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Institut für Angewandte Materialien Werkstoffprozesstechnik

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 AI protective layer
- Enabling the use of high voltage materials
- Pre-formation of a sufficient protective layer

Mechanism*



 $AI[TFSA]_x^{3-x}(bulk)$ \checkmark $AI[TFSA]_x^{3-x}(electrode)$ + O_2 + e^{-1}

- Conducting salts are able to destroy the passivation layer
- Unprotected AI 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



2.0 - 4.0 V Potential range = 3 - x V (x = 4 - 5 V)20-45V Solvent: ammonium-based ionic liquid cm⁻² 20-47V propylene carbonate (1:1) Ā Conducting salt: lithium bis(trifluoromethanesulfonyl)azanide (= LiTFSA) 2.0 - 5.0 V Critical potential at 4.6 V vs. Li/Li+ 30 30 cycles at 1 mV s⁻¹ 40 10 20 t/h

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



Surface modification of AI 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⁺
- AllLi Swagelok cells
- 20 cvcles at 0.1 mV s⁻¹
- \leq

Strong dependence of corrosion pits from solvent mixture and salt concentration



SC3-10

C3-15





| 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 _e / LiBOB | 4.6 |

Enhance of LiBOB concentration improves the oxidative AI 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 AI salts as prerequisite for AI dissolution

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* 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.



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