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Multi-physics Model for a Vanadium Redox Flow Battery

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Abstract

The raising global warming concerns, rising oil prices and the increasing electricity demand have led to an acceleration of the renewable energy contribution. Due to the fluctuating nature of renewable energy generation, the problem of matching the supply to meet the demand has emerged. Therefore, energy storage has become essential to compensate this fluctuation. The all- vanadium redox-flow battery (VRB) is a promising and attractive candidate due to its long lifetime and the possibility of independent scale-up of nominal power and nominal energy. The present paper presents a VRB model accounting for the electrochemical reactions, pump losses, temperature changes within the VRB and aging prediction. The model is applicable for a wide range of different VRBs with different nominal power ratings, nominal capacities and different vanadium and sulfuric acid concentrations. The modeling results are discussed and proven to be consistent with current research in this field.

1. Introduction

Worries about climate change, rising oil prices and the peak oil scenario have led to an increase in renewable energy generation. Due to the intermittent nature of renewable energy generation, the problem of matching the energy.
supply to meet the demand has emerged [1]. Especially in case of stand-alone electricity generation and small grids, where the grid itself cannot provide the balancing of power generation and demand, energy storage has become essential to compensate the fluctuations of renewable energies [2]. The all-vanadium redox-flow battery (VRB) is a promising candidate for balancing energy supply and demand in such systems [2]. Its long lifetimes and the possibility of independent scale-up of nominal power and nominal energy make it attractive for the usage in off-grid applications.

VRBs are electrochemical storage systems which consist of two tanks containing the electrolytes with the redox couples $V^{2+}/V^{3+}$ in the negative and $VO^{2+}/VO_2^{+}$ in the positive half-cell [3]. These electrolytes are circulated from the reservoirs to the stacks using two pumps in order to enable the main electrochemical reaction at the cells’ inert electrode ([3], [4]):

$$V^{2+} \rightleftharpoons V^{3+} + e^- \quad \text{(negative half-cell)}$$

$$VO_2^{+} + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O \quad \text{(positive half-cell)}$$

Modeling is an important tool to predict the behavior of the VRB as input parameters change: It can reduce the costs of laboratory testing since prediction can be based on a limited number of tests [5].

For a prediction of the aging behavior and the lifetime of a VRB under different environmental conditions, at least six input parameters are needed: The temperature of the stack and the tanks, the battery’s SOC, the concentrations of V(IV) and V(V) and the corrosion current. Until now, no multi-physics model exists which is able to determine all of these parameters.

The present paper presents a new VRB model which combines existing models with new approaches in order to obtain all input parameters necessary for an aging prediction. The model includes an electrochemical model accounting for the electrochemical reactions including three side reactions ($H^+$ evolution, $CO_2$ evolution and vanadium diffusion through the membrane), a mechanical model for the pump losses of the VRB, a temperature model for the prediction of the temperature changes within the VRB and a VRB control model which determines the flow rate of the electrolyte. Future work will include an aging model for the VRB. The model is applicable for VRBs with different capacities and nominal power ratings. The VRB model was implemented in MATLAB Simulink.

2. The Multi-physics model

The multi-physics model consists of five sub-models (Figure 1): The VRB control system determines the flow rate of the electrolyte $Q$ based on Faraday’s law of electrolysis:

$$Q = \frac{2 \times b \times N_{cell} \times i(t)}{z \times F \times c_{Vanadium} \times SOC_{min} \times [s]}$$  \hspace{1cm} (1)$$

where $b$ is a sign factor which is 1 during charging and -1 during discharging, $N_{cell}$ is the number of cells, $i(t)$ is the charging or discharging current as a function of time, $z$ is the number of electrons transferred during the redox reaction which is 1 for the VRB, $c_{Vanadium}$ is the total vanadium concentration of each tank and $SOC_{min}$ is the minimum state-of-charge.
The mechanical model determines the pump power of the two pumps based on the pressure drop across the hydraulic system [6]:

$$P_{pump} = 2 \times \frac{1}{\eta_{pump}} \times \Delta p_{system} \times Q \quad [W]$$  \hspace{1cm} (2)

where $P_{pump}$ is the power loss of the two pumps in [W], $\eta_{pump}$ is the pump efficiency, $Q$ is the electrolyte flow rate in $[m^3/s]$ and $\Delta p_{system}$ is the pressure drop across the hydraulic circuit in [Pa], which is the sum of the pressure drop in the pipes $\Delta p_{pipes}$ and in the stack $\Delta p_{stack}$. The stack power can then be determined based on the battery system power $P_{VRB}$ and the pump power:

$$P_{VRB} = P_{stack} + P_{pump} \quad [W]$$  \hspace{1cm} (3)

The battery system power $P_{VRB}$ is the power which is delivered to the battery during charging or taken from the battery for the external load during discharging.

In the electrochemical model, the power $P_{charge/discharge}$ which is charged or discharged from the battery is determined as well as the power losses $P_{side~reactions}$ due to the three side reactions (the losses due to the flow of vanadium ion diffusion, the losses due to CO$_2$ evolution and due to H$^+$ evolution):

$$P_{stack} = P_{charge/discharge} + P_{side~reactions} \quad [W]$$  \hspace{1cm} (4)

The stack voltage can be described by the equilibrium voltage $E_{Eq}$ and the sum of overpotentials:

$$U_{stack} = N_{cell} \times (E_{eq} - \eta_{act} - \eta_{conc} - \eta_{ohm} - \eta_{ionic}) \quad [V]$$  \hspace{1cm} (5)

where $N_{cell}$ is the number of cells per stack that are connected in series, $E$ is the equilibrium voltage in [V], $\eta_{act}$ is the activation overpotential necessary to sustain the rate of the electrochemical reaction in [V], $\eta_{conc}$ [V] is the concentration overpotential due to concentration differences between the bulk electrolyte and the electrolyte surface and $\eta_{ohm}$ and $\eta_{ionic}$ [V] are the ohmic and ionic overpotential due to the electrical resistance of the electrodes, bipolar plates, current collector plates, the electrolyte and membrane [4].

The battery state of charge is determined as the minimum of the vanadium concentrations in the two half-cells:
\[
SOC = \min \left( \frac{c_{V(II)}}{c_{V(II)} + c_{V(III)}}, \frac{c_{V(I)}}{c_{V(I)} + c_{V(II)}} \right) [-]
\]  

where \(c_i\) are the concentrations of the different vanadium species in \(\text{mol} \ L^{-1}\).

The concentration changes of the different vanadium species due to the diffusion of vanadium ions through the membrane can be described by the following equation:

\[
\frac{d\tilde{c}_i}{dt}(t, T) = \left( + \frac{i \cdot A}{F} - \frac{\alpha_{H_i} \cdot k_2(T) \cdot c_{H_i} \cdot S}{d} - \frac{\alpha_{V_1} \cdot k_3(T) \cdot c_{V_1} \cdot S}{d} - \frac{\alpha_{V_2} \cdot k_4(T) \cdot c_{V_2} \cdot S}{d} ight) \cdot \frac{1}{V_h} \left(\frac{\text{mol}}{\text{m}^3}\right)
\]

where \(\tilde{c}_i\) with \(i = II..V\) are the concentrations of the vanadium species in \(\text{mol} \ L^{-1}\), \(k_i\) with \(i = 2..5\) are the temperature dependent diffusion coefficients of the different vanadium species in \(\text{dm}^2 \ \text{s}^{-1}\), \(V_h\) is the volume of one half-cell solution [L], \(i\) is the current density in \(\text{A} \ \text{cm}^{-2}\), \(A\) is the electrode surface area in \(\text{cm}^2\), \(F\) is the Faraday constant which is 96 485 \(\frac{\text{C}}{\text{mol}}\), \(d\) is the thickness of the membrane in \(\text{dm}\) and \(S\) is the membrane area in \(\text{dm}^2\). The signs ‘+’ and ‘−’ stand for the process of charging and discharging.

The hydrogen model determines the hydrogen evolution current \(I_{H_2}\) based on the coulombic efficiency \(\eta_{V(III) \to V(II)}\), which is a function of the polarization potential, the sulfuric acid concentration and V(III) concentration:

\[
I_{H_2} = \left( 1 - \eta_{V(III) \to V(II)} \right) \cdot I_{V(III) \to V(II)} [A]
\]

In this equation, \(I_{V(III) \to V(II)}\) is the current for the conversion of V(III) to V(II) during charging. The coulombic efficiency \(\eta_{V(III) \to V(II)}\) at different polarization potentials, sulfuric acid and V(III) concentrations can be determined using the data from a systematic investigation published in [7].

The corrosion current model is used to set the right voltage limits (in order to prevent corrosion). It is based on measurements published in [8]. The current can be described by the following equation:

\[
i_{\text{corr}}(t_{\text{pol}}, E_{\text{initial}}, E^+) = \begin{cases} 
0, & \text{for } t_{\text{pol}} \leq 0 \cup E^+ < E_{\text{initial}} \\
\tilde{i}_{\text{corr, initial}} + t_{\text{pol}} \cdot \left( \frac{\tilde{i}_{\text{corr, max}} - \tilde{i}_{\text{corr, initial}}}{t_{\text{pol, max}}} \right), & \text{for } 0 < t_{\text{pol}} < t_{\text{pol, max}} \cap E^+ \geq E_{\text{initial}} \\
\tilde{i}_{\text{corr, max}}, & \text{for } t_{\text{pol}} \geq t_{\text{pol, max}} \cap E^+ \geq E_{\text{initial}}
\end{cases}
\]

where \(t_{\text{pol}}\) is the polarization time [s], \(E^+\) is the positive electrode potential, \(i_{\text{corr, initial}}\) is the initial corrosion current density (the corrosion current density at the moment at which the corrosion process starts) [A/m²], \(i_{\text{corr, max}}\) is the maximum value of the corrosion current density and \(t_{\text{pol, max}}\) is the polarization time [s], after which the maximum value of the corrosion current density is reached.

The initial corrosion potential \(E_{\text{initial}}\) [V] is based on measurements published in [8], while for the initial corrosion
current density, its maximum value and the time \( t_{\text{pol, max}} \), can then be described by the following equations which are based on the measurements in [8] as well:

\[
i_{\text{corr, initial}} = 0.025 \frac{A}{cm^2} \cdot 2 \frac{E_{\text{pol}} - 1.75 V}{0.05 V} \left[ \frac{A}{cm^2} \right] (10)
\]

\[
i_{\text{corr, max}} = 0.144 \frac{A}{cm^2} \cdot 1.125 \frac{E_{\text{pol}} - 1.75 V}{0.05 V} \left[ \frac{A}{cm^2} \right] (11)
\]

\[
t_{\text{pol, max}} = 7200 s \cdot 2 \frac{E_{\text{pol}} - 1.75 V}{0.05 V} [s] (12)
\]

The temperature model determines the stack temperature \( T_s [K] \) and tank temperature \( T_t [K] \) based on the law of energy conservation [9]:

\[
\begin{bmatrix}
\frac{dT_s}{dt}
\end{bmatrix} = \begin{bmatrix}
-\frac{Q}{V_{\text{stack}}} \cdot 2
\frac{Q}{V_{\text{stack}}} \cdot 2
\end{bmatrix} \begin{bmatrix}
\frac{V_{\text{tank}}}{C_p \cdot \rho \cdot V_{\text{tank}}}
\end{bmatrix} \begin{bmatrix}
T_s
T_t
\end{bmatrix} + \beta \frac{[K]}{[s]} (13)
\]

Where:

\[
\beta = \begin{bmatrix}
\frac{P^2 \cdot R_{\text{stack}}}{C_p \cdot \rho \cdot V_s} \\
UA \cdot \frac{T_{\text{air}}}{C_p \cdot \rho \cdot V_{\text{tank}}} + \frac{1}{C_p \cdot \rho \cdot V_{\text{tank}}} (P_{\text{heating}} - P_{\text{cooling}})
\end{bmatrix} \frac{[K]}{[s]} (14)
\]

and \( T_{\text{air}} [K] \) is the air temperature, \( P^2 \cdot R_{\text{stack}} [W] \) is the heat generation due to charging or discharging \( P_{\text{heating}} \) and \( P_{\text{cooling}} [W] \) are power for the battery heating and cooling, \( Q \) is the electrolyte flow rate [m³/s], \( V_{\text{stack}} \) is the volume of the stack [m³], \( C_p \) is the heat capacity of the electrolyte [J/K⁻¹•kg⁻¹], \( \rho \) is the electrolyte density [kg/m³], \( V_{\text{tank}} \) is the volume of the one VRB tank [m³] and \( UA \) is the heat transfer through the tank wall [W/K⁻¹]. It is assumed that the flow rate of the positive and negative electrolyte is equal \((Q = Q_+ = Q_-)\) as are the temperatures in the tanks on the positive and negative side \((T_t = T_+ = T_-)\), the volumes of the tanks \((V_t = V_+ = V_-)\) and the heat transfer of the tanks \((U_A = U_+ + U_-)\).

3. Results and Discussion

The vanadium redox flow model is integrated into a model for an off-grid PV- wind- diesel battery hybrid system to supply the energy to a 3 kW telecommunication base station. Detailed information about the system can be found in [10].

The resulting flow rate and the mechanical pumping power vary with VRB system power. The mechanical pumping power \( P_{\text{pump}} \) is shown in Figure 2. It is in the range lies between 2 and 6% of the VRB power. This is consistent with the statements of Skyllas-Kazacos and co-workers, who assume that 2-3% of energy losses within the VRB are
expected to be due to pumping the electrolyte. However, if the battery is operating at low power or is charging at high SOC or discharging at low SOC, higher power losses are expected [11].

Figure 2: Mechanical power for the pumping of the electrolyte over a simulation period of one week

At the beginning of the simulation, the battery is fully charged and is then cycled several times. The resulting stack current is shown in Figure 3. The figure demonstrates that the battery is charged and discharged according to the fluctuating power provided by the renewables, and discharged according to the requested power by the load.

Figure 3: Stack current simulated over a period of one week

This current profile leads to repeated charging and discharging which can be seen in Figure 3. The battery’s maximum state of charge ($SOC_{\text{max}}$) is set to 100%, the minimum state of charge ($SOC_{\text{min}}$) to 5%. Figure 4 illustrates that the VRB is usually not entirely charged through the PV panels and wind turbine as their power production is fluctuating.
During charging and discharging, heat is generated. The charge resistance for the stack of 39 cells is $R_{\text{charge}} = 0.0515 \ \Omega$, while the discharge resistance is $R_{\text{discharge}} = 0.0555 \ \Omega$.

Figure 5: shows the voltage of the stack, which varies between 25.74 V and 78 V. The major voltage drops which can be seen in the figure are due to overpotentials during charging and discharging, mainly the ohmic overpotential.

The voltage of one cell then varies between 0.67 V and 2.0 V. This is accordance with the experimental measurements and analytical determination of the cell voltage presented by Shah et. al. Their measurement of cell voltage varies between 0.6 V and about 1.9 V.

The equilibrium potential varies between the voltage of 1.2 V and 1.48 V depending on the vanadium concentration. This result is similar to the values published in [13], [5] and [4].

The results of the model for the Vanadium ion diffusion through the membrane are shown in Figure 6 for a simulation period of 300 hours. The figure demonstrates that per 10 minutes the concentration of the different vanadium species changes in the range of $10^{-3}$. 
The temperature is simulated over a period of one year. The results are shown in Figure 7. The stack and tank temperature varies between 10°C and 26°C. The lower limit of the temperature is set to 10°C. Due to the heating of the tanks electrolyte, the temperatures do not fall below this limit despite the cold air temperature during winter time. The tank temperature is slightly lower than the stack temperature which cannot be seen in the figure below due to the proximity of both values. This proximity exists because the flow rate is high.
Figure 7: The temperature of the stack and the tanks over a period of one year

Figure 8 shows the power needed for the heating of the electrolyte over a period of one year. The heating is necessary to assure that the electrolyte temperature does not fall below a minimum temperature of 10°C despite the low temperatures during winter time.

Figure 8: The heating power of the VRB over a period of one year

1 Conclusion and Outlook

The all-vanadium redox flow battery (VRB) is a promising candidate for balancing power generation and demand in autonomous electricity generation systems [5]. Modeling is an important tool to predict the VRBs behavior over extended periods of time based on a limited amount of laboratory tests [5]. Until now, no multi-physics model which captures the VRBs behavior over extended periods of time has been developed.

Therefore, a multi-physics VRB model has been developed and presented in this paper which takes into account most physical and chemical effects occurring in the VRB in order to allow for meaningful predictions of the batteries behavior in various applications. Among the effects taken into account in this model are the mechanical losses of the pumps and the electrochemical reactions in the stack including side reactions such as the hydrogen evolution, CO₂ evolution or vanadium cross-over through the membrane. Furthermore, the model takes into account the temperature changes within the battery due to varying environmental air temperatures and heat generation in the stack. The model is applicable to VRBs of different energy and power ratings, membranes, and SOC limits.

The proposed model is simulated and the results are presented. The presented results demonstrate that the model is
able to predict aspects of VRB behavior included in the model well in comparison to the simulation and experimental results published by other groups.

References


