



## A coupled-physics model for the vanadium oxygen fuel cell



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### HIGHLIGHTS

- A stationary model for the vanadium oxygen fuel cell is developed.
- The transient cell behavior is modeled by introducing a logistic function.
- Simulated data on basis of this model are in good agreement with experimental data.
- Optimization of the oxygen cathode will contribute the most to system improvement.

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### ABSTRACT

A stationary two-dimensional model for the vanadium oxygen fuel cell is developed. The model consists of a single cell with two membranes, set up as of two half-cells and an intermediate chamber. The transport and balance of mass, momentum and charge are linked to the electrochemical reaction kinetics of the vanadium species and oxygen. The kinetic model for the cathode half-cell is extended by an empirical logistic function to describe the transient behavior of the half-cell. Additionally, experiments are conducted on a single vanadium oxygen fuel cell with 40 cm<sup>2</sup> active membrane area. The experimental results are used to validate the simulation data. The effects of constant current discharging, polarization behavior and different flow rates on the cathode overpotential are studied by means of this model.

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### 1. Introduction

Redox flow batteries are a promising energy storage medium for load leveling and peak shaving of fluctuating electricity production. This is crucial for the grid integration of electrical energy from renewable sources like wind and solar, which show an intermittent electricity generation pattern. One of these batteries' defining features is the electrolyte, which remains liquid at all times. This electrolyte is stored in separate tanks and pumped through the stack. The battery system can therefore be charged either by an electric current or by replenishing the Vanadium V<sup>2+</sup> solution. The latter method makes this system attractive for use in a hybrid or fully electric car. Redox flow batteries are suitable for scale-up

because of the division between energy conversion in the stack and energy storage in the tanks. Scale-up, optimization and large-scale assembly processes are challenges that must be met to ensure the economic viability of redox flow battery systems (Tables 1–4).

The most common type of redox flow battery is the all-vanadium redox flow battery [1,2]. Typical concentrations in this battery vary between 1.4 and 2.0 M. This results in a system whose energy density is comparable to lead-acid batteries. The concentration of the vanadium in the electrolyte can be increased to 2.5 M without loss of chemical stability [3], increasing the energy density. When the application requires an even higher energy density one half-cell or both are changed to another redox system. One possible system features an oxygen cathode fed by ambient air [4] instead of the tetravalent and pentavalent vanadium redox couple, thus eliminating one tank from the system. This could improve redox flow batteries for hybrid electric vehicles [5].

The components of a vanadium oxygen redox fuel cell were investigated by MENICTAS and SKYLLAS-KAZACOS [6] using two

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**Table 1**  
Geometry values.

Symbol	Quantity	Size
$h$	Cell height [mm]	77
$w$	Cell width [mm]	52
$l_{elec}$	Electrode thickness [mm]	3
$l_{felt,1}$	Graphite felt thickness [mm]	3
$l_{membrane}$	Membrane thickness [mm]	0.18
$l_{middle}$	Middle cell thickness [mm]	7.8
$V_t$	Volume of $V^{2+}/V^{3+}$ tank [l]	1

experimental setups, one in a single cell and another in a stack with five cells. They reported a voltage efficiency of 79% for the five cell stack at 10 mA cm<sup>-2</sup>. They further reported problems with the delamination of the catalyst layer for some tested catalyst coated membranes which resulted in a loss of performance after a few hours but could achieve a 120 h lifetime without performance problems employing a thicker Nafion® 117 membrane. HOSSEINY et al. [7] used different membrane electrode assemblies in their vanadium oxygen fuel cell. Our experimental setup was first presented by NOACK et al. [8]. We reported a power loss during the discharge cycle that was attributed to hydrogen evolution at the platinum catalyst particles in the cathode half-cell while achieving a maximum of nearly 50 mW cm<sup>-2</sup> with this design. With a design employing two membranes [9,10] the lifetime was extended to over 250 h at 25 mA cm<sup>-2</sup> without any serious performance loss.

The electrolyte solution of the anode half-cell contains bivalent vanadium ions representing the charged state of the system. Some of these ions cross the membrane because of diffusion and electromigration [11]. In an all-vanadium redox flow battery, this causes a small amount of self-discharge.

In a vanadium oxygen fuel cell, by contrast, the bivalent vanadium ions reduce the potential at the platinum catalyst particles and therefore lead to the decomposition of the acidic electrolyte [12].

Due to the low cathodic overpotential of platinum, hydrogen molecules are formed as a byproduct of the reaction. This hydrogen evolution acts as a dynamic hydrogen electrode within the cathode half-cell, replacing the anode half-cell reaction in the vicinity and therefore lowering the cell potential. Another power loss mechanism is based on the oxygen molecules in the cathode half-cell, which react with the hydrogen at the platinum catalyst. As a result of these processes, the catalyst layer is damaged or even delaminated [6,9], increasing the internal resistance of the cell. This is an obstacle to the long term operation of the cell.

**Table 2**  
Initial and boundary values.

Symbol	Quantity	Size
$p_{out}$	Total pressure at the outlets [Pa]	$1.013 \times 10^5$
$S_s$	State-of-charge at the beginning [1]	0.995
$S_e$	State-of-charge at the end [1]	0.005
$T$	Cell temperature [K]	298.16
$c_1^{tot}(V^{2+}/V^{3+})$	Total concentration of vanadium ions [mol m <sup>-3</sup> ]	1600
$c_1^0(H^+)$	Inlet concentration of hydrogen ions, $S = 0$ [mol m <sup>-3</sup> ]	2000
$c_1^0(HSO_4^-)$	Inlet concentration of hydrogen ions [mol m <sup>-3</sup> ]	2000
$c_2^0(V^{2+})$	Inlet concentration of bivalent vanadium ions [mol m <sup>-3</sup> ]	800
$c_2^0(V^{3+})$	Inlet concentration of trivalent vanadium ions [mol m <sup>-3</sup> ]	800
$c_2^0(H^+)$	Inlet concentration of hydrogen ions [mol m <sup>-3</sup> ]	2000
$c_2^0(HSO_4^-)$	Inlet concentration of hydrogen ions [mol m <sup>-3</sup> ]	2000
$w_{in,3}^0(H_2O)$	Mass fraction of water at the inlet [1]	0.023
$w_{in,3}^0(O_2)$	Mass fraction of oxygen at the inlet [1]	0.228
$w_{in,3}^0(N_2)$	Mass fraction of nitrogen at the inlet [1]	0.743

**Table 3**  
Default values of the constants related to electrochemistry.

Symbol	Quantity	Size	Origin
$c$	Logistic function constant [1]	350	Fitted
$E_1^{00}$	Equilibrium potential, $V^{2+}/V^{3+}$ [V]	-0.255	[27]
$E_3^{00}$	Equilibrium potential, $\frac{1}{2}O_2/H_2O$ [V]	1.229	[27]
$j_3^s$	Interfacial current density, anode A m <sup>-2</sup>	1	[28]
$k$	Logistic function constant [1]	6.5	Fitted
$k_1$	Electrochemical rate constant, anode [m s <sup>-1</sup> ]	$1.7 \times 10^{-7}$	[1]
$S_{Vf}$	Surface area to volume ratio, graphite felt [m <sup>2</sup> m <sup>-3</sup> ]	$1.0 \times 10^{-5}$	[29]
$S_{V,mea}$	Surface area to volume ratio, MEA [m <sup>2</sup> m <sup>-3</sup> ]	303	[28]
$\alpha_{a,1}$	Anodic transfer coefficient, anode [1]	0.5	Estimated
$\alpha_{c,1}$	Cathodic transfer coefficient, anode [1]	0.5	Estimated
$\alpha_{a,3}$	Anodic transfer coefficient, cathode [1]	0	Estimated
$\alpha_{c,3}$	Cathodic transfer coefficient, cathode [1]	1	Estimated
$\sigma_{cep}$	Specific electric conductivity of the carbon composite plates [S m <sup>-1</sup> ]	1000	Estimated
$\sigma_f$	Specific electric conductivity of the graphite felt [S m <sup>-1</sup> ]	370	[29]

This challenge can be approached by introducing an intermediate chamber to the cell setup [9] and therefore preventing contact between the bivalent vanadium ions and the platinum catalyst particles. The intermediate chamber, hereafter called the “middle cell”, adds another electrolyte between anode and cathode half-cells. The electrolyte solutions of the anode half-cell and the middle cell have the same concentration of vanadium ions but a different composition. This is intended to reduce the osmotic drag and therefore reduce the number of bivalent vanadium ions crossing the membrane. The remaining ions then react with tetravalent vanadium ions in a comproportionation reaction to trivalent vanadium ions.

The emphasis of this work is to present a theoretical model for the vanadium oxygen fuel cell; further experimental work has been done by NOACK et al. [10].

## 2. Experimental details

A filter press setup was used analogously to other flow batteries. In Fig. 1 a schematic drawing of the setup is shown. From left to right, the drawing shows a carbon composite plate (1), a porous electrode for the anode half-cell (2), a cation-sensitive membrane (3), the middle cell (4), another cation-sensitive membrane (5) with a membrane electrode assembly (6), a gas diffusion layer (7) and another carbon composite plate (8).

The flow frames of the compartments were made from polyvinyl chloride polymer plates. The compartments were 52 by 77 mm,

**Table 4**  
Default values for constants related to the transport of charge and mass.

Symbol	Quantity	Size	Origin
$D_{H_2O-N_2}$	Binary diffusion coefficient [m <sup>2</sup> s <sup>-1</sup> ]	$2.42 \times 10^{-5}$	[27]
$D_{H_2O-O_2}$	Binary diffusion coefficient [m <sup>2</sup> s <sup>-1</sup> ]	$2.44 \times 10^{-5}$	[27]
$D_{N_2-O_2}$	Binary diffusion coefficient [m <sup>2</sup> s <sup>-1</sup> ]	$2.02 \times 10^{-5}$	[27]
$D_{H^+}$	Diffusion coefficient [m <sup>2</sup> s <sup>-1</sup> ]	$9.31 \times 10^{-9}$	[30]
$D_{HSO_4^-}$	Diffusion coefficient [m <sup>2</sup> s <sup>-1</sup> ]	$1.33 \times 10^{-9}$	[30]
$D_{SO_4^{2-}}$	Diffusion coefficient [m <sup>2</sup> s <sup>-1</sup> ]	$1.07 \times 10^{-9}$	[30]
$D_{V^{2+}}$	Diffusion coefficient [m <sup>2</sup> s <sup>-1</sup> ]	$2.40 \times 10^{-10}$	[31]
$D_{V^{3+}}$	Diffusion coefficient [m <sup>2</sup> s <sup>-1</sup> ]	$2.40 \times 10^{-10}$	[31]
$\epsilon_f$	Graphite felt porosity [1]	0.7	[18]
$K$	KARMAN-KOZENY constant [1]	5.55	[18]
$\mu_1$	Dynamic viscosity of $V^{2+}/V^{3+}$ electrolyte [Pa s]	$3.5 \times 10^{-3}$	Measured
$\mu_2$	Dynamic viscosity of $V^{3+}/VO^{2+}$ electrolyte [Pa s]	$7.6 \times 10^{-3}$	Measured

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