Multi-observable monitoring for consistent state of health and capacity fade observables of vanadium flow batteries

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Outline

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Introduction
- Vanadium flow batteries
- SoC measurement approaches
- SoH processes and quantities

Experimental
- Multi SoC/SoH observable measurements
- Long term runs
- Temperature correctured observables

Results
- Long term SoC measurements
- Reference SoC
- Stepwise SoC & SoH estimation
- Multi observable SoC & SoH estimation

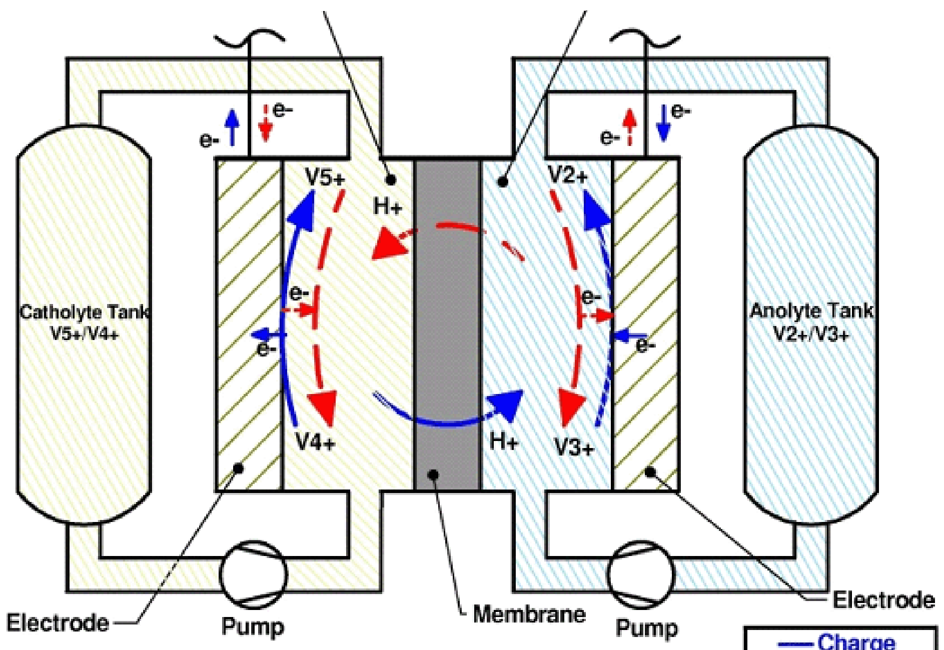
Conclusion & Next steps

Introduction - Flow batteries (FB) & state of charge (SoC)

Redox flow batteries

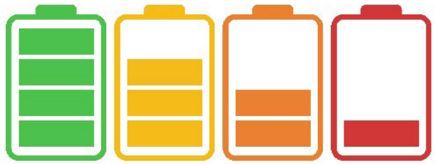
- Electrochemical energy storage (4-12 h)
- Power and energy independently salable
- Very high cycle life
- Range of cell chemistries
- **All vanadium chemistry (VFB) established and used for this feasibility study**

Positive half cell **Negative half cell**



$E_p^0 = 1.004V$ $E_n^0 = -0.255V$

State of charge

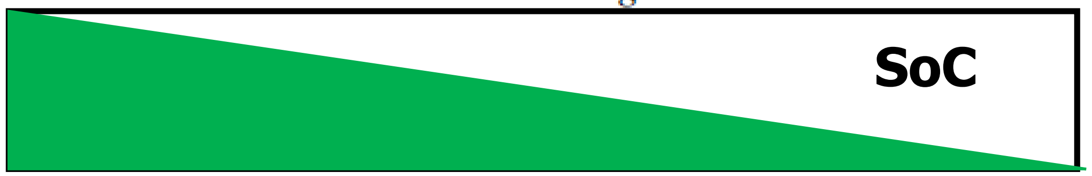


Neg. half cell

$$V^{2+} \underset{charge}{\overset{discharge}{\rightleftharpoons}} V^{3+} + e^-$$

Pos. half cell

$$VO_2^+ + 2H^+ + e^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} VO^{2+} + H_2O$$



- Half cell specific

$$SoC_p = \frac{n_{V5}}{n_{V4} + n_{V5}} \qquad SoC_n = \frac{n_{V2}}{n_{V2} + n_{V3}}$$

- Cell level

$$SoC = \frac{n_{V2} + n_{V5}}{n_{V2} + n_{V3} + n_{V4} + n_{V5}}$$

$$\Rightarrow \frac{min(n_{V2}, n_{V5})}{min(n_{V2}, n_{V5}) + min(n_{V3}, n_{V4})}$$

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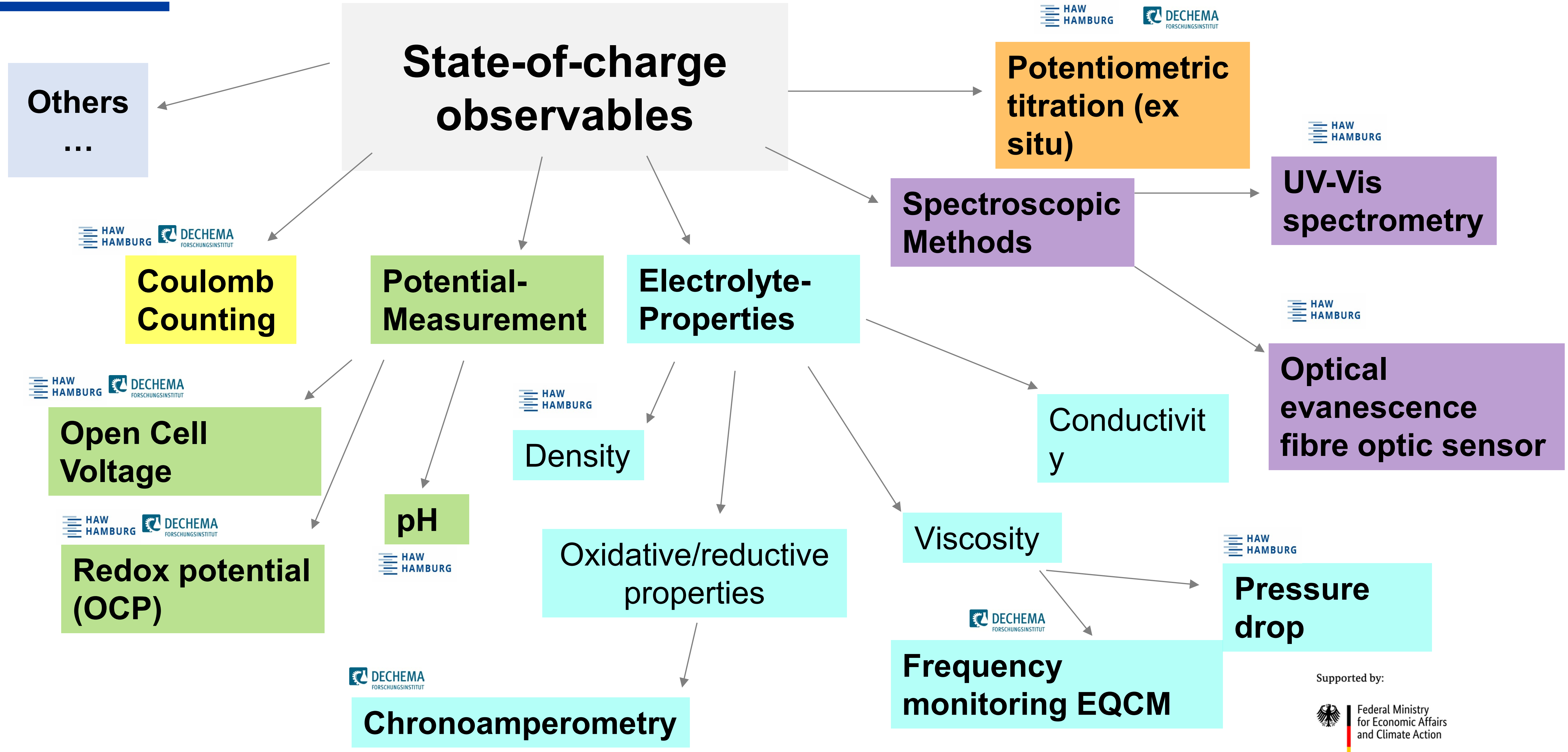
Journal of Power Sources 624 (2024) 235487

Introduction - SoC measurement approaches



Seed project „Vanadium Monitoring System“ with DECHEMA 2021/24

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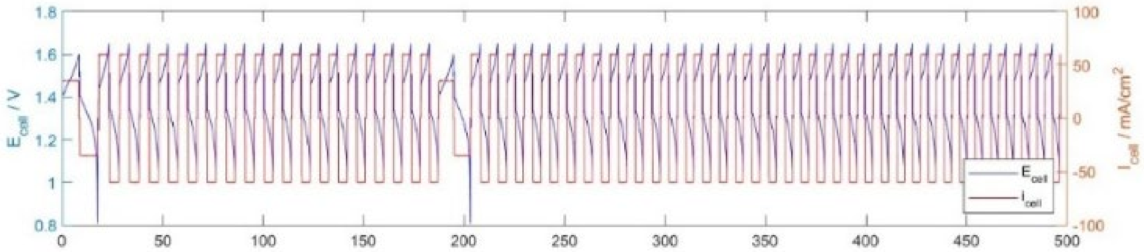
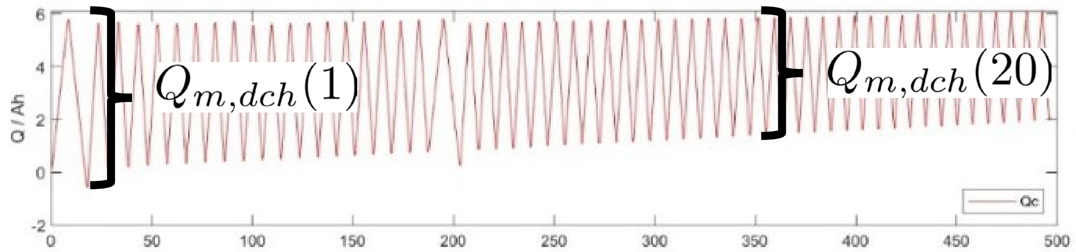
Introduction – State of health (SoH) processes and quantities

State of Health $SoH(cycle\ i) = \dfrac{Q_m(i)}{Q_m(1)}$

- Capacity Q_m decrease over cycles **L1 data**





- Discharge capacities – cell level
  - operation parameters
  - electrode & electrolyte aging

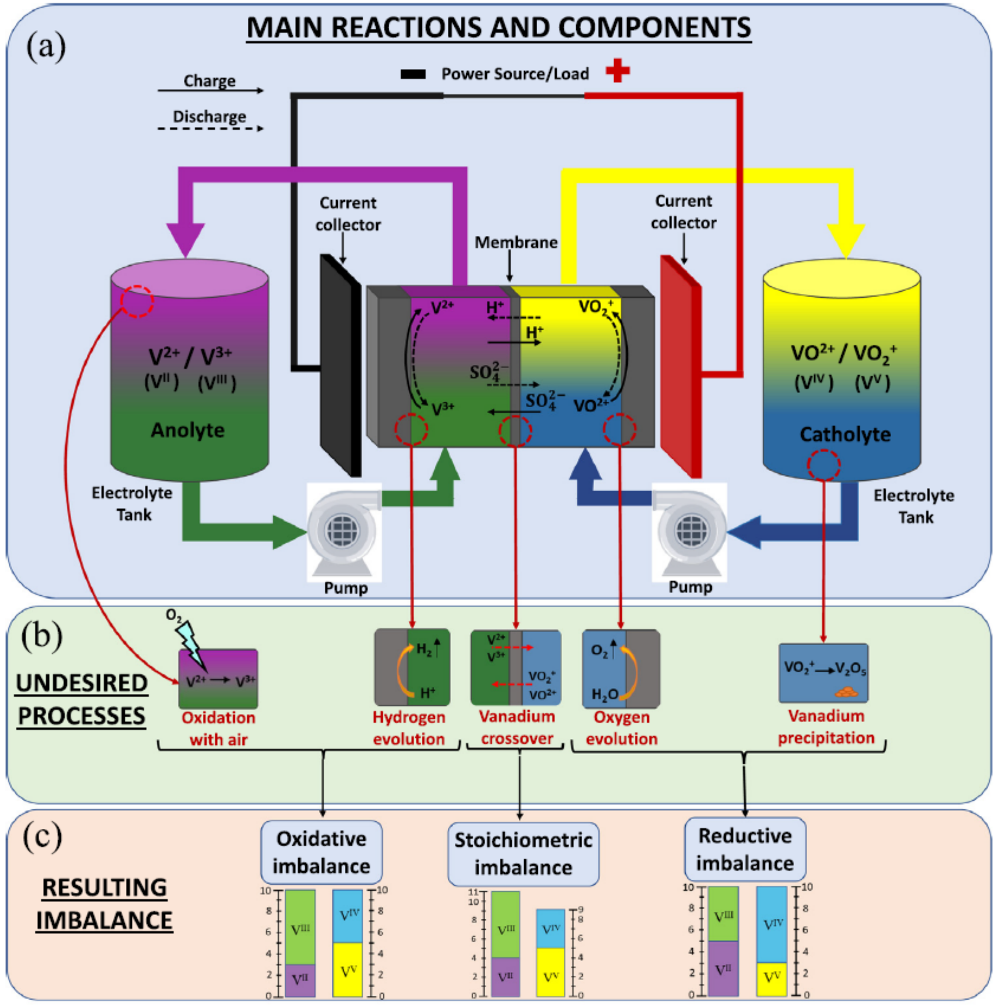
$$SoH_{dch}(i) = \frac{Q_{m,dch}(i)}{Q_{m,dch}(1)}$$

- Totally available charge carriers - half cells
  - indirect observation
  - electrolyte aging

$$SoH_{tot}(i) = \frac{Q_{m,tot}(i)}{Q_{m,tot}(1)}$$

Long term electrolyte changes

- Species crossover ⇒ stochiometric imbalance
- Side reactions ⇒ oxid./reductive imbalance



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Experimental - Multi obervable measurements for SoC & SoH

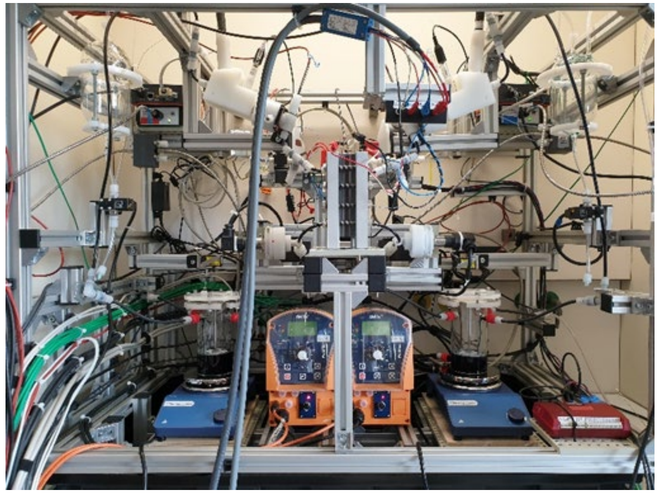
Observables (half cell specific)

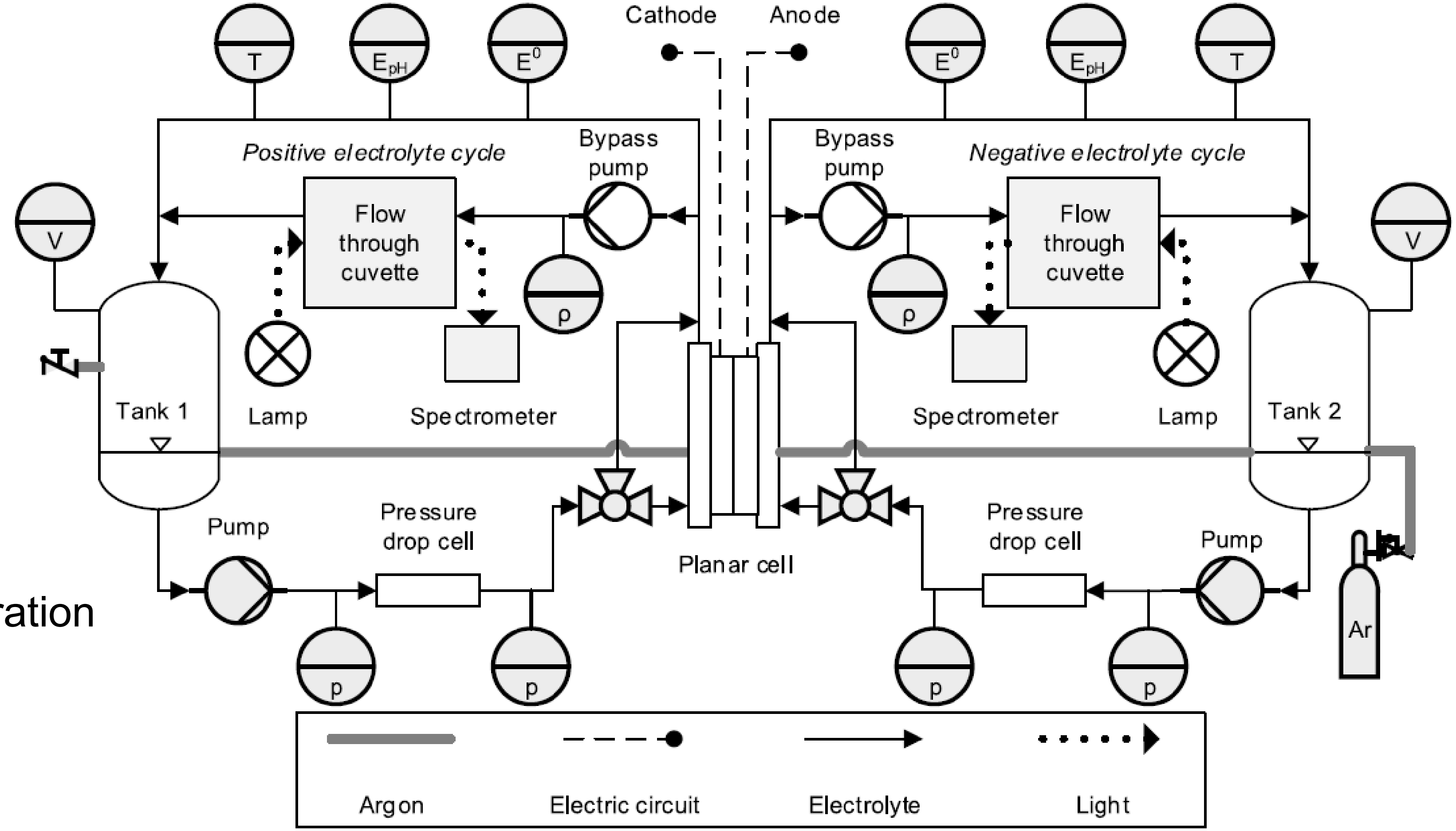
In situ measurements

- E0 - E^0 - electrolyte potential
- rh - ρ - electrolyte density [5]
- dp - p - pressure drop
- Ve - V - electrolyte volume
- pH - E_{pH} - pH potential
- A1/2/3 - UVvis absorptions
  - neg. half cell: 400, 600, 800 nm
  - pos. half cell: 560, 450, 760 nm

Ex situ measurements

- V concentrations from potentiometric titration





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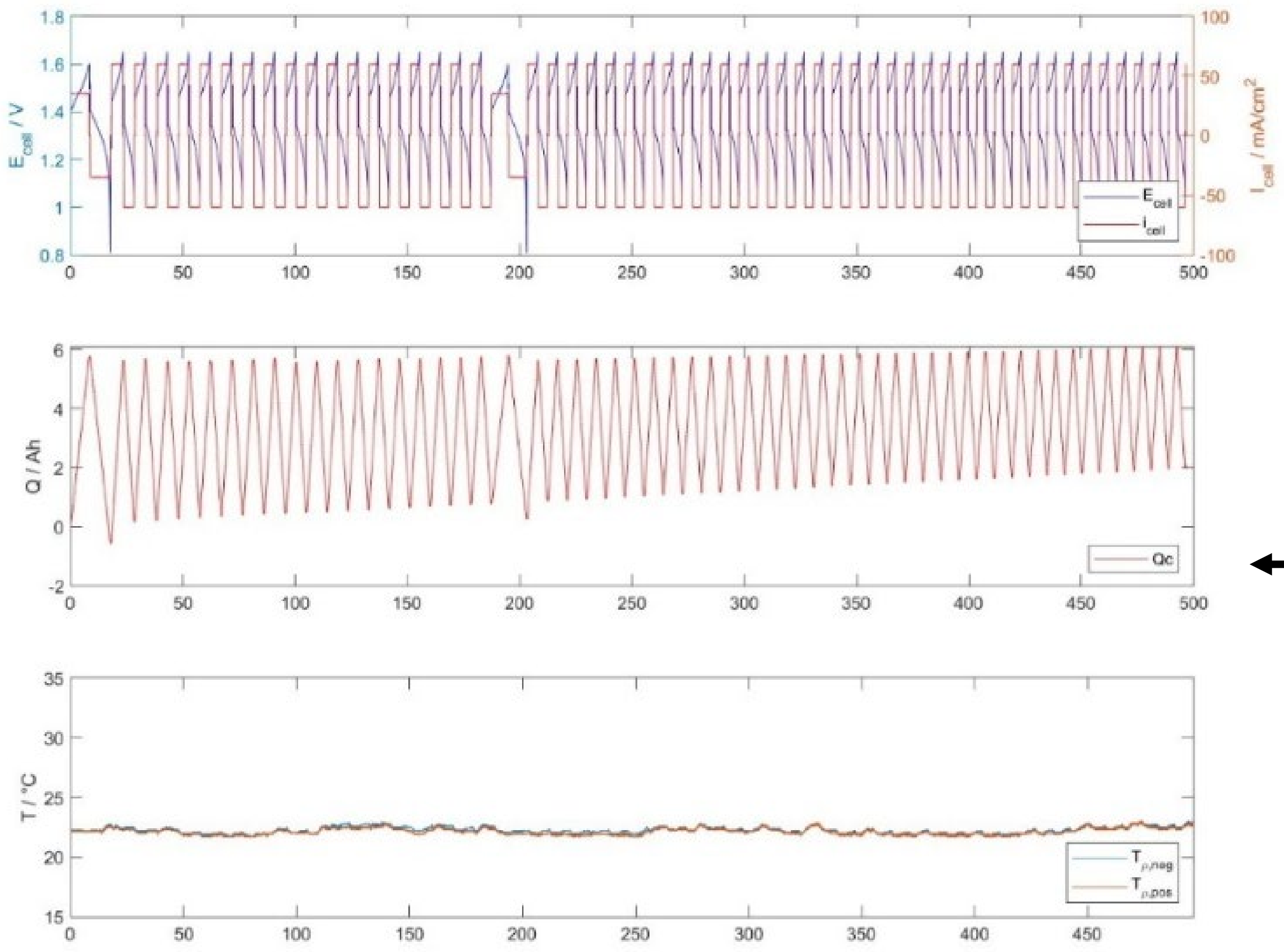
Experimental – Long term cycling



Study	Theoretical capacity[a] / A h	Transferred charge[b] / A h	Capacity turnover[c]	Current density / mA cm^{-2}	Potential limits / V
[25]	4.3 A h	154 A h	36	35 mA cm^{-2}	0.8 V to 1.7 V
[37]	0.6 A h	91 A h	152	40 mA cm^{-2}	−0.6 V to 0.6 V
Present study	8.6 A h	533 A h	62	60 mA cm^{-2}	1 V to 1.65 V

Long term runs

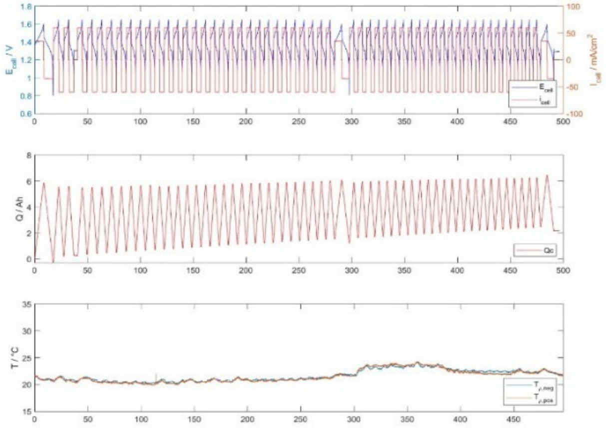
- 500 – 1,000 h of cycling
- 50 -180 charge discharge cycles
- 60 mA/cm^2 - PinflowES flow-by cell (20 cm^2)
- 200 ml half cell electrolyte volume
  GfE : 1.6 mol/l V content
- electrolyte withdrawal for titration

Cation exchange membranes

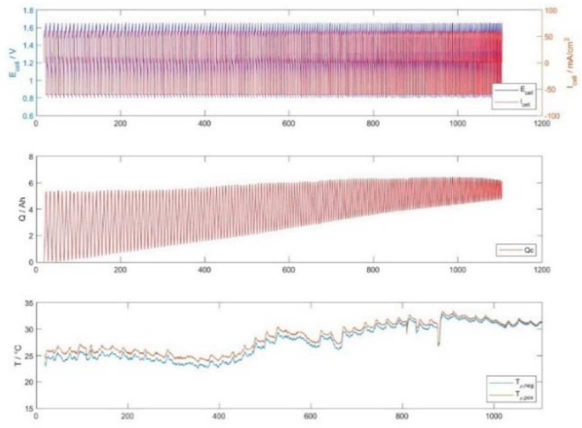
L1

- Fumatech F10100
- Nafion N212

L2



L3



Experimental – Long term data SoC & SoH observables

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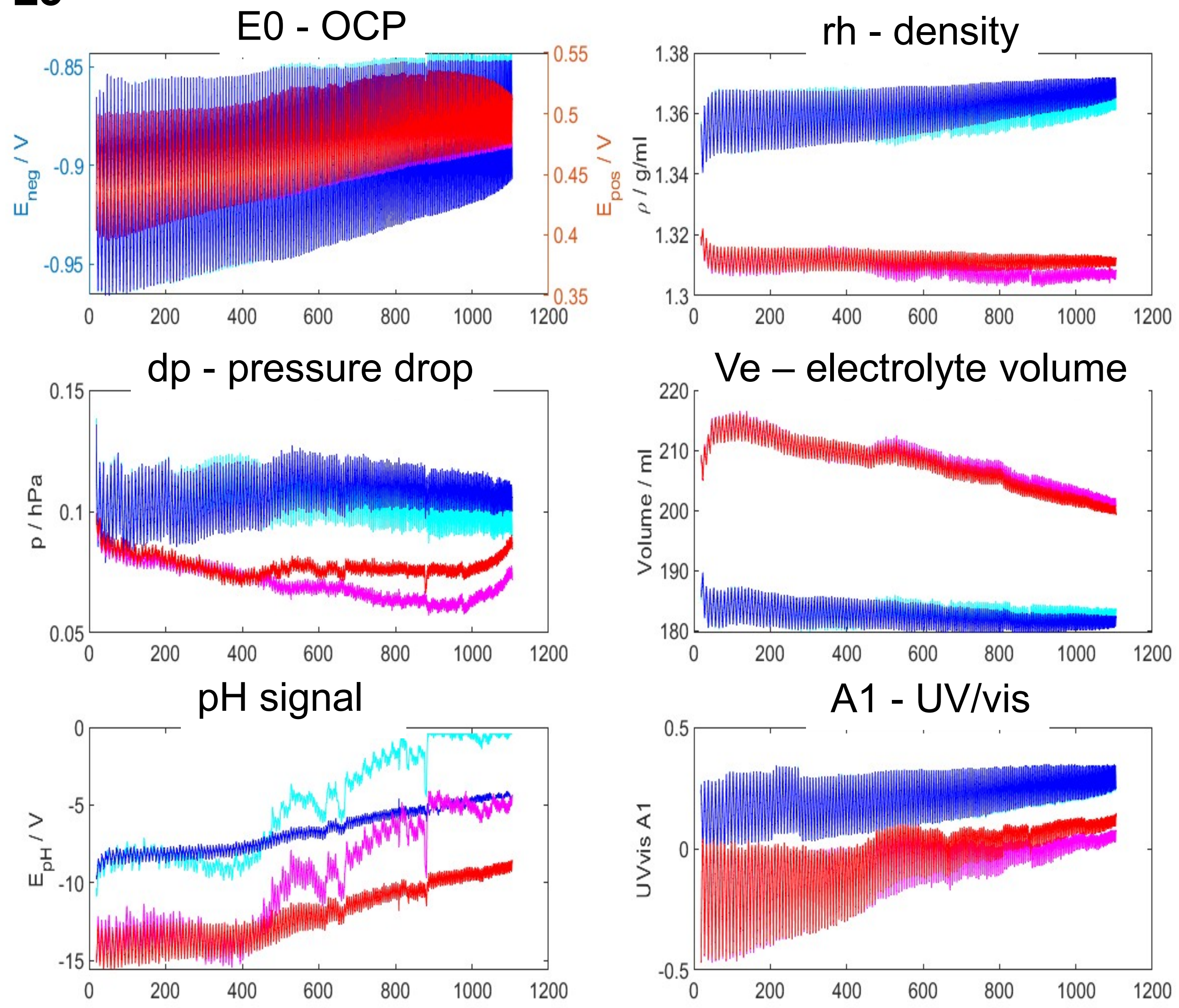
L3



Short term changes ⇒ SoC

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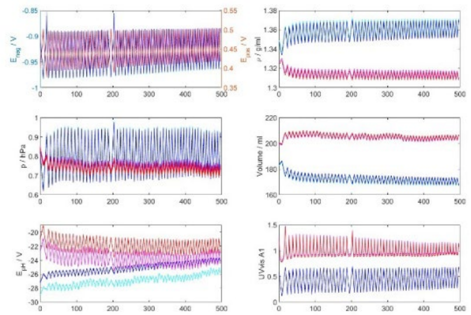
Electrochimica Acta 517 (2025) 145707

Temperature corrections

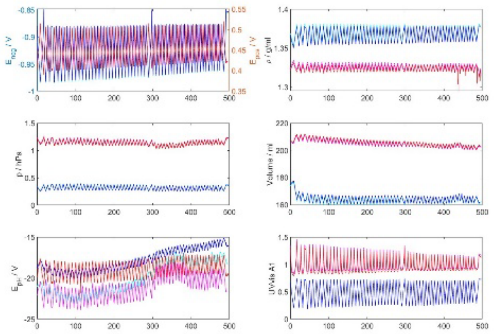
- *Positive half cell*
  - original
  - **corrected**
- *Negative half cell*
  - original
  - **corrected**

Long term changes ⇒ SoH

L1



L2



Results – Reference SoC from cycle specific fits

SoC fit in each cycle

- E^0 (ΔQ, T) half cell specific

S. Ressel et al. Journal of Power Sources 378 (2018) 776–783

T. Struckmann, P. Kuhn and S. Ressel Electrochimica Acta 362 (2020) 137174

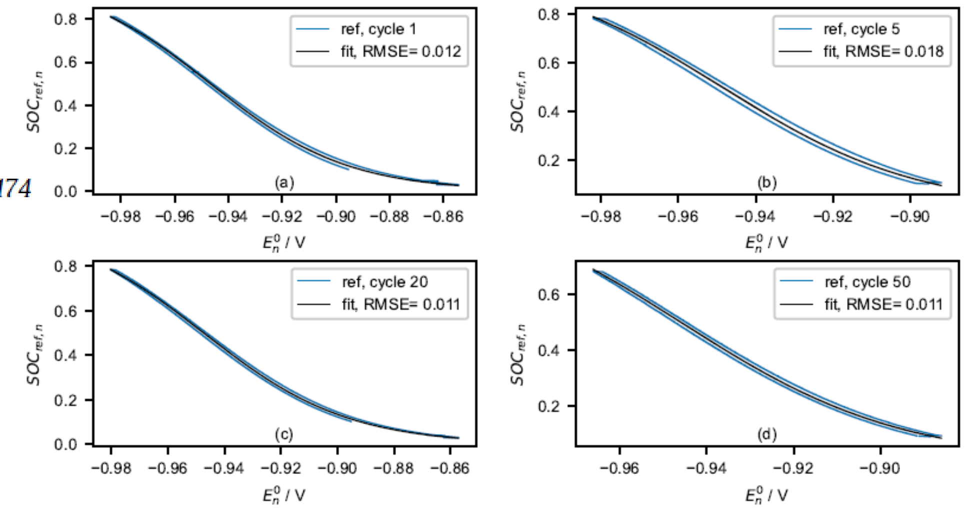
- SoC from Coulomb counting

$$E_n^0 = E_n^{0\prime} + \frac{RT_n}{F}\ln\left(\frac{1 - SOC_n}{SOC_n}\right)$$

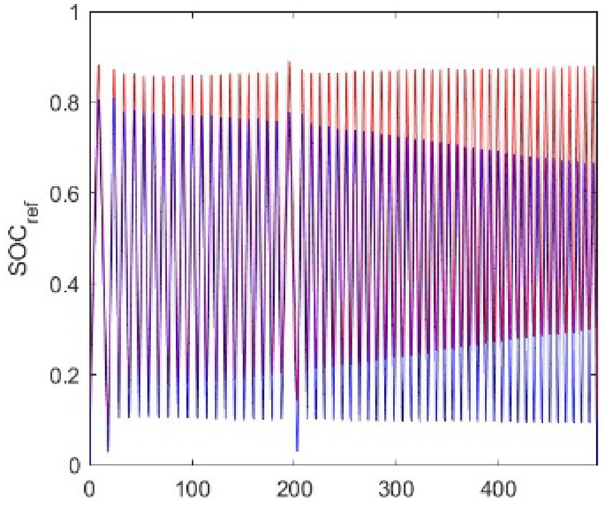
$$E_p^0 = E_p^{0\prime} + \frac{RT_p}{F}\ln\left(\frac{SOC_p}{1 - SOC_p}\cdot\left(\frac{c_{H^+,p}(SOC_p)}{c_{H^+_{ref}}}\right)^2\right).$$

$$SOC_{ref,n/p}(\Delta Q) = m_{n/p}\cdot\Delta Q + SOC_{0,n/p}.$$

$\Rightarrow$ cycle specific fit parameters
  - potential *$E^{0\prime}$*
  - total capacity
    $1/m = Q_{m,fit}$



L1



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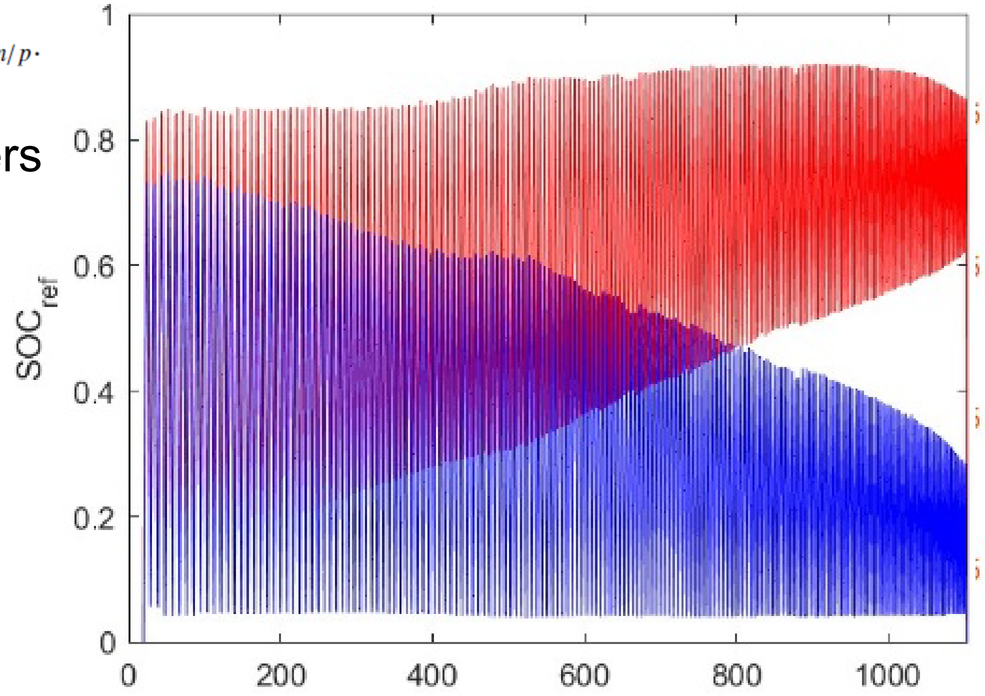
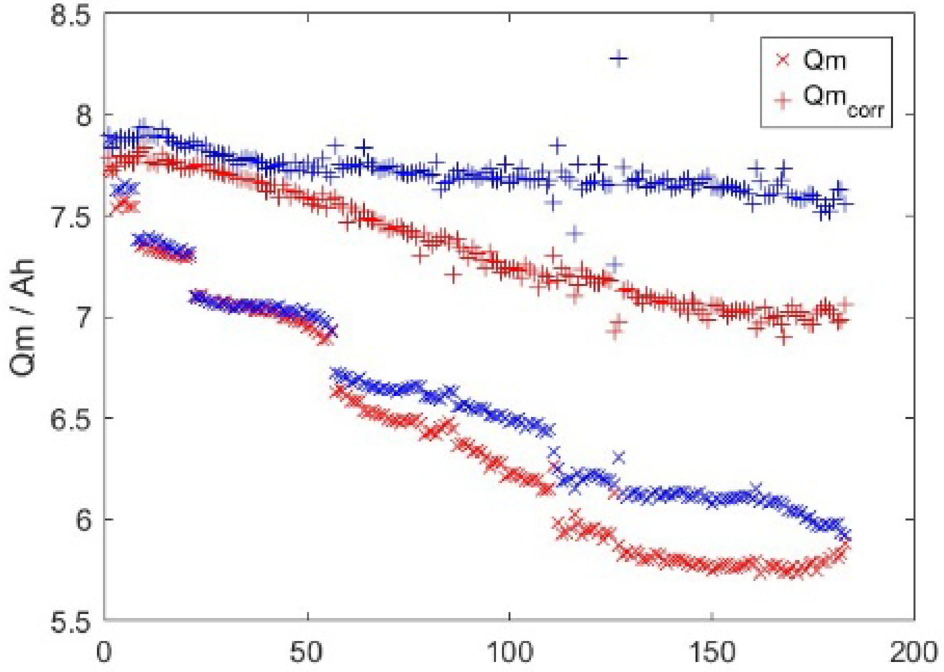
L3 – reference SoCs and total half cell capacities





Results – Reference SoH from discharge & total capacities

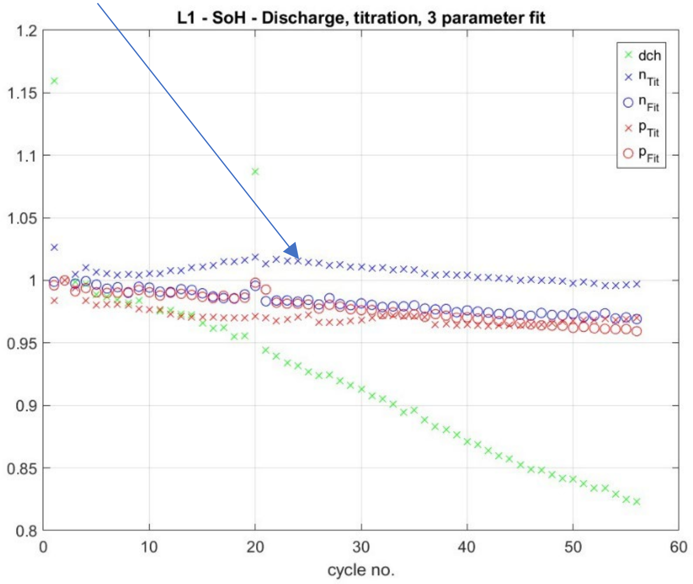
- Reference cycles i_0 = 2-4 (1. cycle „deep cycle“)
- Discharge capacity

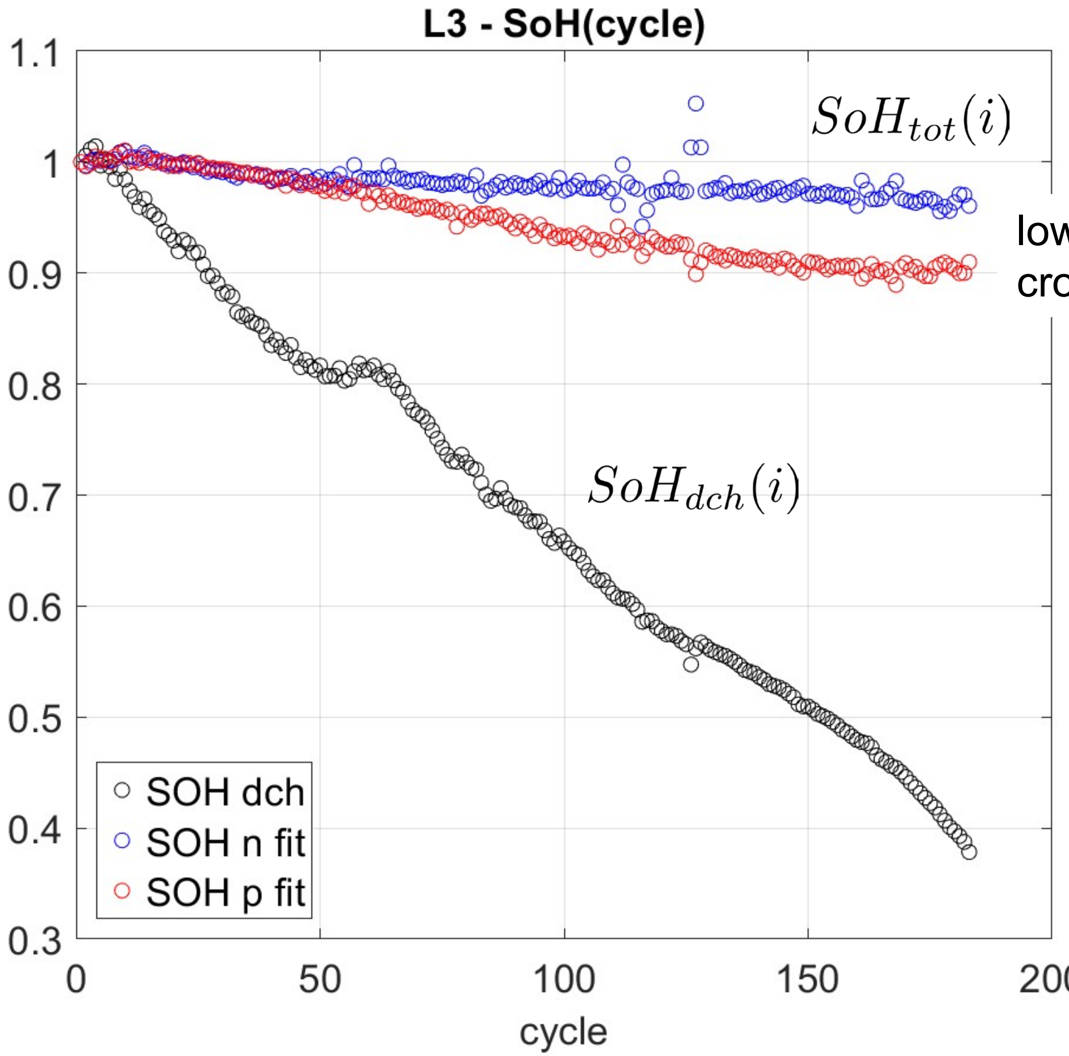
$$SoH_{dch}(i) = \frac{Q_{m,dch}(i)}{Q_{m,dch}(i_0)}$$

- Total capacity from SoC fit

  consistent to titration

$$SoH_{tot}(i) = \frac{Q_{m,tot}(i)}{Q_{m,tot}(i_0)}$$





low V crossover

- Capacity decay in long term runs L1/2/3 dominated by side reations

Results – Stepwise $\mathbf{SoC}_{n/p}$ and SoH_{dch} estimation

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1) SoC estimation from half cell potentials $E^0_{n/p}$

$$SoC_{n/p}(t) = f_{n/p}(E^0_{n/p}, T_{n/p})$$

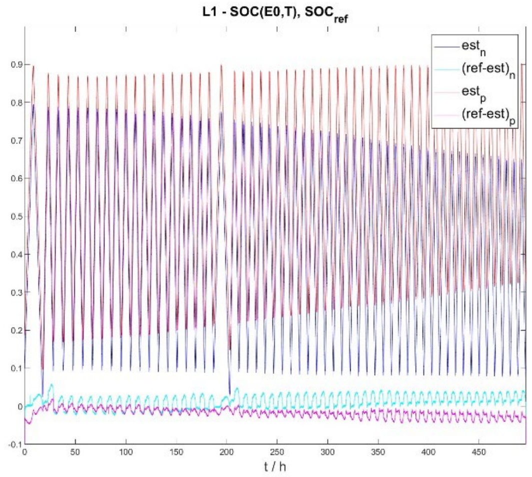
- half cell specific SoCs

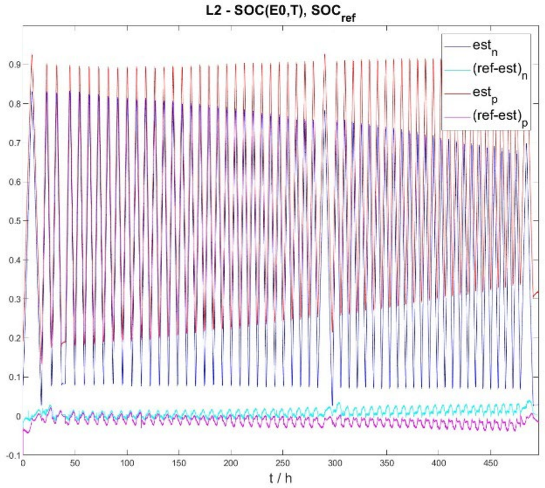
$$E_n^0 = E_n^{0'} + \frac{RT_n}{F}\ln\left(\frac{1-SOC_n}{SOC_n}\right)$$

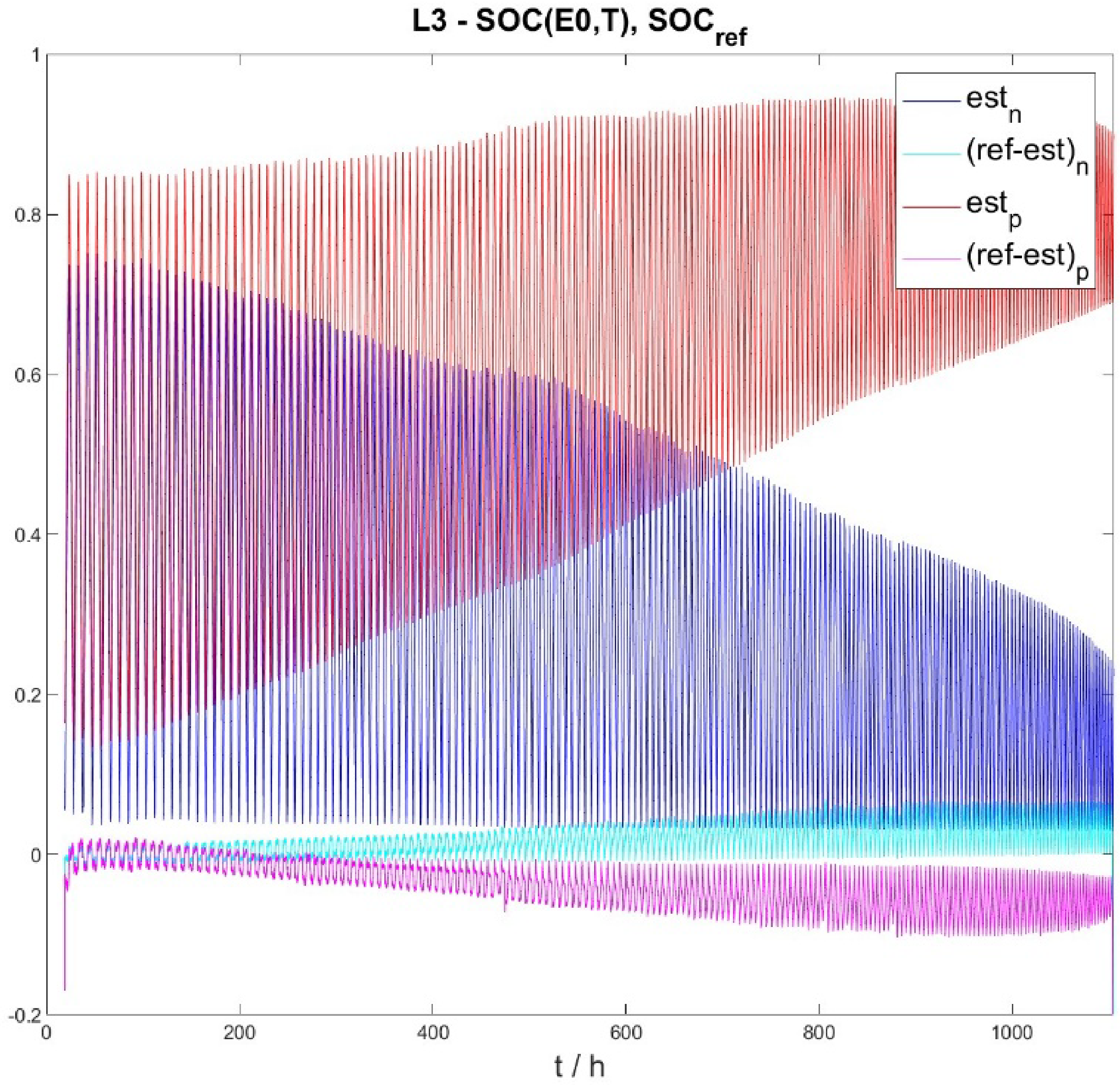
$$E_p^0 = E_p^{0'} + \frac{RT_p}{F}\ln\left(\frac{SOC_p}{1-SOC_p}\cdot\left(\frac{c_{H^+,p}(SOC_p)}{c_{H^+_{ref}}}\right)^2\right).$$

- stable method
- low estimation errors RMSE (root mean squared error)

hc/run	L1	L2	L3
neg	0.021	0.013	0.026
pos	0.022	0.017	0.047







Results – Stepwise $SoC_{n/p}$ and $\mathbf{SoH_{dch}}$ estimation

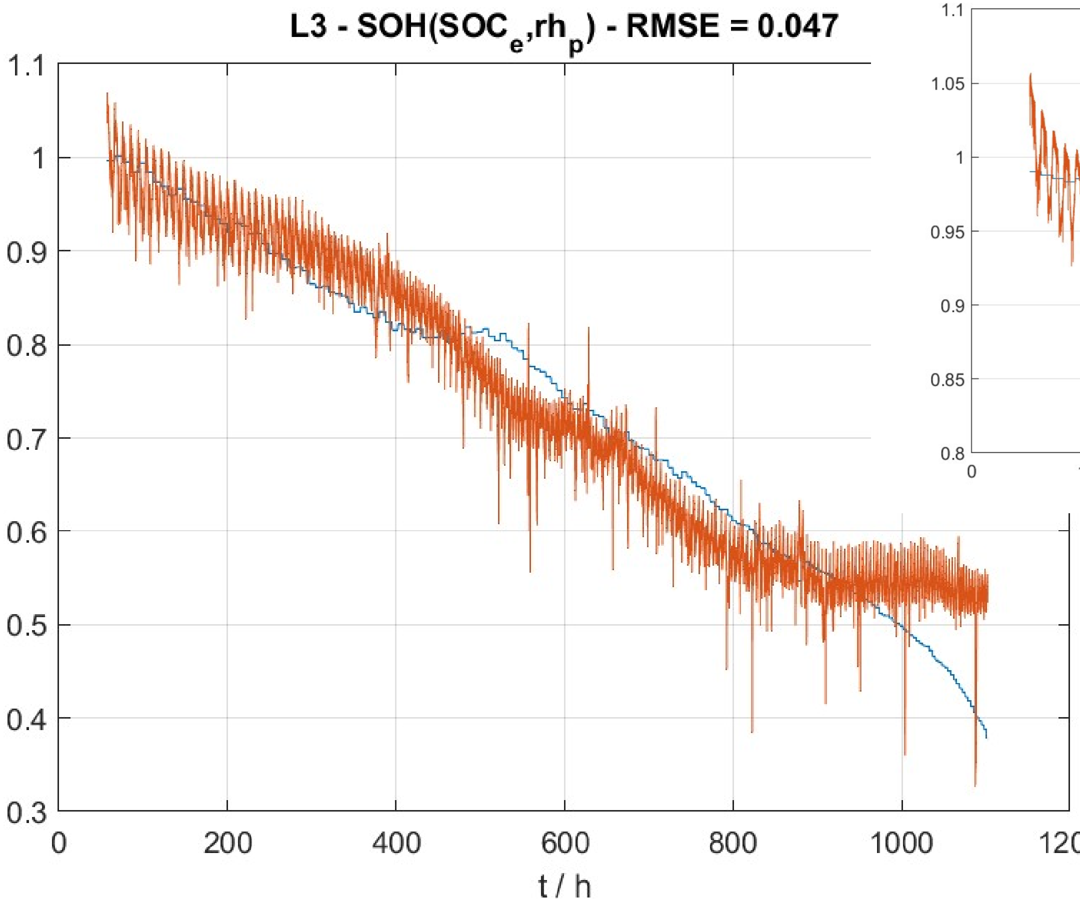
2) SoH from SoC_{est} and observable obs

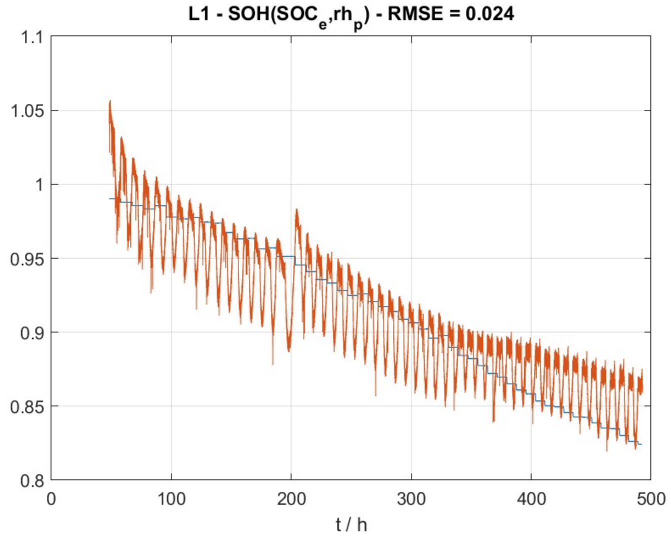
Run	L1	L2	L3
σ_{SOHexp}	**0.052**	0.049	**0.17**

- linear model $$SoH(t) = a \cdot SCo_{est}(t) + b \cdot obs(t) + c$$
- **SoC_{est} corrects** for short term SoC changes of **long term SoH sensitive observable obs**

SOH(SOC_{est}, obs) - RMSE percentage

	L1n	L1p	L2n	L2p	L3n	L3p
E0	0.9917	0.9859	0.9933	0.9828	0.9043	0.8375
rh	0.5642	0.4565	0.9393	0.9345	0.3893	0.2828
dp	0.8633	0.9478	0.4805	0.9763	0.8691	0.8476
Ve	0.3552	0.5833	0.9085	0.2884	0.7538	0.1224
pH	0.2422	0.4552	0.2768	0.4434	0.2164	0.2557
A1	0.9806	0.9852	0.7546	0.9522	0.7813	0.6373
A2	0.6786	0.9883	0.5583	0.9899	0.5854	0.7769
A3	0.6466	0.9858	0.5232	0.9832	0.8811	0.8483





Results – Multi observable $\mathbf{SoC}_{n/p}$ and SoH_{dch} estimation

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SoC estimation

- prediction from $SOC(E^0_{n/p})$
- correction from additional observable $obs_{n/p}$

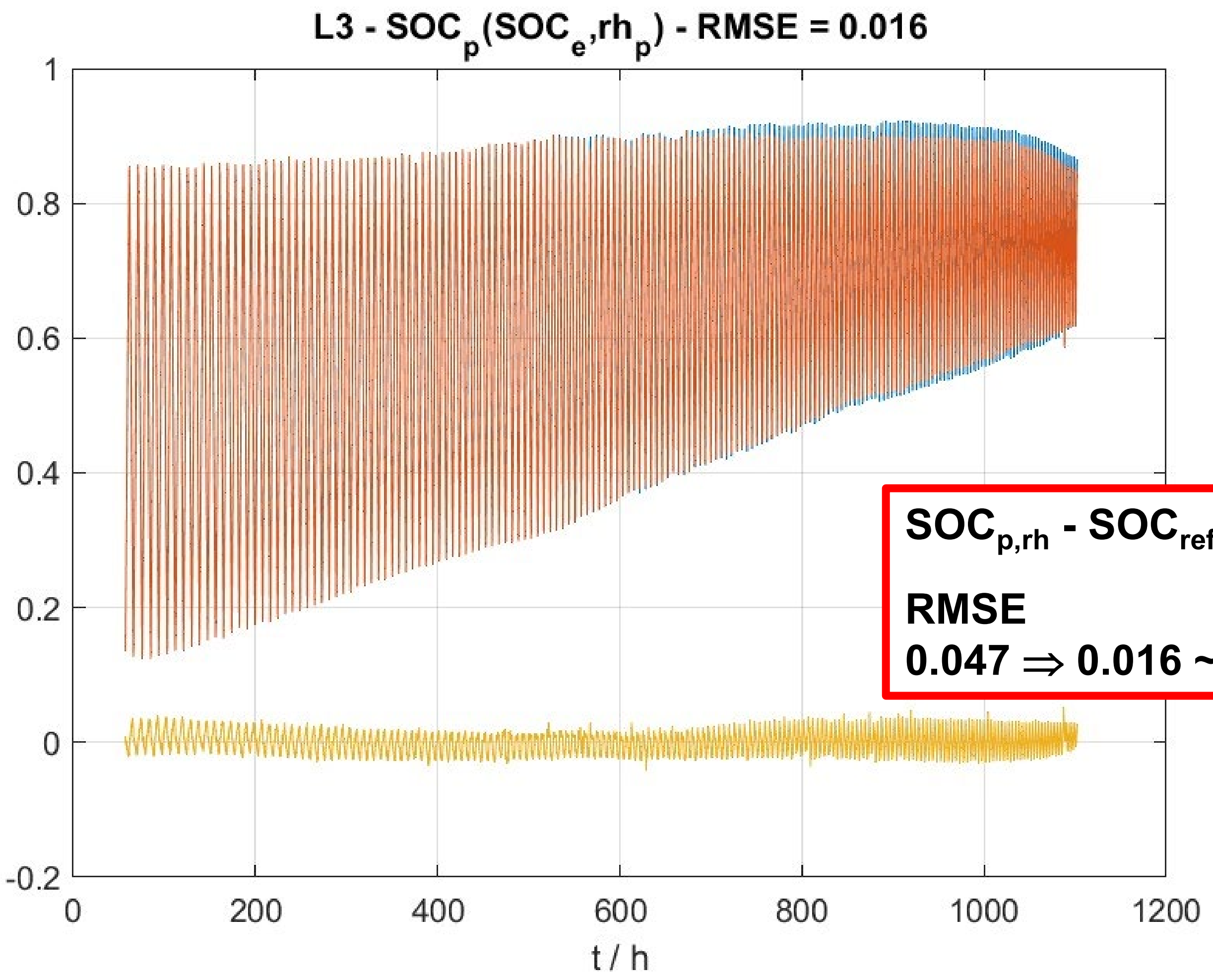
$$\begin{pmatrix} SoC_n(t) \\ SoC_p(t) \\ SoH(t) \end{pmatrix} = \begin{pmatrix} a_{C,n} \cdot SoC_{est,n}(t) + b_{C,n} \cdot obs_n(t) + c_{C,n} \\ a_{C,p} \cdot SoC_{est,p}(t) + b_{C,p} \cdot obs_p(t) + c_{C,p} \\ a_H \cdot obs1(t) + b_H \cdot obs2(t) + c_H \end{pmatrix}$$

Promising estimation error reductions

SOC(SOC_{est}, obs) - RMSE percentage

	L1n	L1p	L2n	L2p	L3n	L3p
E0	0.7871	0.4836	0.7162	0.557	0.6299	0.5395
rh	0.7509	0.4359	0.7002	0.5767	0.4826	0.3337
dp	0.5676	0.4979	0.5847	0.5765	0.6745	0.5468
Ve	0.7062	0.3862	0.7364	0.4892	0.5493	0.375
pH	0.6526	0.3896	0.538	0.5205	0.4333	0.3895
A1	0.627	0.4916	0.7023	0.575	0.6427	0.3862
A2	0.7701	0.4812	0.646	0.5556	0.5568	0.4225
A3	0.7361	0.4862	0.6246	0.5598	0.6721	0.4987

Color scale: 0.35 – 0.75



$SOC_{p,rh}$ - SOC_{ref}

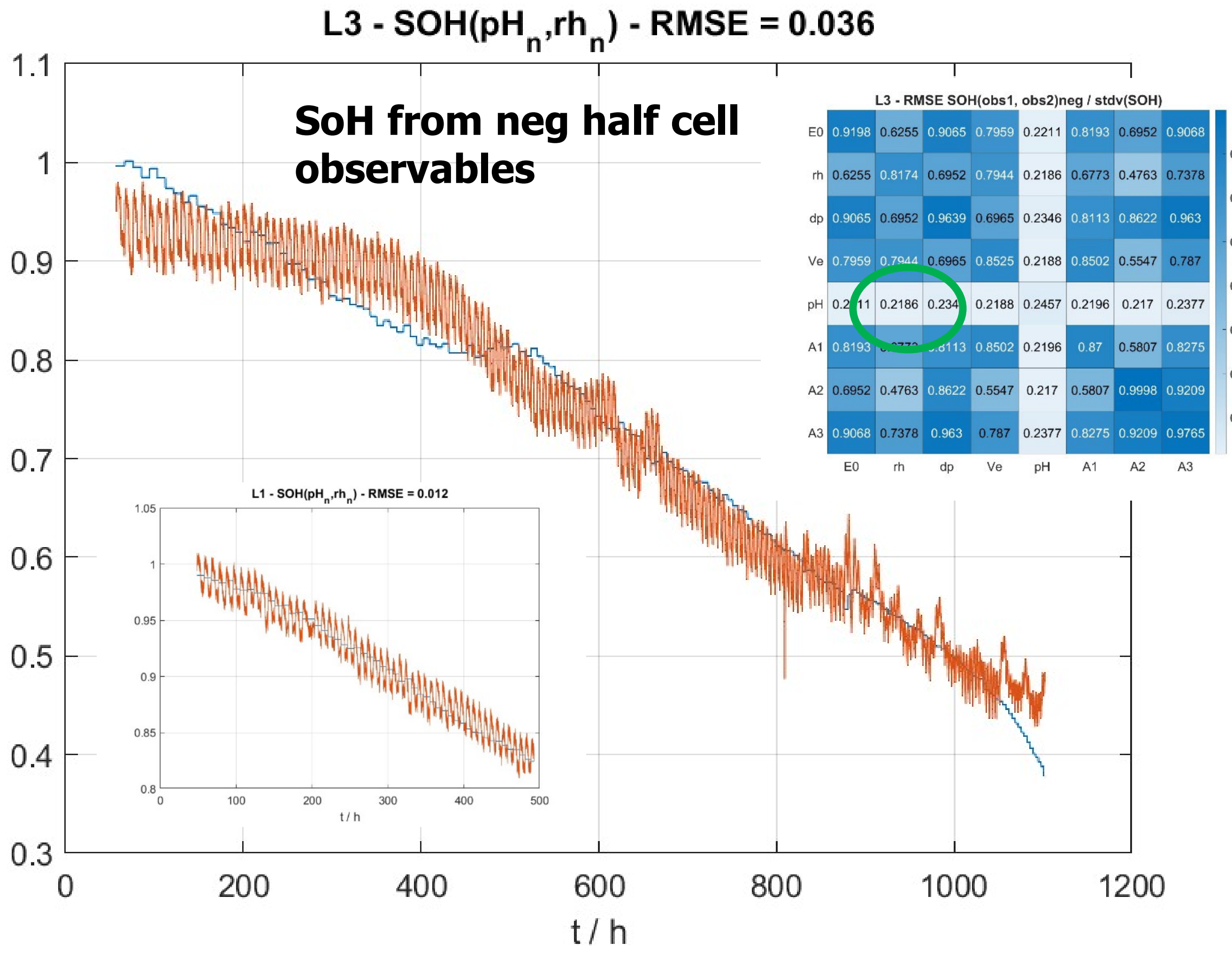
RMSE
0.047 ⇒ 0.016 ~ 33%

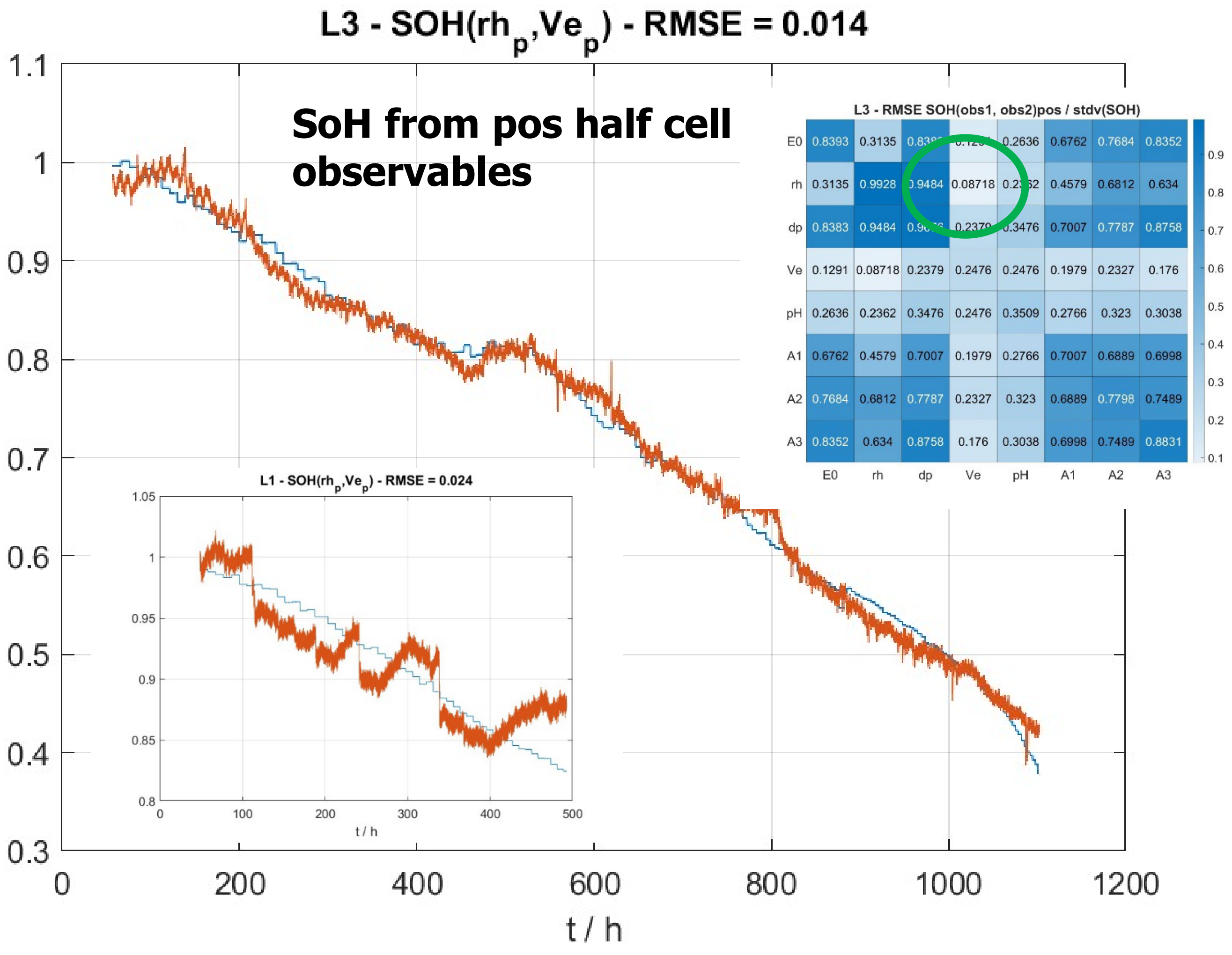
Results – Multi observable $SoC_{n/p}$ and $\mathbf{SoH_{dch}}$ estimation

SoH estimation

- from 2 observables obs1, obs2
- elimination of short term SoC dependence

$$\begin{pmatrix} SoC_n(t) \\ SoC_p(t) \\ SoH(t) \end{pmatrix} = \begin{pmatrix} a_{C,n} \cdot SoC_{est,n}(t) + b_{C,n} \cdot obs_n(t) + c_{C,n} \\ a_{C,p} \cdot SoC_{est,p}(t) + b_{C,p} \cdot obs_p(t) + c_{C,p} \\ \boxed{a_H \cdot obs1(t) + b_H \cdot obs2(t) + c_H} \end{pmatrix}$$





Conclusions & Next steps

Stepwise SoC & SoH estimation

- SoC estimation from half cell electrolyte potentials stable
- SoH from SoC and one additional observable with promising results

Multi-observable SoC & SoH estimation

- Significant SoC error reduction with one additional variable possible
- SoH from two observables with promising results – but further analysis necessary

Next steps

- Analysis
  - Multivariate analysis – PCA and PLS for multiple observables
  - Incorporation of multi observable data in combined SoC – SoH model
- Experiment
  - Long term runs with dominating V crossover
  - Long term runs with varying current and flow rates

Many thanks for your attention