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A two dimensional numerical model of the membrane-divided soluble lead flow battery

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**Abstract**

Dividing the soluble lead flow battery (SLFB) is known to improve the cycle life of the SLFB by preventing failure mechanisms such as short-circuiting and by allowing electrode specific electrolyte additives. Modelling (SLFB) is a complex multiphysics problem due to the electrolyte flow, composition changes and reaction environment geometry variations associated with the deposition and dissolution of the active material as a function of state of charge. Here we studied the membrane divided SLFB using a two-dimensional, transient, numerical model, built in COMSOL Multiphysics. Divided cells using cationic and anionic ion-exchange membranes and simple, porous separators are compared with the undivided SLFB. The model successfully predicts the complex, non-linear relationship between Pb2+ ion concentration and conductivity of the electrolyte as a function of free acid concentration. There is a deviation of less than 22 mS cm-1 between the simulated electrolyte conductivity and the experimental data. We show the conductivity of the Nafion-115 membrane in the SLFB dominated the potential drop across the membrane. However, at higher current densities, the Donnan potential becomes more dominant.

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1. Introduction

The soluble lead flow battery (SLFB) is a hybrid flow battery in which solid lead is electroplated onto the negative electrode and solid lead dioxide is electroplated onto the positive electrode during charging. During discharge, the solid phases are electrochemically dissolved back into the electrolyte as Pb2+, the active species in both half-reactions, see eq( 1 )-( 3 ). Because of this, the SLFB can operate in an undivided manner as there is a physical separation of the active materials in the charged state, which prevents self-discharge.

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| --- | --- | --- | --- |
|  | |  | ( 1 ) |
|  | |  | ( 2 ) |
|  |  | | ( 3 ) |

Despite the advantage of a single electrolyte and simplified reaction chamber, however, a review of the SLFB highlights the relatively low cycle life of the undivided system. 2000 cycles have been achieved in a beaker cell, but this drops to 100 in a flow cell with no maintenance cycle [1]. Krishna et al. showed that by including a separator, the cycle life of the SLFB can be improved to over 150 cycles [2]. In the same study the undivided cell failed after just 10 cycles. The separator acts as a physical barrier to prevent failure by electrical shorting of uneven deposit growths and, when an ion exchange membrane is used, electrode specific additives may be included in the electrolytes.

Studies which model the SLFB have investigated variation in applied and local current density [3, 4], possible morphology of the PbO2 deposit [5], convection currents driven by Pb2+ concentration [4-7], novel electrode designs to increase the relative area of the positive electrode [4, 8]. However, all these models the undivided SLFB configuration.

Simulations by Nandanwar and Kumar suggest control of flow rate and direction provide more even current distribution leading to reduced unevn deposit growth which may lead to an increase in cycle life [4]. Additives are also known to improve the smoothness of deposits [9] and regular chemical [10], or electrochemical, [11], maintenance cycles are shown to reset the deposits to close to initial conditions. However, maintenance cycles may add cost and restrict the freedom of operation of the SLFB, so reducing their required frequency is beneficial. As neither flow control nor additives lead to completely smooth deposits, and as a separator provides a physical barrier to shorting and allows for the possibility of better performing, electrode specific additives, dividing the SLFB remains beneficial.

While ion-exchange membranes in flow batteries, such as the vanadium redox flow battery [12], have been modelled, simulation of the SLFB remains exclusively of the undivided setup. In this paper, we develop a novel model for the ion exchange, fully-divided SLFB, which is validated using experimental results for a Nafion 115 divided cell.

1. Model setup

A numerical model of the divided SLFB was developed in COMSOL Multiphysics. The equations for the electrolyte and the electrode equations are as used in our previous paper [13], the following section highlights any differences. The flow of the electrolyte was modelled using the Navier-Stokes for conservation of mass and momentum. The Nernst-Planck equation was employed to simulate the mass transport of species in solution. Three domains between the active electrode surfaces are used when implementing the model: two containing electrolyte and a further membrane domain. Validation was completed using steady-state, one-dimensional models. The model for validation of the electrolyte conductivity was competed using a single electrolyte domain. Validation for the membrane used the same three domains as the two-dimensional model. As with previous SLFB models, only a single side reaction is assumed at the positive electrode:

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| --- | --- | --- |
|  |  | ( 4 ) |

This side reaction is a simplification of the mechanism which gives the SLFB its characteristic two-step charging voltage which is seen during the second and subsequent charges. The cell potential begins at a lower voltage than the first charge before rising sharply, once PbO is fully converted to PbO2, to close to the first charge voltage for the remainder of the charge.

* 1. Assumptions

In all models, the electrolyte is defined as being composed of only the following ions in water: Pb2+, H+ and CH3SO3-. Methanesulfonic acid is assumed to dissociate fully into H+ and CH3SO3-. The electroneutrality assumption is also employed.

The two-dimensional model further assumes laminar flow within the reaction chamber and perfect mixing in the reservoir. Hence the inlet concentration (averaged over the inlet length) is set to be the volumetric integral of the outlet and reservoir concentration.

* 1. Governing equations

The membrane domain is a porous medium, so the effective diffusion coefficient, Di,eff­, is lower than in the free electrolyte. The Bruggeman correlation is used for calculating the effective diffusion coefficients in the membrane from the porosity, ϵ [12]:

|  |  |  |
| --- | --- | --- |
|  |  | ( 5 ) |

Where Di,eff is used to calculate mobility, um,i becomes um,I,eff. In the membrane, effective diffusion coefficients and mobilities are used. It is assumed there is negligible flow, so the Nernst-Planck equation becomes:

|  |  |  |
| --- | --- | --- |
|  |  | ( 6 ) |

* 1. Boundary conditions
     1. Two-dimensional model

The boundary conditions used were largely the same as in our previous publication [13]. But briefly, the following conditions were employed, Butler-Volmer equations for the kinetics, the Nernst equations to define the equilibrium potential, a constant parabolic velocity profile at the inlet, zero diffusion and current normal to the boundary and zero gauge pressure at the outlet, no-slip wall conditions, a negative electrode potential of 0 V and an average current density equal to the applied current density at the positive electrode.

As there are significant changes of concentration and potential at the membrane boundaries, Donnan potentials may be used to prevent the need for meshing on a nm scale. This gives two values for concentration and electrolyte potential at the membrane-electrolyte interface – one approaching from the electrolyte domain and another approaching from within the membrane, denoted by subscripts 1 and 2 respectively [14]. To do this, the electrochemical potentials for both conditions are set to be equal.

|  |  |  |
| --- | --- | --- |
|  |  | ( 7 ) |
|  |  | ( 8 ) |
|  |  | ( 9 ) |

Where is the electrochemical potential and ci,ref is an arbitrary reference concentration.

* + 1. One-dimensional model

The one-dimensional conductivity validation model used constant concentrations at both boundaries. Potentials at the boundaries were fixed, the boundary potentials were set to 0.1 V and 0 V for the positive and negative respectively.

The one-dimensional model for potential-drop across the membrane also used constant concentrations at each external boundary. A constant current was applied at the positive boundary and a potential of 0 V was applied to the negative boundary.

1. Numerical details

The simulations were run using COMSOL Multiphysics 5.4. Transient simulations used a multifrontal massively parallel sparse direct solver (MUMPS) using backward differentiation formula (BDF) time-stepping and stationary simulations used a parallel direct solver (PARDISO). Default COMSOL values were used for both.

A rectangular mesh with 40 elements vertically by 10 elements horizontally for each electrolyte domain and 5 elements across the membrane domain's width was used. A further 15 boundary layer elements at each electrode boundary and another 5 on the electrolyte side of each membrane-electrolyte boundary were used.

1. Results and discussion
   1. Model validation 1D model

The simple Nernst-Einstein relation is commonly used to calculate the mobility of mobile ions in electrolytes. However, this gives a linear relationship for conductivity vs concentration, as presented in Figure 1a. Krishna et al. have shown that this relationship is non-linear [15]. There is a positive correlation between conductivity and concentration at low concentrations and a negative correlation at higher concentrations. By using eq ( 10 ) in place of the Nernst-Einstein equation, a much closer fit is achieved. The simulated conductivity *vs* concentration of H+ and Pb2+ in an electrolyte with a CH3SO3- counter ion is shown against the experimental data gathered by Krishna et al. in Figure 1b. The model successfully predicts the complex, non-linear relationship between Pb2+ ion concentration and conductivity of the electrolyte as a function of free acid concentration. The model closely matches the experimental data, with a maximum deviation of 22 mS cm-1 and an R2 value of 0.985.

Using a correction factor for the mobility derived from Kohlrausch's square-root law, mobility is defined as:

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| --- | --- | --- |
|  |  | ( 10 ) |

*γcorr* can be related to the activity coefficient, *γi*:

|  |  |  |
| --- | --- | --- |
|  |  | ( 11 ) |

γi is calculated using a variation on the Debye-Hückel equations:

|  |  |  |
| --- | --- | --- |
|  |  | ( 12 ) |

A (0.51) and B(3.29) are constants, a0 is an empirically fitted function with constants δ­i (δH+=0.94331, δPb2+=3.52243, δCH3SO3-=0.18444), and I is the ionic strength:

|  |  |  |
| --- | --- | --- |
|  |  | ( 13 ) |
|  |  | ( 14 ) |

Using this method for calculating mobility in both the electrolyte and the membrane, it is possible to calculate the potential drop across the membrane. Using a Nafion 115 ion exchange membrane, Figure 2 shows the experimental results gathered by Krishna et al. [2], the results by simulating the same technique they used and the simulated potential drop between boundaries at different electrolyte concentrations simulating different Pb2+ utilisations. A reasonable match is found with R2 values of 0.705 and 0.751.

The concentration distributions across the membrane domain and electrolyte domains which extend 2 mm to either side of the membrane, displayed in Figure 3, show the majority of the potential drop across the membrane is due to the resistance of the membrane.



Figure : Simulated and experimental electrolyte conductivity vs concentration of Pb2+ and H+ ions. (a) shows the conductivity calculated using the modified equation for mobility and (b) shows the conductivity using the simple Nernst-Einstein equation. Experimental data from [15].

(a)

(b)

* 1. Divided cell 2D model

In the 2D simulations, as seen in Figure 3, the concentration of each species varies between membrane boundaries, leading to an increase in Donnan potential drop. This is exacerbated with an increase in current density. However, Figure 4, which shows the potential distribution over a 2D simulated flow cell when the cell is run at currents of 10, 20, 30 and 50 mA cm-2 shows the potential drop within the membrane, also increases. In the electrolyte domain, the potential increases almost linearly with distance through the electrolyte. At the membrane-electrolyte interface, however, there are significant changes in the electrolyte – as expected from the concentration profile. Table 1 displays the total potential difference across the membrane, the potential difference due to Donnan potentials and the potential difference within the membrane due to its conductivity. This shows that the membrane conductivity dominates the potential drop across the membrane during both charge and discharge. However, as current density is increased, the ratio of membrane conductivity to Donnan drop decreases.



Figure : Experimental and simulated potential drop across the membranes, (a), and across the electrolyte at different Pb2+ utilisation, (b). A current density of 171 mA cm-1 is used. The two simulated techniques used in (a). One measuring the potential drop between the electrolyte side of the membrane boundaries and another which mimics the experimental technique of measuring the potential difference between points 2 mm either side of the membrane minus the potential drop over an equivalent distance of electrolyte only.

(a)

(b)

Table : Breakdown of potential drop across the membrane during charge and discharge. Current densities of 10, 20, 30 and 50 mA cm-1 are used.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | Potential during charge (mV) | | | Potential during discharge (mV) | | |
| Current Density (mA cm-2) | Donnan (φD) | Conductivity (φC) | Ratio (φC/φD) | Donnan (φD) | Conductivity (φC) | Ratio (φC/φD) |
| 10 | 0.0149 | 1.48 | 84 | 0.0230 | 2.04 | 89 |
| 20 | 0.0487 | 3.99 | 82 | 0.0473 | 4.02 | 85 |
| 30 | 0.0753 | 5.89 | 78 | 0.0728 | 5.94 | 82 |
| 50 | 0.131 | 9.34 | 71 | 0.134 | 9.79 | 73 |

1. Conclusions and further work



Figure : Simulated concentration profiles for each species over the width of the cell during charge (a) and during discharge (b) with an applied current density of 50 mA cm-2. A spike/trough in each of the species is seen in the membrane.

(a)

(b)

This study presents a transient 2-D model, which simulates the operation of the divided SLFB for the first time. The model simulates the electrode reactions and predicts the concentration of all ionic species in the electrolyte and the membrane. Using an improved method for modelling ionic mobility, novel in its application to the SLFB, the model can predict the potential drop due to the change in concentration between electrolyte and membrane domains. However, it shows the resistance to ion movement in the membrane still contributes to the majority of the potential drop across the membrane over the operating range of the SLFB.

This study has set the basis allowing for further development of this model with the inclusion of electrode specific additives, which could lead to an in-depth study considering optimised membrane parameters such as anionic/cationic selection, concentration of the fixed charge within the membrane, porosity and tortuosity of the fixed matrix and dimensions of the membrane and cell. In short, it provides a predictive tool for the electrochemical voltage behaviour when incorporating membranes and additives into the SLFB.



Figure : Electrolyte potential distribution across the midpoint of the cell during charge (a) and discharge (b).

(a)

(b)

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