**2D modelling of a molten carbonate cell for steam electrolysis**

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**1.Introduction**

It is well known that one of the biggest issues with the use of renewable sources consists in their inherent intermittency. In this context, processes that can convert electrical energy into chemical energy represent a viable solution to reduce the imbalance between the rates of production and demand of electricity. These processes are generally referred to as Power-to-Gas (PtG) or Power-to-Liquid (PtL), depending on the physical state of the components used to store the chemical energy. Steam electrolysis falls under the first category, as it allows the production of hydrogen. Compared to water electrolysis, in the steam-based process part of the required energy is provided as heat, thereby allowing a reduction in the amount of electrical energy to be provided. Naturally, the increase in operating temperature of any process is accompanied by mater-related problems. In this context, steam electrolysis based on the use of a molten carbonate electrolyte is interesting because it operates at temperatures around 600°C, which is about 200°C lower than steam electrolysis in solid oxide cells. The lower temperature level is advantageous not only because of the lower strain on the materials, but also because it allows coupling the electrolysis process with mid-scale solar concentrating systems.

 The net electrolysis reaction is

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| --- | --- | --- |
|  | $$H\_{2}O\rightarrow H\_{2}+\frac{1}{2}O\_{2}$$ | (1) |

 and, in molten carbonate cells, it is the result of reduction reaction at the cathode

|  |  |  |
| --- | --- | --- |
|  | $$H\_{2}O+CO\_{2}+2e^{-}\rightarrow CO\_{3}^{2-}+H\_{2}$$ | (2) |

and an oxidation reaction at the anode

|  |  |  |
| --- | --- | --- |
|  | $$CO\_{3}^{2-}\rightarrow CO\_{2}+\frac{1}{2}O\_{2}+2e^{-}$$ | (3) |

Although molten carbonate cells for the electrolysis of water or carbon dioxide have been receiving significant attention in the past years, a literature review has highlighted a complete lack of modelling studies that go beyond so-called “lumped parameter” models capable of describing the correlation between current density and applied voltage without entering into the detail of the cell geometry or operating conditions.

In the present work a 1D model accounting for activation and ohmic overpotentials was developed for a preliminary analysis of experimental data available in the literature [1]. The model was then extended to cells operating at temperatures lower than 550°C. The main difference between the two models (high and mid-temperature) lies in the fact that, while at temperatures higher than 550°C it is possible to work with binary mixtures of Li, Na, or K carbonates, operating below 550°C requires the use of a specific carbonate mixture whose melting temperature is lower than 400°C. The use of a eutectic ternary mixture of Li, Na and K was proposed [2]. Such a mixture is characterized by a different dependence of the ionic conductivity on temperature, which needs to be accounted for when describing ohmic losses. Subsequently, a 2D model, accounting for chemical, electrochemical, and heat transport phenomena was developed. The results have highlighted the importance of ohmic losses in the performance of the cell and have indicated that activation overpotentials at the cathode are negligible.

**2. Methods**

The model was developed for a planar cell made up of porous electrodes separated by a molten carbonate electrolytic matrix. A schematic representation of the cell is shown in Figure 1. A 1D model accounting for ohmic and activation losses was initially developed to analyze experimental data available in the literature [REF]. The 2D model also accounts for gas flow in the square gas channels running parallel to the electrodes. The cathodic gas was considered to be an equimolar mixture of H2O, CO2, H2, and N2; the gas fed to the anode channel was instead a mixture containing 50% N2, 25% O2, and 25% CO2.



***ANODE***

***CATHODE***

*ANODE GAS CHANNEL*

*ELECTROLYTE*

*CATHODE GAS CHANNEL*

**Figure 1.** Schematic representation of the modeled electrolysis cell

The 2D model accounted for

* heat transport
* mass transport
* electrochemical reactions (2) and (3) at the cathode and anode, respectively
* reverse water-gas shift reaction in the cathode channel
* heat effects due to the electrochemical and chemical reactions, as well as Joule heating

It is worth noting that the rate of the electrochemical oxidation semi-reaction taking place at the anode was modelled using the Butler-Volmer rate expression with a reference exchange current density evaluated from the 1D model. On the other hand, the analysis of the experimental data showed that the cathodic reaction was very fast, and therefore offered no significant resistance (infinite exchange current density at the cathode).

**3. Results and discussion**

Figure 2 shows an example of current-potential curves evaluated from the 1D model at different temperatures and considering the exchange current density at the cathode to be sufficiently high as to not have any effect on the performance of the cell. The exchange current density at the anode, on the other hand, was fitted from the experimental data [1 The agreement of the experimental (points) and numerical results confirms the validity of assuming negligible activation overpotentials at the cathode. In addition, the shape of the curves suggests that polarization losses are negligible under the entire range of operating conditions investigated, as highlighted by the fact that the slope of the curves does not increase at high current densities.

**Figure 2.** Current-potential curves evaluated from the 1D model at temperatures ranging from 843 (light blue) to 923 K (dark blue) and comparison with experimental data (points) available in [1].

Extending the model to the lower temperature range allowed to carry a sensitivity analysis on the main process parameters, in order to gain insight on this novel process. Figures 3-5 show the effect of varying the effective ionic conductivity of the electrolyte matrix, the thickness of the electrolyte layer, and the exchange current density at the anode, respectively. The base case values of these parameters, determined from the analysis of experimental data, were 2.82 S/m for the effective ionic conductivity, 0.7 mm for the matrix thickness and 2x10-2 mA/cm2 for the anodic exchange current density. It is interesting to note that the Ohmic resistances seem to have a stronger effect on the overall performance of the cell, suggesting that the correct choice of electrolyte and of its supporting matrix is crucial.



**Figure 3.** Current-potential curves evaluated from the 1D model at 763 K and effective ionic conductivities of the electrolyte of 2, 2.5, 2.82, 3 e 3.5 S/m.



**Matrix thickness**

**Figure 4.** Current-potential curves evaluated from the 1D model at 763 K and thicknesses of the electrolyte layer ranging from 0.1 to 1.3 mm.



**Figure 5.** Current-potential curves evaluated from the 1D model at 763 K and exchange current densities at the anode of 1x10-2, 1.5x10-2, 2x10-2, 2.5x10-2, e 3x10-2 mA/cm2.

The 2D model allowed to determine temperature profiles within the cell and concentration profiles in the gas channels running parallel to the electrode. The temperature was found to be virtually uniform throughout the cell. Typical concentration profiles of hydrogen and water in the cathodic gas channels are reported in Figures 5-8 for a cell operating at 883 K and with an applied potential of 1.5 V and 1.29 V. It is clear that the increase in applied potential favors hydrogen production. The negligible gradients in the direction transversal to that of the main gas flow confirm the finding made with the 1D model that concentration overpotentials are negligible.



**Figure 5.** Water concentration profiles in terms of molar (a) and mass (b) fractions a 5, 25, 65, and 85 mm from the inlet section at 883 K and applied voltage of 1.5 V.



**Figure 6.** Hydrogen concentration profiles in terms of molar (a) and mass (b) fractions a 5, 25, 65, and 85 mm from the inlet section at 883 K and applied voltage of 1.5 V.



**Figure 7.** Water concentration profiles in terms of molar (a) and mass (b) fractions a 5, 25, 65, and 85 mm from the inlet section at 883 K and applied voltage of 1.29 V.



**Figure 8.** Hydrogen concentration profiles in terms of molar (a) and mass (b) fractions a 5, 25, 65, and 85 mm from the inlet section at 883 K and applied voltage of 1.29 V.

**4. Conclusions**

1D and 2D models were developed to describe the behavior of electrolysis cells operating with different mixtures of molten carbonates. It was found that the cathodic activation overpotential is negligible, whereas Ohmic losses in the electrolyte matrix have a significant effect on the performance of the cell. The 2D model allows to account for different mass transport and electrochemical phenomena occurring within the cell, thereby allowing to gain more insight on the mechanisms causing the observed overpotentials. More specifically, the 2D model confirmed that concentration overpotentials are not significant under the range of operating conditions investigated and that temperature gradients may also be neglected.

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