

Influence of Post-Calendering on Physicochemical Parameters and Performance of Dry Processed LiFePO_4 -based Electrodes



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Motivation

Porosity in Dry-Processing

- Electrode film gets stretched and compacted in constant ratio during repeated calendering using friction
- Porosity roughly stays constant through friction over course of film thinning
- Final electrode porosity determined via lamination step

Post-Calendering as Concept

- Post-calendering opportunity to change porosity after lamination
- Calendering at ambient temperature offers different polytetrafluorethylene (PTFE) response on compaction
- Decrease in porosity, increases energy density on electrode and cell level

Goal:

Test viability and investigate influence of ambient post-calendering on physicochemical parameters and electrode performance

Electrode Processing

Granulation (Eirich EL1 Mixer)

- Premixing (LFP+CB) 10 min @ 25 m s⁻¹
- Cooling <40 °C
- Addition of PTFE ~2 min @ 5 m s⁻¹
- Fibrillation 30 min @ 25 m s⁻¹
- Low Shear Fibrillation 4 min @ 4 m s⁻¹
- Cooling <25° C
- Homogenisation 15 s @ 15 m s⁻¹

Cathode Composition:

95wt.% LFP400 (IBUtec), 3wt.% C65 (TIMCAL), 2wt.% PTFE (DAIKIN)

Calendering (MSK-HRP22; MTI Corp)

Step	Gap width	Rot. Speed	Friction
1	300 µm	1.0 rpm	60%
2	225 µm	1.0 rpm	60%
3	150 µm	1.0 rpm	60%
4	80 µm	1.0 rpm	60%
5	50 µm (Lamination)	1.0 rpm	0%
Postcalendering to 50, 40, 30% theo. porosity			0%

Electrode Characterization

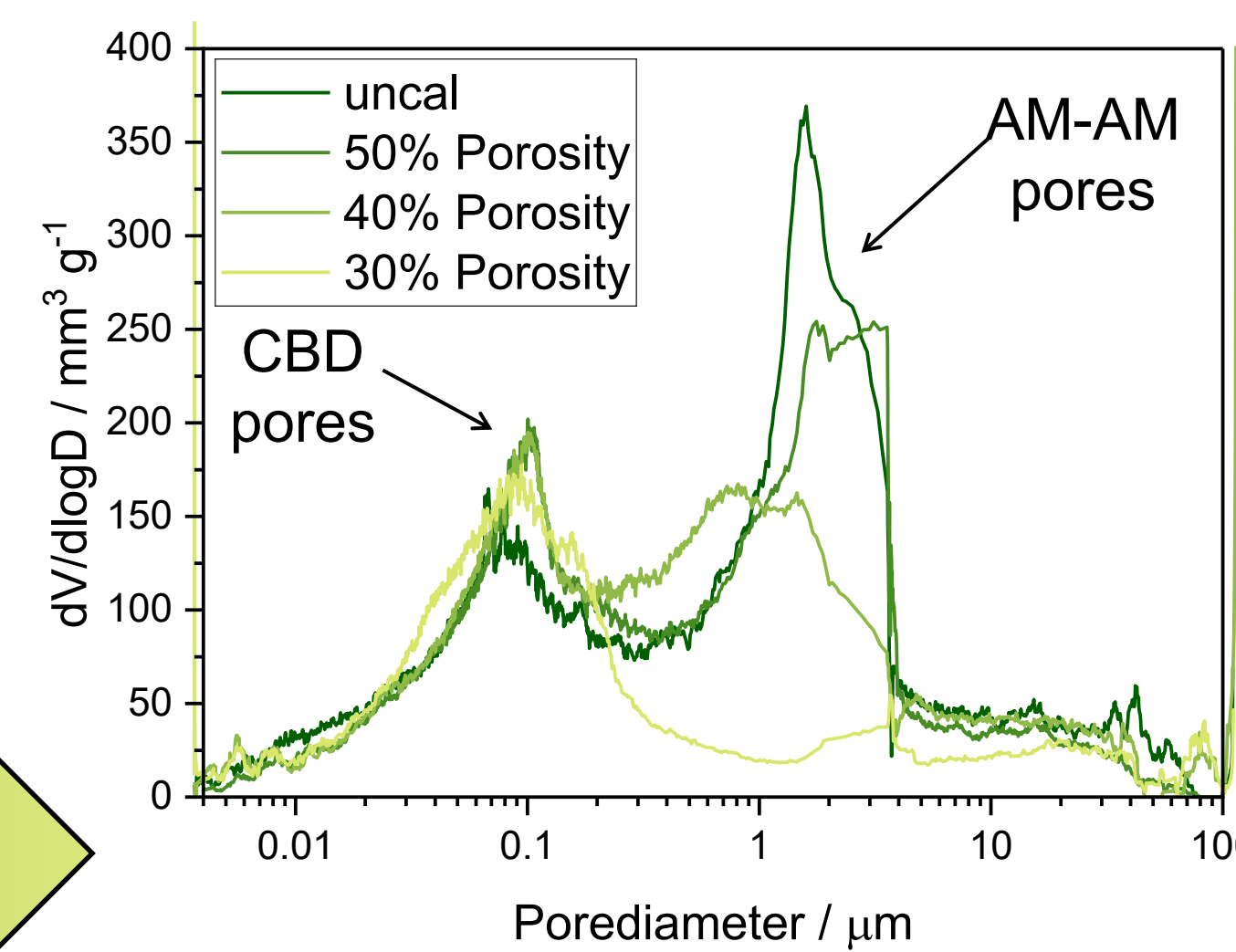
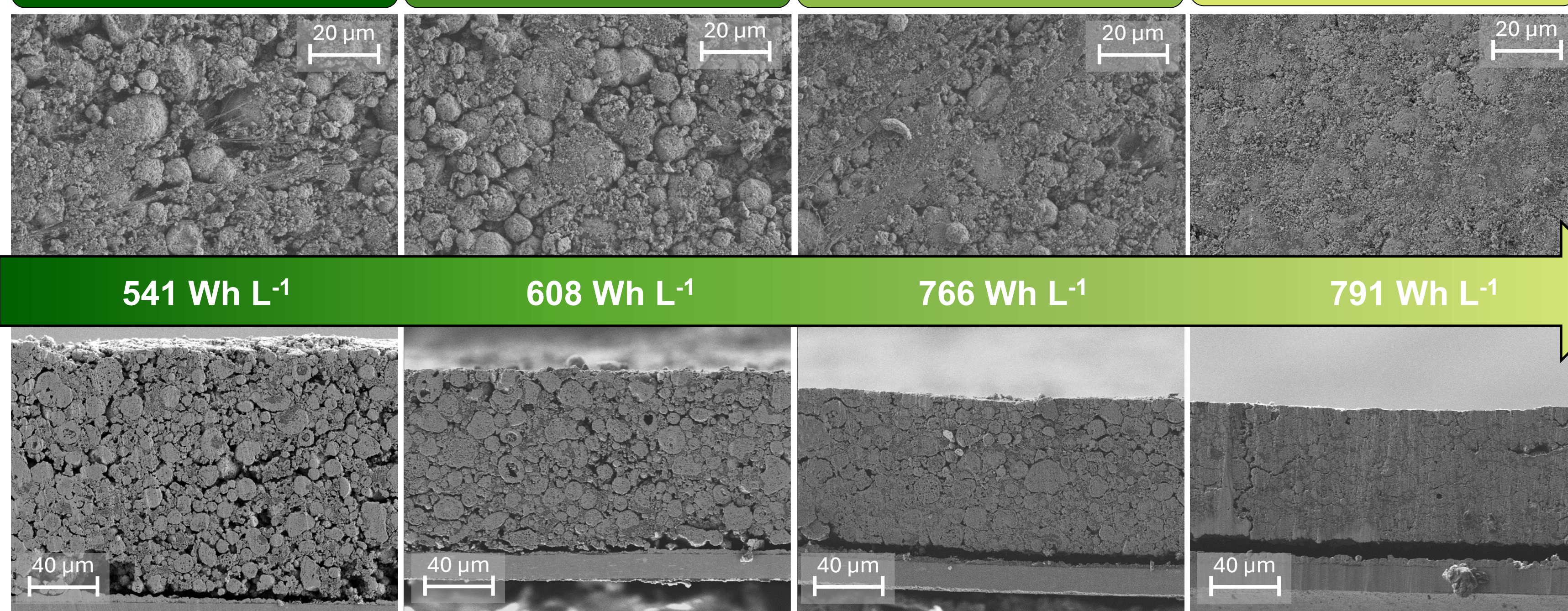
Energy Density increase on electrode level up to ~800 Wh L⁻¹ (+46%) by decreasing porosity

Uncal

50% Porosity

40% Porosity

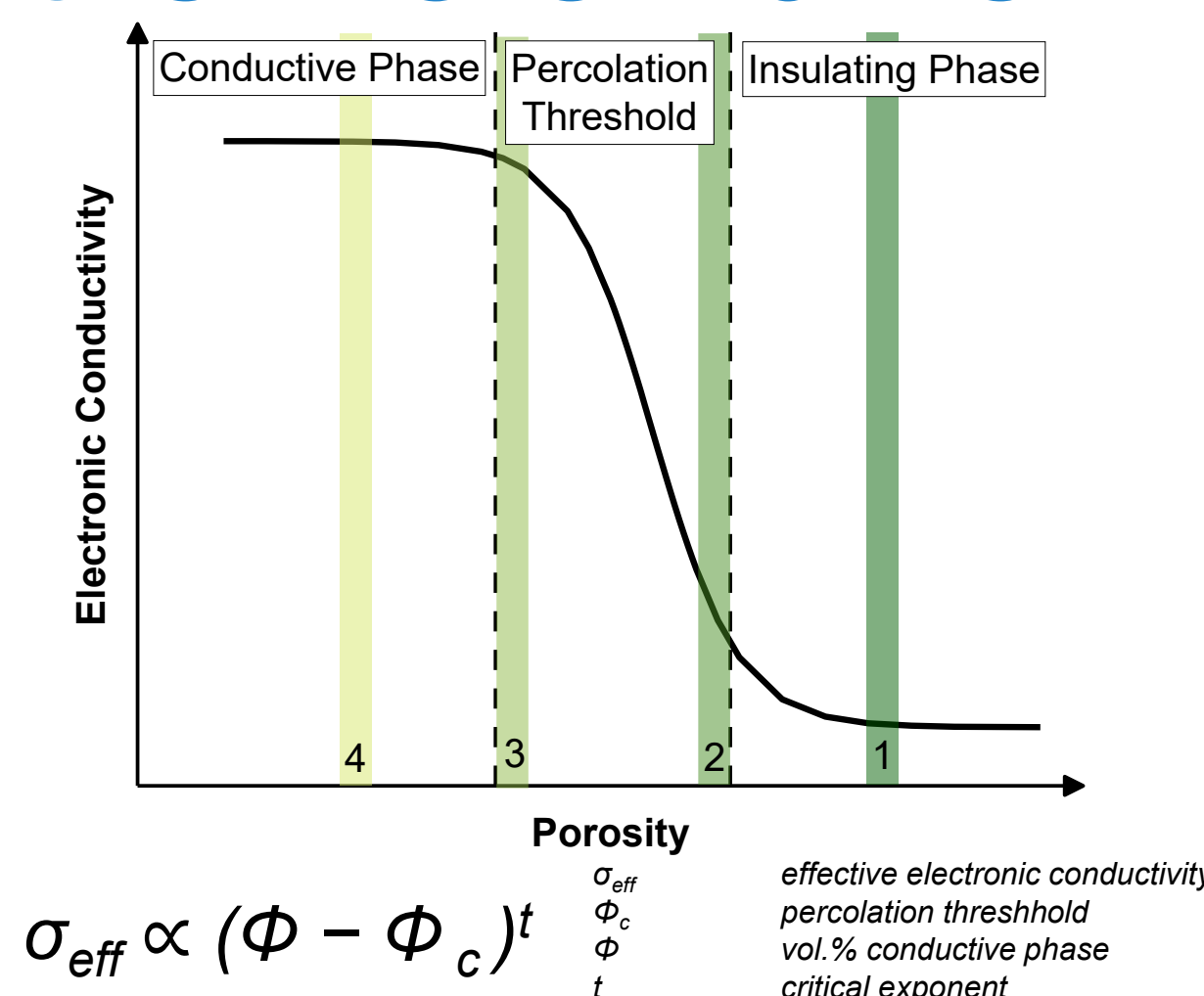
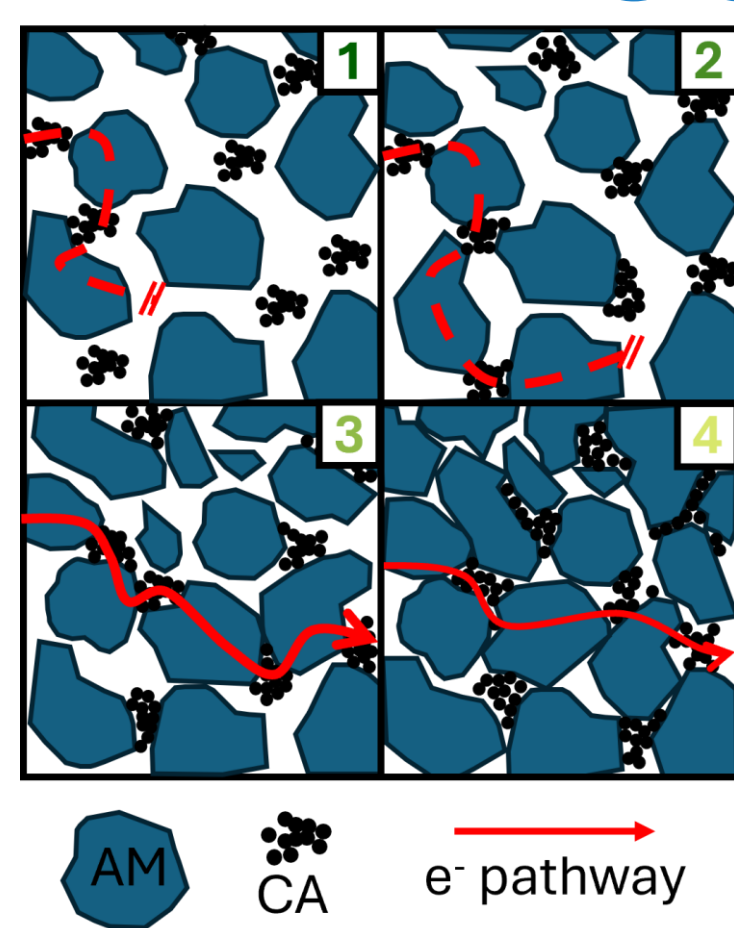
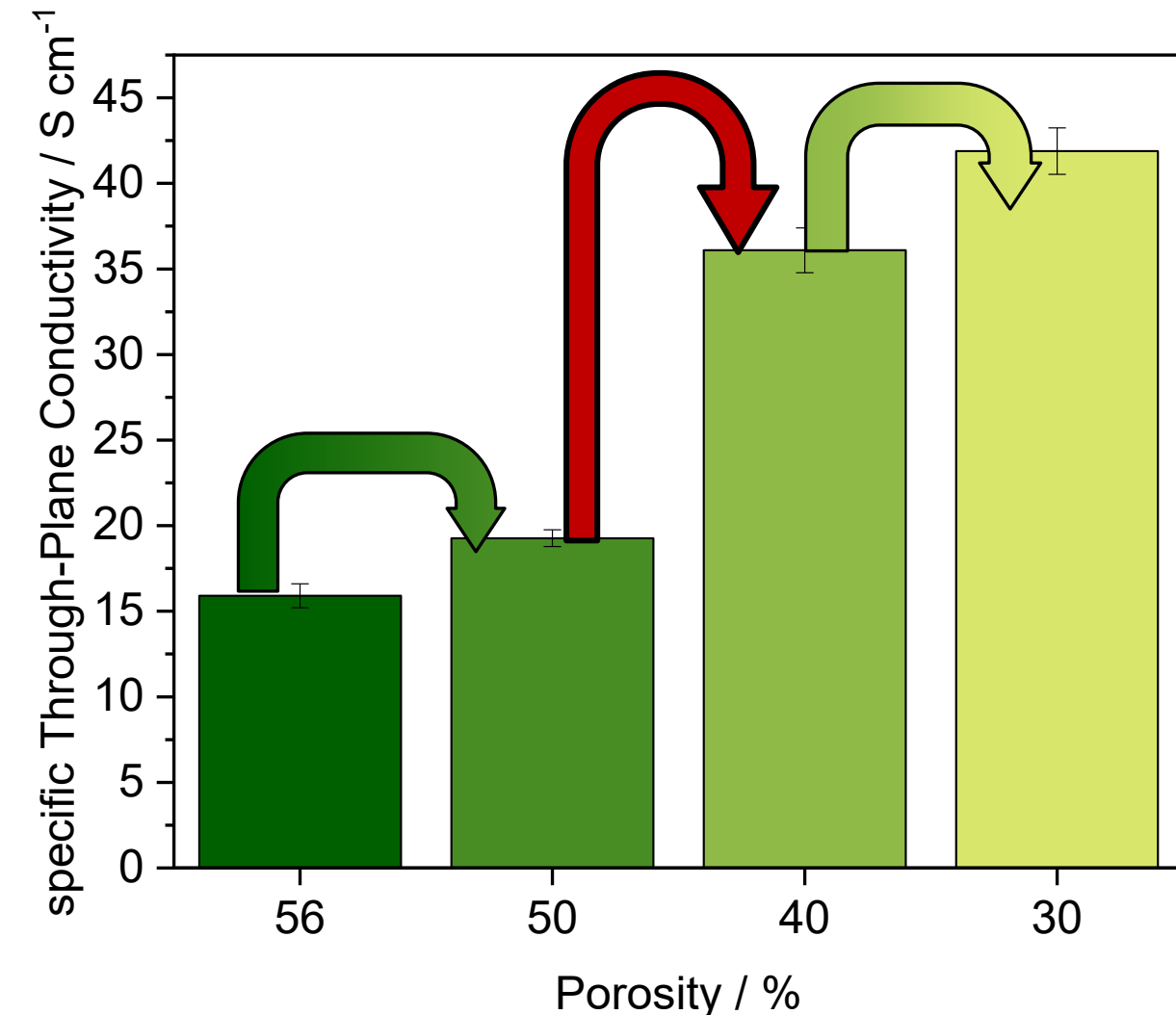
30% Porosity



	Uncal	50%	40%	30%
Porosity by MIP / %	53.97	25.01	17.05	12.19
Inaccessible Porosity / %	0.29	52.37	66.63	69.70
Pore Volume / mm³g ⁻¹	376.82	351.83	339.30	87.34
Average Pore Diameter / nm	109.40	97.38	87.34	53.83

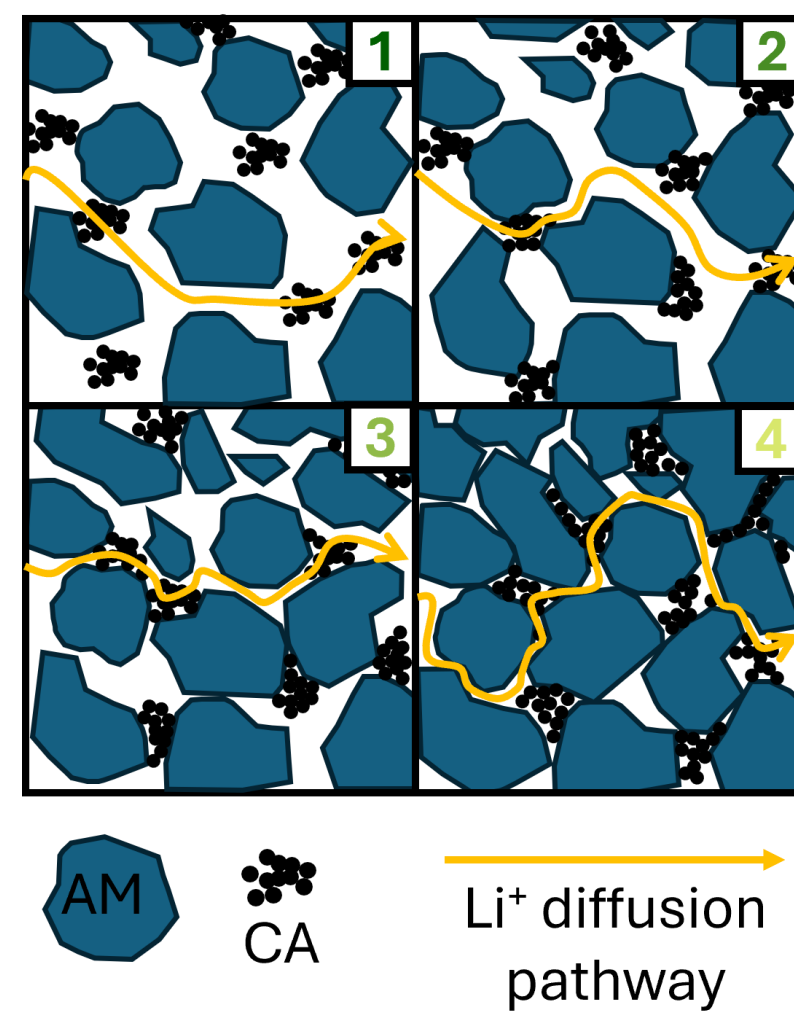
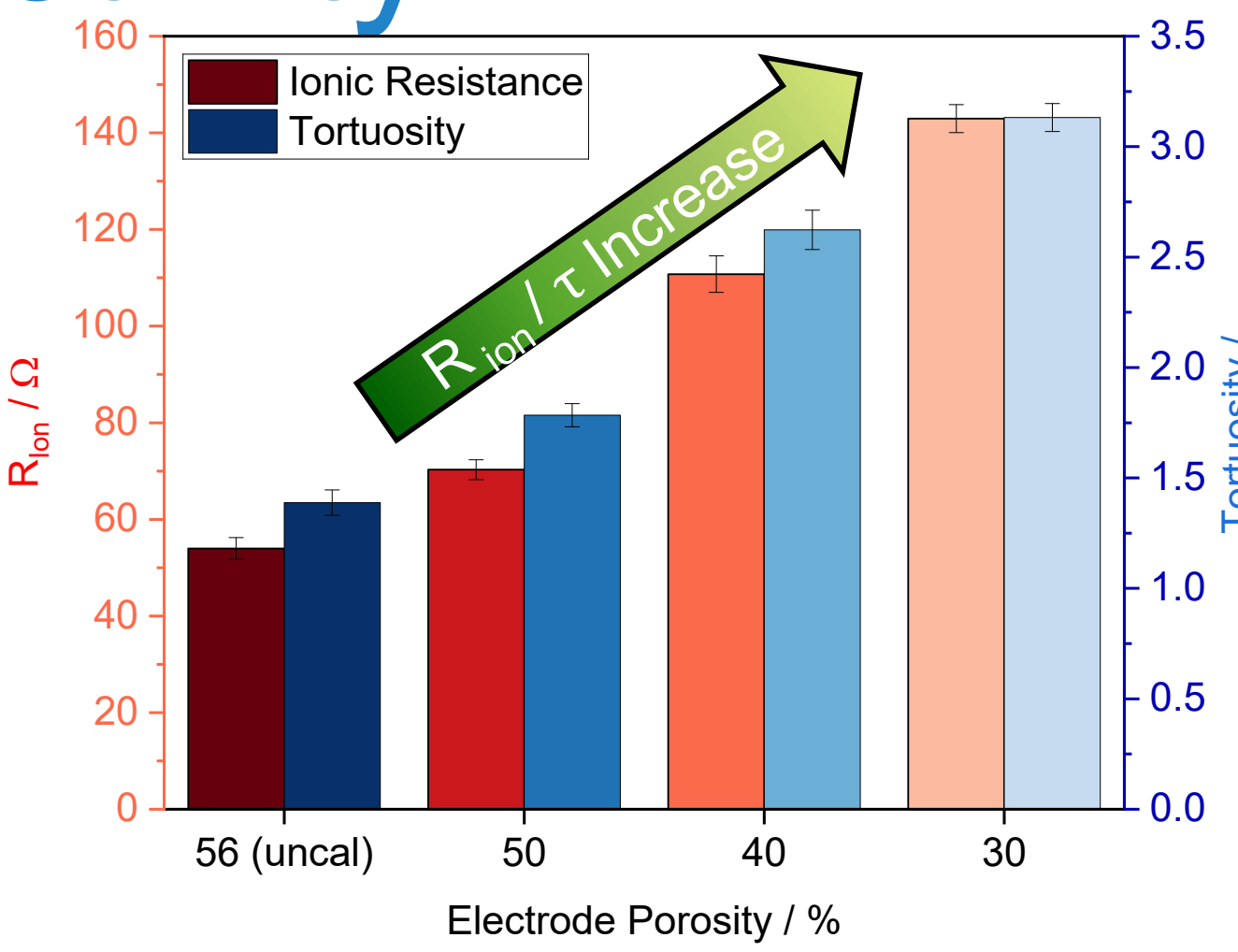
- Shift in accesible porosity after postcalendering determined by MIP
- Decrease in pore volume/ diameter
- Mainly shrinkage of pores between active material, CBD pores unaffected
- Drastic decrease of pore volume from 40 to 30%

Electronic and Ionic Conductivity



$$\frac{\tau}{\varepsilon} = \frac{R_{ion} A \kappa}{2 d}$$

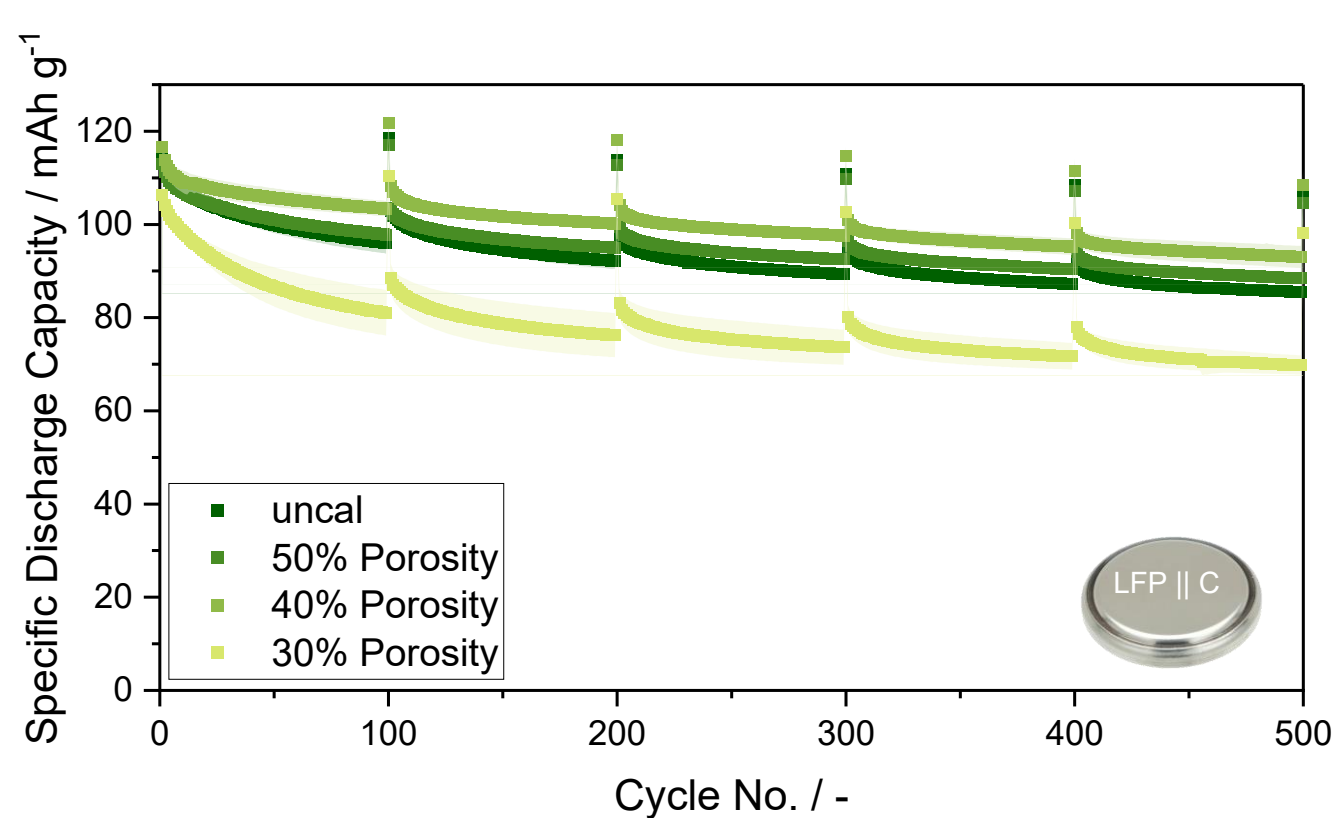
Determined via PEIS measurement of symmetric cells with blocking conditions



- Small increase in electronic conductivity from 56% to 50%, as well as 40% to 30% porosity
- Large increase in conductivity from 50 to 40% porosity
- Increase of volumetric conductive filler content by compression
- Percolation threshold is surpassed between 50 and 40% porosity

- Almost linear increase of ionic resistance and tortuosity with higher degree of compression
- Reduced porosity cannot compensate increase of ionic resistance, resulting in increased τ

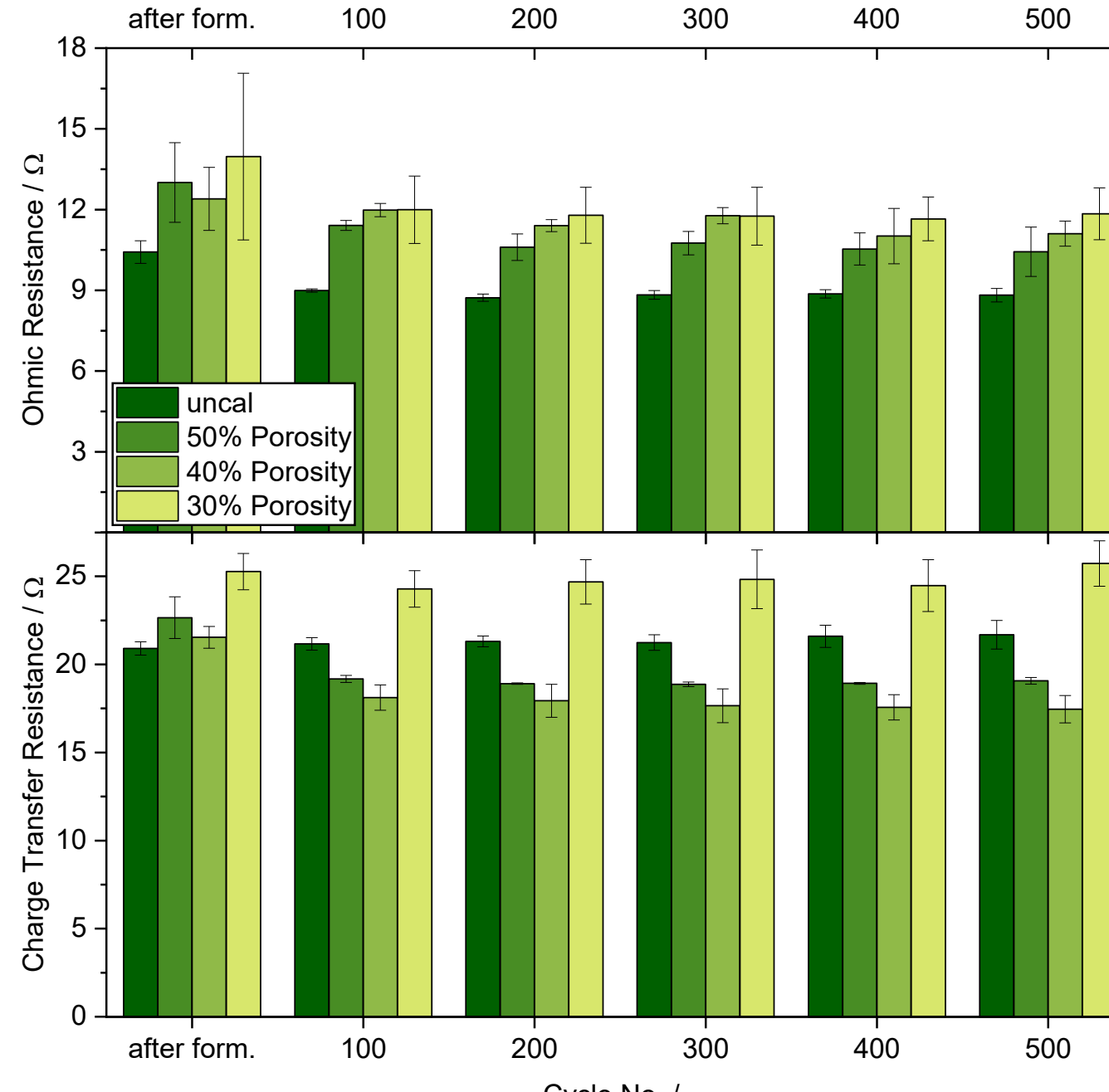
Electrochemical Performance



- Compaction has a negligible impact on C-rate performance in coin cells against Li metal
- Optimum in specific discharge capacity at 40% porosity

Pulse test during recovery steps every 100th cycle, showed no increase of resistances over cycle life for any electrode variation after formation:

- R_{Ω} rises with decreasing porosity
- Ionic conductivity of electrolyte in cell/composite deteriorates with decreasing porosity
- Fewer/narrower pores, more tortuous composite electrode structure, greater diffusion resistance
- R_{CT} reduces with decreasing porosity up to 40% porosity
- Improved electronic percolation network
- Improved particle contact and more available electrochemically active reaction sides result in lower R_{CT}
- Large increase in R_{CT} at 30% porosity, due to depletion of triple-phase boundaries and loss of electrolyte availability



Conclusion

- Porosity strongly influences balance between electronic and ionic transport inside electrode composite
- Post-calendering viable unit operation to adjust electrode porosity after lamination and boost energy density on electrode level
- Reducing porosity improves mechanical integrity, adhesion, electronic conductivity and electrochemical performance up to a certain point
- Excessive compaction leads to increased tortuosities, reduced electrolyte accessability and loss of triple-phase boundaries, which impairs ionic transport and charge transfer kinetics
- Optimal performance achieved at intermediate porosities, where the trade-off between improved electronic conductivity an acceptable ionic transport yields highest specific capacity, rate capability and cycling stability

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