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Lithium-ion battery liquid electrolyte characterization with programmed-current derivative chronopotentiometry (PCDC)

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Summary

- Development of safe electrolytes for energy storage (battery applications)

- Investigation of lithium mobility in liquid battery electrolytes via programmed current chronopotentiometry measurements

Motivation

The measure of Li transference numbers can be achieved by different methods including pulsed field gradient nuclear magnetic resonance, Bruce-Vincent/potentiostatic polarization, galvanostatic polarization, moving boundary method and electromotive force method.

- Significant differences among these methods are found due to different assumptions and experimental conditions during the measurement

- Prerequisites are necessary which restrict the electrolyte formulations

- The behavior of the electrolyte in the Li-ion cell and in particular the Li-cell performance can be predicted only in a very limiting manner based on the knowledge of Li transference numbers

- The measure of the lithium mobility in the electrolyte is investigated with **programmed current derivative chronopotentiometry (PCDC)**

Measurement of the lithium mobility via programmed-current derivative chronopotentiometry

A current (I) respectively current density (j) that increases linearly with time is imposed to Li|Li Swagelok-cells with several layers of glass fibre separators. Above a certain applied current limit the voltage increases in a dramatic fashion because no more Li ions can be delivered by the electrolyte. That way, I_{max} corresponds to the maximum accessible lithium ion flux under applied current conditions.

- Li||Li cell configuration

- Applying a time-dependent current
$I(t) = \beta \cdot t$ ($\beta = 100$ µAs^{-1})

- A current corresponds to a specific electrode reaction

- Measuring the voltage response

- Determining the current limit

- It is shown that neither the deposition nor the dissolution of lithium is rate-dependent

- The ionic polarization inside the cell should be in same order of magnitude

- Therefore, a pre-polarization at 1 mA s^{-1} is performed up to identical potential differences (0.7 V vs. Li/Li$^+$)

- The observed potential increases with ascending current based on solvation effects, lithium dissolution, lithium plating or interactions with separator material in the electrolyte which hamper the movement of the Li-ions

- In case of lithium as active electrode material, the electrode area A varies within the experiment because of lithium dendritic growth

- A continuous decrease of the Li-Li distance due to dendritic Li deposition affects the electric field inside the cell

- Nevertheless, the experiments reveal that these effects are small compared to the voltage jump due to discontinued Li$^+$ flux
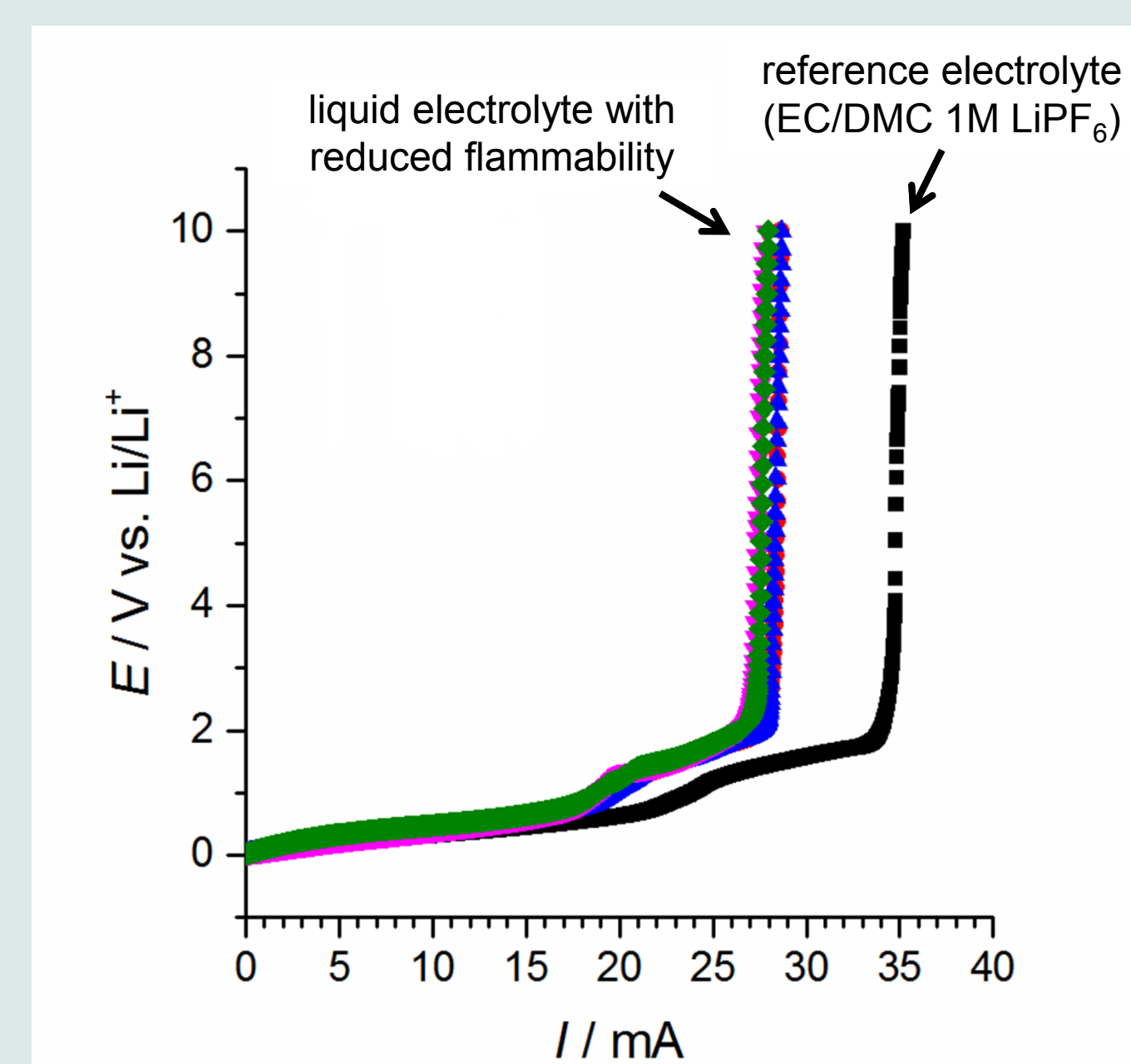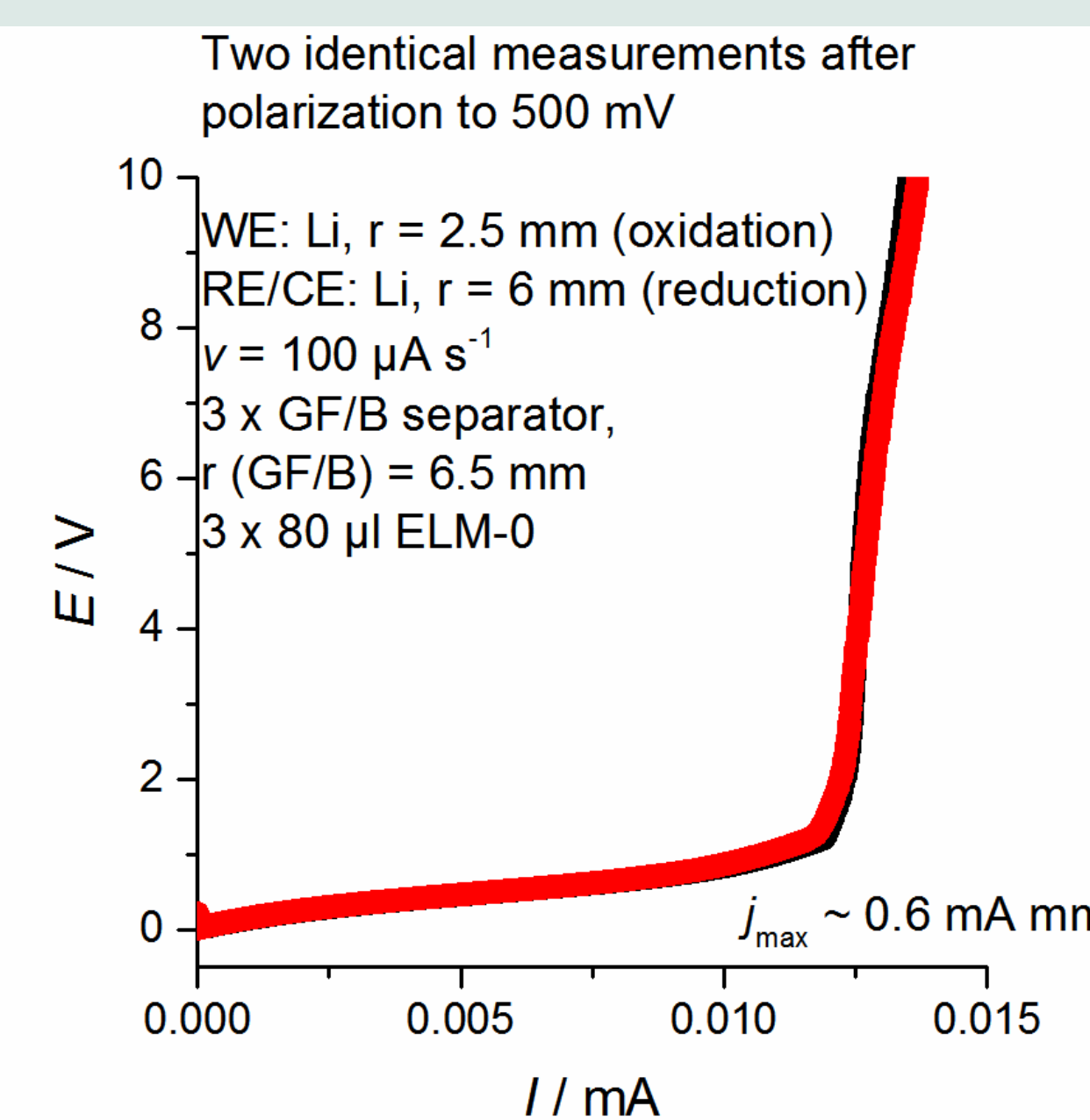

Potential (vs. Li/Li$^+$) *versus* current during programmed-current chronopotentiometry (working electrode: lithium, counter/reference electrode: lithium, four-layer glass fiber separators GF/B).
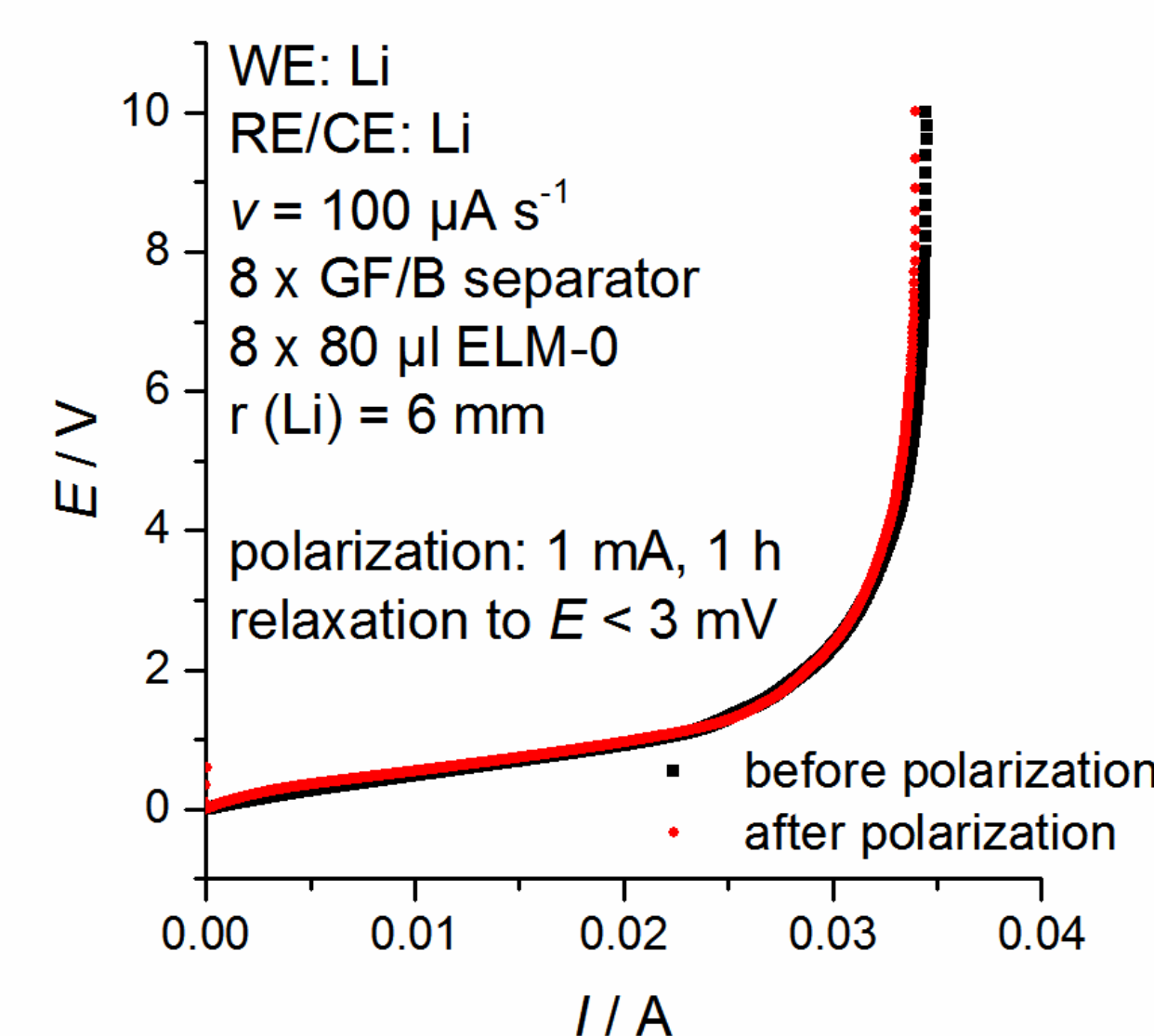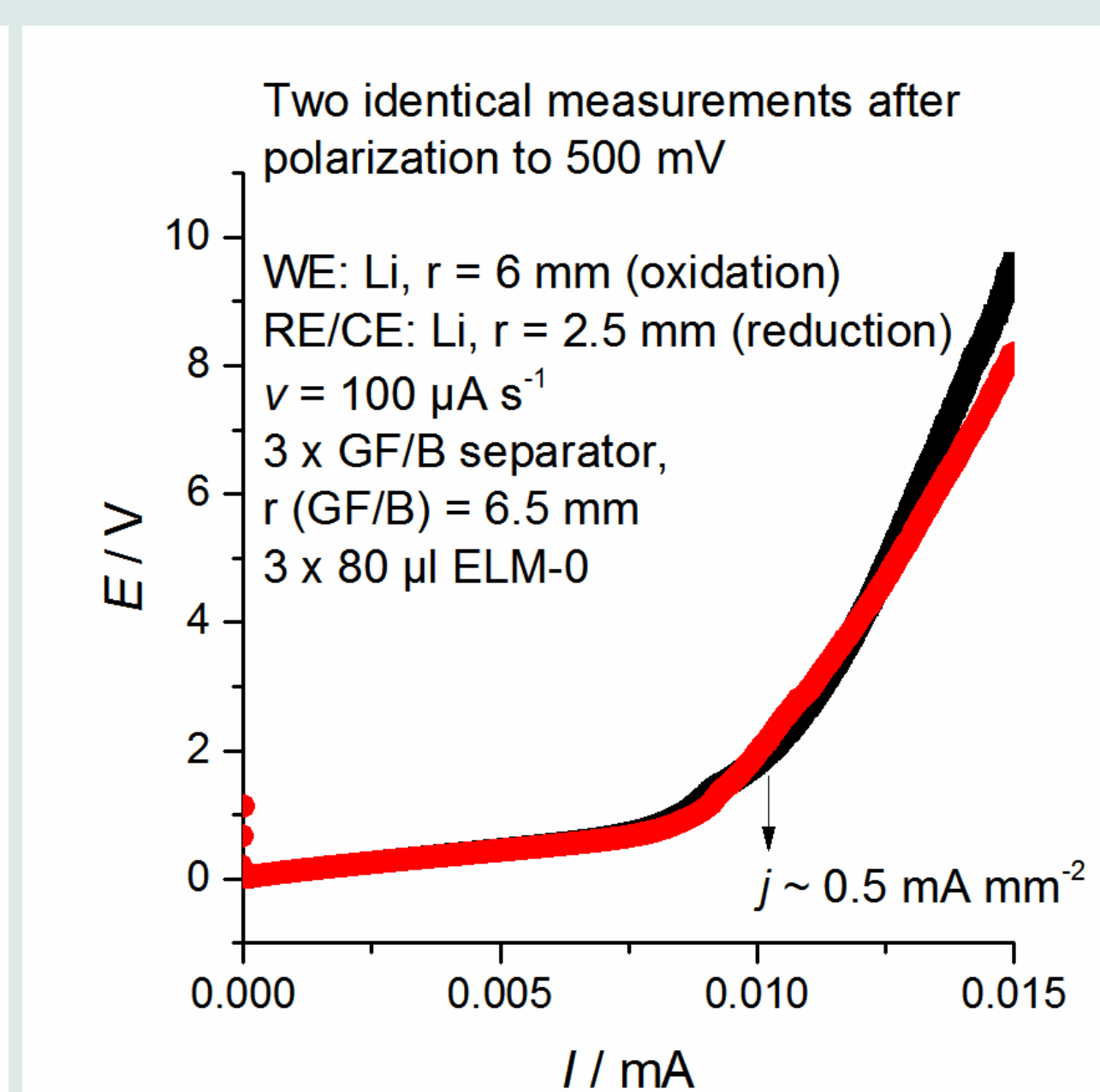

Potential (vs. Li/Li$^+$) *versus* current during programmed-current chronopotentiometry (working electrode: lithium, counter/reference electrode: lithium, eight layer glass fiber separators GF/B (d = 13 mm); b = 100 µA s^{-1}). Between both measurements, a polarization at 1 mA was applied for 1h. Thereafter, it was waited after the potential difference was dropped below 3 mV.
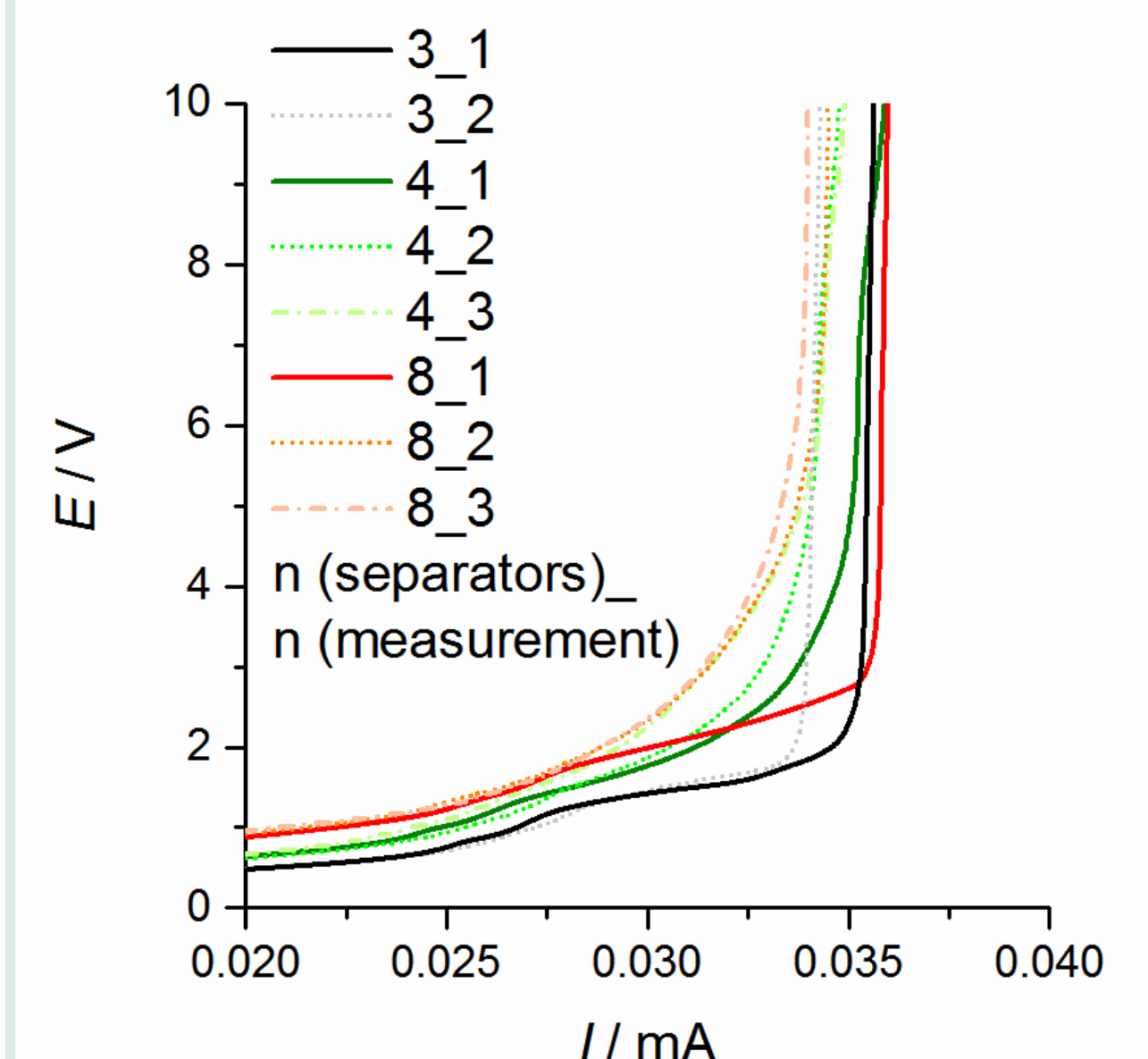
Potential (vs. Li/Li$^+$) *versus* current during programmed-current chronopotentiometry (working electrode: lithium, counter/reference electrode: lithium, b = 100 µA s^{-1}, electrolyte: ELM-0). The first number represents the layers of separators (GF/B) and the second number represents the number of measurement of each cell. A relaxation to E < 5 mV is obtained within a few hours.

Potential (vs. Li/Li$^+$) *versus* current during programmed-current chronopotentiometry (working electrode: lithium, counter/ reference electrode: lithium, b = 100 µA s^{-1}, electrolyte: ELM-0).

Potential (vs. Li/Li$^+$) *versus* current during programmed-current chronopotentiometry (working electrode: lithium, counter/reference electrode: lithium, b = 100 µA s^{-1}, electrolyte: ELM-0).

- The current limit is significantly affected by the electrode area

- Lithium plating onto stainless steel or metallic electrodes

- Lithium plating and dissolution not rate-determining

- Both individual potential plateaus (observed within the first measurements) disappear continually after several successive measurements

- Formation of Helmholtz double layers at Li and dendritic lithium surfaces is supposed which becomes more pronounced at high current densities

- The critical current decreases slightly within the first 1-3 galvanostatic measurements (~ 2 – 4 mA) and then remains more or less constant

- This can be attributed to irreversible reactions at the beginning, e.g. removing very thin layers onto Li (Li$_2$O or Li$_3$N) electrochemically

- Different numbers of separator layers (distance between Li-Li-electrodes) do not affect the current limit significantly

- The current jump between 4 – 10 V vs. Li/Li$^+$ can be seen as current limit

- Dendritic growth and differences in the Li-Li distance do not have a significant effect on the critical current jump

Conclusions and outlook

- Presentation of a novel approach for quantification of the lithium mobility

- Possibility for preliminary investigation of lithium-ion battery electrolytes (novel pre-screening method for liquid electrolytes)

- Comparison of various liquid electrolytes is possible including ionic liquids

- Cell performance may be different based on specific electrode reactions

References

- Hofmann et al., "*Novel Electrolyte Mixtures Based on Dimethyl Sulfone, Ethylene Carbonate and LiPF$_6$ for Lithium-Ion Batteries*", J. Power Source 298, 322-330 (2015).

Acknowledgements

* C/n: current rate when the cell is charged or discharged completely in n h