Karlsruhe Institute of Technology

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The Growth Mechanism of Lithium Dendrites and its Coupling to Mechanical Stress

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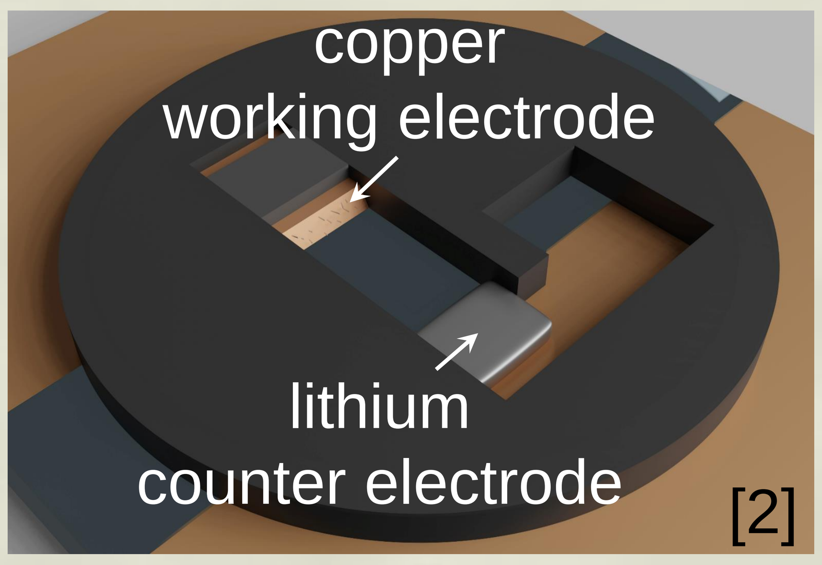
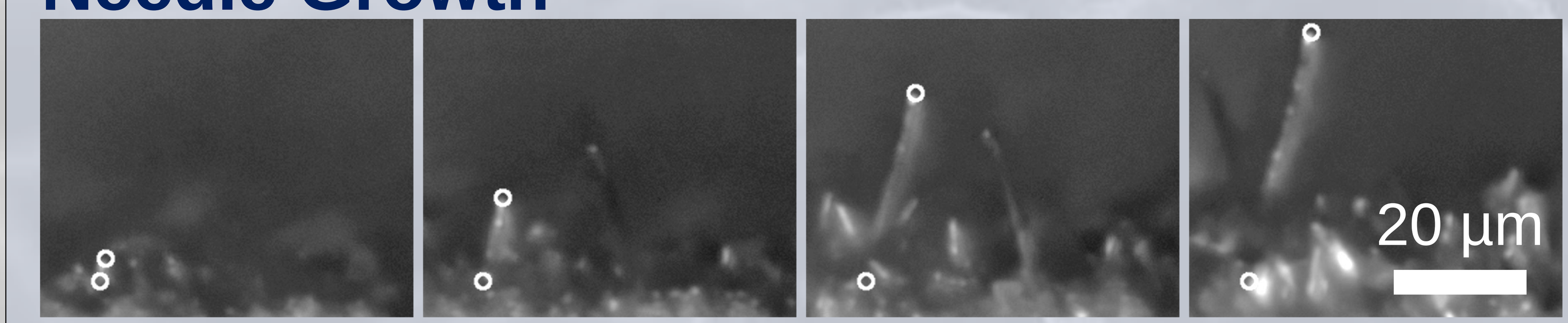
Lithium metal anodes have the potential to increase the energy density of rechargeable batteries significantly. However, safety concerns hinder their commercialization.[1] They typically exhibit poor Coulombic efficiencies and tend to form dendritic deposits, which can result in internal short circuits.[1] In spite of many detailed models of electrodeposition, the behavior of lithium still deserves further research: mechanisms described in literature are often contradictory and their application range is not clear.

Experimental



- Electrodeposition of Li on a prelithiated Cu block in a 1 M $LiPF_6$ in EC/DMC (1:1) electrolyte.
- *Operando* observation of the electrodeposition with a light microscope at the physical resolution limit with extended depth of field.
- Galvanostatic deposition: 50 µA cm^{-2}

Needle Growth

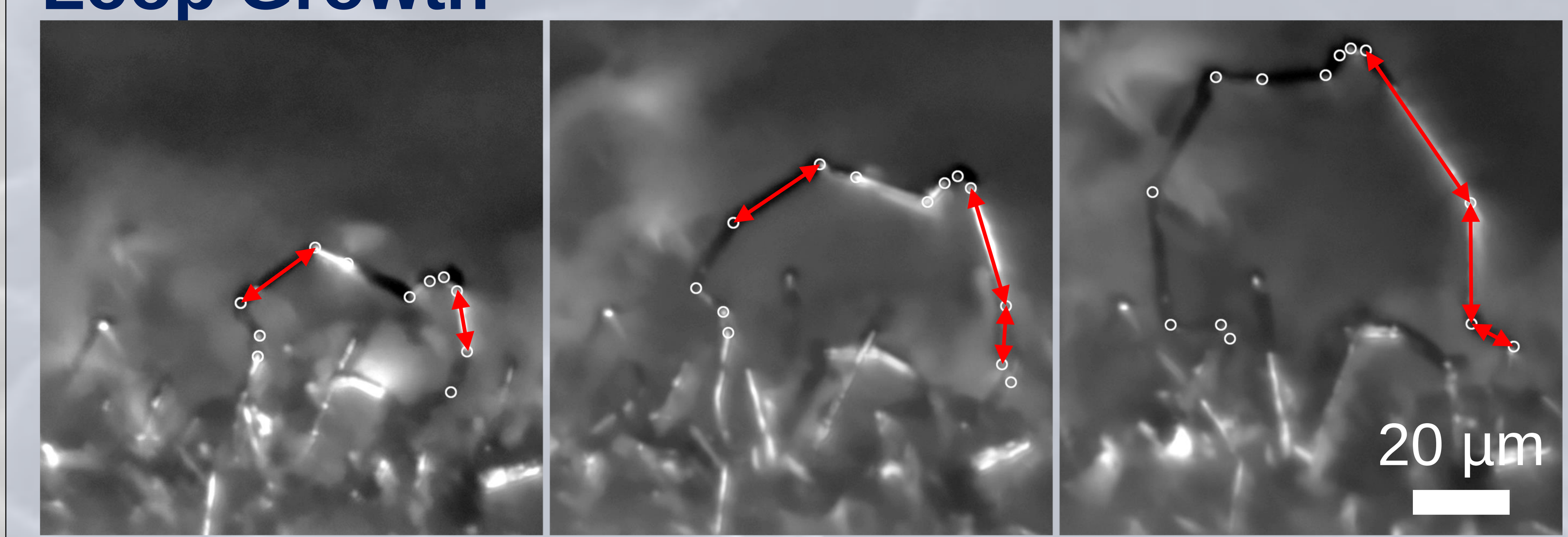


[3]

$l = 3.5\ \mu m$ | $l = 12.9\ \mu m$ | $l = 29.6\ \mu m$ | $l = 39.1\ \mu m$

$v = 1.6\ \mu m/h$ | $v = 2.8\ \mu m/h$ | $v = 1.6\ \mu m/h$

Loop Growth



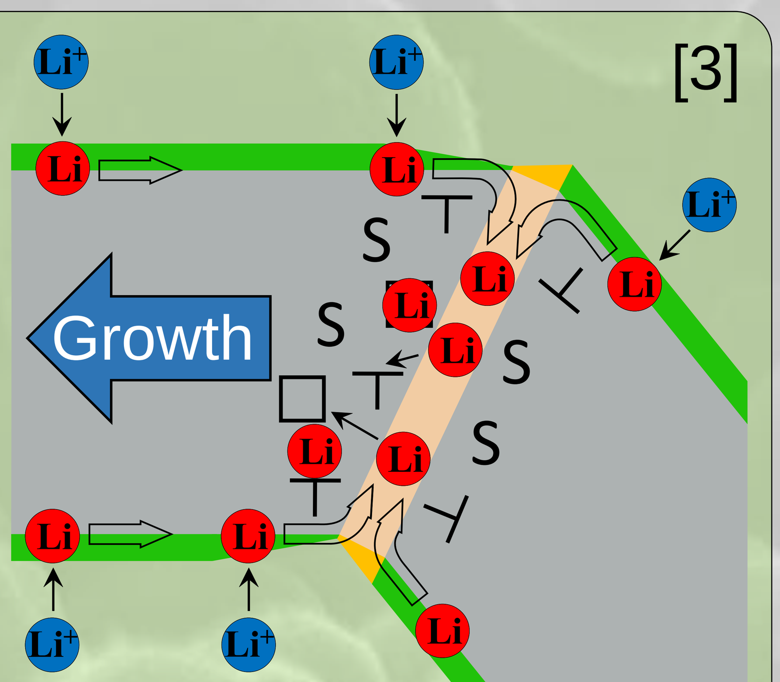
[3]

- Needles growth from their base
- The growth rate accelerates first and diminishes later

Loops, structures attached to the electrode at both ends, occur later during deposition and grow very differently despite identical electrochemical conditions:

- Loops grow at kinks by elongating individual segments.
- EBSD shows that kinks coincide with grain boundaries.
- A few segments (marked red) dominate growth
- These segments change over time
- Segments can grow significantly faster than needles
- The growth rate does not diminish
- The growth of loops dominates the electrodeposition for longer deposition times

Growth Mechanism



- Diffusive processes are very facile as room temperature is ≈2/3 T_m of Li.
- Adatoms diffuse from the surface into grain boundaries (GBs).
- Within the GB atoms move into dislocations / vacancies and thereby enter the bulk.
- Continuous insertion at these crystalline defects results in the growth of segments or needles, e.g., by climb.

Stimulation by Mechanical Stress

- Mechanical stress can generate plasticity and hence fuel the growth by the continuous formation of new insertion sites.
- Growth of loops inevitably induces stresses and the growth may be self-sustaining, while defects in needles may heal and the growth diminishes.

References

[1] X.B. Cheng *et al.*, *Chem. Rev.*, 2017, 117, 15, 10403–10473.
[2] J. Becherer *et al.*, *ChemElectroChem*, 2021, 8, 20, 3882–3893.
[3] J. Becherer *et al.*, *J. Mater. Chem. A*, 2022, 10, 5530–5539.

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