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# Experimental validation of a vanadium redox flow battery model via Particle Swarm Optimization (O-2AB-V)

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## 1. Introduction

Among all types of energy storage systems (ESS), vanadium redox flow batteries (VRFB) stand out for their high efficiency (70-90 %), long life cycle, safety and the possibility to decouple both energy and power sizes [1].

One of the main challenges in the study and analysis of VRFB consists on the correct characterization of its performance through mathematical models. The importance of developing mathematical models is reflected in the literature, where numerous studies widely validated and referenced can be found, such as the electrochemical model developed by M. Skyllas-Kazacos [2], who pioneered the use of vanadium in redox flow batteries.

Models can be classified as static or dynamic, depending on whether the effect of time is taken into account, and as distributed or lumped parameter models, depending on the space dimension [3]. Tools as COMSOL are used to analyze and develop distributed parameter models, to study effects of flow design, components materials or degradation mechanisms [4]. However, for control purposes, the distributed models are rarely used due to its complexity and relevant computational cost, both in resources and time. For that reason, a vast majority of works in the literature concerning VRFB control, use lumped parameters models.

Most of these lumped parameters models use different hypothesis to relax the problem, facilitating its understanding and analysis. This is the case of Skyllas-Kazacos electrochemical models mentioned, where the same flow rate is considered in both semicells, same species concentration inside the cell and tanks, as well as a constant temperature to estimate the open circuit voltage (OCV) by means of the Nernst equation [5]. Therefore, it is necessary to develop an analysis in order to define which variables and parameters will be modelled, and under which assumptions.

Thus, in this work, a complete model that considers the most important effects of a VRFB is presented. It can be divided into four submodels, according to the previous parameters, which are: electrochemical, voltage, thermal and hydraulic ones.

This model has been developed in a Matlab-Simulink environment as a tool to analyze the performance of a VRFB in a wide range of possibilities, examining the behaviour of the species and the voltage, temperature and pressure variables, incorporating some improvements with respect to

other works. For all submodels, a clear distinction is made between both sides of the system (catholyte and anolyte semicells), not only in terms of dimensions and flow rates, but also on the initial conditions.

## 2. Model formulation

The model presented in this work can be decomposed in different submodels. The inputs are the charge/discharge current  $I$ , the flow rates for both catholyte and anolyte  $q_+$  and  $q_-$ , and the room temperature  $T_{air}$ .

### 2.1 Electrochemical

The electrochemical model presented in this work shows the evolution of the species concentration distinguishing between anolyte (-) and catholyte (+) semicells, as well as cell and tank components  $c^c$  and  $c^t$ , respectively. Moreover, as an improvement over other works, it considers the real temperature of the electrolyte inside the cell which comes from the thermal model, and includes hydrogen ions and water.

The behavior of the vanadium species, as well as the hydrogen ions and water concentration, can be used not only to determine the state of charge (SOC), but also to compute the state of health (SOH), as it considers the main ion transport methods such as diffusion, migration and convection [6].

On the one hand, the evolution of species concentration inside the cell can be formulated by the following differential equation:

$$v_k^c \frac{\partial c_i^c}{\partial t} = q_k (c_i^t - c_i^c) \pm \frac{I}{F} + \nabla \vec{n}_i$$

where the subscript  $i$  defines the species, subscript  $k$  is used to differentiate between anolyte and catholyte semicells,  $v_k^c$  is the electrolyte volume of the semicell,  $F$  is the Faraday constant and  $\nabla \vec{n}_i$  represents the ion transport mechanisms.

On the other hand, the behaviour in the tanks is defined by the expression:

$$v_k^t \frac{\partial c_i^t}{\partial t} = q_k (c_i^c - c_i^t)$$

where  $v_k^t$  is the electrolyte volume of each tank.

### 2.2 Thermal

The thermal model is formulated to calculate the temperature inside the whole system, namely: both tanks, pipes line connections and the cell temperature  $T^c$ . It

considers the effect of the current by the Ohm's law, and also the heat generated in each pump thanks to its particular hydraulic model [7].

In order to compute the temperature in any part of the system, the following expression can be used:

$$v_k^i c_p \rho \frac{\partial T^i}{\partial t} = q_k c_p \rho (T^{in} - T^i) + u^i s^i (T_{air} - T^i)$$

where superscript  $i$  is used to distinguish between the system part,  $c_p$  is the specific heat capacity of the electrolyte,  $\rho$  is the electrolyte density,  $T^{in}$  is the temperature of the inlet electrolyte flux,  $u^i$  is the overall heat transfer coefficient that depends on each material and  $s^i$  is the surface in contact with the room temperature  $T_{air}$ .

On the one hand, considering the temperature inside the cell, the effect of the current must be considered adding the factor  $r \cdot I^2$  where  $r$  is the cell resistance. On the other hand, considering the temperature inside the pipe lines where the pumps are connected, the heat generated by the pumps of the catholyte ( $W_+$ ) and anolyte ( $W_-$ ) parts must also be added.

### 2.3 Voltage

The voltage model analyzes the voltage drop,  $V$ , between the cell terminals. Unlike the vast majority of works that only include the OCV without accounting for the Donnan effect considering the hydrogen ions, this one does take it into account jointly with the different overpotentials [8].

Thus, the complete expression of the cell voltage used here is the following one:

$$V = E^\theta + \frac{R \cdot T^c}{F} \ln \left( \frac{c_2^c \cdot c_5^c \cdot (c_{H^+}^c)^3}{c_3^c \cdot c_4^c \cdot c_{H^-}^c} \right) + \eta$$

$E^\theta$  being the standard electrode potential,  $R$  the ideal gas constant and  $\eta$  the overpotentials [9].

### 2.4 Hydraulic

The hydraulic model is used to calculate the power that the pumps must supply in order to maintain the electrolytes flowing at a certain rate, considering the pressure drop in the pipes and inside the cell [10].

On the one hand, the pressure drop in the pipes line ( $\Delta p_k^l$ ) can be computed by means of the following equation:

$$\Delta p_k^l = f \frac{l_k^l \rho v_k^2}{d_k^l 2}$$

where  $l_k^l$  is the length of the pipes line,  $d_k^l$  is the diameter and  $v_k$  is the electrolyte velocity that can be computed as:

$$v_k = \frac{q_k}{s_k^l}$$

$s_k^l$  being the pipe section surface.

Finally, the pressure drop inside the cell can be divided in two main parts. On the one hand, the pressure drop in the flow frames, which is calculated using the same expression of the pipe lines but considering the different flow sections:

$$\Delta p_k^f = f \frac{l_k^f \rho v_k^2}{d_k^f 2}$$

where  $l_k^f$  and  $d_k^f$  are the same variables of length and diameter but for the flow frames.

On the other hand, the pressure drop inside the electrodes can be calculated using the expression:

$$\Delta p_k^e = \frac{\mu q_k K_{ck} (1 - \varepsilon)^2 h_k^e w_k^e}{d_k^e \varepsilon^3 l_k^e}$$

where  $\mu$  is the electrolyte viscosity,  $K_{ck}$  is the Kozeny-Carman constant,  $\varepsilon$  is the electrode porosity,  $d_k^e$  is the diameter of the electrode fibres and  $h_k^e$ ,  $w_k^e$  and  $l_k^e$  are respectively, the height, length and thickness of the electrodes.

Finally, it is possible to compute the heat generated by the pumps considering these pressure drops as:

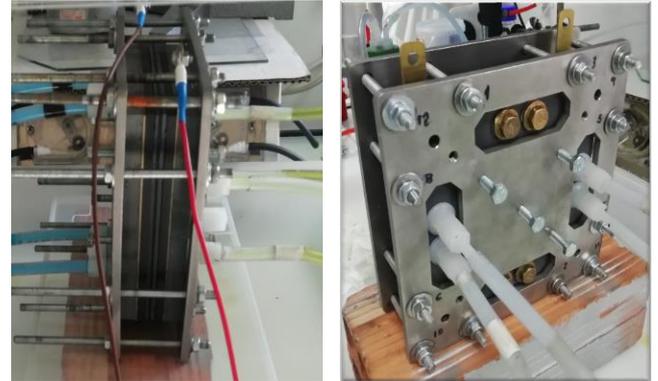
$$W_k = (\Delta p_k^l + \Delta p_k^f + \Delta p_k^e) \cdot q_k$$

## 3. Experimental design

A real VRFB single cell has been developed by the LIFTEC research team (see Fig. 1), and consists of two 7x7 cm<sup>2</sup> carbon felt electrodes separated by a Nafion-117 membrane. The electrolytes for both anolyte and catholyte consist of a 2 M solution of sulphuric acid with a concentration 1.7 M of vanadium, using 80 ml for each of them.

The experiment carried out consists of a discharge cycle at constant current where the voltage has been measured taking samples every 1 second, without imposing any initial conditions in terms of initial species concentration.

Fig. 1 VRFB single cell assembled in the LIFTEC center.



### 3.1 Experimental validation

Despite the fact that many of the variables and parameters of the system are known or can be measured, there is no information available about some others and they need to be estimated. For this purpose, the use of an estimation method is required. An offline estimator based on the Particle Swarm Optimization (PSO) technique is proposed in this research. The main reason to choose this offline estimation technique is that can be implemented easily in MATLAB and is computational efficiency compared with other mathematical algorithms or heuristic techniques [11].

The parameters and variables that have been considered in this work are the initial species concentrations, and the parameters related with the different overpotentials, which are the cell resistance  $r$ , the charge transfer coefficients  $\alpha$ , and the reaction rate constant  $\beta$ .

Defining the set of parameters to be estimated as  $\mathbf{p} = [c_2(\mathbf{0}), c_3(\mathbf{0}), c_4(\mathbf{0}), c_5(\mathbf{0}), c_{H^+}(\mathbf{0}), r, \alpha, \beta]$ , it is possible to formulate the following optimization problem [12]:

$$\min_{\mathbf{p}} \sum_{j=1}^{n_j} |V_j - \hat{V}_j|$$

$$\text{subject to } \hat{V}_j = f(\mathbf{p})$$

$$\mathbf{c}(\mathbf{p}) \leq \mathbf{0}$$

where  $n_j$  is the number of samples of the output measure  $V_j$ , which must be equal to the total points of the estimated one  $\hat{V}_j$  that is computed by means of  $f(\mathbf{p})$ , which is the voltage function used in this work that depends on the complete model variables. Finally,  $\mathbf{c}(\mathbf{p})$  is the constraint vector of parameters.

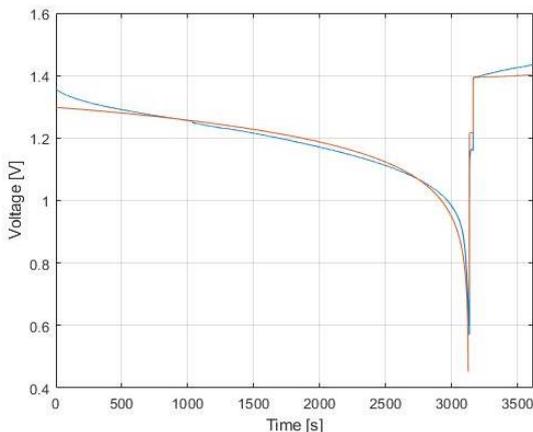


Fig. 2. Real (blue) and estimated (red) voltage profiles for a discharging process of the experimental cell.

#### 4. Results

A discharging profile with a constant current of 3 A has been used as a first step in order to validate the estimated parameters of the PSO method. Fig. 2 shows the experimental profile applied to the single cell and the one obtained with the calibrated model. As can be observed the agreement is reasonably good, presenting a similar semblance in terms of voltage computation. The estimation of the ohmic and activation overpotential coefficients makes it possible to obtain a correct estimation both in the low and high concentration periods.

#### 5. Conclusions

This work presents a new dynamic model of a VRFB that allows to consider the most important variables and effects that occur during the system operation. The calibration performed using the PSO technique has achieved very accurate results with the real data obtained from a discharge experiment, validating the presented model. In this way, the need for a model that considers different variables has also been demonstrated. As future improvements, it would be interesting to analyze the robustness of the model for the case of a stack composed by different cells where the bypass currents can have an important effect. Another line of work, could be related with long term operation, analysing and validating the effect of ion transport mechanism, as well as possible degradation of the electrolyte and components.

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