Long term multi-observable data for a state of charge and crossover description of vanadium flow batteries

Thorsten Struckmann[1)], Niklas Janshen[1),2)]
1) Hamburg University of Applied Sciences, Heinrich-Blasius –Institut for Physical Technologies. Hamburg, Germany
2) Instituto de Tecnología Química, (Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas), València, Spain

Introduction

- State of charge (SOC), state of health (SOH) and crossover in flow batteries is usually described by considering only one or two observables [1, 2, 3]
- Correlated multi-observable data are needed for a comparative estimation method evaluation [4]
- We present in-situ measurement data of two long term VFB cycling runs featuring two different cation exchange membranes
- Cycling data and SOC calibration parameters allow for a stability analysis of SOC estimation methods and empirical modelling
- The approach is transferrable to different redox flow chemistries

Experimental

Long term runs: 500h of charge/discharge cycling, more than 50 charge discharge cycles (60 mA/cm^2, 200 ml half cell electrolyte volume), repeated electrolyte withdrawal for titration

Membranes: Cation exchange membranes Fumatech F10100 (L1) and Nafion N212 (L2)

Observables (half cell specific)
In situ measurements [4]:
- E^0 - Electrolyte potential
- r - electrolyte density [5]
- p - pressure drop
- V - electrolyte volume
- E_{pH} - pH potential
- A - UVvis absorptions
  neg. half cell: 400, 600, 800 nm
  pos. half cell: 450, 560, 760 nm

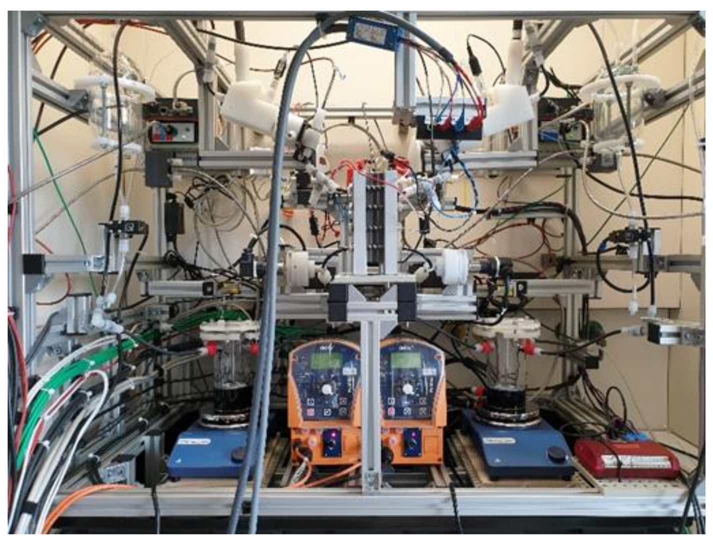


Fig. 1 - Multi-observable test rig [4]

Ex situ measurements: V concentrations from potentiometric titration

Half cell reference SOC and SOH: Reference SOC and capacities from fits of electrolyte potential and transferred charge in each cycle [3,4]. SOH from normalized capacities: SOH(t) = $Q_{max}(t)/Q_{max}(t_0)$

Results

Cycling data

- Constant current runs in 1.1-1,65V cell voltage range. „Deep discharge“ E_{cell} range in two cycles
- Trend in transferred charge Q(t) indicates crossover and side reactions
- Temperatures nearly constant ⇒ no temperature corrections needed

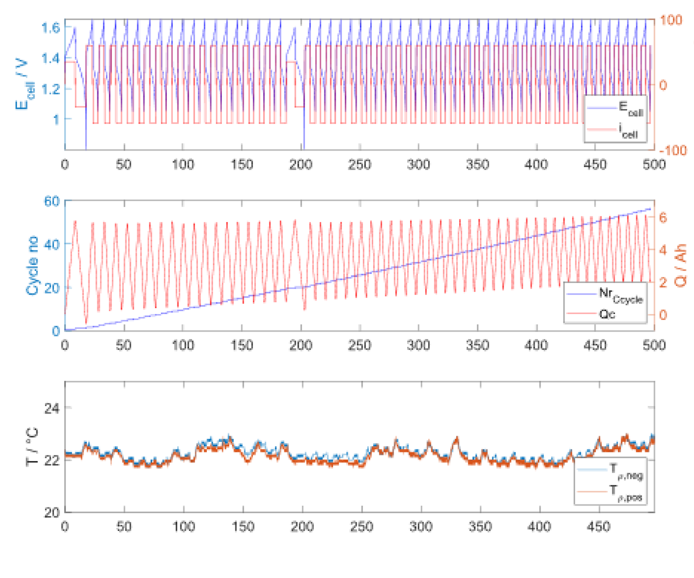
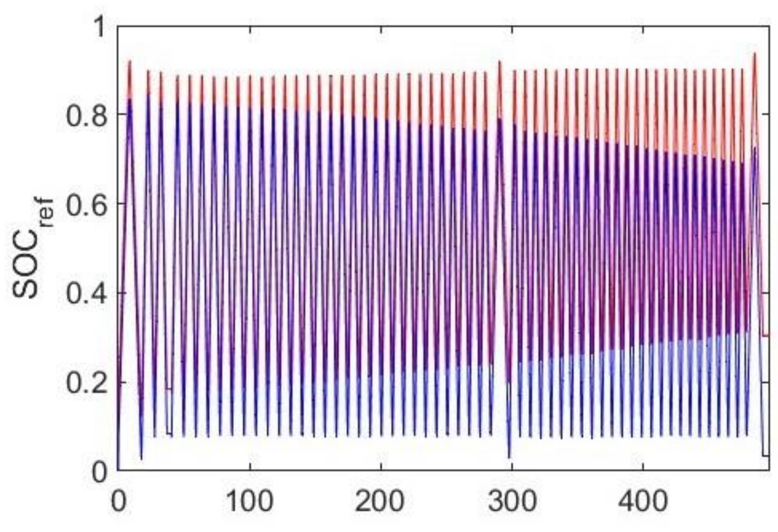


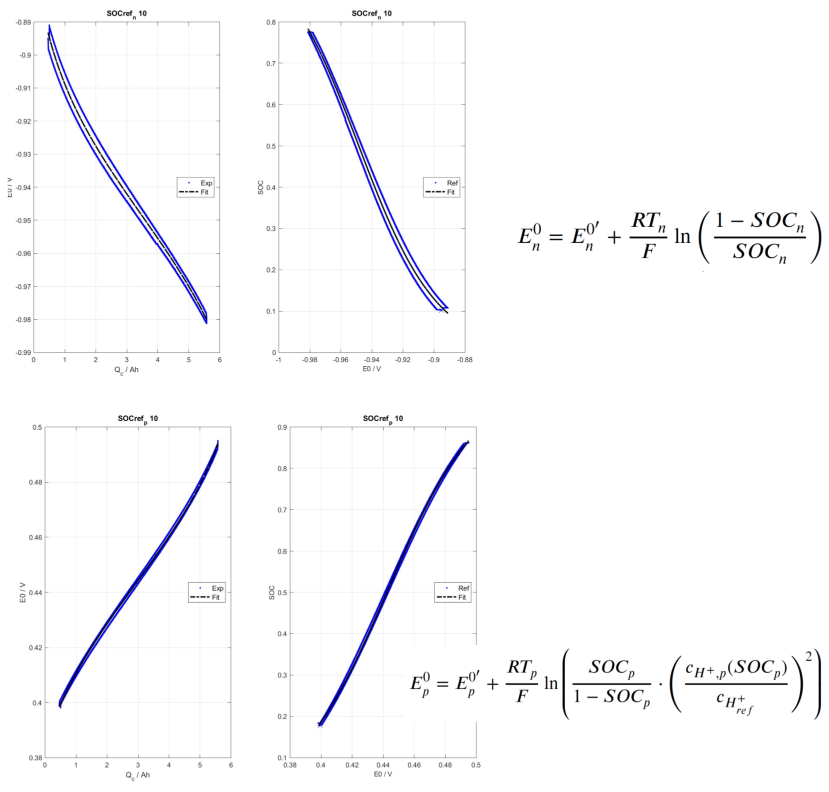
Fig. 2– Cycling data E_{cell}/i, Q, T (L1)

Reference SOCs



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

Fig. 3 - Cycle specific ref. SOCs (L2). Red/blue: pos./neg. half cell



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

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

Fig. 4 - Ref. SOC calibration (L1, cycle 10). Top/bottom: neg./pos. half cell

Observables dependent on reference SOC

- Correlated data for ΔSOC ~ 60-80%
- Low-intermediate crossover ΔSOH ~ 2–6%
- Individual SOC dependencies for E, r, p, V, A
- High temperature sensitivity for E_{pH}

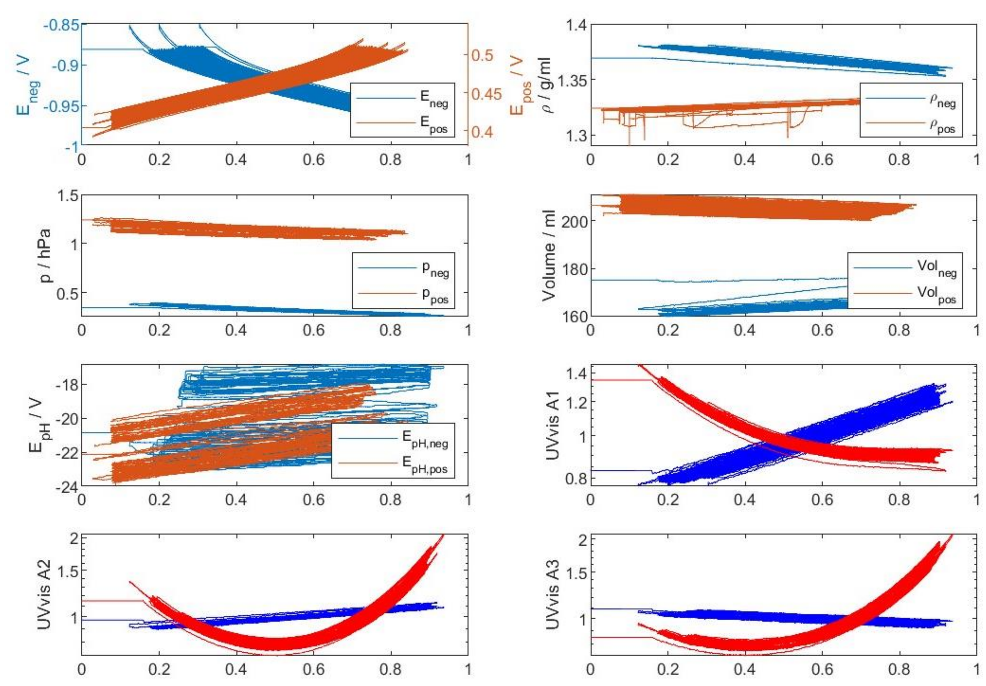


Fig. 5 - In-situ data over reference SOC (L2). Red/blue: pos./neg. half cell

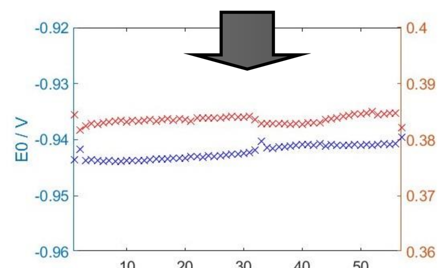
Calibration parameter stability over 50 cycles/500 h

- SOC from r, p, V, E_{pH}

$$SOC(obs) = a \cdot obs + b$$

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

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



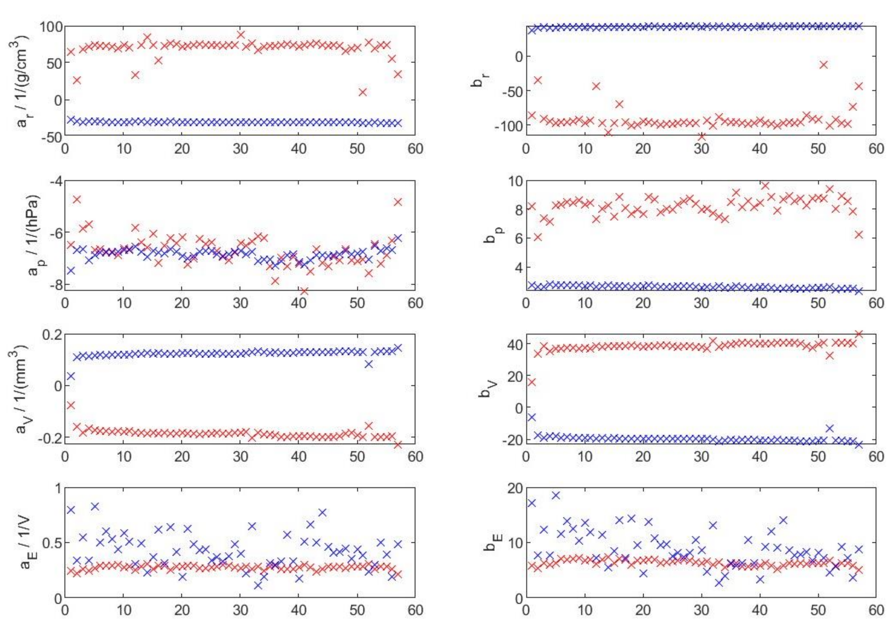


Fig. 6 - Left: potential parameter for SOC(E); right: coefficients of linear SOC estimation from r, p, V, E_{pH} (L2); Red/blue: pos./neg. half cell

Conclusions and Outlook

- Long term data basis (>50 cycles/500 h, 2 membranes) for comparative evaluation of SOC estimation methods (complement to [4])
- Stable reference SOC determination
- Stable SOC (re-)calibrations for selected observables

⇒ Measurement of high crossover scenario (ΔSOH > 10%) data
⇒ Parametrization of SOH and crossover models

Acknowledgements

This research is conducted in close cooperation with the DECHEMA Research Institute within the research project VaMoS which is funded by the German Federal Ministry for Economic Affairs and Climate Action (IGF: 21599 N2).

References

[1] O. Nolte, I. Volodin, C. Stolze, M. Hager, U. Schubert, Materials Horizons. 2021 8, 1866.
[2] T. Haisch, H. Ji, L. Holtz, T. Struckmann, C. Weidlich, Membranes. 2021, 11, 232.
[3] T. Struckmann, P. Kuhn, S. Ressel, Electrochim. Acta. 2020, 362, 137174.
[4] N. Janshen, S. Ressel, A. Chica, T. Struckmann, Electrochimica Acta, 2024, 490, 144239.
[5] S. Ressel, F. Bill, L. Holtz, N. Janshen, A. Chica, T. Flower, C. Weidlich, T. Struckmann, J. Power Sources. 2018, 378, 776

Contact

e-mail: thorsten.struckmann@haw-hamburg.de
phone: +49 40 428 75-8736

Supported by:
Federal Ministry for Economic Affairs and Climate Action
on the basis of a decision by the German Bundestag