Transient ion exchange of anion exchange membranes exposed to carbon dioxide

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HIGHLIGHTS

- Theoretical investigation of ion exchange process in an AEM exposed to CO_2.
- Model studies transient behavior of CO_3^{2-} and HCO_3^- formation.
- CO_2 hydration found to be the rate limiting kinetic step.
- CO_2 diffusion has a significant effect of the rate of ion conversion.

ARTICLE INFO

ABSTRACT

A common issue with anion exchange membranes (AEMs) is carbon dioxide contamination which causes a conversion from the hydroxide form to a mixed carbonate/bicarbonate form. In the mixed ionic form the membrane suffers from lower conductivity due to the larger and heavier ions having a lower mobility. The purpose of this study is to develop a theoretical model of the transient ion exchange process and elucidate the nature of the conversion of the AEM from a hydroxide form to a carbonate/bicarbonate form. Experimental data available from the literature providing the anion concentrations versus time are used for comparison. The prevalent mechanisms are discussed and the governing equations are cast in a dimensionless form. Extensions are then made to conductivity predictions.

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1. Introduction

The anion exchange membrane fuel cell (AEMFC) has potential application as a portable power source [1]. One of the competing technologies is the proton exchange membrane fuel cell (PEMFC). The PEMFC is a comparatively mature technology; however, there are a number of factors which make the AEMFC attractive as a substitute. Some of the advantages of the AEMFC include more facile electrochemical kinetics which can enable the reduction or replacement of some platinum group catalysts, an alkaline environment which can support less expensive packaging materials, and opportunities to simplify the balance of plant at the system level [1–7].

State of the art AEMs are similar in concept to the benchmark PEM Nafion, produced by DuPont. The AEM membranes consist of a polymer backbone material with an embedded functional group, benzyltrimethylammonium hydroxide for example. As the membrane becomes hydrated, the anions (e.g., hydroxide) dissociate from the fixed cationic group (i.e., side chain) and act as charge carriers for ion transport. It is believed that the mechanisms for ion transport in the AEMs may be similar to that described for the PEM [8–12]. In this case the overall transport consists of several components which can include en masse diffusion, migration, convection, Grotthuss behavior, and site hopping between the fixed cationic side chain groups [13–16].

There are a variety of AEMs which have been synthesized. The list of materials that have been developed, including with methods

Nomenclature

C_i	species concentration (mol cm^{-3})
C_i^{ref}	reference concentration (mol cm^{-3})
D_{i,H_2O}	species/water diffusivity (cm^2 s^{-1})
D_i^{eff}	effective species diffusivity (cm^2 s^{-1})
F	Faraday's constant (C mol^{-1})
IEC	ion exchange capacity (mol g^{-1})
J_i	species flux (mol cm^{-2} s^{-1})
k_{abs}	absorption coefficient (cm s^{-1})
k_H	Henry's constant (cm^2 N^{-1})
k_j^+	forward kinetic rate constant (cm^3 mol^{-1} s^{-1})
k_j^-	reverse kinetic rate constant (s^{-1}, cm^3 mol^{-1} s^{-1})
K_j	equilibrium constant (mol cm^{-3}, mol^2 cm^{-6})
L	membrane thickness (cm)
$M_{H_2O_{(j)}}$	molecular mass of water (g mol^{-1})
$M_{i,k}^*$	reduced molecular mass (g mol^{-1})

$P_{CO_2}^{gas}$	partial pressure of CO$_2$ (N cm^{-2})
q	Bruggeman exponent
R	ideal gas constant (J mol^{-1} K^{-1})
$\dot{R}_i$	species kinetic source terms (mol cm^{-3} s^{-1})
t	time (s)
T	temperature (K)
x	position (cm)
z_i	valance

Greek

α	degree of dissociation
ε	porosity
λ	water content
$\rho_{H_2O_{(l)}}$	density of water (g cm^{-3})
ρ_m	membrane density (g cm^{-3})
σ	ionic conductivity (S cm^{-1})

that are analogous to those which have been developed and used within the PEM community, is too exhaustive to review here and interested readers are pointed toward reviews on the subject [17,18]. One common technique involves the functionalization of a polymer, such as polysulfone, via chloromethylation followed by a quaternization step using trimethylamine [19–22]. The resulting membranes can then be exchanged to a hydroxide form by performing ion exchange in a base solution, such as KOH. Varcoe and co-workers [1,23–25] developed membranes which consist of preformed films of fluorinated ethylene propylene (FEP) or ethylene tetrafluoroethylene (ETFE) which are radiation grafted with vinylbenzyl chloride before subsequently being quaternized with trimethylamine and alkanized. The group reported favorable mechanical properties and reasonable ionic conductivities (30 mS/cm vs. Nafion's reported 90 mS/cm for fully hydrated conditions at 30 °C). The Tokuyama Corporation's A201 and A901 membranes are also worth mentioning due to the wide variety of investigations published on them [26–30]. Being produced through a commercial manufacturing process, they tend to have relatively consistent properties and reasonable conductivities (~20 mS/cm at 23 °C in saturated conditions [26]).

For AEMs to become a practical material for fuel cell applications, the community has identified several issues which must be adequately addressed [31]. Among these issues are:

- *Stability* – Chemical degradation of the AEM materials are commonly reported due to nucleophilic attack or the Hoffman elimination process [1,19].
- *Ionic conductivity* – AEMs display lower ionic conductivities than their PEM counterparts. This is expected, in part, because hydroxide (and carbonate/bicarbonate) ions have a lower mobility in water. Anion-exchange cation groups tend not to dissociate as freely as the sulfonic acid groups found in Nafion, meaning the ions are more confined within the membrane. To some degree, the conductivity of the AEMs can be increased by increasing the ion exchange capacity (IEC) but this comes at the price of mechanical stability since increasing the number of functional groups can cause a higher degree of swelling at fully hydrated conditions and brittleness in the dry state [19].
- *Carbon dioxide interaction* – Exposure of the AEM to carbon dioxide causes an ion exchange process. The counter-ions in the membrane convert from a hydroxide to a carbonate/bicarbonate composition [26,27,29,30]. These bulkier anions have lower

mobility in the membrane than the hydroxide, leading to the lower conductivities. While conductivity suffers, it has been noted by Vega et al. that the stability of the membrane is improved in the carbonate/bicarbonate form [32]. Literature has already shown that the hydroxide anions can be completely displaced even in the presence of air which contains roughly 385 ppm carbon dioxide. It has however, been reported that carbonate/bicarbonate ions can be displaced from the operating fuel cell via what is commonly referred to as the self-purging mechanism [27,29].

The focus of the present study is on the carbon dioxide interaction issue. This issue is directly linked to two commonly reported shortcomings of AEMs: ionic conductivity and stability. Carbon dioxide contamination lowers ionic conductivity which can be recovered by increasing the ionic membrane's ionic content (IEC) but with a negative impact on the mechanical stability. However, it has been noted that the carbonate/bicarbonate form of the membrane is markedly more stable than the hydroxide form giving incentive to investigate operating the fuel cell with a carbonate/bicarbonate form membrane. Whichever route is chosen, understanding the fundamental interaction between AEMs and carbon dioxide is important for fuel cell design. This research will seek to employ modeling techniques to understand the ion exchange process between the hydroxide anions and the carbonate/bicarbonate anions. In developing the model, comparisons will be made to titration data available in the literature as a means of validation [27,33]. Dimensional analysis on the governing equations is performed with calculated Thiele moduli used to help explain the prevalent physics in the system. Finally, an extension to calculate membrane conductivity is made.

2. Theory

Ion exchange measurements of an AEM have been made by Varcoe et al. on their ETFE membranes [33] as well as the Tokuyama Corporation on their A201 membranes [27]. These membranes, initially in a hydroxide form, were exposed to normal atmospheric air containing carbon dioxide under open circuit conditions (the membranes did not have electrodes). Warder's titration method was used by the groups to measure the IEC contributions of hydroxide, carbonate, and bicarbonate in their respective membranes over time upon exposure to air containing carbon dioxide starting