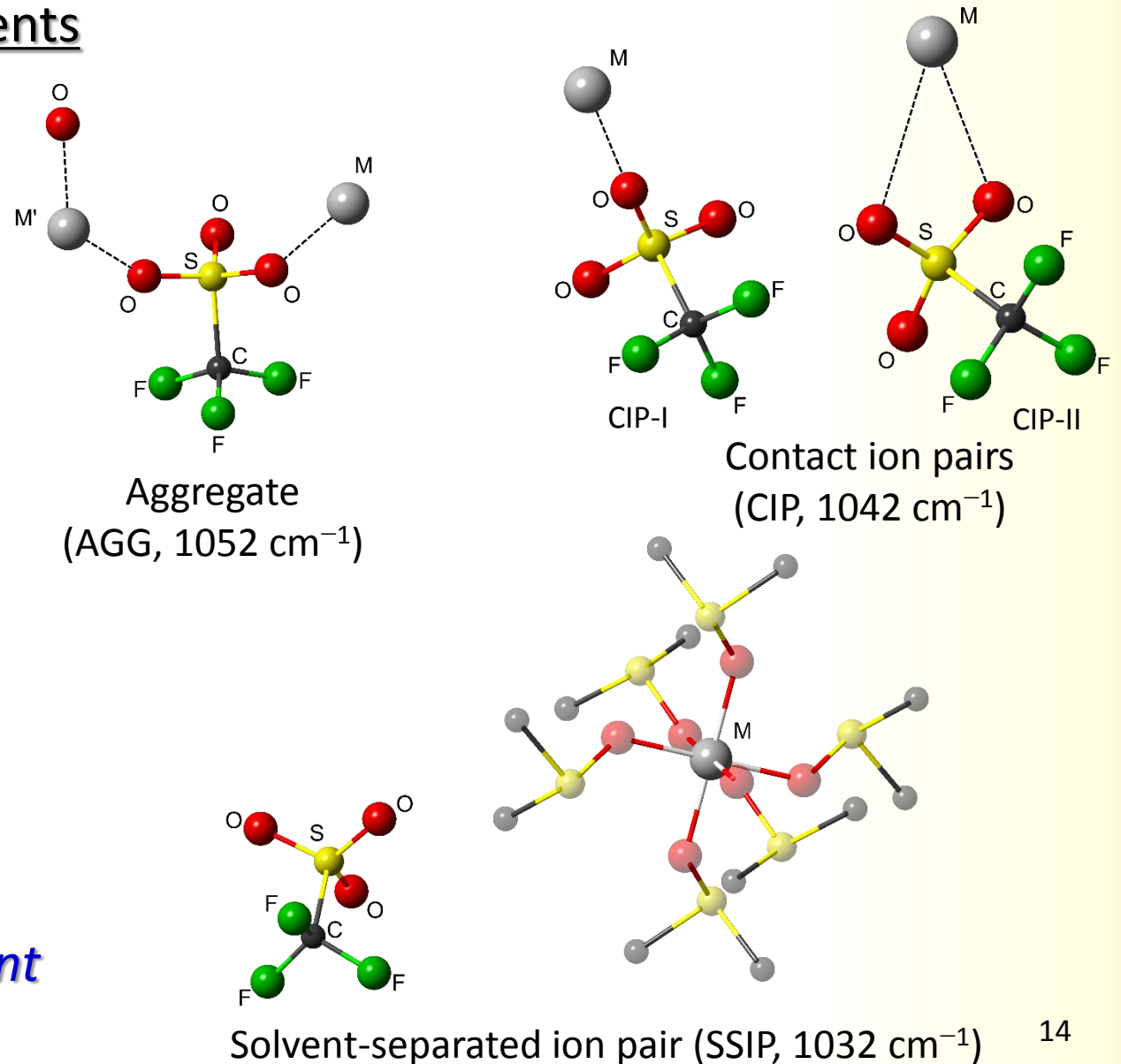
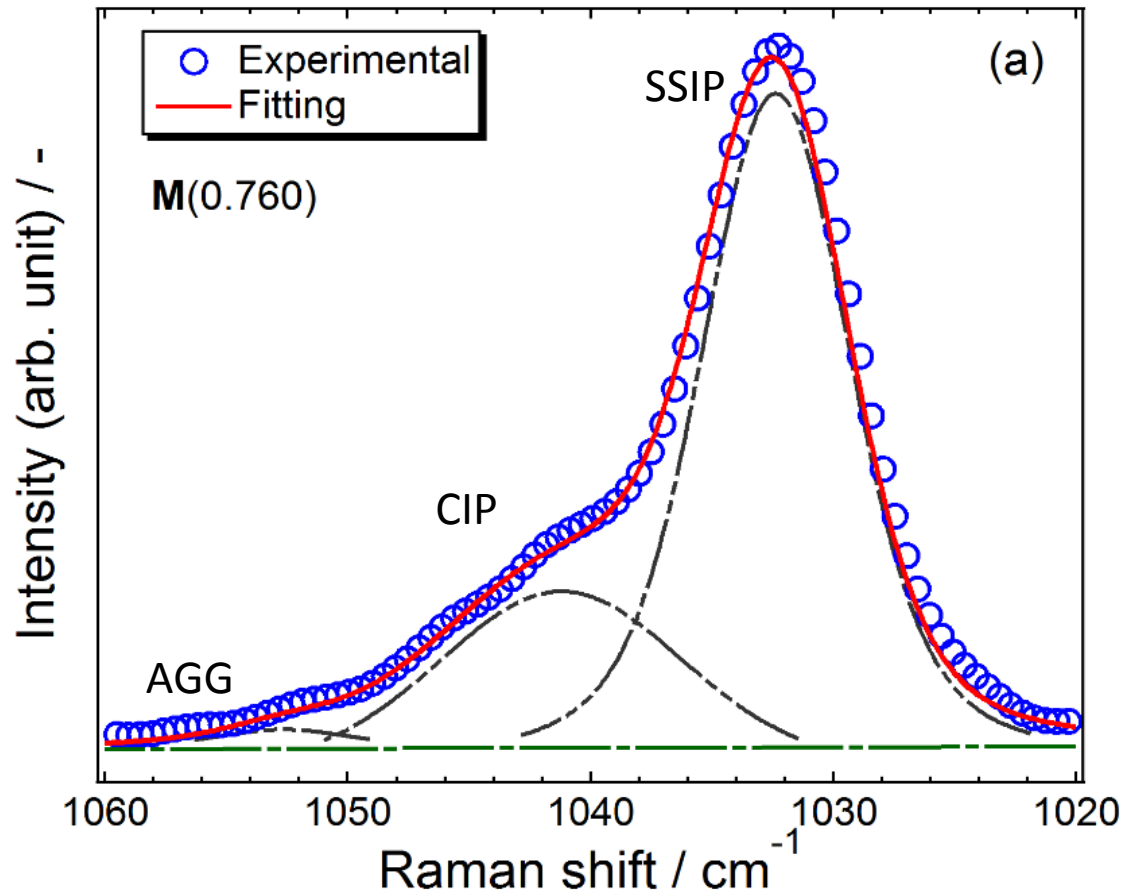


- Cond. max. $X_{NMA} = 0.76$ (M(0.760))

- Decoupling of the Al conduction mechanism from viscosity

Electrolyte Optimization: Salt Dissociation

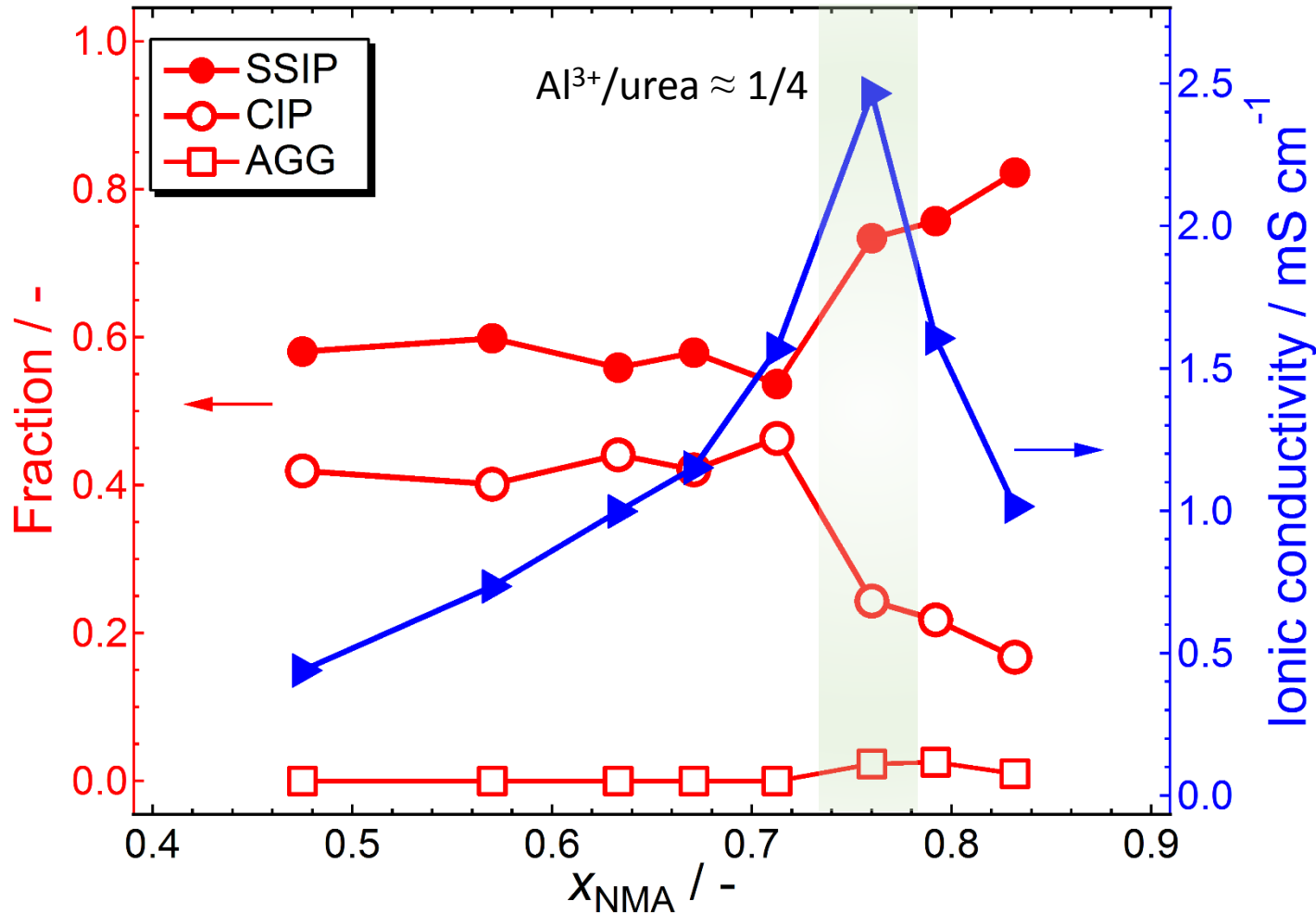
✓ Change in salt dissociation and assignments



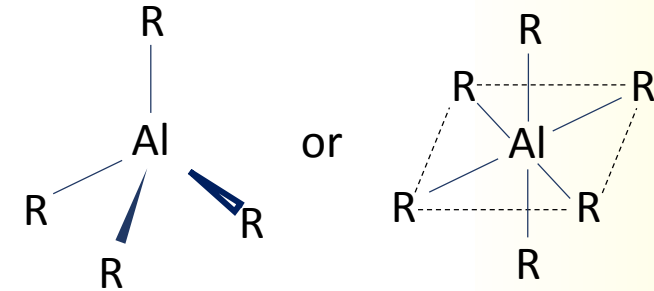
- The speciation is *composition dependent*

Electrolyte Optimization: Salt Dissociation

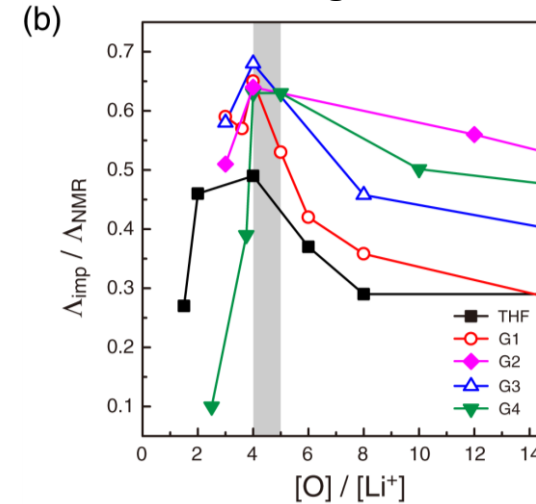
✓ Dissociation = function of x_{NMA}



Preferential coordination number of Al^{3+}



e.g.: LiTFSI/ether system

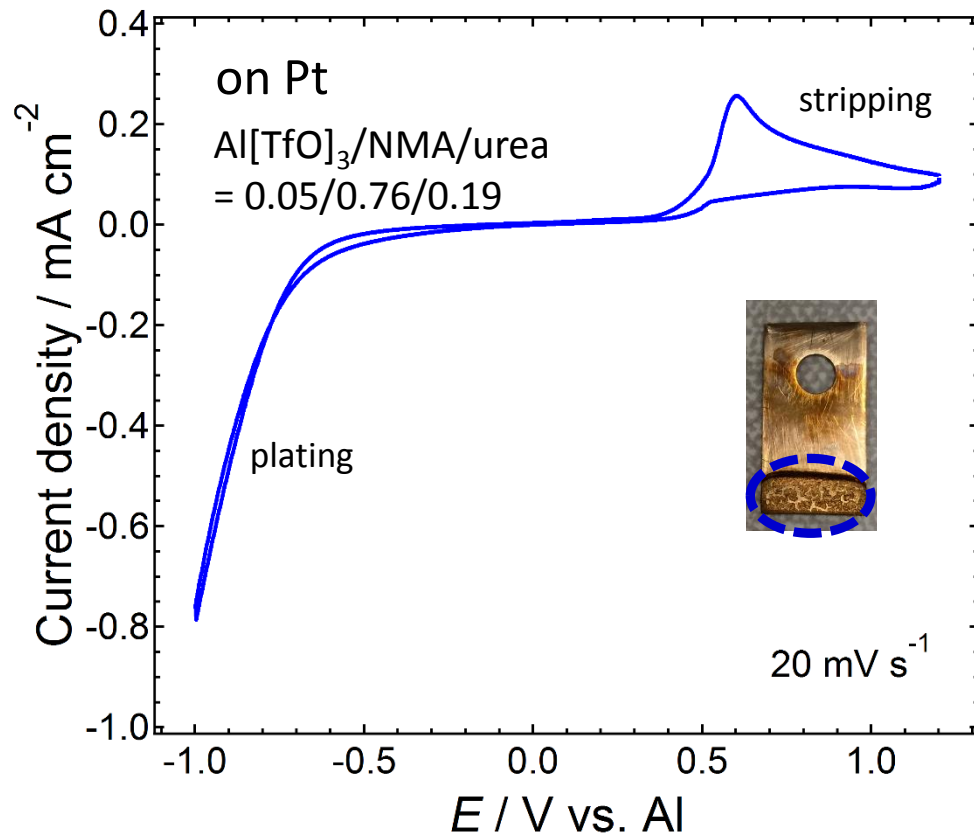


C. Zhang et al., *J. Phys. Chem. B* **2014**, *118*, 5144.

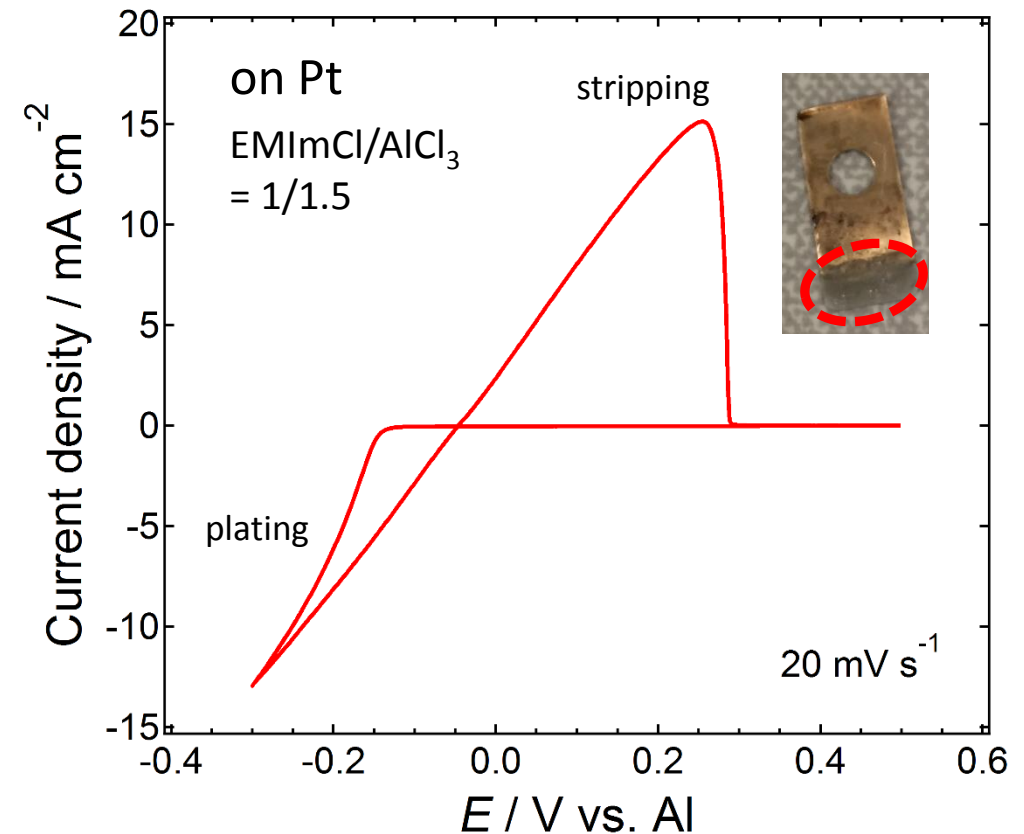
Low dielectric solvents play multiple roles to facilitate/suppress salt dissociation, depending on the composition.

- Multiple roles of urea behind complex salt dissociation behaviour

Optimized ternary electrolyte



Conventional AlCl₃-based electrolyte



- *Some reversible electrochemistry found*
- *Modest compared to an AlCl₃-based electrolyte*

Intermediate Summary

- *The extremely reactive nature of AlCl_3 -based electrolytes is problematic*
- *AlCl_3 -free non-aqueous Al electrolytes based on $\text{Al}[\text{TfO}]_3$, NMA, and urea =>*
 - *unprecedented solvation ability for Al-salt*
 - *remarkable ion transport*
- *For the special case of $\text{M}(0.760)$ =>*
 - *the properties and the dissociation state of $\text{Al}[\text{TfO}]_3$ drastically changes*
 - *modestly electrochemically active*

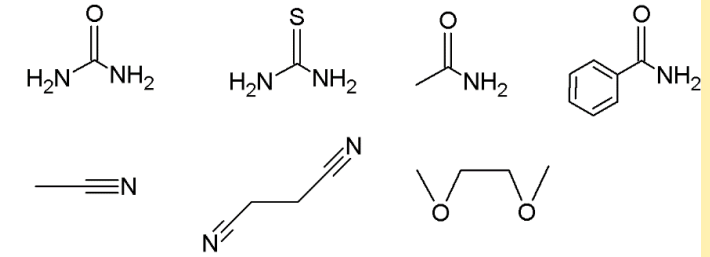
T. Mandai and P. Johansson, *J. Mater. Chem. A* **2015**, 3, 12230–12239.

Another approach possible?! =>

Possible Candidates for Al-Electrolytes

➤ Deep Eutectic Solvents (DESs)

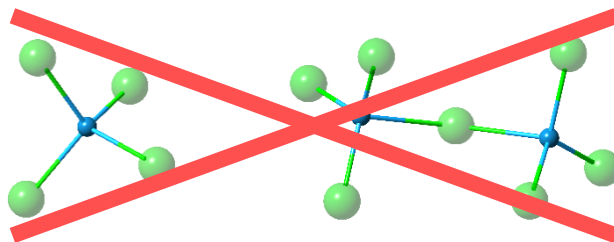
- Present system
- Optimize compositions and/or choices of fertilizers/salts



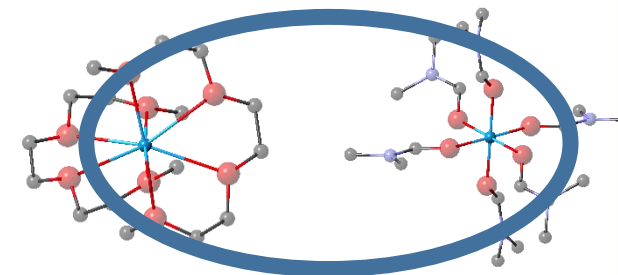
Chemical structure of fertilizers

➤ Cationic solvates: Solvate Ionic Liquids, Liquid Metal Salts (LMSs)

IL based electrolytes with the electrochemical activity being **cationic** rather than anionic



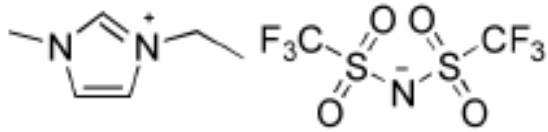
Anionic $[\text{Al}_n\text{Cl}_{3n+1}]^-$



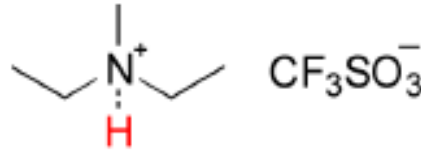
Cationic $[\text{Al}(\text{Ligand})_n]^{3+}$

What are Solvate Ionic Liquids and LMSs?

1. Aprotic ILs



2. Protic ILs



Lewis acid



+

Lewis base



→

Anion



+

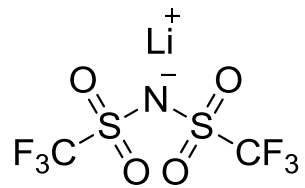


→



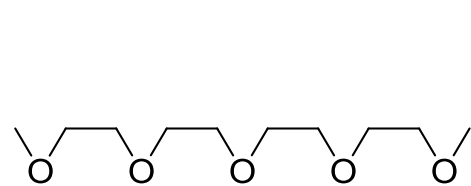
3. Solvate ILs LMSs

New family of ILs; incorporating solvate ions as cationic/anionic components

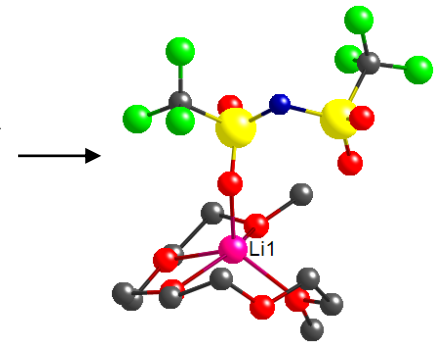


Li[TFSI]

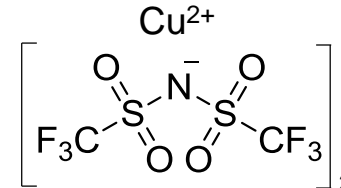
+



G4

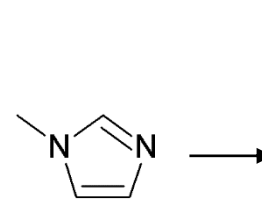


[Li(G4)][TFSI]

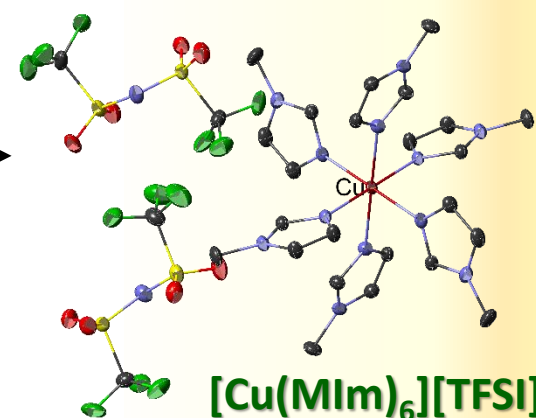


Cu[TFSI]₂

+



MIm



[Cu(MIm)₆][TFSI]₂

C. A. Angell et al., *Faraday Discuss.* **2011**, 154, 9;

T. Mandai et al., *Phys. Chem. Chem. Phys.* **2014**, 16, 8761.

T. V. Hoogerstraete et al.,

CrystEngComm **2012**, 14, 4902.

Lewis acid



+

Lewis base

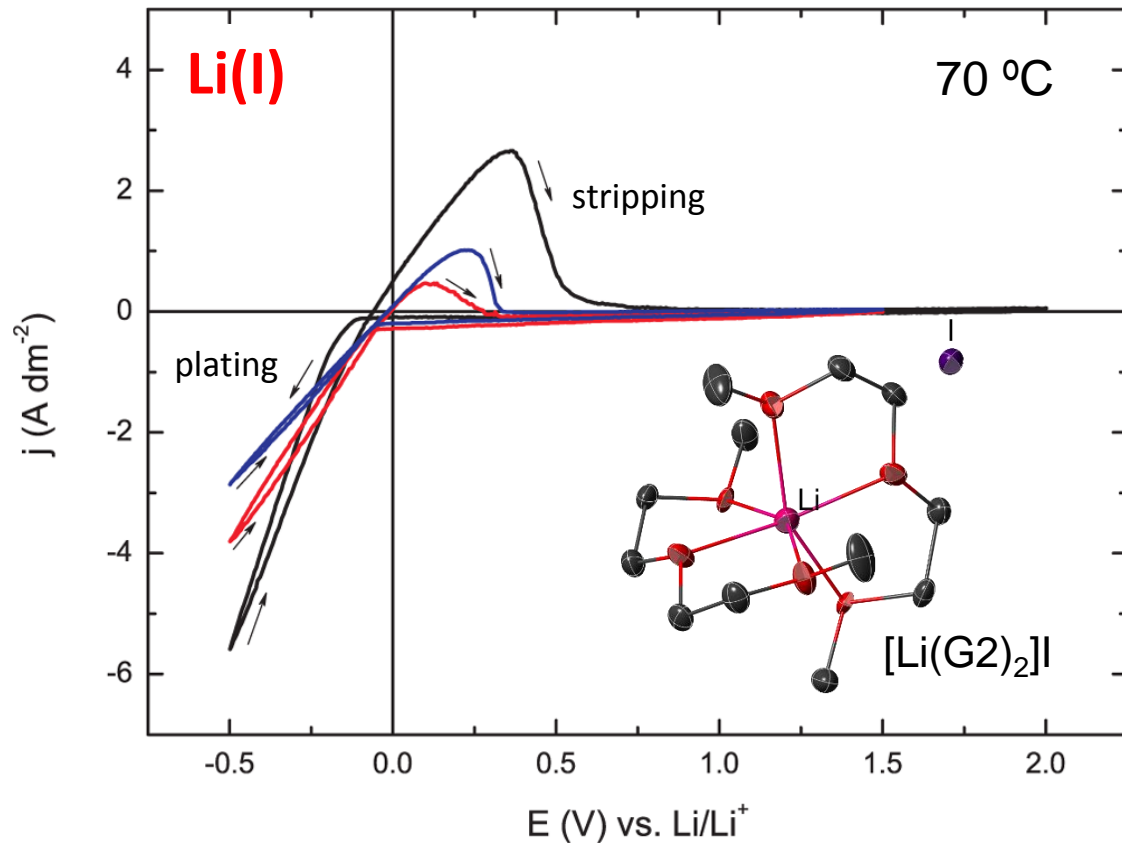
n Ligand

→

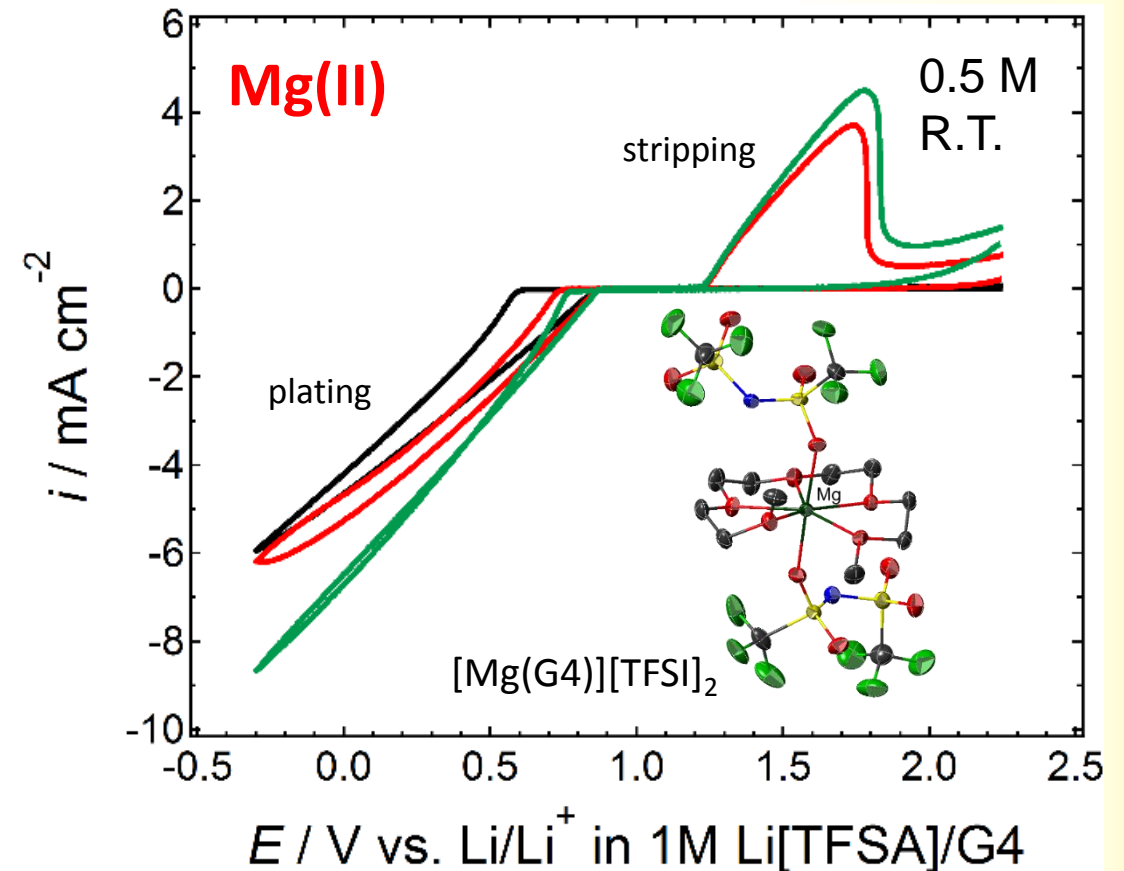
Cation



Potential of Solvate ILs as Electrolytes



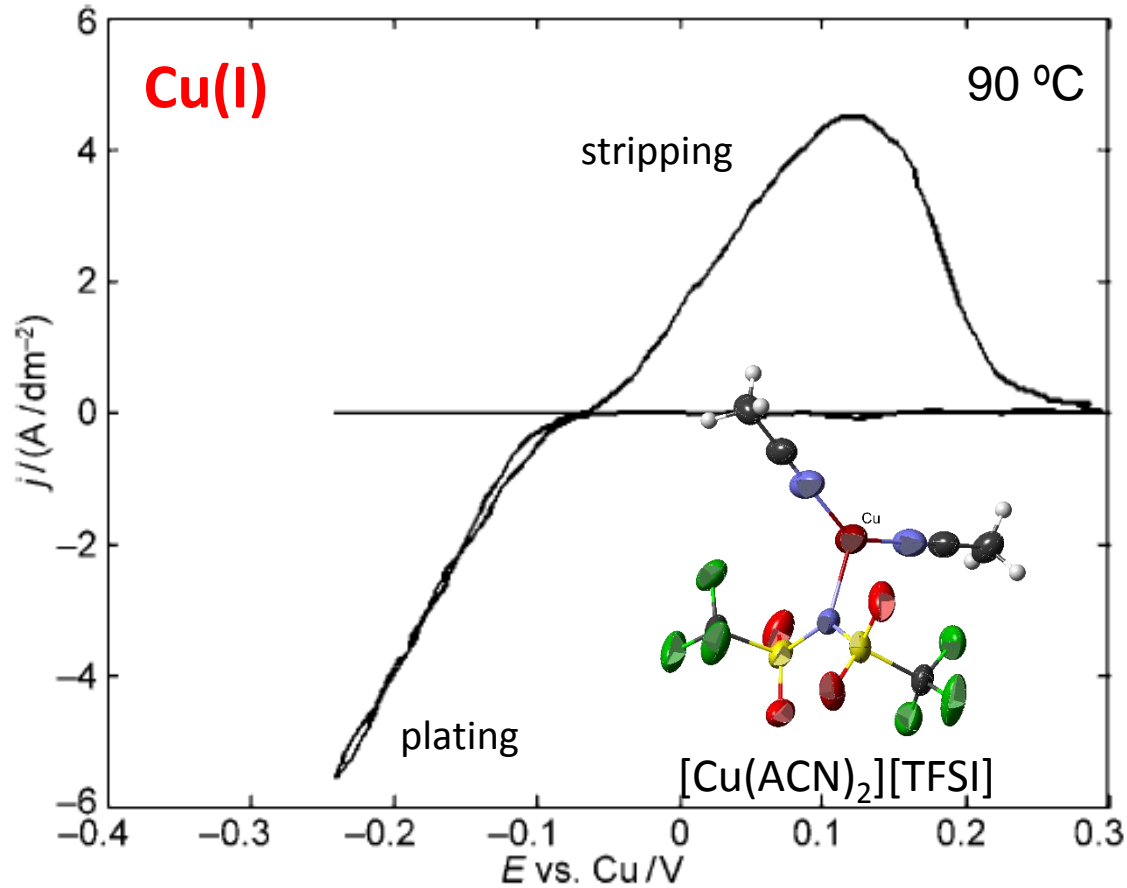
G. Vanhoutte, et al., *J. Phys. Chem. C* **2014**, *118*, 2015.



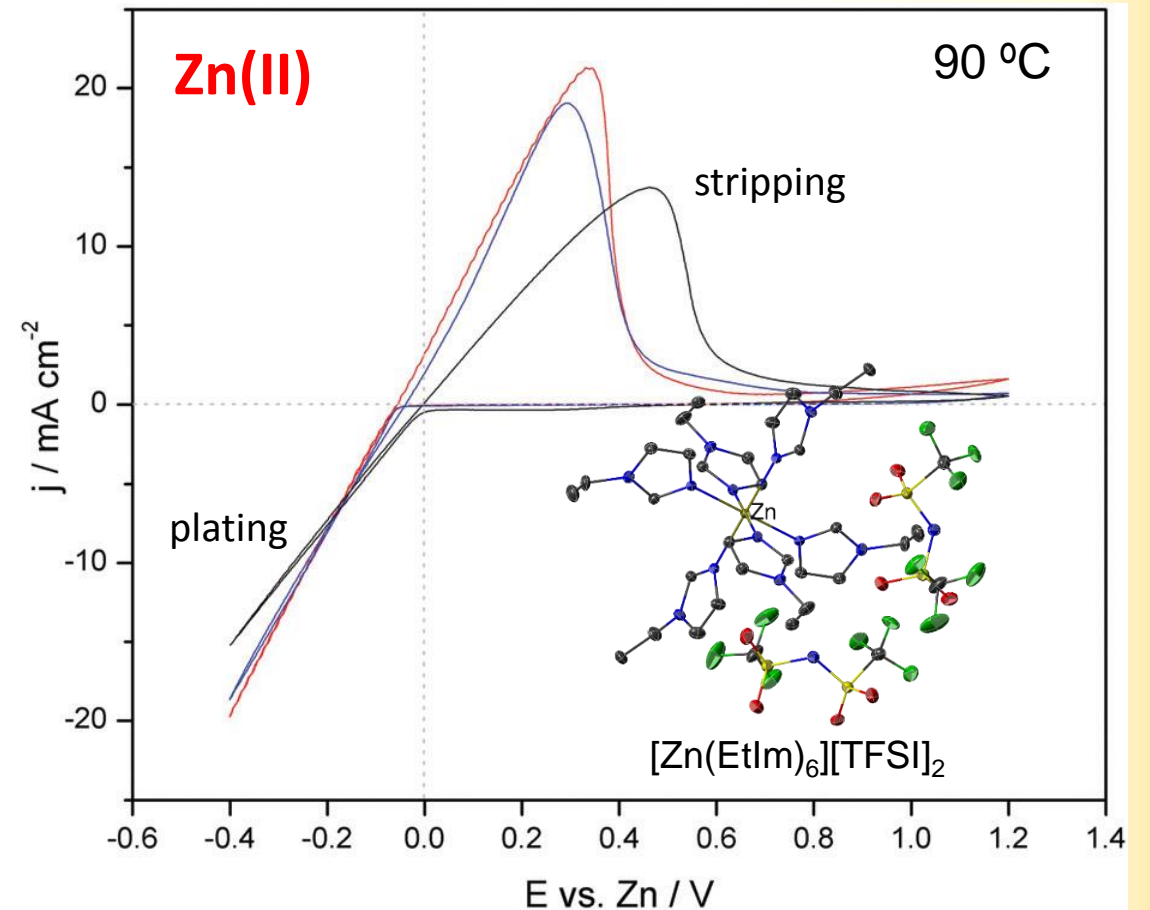
T. Mandai, M. Watanabe, et al., *J. Phys. Chem. C*, submitted.

- Solvate IL electrolytes allow reversible electroplating/stripping of metals

Electroplating of Metals from LMSs



N. R. Brooks, et al., *Chem. Eur. J* **2011**, *17*, 5054.



M. Steichen, et al., *Dalton Trans.* **2014**, *43*, 12329.

Cationic solvates have promise for multivalent metal batteries

Concluding Remarks

- *Multivalent based electrochemical energy storage systems, especially **Al metal**, have promise with respect to growing demands.*
- *AlCl₃-based electrolytes are highly reactive and corrosive => Development of **AlCl₃-free electrolytes** is crucial for practical Al batteries.*
- *Novel electrolytes based on **DESs** or **cationic Al complexes** are promising.*

*Chalmers Area of Advance Materials Science and the
Swedish Energy Agency programme “Batterifonden”*

Chalmers Areas of Advance Energy and Transport

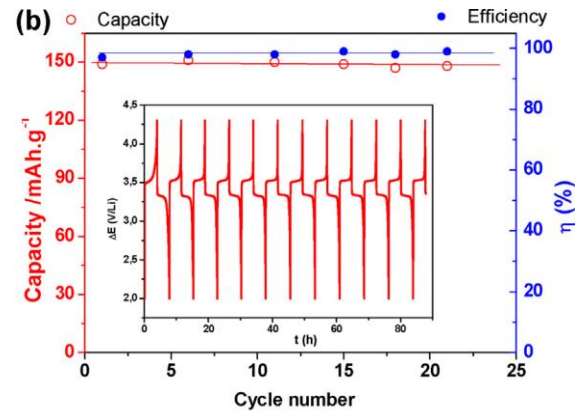


“BASF open innovation contest on Energy Storage”

Appendix



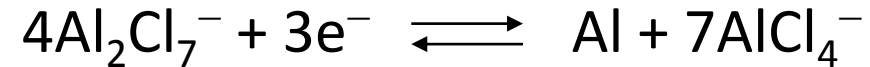
✓ Li[TFSA] with urea, acetamide, or NMA binary electrolyte



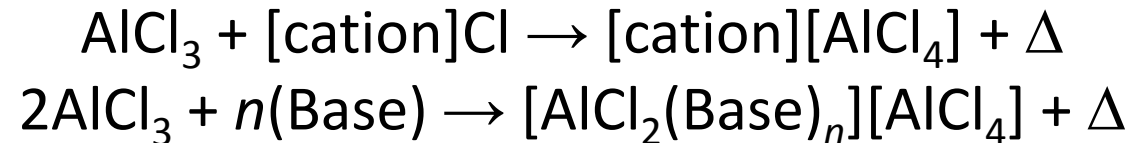
H. Liang et al., *J. Phys. Chem. B* **2001**, *105*, 9966; Y. Hu et al., *Electrochem. Commun.* **2004**, *6*, 28; A. Boisset et al., *Electrochim. Acta* **2013**, *102*, 120.

Electrochemical Reaction of the $AlCl_3$ -based

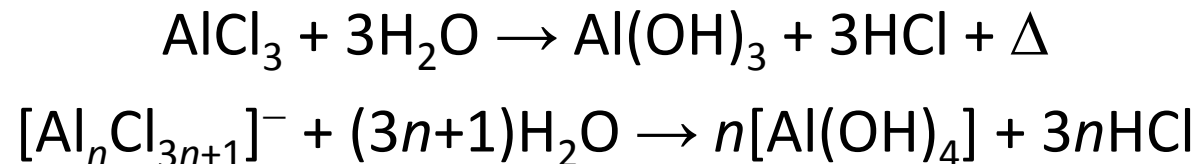
- ✓ During plating and stripping



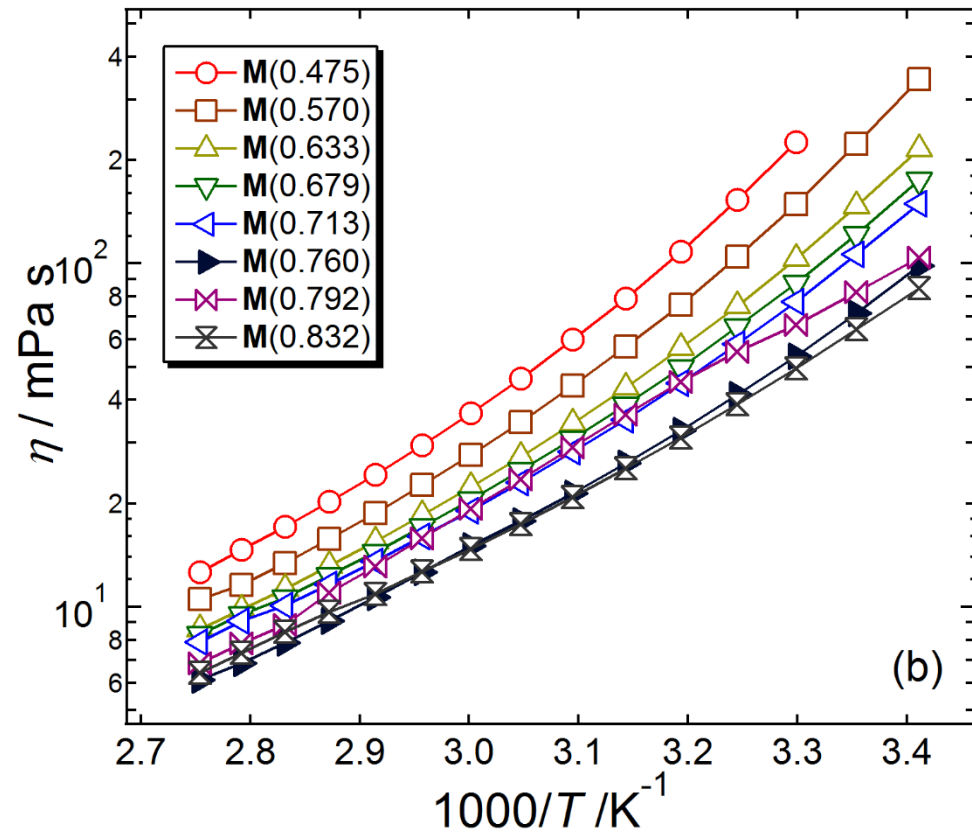
- ✓ Preparation of electrolytes



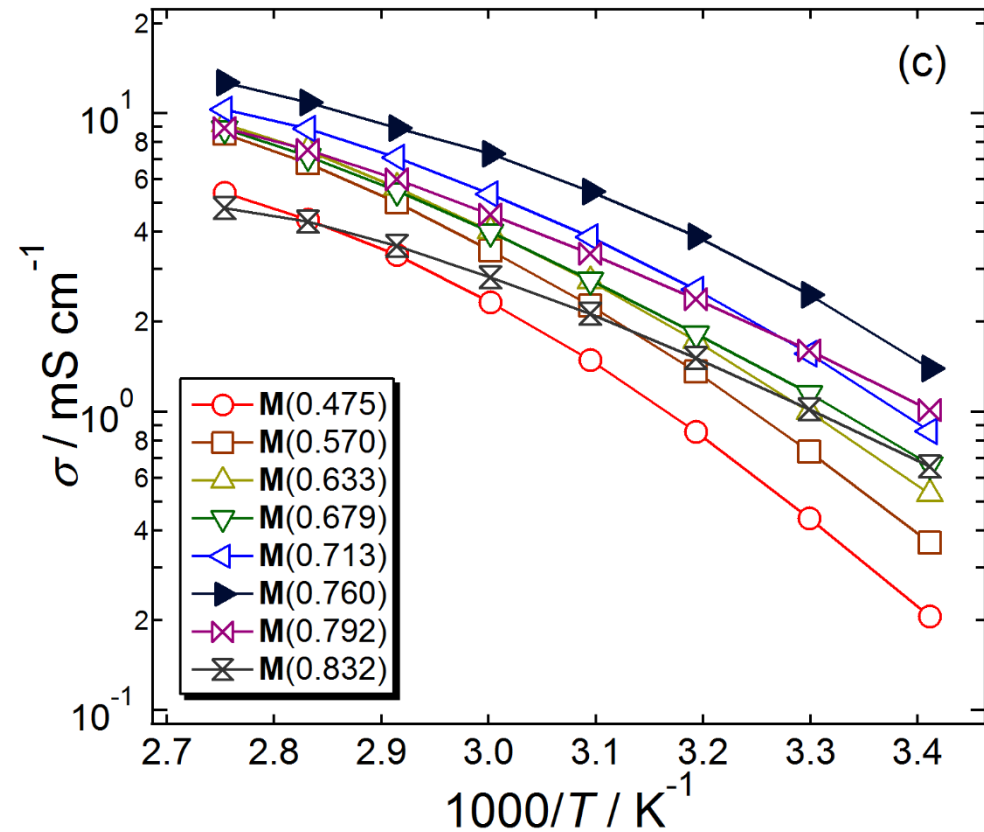
- ✓ Reaction of $AlCl_3$ and electrolytes with water



Electrolyte Optimization: Arrhenius Plot

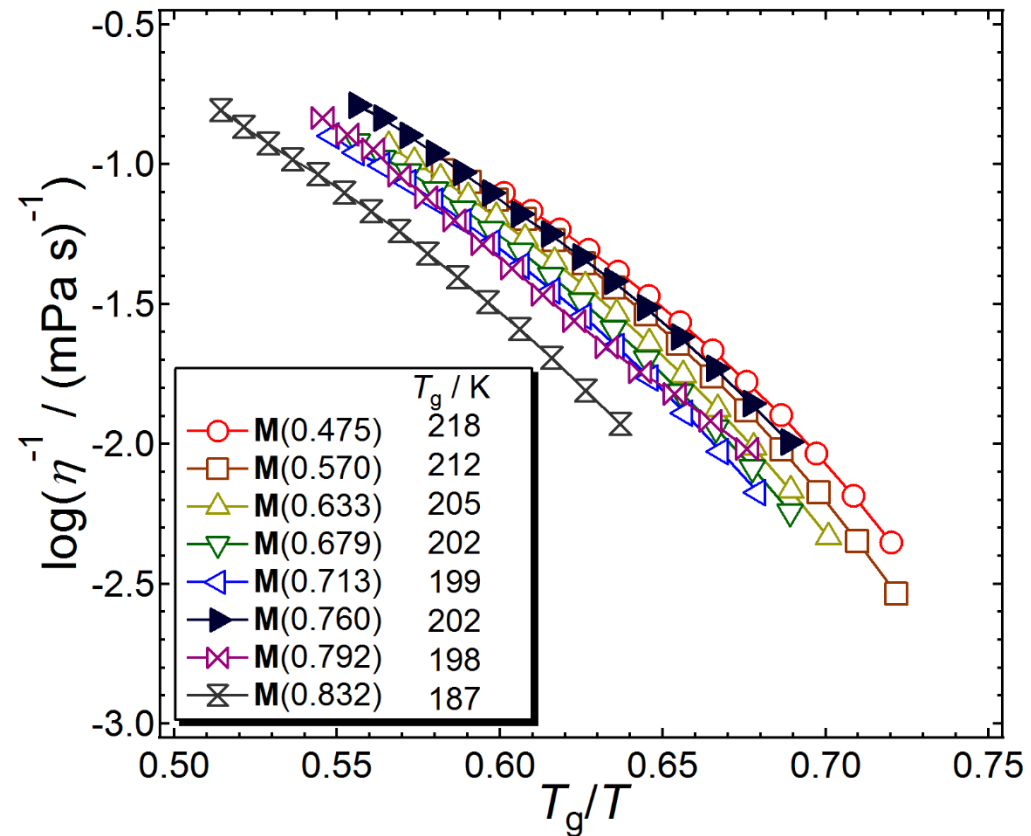


$$\eta = \frac{\sqrt{T}}{A_\eta} \exp \left[\frac{B_\eta}{T - T_{0,\eta}} \right]$$



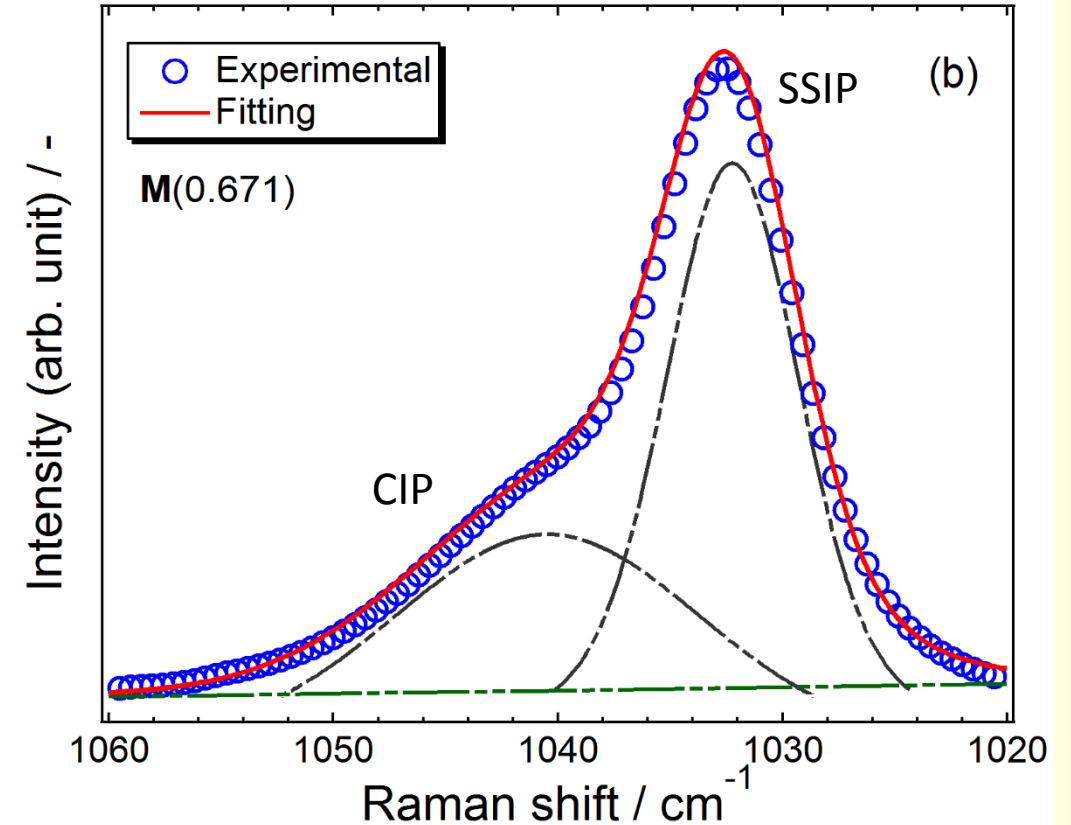
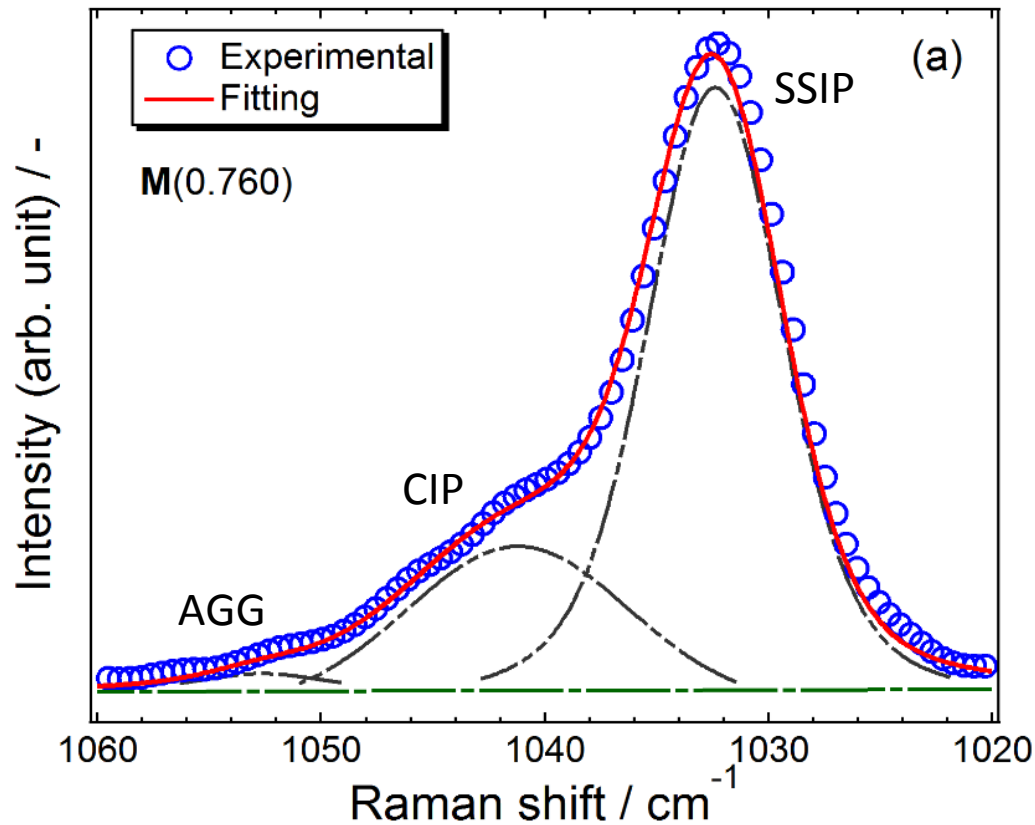
$$\sigma = \frac{A_\sigma}{\sqrt{T}} \exp \left[\frac{-B_\sigma}{T - T_{0,\sigma}} \right]$$

Electrolyte Optimization: Fluidity



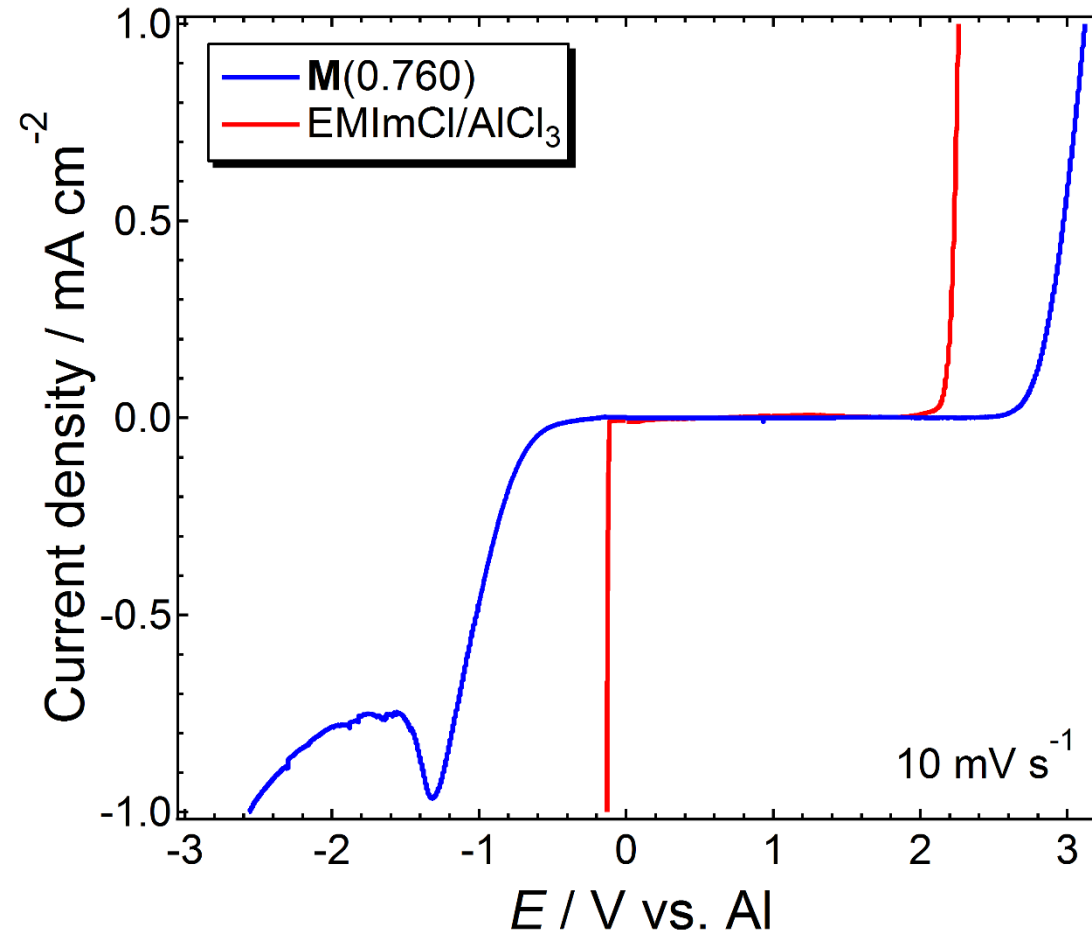
Electrolyte Optimization: Salt Dissociation

✓ Fitting by Voigt (G/L) functions



- Deconvolution of spectra \Rightarrow 2-3 bands; SSIP, CIPs, and AGG
- Number of bands composition dependent

Electrochemical Stability Window



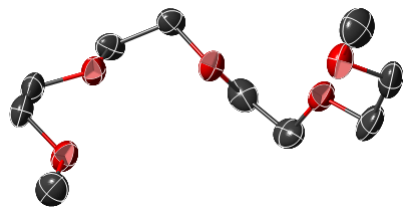
Criteria for Solvate ILs

1. Form a *solvate compound* between an ion and a ligand(s) in a certain stoichiometric ratio.
2. Consist entirely of complex ions (solvates) and their counter ions *in the molten state*.
3. Show no physicochemical properties based on both pure ligands and precursor salts under using conditions.
4. Have a *melting point below 100 °C*, which satisfies the criterion for typical ILs.
5. Have a *negligible vapor pressure* under typical application conditions.

Phys. Chem. Chem. Phys.,
2014, **16**, 8761.

For glyme-salt systems,

Cation–Glyme interaction competes with Cation–Anion interaction.

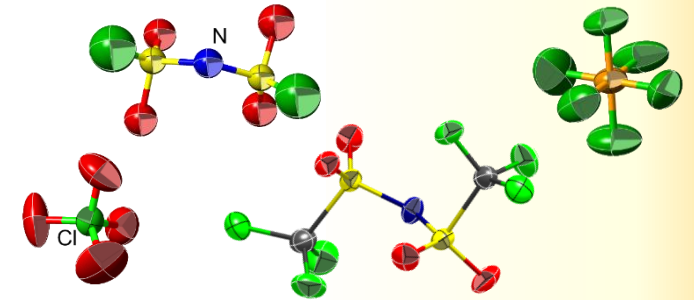


Chelating ability of
Glymes (K_{complex})



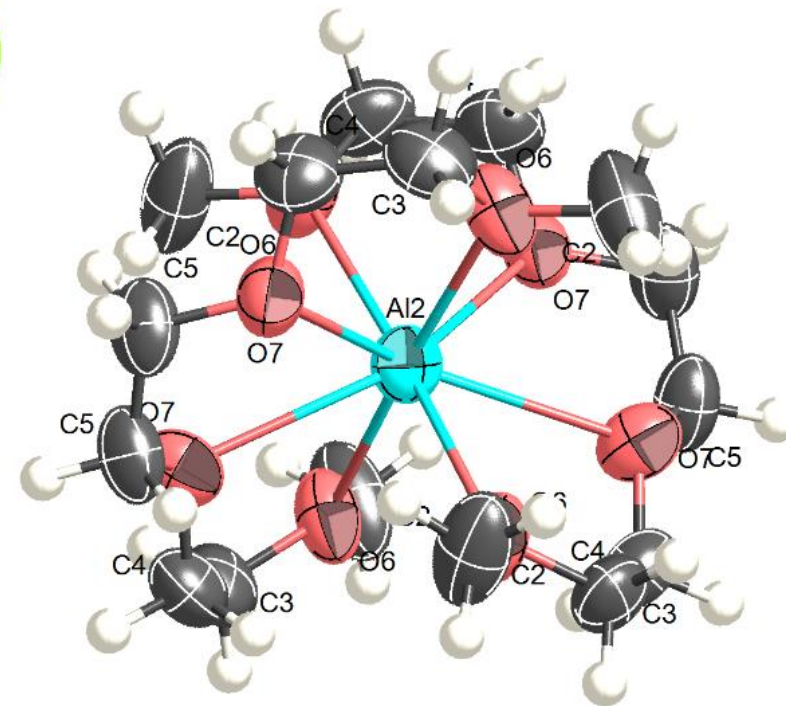
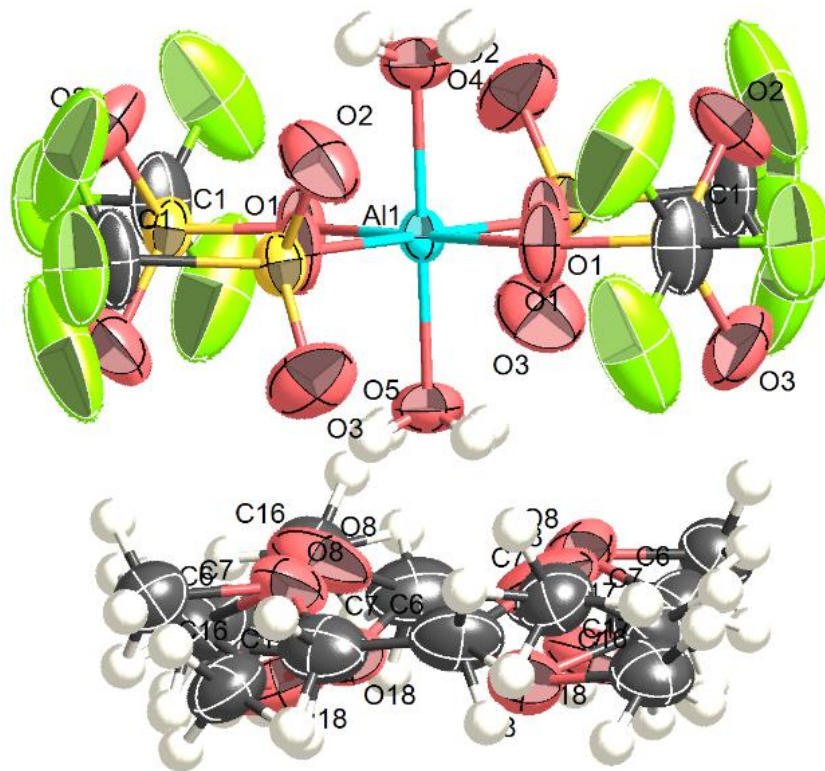
M^+

Lewis acidity of
Cations ($E_{M^+X^-}$)



Lewis basicity of
Anions ($E_{M^+X^-}$)

ORTEP Diagram of $[Al(G3)_2][Al(TfO)_4(OH)_2] \cdot G3$



Exceptionally Large Al–O Separation

