MATHEMATICAL MODELING AND SIMULATION OF CO$_2$ REMOVAL FROM AN ALKALINE SOLUTION FOR FUEL CELLS APPLICATIONS

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ABSTRACT

In order to reduce oil dependency and reduce CO$_2$ emissions stabilizing the greenhouse effect on the planet, the search for new renewable energy sources has been intensified, with a particular interest in hydrogen based solutions. Hydrogen can be used in fuel cells, which have several applications. Fuel Cells are among the environmentally friendly energy conversion systems for the 21st century with simple components such as membrane, catalyst, rearrangeable configurations that allow them to accommodate space limitations, and their use of hydrogen and oxygen. There are many types of fuel cells that are distinguished by the electrolyte type and their operating temperature. Alkaline Membrane Fuel Cells (AMFCs) and Proton-Exchange Membrane Fuel Cells (PEMFCs) are major types that work in low temperatures and produce only H$_2$O and electricity as part of the electrochemical reaction. AMFC is a fuel cell that has more affordable membranes, when compared to the PEMFC that uses a polymeric membrane with high cost, making applications more expensive. In AMFCs, the alkaline membrane used, is a simple filter paper saturated with KOH solution that allows ions to pass through the membrane, however, suffers CO$_2$ poisoning when it gets in contact to the carbon dioxide present in the air, reacting in the KOH and capturing hydroxyl ions. The poisoning will generate chemical compounds that will interfere with the energy generation and efficiency of the fuel cell. The main cause of the decreasing performance of carbonate formation is the precipitation of large metal carbonate crystals such as K$_2$CO$_3$ and the formation of H$_2$O in the membrane, decreasing KOH concentration. If not addressed, this issue will limit the use of AMFC to pure oxygen applications only, instead of the air itself, which restricts the applicability of the technology. This study presents a mathematical model of a purifier that reduces the concentration of CO$_2$ present in the air, improving conditions to be used in AMFC for mobile applications as automotive vehicles and without the need to use pure oxygen.

INTRODUCTION

It is expected that the human population will reach about 9 billion people by 2050 and with this, energy consumption and CO$_2$ emissions will also increase, which may lead to an intensification of climate change and an increase in the greenhouse effect. The need to develop new clean and renewable energy conversion processes has advanced considerably. (Masnadi et al., 2015).

The awareness in climate change and repeated oil crises have increased research and investments in renewable energy sources and technologies that use clean energy with less or no CO$_2$ emissions to control the greenhouse gas effect and achieve the targets to limit global warming to the 1.5 ºC scenario by 2100 (Wang et al., 2011).

In this context, Fuel cells (FC) are a promising technology that can contribute in the global efforts to transform energy conversion approaches. However, there remain technological challenges that limit their use, for example, the need for expensive and rare catalysts (Pan et al., 2017). The use of hydrogen fuel cells is attractive for stationary stacks and some

mobile applications like automotive vehicles because their high energy conversion efficiency of up to 60% and their lack of CO_2 emissions (Negro et al., 2018).

Even with high cost, fuel cells have been used in several applications like vehicles, stationary power plants, trains, and other hybrid systems. The drive to include fuel cells in these applications is in part due to their high energy conversion efficiency, their simple functionality, the absence of noise and harmful emissions. (Benipal et al., 2018).

The alkaline electrolyte was one of the first ones to appear in the context of fuel cells technologies that use hydrogen to provide electricity in alkaline fuel cell (AFC). AFCs use a solution of potassium hydroxide (KOH) as a liquid electrolyte that allows the passage of ions (Gülzow and Schulze, 2014). However, the use of pure oxygen is necessary because the presence of CO_2 leads to reactions forming potassium carbonate and "poisoning" the cell (Merle; Wessling and Nijmeijer, 2011). This problem has led to efforts to incorporate anionic exchange membrane (AEM) in order to effectively replace the liquid electrolyte in the AFC.
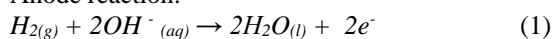
In part the search for new solutions to avoid poisoning in FC led to the development of a proton exchange membrane fuel cell (PEMFC), which over the years has gained popularity. PEMFC works with hydrogen ions in the membrane and avoid the problem with the formation of potassium carbonate seen by AFC. Today PEMFC is used in several applications even with its high cost (Wu, 2016). However, according to Ogata et al. (2016) alkaline membrane fuel cell (AMFC) has the potential to be competitive with PEMFC, as the alkaline membrane is cheaper and can be more favorable for power generation.

The purpose of this work is to use mathematical modeling and simulation to explore the possibility to filter carbon dioxide from the air used in AMFC. The study also involves a parametric analysis applying mass transfer and henry law to know how efficiently the filter can contain the CO_2.
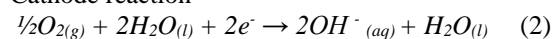
ALKALINE MEMBRANE FUEL CELL (AMFC)

For FC to produce electrical energy, it must be continuously fed with fuel and an oxidizer. This feeding of reagents is especially important when the current intensity is high, as the consumption rate of reagents becomes fast and can become a limiting factor for the overall reaction. For this reason, oxygen inlet control is necessary. The overall reactions are given by:
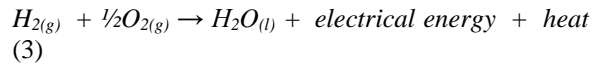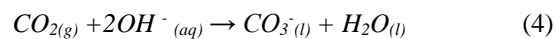
Anode reaction:
$$H_{2(g)} + 2OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + 2e^- \qquad (1)$$

Cathode reaction
$$\tfrac{1}{2}O_{2(g)} + 2H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)} + H_2O_{(l)} \quad (2)$$

Overall Cell reaction:
$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} + electrical\ energy\ +\ heat \qquad (3)$$

AMFC operation is influenced by parameters such as temperature, pressure, and relative humidity of the membrane and of the gas. The membrane allows the exchange of ions and should prevent the transfer of hydrogen from the anode to the cathode. Besides the good ionic conductivity, the membrane can also provide some mechanical stability (Merle; Wessling and Nijmeijer, 2011).

ELECTROLYTE POISONINGS

KOH is one of the best electrolytes to be used in AFC because of its high ionic conductivity, however, KOH solution is very reactive and sensitive to CO_2 in the air, which will react with the hydroxides ions to form carbonates (Schulze and Gülzow, 2004), according to the following reaction:

$$CO_{2(g)} + 2OH^-_{(aq)} \rightarrow CO_3^-_{(l)} + H_2O_{(l)} \qquad (4)$$

$$CO_{2(g)} + 2KOH_{(aq)} \rightarrow K_2CO_{3(s)} + H_2O_{(l)} \qquad (5)$$

The main problem with the formation of carbonate is the decreasing performance of FC, as precipitation of large metal carbonate crystals like K_2CO_3 modifies the composition of the electrolyte and reduces its ionic conductivity. Other problems are related to precipitation of carbonate that may block the pores of the gas diffusion layer (Laminier and Dicks, 2002).

Using membranes instead of liquid electrolytes helped to mitigate the effects caused by CO_2 contamination in the fuel cell, preventing the formation of precipitated carbonates and large crystals that will not be formed to block the gas diffusion electrodes. Other benefits of using the anion exchange membrane include the volumetric stability and easy handling, the reduction of overall size and weight which consequently expands the range of applications, improves efficiency and slows down performance degradation with time.

In spite of their early start, AMFCs are still in an early stage of development. There is a need to identify optimal operating parameters and addressing CO_2 poisoning. it was thought that just changing the liquid electrolyte of the AFC for the alkaline exchange membrane would solve the problem with carbon dioxide, although in smaller amounts carbon dioxide still reacts in membrane and affects the performance of the AMFC along of time (Zheng et al., 2019).

METHODS

As previously stated, AMFCs normally use air taken from the environment as an oxidant for the

reaction to take place and generate electricity, avoiding the use of high purity O_2 for reasons of practicality in use and economic viability. It was reported that the carbonation reaction in the AMFC can be alleviated to tolerable degrees that do not influence so significantly the effectiveness and permanence of the fuel cell, if this concentration of CO_2 can be reduced to scales of 5ppm or less (Gottesfeld et al., 2018). It is of critical importance to significantly reduce the CO_2 concentration in the ambient airflow before feeding it to the cathode of the air-fed AMFCs. Recent efforts (e.g., (Raimundo et al., 2020) and (Liang et al. 2022)), are exploring practical applications using chemistry reactions and membrane systems to mitigate contamination.

To contribute to recent works that have been exploring the containment of CO_2 to prevent its reaction with the alkaline membrane, this work will model and simulate a purifier that filters carbon dioxide when it passes along with the air through a KOH solution. Figure 1 shows a simple schematic of the system. How this system was designed where ambient air enters the cylinder with a certain amount of H_2O and KOH in low concentration.


Figure 1. The model of filter idealized

The strategy adopted for this work aims at passing ambient air through a layer of KOH and H_2O which, when in contact with CO_2, leads to the formation of carbonates that would otherwise be formed inside the AMFC.

The formation of the carbonate proceeds in two steps. Initially, the CO_2 reacts with H_2O and forms the intermediary and unstable acid, H_2CO_3 according to Eq. (6) (Pocker and Bjorkquist, 1977). Notice that this reaction is reversible. The H_2CO_3 reacts with the KOH to from the carbonate (K_2CO_3) which should precipitate in the liquid solution (see Eq. 7).

Reaction (7) is ideal for the objective of the work since the reaction is irreversible and the carbonate would remain in the solution of KOH and would not be taken to the membrane along with the air. This work will not include the chemical species K_2CO_3 of the reaction (7), because the calculation is based on the mass transfer that occurs when entering and leaving the purifier, in line with the objective of

the work, we consider that the potassium carbonate remained in the solution.

$$H_2O_{(l)} + CO_{2(g)} \quad H_2CO_{3(l)} \tag{6}$$

$$H_2CO_{3(l)} + 2KOH_{(aq)} \quad 2H_2O + K_2CO_{3(s)} \tag{7}$$
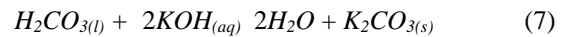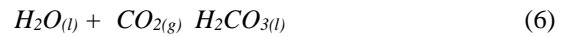
Therefore, the calculations and the simulation will be based on the mass transfer that occurs between the CO_2 entering the system and the liquid phase. The absorption will occur in equilibrium at the gas-liquid interface and in accordance with Henry's law (Seaderet et al., 2016; Han et al., 2013).

MATHEMATICAL MODELING

Using Henry's Law to describe the reaction presented in the Eq. (6), we have:

$$\frac{d[CO_2]}{dt} = \frac{k_L A_1 ([CO_2]-[CO_{2,L}])}{V_L} - \frac{k_L A_2 ([CO_{2,L}]-[CO_{2,L}])}{V_L} - k_1 [CO_{2,L}] + k_2 [H_2CO_3] \tag{8}$$

where, $[CO_2]$ is the inlet carbon dioxide concentration, mol/mL. $[CO_2]$ is the carbon dioxide concentration in the alkaline solution, mol/mL; $[CO_2]$ is the inlet carbon dioxide concentration, mol/mL; $[H_2CO_3]$ is the carbonic acid concentration, mol/mL; k_L is the mass transfer coefficient by convection, cm/s; k_1 is the carbon dioxide kinetic rate, s⁻¹; k_2 is the carbon acid kinetic rate, s⁻¹; A_1 and A_2 are the inlet and outlet area, respectively, cm² and V_L is total volume of the reactants, mL.

The Henry's law coefficient and partial pressure were used to find the carbon dioxide concentration in the air that enters the filter (Seaderet et al., 2016):

$$[CO_2]=H_e \, p_{CO2} \tag{9}$$

where, H_e is the Henry's law coefficient, mol/mL.atm and p_{CO2} is the carbon dioxide partial pressure, atm.

Eq. (10) represents the reaction of CO_2 into H_2CO_3 in the alkaline solution.

$$\frac{d[H_2CO_3]}{dt} = k_1 [CO_{2,L}] - k_2 [H_2CO_3] - k_3 [H_2CO_3][KOH] \tag{10}$$

where k_3 is the potassium hydroxide kinetic rate, s⁻¹; $[KOH]$ is the solution concentration of potassium hydroxide, mol/mL .

Eq. (11) represents the reaction of KOH with H_2CO_3, shown in the Eq. (7), generating potassium carbonate (K_2CO_3). Potassium carbonate is not taken into account in the Eq. (11) because it is a final product of the reaction and does not generate any

other product, therefore, the Eq. (7) it is an irreversible reaction.

$$\frac{d[KOH]}{dt} = -2k_1[H_2CO_3][KOH] \qquad (11)$$

We define the efficiency of the filter as follows:

$$\eta = 100 - 100 \frac{k_1 A_2 [co_{2,L}]}{k_1 A_2 ([co_2] - [co_{2,L}])} \qquad (12)$$

The efficiency of the filter expresses the ratio of CO_2 entering the system to the CO_2 leaving the system. The carbonates formed are not considered because it is an irreversible reaction and it does not leave the filter.

The concentrations $[CO_{2,L}]$, $[H_2CO_3]$ and $[KOH]$ are determined by solving the system of differential equations of second and third order, composed by the Eq. (8), (10) and (11) with the initial and geometric parameters as shown in Table 1.

Table 1. Parameters fixed to simulate equations

Symbol	Parameter	Value	Units
A_1, A_2	Area	1.0	cm^2
k_L	Convection mass transfer coefficient	0.04 (Han et al., 2013)	cm/s
$[KOH]_i$	Initial KOH concentration	0.001	mol/mL
He	Henry's law coefficient	0.000034 (Pandis and Seinfel, 1989)	mol/mL.atm
k_1	Kinetic rate of CO_2	0.04 (Han et al., 2013)	s^{-1}
k_2	Kinetic rate of H_2CO_3	18 (Stumm and Morgan, 1996)	s^{-1}
k_3	Kinetic rate of KOH	2050 (Stumm and Morgan, 1996)	s^{-1}
p_{CO_2}	CO_2 partial pressure	0.00039 (Pandis and Seinfel, 1989)	atm

V_L	Volume of filter	200	mL

RESULTS AND DISCUSSION

The results show the influence of [KOH], A_2 and total volume of reactants V_L.

Figure 2 shows the effect of KOH concentration on the efficiency. It is observed that the *CO₂* removal efficiency increases with the KOH concentration. We can then select a specific KOH concentration based on a desired efficiency. It can be seen that with a relatively low KOH concentration (0.004 mol/mL) we can reach efficiency above 95%.

In Figure 3, we explore the effect of the outlet area. We observed that the bigger the outlet area (Fig. 1) the lower the efficiency. A bigger outlet area reduces the contact time between the air/CO₂ and the alkaline solution, reducing the formation of carbonic acid, consequently reducing the efficiency of the filter.
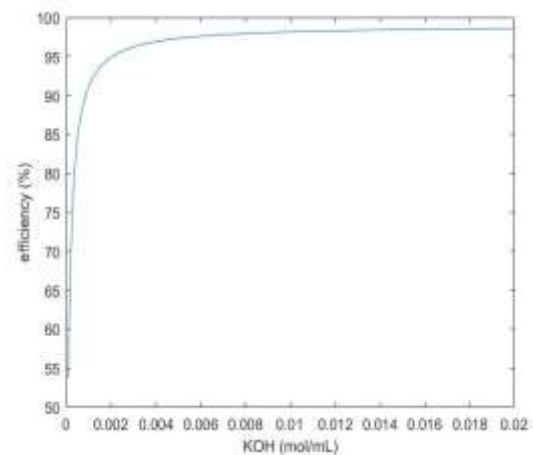

Figure 2. Steady state efficiency of the filter as a function of KOH concentration.
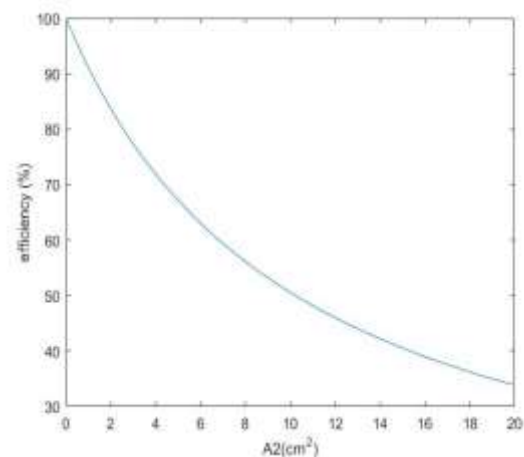

Figure 3. Steady state efficiency of the filter as a function of the outlet area.

Another important parameter to be evaluated is the time that the system takes to reach steady state. Fig. 4 shows that the efficiency is 100% at t=0s because at the beginning there is no CO_2. As the time progresses the $[CO_{2,L}]$ increases and according to the Eq. (12) the efficiency decreases until it reaches a lower limit (approximately 85%).

In Figure 5, the same analysis was performed in relation to efficiency, the volume was varied to determine which reactant volume will deliver the highest efficiency. We can observe that the efficiency does not change significantly for volumes above 600 mL. Higher volumes will demand more unnecessary KOH which would only increase the cost of the process and require larger spaces.
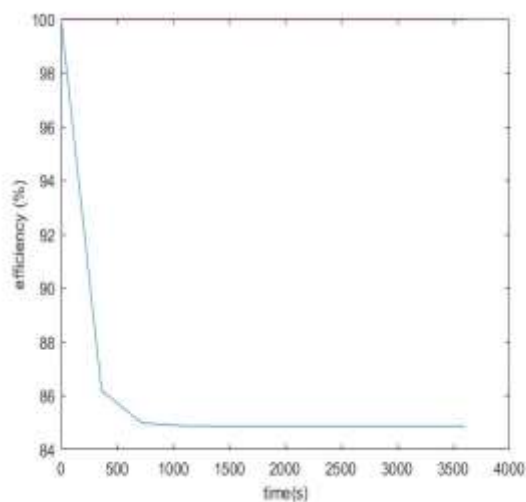

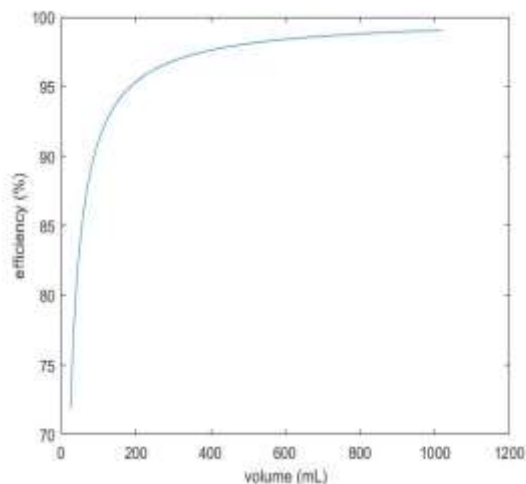Figure 4. Determination of the steady state efficiency.

Figure 5. Steady state efficiency as a function of the reaction total volume.

According to the aforementioned results, it can be stated that the system has the potential to become part of fuel cells systems, since the alkaline membrane fuel cells have efficiency decreased due to CO_2 poisoning.

The results are very satisfactory since the filter reaches high efficiency in the robust and simplified way in which it is presented.

CONCLUSIONS

This study presented a mathematical model and simulation of a carbon dioxide filter to solve a problem that has been gaining more attention in recent years, which is the poisoning of alkaline membrane fuel cells (AMFC) by carbon dioxide. AMFC has the economic and power output competitive capacity for large applications. Still, poisoning by CO_2 is herein proposed to be solved by a carbon dioxide filter that allows cleaner and contaminant-free ambient air to enter the fuel cell.

The simulation results show a high capacity of the system to retain carbon dioxide in the KOH solution and make the air free of contaminants, doing the application more helpful and possibilities more advantageous for AMFC and increasing its use.

The results presented show a clear possibility of real applications. The simulations also show great gains in the use of the filter, due to the high efficiency of 95% using a low concentration of KOH, high filtering capacity for small volumes of solution, and no need for high investments for construction.

There is a need for laboratory experiments to validate the simulation, but the results show a great possibility to apply in AMFCs and can solve the years-long problem of membrane poisoning. There are opportunities for improvement in their design and membrane development to improve efficiency and make the system more compact and user-friendly.

ACKNOWLEDGEMENTS

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