Karlsruhe Institute of Technology

Institut für Angewandte Materialien
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# Anodic Aluminum Dissolution in Electrolytes for Lithium-Ion Batteries

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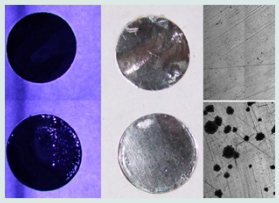
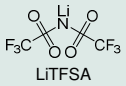
## Summary

- Investigation of the compatibility of aluminum in Li-ion cells for high voltage applications
- Strong dependence of Al dissolution on solvents and conducting salts
- Additives are able to prevent anodic aluminum dissolution considerably



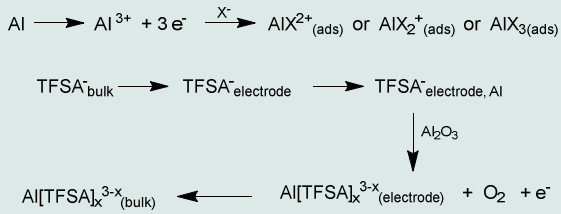
## Motivation

- Use of less-toxic conducting salts in Li-ion cells
- Understanding of the passivation layer on aluminum
- Specific formation of an Al protective layer
- Enabling the use of high voltage materials
- Pre-formation of a sufficient protective layer




LiTFSA

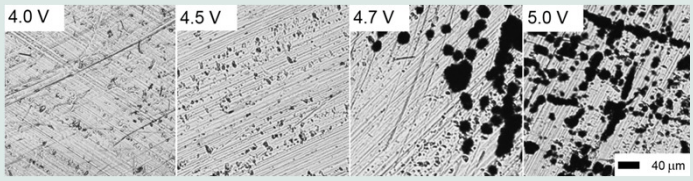
## Mechanism*



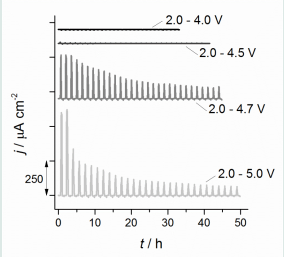

- Conducting salts are able to destroy the passivation layer
- Unprotected Al can react readily at common potentials applied in a Li-ion cell (< 4.2 V)
- In common electrolytes: formation of a stable lithiumoxyfluoride layer
- Al salts have to be soluble for continual dissolution

## Potential range

- Strong dependence of pitting corrosion on potential range
- Study of Al|Li Swagelok® cells



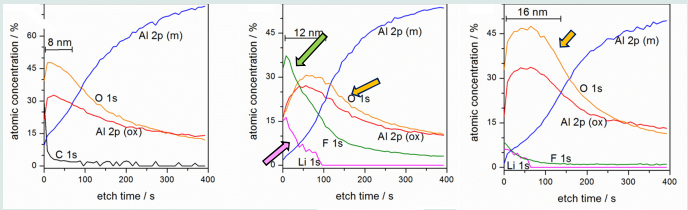

- Potential range = 3 – *x* V (*x* = 4 – 5 V)
- Solvent:
  ammonium-based ionic liquid
  propylene carbonate (1:1)
- Conducting salt: lithium bis(trifluoro-methanesulfonyl)azanide (= LiTFSA)
- Critical potential at 4.6 V vs. Li/Li+
- 30 cycles at 1 mV s-1




**Critical potential is highly dependent from solvent, conducting salt and additives**

## Composition of the aluminum surface

- Cycling Swagelok cells (Al|Li, 3 – 5 V vs. Li/Li+) at 0.1 mV s-1
- Analysis of the aluminum surface via XPS (depth profiling)
- F and Li rich species can be detected in the surface layer substituting O containing species by using conducting salts with "available" fluorine ions

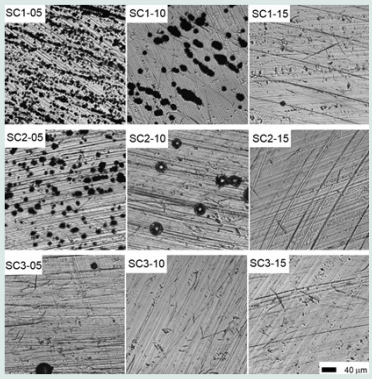



**aluminum reference (without cycling)** | **$LiBF_4$ (after cycling)** | **$LiN(SO_2CF_3)_2$ (after cycling)**

**Surface modification of Al by conducting salts under cycling**

## Effect of conducting salt concentration and LiBOB as additive

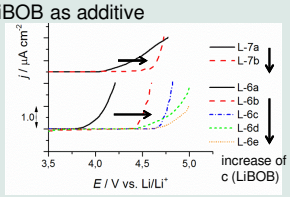
- SC1: propylene carbonat + ammonium based ionic liquid
- SC2: sulfolane
- SC3: sulfolane + ammonium based ionic liquid
- Conducting salt: LiTFSA
  (0.5 – 1.0 – 1.5 mol kg-1)
- E = 3 – 5 V vs. Li/Li+
- Al|Li Swagelok cells
- 20 cycles at 0.1 mV s-1




0.5 mol/kg 1.0 mol/kg 1.5 mol/kg

**Strong dependence of corrosion pits from solvent mixture and salt concentration**

LiBOB as additive




| sample | conducting salt | $E_{crit}$ / V vs. Li/Li+ (first cycle) |
|---|---|---|
| L-6a | LiOTf / LiBOB | 4.0 |
| L-6b | LiOTf / LiBOB | 4.4 |
| L-6c | LiOTf / LiBOB | 4.6 |
| L-6d | LiOTf / LiBOB | 4.5 |
| L-6e | LiOTf / LiBOB | > 4.7 |
| L-7a | $LiPF_6$ / LiBOB | 4.1 |
| L-7b | $LiPF_6$ / LiBOB | 4.6 |

**Enhance of LiBOB concentration improves the oxidative Al stability**

## Conclusions

- Anodic aluminum dissolution is critical in high voltage applications
- Additives can improve the oxidative stability significantly
- Conducting salts affect the formation of the Al surface layer greatly
- Ionic liquid based solvents are able to reduce the aluminum dissolution
- Solvation of Al salts as prerequisite for Al dissolution

## Acknowledgements

We acknowledge IoLiTec Ionic Liquids Technologies GmbH for kindly providing ionic liquids and Dr. Martin Tosoni for helpful discussions.

- * Wang et al., *Electrochim. Acta* 45 (2000) 2677.
- Hofmann et al. *Electrochim. Acta* 116 (2014) 388; Hofmann et al. *J. Electrochem. Soc.* 161 (2014) A431.