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# Development of a Reliable Reference Electrode to Investigate the Effects of Lithium Plating on Battery Durability

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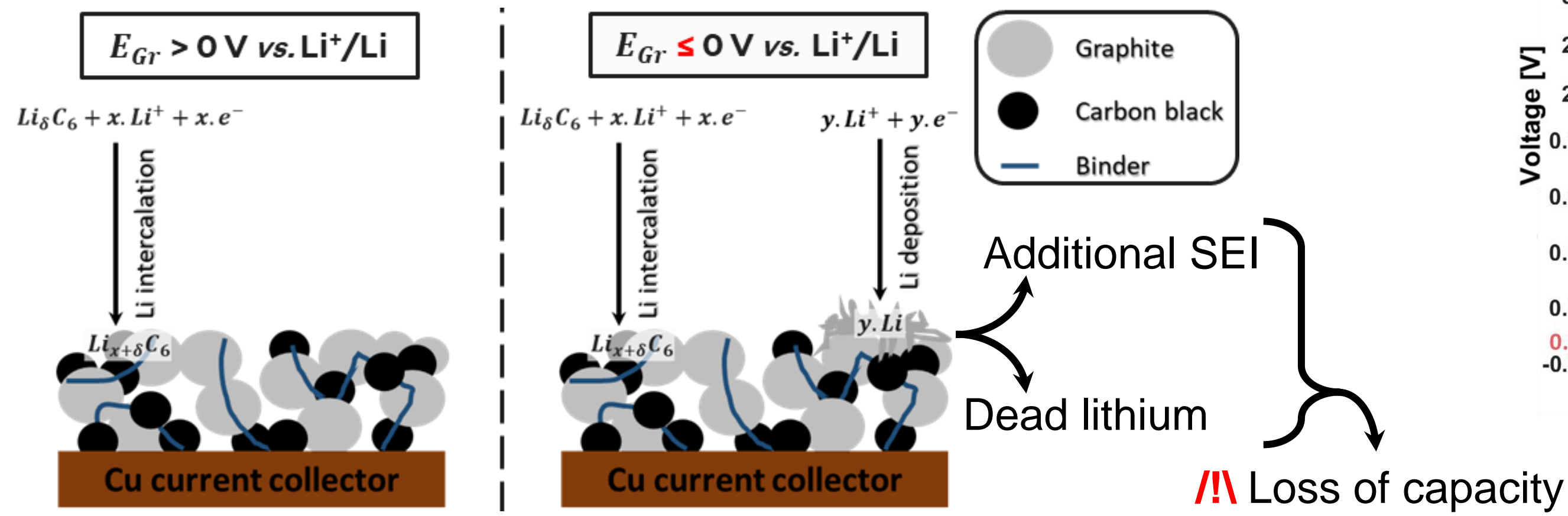
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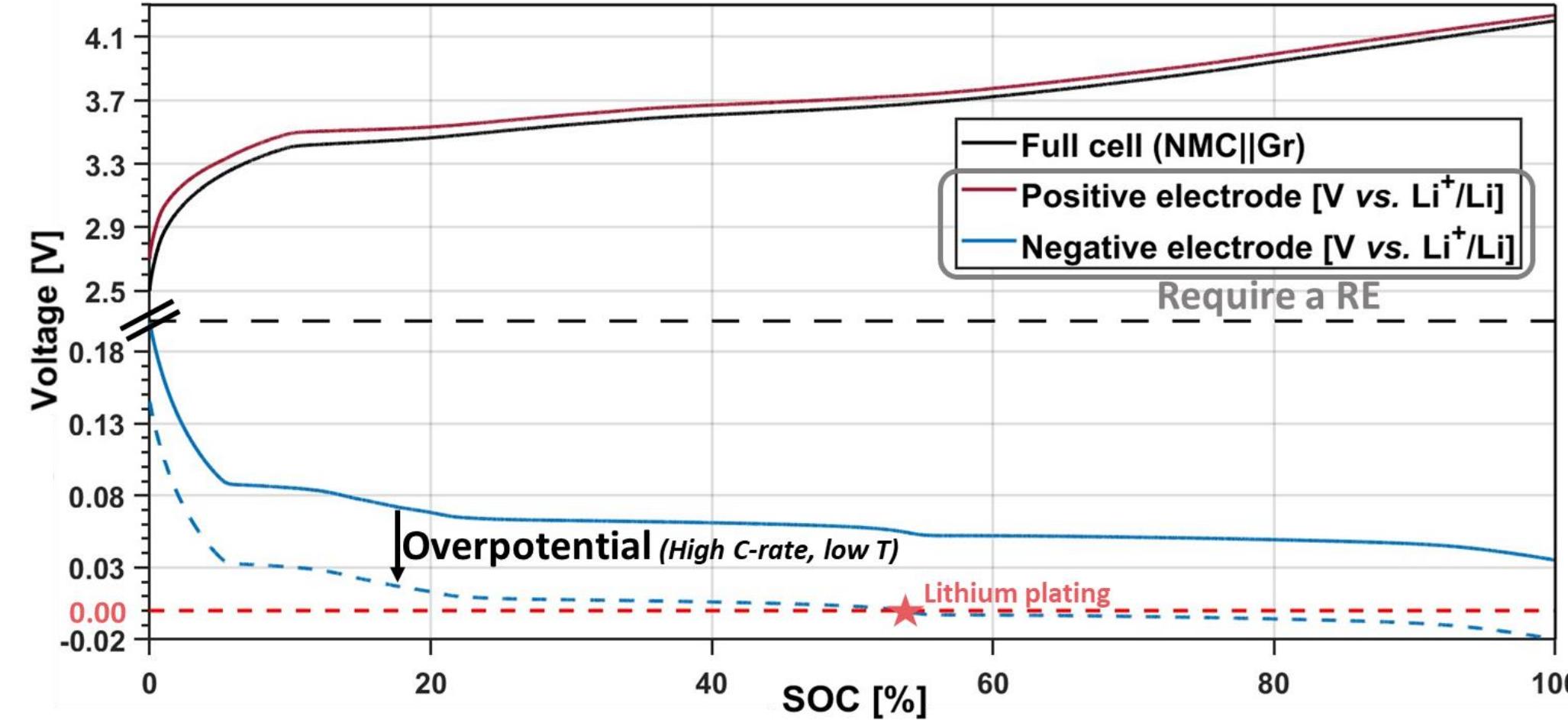
## Context

**New European legislation on battery durability:**  
SOH > 72% over 8y/160 000km (implementation in 2030)<sup>1</sup>

Investigation of degradation mechanisms such as **Li plating**



**How to detect Li plating? The Reference Electrode (RE)**



**Main RE challenges:**

- Reliability  
→ Li plating at 0 V vs. RE??
- Size & position  
→ Minimize cell perturbations<sup>2</sup>
- Long-term stability  
→ Max 1000h at C/5 for LiFePO<sub>4</sub><sup>3</sup>

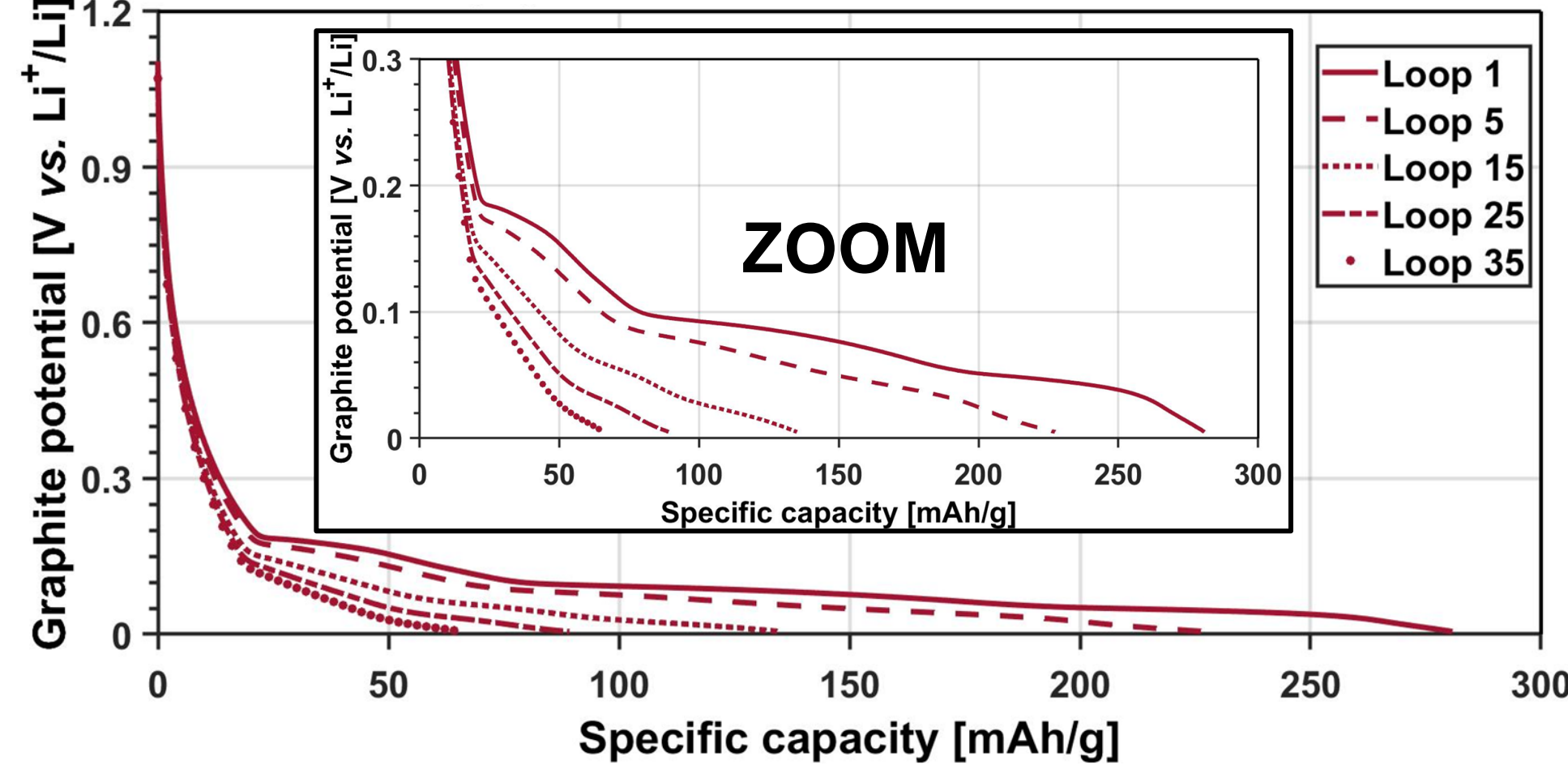
**Objective: Development of a reliable reference electrode**

## Li plating investigation

**Additional Li plating detection techniques required:** - Confirm the RE measurement

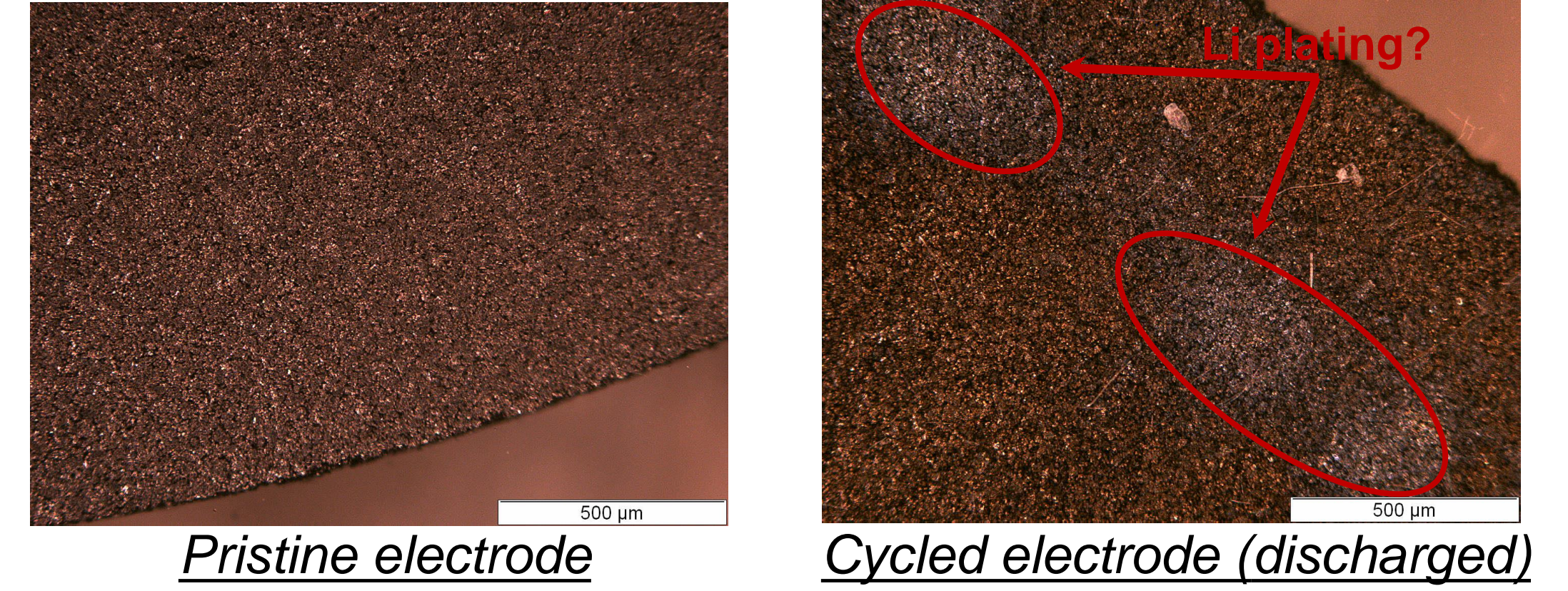
- Test the validity of the 0 V vs. Li<sup>+</sup>/Li criterion

**Specific capacity of graphite as a function of the loop (at C/5)**



Capacity retention (at C/20) = 67% } **Li plating expected**

**Optical microscopy analysis of graphite electrodes**

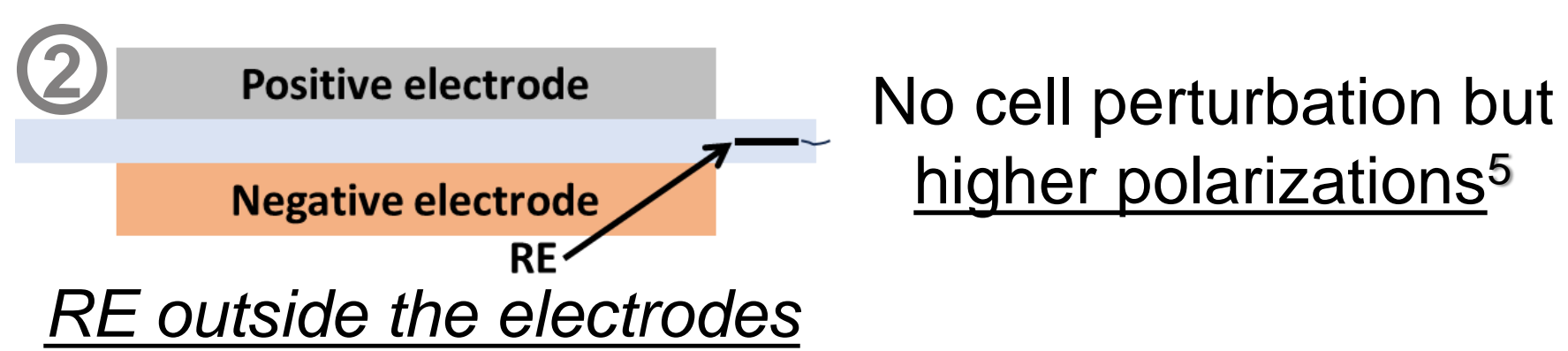
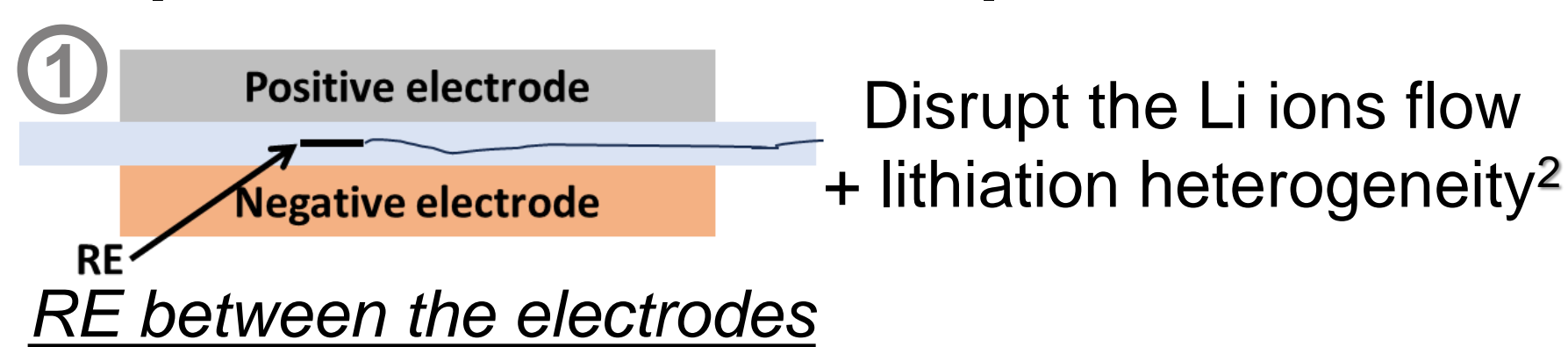


Gray areas on graphite electrode after aging → Li plating?

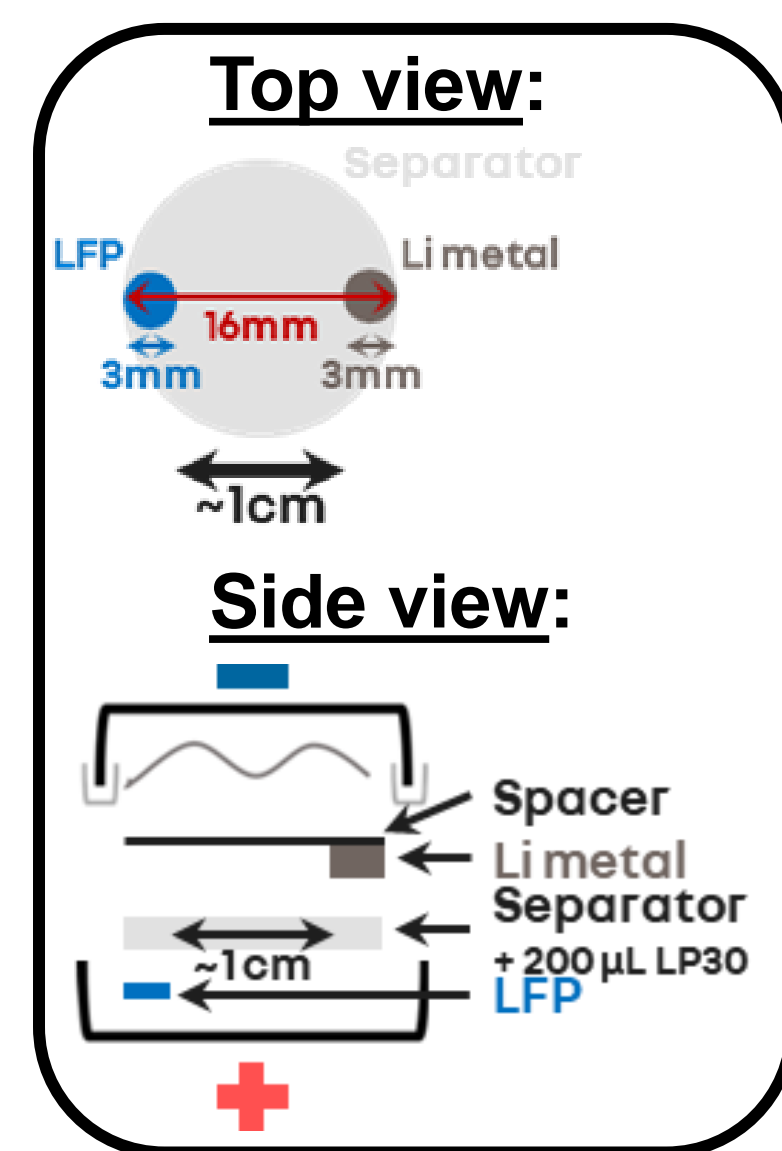
Possible explanations: pressure / higher current densities<sup>4</sup>

## Electrochemical signature of the reference electrode

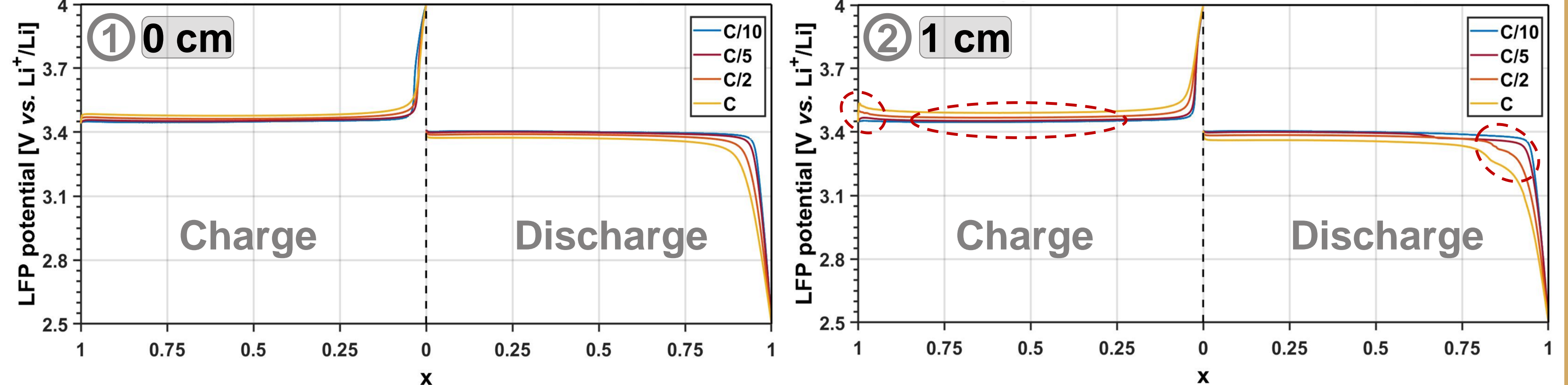
**Two possibilities for the RE placement:**



Choice of LFP for the RE (flat plateau at 3.4 V vs. Li<sup>+</sup>/Li)  
What about 1 cm?



**LFP potential profile as a function of lithium concentration for both configurations**



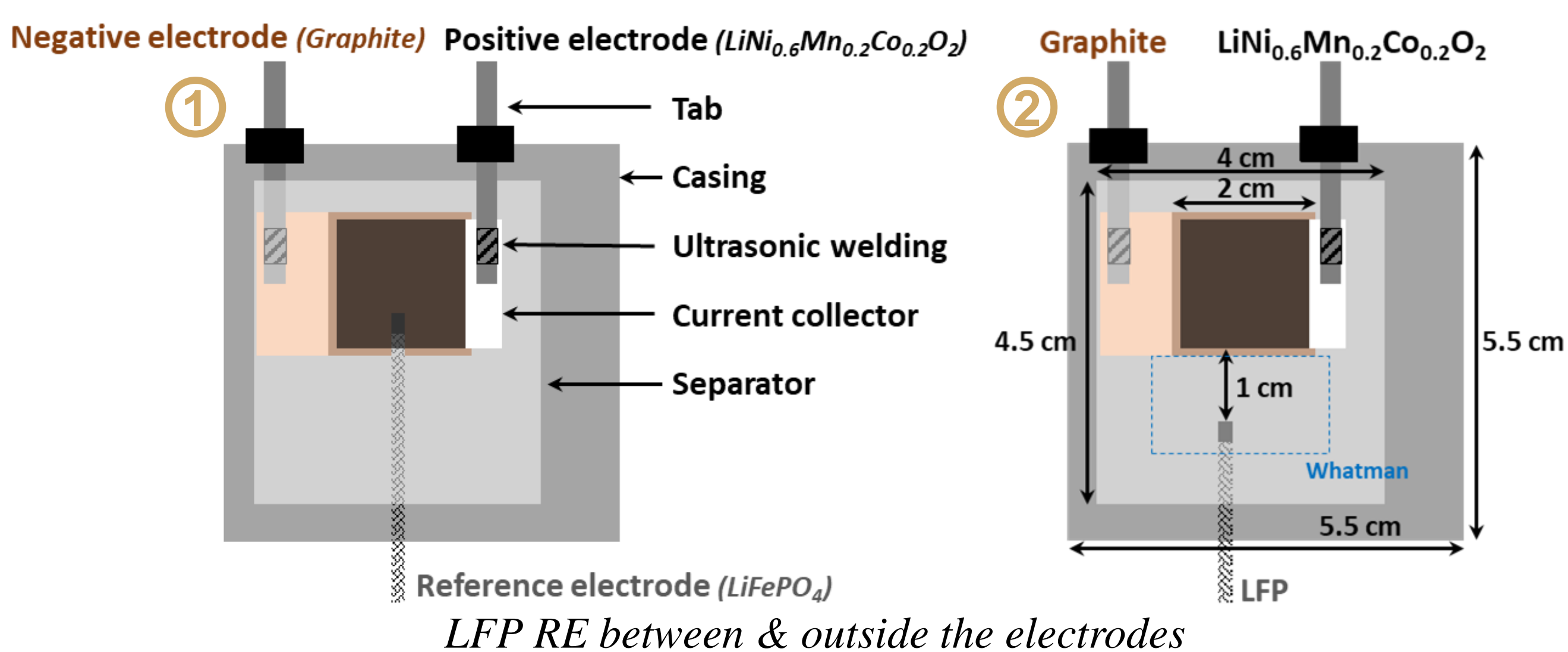
Higher polarization for 1 cm configuration but still the LFP flat potential plateau



Reduction of Li<sup>+</sup> on spacer during discharge?  
→ Insulation of the spacer with Kapton tape

## Three-electrode pouch cells

**Two setups under development:**



**RE position investigation:** What about lithiation heterogeneity and RE artifacts?

## Perspectives

- Additional optical characterizations & XRD analysis  
→ Confirm the nature of gray areas
- Optical microscopy with operando cell
- Proposal accepted at the ESRF  
→ Quantification of negative electrode lithiation (heterogeneity near the RE?)  
→ Quantification of RE artifacts (correlation between XRD signals and RE measurement)

**References:**

- [1] Euro 7, Regulation (EU) 2024/1257, Annex II (2024)
- [2] Y. Li et al., J. Power Sources, 481. 228933 (2021)
- [3] Z. Ahmed et al., Energy Technol., 10. 2200248 (2022)
- [4] F. Ringbeck et al., J. Electrochem. Soc., 167. 090536 (2020)
- [5] D.W. Dees et al., J. Power Sources, 174. 1001 (2007)