Karlsruhe Institute of Technology

Institute for Applied Materials

Water-induced Influences on Active Materials in Lithium Ion Batteries

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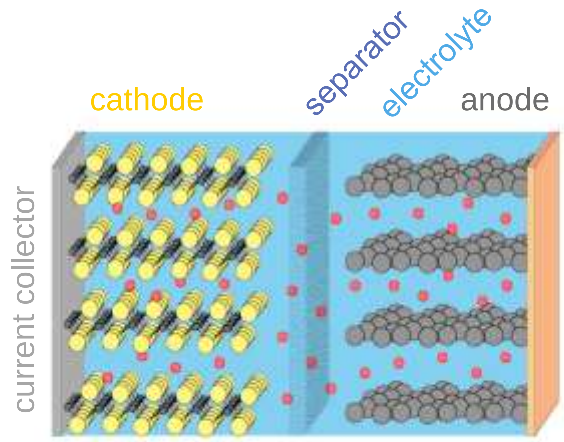
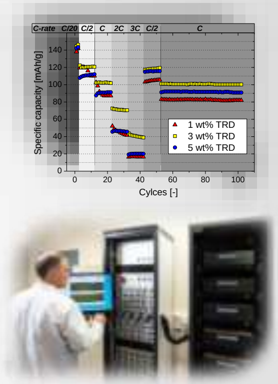
INSTITUTE FOR APPLIED MATERIALS – ENERGY STORAGE SYSTEMS (IAM-ESS)

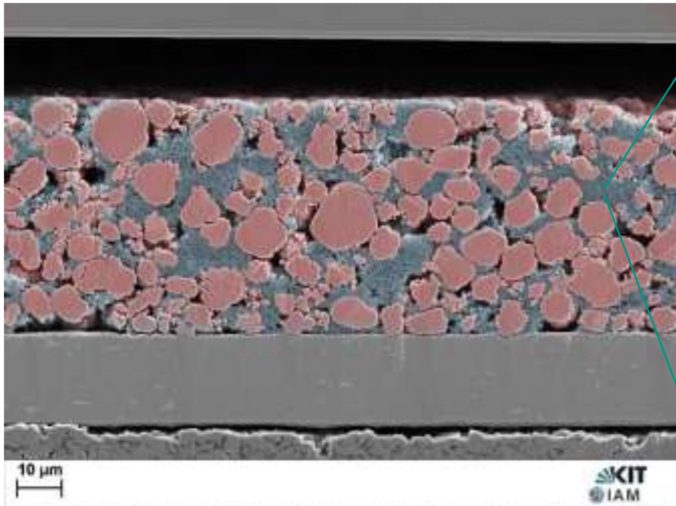
Manufacturing of Lithium Ion Batteries

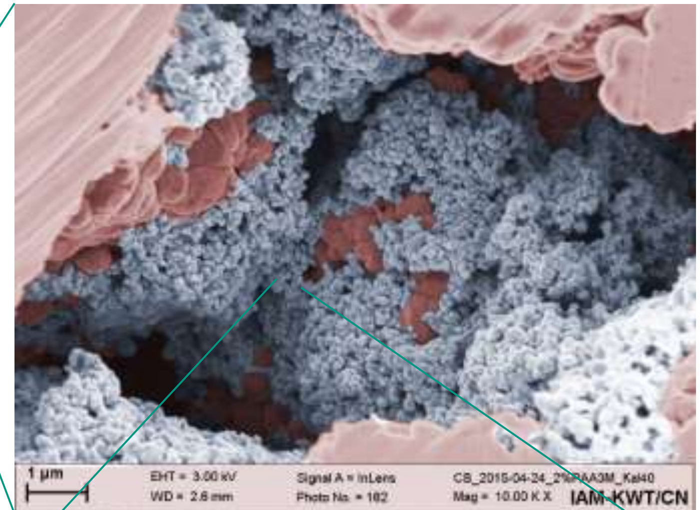


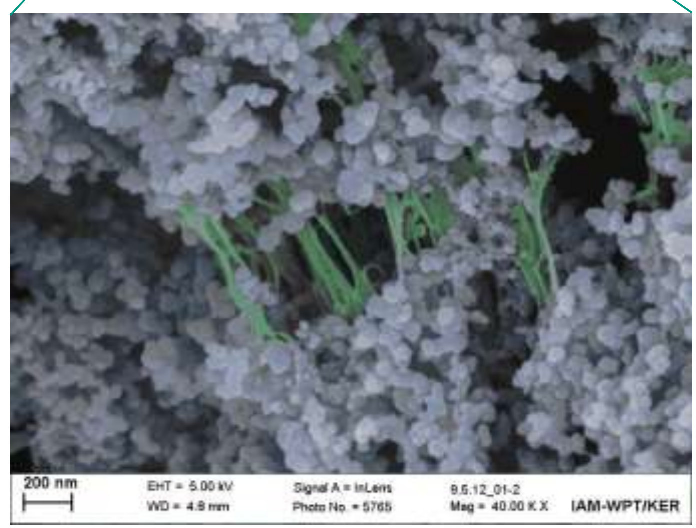


Slurry Processing → **Electrode Fabrication** → **Cell Assembling** → **Electrochemical Characterization**

Electrode Components





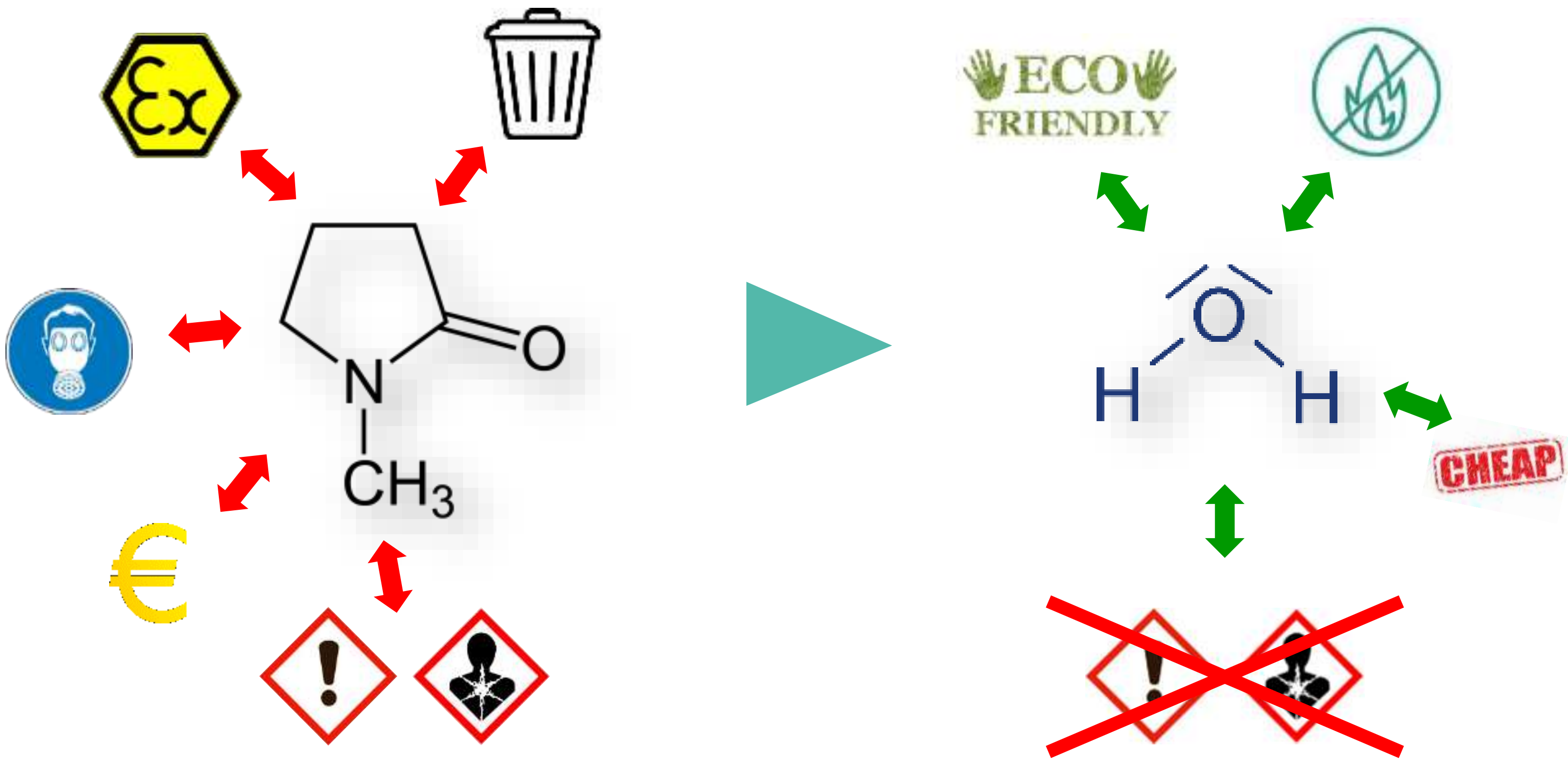


Binder

- Active material
- Conductive Additives
- Binder
- Porosity

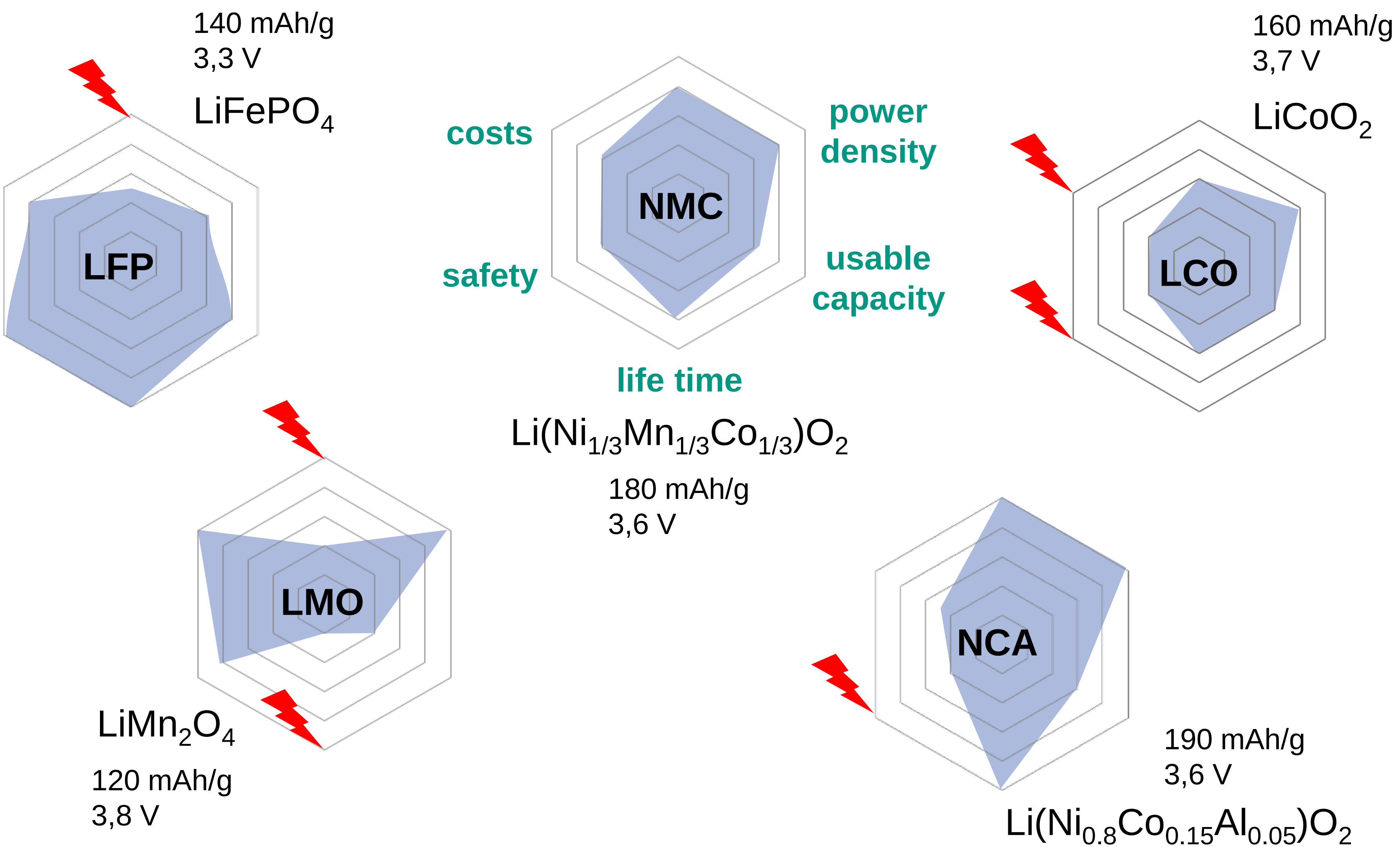
Aqueous Processing of Electrodes

- Substitution of the harmful and expensive N-Methyl-2-Pyrrolidone (NMP) by inexpensive and eco-friendly water

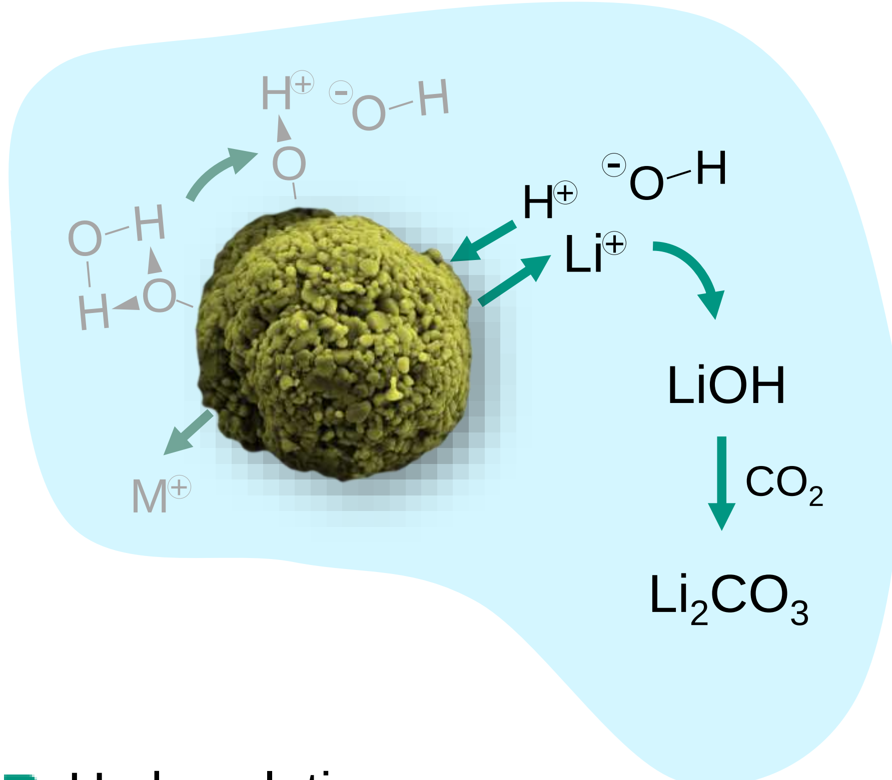


since 2011 on SVHC candidate list
(Substances of Very High Concern)

Cathode Materials

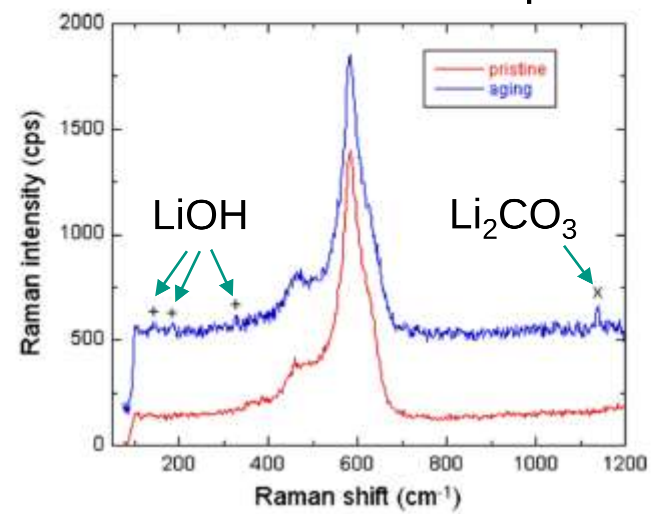


Interaction of Cathode Materials with Water



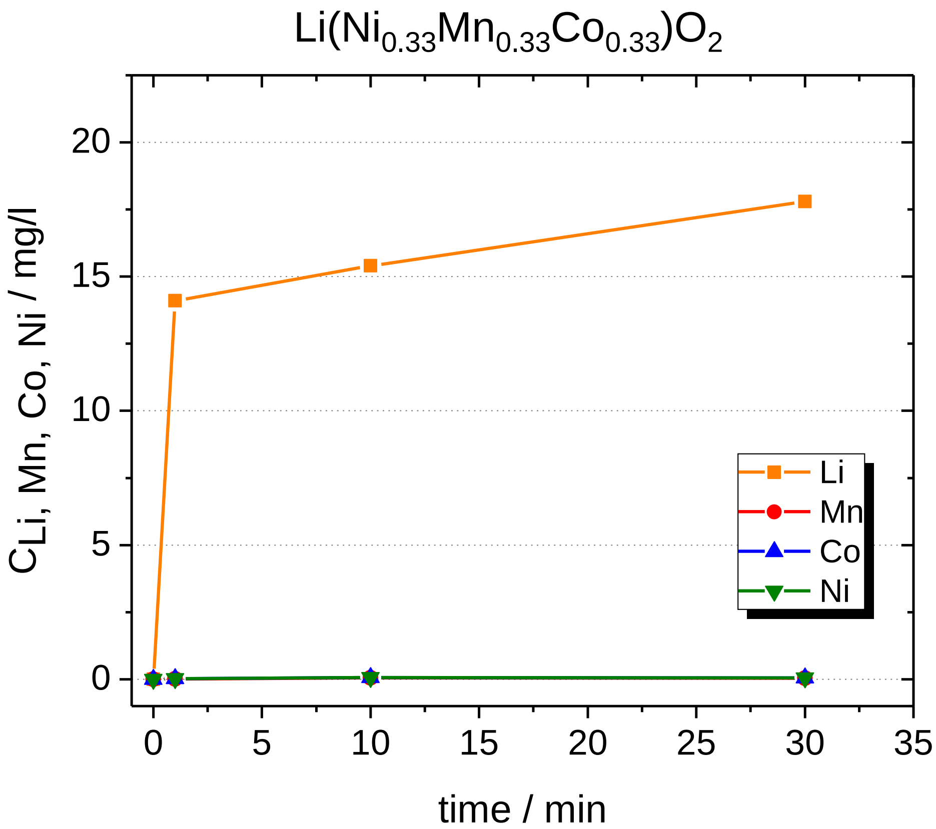
- Hydroxylation
- Leaching of cations
- Proton exchange

NMC in humid atmosphere



Source: Zhang et al, J. Power Sources 196 (2011)

Leaching of Cations from NMC

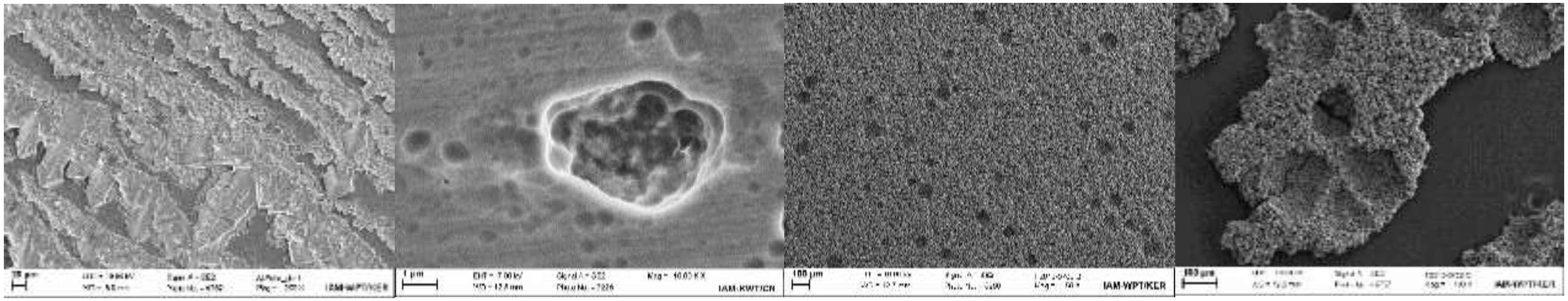


- After 30 min leaching time
  - Lithium loss 0.5%
  - Leaching layer ≈ 7 nm thick
- Recommendations
  - Crucial for nano materials
  - Store in dry chamber
  - Coating of active materials

5 wt.% NMC111 in water
pH 11 (native), T = 21 °C
ICP-OES

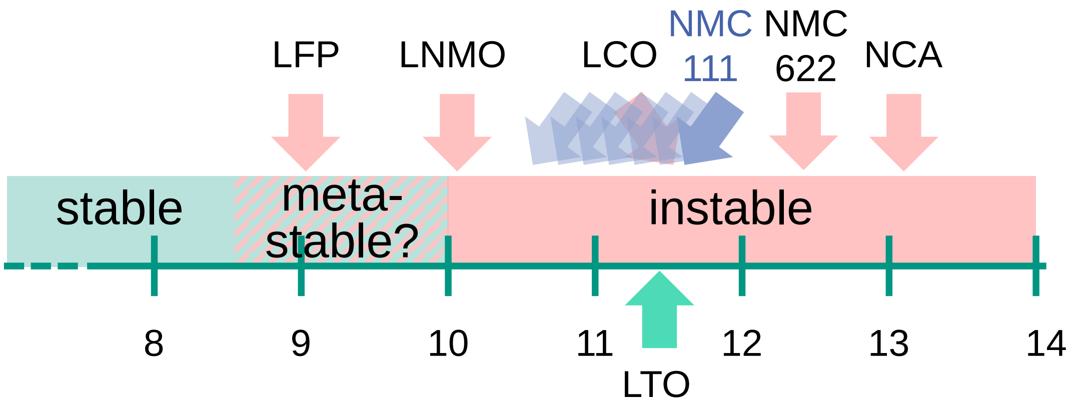
Corrosion of Aluminum Foils

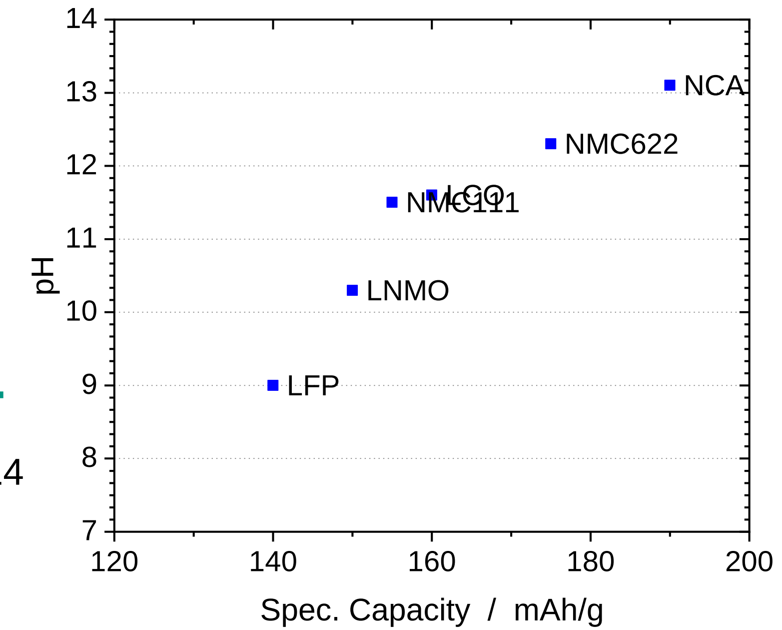
- Stability range of aluminum between pH 4 – 8.5
- Problems caused by extreme pH
  - Dissolution of protective oxide layer
  - Formation of water soluble Al species
  - Pitting of aluminum foil
  - Formation of hydrogen gas bubbles
  - Foaming of electrodes



Impact on pH of Aqueous Slurry

- Formation of LiOH leads to an increase of the pH
- Native pH depends on product and storage conditions
- Does a metastable range exist?
  (depending on exposure time and temperature)





Countermeasures

- pH reduction by acid addition
  (Li et al., JMaterSci 42 (2007) 5773–5777)

  pH ↓

- Addition of amphoteric oxidic additives
  (M. Memm et al., Electrochim. Acta 260 (2018) 664 – 673)

  pH ↓

- Pressurized CO_2 Gas Treatment
  (K. Kimura et al., J. Electrochem. Soc. 165 (2018) A16-A20)

  pH ↓

- Carbon coating on aluminum current collector
  (I. Doberdò et al., JPowerSources 248 (2014) 1000-1006)

- Particle coating with VO_x
  (N. Laszczynski et al., ChemElectroChem 2 (2015) 1768 – 1773)

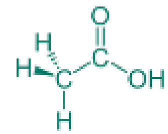
  

- In-situ coating by adding of phosphoric acid
  (N. Loeffler et al., ChemSusChem 9 (2016) 1112 – 1117)

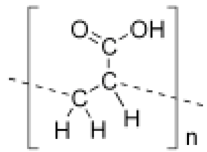
  

Adjustment of pH by Addition of Acid

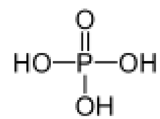
- Acetic acid (HAc)



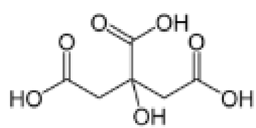
- Polyacrylic acid (PAA)
  (MW = 2.000, 450.000 and 1.250.000 g/mol)



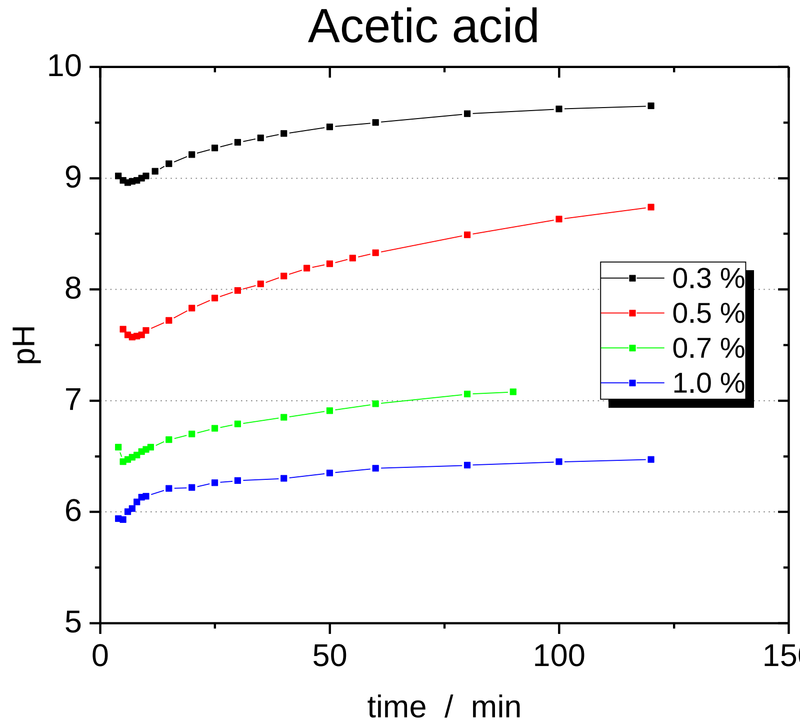
- Phosphoric acid (PA)



- Citric acid



Slurry composition	
Li($Ni_{0.33}Mn_{0.33}Co_{0.33}$)$O_2$	100
Carbon black (Super C65)	3
CMC (CRT2000PA)	2
Latex binder (TRD202A)	3
+ Acid	x

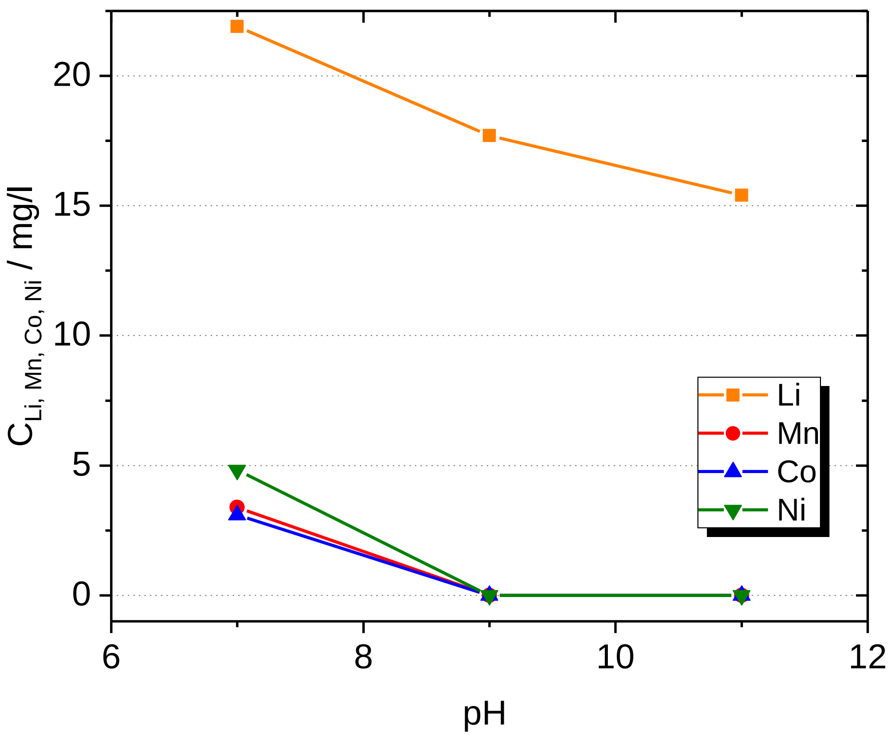


Rule of thumb: 0.5 – 1 wt.% of acid required for pH 7

Impact of pH Reduction on Cation Solubility

- Lithium leaching is minimal at native pH
- Dissolution of transition metal ions is detectable at lower pH

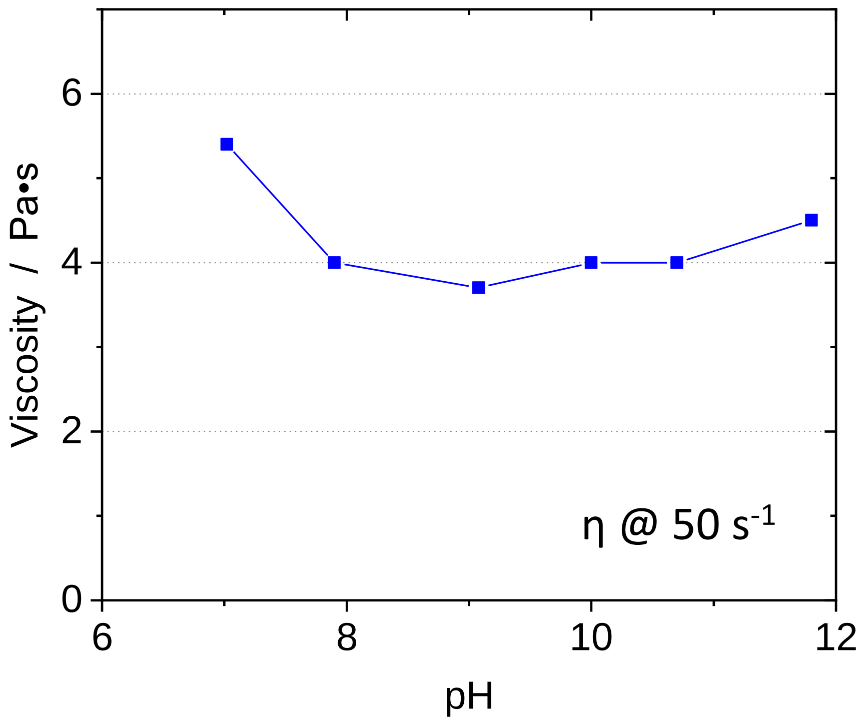
$Li(Ni_{0.33}Mn_{0.33}Co_{0.33})O_2$



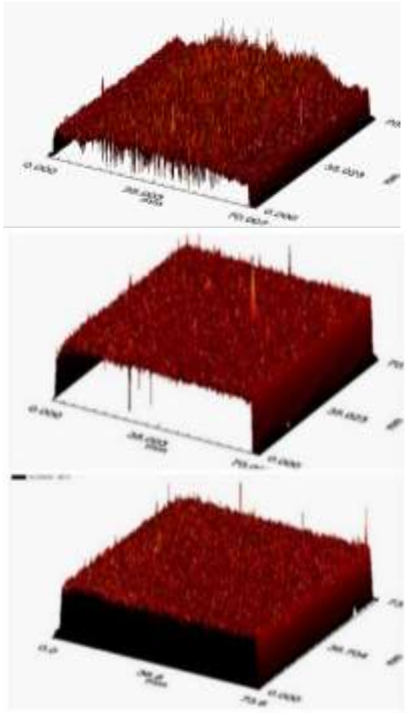
5 wt.% NMC in water
pH modified by HCl
Leaching time 10 min

Impact of Acetic Acid on Slurry Rheology

- Moderate decrease of viscosity
- Viscosity rises again at neutral zone



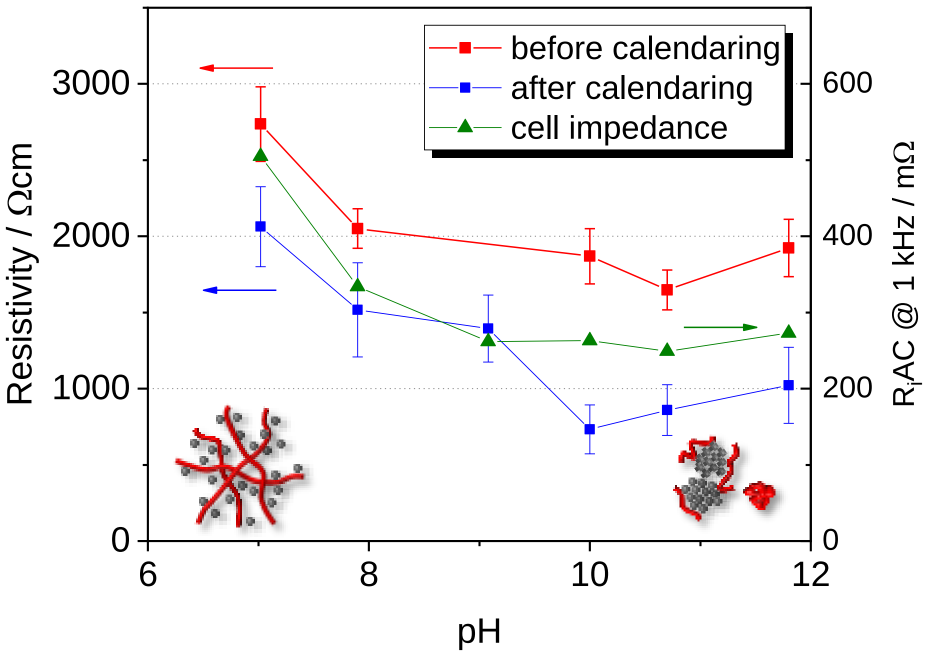
Electrode topography

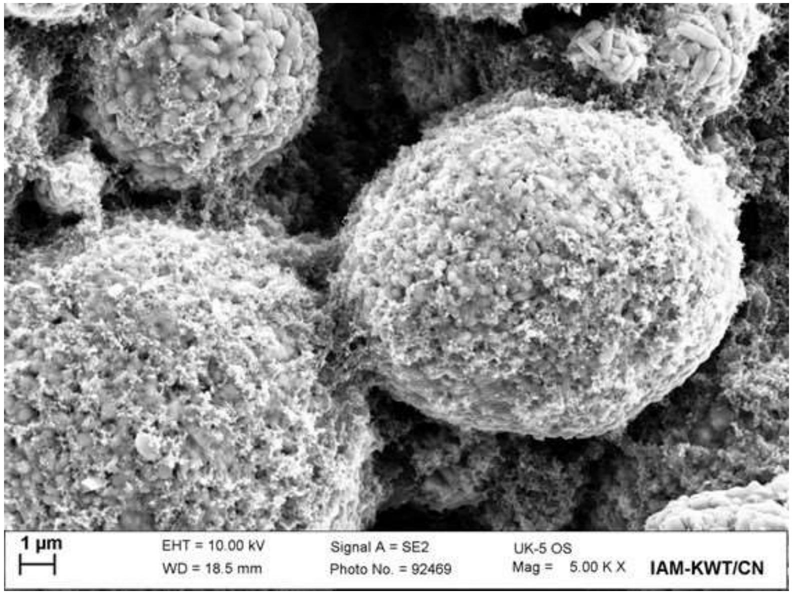


- Decrease of surface roughness
  → Deletion of agglomerates from carbon black

Impact of Acetic Acid on Coating Resistivity

- Increase of DC (electrode) and AC (cell) resistance at low pH
- Formation of small carbon black fragments
  - Unfolding of CMC chains → more entanglement and bridging
  - Loss of electrical connection for isolated fragments

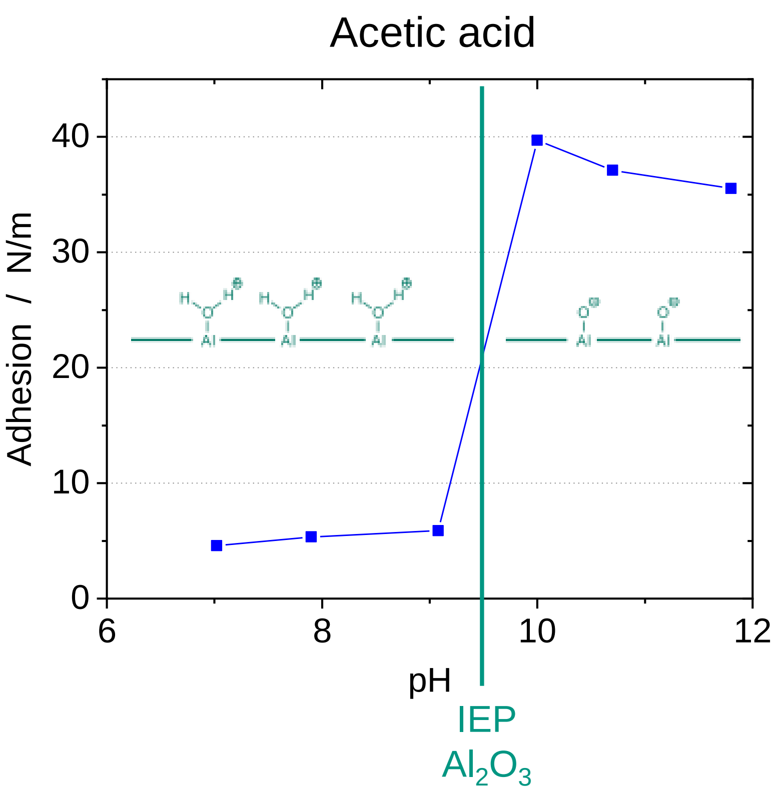


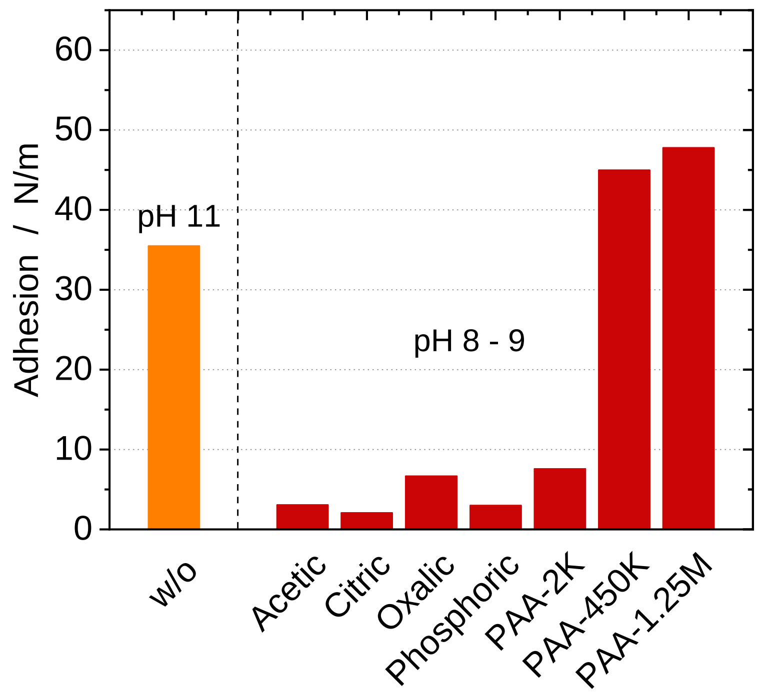


NMC particles with homogeneously distributed carbon black fragments at pH7

Adhesion Strength after Acid Addition

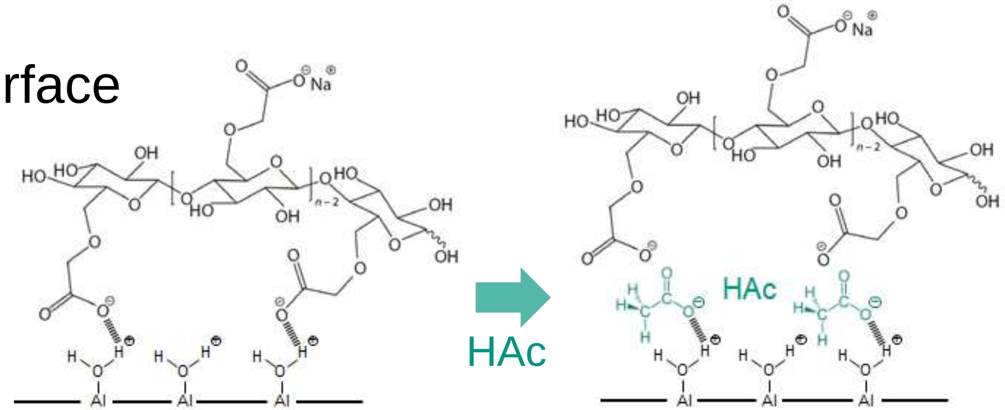
- Massive loss of adhesion strength with most acids
- Good adhesion with high molecular weight PAA (binder capability!)
- Besides pH, adhesion drop depends on composition and processing



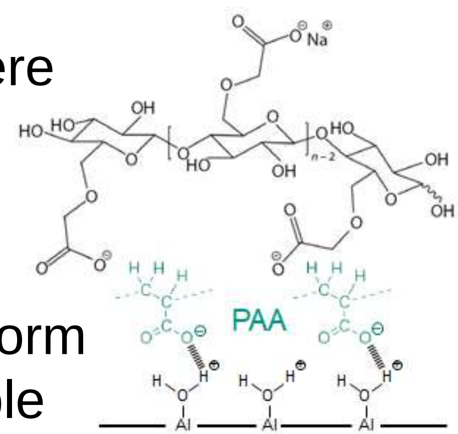


Adhesion Failure

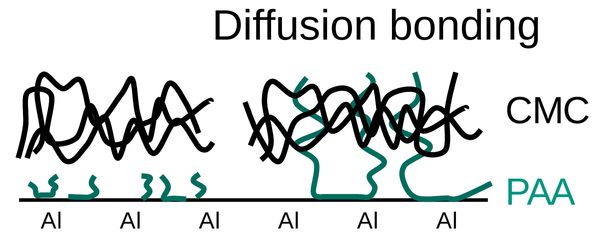
- Below the IEP, the alumina surface has a positive charge
- Anions from the dissociated acids are strong Lewis bases, replacing existing interactions



- Small PAA molecules adhere as a thin layer preventing straight interaction with functional binder groups
- Extended PAA molecules form loops and tails, which enable diffusion bonding by creating an interdiffusion layer with the binder



PAA

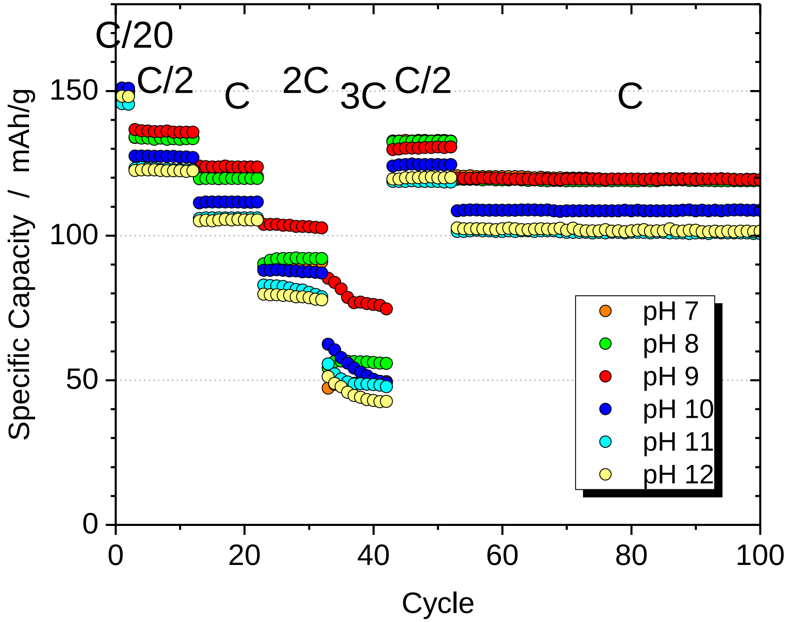


2K 450K

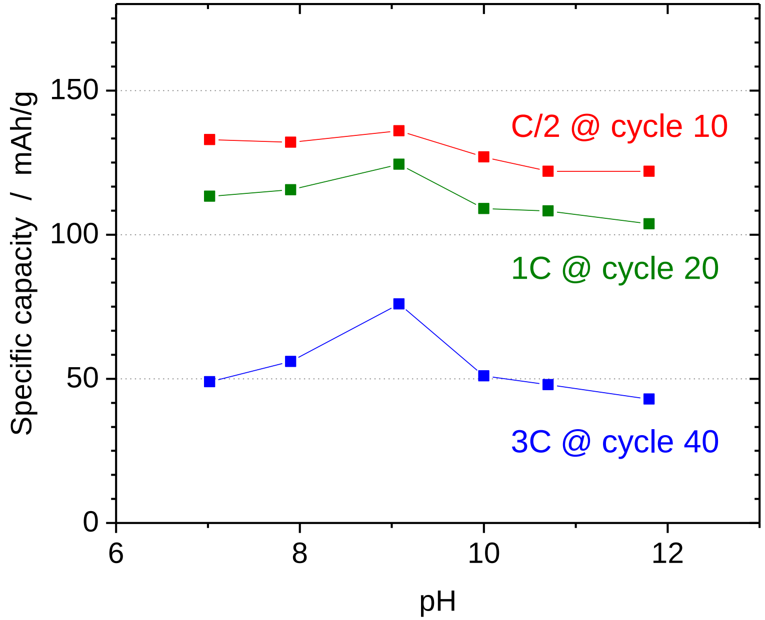
Electrochemical Properties with Acetic Acid

- Maximum of specific capacity at pH 9

pouch cells, 11.4-14 mg/cm^2, graphite anode, LP 30, CC, 3.0 – 4.2 V

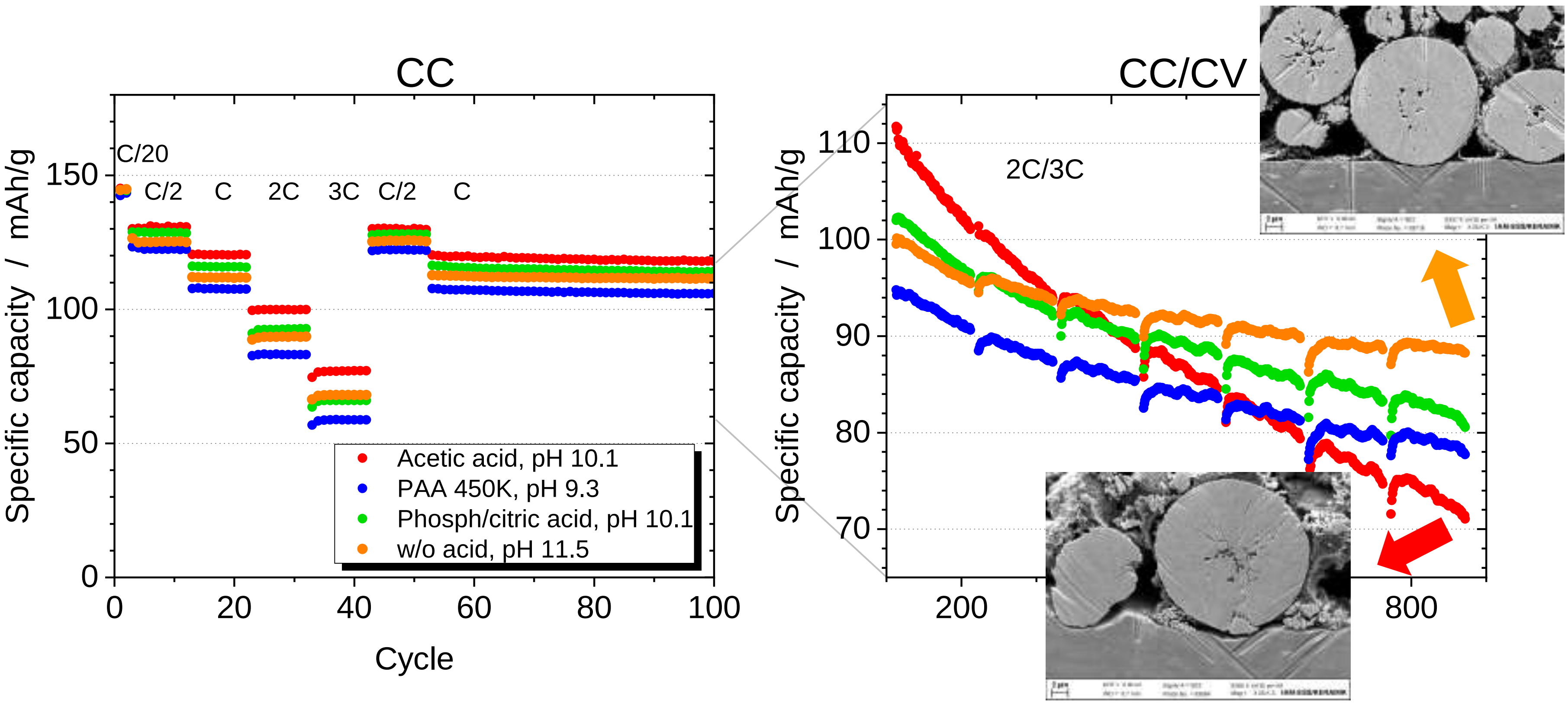


Values corrected for different mass loadings



Electrochemical Results

- Higher inital capacity for acetic acid, but also high degradation
- Best long-term stability for acid free slurry



pouch cells, 10.9-12.3 mg/cm^2, graphite anode, LP 30, 3.0 – 4.2 V

Summary

- Challenges for aqueous processing of cathode materials
  - Leaching of lithium ions, lithium loss by formation of Li_2CO_3
  - Corrosion of aluminum foil due to high pH value of slurry
- Investigated approach: Decrease of pH by addition of acids
  - Lowering of corrosion effects
  - Significant drop of adhesion strength (for acids with low molecular weight)
  - Acetic acid gives high initial capacity, but strong degradation
  - Best long-term stability without acid addition
    - ➡ Better understanding of the influence of the acid required
    - ➡ Invest more effort in the minimization of lithium leaching

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Thank you for your attention.