Theoretical and experimental modelling and simulation of a vanadium flow battery system considering self-discharge

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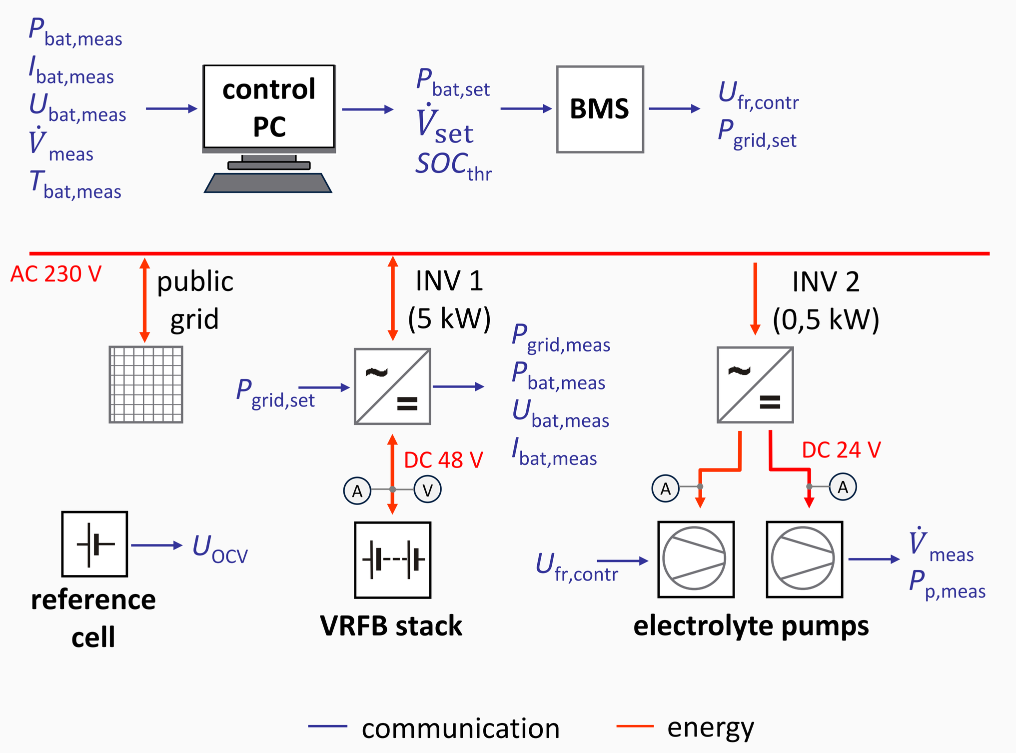
1) Motivation and objectives

- Investigation of self-discharge mechanisms is instrumental in enhancing the efficiency and durability of vanadium flow battery systems (VFBS)
- Improvement of battery management (BMS) and energy management system (EMS) of VFBS
- Utilisation of advanced models for dynamic loss and self-discharge behaviour (particularly during standby)
- Presentation of test system for experimental investigations of a VFBS
- Description of the developed system and self-discharge models for different operation modes
- Investigations and comparison of experimental and theoretical, model-based simulation results

2) Experimental system

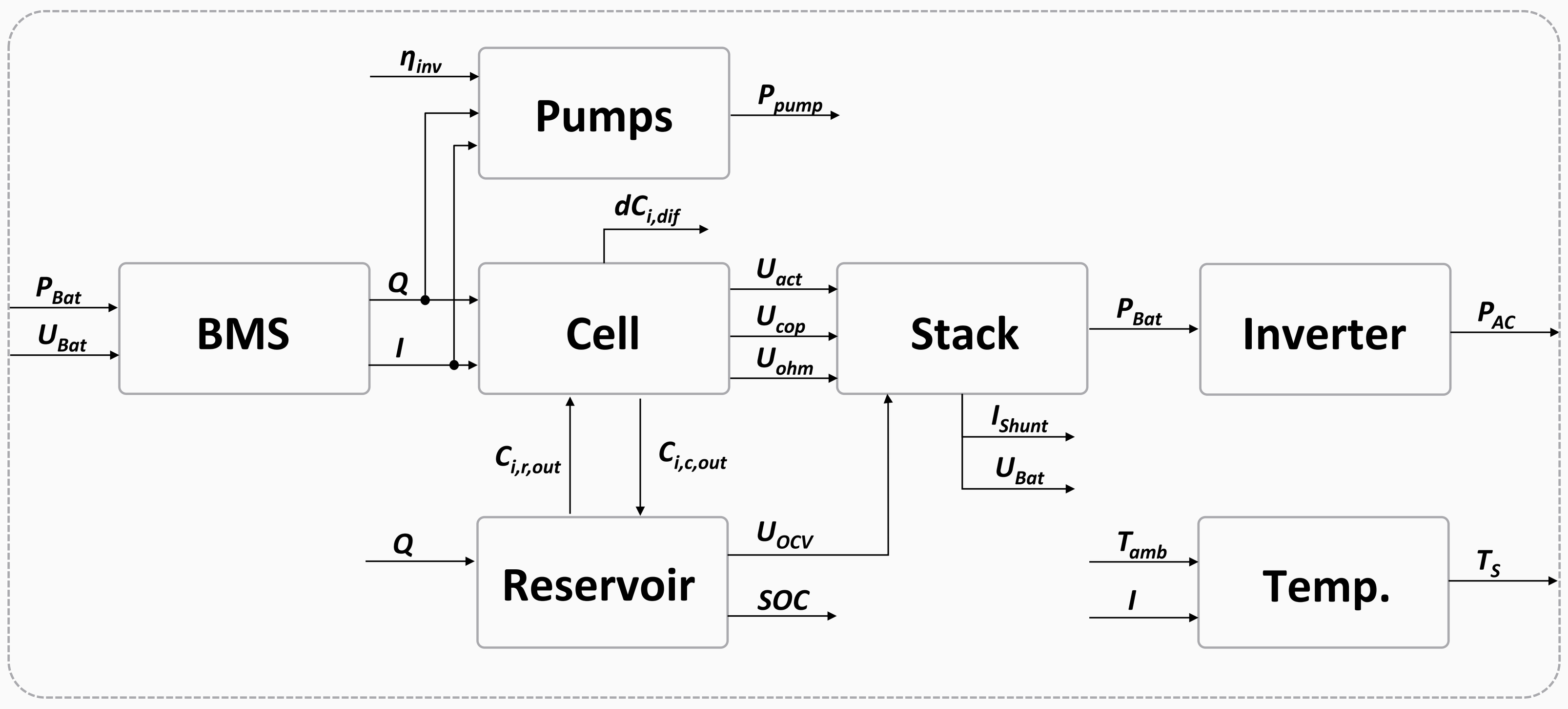


Characteristic	Value
E_{gross} / $E_{@SOC\ 5\text{-}95\%}$	18 /15 kWh
$P_{DC,max}$	5 kW
n_c	40
V_{neg} / V_{pos}	420 / 430 l
I_{max}	100 A
U_m	48 V
P_{Pump}	250 W

- Adapted commercial VFBS (stationary, grid-connected application)
- Additional measuring devices for precise model validation and develop experimental based models (Pumps)

3) VFBS model approach with standby

Multi-physical model: electrochemical models for estimation of over-voltages and concentrations; empirical models for hydraulic behaviour (pumps) and inverters; equivalent circuit model for shunt-currents [1]



Operating modes:

1. Operation
- Pumps and inverter active
- $\dot{V} > 0$ & $I \neq 0$

2. Partial standby
- Inverter standby, pumps running (throttled)
- $\dot{V} > 0$ & $I = 0$

3. Deep standby
- Inverter and pumps off
- $\dot{V} = 0$ & $I = 0$

Self-discharge:

- No reports of effects on self-discharge processes during or after deep standby related to the reservoirs in literature so far
- During long standby periods accumulation of V^{3+} ions in the positive half-cells and V^{4+} ions in the negative half-cells can occur
- After recommissioning a mass transport from cells to reservoirs take place and can leads to following self-discharge reactions

Positive reservoir: $VO_2^+ + V^{3+} \rightarrow 2VO^{2+}$

Negative reservoir: $V^{2+} + VO^{2+} + 2H^+ \rightarrow 2V^{3+} + H_2O$

- Mathematical relationship based on chemical equilibrium and mass balance has been derived for estimating the overall gradients (c, n)

Negative reservoir	Positive reservoir
$\Delta n_{r,2}^{neg} = -n_{c,4}^{neg}$	$\Delta n_{r,4}^{pos} = 2 \cdot n_{c,3}^{pos} + n_{c,4}^{pos}$
$\Delta n_{r,3}^{neg} = 2 \cdot n_{c,4}^{neg} + n_{c,3}^{neg}$	$\Delta n_{r,5}^{pos} = -n_{c,3}^{pos}$
$\Delta c_{r,3}^{neg} = \frac{2 \cdot c_{c,4}^{neg} \cdot V_{hc} + c_{c,3}^{neg} \cdot V_{hc}}{V_r}$	$\Delta c_{r,4}^{pos} = \frac{2 \cdot c_{c,3}^{pos} \cdot V_{hc} + c_{c,4}^{pos} \cdot V_{hc}}{V_r}$
$\Delta c_{r,2}^{neg} = \frac{-c_{c,4}^{neg} \cdot V_{hc}}{V_r}$	$\Delta c_{r,5}^{pos} = \frac{-c_{c,3}^{pos} \cdot V_{hc}}{V_r}$

- Change in concentration for the reservoirs and cells with respect to the temporal interval during the process of recommissioning (pre-running), can be calculated by utilising the following equations

$$V_r \frac{d}{dt}\begin{pmatrix} c_{r,2} \\ c_{r,3} \\ c_{r,4} \\ c_{r,5} \end{pmatrix} = \begin{pmatrix} \dot{V}_{neg} \\ \dot{V}_{neg} \\ \dot{V}_{pos} \\ \dot{V}_{pos} \end{pmatrix} \circ \left(\begin{pmatrix} c_{c,2,out} \\ c_{c,3,out} \\ c_{c,4,out} \\ c_{c,5,out} \end{pmatrix} + \begin{pmatrix} -c_{c,4,out}^{neg} \\ 2c_{c,4,out}^{neg} \\ 2c_{c,3,out}^{pos} \\ -c_{c,3,out}^{pos} \end{pmatrix} - \begin{pmatrix} c_{r,2} \\ c_{r,3} \\ c_{r,4} \\ c_{r,5} \end{pmatrix} \right)$$

Negative half-cells: $V_c \frac{dc_{c,4}^{neg}}{dt} = \dot{V}_{c,neg} \cdot -c_{c,4}^{neg}$

Positive half-cells: $V_c \frac{dc_{c,3}^{pos}}{dt} = \dot{V}_{c,neg} \cdot -c_{c,3}^{pos}$

[1] Beyer, R.; Bocklisch, T.: "Theoretical and Experimental Investigation of Voltage Current Characteristic, Losses and Self-discharge of a Vanadium Redox Flow Battery System", Proceedings of the International Renewable Energy Storage Conference (IRES 2022), PP. 47–62., Atlantis Press, 2023, doi: 10.2991/978-94-6463-156-2_5

4) Experiments and simulation

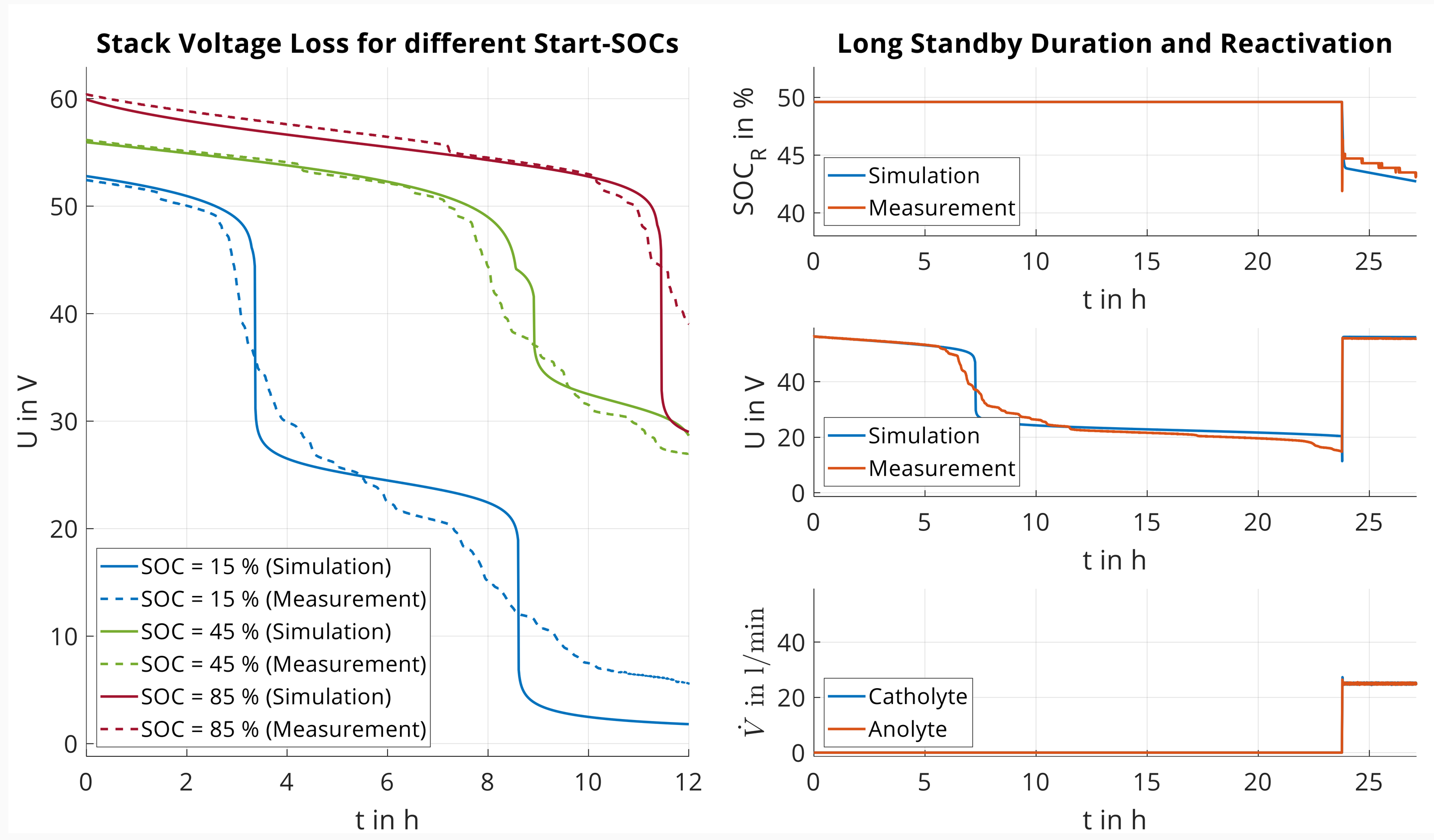
Experiments: critical analysis and comparison for different working points, start SOC's, durations and flow rates with deep and partial standby

Experiment	SOC_0 [%]	Duration [h]	$sgn(I_{t-1})$	$\dot{V}$ [l/min]	ΔSOC [%]	Losses [kWh]
Partial standby	5	3	0	5	1,98	0,45 (0,09)
	5	3	0	15	2,55	0,97 (0,51)
	5	6	-1	5	2,52	0,69
	10	3	0	5	1,21	0,33 (0,12)
	10	6	+1	5	2,52	0,64(0,24)
			0		2,64	0,72(0,24)
	10	12	0	5	5,35	1,44 (0,48)
	50	24	0	5	8,52	2,49 (0,96)
	50	24	0	15	8,52	5,14 (3,61)
Deep standby	5	3	+1	-	1,63	0,33 (0,04)
	5	6	-1	-	4,7	0,88 (0,04)
	10	3	+1	-	1,11	0,24 (0,04)
	10	3	-1	-	1,47	0,3 (0,04)
	10	12	+1	-	3,62	0,69 (0,04)
		13			4,01	0,76 (0,04)
	50	24	+1	-	4,89	0,92 (0,04)
	73	24	0	-	7,47	1,41 (0,04)
	73	48	0	-	9,43	1,77 (0,04)
	73	63	0	-	11	2,05 (0,04)
	73	96	-1	-	11,82	2,2 (0,04)

- High energy losses after long standby phases in partial state mainly due to pump power and dependent on flow rate
- High energy loss for deep standby only after very long durations (96h)
- Losses are dependent on applied current direction instantly before standby (discharge: sgn(It-1) = -1; charge: sgn(It-1) = +1)

Simulation based analysis:

- Prediction of voltage losses and SOC drop is necessary to derive recommendations for action for the BMS, particularly flow rate controller
- SOC change of 6 % after 24 h, can be assumed significantly higher if start SOC is higher or cell concentrations reach equimolar state



5) Conclusions and outlook

- Novel contribution of understanding the self-discharge processes of VFBS
- Standby have a significant impact on the changes of reservoir concentrations and leads to SOC-drops after phases of deep standby
- Simulation data demonstrate qualitative agreement to the measurements
- **Next steps:** scale up system model to simulate larger systems MW-range
- Development of model predictive flow rate controllers
- Superordinate target is the investigation of a control strategies for VFBS and also within a hybrid energy storage configuration

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