

Modeling the Vanadium Oxygen Fuel Cell

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Introduction: In order to increase the energy density of redox flow batteries, the combination of a redox flow battery vanadium anode and a fuel cell air/oxygen cathode has been proposed [1, 2]. The resulting system is a vanadium air battery or, if used only in discharge mode, a vanadium oxygen fuel cell. A schematic drawing is shown in figure 1.

Water is formed during the oxygen reduction reaction at the cathode side. In the course of the cell operation, this leads to a reduction of the surface of the platinum catalyst available for the reaction, also called “flooding”. This is a nonsteady phenomenon. In this work, we wanted to expand a steady-state model of the vanadium oxygen fuel cell to be able to represent the effects of the catalyst flooding, therefore saving computational time over a fully time-dependent model.

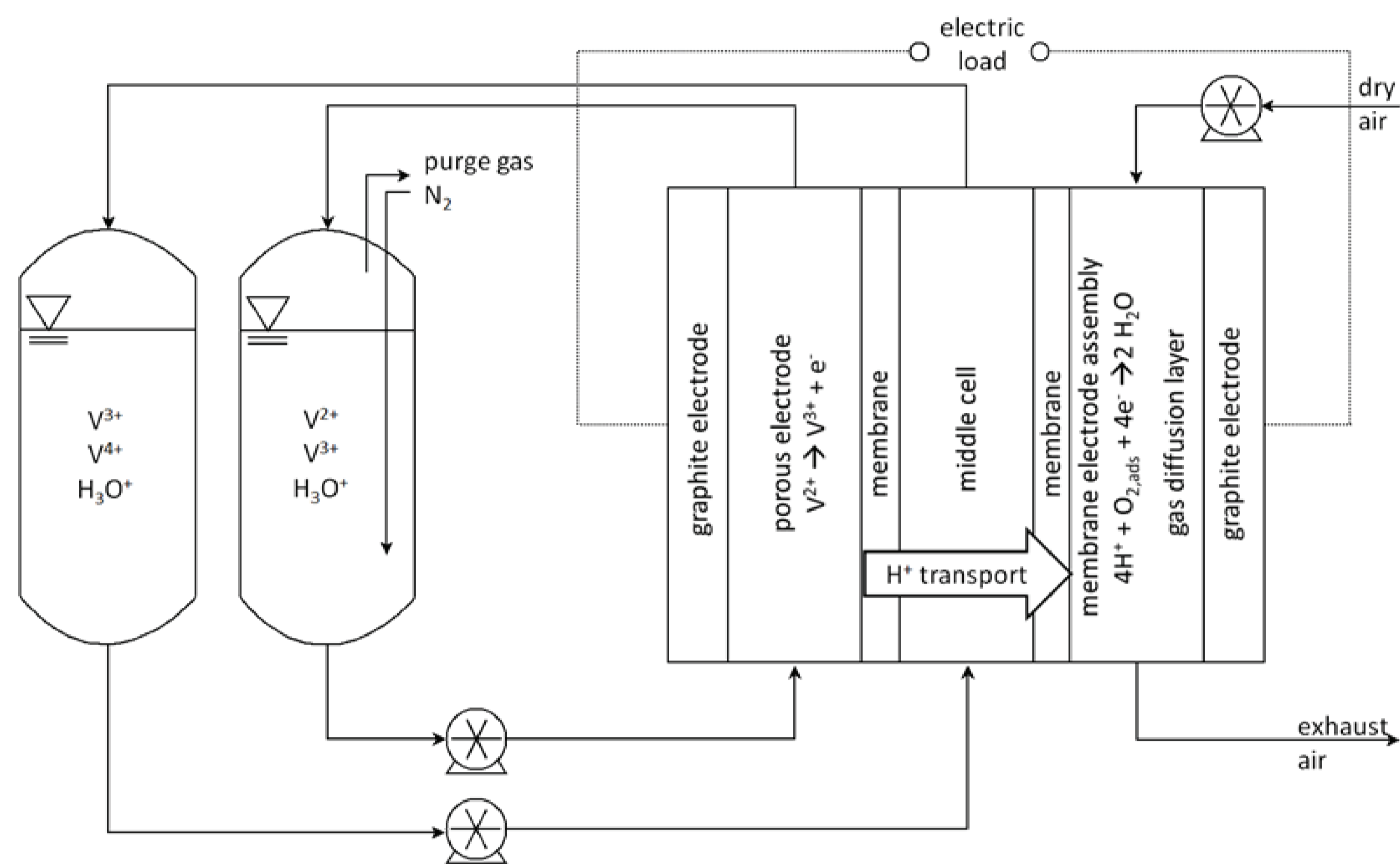


Figure 1. Process diagram of a vanadium oxygen fuel cell [3]

Methods: The steady-state model has been developed using the battery & fuel cell module of COMSOL Multiphysics. For given inlet concentrations of the reactants and current, the isothermal simulation yields the resulting operational parameters. The model geometry is shown in figure 2. The oxygen reduction reaction takes place at the platinum particles in the domain (6) next to the membrane (5). The oxygen is supplied by the gas diffusion electrode (7).

The electrochemical conversion is modeled by an adjusted BUTLER-VOLMER equation

$$j_{cath} = S_V \Psi j_{cath}^0 \frac{c^s(O_2)}{c_{ref}(O_2)} \left(-exp \left\{ -\frac{\alpha_c \mathfrak{F}}{RT} \eta_c \right\} \right), \quad (1)$$

the logistic function $\Psi(t)$ represents the loss of catalyst surface

$$\Psi(t) = \frac{1}{1 + c \exp\{k(t - t_0)\}}, \quad (2)$$

and the inlet concentrations are calculated from the state-of-charge which can be calculated for a galvanostatic discharge regime as

$$SOC(t) = SOC_{start} - \frac{t - t_{start}}{t_{end} - t_{start}} \Delta SOC. \quad (3)$$

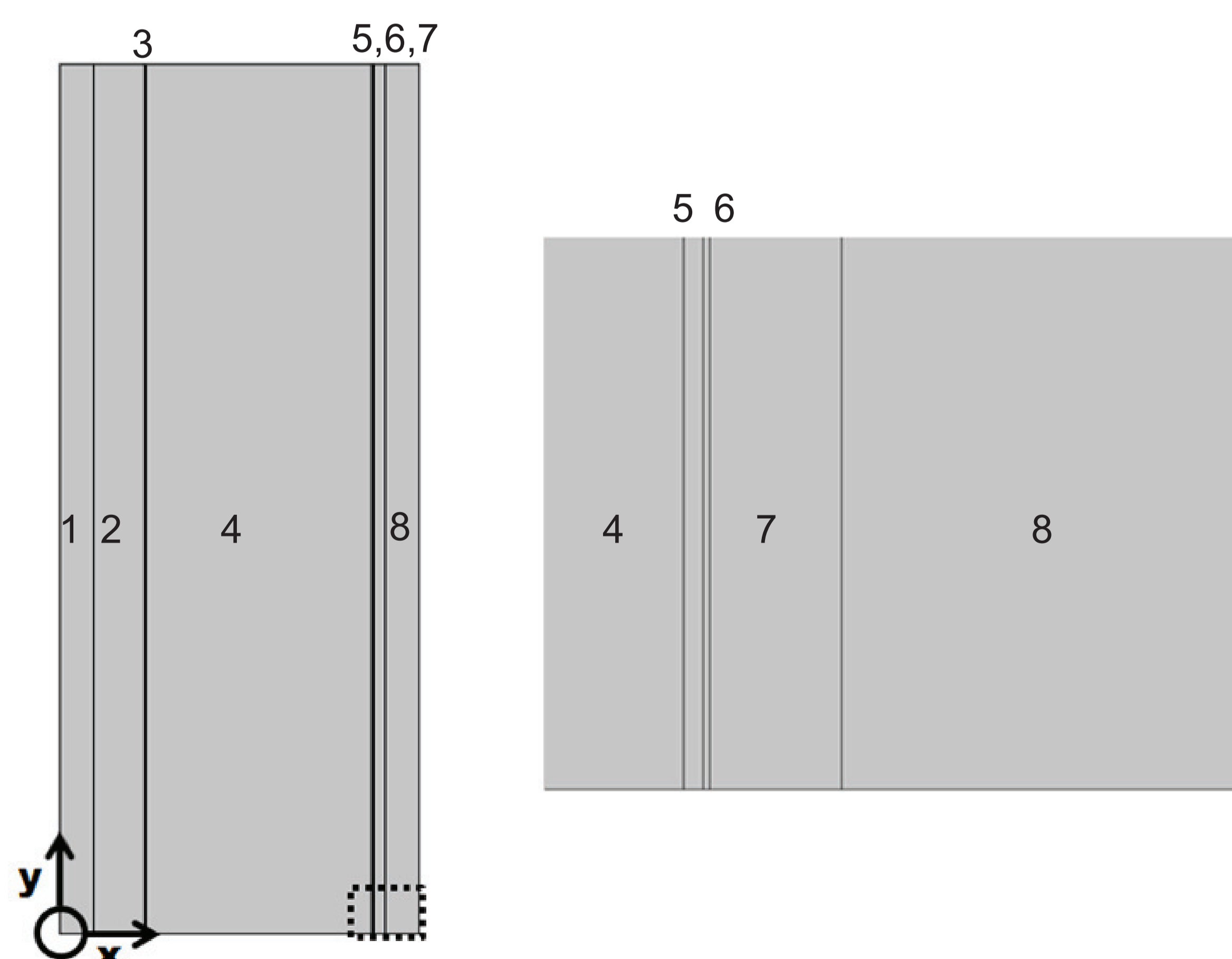


Figure 2. The 2D model geometry (left-hand complete, right-hand magnified part) 1,8 carbon electrodes 2 porous electrode (anode) 3, 5 membrane 4 middle cell 6 layer with catalyst particles 7 gas diffusion electrode

Results: Measured and simulated values for the terminal voltage of a single cell are presented in figure 3. There is a significant gap between the measurement (black line) and the simulation without the logistic function (2) (blue line). This is due to flooding of the platinum catalyst particles. With the correction of the logistic function, the simulation (red line) is in good agreement with the measured data.

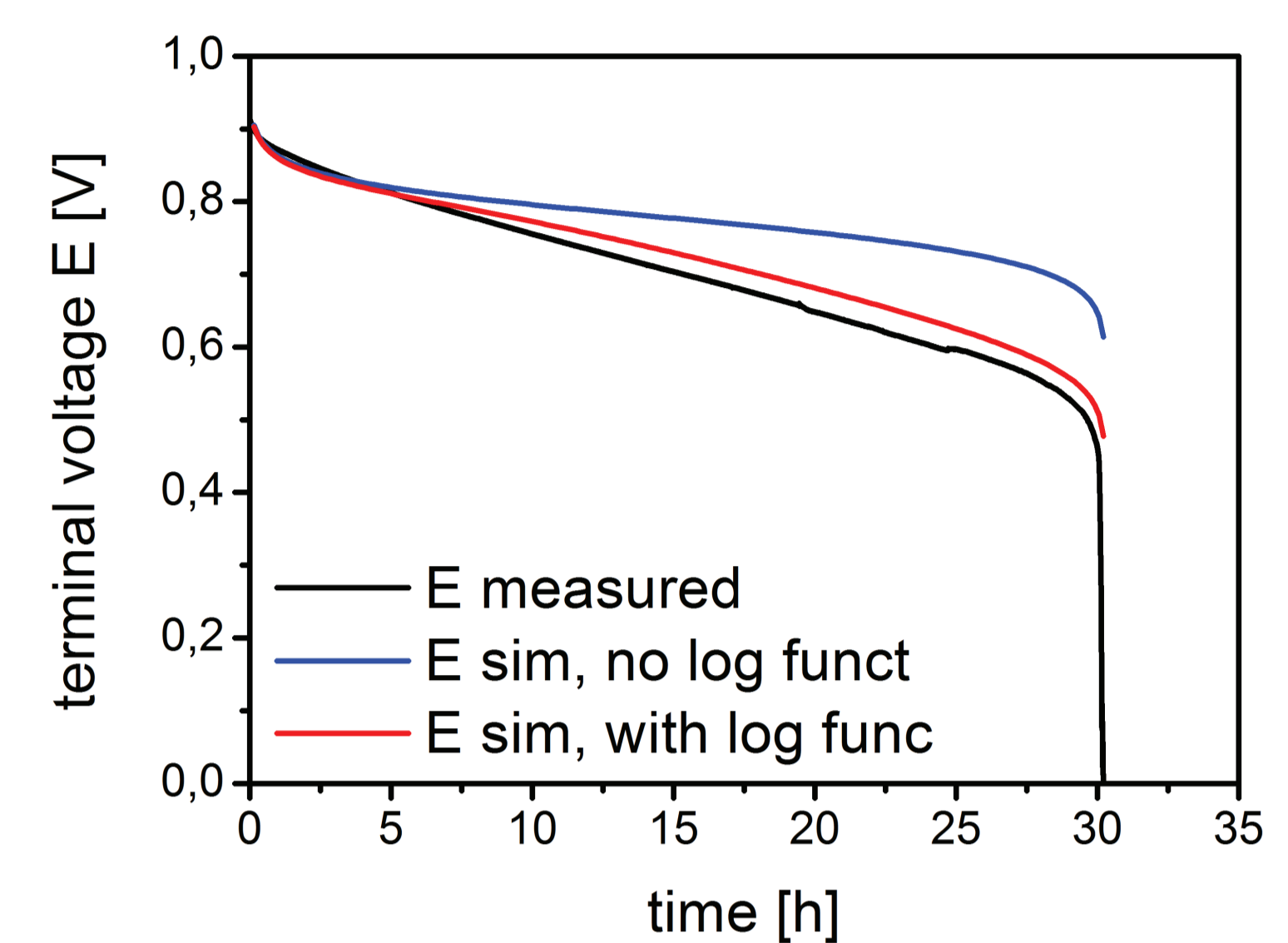


Figure 3. Comparison of experimental and simulated discharge process

The logistic function (2) increases the overpotential η_c for a given j_{cath} in eq. (3). This is also in good agreement with the measurements. The measured and simulated overpotentials in the cathode are shown in figure 4. Due to the fitted parameters of the logistic function, the simulated overpotential shows a different curvature from the measurement at the start of the discharge cycle but runs parallel after the initial mismatch.

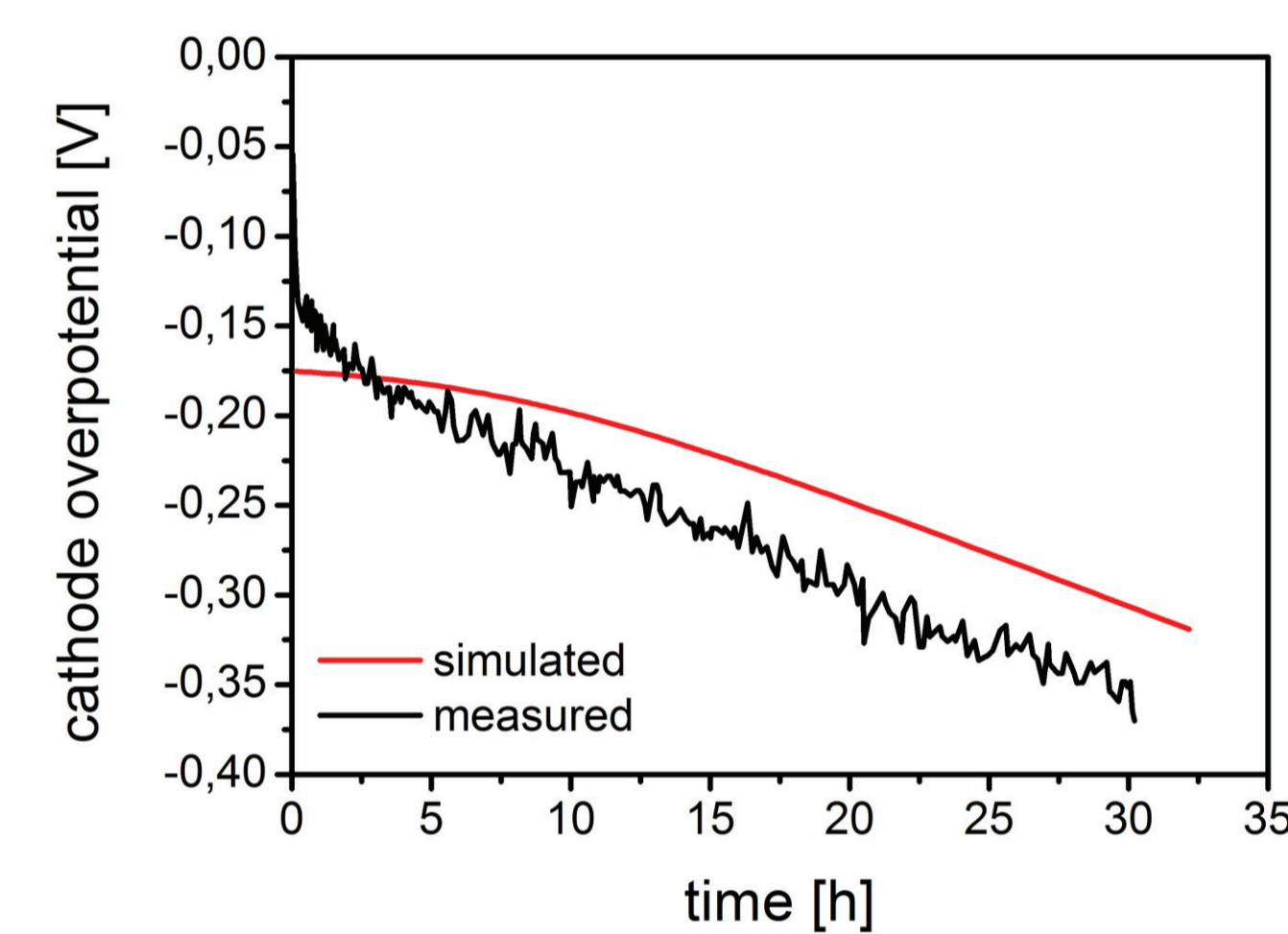


Figure 4. Overpotential at the cathode half-cell during discharge cycle

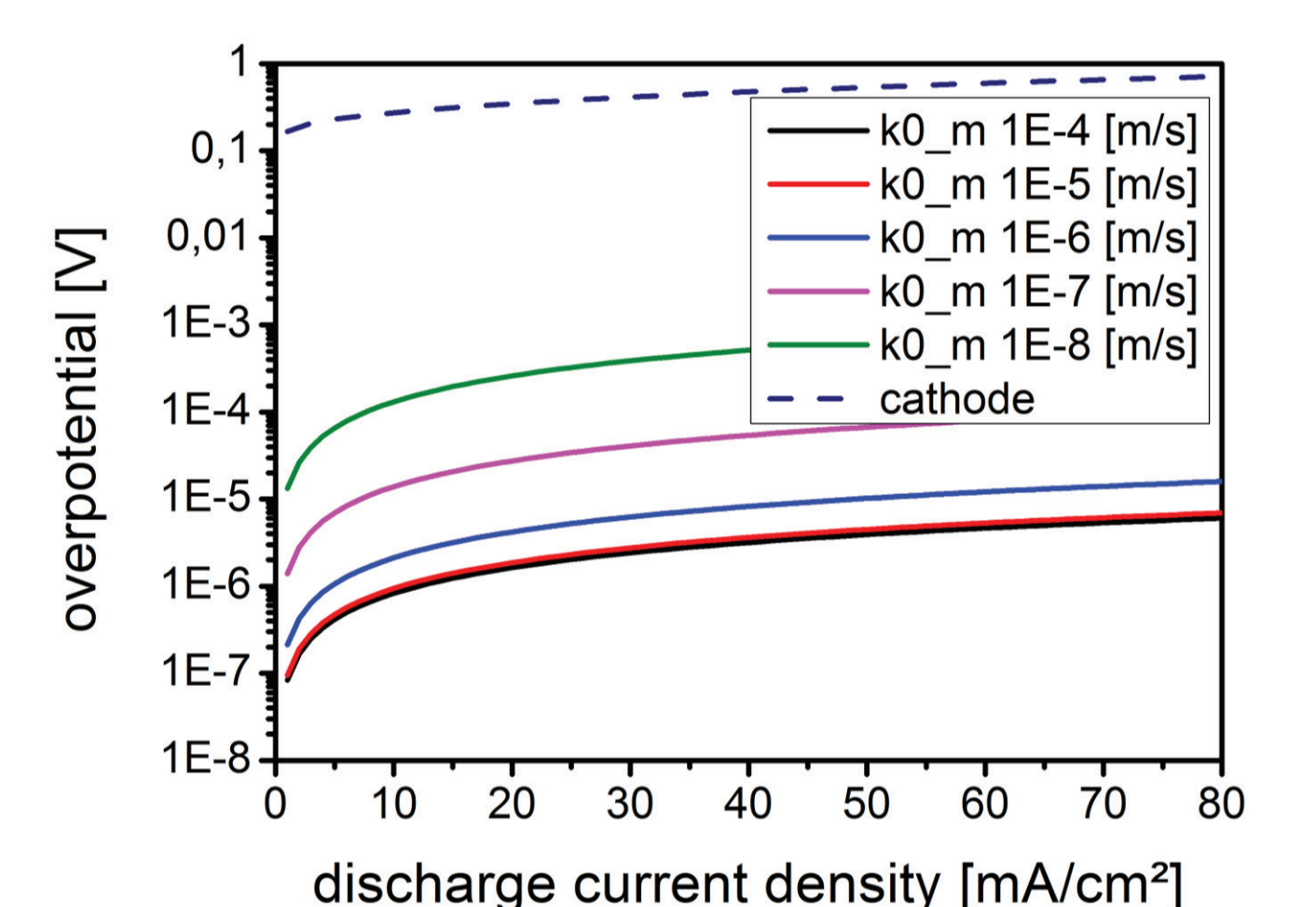


Figure 5. Anodic and cathodic overpotentials for different rate constants

The logistic function (2) increases the overpotential η_c for a given j_{cath} in eq. (3). This is also in good agreement with the measurements. The measured and simulated overpotentials in the cathode are shown in figure 4. Due to the fitted parameters of the logistic function, the simulated overpotential shows a different curvature from the measurement at the start of the discharge cycle but runs parallel after the initial mismatch.

The cathode contributes far more to the voltage losses of the cell than the anode. This is illustrated in figure 5; even for slow rate constants, the anodic overpotentials are orders of magnitude smaller than the cathodic ones. Therefore, it is justified to apply the correction only to the cathode.

Conclusions: The proposed modification of the BUTLER-VOLMER equation allows to examine the transient phenomenon of flooding with a simpler, steady-state model. The logistic function is a measure of the speed and the intensity of the cathode degradation. Employing this metric, different cell designs can be evaluated for optimization.

References:

1. H. Kaneko, A. Negishi, K. Nozaki, K. Sato, M. Nakajima, US Patent 5,318,865 (1992)
2. J. Noack, T. Berger, K. Pinkwart, J. Tübke, DE Patent 1020 1110 7185 (2011)
3. F.T. Wandschneider, M. Küttinger, P. Fischer, K. Pinkwart, J. Tübke, H. Nirschl, A coupled-physics model for the vanadium oxygen fuel cell, submitted to the Journal of Power Sources (2013)

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