



# A numerical model for a soluble lead-acid flow battery comprising a three-dimensional honeycomb-shaped positive electrode



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## HIGHLIGHTS

- New reactor for a soluble lead-acid flow battery with a honeycomb-shaped electrode.
- Simulation of the influence of the honeycomb dimensions on the cell characteristics.
- Experimental measurement of kinetic parameters for the Pb<sup>2+</sup>/Pb and PbO<sub>2</sub>/Pb systems.

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## ABSTRACT

A novel reactor design is proposed for the soluble lead-acid flow battery (SLFB), in which a three-dimensional honeycomb-shaped positive PbO<sub>2</sub>-electrode is sandwiched between two planar negative electrodes. A two-dimensional stationary model is developed to predict the electrochemical behaviour of the cell, especially the current distribution over the positive structure and the cell voltage, as a function of the honeycomb dimensions and the electrolyte composition. The model includes several experimentally-based parameters measured over a wide range of electrolyte compositions. The results show that the positive current distribution is almost entirely determined by geometrical effects, with little influence from the hydrodynamic. It is also suggested that an increase in the electrolyte acidity diminishes the overvoltage during discharge but leads at the same time to a more heterogeneous reaction rate distribution on account of the faster kinetics of PbO<sub>2</sub> dissolution. Finally, the cycling of experimental mono-cells is performed and the voltage response is in fairly good accordance with the model predictions.

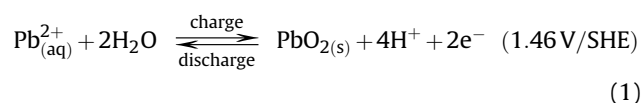
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## 1. Introduction

The soluble lead-acid flow battery (SLFB) has been developed over the last ten years as a possible low-cost solution for the stationary storage of electricity. As part of the redox flow batteries (RFBs), it involves solution-based electro-active species stored in an external electrolyte reservoir, but differs from the traditional RFBs in that it works with undivided cells since the same species (aqueous Pb<sup>2+</sup>) reacts at both electrodes. As a consequence, no ion-selective membrane is required, allowing the use of a single electrolyte, which commonly consists of a solution of lead methanesulfonate salt, Pb(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, in methanesulfonic

acid (CH<sub>3</sub>SO<sub>3</sub>H). It is also different from numerous RFBs such as the all-vanadium or zinc-bromine systems because the reactants and products are not all soluble but, instead, solid phases are alternatively formed and dissolved during operation. These are lead dioxide (PbO<sub>2</sub>) at the positive electrode and lead (Pb) at the negative electrode, deposited during the charge periods and dissolved back into the electrolyte during the discharge periods, according to the following reactions:

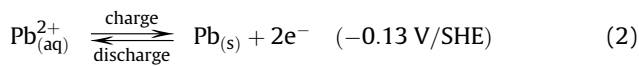
- at the positive electrode:



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- at the negative electrode:



So far, studies of the SLFB [1–10] have focused on mono-cells, or stack of cells, comprising two planar facing electrodes with the electrolyte flowing in-between. The charge efficiency of the system ( $\sim 80\text{--}90\%$ ) is determined by the inability of lead dioxide to be completely dissolved after discharge. This phenomenon is most probably associated with the formation of complex oxides at the electrode surface [11]. The voltage and energy efficiencies are close to 75% and 60%, respectively, with a current density of  $20 \text{ mA cm}^{-2}$  and an inter-electrode gap of  $1.2 \text{ cm}$  [8]. These inefficiencies could be related to the sluggish kinetics associated with the deposition and dissolution of lead dioxide (reaction (1)), which induce significant overvoltages, in addition to the ohmic drops. Considering that, up to now, no solution has been found to improve the reversibility of reaction (1), the only possibility to decrease the charge transfer overvoltages seems to be a significant decrease in the current density. This implies a significant enhancement of the specific surface area of the positive electrode through the use of a three-dimensional matrix. The structure proposed here is a honeycomb matrix made up of hexagonal alveoli. A preliminary numerical study of the system could be of great assistance with choosing suitable dimensions and this is the subject of the present paper.

Several models (stationary or dynamic) of RFBs can be found in the literature, especially for the all-vanadium system. They are all based on mass, charge and momentum (transport) conservation equations combined with charge transfer kinetics relation at the electrodes. Examples for the all-vanadium technology are the transient 2-D model developed by Shah et al. [12] assessing the effect of variations in the species concentration, electrolyte flow and electrode porosity on the cell characteristics, or the 3-D model of Xu et al. [13] which studies various flow field designs for supplying electrolyte to the electrodes. In these studies, the microscopic scale of the electrodes porosity (usually made of carbon fibres) is statistically treated via additional terms in the mass transport equations. It affects the diffusion coefficients of the active species, the electrolyte and matrix conductivity as well as the electrolyte flow and, as a consequence, the concentration distribution of the soluble species and the performance of the battery.

Up to now, the soluble lead flow battery has been the subject of a single modelling attempt. The authors, Shah and co-workers [14], proposed a two-dimensional transient simulation of a mono-cell comprising  $10 \times 10 \text{ cm}^2$  planar electrodes, based on classical conservation laws and Butler–Volmer kinetics relations. The side (solid state) reaction involving  $\text{PbO}_x$  at the positive electrode during charge was considered in addition to the main liquid–solid reaction (1) and the kinetics parameters of each reaction were adjusted to capture the complex voltage transient of an experimental cell.

In the present paper, a two-dimensional stationary model of the SLFB is developed on the basis of a new reactor design, involving the three-dimensional honeycomb structure proposed for the positive electrode and two planar negative electrodes. It relies on the mass, charge and momentum conservation principles and on experiments specially conducted for determining some useful parameters (kinetics of reactions, electrolyte conductivity and electrochemical potentials). As opposed to the previous model of the SLFB, no time dependence is considered due to the fact that the voltage transient of the positive electrode appeared to be strongly influenced by morphological changes that arise at the surface of the  $\text{PbO}_2$  [15] and are not theoretically predictable. Rather, the purpose

of this study is to predict the main charge–discharge behaviour of the system (current densities, voltage components, species concentration...) over a wide range of electrolyte compositions and geometrical dimensions of the reactor. Because 3-D structures are generally associated to non-uniformities of the reaction rate over their surface owing to mass and charge transport limitations and leading to a non-fully or unbalanced utilization of the electrode, special attention is paid to study and quantify the uniformity of the current distribution on the positive electrode.

The innovative reactor design is presented in Section 2 together with the 2-D representation created for the simulations. The assumptions, the governing equations and boundary conditions are further presented and numerical details for the resolution are given. Section 3 contains details on the experiments conducted in this study. Section 4 presents the results of the preliminary experiments conducted to supply adequate parameters to the model. The simulation results are presented in Section 5. Firstly, assessments of the velocity field, ionic potential, species concentration and current density distributions throughout the entire reactor are reported. Then attention is drawn to the current distribution within the positive structure and to the cell voltage, studying the influence of the honeycomb dimensions (length and diameter of the alveoli) as well as of the electrolyte composition. Finally, a few results obtained with experimental flow cells are reported to illustrate the feasibility of the reactor and the data were compared to the model predictions.

## 2. Model

### 2.1. Geometry of the 3-D reactor

The reactor considered in this paper is a mono-cell made up of a high-specific surface area positive electrode and two negative electrodes. The positive electrode has a three-dimensional honeycomb structure consisting of a compact assembly of hexagonal crossing alveoli, or channels, and is sandwiched between two planar negative electrodes so that the channels of the positive electrode are perpendicular to the planes of the negative electrodes. A schematic representation of the mono-cell reactor is given in Fig. 1(a) together with a front view of the honeycomb electrode in Fig. 1(b). The electrolyte is supplied and released so that it can flow through the positive structure (flow-through configuration). For this purpose, holes can be drilled into the negative electrodes, as represented in Fig. 1(a). The electrolyte can also be supplied and/or released in the interelectrode gaps located on the bottom and the top faces, along the  $(x,y)$  plane, or on the vertical faces along the  $(x,z)$  plane.

The three relevant dimensions of the reactor are: (1) the length of the channels, which is the thickness of the positive electrode along the  $x$  axis, referred to as  $L_c$ ; (2) the diameter of the channels, i.e. the distance between two opposite walls of the hexagons, referred to as  $D_c$ ; (3) the inter-electrodes distance  $E$ . The total area  $A^+$  developed by the positive electrode is the area  $A_c$  developed by the wall of each channel multiplied by the number  $N_c$  of channels:

$$A^+ = N_c A_c \quad (3)$$

Given that each of the six sides of the hexagons is  $D_c/\sqrt{3}$  in length,  $A_c$  is given by:

$$A_c = \frac{6D_c L_c}{\sqrt{3}} \quad (4)$$

The section  $S$  of the reactor in the  $(y,z)$  plane, which is also the area of the negative plates, divided by the section of each hexagon,

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