Karlsruhe Institute of Technology

# Surface Modification of Nanoscale $LiNi_{0.5}Mn_{1.5}O_4$ with (Lithium) Metal Fluorides for Application as Cathode Material in Lithium-Ion Batteries

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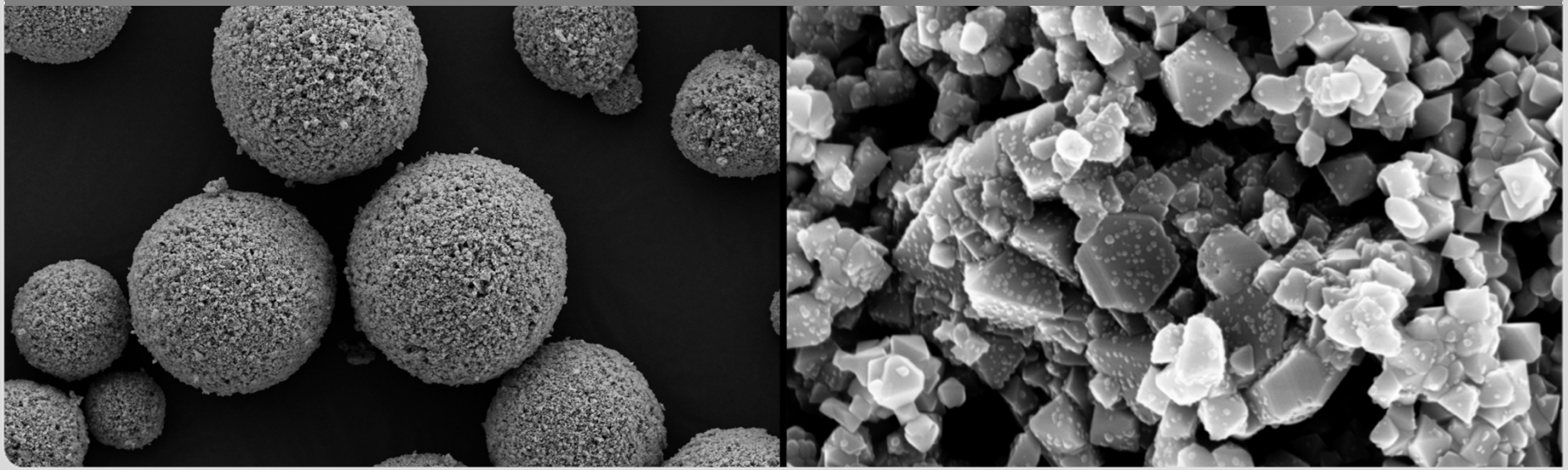


# Fundamentals and Motivation

## Why do we use high voltage spinels?

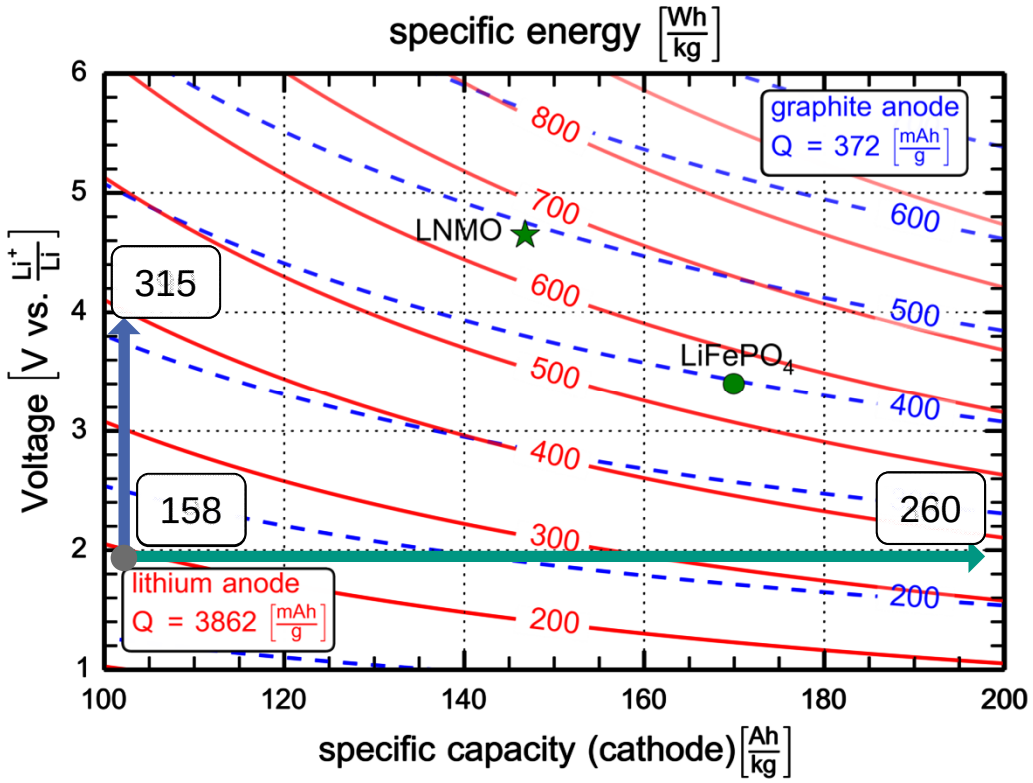
**Options for improvement of the energy density**

$$w = \frac{U \cdot n \cdot F}{M}$$

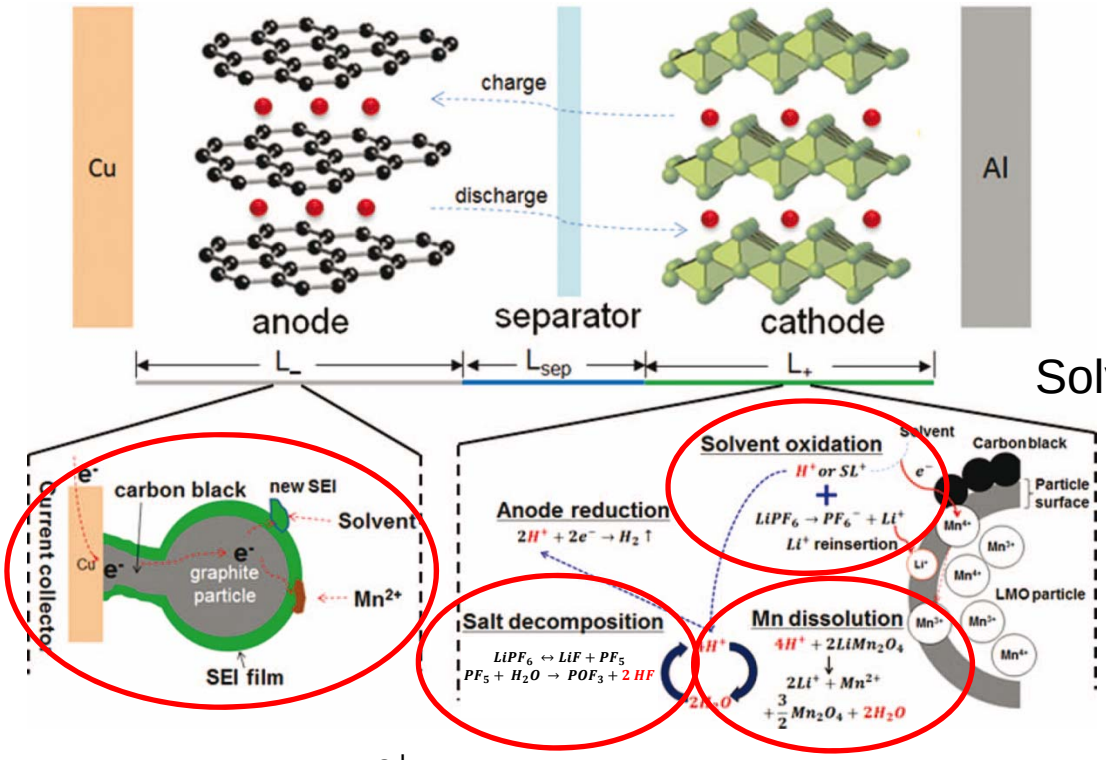
Increase of cathode capacity ($M = m_K + m_A$)

Increase of cell voltage

| | energy vs. Li [Wh kg$^{-1}$] | energy vs. C [Wh kg$^{-1}$] |
|---|---|---|
| LFP | 545 | 391 |
| LNMO | 650 | 484 |



# Fundamentals and Motivation
## Degradation




Solvent oxidation

Loss of Li (SEI)
Deposition of metal ions (e.g. $Mn^{2+}$)

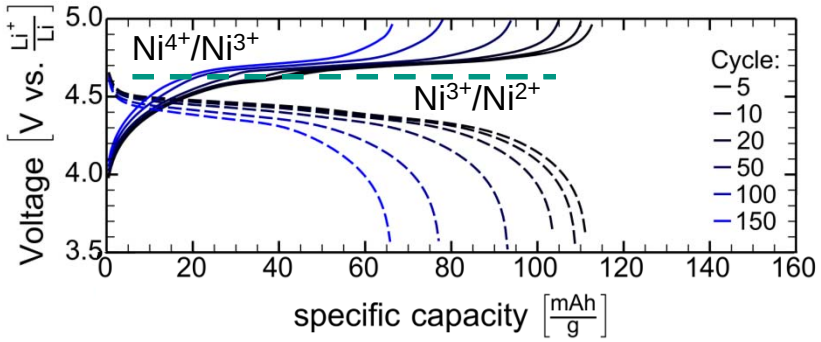
Dissolution of metal ions

Formation of HF and decomposition of AM

[after Lin et al., Journal of the Electrochemical Society, **160** (2013) A1701-A1710 ]

# Fundamentals and Motivation

- **Example: 3 electrode cell (spinel vs. graphite)**




- **Spinel/graphite:**
  - Both Ni redox couples observable
  - No $Mn^{4+}/Mn^{3+}$-plateau
- **Spinel/reference:**
  - Shift of the transition between the Ni redox couples to lower capacities
  - End of Discharge at 4.6 V
- **Graphite/reference:**
  - Voltage rise when all lithium is deintercalated

➢ **Loss of active lithium**

**cycling conditions: C/2, GF/C, LP30**

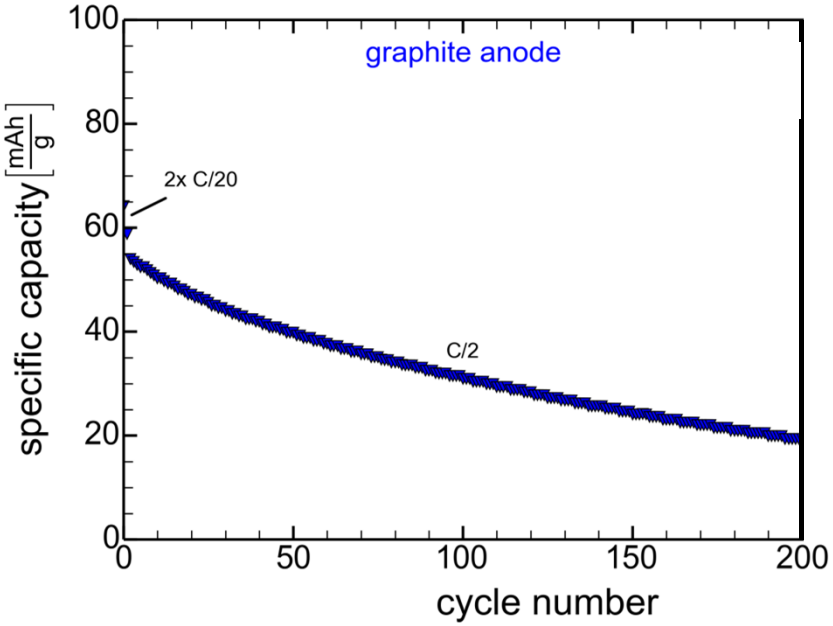
HA2

C-rate; Separator, Elektrolyt
Zyklus

Höweling, Andres; 17.09.2014

# Fundamentals and Motivation

- **Example: Change of anode**




  - Rise of capacity
    - Lithium metal anode compensates for loss of active lithium

➢ **No degradation of active material!!**

➢ **Coating of active material is essential!!**

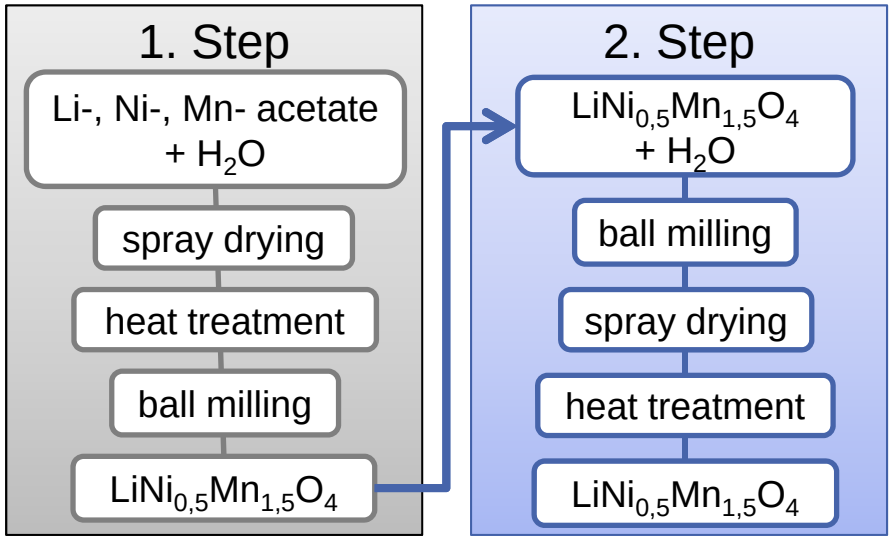
**cycling conditions: GF/C, LP30**

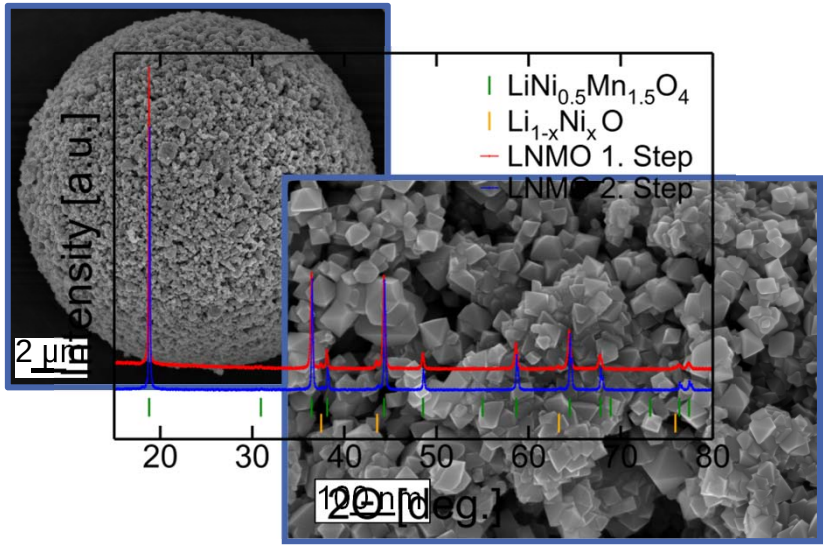
# Coating: Requirements

- Prevent dissolution of metal ions (reduce HF formation)
  - Resistance is reduced
- Electrochemical and chemical inactive
- Covering the surface of the active material
  - Inhibit parasitic reactions

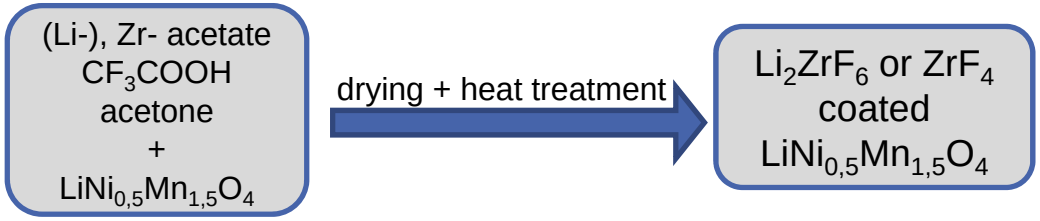
[after Chen et al., J. Mater. Chem. **20** (2010) 7606-7612]

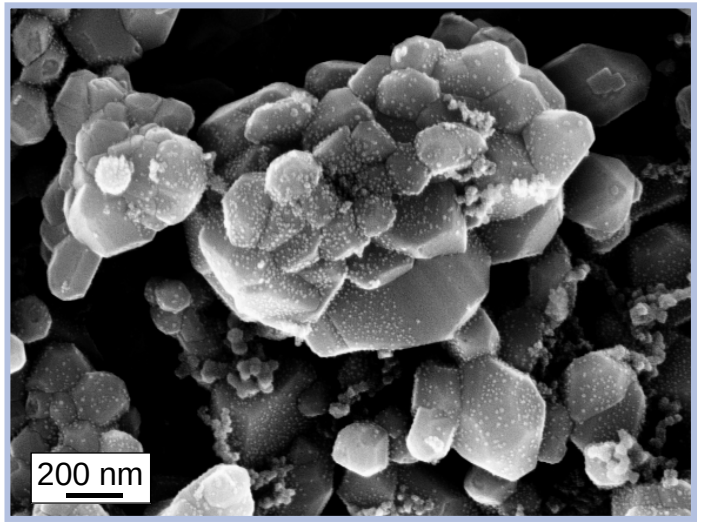
# Synthesis



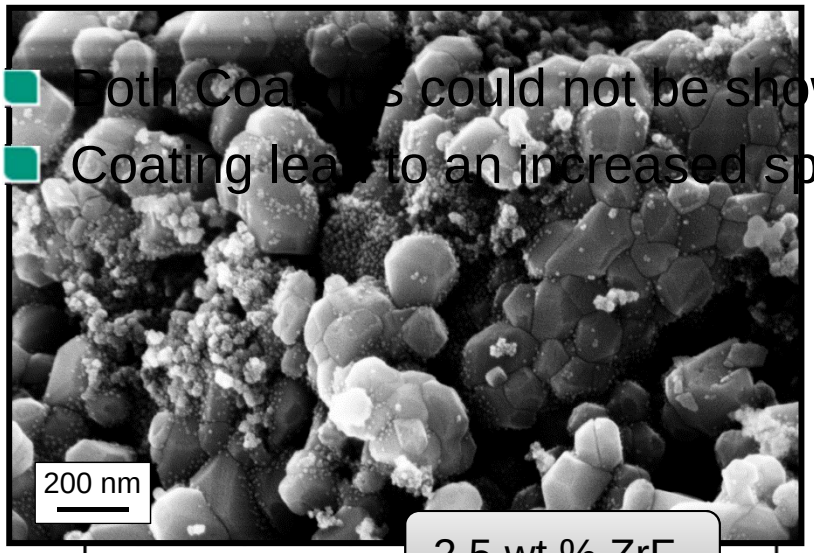

## Surface modification with $Li_2ZrF_6$ and $ZrF_4$

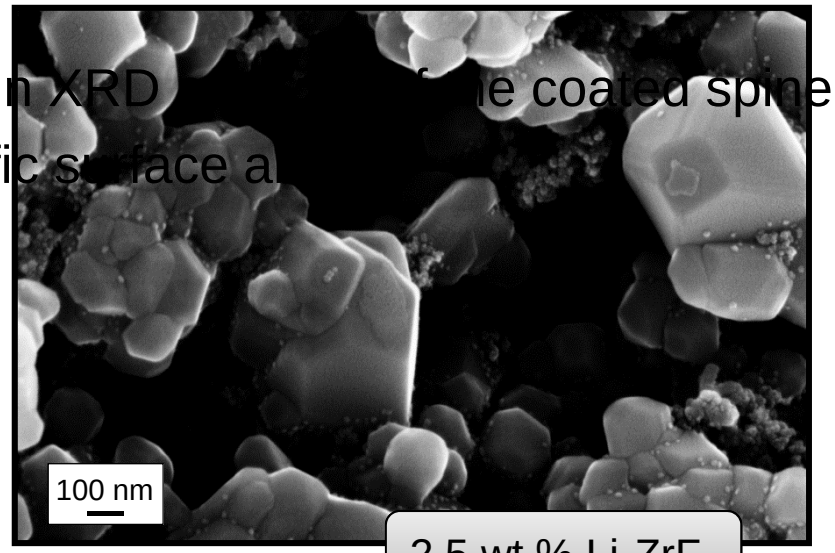


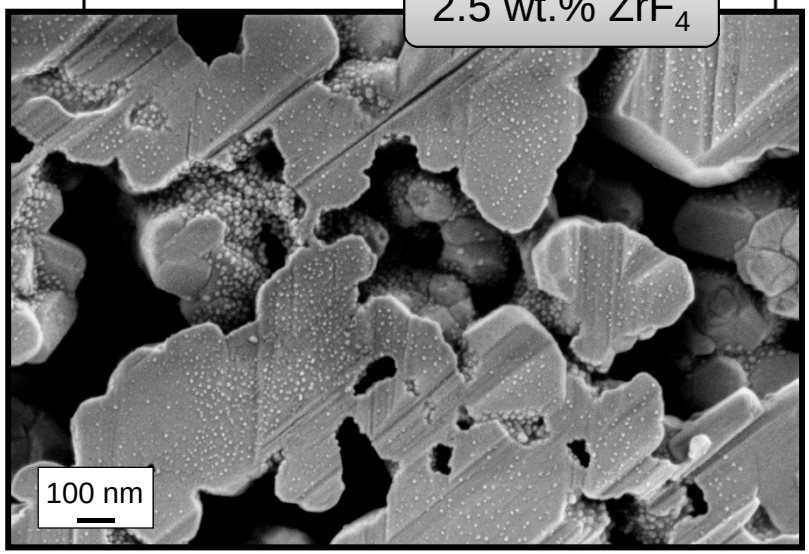
# Powder Properties & Morphology

- Both Coatings could not be shown in XRD [illegible] coated spinel
- Coating leads to an increased specific surface a[illegible]

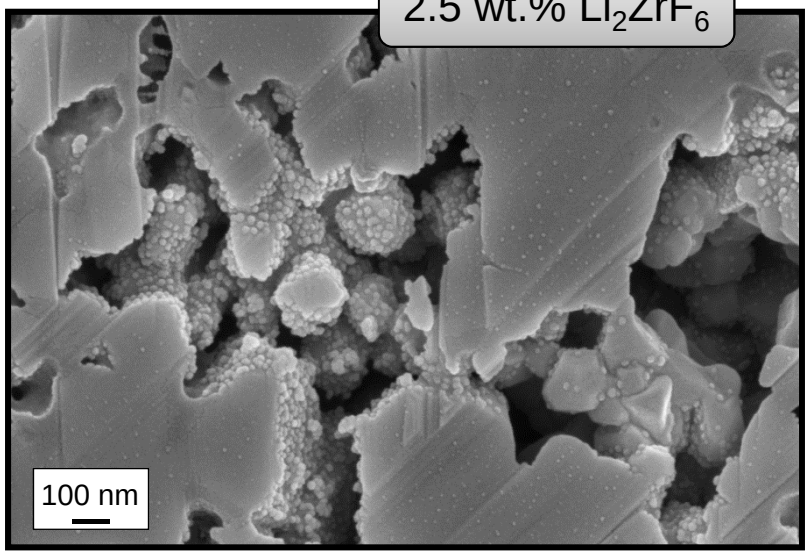


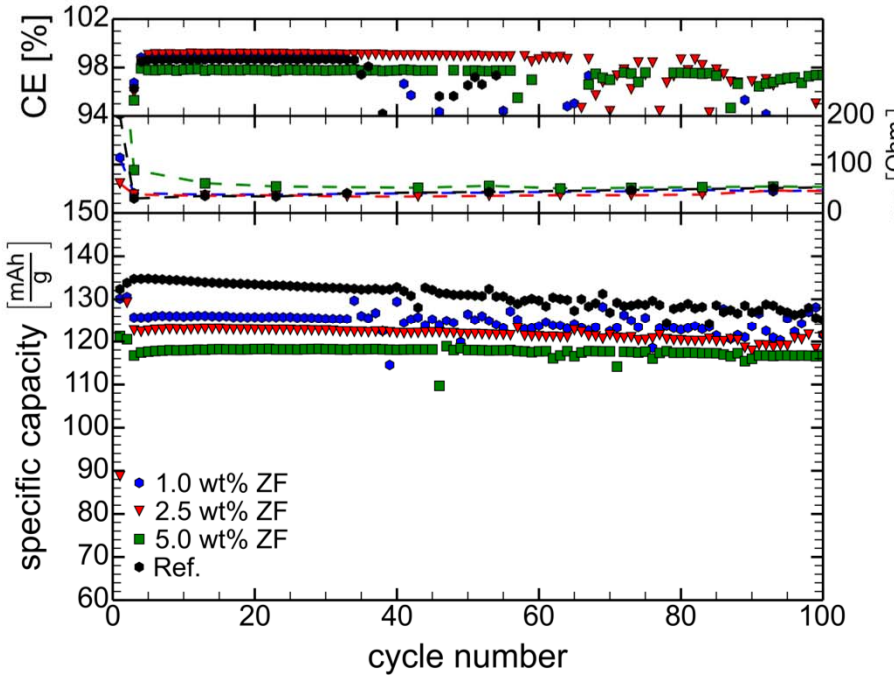

2.5 wt.% $ZrF_4$

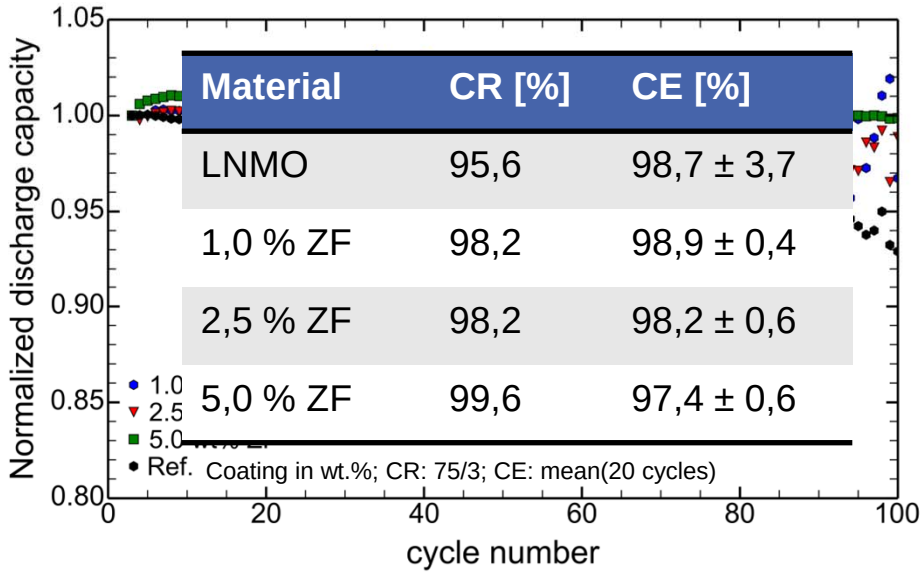



2.5 wt.% $Li_2ZrF_6$



# $ZrF_4$ – Cycling Stability (C/2 @20°C)



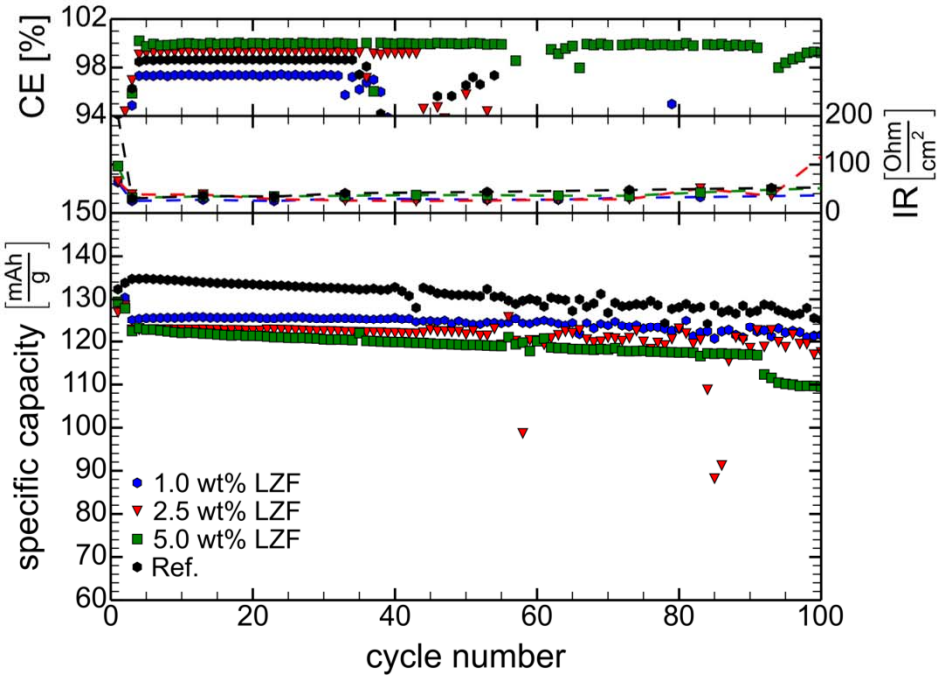

| Material | CR [%] | CE [%] |
|---|---|---|
| LNMO | 95,6 | 98,7 ± 3,7 |
| 1,0 % ZF | 98,2 | 98,9 ± 0,4 |
| 2,5 % ZF | 98,2 | 98,2 ± 0,6 |
| 5,0 % ZF | 99,6 | 97,4 ± 0,6 |

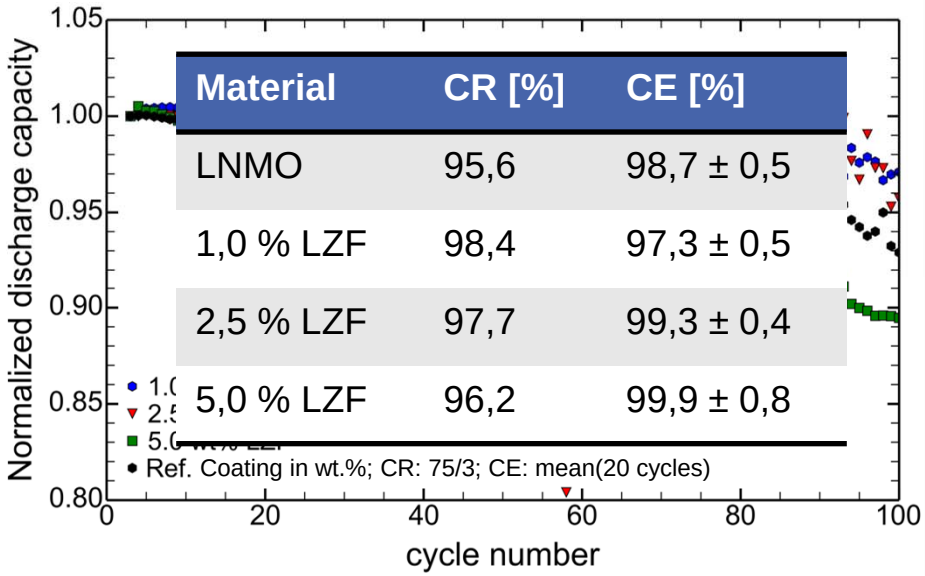
Coating in wt.%; CR: 75/3; CE: mean(20 cycles)

- Initial capacity decreases with coating content
- Capacity loss can be reduced by coating

**cycling conditions: GF/C, LP30**

# $Li_2ZrF_6$ – Cycling Stability (C/2 @20°C)



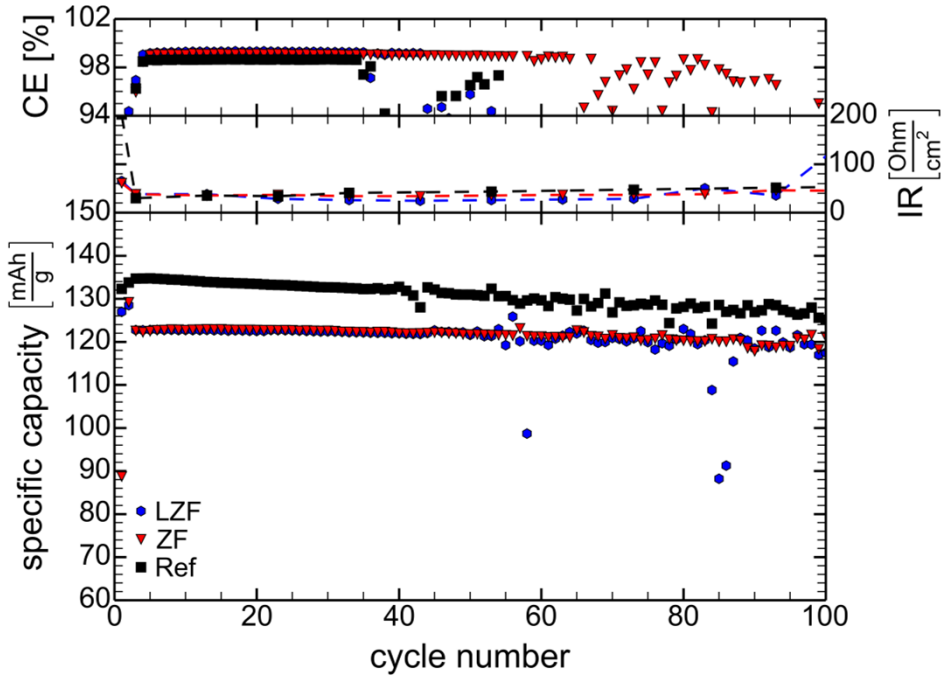



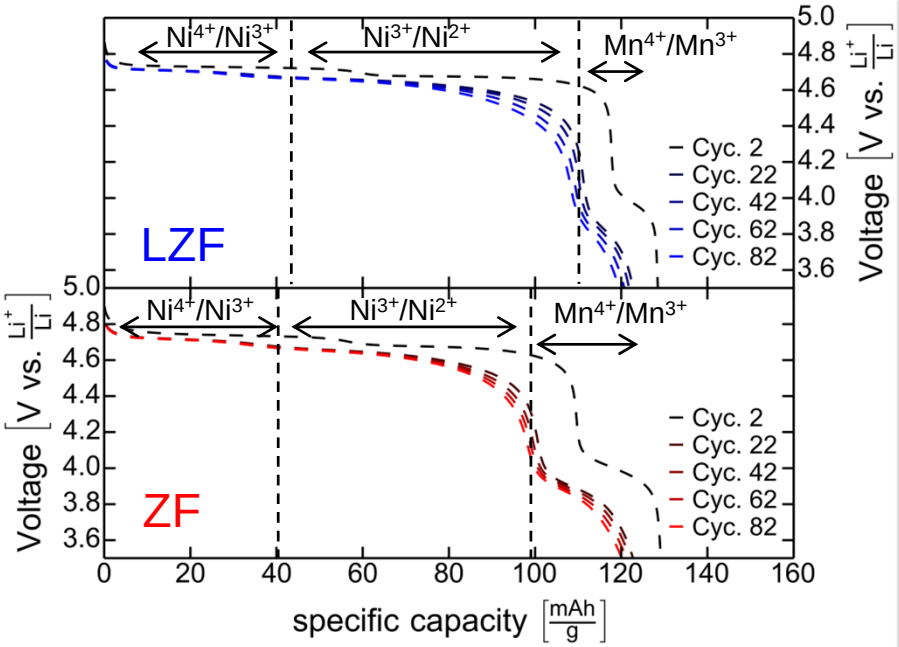

| Material | CR [%] | CE [%] |
|---|---|---|
| LNMO | 95,6 | 98,7 ± 0,5 |
| 1,0 % LZF | 98,4 | 97,3 ± 0,5 |
| 2,5 % LZF | 97,7 | 99,3 ± 0,4 |
| 5,0 % LZF | 96,2 | 99,9 ± 0,8 |

- Similar to the $ZrF_4$ coating, the initial capacity decreases
- Coating with 1.0 or 2.5 wt% $Li_2ZrF_6$ lead to reduced capacity fade

**cycling conditions: GF/C, LP30**

# Comparison of 2.5 wt.% Coatings (C/2 @20°C)

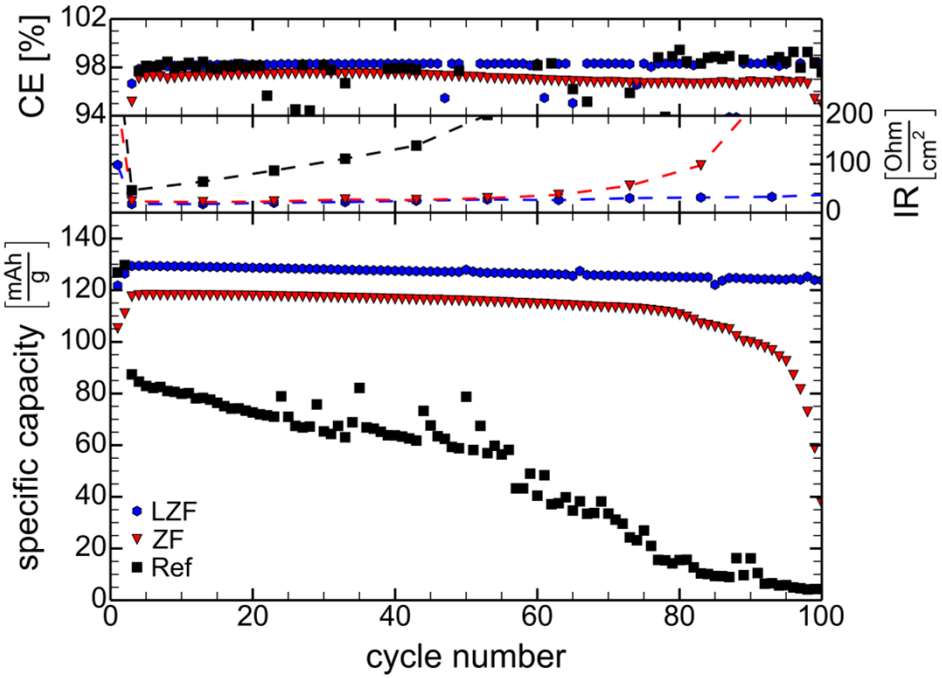


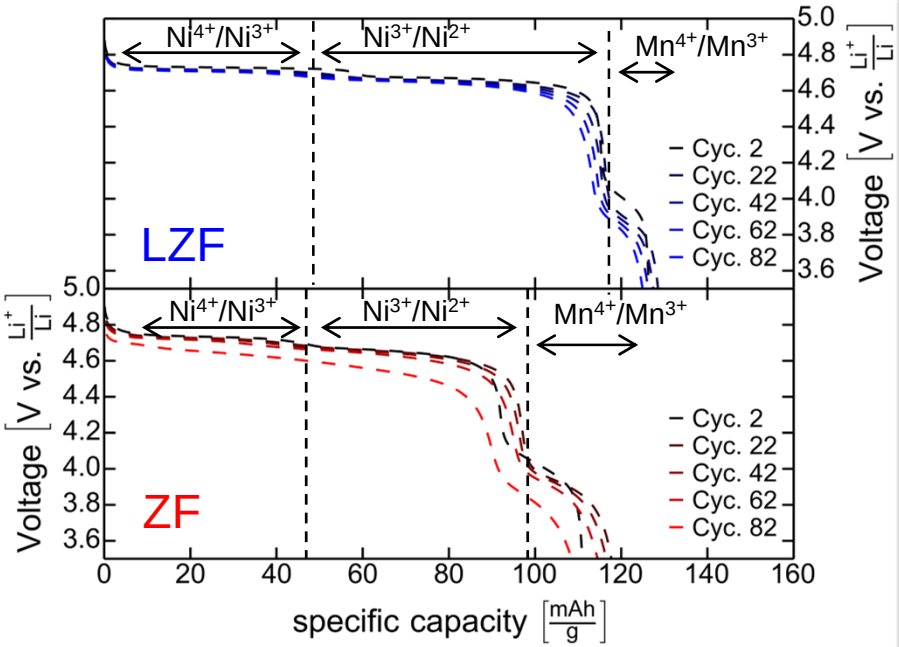




- **Coating leads to lower initial capacities**
- **The capacity loss per cycle can be reduced by coating**
- **Changes in the electrochemistry occur due to partial doping**

**cycling conditions: GF/C, LP30**

# Comparison of 2.5 wt.% Coatings (C/2 @40°C)



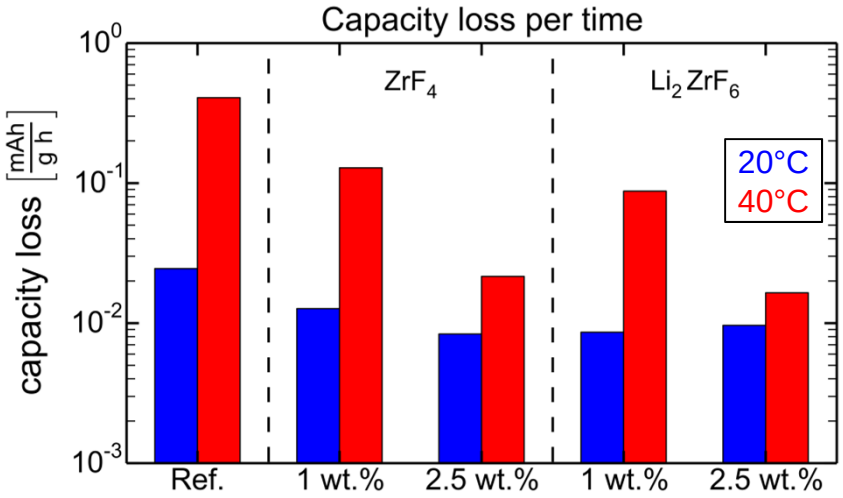




- The uncoated spinel suffers from severe capacity fade
- Coated samples exhibit excellent capacity retention
- Abrupt capacity loss occurs because of a rising internal resistance

**cycling conditions: GF/C, LP30**

# Conclusion

- Coating with $ZrF_4$ and $Li_2ZrF_6$ was performed by a simple sol-gel route
- Significant improvement of capacity retention is achieved




- High temperatures during coating process can lead to partial doping
  - Influences stability
  - Can have an impact on energy density

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