

# New Methods for State-of-Charge Monitoring in VFB: Chronoamperometric Measurements

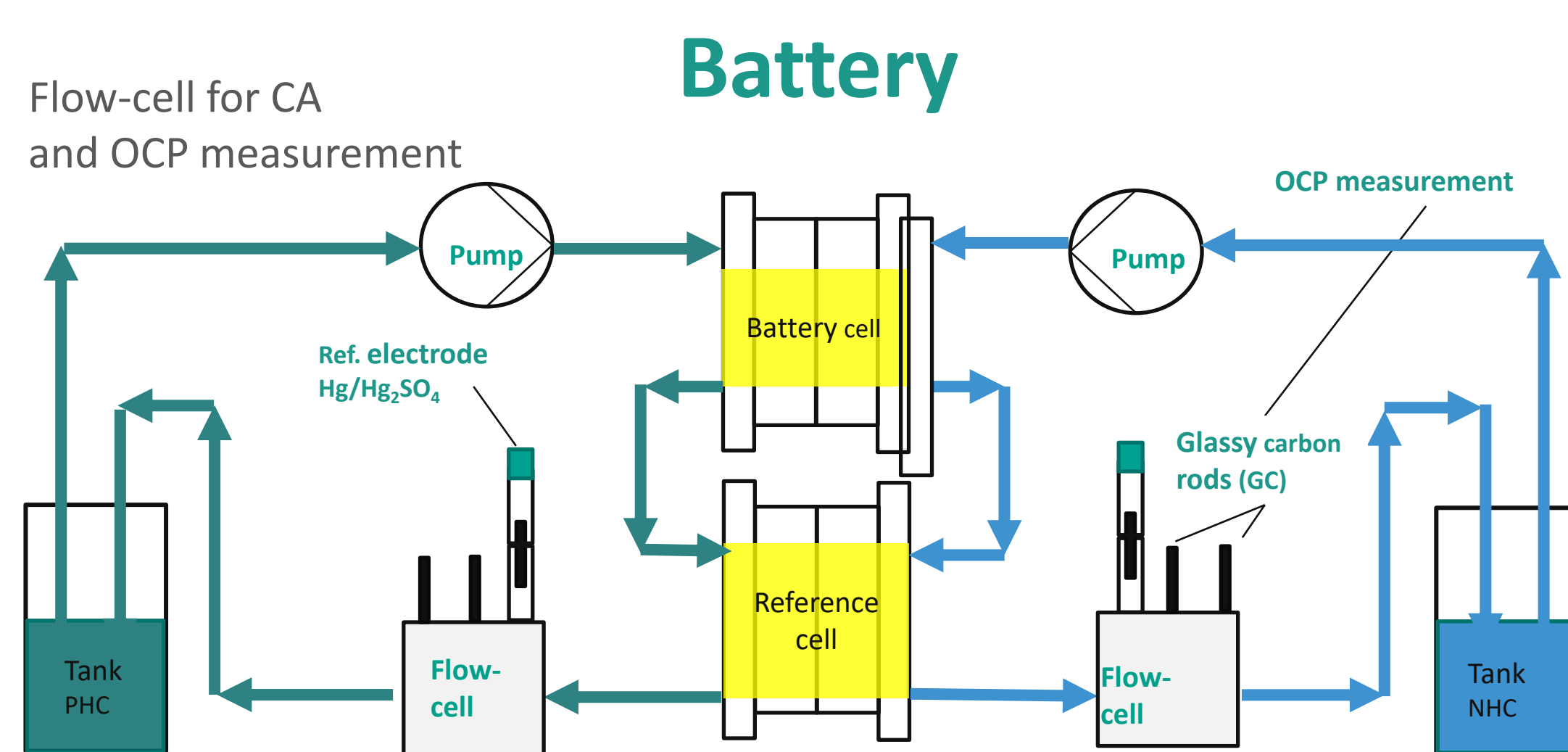
M. Valencia, C. Weidlich, F. Lulay, M. Wieland | [meiser.valencia@dechema.de](mailto:meiser.valencia@dechema.de)

DECHEMA-Forschungsinstitut, Theodor-Heuss-Allee 25, 60486 Frankfurt am Main

## Scope

- Within the project “VaMos” (*Development of online methods for State-of-Charge-monitoring*), several analytical methods have been used in order to predict the State-of-Charge (SoC) of Vanadium-Redox-Flow-Batteries. [1] - [4]
- We show the feasibility of chronoamperometric (CA) analysis [5] by using of low-cost electrodes. For this purpose three different Setups at both half-cells - positive (PHC) and negative (NHC) - were investigated. The limiting currents ( $i_l$ ) show a good correlation with the SoC of the VRFB.

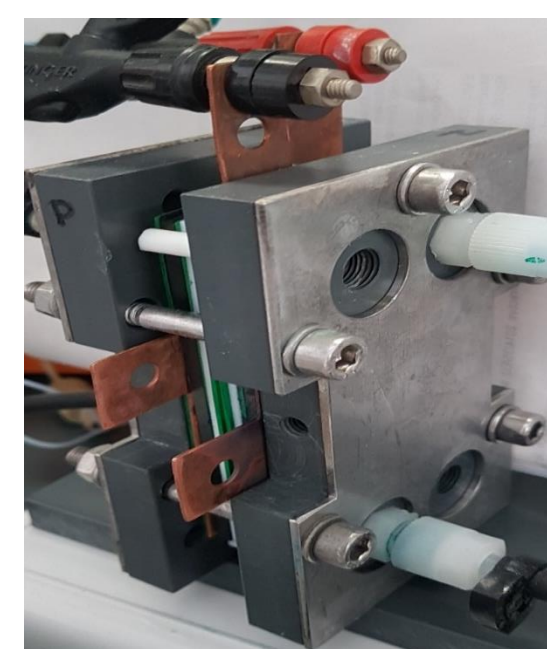
1



## Battery

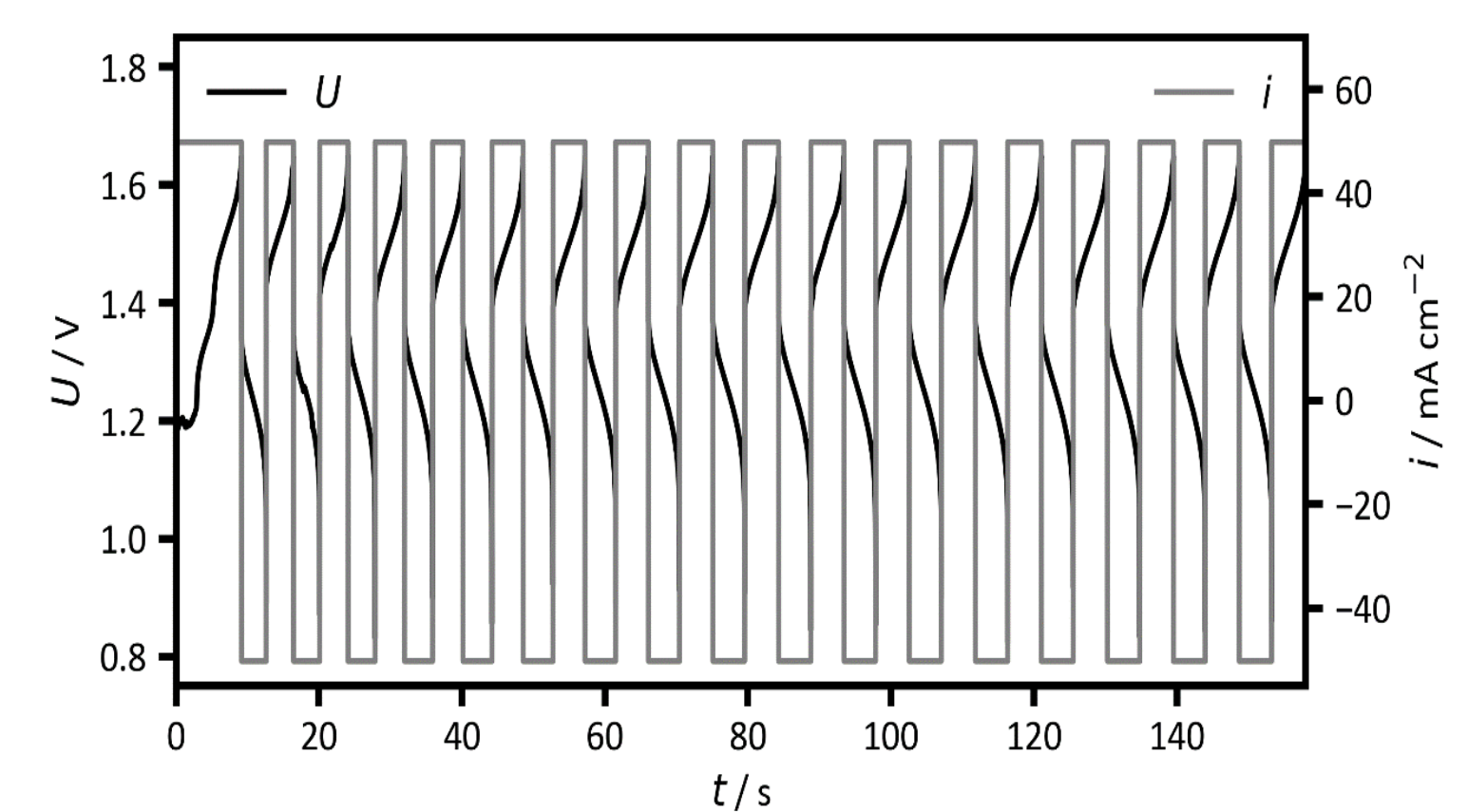
## Battery cell

10 cm<sup>2</sup>, fumasep®F10100, fumatech, Sigracell®GFD 4.6, SGL, 1.6 M V in 2 M H<sub>2</sub>SO<sub>4</sub>, GfE



- Charge / Discharge 0.5/-0.5 A; 0.8/1.75 V
- Electrolyte flow approx. 50 mL/min

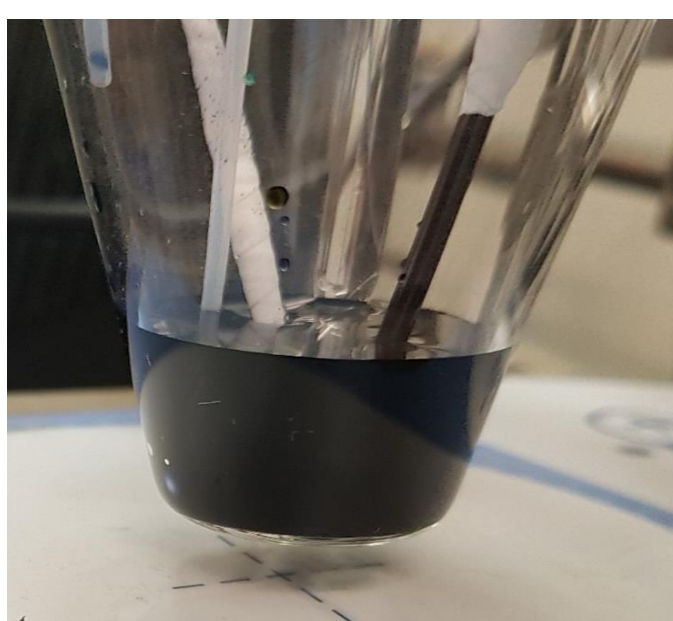
## Battery operation



2

## Test Setup for the CA Measurement

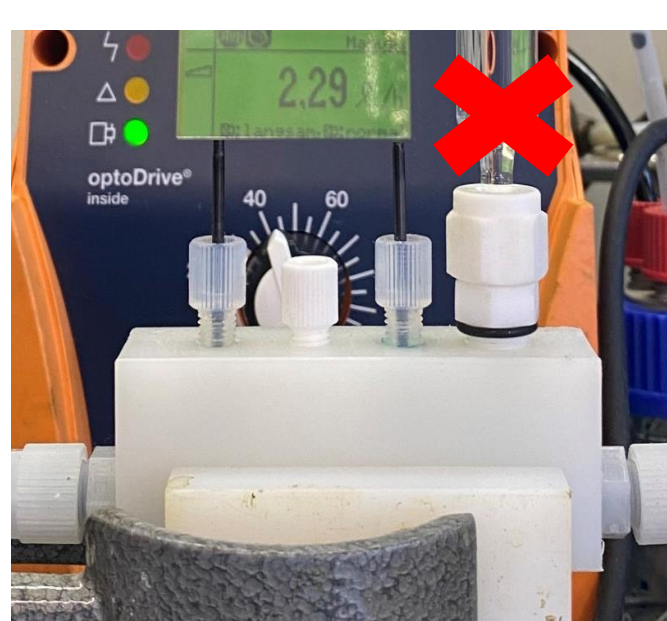
### a) Ex-Situ three-electrodes



### b) In-Situ three-electrodes



### c) In-Situ two-electrodes



## a) Ex-Situ approach

- Battery run with 100 ml electrolyte in NHC, 60 ml electrolyte in PHC, 7 ml in CA cell convection free
- Three-electrode setup: WE: microelectrode (33μm Ø) CE: GC rod RE: Hg/Hg<sub>2</sub>SO<sub>4</sub>
- Multistep Chronoamperometry
- Withdrawal of 0.5 ml for titration

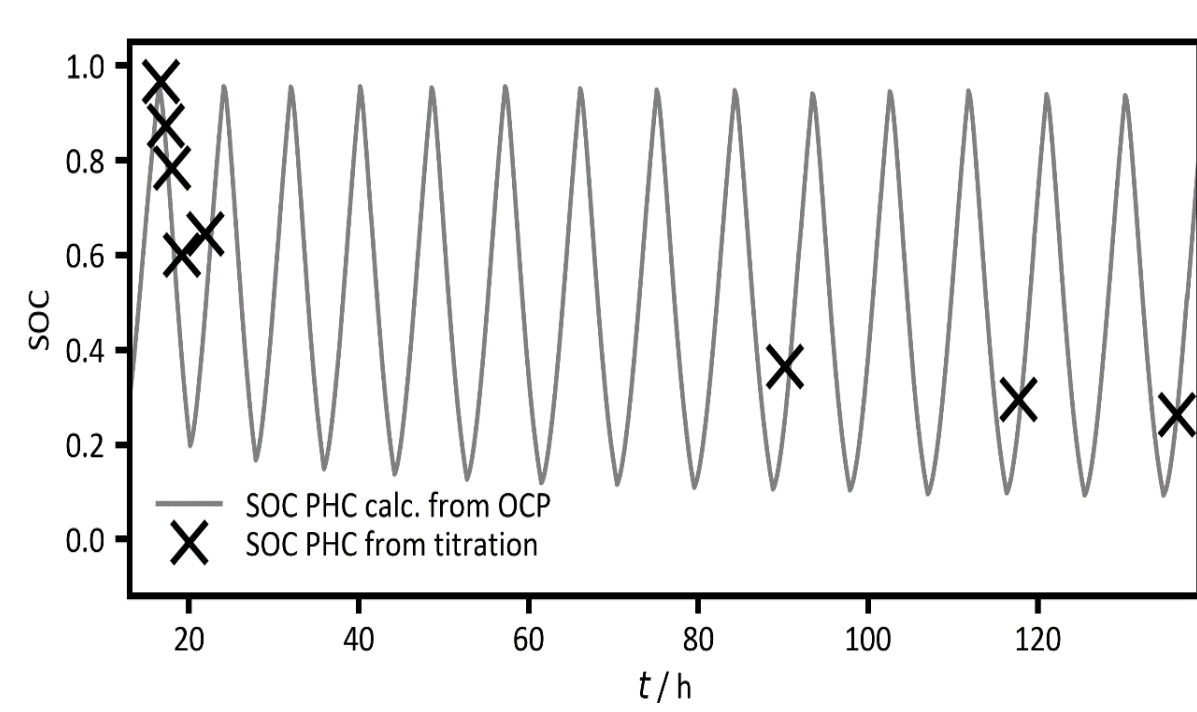
## b) and c) In-Situ approach

- Battery run with equal amount of electrolyte in both NHC and PHC approx. 125 mL
- Three-electrode setup: WE: GC rod (2mm Ø) CE: GC rod (2mm Ø) RE: Hg/Hg<sub>2</sub>SO<sub>4</sub>
- Two-electrode setup: WE and CE: GC rod (2mm Ø)
- Chronoamperometry measurements up to 60 s
- Vanadium-electrolyte flow approx. 50 mL/min

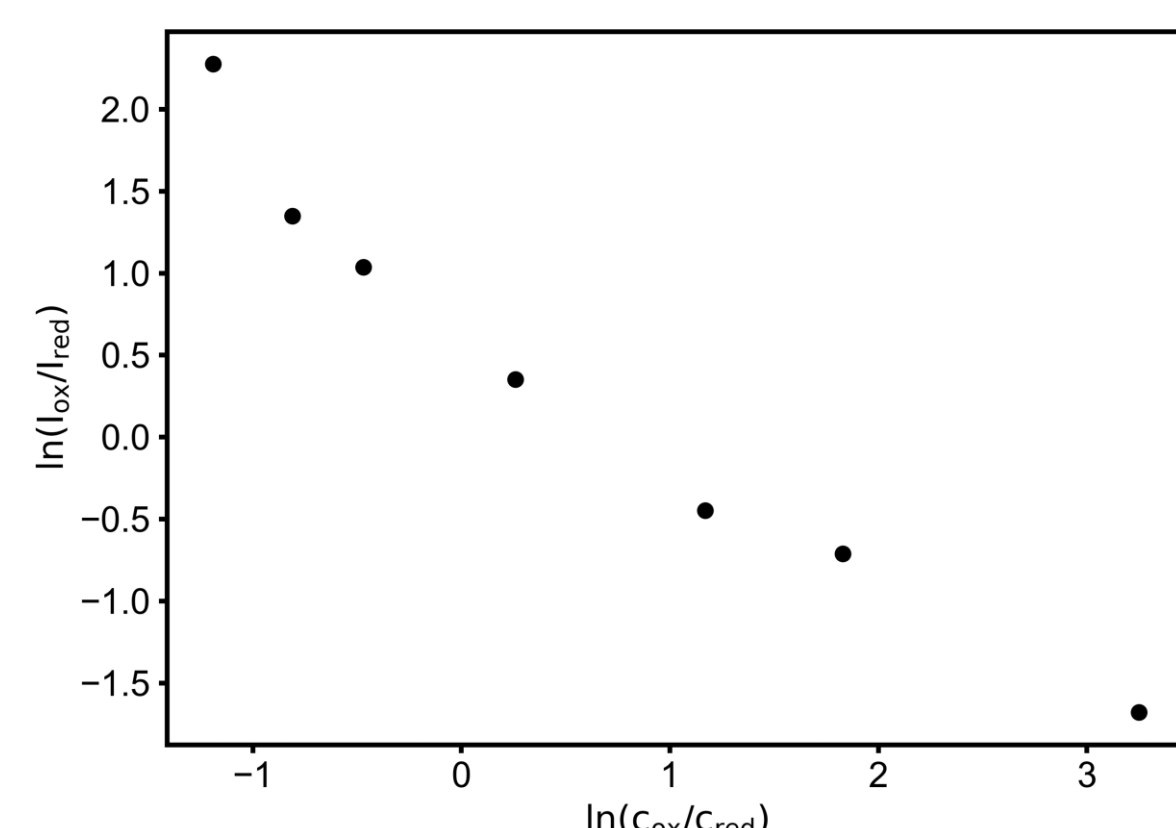
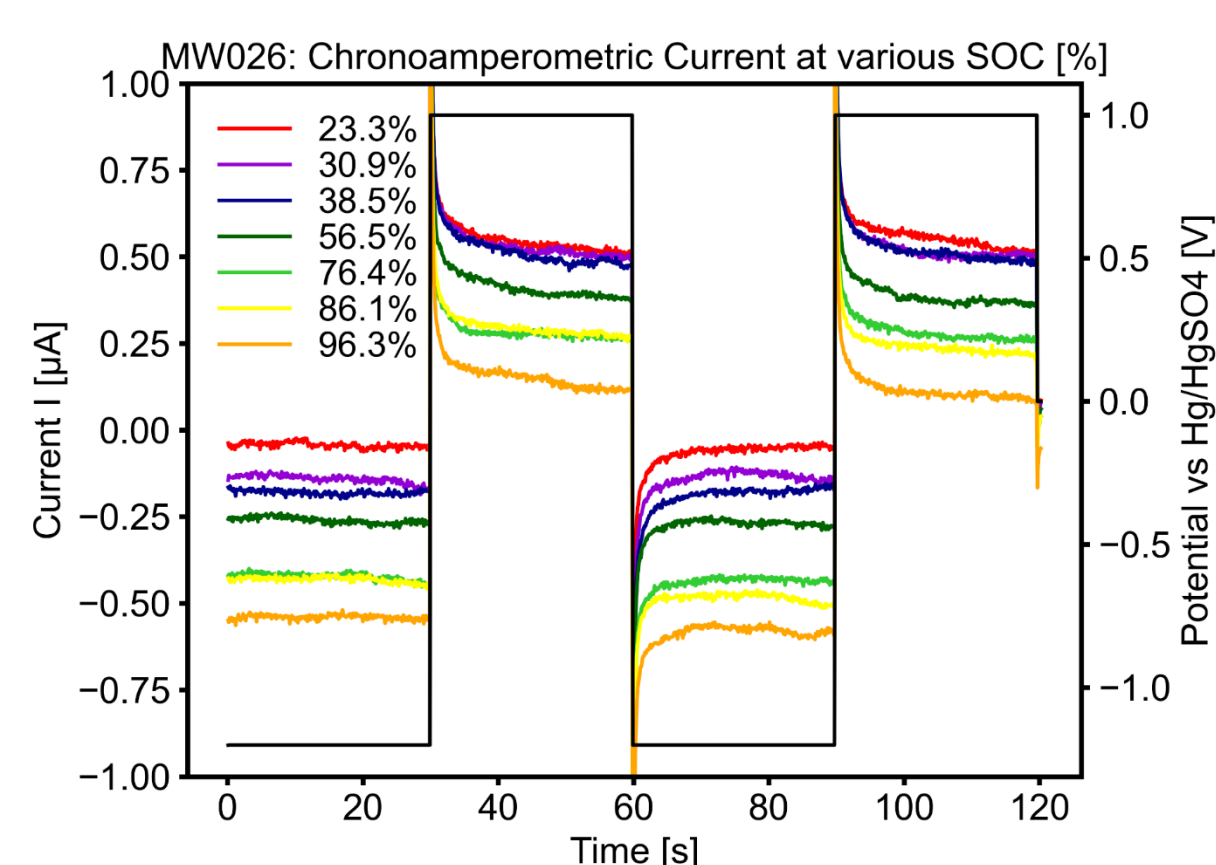
3

## CA Measurement Ex-Situ PHC

4

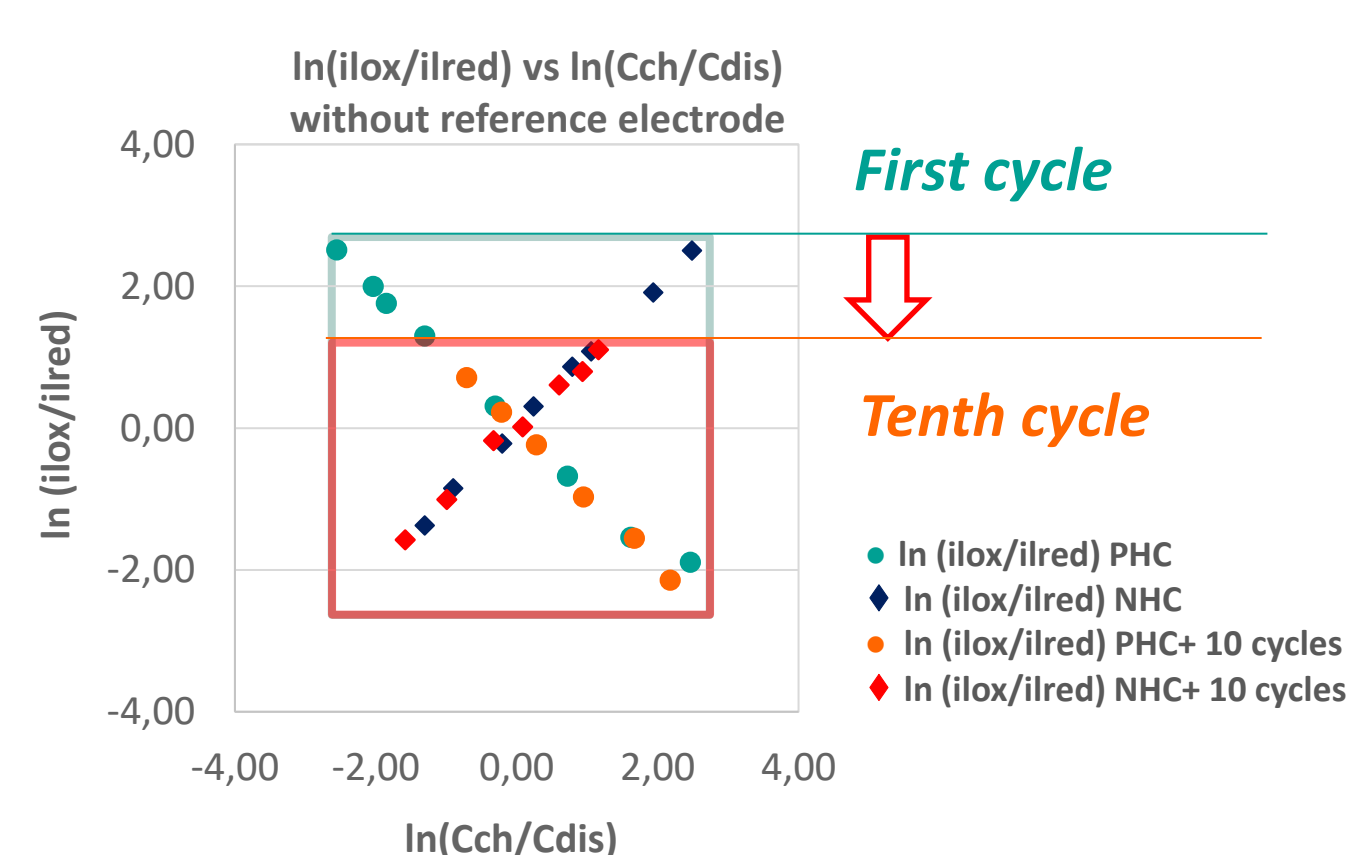
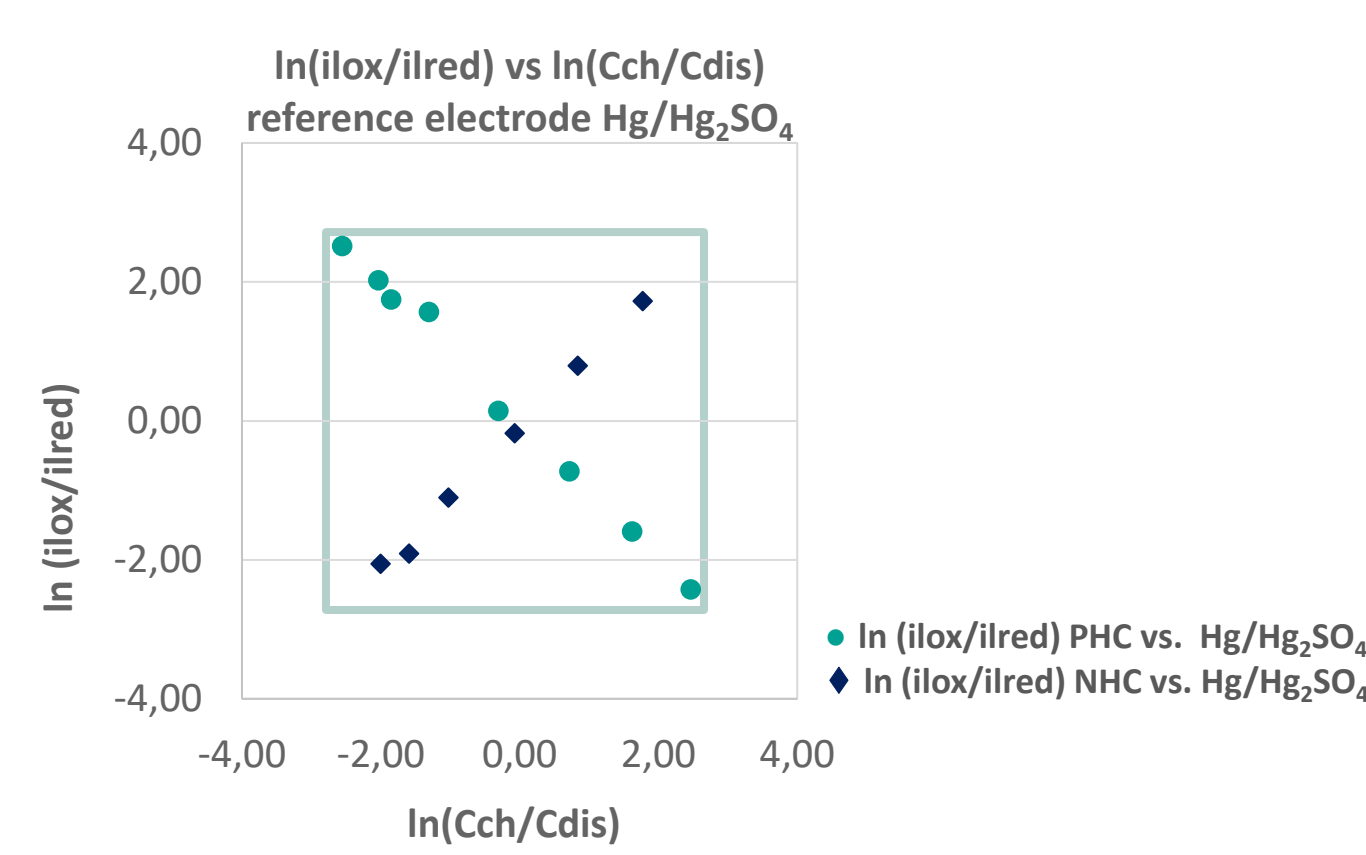


- CA at the first cycle and after 10, 13, and 15 cycles.
- The oxidation and reduction limiting currents were calculated using the CA analysis
- Oxidation: limiting currents (i<sub>lox</sub>), assigned to the V<sup>4+</sup> species, decrease with increasing SoC
- Reduction: limiting currents (i<sub>lred</sub>), assigned to the V<sup>5+</sup> species, increase with increasing SoC
- A linear correlation between  $\ln$  of the ratio  $i_{lox}/i_{lred}$  and the concentration ratio of V<sup>5+</sup>/V<sup>4+</sup> have been established



## CA In-Situ at PHC and NHC

5



- Whereas at the **PHC** the limiting reduction currents assigned to the V<sup>5+</sup> species increase with SoC and a negative slope is calculated, at the **NHC**, the limiting oxidation currents are assigned to the V<sup>2+</sup> species and a positive slope is calculated.
- For the three-electrode but also for the simplified two-electrode setup a linear correlation between  $\ln$  of the ratio  $i_{lox}/i_{lred}$  and the  $\ln$  of the concentration ratio of charged (ch)/discharged (dis) V-species V<sup>5+</sup>/V<sup>4+</sup> (PHC) and V<sup>2+</sup>/V<sup>3+</sup> (NHC) can be shown.
- After 10 cycles an electrolyte shift was observed as a consequence of the crossover an detected by increasing the V<sup>4+</sup> concentration (average oxidation state of 3.55). The chronoamperometric analysis of the system shows as a result also a shift from higher to lower  $\ln(i_{lox}/i_{lred})$  values.

## Literature

- [1] T. Haisch, Electrochimica Acta, Bd. 336, 35573, 2020. [2] S. Ressel, Journal of Power Sources, 776-783, 2018. [3] T. Struckmann, Electrochimica Acta, p. 137174, 2020. [4] T. Haisch, Membranes, Bd. 11, 232, 2021. [5] C. Stolze, Chemistry of Materials, 5363-5369, 2019.

6