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Sol-gel surface coating of cathode materials for lithium ion batteries

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Motivation

Lithium ion batteries play an important role in the field of electromobility and stationary energy storage. Unfortunately, major issues with respect to cathode degradation arise due to metal ion dissolution, cation disorder or phase transitions. The sol-gel method is a useful and widely used strategy to apply functional cathode coatings to prevent these unwanted side reactions and reduce heat generation during cycling resulting in an improved electrochemical performance.

Different sol-gel coatings on planar model electrodes are evaluated with regard to material compatibility and electrochemical performance. To ensure optimal coating conditions, surface pretreatment and wettability, precursor selection, dip/spin coating process as well as heat treatment parameters are equally taken into account. In consideration of economic aspects, suitable coating materials are transferred to commercial cathode materials in powder form.

Planar substrates

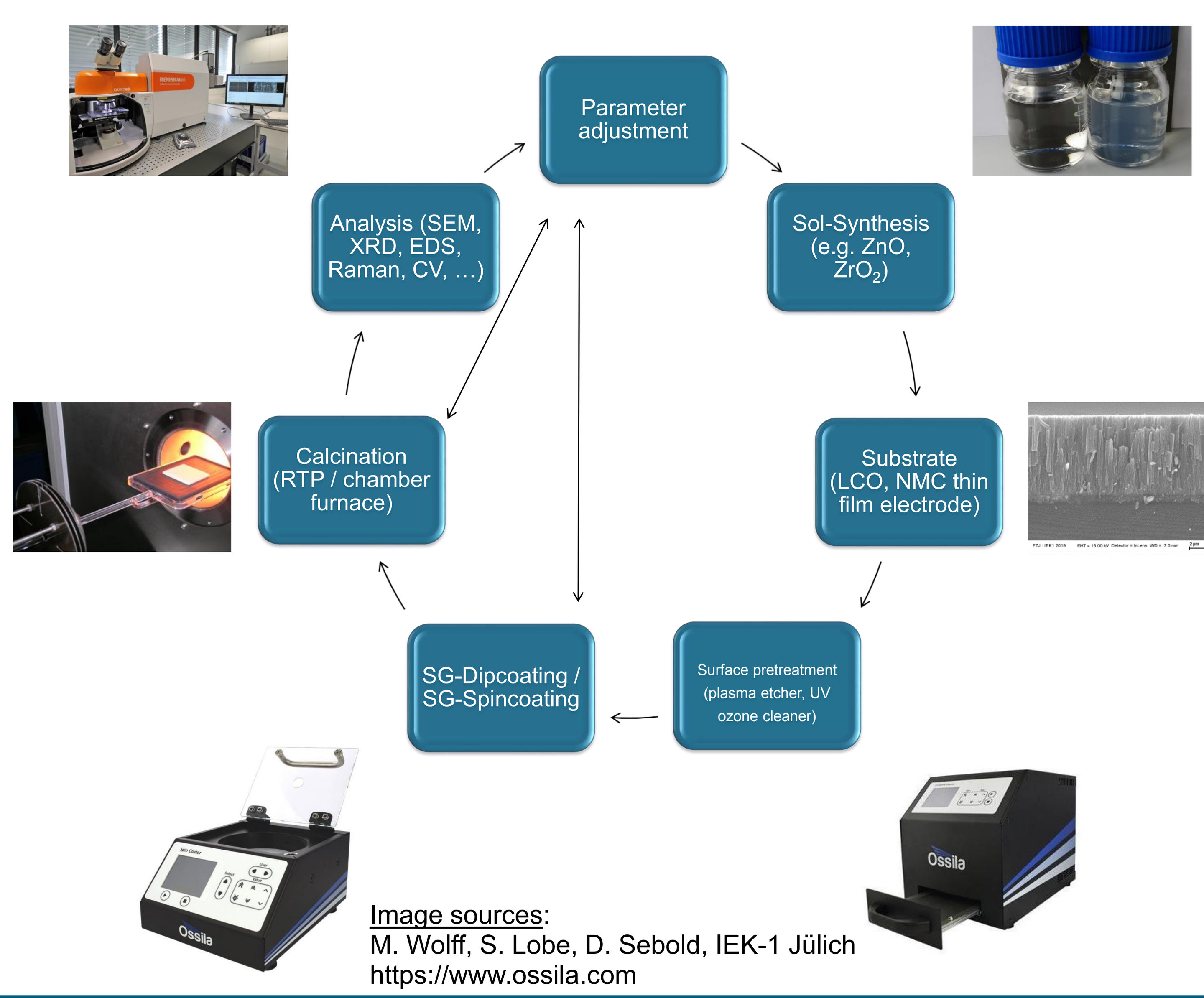

Image sources:
M. Wolff, S. Lobe, D. Sebold, IEK-1 Jülich
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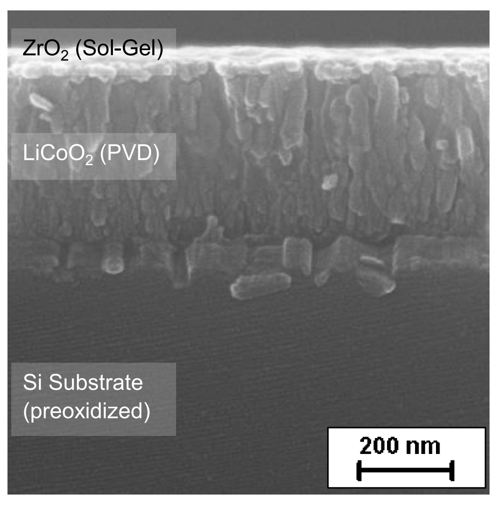
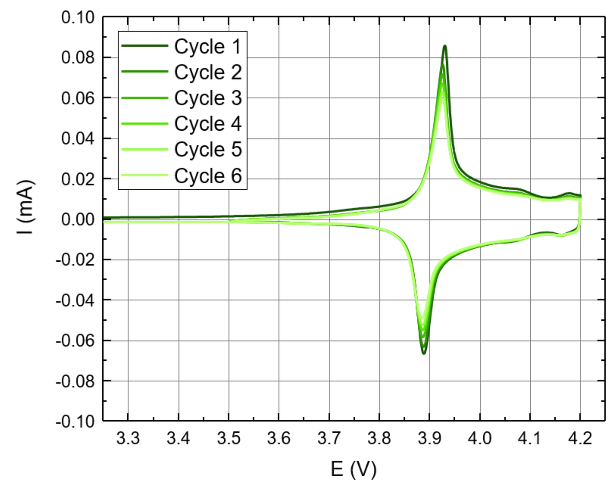
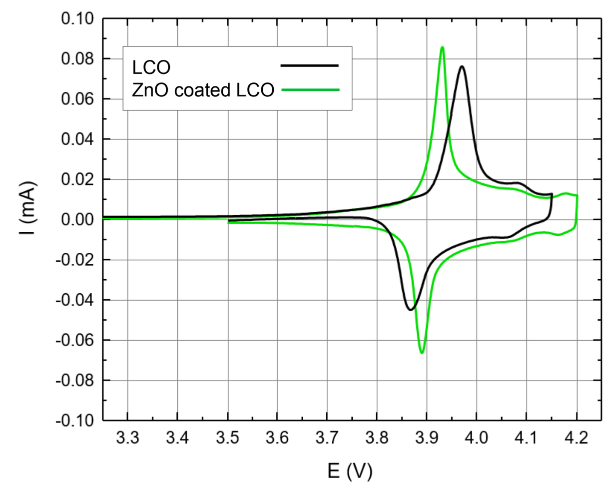


ZrO_2-coated $LiCoO_2$ (LCO) thin film cathode



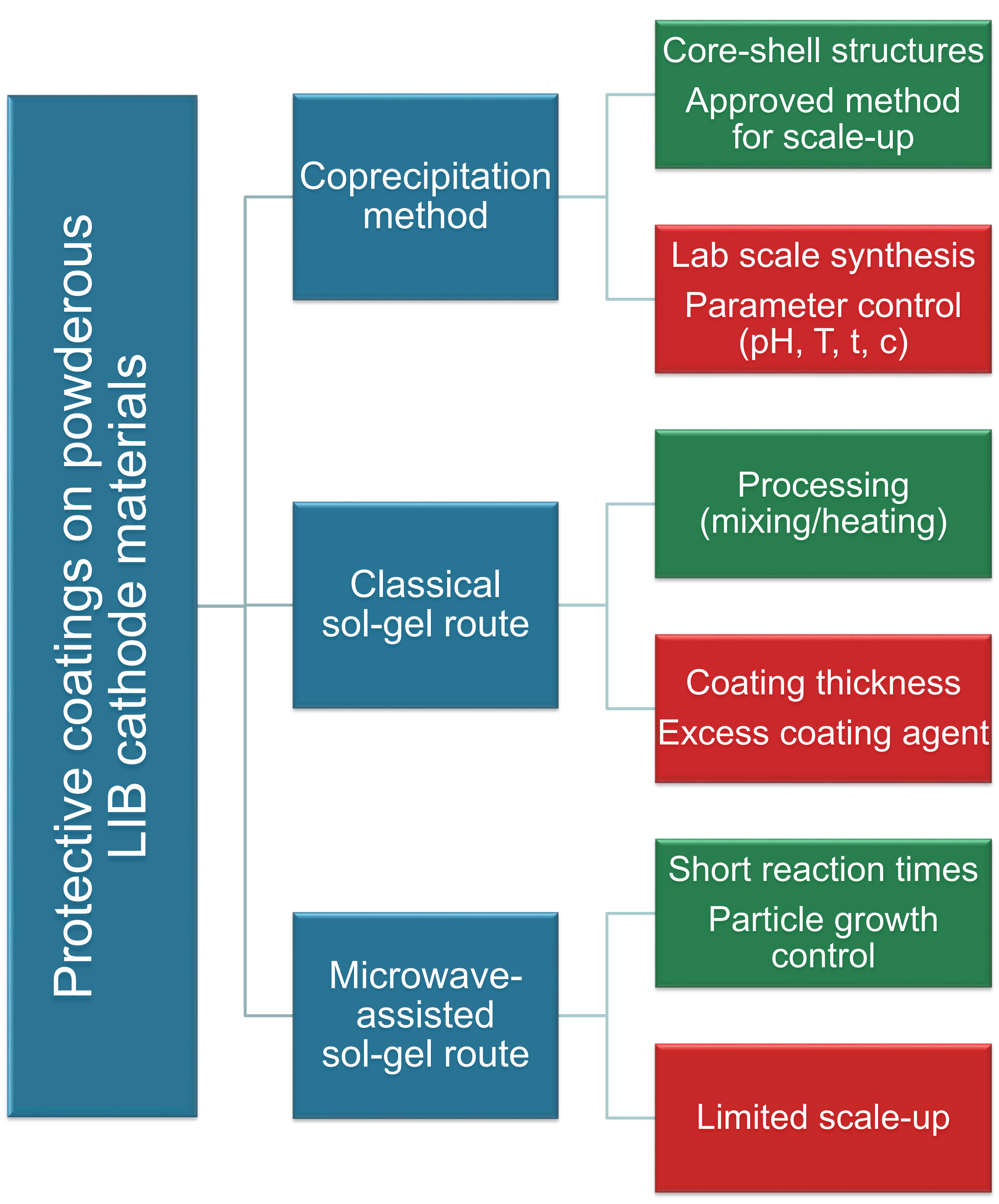
Cyclic Voltammetric (CV) measurement of ZnO coated LCO

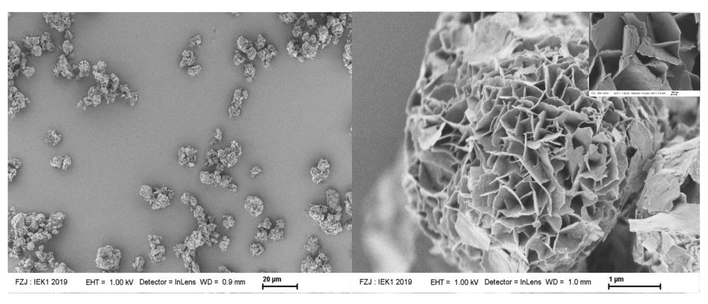


CV of untreated vs. coated LCO thin film cathode

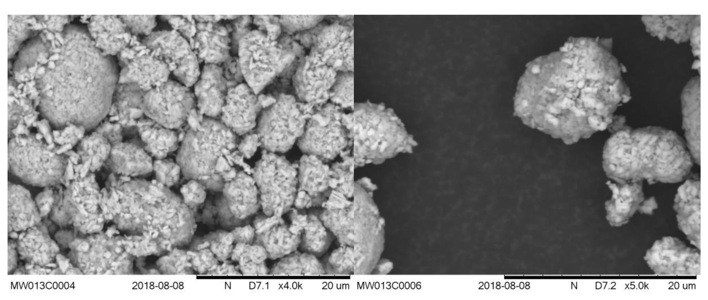
Aim:	Ultra-thin (d < 50 nm) metal oxide coatings (e.g. ZrO_2, ZnO) on thin-film cathodes (e.g. $LiCoO_2$ (LCO), $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$(NMC622))
Methods:	Dip-Coating, Spin-Coating (Cleanroom, ISO 5)
Substrate:	sputter deposited $LiCoO_2$ on Si(100)
Sols:	Metal precursors (e.g. $Zn(OAc)_2$) in non-aqueous solvents (e.g. EtOH, PrOH) with different sol stabilizers
Results:	ZnO coated LCO thin-film cathodes show improved cyclability compared to untreated cathodes

Powders

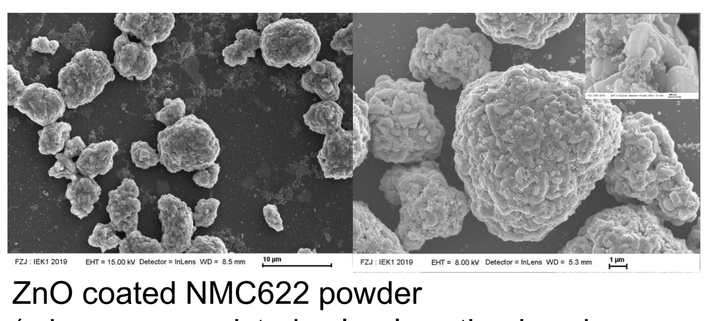




NMC622/NMC111 composite (coprecipitation method using metal sulfates, sodium hydroxide and ammonia solution)



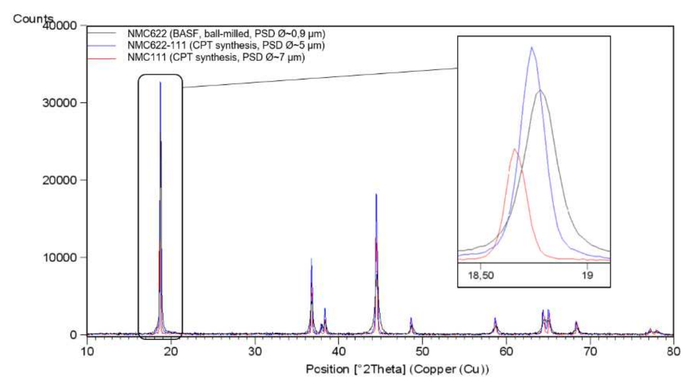
ZrO_2 coated NMC622 powder (sol-gel synthesis using zirconium propoxide and isopropyl alcohol)



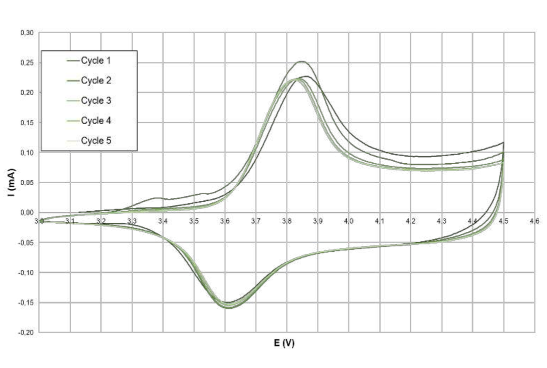
ZnO coated NMC622 powder (microwave-assisted sol-gel synthesis using zinc acetate and benzyl alcohol [1])

Aim: NMC ($LiNi_xMn_yCo_zO_2$, x+y+z=1) Core-Shell structures with Ni-rich core and Ni-poor shell

Results: composite NMC622/NM111 microspheres composed of aggregated nanoplatelets



XRD measurement of NMC composite in comparison with single phase compounds



Cyclic Voltammetric measurement of NMC622/NMC111

Planned measures: surface modification with ZrO_2 and ZnO, doping with Zr and Zn; TEM measurements

Aim: Ultra-thin coatings of ZnO on commercial cathode materials through a one-pot synthesis in a laboratory microwave

Results: partial coating of NMC622 cathode powder with nanoscaled ZnO particles

Planned measures: electrochemical testing, improvement of particle surface coverage

Conclusion

Sol-gel derived ZnO and ZrO_2 coatings have been identified as suitable coating material for planar thin-film $LiCoO_2$ cathodes. CV measurements confirm an improved performance compared to uncoated cathodes. Aiming for a transfer of results to powderous cathode materials, different wet-chemical process strategies have been evaluted, whereas syntheses via coprecipitation method and microwave-assisted sol-gel route show the most promising results so far.

References: [1] I. Bilecka, L. Luo, I. Djerdj, M. D. Rossell, M. Jagodic, Z. Jaglicic, Y. Masubuchi, S. Kikkawa, M. Niederberger, *J. Phys. Chem. C* **2011**, *115*, 1484–1495

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