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Anodic dissolution of aluminum in Li-ion cells in terms of the electrolyte

Seminar-Vortrag HIU

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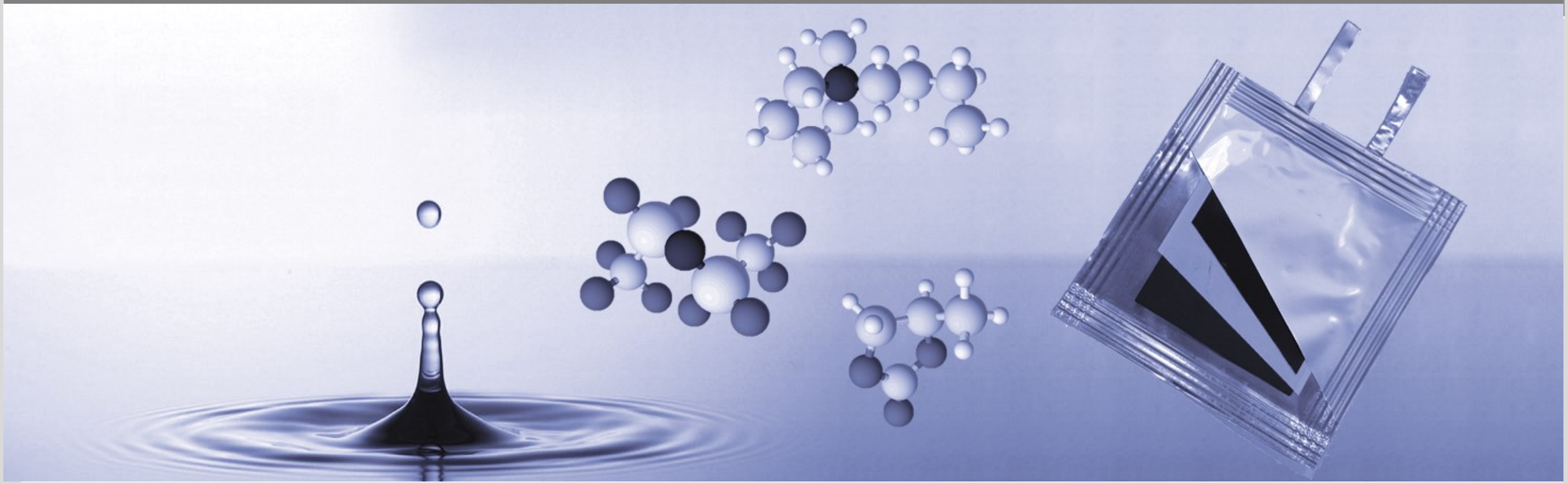

Outline

- Li-ion battery research at IAM-WPT
- Electrolytes in Li-ion cells
- Mechanism of aluminum dissolution
- Influence of electrolyte composition on aluminum “corrosion” – conducting salt, solvents and additives

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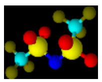
Energy storage systems: Li-ion batteries

technology step

research and development

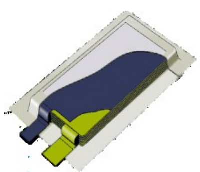
cathode → electrode preparation

anode → electrode preparation

electrolyte → cell manufacturing, electrolyte filling

processing

electrode preparation



cells

cell manufacturing, electrolyte filling

---- at IAM-WPT ----

batteries

cell assembling and battery management

-- at KIT --

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Electrolyte research at IAM-WPT

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Issues

- High voltage electrolytes
- Improve of Safety
- Interfaces
- Structure-property relationships
- Structure-activity relationships

Focus of research

- Ionic liquids and new solvents
- Interaction of cell parts
- Additives
- Current collectors (aluminum)
- Conducting salts
- Electrolyte formulation

Systems

- Liquid electrolytes
- Gel polymer electrolytes
- New materials
- Li-ion cells
- solar cells

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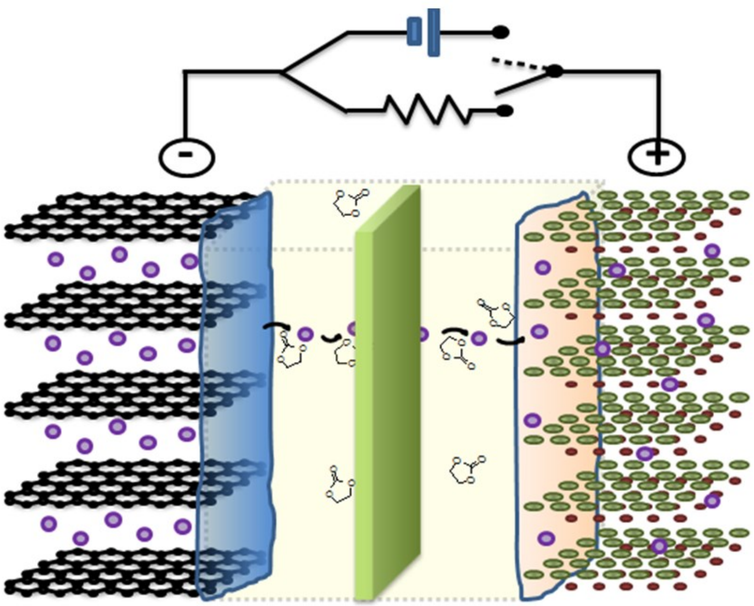
Electrolytes in Li-ion cells: basics

"Chemical compounds which are able to form ionic crystals in solid state and are composed of ions under liquid or molten conditions or when dissolved in a solvent.

lithium salt + matrix + additives

- Enable the lithium transport through the cell
- Basis for the current flow
- Solid electrolyte interface
- Interact with all parts inside the cell



** http://www.itwissen.info

Electrolytes in Li-ion cells: requirements

- Nonflammable liquid electrolytes with adequate Li ion conductivity
- Inherent safety
- Infinite cycling
- Low cost
- Non-toxic salts and solvents
- Improved low-temperature performance
- Effective redox shuttles for overcharge protection
- Electrolyte additives for effective SEI layer formation
- Stable ionic liquids and solid polymer electrolytes with acceptable conductivity

Electrolytes in Li-ion cells: state of the art

State of the art:

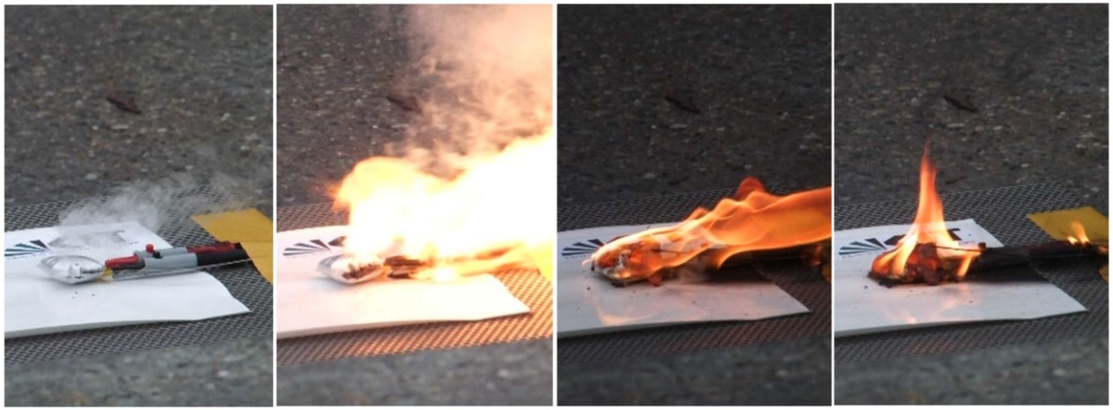
- Carbonate-based electrolytes (z.B. EC/DMC + 1M $LiPF_6$)
- Gel polymer electrolytes with liquids (carbonate based)

Composition:

- Mixture of organic carbonates
- $LiPF_6$ (1 mol/l)
- Additives

Properties:

- Stable up to 4.2 V vs. Li/Li^+
- Highly flammable (flash point EC/DMC: 24°C)
- Temperatures up to 60 °C



Electrolytes in Li-ion cells: research

- Replacement of $LiPF_6$
- Use of electrolytes
  - New electrolytes for new electrode materials
  - Electrolyte uptake
  - Range of temperature
  - Intercalation of solvents (graphite)
- Electrolytes for high voltage applications
  - New solvents at $E > 4.2 – 4.5$ V vs. Li/Li^+
  - Electrolyte decomposition, gas formation
- Safety issues
  - High toxicity of $LiPF_6$
  - Intrinsic fire safety
  - Reduce of leakage

$LiPF_6$

Dimethylcarbonat

→ Interaction of the electrolyte with all parts inside the cell

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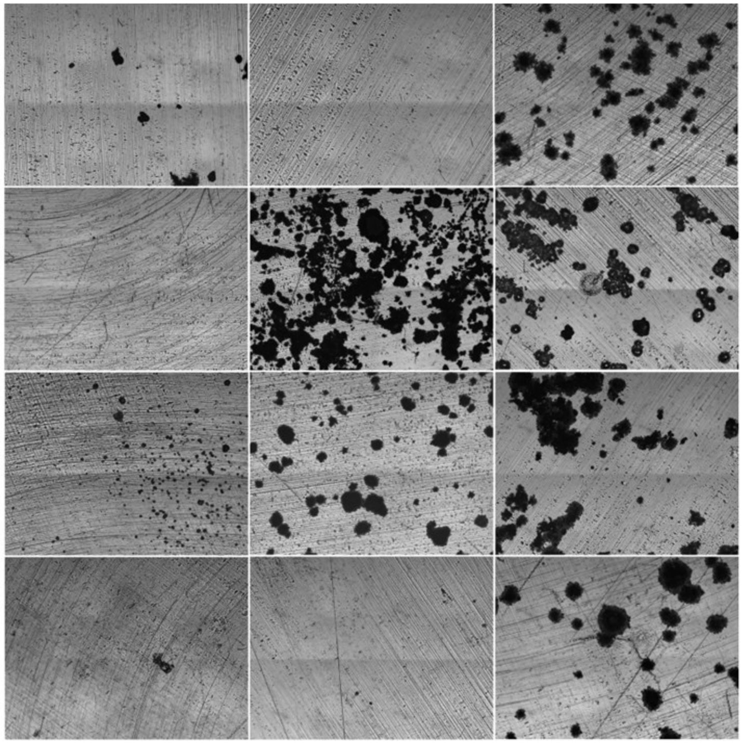
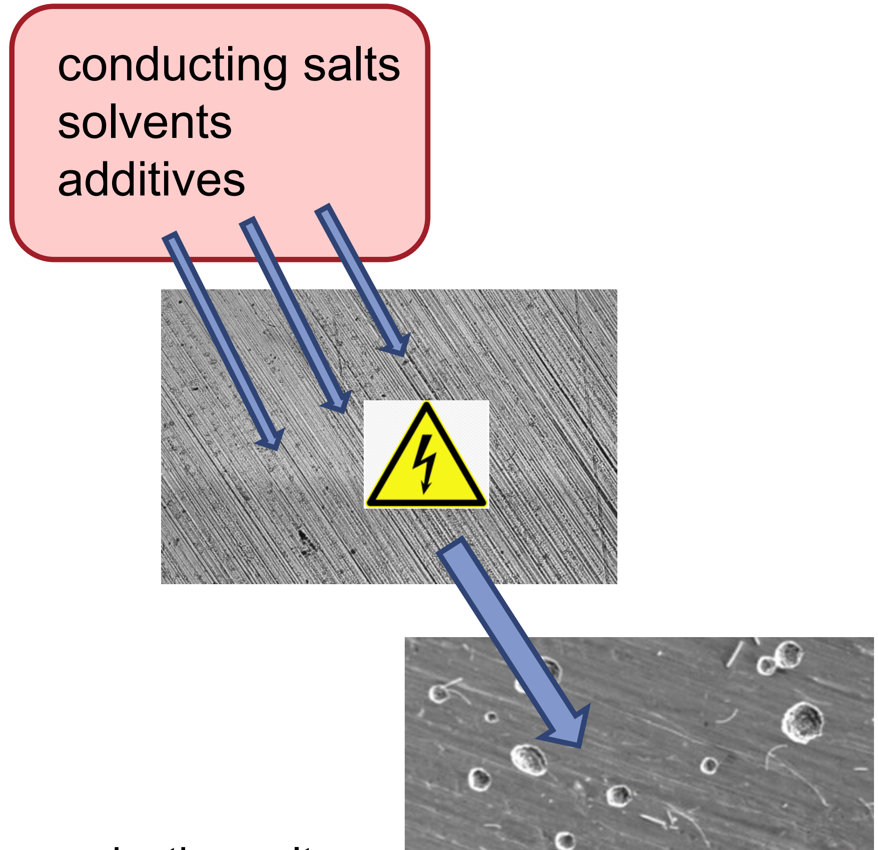
Aluminum dissolution: challenge





Questions:

- Dependence of aluminum corrosion on conducting salt
- Corrosivity of ionic liquids and organic solvents
- Concentration dependence of aluminum corrosion
- Additives for protecting the aluminum surface

A. Hofmann et al. *Electrochim. Acta*, 116, 388–395 (2014).
A. Hofmann et al. *J. Electrochem. Soc.*, 161, A431 – A438 (2014).

Mechanism of aluminum dissolution

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What is aluminum corrosion?

- Electrochemical reaction of aluminum inside the cell
- Anodic dissolution of aluminum (oxidation)

$$Al \rightarrow Al^{3+} + 3e^{-}$$

Why not „corrosion“?

- Corrosion towards „DIN EN ISO 8044“:

  „Reaktion eines metallischen Werkstoffes mit seiner Umgebung, die eine messbare Veränderung des Werkstoffes bewirkt und zu einer Beeinträchtigung der Funktion eines metallischen Bauteils oder eines ganzen Systems führen kann.“

- Corrosion: *without* a potential difference

Where is aluminum inside the cell?

- Current collector for cathode material
- Electrolyte is in contact with aluminum

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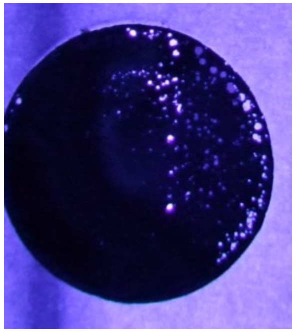
Mechanism of aluminum dissolution

What happens when aluminum dissolves?

- Aluminum dissolves slowly but completely
- Cathode material crumbles away
- Aluminum salts can deposit onto the counter electrode



aluminum disc after cycling, d = 12 mm

Why this is not a problem of today's electrolytes?

- Inert under the conditions which are used today (E < 4.3 V vs. Li/Li^+, today's electrolytes)
- Passivation of aluminum by oxygen (Al_2O_3)
- Passivation of aluminum by fluorine (AlF_3)

When aluminum corrosion plays a role?

- Use of new electrolytes (solvents, conducting salts, additives)
- Use of higher voltages (E > 4.3 V vs. Li/Li^+)
- Replacement of fluorine ($LiPF_6$)

Mechanism of aluminum dissolution

- Multistep process

$$Al \rightarrow Al^{3+} + 3e^{-}$$

$$Al^{3+} + X^{-} \rightarrow AlX^{2+}_{(ads)} \text{ or } AlX^{+}_{2(ads)} \text{ and } AlX_{3(ads)}$$

- Mechanism under involvement of corrosive salts*

$$N(SO_2CF_3)^{-}_{2\,\text{bulk}} \rightarrow N(SO_2CF_3)^{-}_{2\,\text{electrode}} \rightarrow N(SO_2CF_3)^{-}_{2\,\text{electrode(Al)}}$$

$$x\,N(SO_2CF_3)^{-}_{2\,\text{electrode(Al)}} + Al_2O_3 \xrightarrow{3.5\text{ V !}} 2\,[Al(N(SO_2CF_3)_2)_x]^{3+x-}_{\text{electrode}} + 3/2\,O_2 + 6\,e^{-}$$

$$[Al(N(SO_2CF_3)_2)_x]^{3+x-}_{\text{electrode}} \rightarrow [Al(N(SO_2CF_3)_2)_x]^{3+x-}_{\text{bulk}}$$

$$Al \rightarrow Al^{3+}_{\text{electrode}} + 3e^{-}$$

$$Al^{3+}_{\text{electrode}} \rightarrow Al^{3+}_{\text{bluk}}$$

* Wang et al., *Electrochim. Acta* 45 (2000) 2677.

Mechanism of aluminum dissolution

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- Multistep process

$$Al \rightarrow Al^{3+} + 3e^{-}$$

$$Al^{3+} + X^{-} \rightarrow AlX^{2+}_{(ads)} \text{ or } AlX^{+}_{2(ads)} \text{ and } AlX_{3(ads)}$$

- Mechanism under involvement of corrosive salts*

$$N(SO_2CF_3)^{-}_{2\ bulk} \rightarrow N(SO_2CF_3)^{-}_{2\ electrode} \rightarrow N(SO_2CF_3)^{-}_{2\ electrode(Al)}$$

$$x\ N(SO_2CF_3)^{-}_{2\ electrode(Al)} + Al_2O_3 \xrightarrow{3.5\ V\ !} 2\ [Al(N(SO_2CF_3)_2)_x]^{3+x-}_{electrode} + 3/2\ O_2 + 6\ e^{-}$$

$$[Al(N(SO_2CF_3)_2)_x]^{3+x-}_{electrode} \rightarrow [Al(N(SO_2CF_3)_2)_x]^{3+x-}_{bulk}$$

$$Al \rightarrow Al^{3+}_{electrode} + 3e^{-}$$

$$Al^{3+}_{electrode} \rightarrow Al^{3+}_{bluk}$$

* Wang et al., *Electrochim. Acta* 45 (2000) 2677.

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Mechanism of aluminum dissolution

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- Multistep process

$$Al \rightarrow Al^{3+} + 3e^-$$

$$Al^{3+} + X^- \rightarrow AlX^{2+}_{(ads)} \text{ or } AlX^{+}_{2(ads)} \text{ and } AlX_{3(ads)}$$

- Mechanism under involvement of corrosive salts*

$$N(SO_2CF_3)^-_{2\,bulk} \rightarrow N(SO_2CF_3)^-_{2\,electrode} \rightarrow N(SO_2CF_3)^-_{2\,electrode(Al)}$$

Destruction of the surface protecting layer

$$[Al(N(SO_2CF_3)_2)_x]^{3+x-}_{electrode} \rightarrow [Al(N(SO_2CF_3)_2)_x]^{3+x-}_{bulk}$$

Dissolving of Al at low voltages

* Wang et al., *Electrochim. Acta* 45 (2000) 2677.

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Preventing Al dissolution

- Aluminum dissolution prevention by using solvents with low dielectric constants or ionic liquids
- Use of conducting salts or additives which enable a formation of a passivation layer (e.g. LiBF4, lithium bis(oxalato)borate, HF)
- Formation of fluorine containing passivation layer
- Use of conducting salts with large anions in space which are not able to complex and dissolve the Al (e.g. lithium bis(perfluoroethylsulfonyl)imide).
- Use of solvents with functional groups which are less sensitive to reduction

Surface layer composition

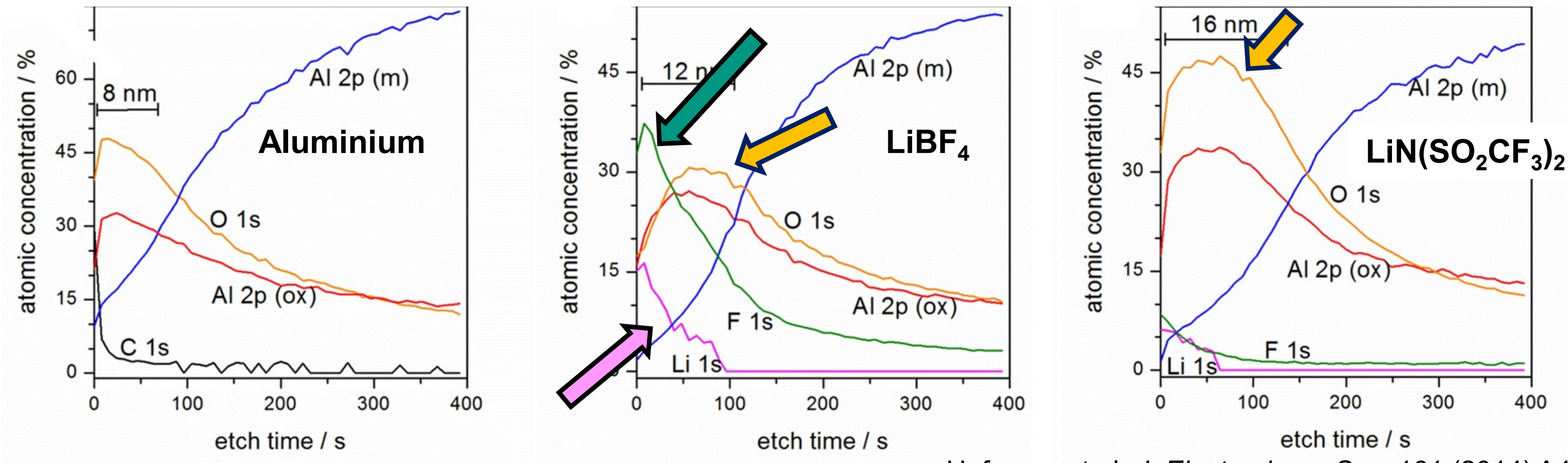
Cells

- Swagelok-cells
- Al | Li
- 3 – 5 V vs. Li/Li^+

X-ray photoelectron spectroscopy

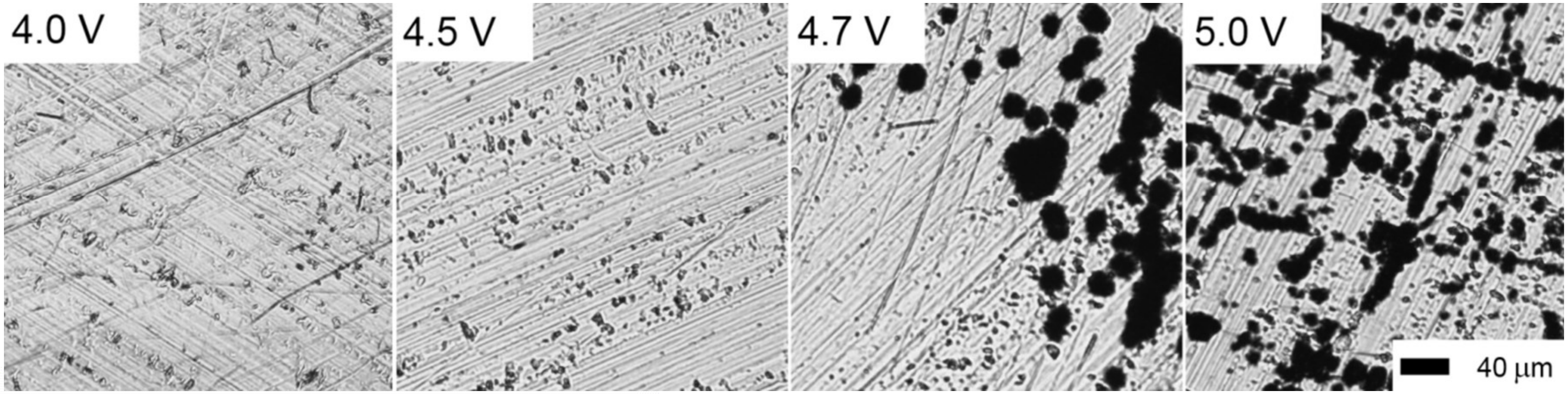
Results

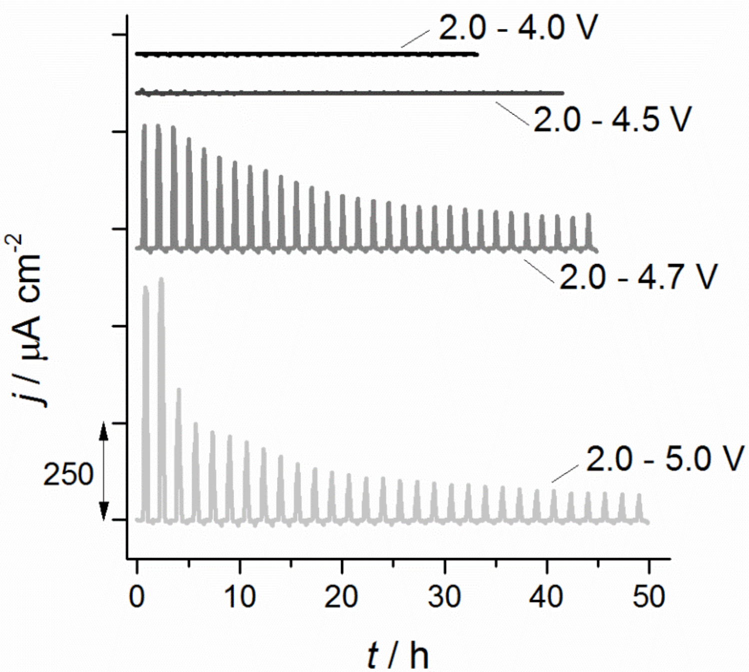
- F and Li can be detected in surface layer
- O-content is decreased
- **F** and **Li** are important for passivation



Hofmann et al. *J. Electrochem. Soc.* 161 (2014) A431

Potential range





- Potential range: 3 – x V (x = 4 – 5 V vs. Li/Li$^+$)
- Solvent: ionic liquid + propylene carbonate
- conducting salt: 1 M $LiN(SO_2CF_3)_2$
- Cells: aluminum | lithium (Swagelok)
- Critical potential at **4.6 V vs. Li/Li$^+$**
- **However**: dependent on solvent!

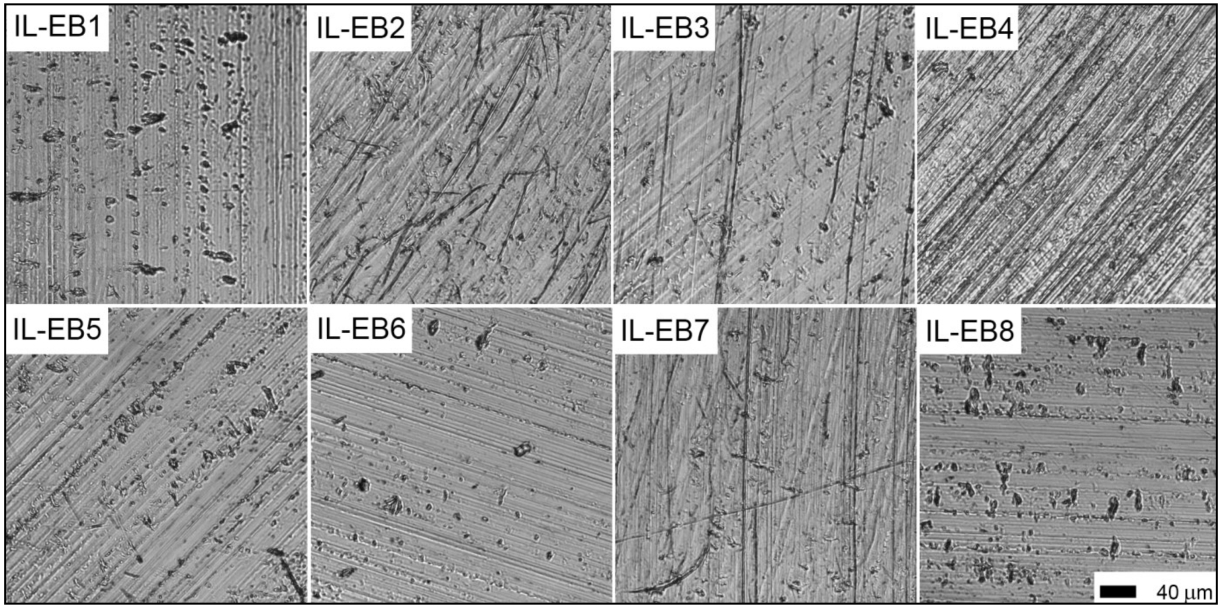
Hofmann et al. *Electrochim. Acta* 116 (2014) 388

Solvents (IL = ionic liquid)

	IL-EB 1	IL-EB 2	IL-EB 3	IL-EB 4	IL-EB 5	IL-EB 6	IL-EB 7	IL-EB 8
solvent	EMIM-BF_4	EMIM- BF_4	EMIM- BF_4	EMIM- BF_4	EMIM- BF_4	EMIM- BF_4	EMIM- BF_4	EMIM- BF_4
Conducting salt/ c[mol/kg]	$LiBF_4$/ 0,25	$LiBF_4$/ 0,5	$LiBF_4$/ 0,75	$LiBF_4$/ 1,0	LiTFSI/ 0,25	LiTFSI/ 0,5	LiTFSI/ 0,75	LiTFSI/ 1,0

EMIM-BF_4: 1-Ethyl-3-methylimidazolium tetrafluoroborate; $LiBF_4$: Lithium tetrafluoroborate; LiTFSI: Lithium bis(trifluoromethanesulfonyl)imide

- Swagelok Cells Al | Li
- 3 – 5 V vs. Li/Li^+
- No sign of Al dissolution even with the use of LiTFSI
- Ionic liquid solvent prevent Al corrosion excellently
- *Explanation:* Unable to dissolve the Al salts in the solvent



Solvents (IL = ionic liquid)

Cells

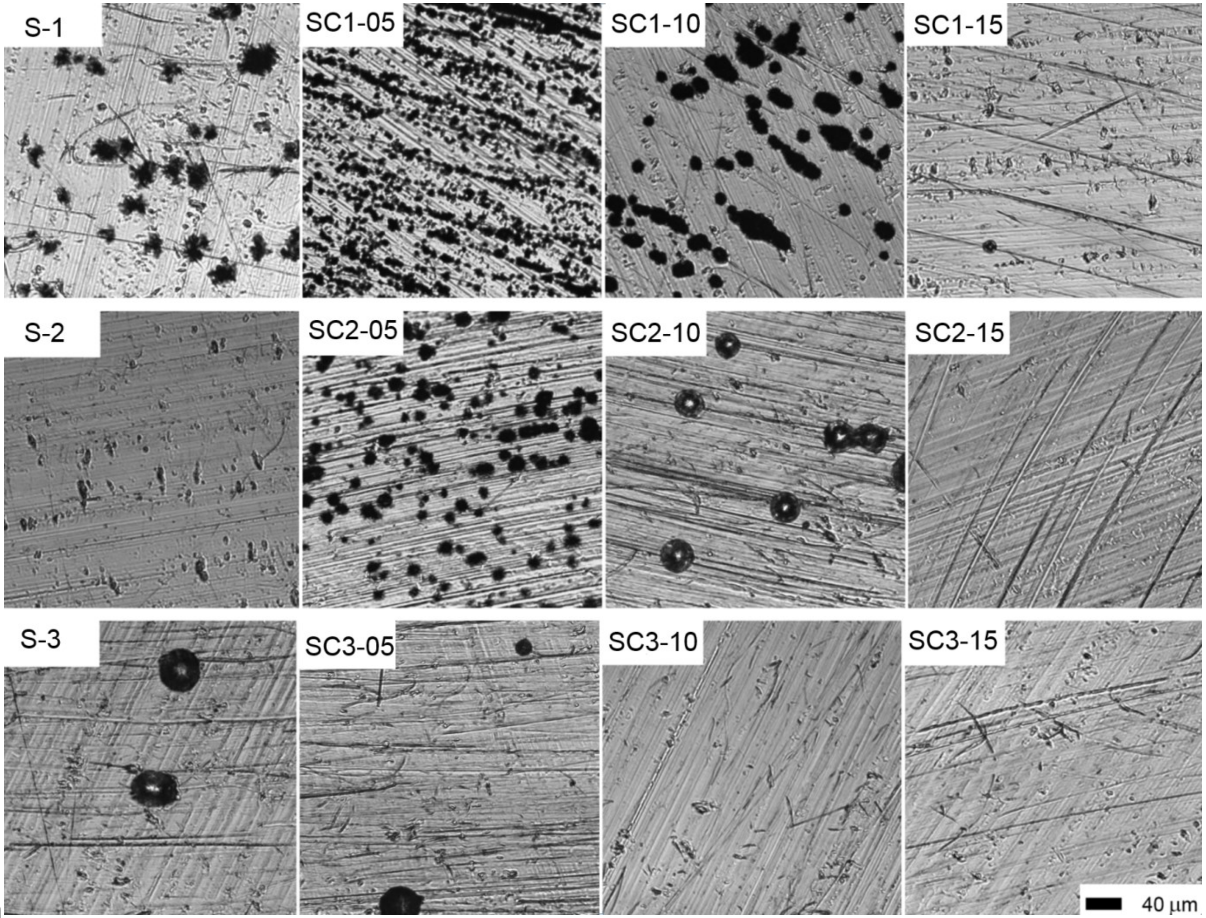
- Swagelok
- Al | Li
- 3 – 5 V vs. Li/Li$^+$

Composition

- **S-1** – PC + IL
- **S-2** – SL
- **S-3** – SL + IL
- $LiN(SO_2CF_3)_2$

Results

- Al more stable if sulfolane is used
- Better stability of Al, if conducting salt concentration is high



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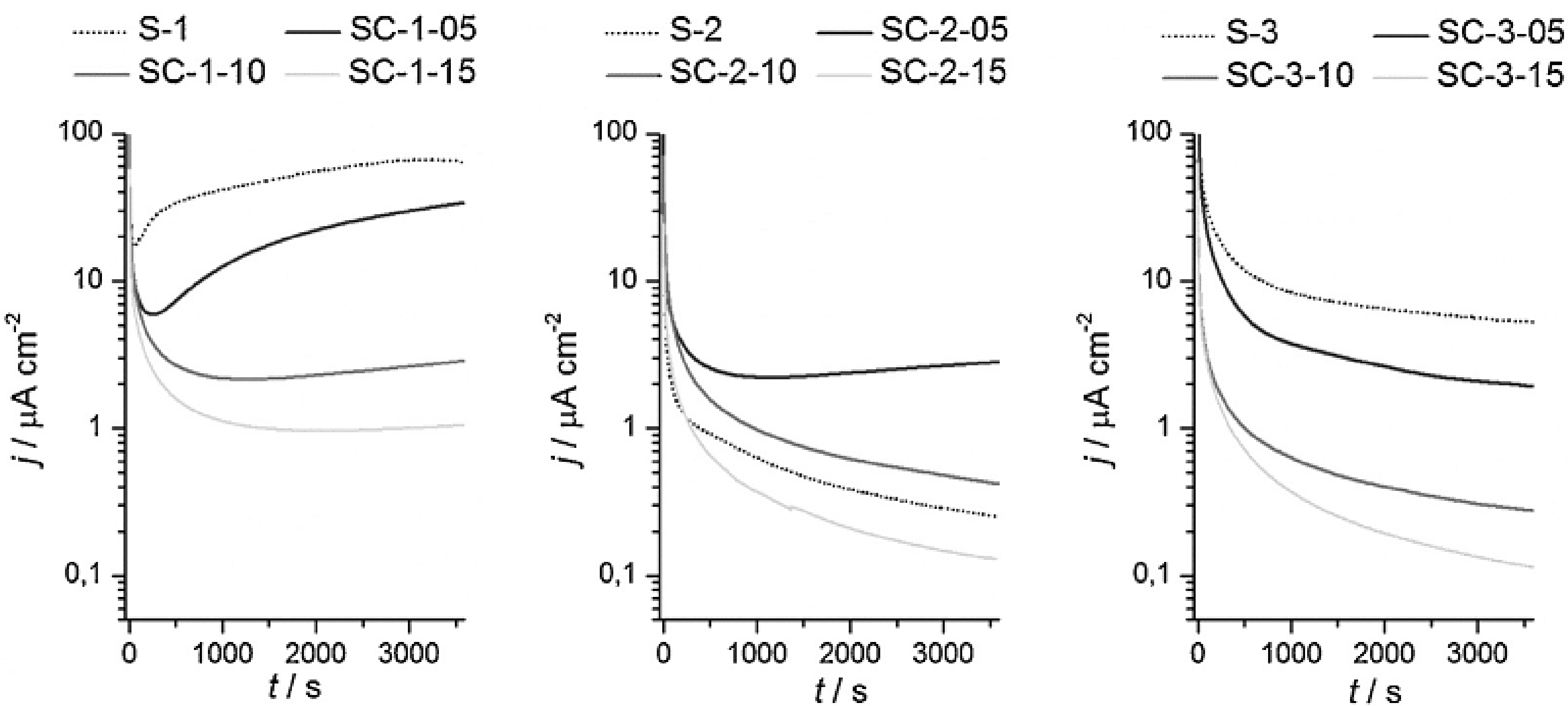
Solvents (IL = ionic liquid)



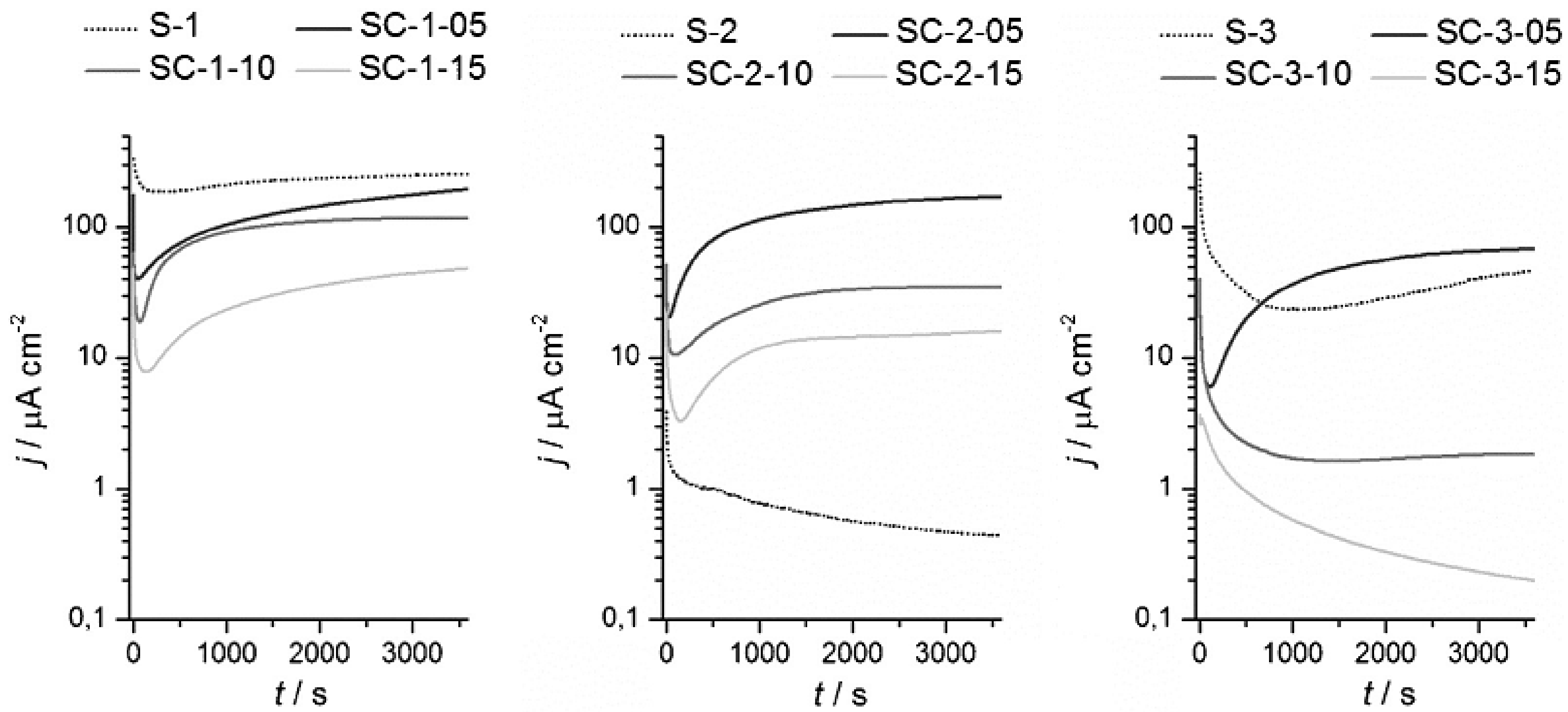
Composition

- **S-1** – PC + IL
- **S-2** – SL
- **S-3** – SL + IL
- $LiN(SO_2CF_3)_2$

Results

- Chronoamperograms at **4.3** V vs. Li/Li+
- Confirmation of the optical results
- Better stability of Al, if conducting salt concentration is high

Solvents (IL = ionic liquid)



Composition

- **S-1** – PC + IL
- **S-2** – SL
- **S-3** – SL + IL
- $LiN(SO_2CF_3)_2$

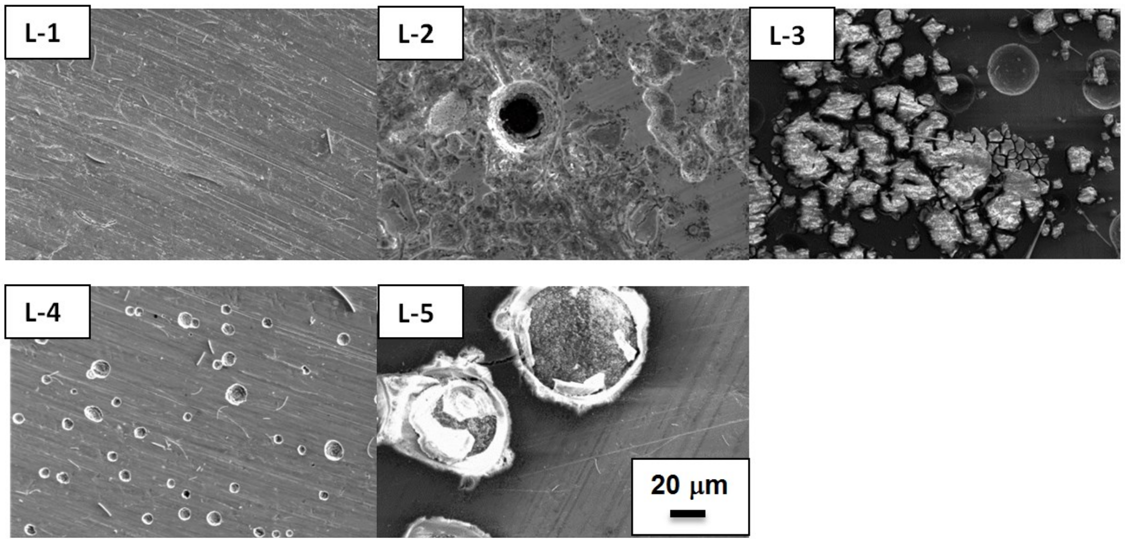
Results

- Chronoamperograms at **5** V vs. Li/Li+
- Confirmation of the optical results
- Better stability of Al, if conducting salt concentration is high and ionic liquid is present

Influence of conducting salt

- Solvent mixture:

  Propylene carbonate and ammonium based ionic liquid



L-1 $LiBF_4$
L-2 $LiOSO_2CF_3$
L-3 $LiClO_4$
L-4 $LiPF_6$
L-5 $LiN(SO_2CF_3)_2$

measurement after 20 cycle; U = 3 – 5 V (0.1 mV/s)

→

- The conducting salts $LiOSO_2CF_3$ and $LiN(SO_2CF_3)_2$ (= LiTFSI) cause severe corrosion
- Much less corrosion in case of conducting salts with readily available F^- ions

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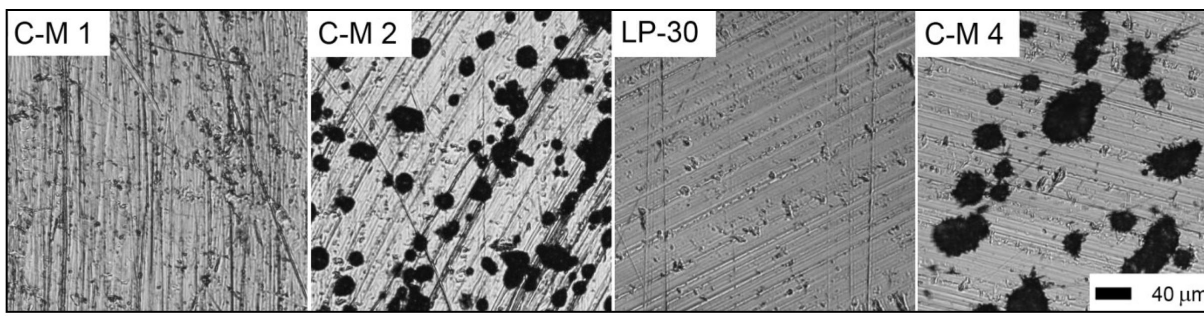
Influence of conducting salt

- Swagelok Cells Al | Li
- 3 – 5 V vs. Li/Li^+
- State of the art solvent mixture (EC/DMC)
- Use of LiTFSI and LiOTf yields in pitting corrosion
- No sign of Al dissolution if $LiBF_4$ or $LiPF_6$ is used up to 5 V vs. Li/Li^+
- *Explanation:* Destruction of the AlF_3 and/or Al_2O_3 layer

	C-M 1	C-M 2	C-M 3	C-M 4
Solvent (1:1 wt.)	EC- DMC	EC- DMC	EC- DMC	EC- DMC
Conducting salt	$LiBF_4$	LiTFSI	$LiPF_6$	LiOTf
c [mol/kg]	1,0	1,0	1,0	1,0

EC: ethylene carbonate; DMC: dimethyl carbonate; $LiBF_4$: Lithium tetrafluoroborate; LiTFSI: Lithium bis(trifluoromethanesulfonyl)imide; $LiPF_6$: lithium hexafluorophosphat; LiOTf: lithium trifluoromethanesulfonate



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Improve by additives (e.g. LiBOB)

Suppress of pitting corrosion using lithium bis(oxalato) borate

Cells

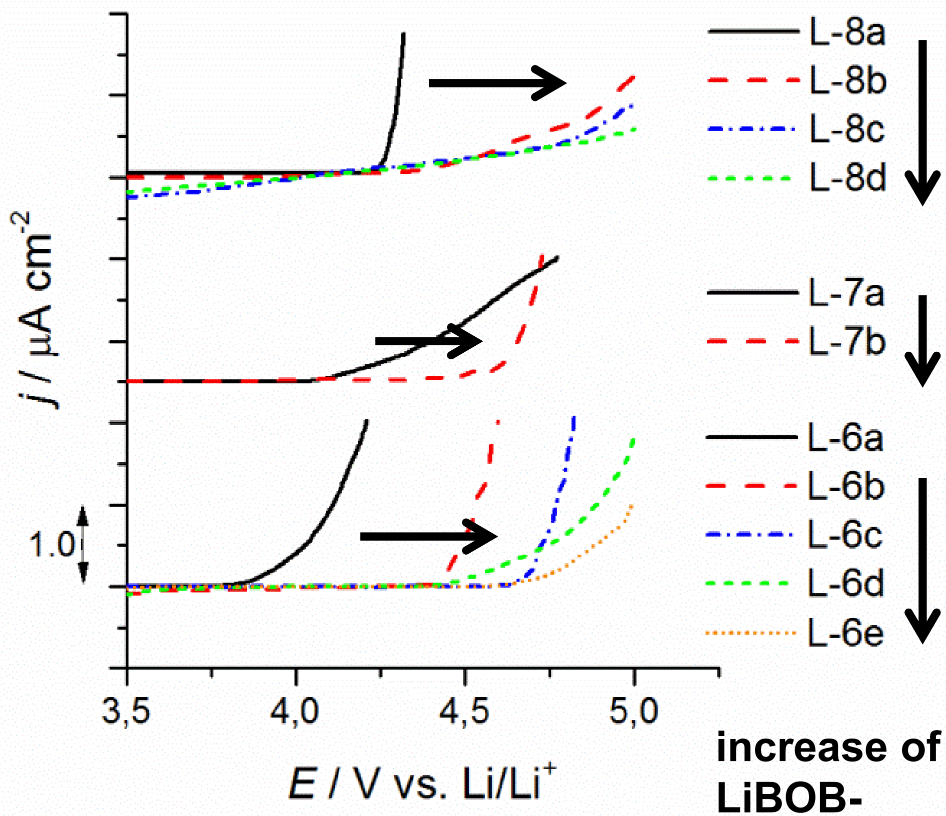
- Swagelok
- Al | Li
- 3 – 5 V vs. Li/Li^+

Composition

- Solvent: ammonium based ionic liquid + propylene carbonate
- **L-8** – LiTFSI + LiBOB
- **L-7** – $LiPF_6$ + LiBOB
- **L-6** – LiOTf + LiBOB

Results

- Better stability of Al, if LiBOB concentration is high



increase of LiBOB-concentration

Hofmann et al. *J. Electrochem. Soc.* 161 (2014) A431

Improve by additives (e.g. LiBOB)

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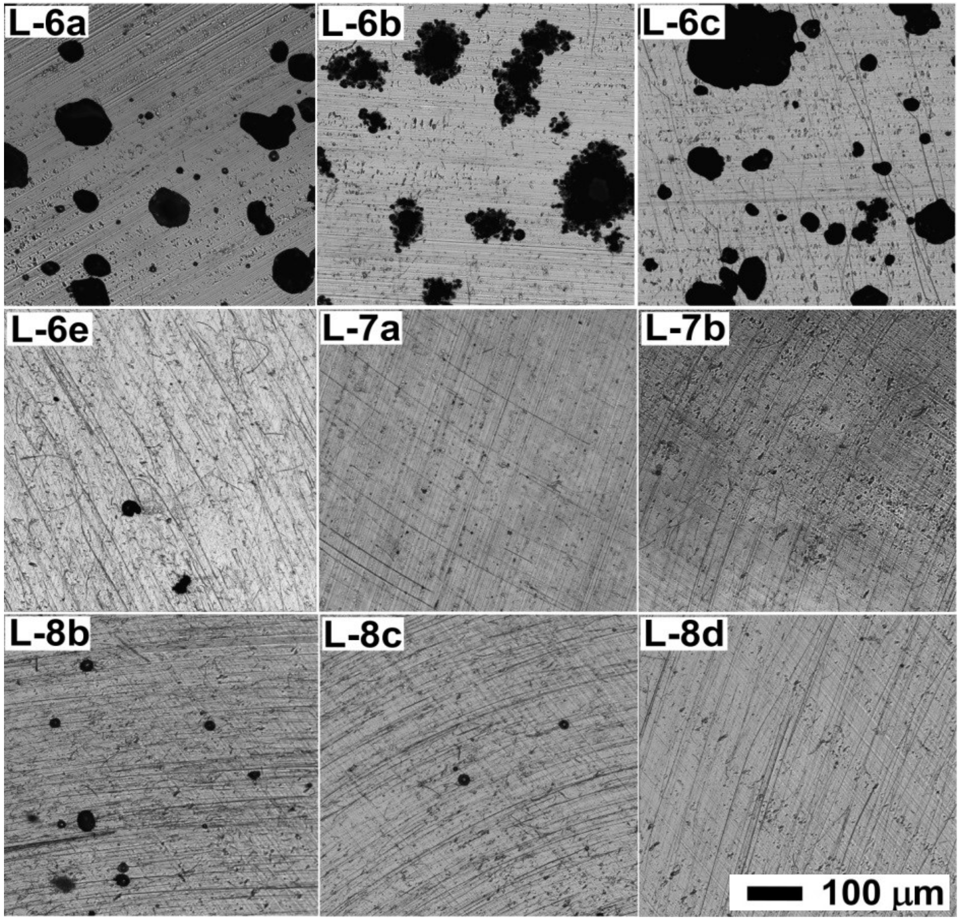
Suppress of pitting corrosion using lithium bis(oxalato) borate

Microscopical analysis of the aluminum foil after 20 cycles at 3–5 V



Composition

- Solvent: ammonium based ionic liquid + propylene carbonate
- **L-8** – LiTFSI + LiBOB
- **L-7** – $LiPF_6$ + LiBOB
- **L-6** – LiOTf + LiBOB

Results

- Less Al dissolution at high concentrations of LiBOB
- Al stability: $LiPF_6$ > LiTFSI > LiOTf

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Conclusion:
Important factors to suppress Al-dissolution:

- Potential range
- Non-corrosive conducting salts
- Additives for additional aluminum protecting layer
- Use of ionic liquids
- Solubility of Al salts in electrolyte
- Conducting salt concentration should be high

→ **Small changes in the electrolyte composition can cause severe effects in cell chemistry!**

Publications

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- A. Hofmann, M. Schulz, T. Hanemann
  “**Gel Electrolytes based on Ionic Liquids for Advanced Lithium Polymer Batteries**”
  Electrochimica Acta, 89, 823-831 (2013).
- A. Hofmann, M. Schulz, T. Hanemann
  „**Effect of Conducting Salts in Ionic Liquid based Electrolytes: Viscosity, Conductivity, and Li-Ion Cell Studies**”
  International Journal of the Electrochemical Science, 8, 10170 - 10189 (2013).
- N. Schweikert, A. Hofmann, M. Schulz, M. Scheuermann, S. T Boles, T. Hanemann, H. Hahn, S. Indris
  “**Suppressed Lithium Dendrite Growth in Lithium Batteries Using Ionic Liquid Electrolytes: Investigation by Electrochemical Impedance Spectroscopy, Scanning Electron Microscopy, and In Situ ^{7}Li Nuclear Magnetic Resonance Spectroscopy**”
  J. Power Sources, 228, 237-243 (2013).
- A. Hofmann, L. Merklein, M. Schulz, T. Hanemann
  “**Anodic Aluminum Dissolution of LiTFSA Containing Electrolytes for Li-Ion-Batteries**”
  Electrochimica Acta, 116, 388–395 (2014).
- A. Hofmann, V. Winkler, M. Schulz, T. Hanemann
  „**Anodic Aluminum Dissolution in Conducting Salt Containing Electrolytes for Lithium-Ion Batteries**”
  Journal of the Electrochemical Society, 161, A431 – A438 (2014).

Acknowledgement

- Prof. Dr. Thomas Hanemann
- Lisa Merklein
- Volker Winkler
- Dr. Michael Schulz
- Dr. Martin Tosoni
- Bing Li
- Oliver Schwindt
- Matthias Migeot

Thank you very much for your attention!

Further information:

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