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TOWARDS MORE SUSTAINABLE BATTERY MATERIALS: INSIGHTS INTO THE FUNDAMENTAL PROPERTIES OF DIFFERENT MATERIAL CLASSES USING SOLID-STATE THIN-FILM MODEL CELLS

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Goals:

Design, synthesis, and study of more sustainable battery materials:

- High performance solid-state batteries
- Minimal use of critical elements
- Fundamental studies of complex redox processes
- Chemical and structural stability of the materials and interfaces

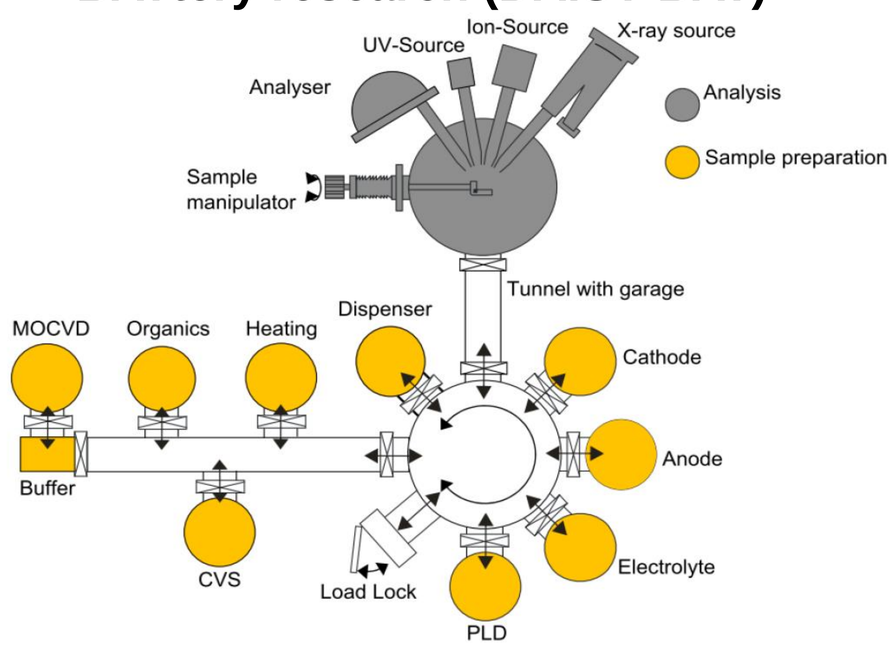
Methods:

- Materials design and simulations with DFT
- Materials synthesis via flexible element substitution using thin-film growth
- Free-standing solid-state thin-film model cells for physical operando investigations
- Flexible combination of solid electrolyte and electrodes

Examples:

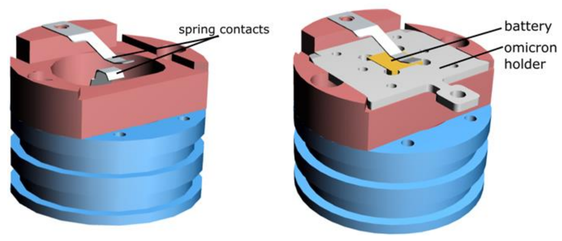
- Solid state electrolytes: β-Alumina, Nasicon, LIPON, Ohara, …
- Cathode materials: Na_xCoO_2, $Li_x(Ni,Mn,Co)O_2$, $LiCoPO_4$-$LiCo_2P_3O_{10}$ (LCP-LCPO)...
- Anode materials: Li, Na
- Thin-film deposition using PLD, Sputtering, Evaporation, MOCVD, …
- Operando studies with XRD, XPS, Raman, XAS…

DArmstadt Integrated SYstem for BATtery research (DAISY-BAT)

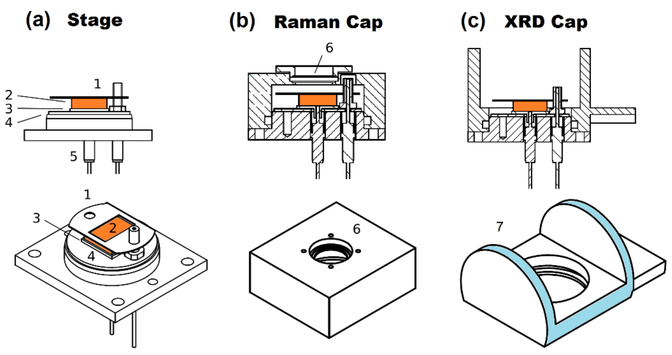


Operando measurements

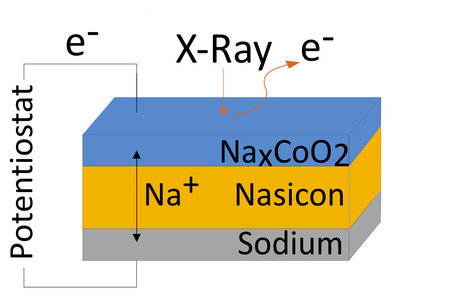
XPS

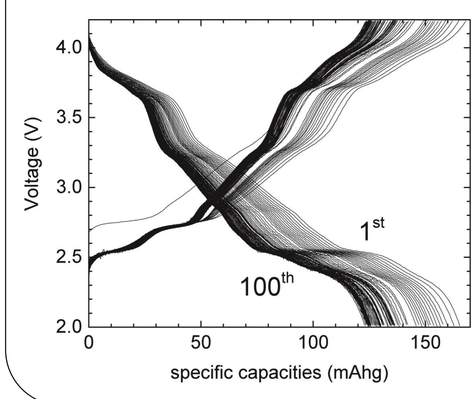


Raman and XRD

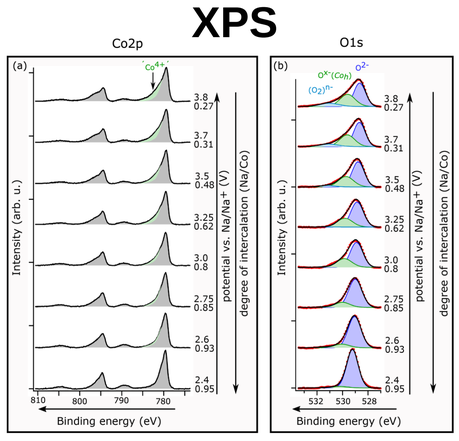


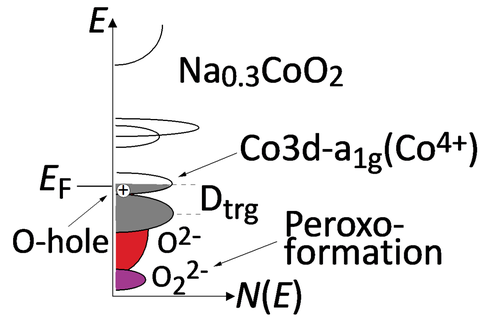
Na solid-state battery



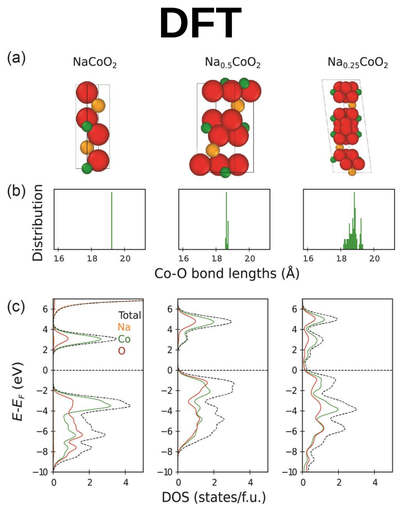


XPS

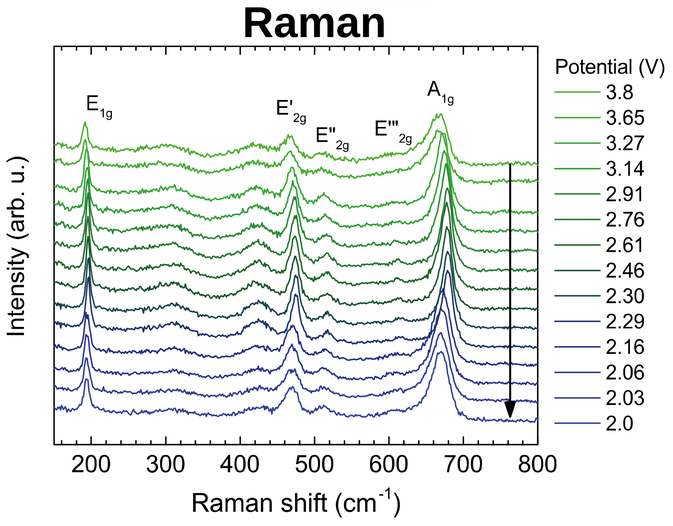




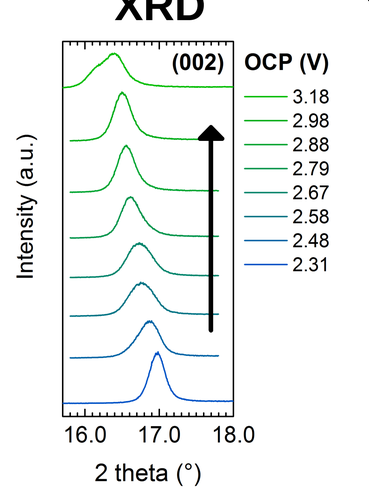
DFT



Raman



XRD



- **Stable Na_xCoO_2/Nasicon and Nasicon/Na interfaces**
- **A mixed cationic-anionic (oxygen) redox behavior is observed**
- **Oxygen redox contribution depends on the covalency of the cathode TM-O bonds**
- **Cathode structural flexibility is important for reversible sodium (de) intercalation**

References

C. Guhl, et al., *Rev. Sci. Instrum.* 89, 073104 (2018)

P. Kehne et al., *J. Power Sources* **409**, 86 (2019)

C. Guhl et al., *Energy Storage Mater.*, **37**, 190 (2021)

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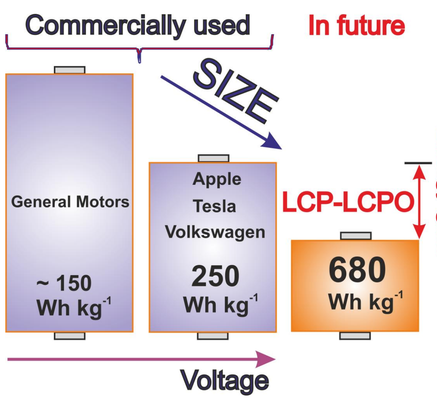
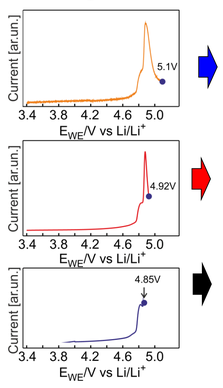
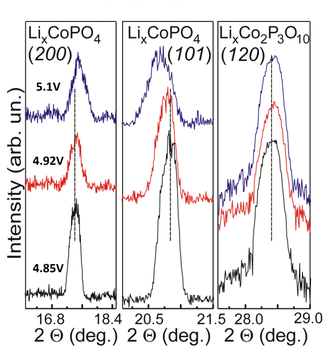
Olivine-based high voltage materials



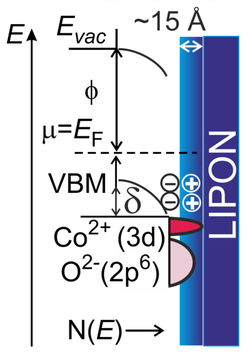
CV



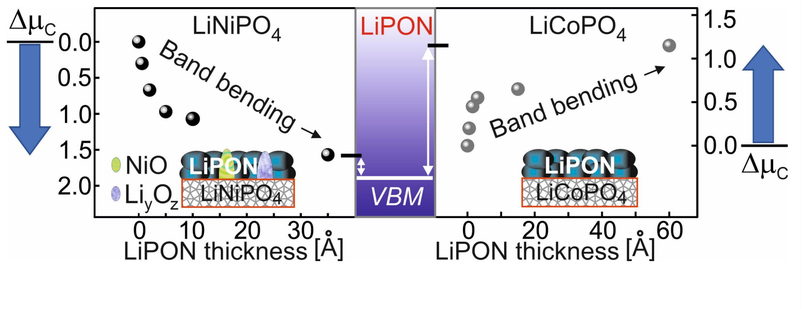
XRD



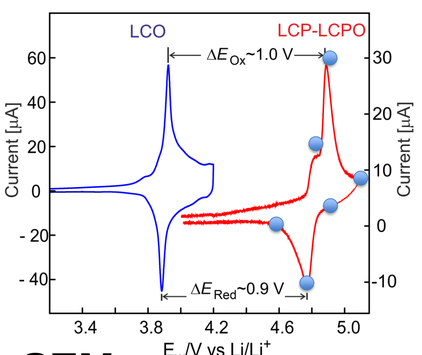
XPS/UPS



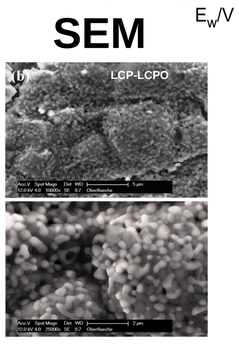
Interfacial $LiMPO_4$/LIPON properties



LCP-LCPO



SEM



LCP-LCPO:

- **Excellent electrochemical activity (no conductive carbon is required)**
- **The inductive effect leads to higher redox potential (by 1 V) as compared to $LiCoO_2$**
- **$Co^{2+} \leftrightarrow Co^{3+}$ redox activity**
- **Olivine structure is stable for delithiated LCP-LCPO (at 5.1 V vs. Li+/Li) even if the material is exposed to atmosphere**
- **Chemically compatible with LiPON-solid electrolyte due to a favorable interfacial charge distribution**

References

C. Cherkashinin, et al., *Adv. Energy. Mater.* **7**, 1602321 (2017)

C. Cherkashinin et al., *J. Chem. Mater*. **6**, 4966 (2018)

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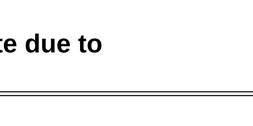
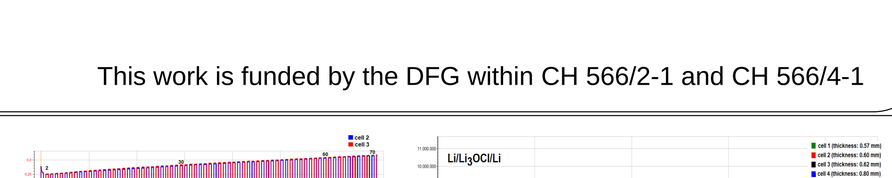
This work is funded by the DFG within CH 566/2-1 and CH 566/4-1

Novel Electrolyte

- **Preliminary work: Solid state synthesis & characterisation (XRD, SEM, DSC, EIS, Plating/Striping) of Li_3OCl Antiperovskite-type electrolyte done in cooperation with VARTA Microbattery**
- **$\sigma_{RT} = 4 \cdot 10^{-5} [S \cdot cm^{-1}]$**
- **Aim: Achieve stability against lithium-metal by use of advanced synthesis methods (Sputtering, PLD)**





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"Towards an All-solid-state lithium-oxygen-battery based on a Li_2OHCl-electrolye and a Nanolithia-cathode" master thesis Mellin, 2020