Development of corrosion protection layers for current collectors

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Introduction: The first approaches of lithium ion batteries with simultaneous lithium and anion intercalation are based on commercial electrolytes consisting of organic solvents and a dissolved Li-salt. These solvents have a limited electrochemical and thermal stability. Therefore in the new dual-ion cell these solvents are replaced by ionic liquids, which are compatible with higher cell voltages. But some anions are corrosive to the aluminum current collector at potentials above 5 V. The approach of depositing an electronically conductive protection layer made of metal oxides is presented in this work.

Corrosion of current collector:

- aluminum oxide layer is locally removed
- Pit corrosion triggered by fluorinated anions like TFSI: bis(trifluoromethylsulfonyl)imide

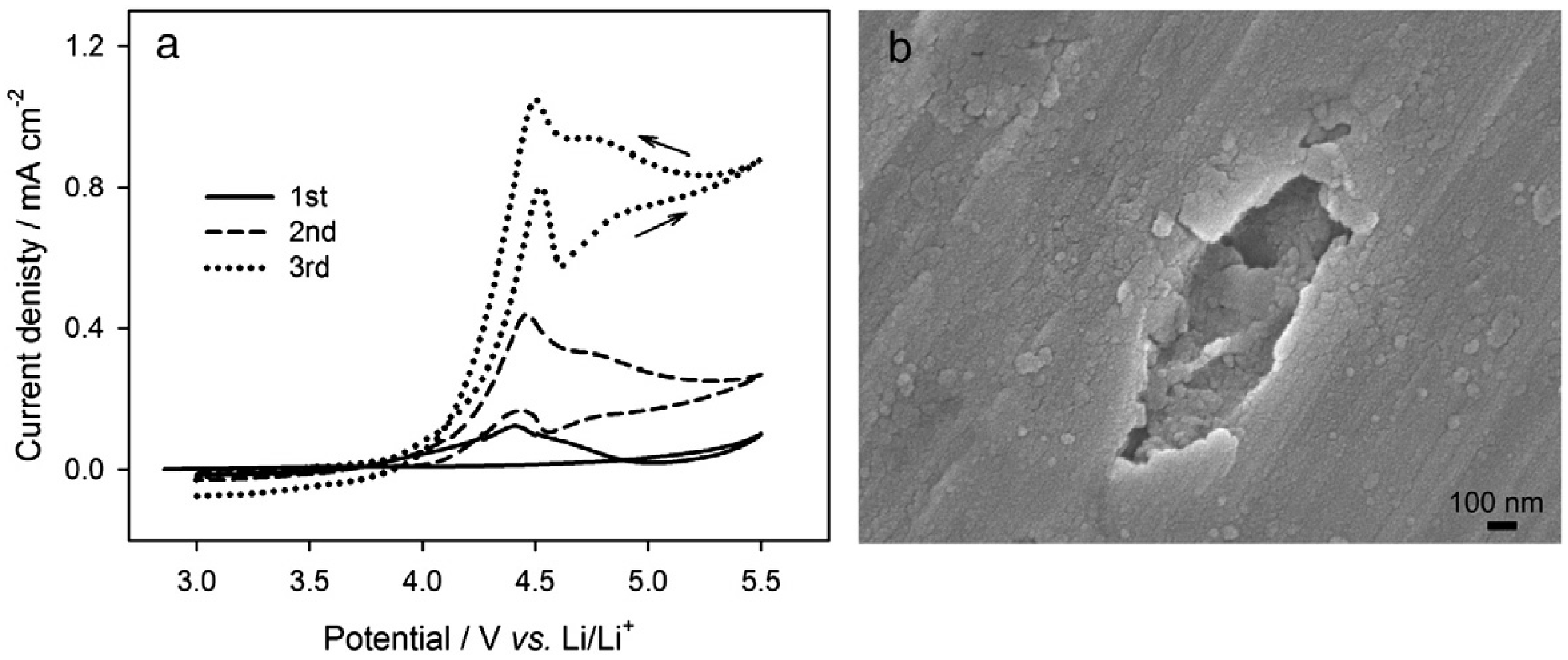

***Figure 1:** Aluminum working electrode in 1 M LiTFSI/PMPyr-FSI electrolyte; (a) cyclic voltametry, 10 mV/s; (b) FE-SEM after CV; from Cho, E. et al., Electrochem. Comm., 2012, 22, 1-3.*

Approach:

- Deposition of thin ceramic layers on aluminum foil by sol-gel method (dip- or spin-coating) and subsequent heat treatment or PVD (reactive sputtering)
- Materials: electronically conductive metal oxides, e.g. CGO, ZnO:Al

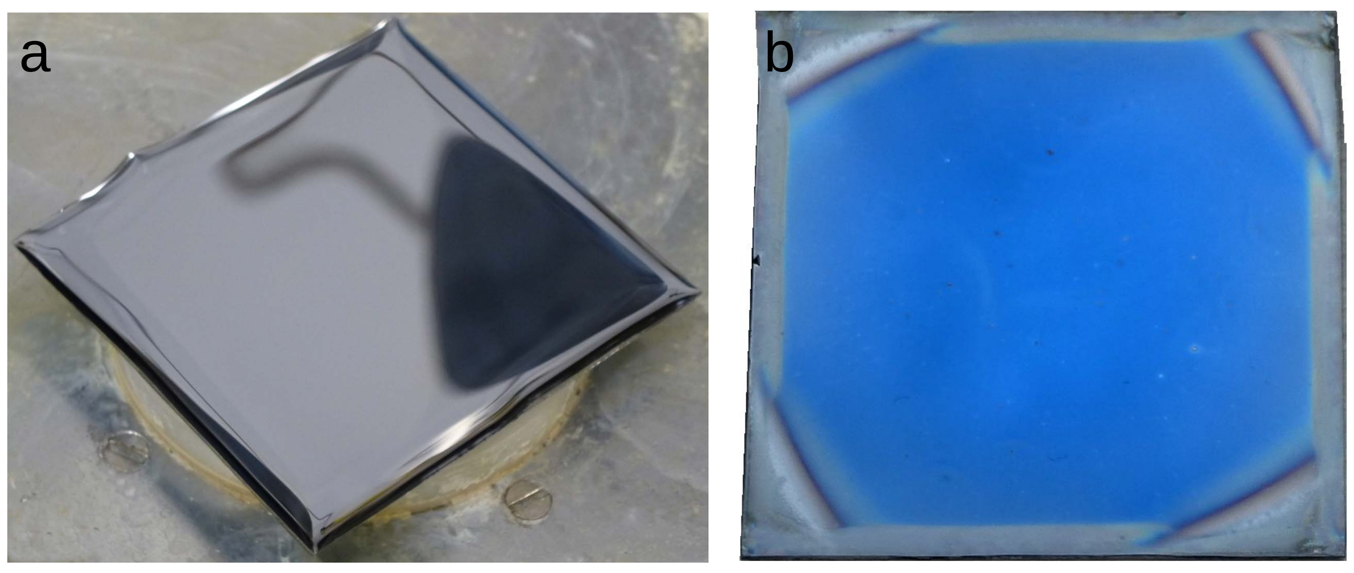

***Figure 2 a:** Sol wetted silicon wafer (5x5 cm²) using 0.15 M ethanolic solution of stabilized particles (sizes 0.7…7 nm).*

***Figure 2 b:** Photo after 2x spin-coating and heat treatment at 500 °C (10 min).*

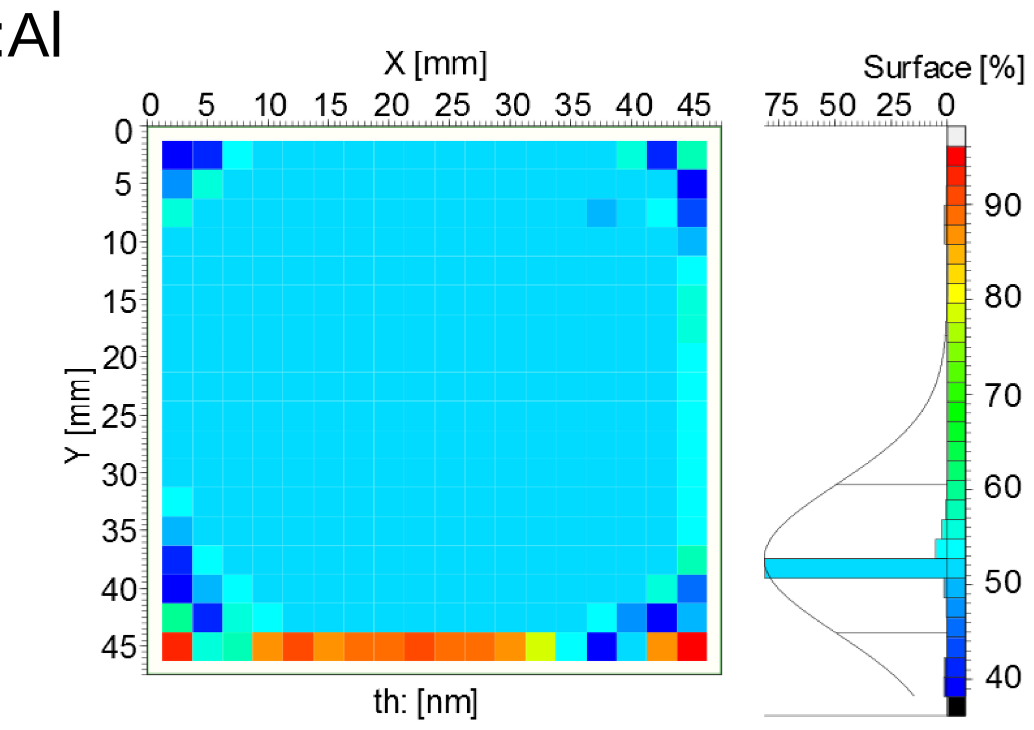

***Figure 3:** Laser ellipsometry graphic of a layer (see figure 3).* Except for the thicker areas at the edges, the film thickness is conformal (52 nm).

Characterization:

- Laser ellipsometry for film thickness
- SEM and XRD for layer structure
- Electrochemical investigation in test cells

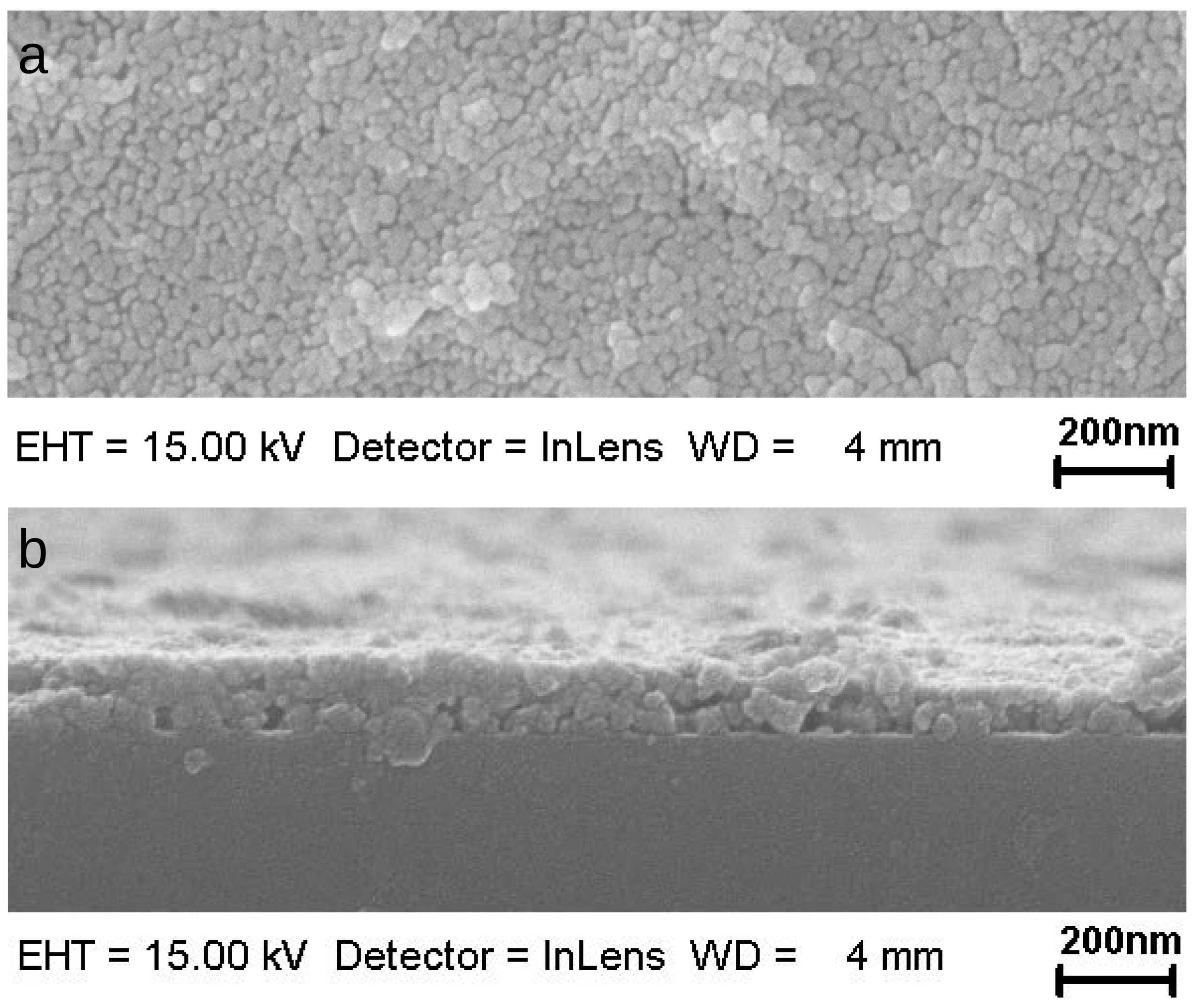

***Figure 4:** SEM image of a ZnO:Al layer, deposited by spin-coating 3x, heated at 500 °C (a) surface, (b) fracture. The microstructure is fine-grained and microporous. The layer covered the substrate completely and had sufficient adhesion.*

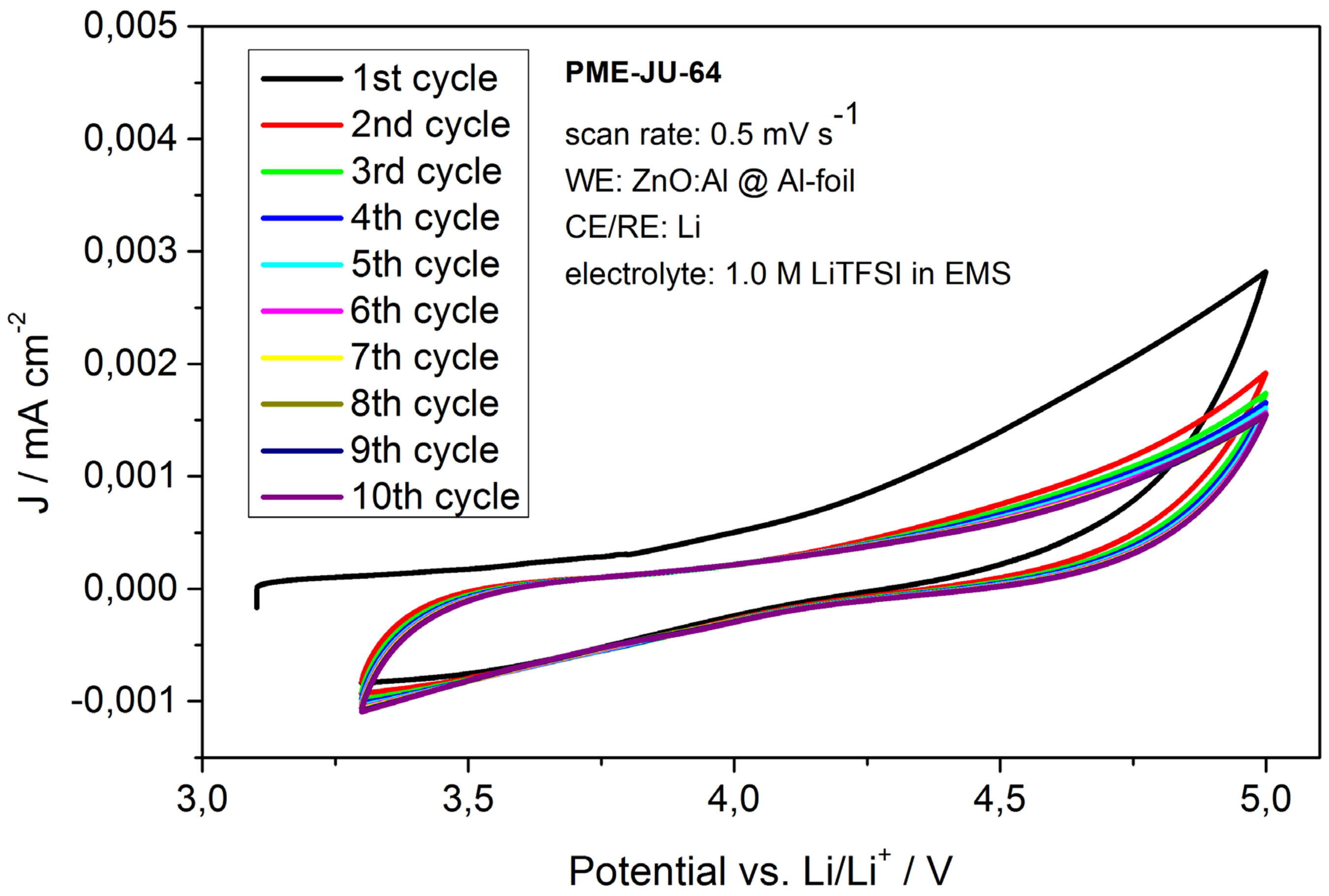

***Figure 5:** CV of ZnO:Al layer on aluminum foil. The low and decreasing current density indicates a suppressed corrosion. Data from P. Meister, MEET Battery research center.*

Conclusion and Outlook:

- Diverse mixed/doped oxides were synthesized and thin homogenous films were deposited on aluminum foil.
- Protection layers were characterized regarding their structure, firstly on silicon wafers.
- Samples of ZnO:Al films showed a promising electrochemical performance in CV tests.
- New materials with different compositions will be deposited and tested.
- The coating procedure will be improved referring to the layer's densification.

Acknowledgements: Financial support by the BMBF project "Insider" (no. DB001089) is gratefully acknowledged.

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