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Modeling the effect of membrane conductivity on the performance of alkaline fuel cells

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HIGHLIGHTS

- We proposed a model for the ionic conductivity of membranes in alkaline media.
- The key model parameters are the solution concentration and the temperature.
- We integrated the proposed description into an alkaline fuel cell model.
- Including the membrane conductivity leads to more accurate results.
- The ohmic overpotentials are highly sensible to temperature variations.

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ABSTRACT

The present work proposes and demonstrates a methodology to capture the effect of operating conditions on ionic conductivity of membranes immersed in alkaline media. Based on reported experimental results for an anion exchange membrane (A-201 by Tokuyama) and a cation exchange membrane (Nafion 211), two novel expressions are developed for the ionic conductivity by incorporating the effects of solution concentration and temperature. The expression for the cationic conductivity is applied in a cell-level model to predict the performance of an alkaline direct borohydride fuel cell; it is found that the membrane ionic conductivity significantly affects the cell performance and capturing its functionality is essential to accurately predict the fuel cell performance.

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1. Introduction

Fuel cells offer several advantages over conventional energy systems; they are (i) far more efficient, (ii) scalable to small sizes, and (iii) environmentally friendly. Their development is frequently guided by numerical modeling techniques (e.g. CFD, multiphysics modeling, etc.) that build on the availability of analytical descriptions of the performance of key fuel cell components.

The simulation of alkaline fuel cells has grown in the last few years; Verma and Basu [1] developed a mathematical model for methanol, ethanol, and sodium borohydride fuel cells which includes the electrooxidation mechanisms of these fuels. An et al. [2] formulated a model for direct ethanol fuel cells that incorporates the activation and concentration losses in the cell. Shah [3] numerically captured the effect of hydrogen evolution due to incomplete reactions in direct borohydride fuel cells (DBFC). However, current mathematical models ignore the fact that the membrane conductivity varies with temperature and solution concentration [4–6]. A suitable methodology for describing the ionic conductivity is required to accomplish a better numerical prediction.

Different studies have tried to capture the ionic conductivity of membranes immersed in alkaline media. Stegen et al. [7] developed a model for Na^+ ions based on the Maxwell–Stefan theory; in this model, the binary diffusivities were fitted to experimental values in a chloralkali process at standard conditions. Grew et al. [8] proposed a model for OH^- ions based on the same theory but assuming that these anions behave analogous to protons; the percolation

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Nomenclature

A_0	frequency factor (S cm^{-1})
C	constant in the exponential term in Eq. (1) (dimensionless)
C_k	molar concentration of species k (M)
E_a	activation barrier (J mol^{-1})
E_{cell}	operating cell voltage (V)
E_r	reversible open circuit voltage (V)
F	Faraday constant (96485 C mol^{-1})
j	current density (A cm^{-2})
$K_{H_2O_2}$	constant for hydrogen peroxide reduction (mol cm^{-2} s^{-1})
K_{NaBH_4}	constant for sodium borohydride oxidation (mol cm^{-2} s^{-1})
n	number of electrons transferred in the electrochemical reaction (dimensionless)
R	universal gas constant (8.314 J mol^{-1} K^{-1})
T	operating temperature (K)
t	thickness (μm)

Greek letters

α	charge transfer coefficient (dimensionless)
η_{act}	activation overpotential (V)
η_{ohm}	ohmic overpotential (V)
Λ	molar conductance (S cm^2 mol^{-1})
σ	membrane ionic conductivity (mS cm^{-1})

Subscripts/Superscripts

ξ	CEM or AEM
AEM	anion exchange membrane
CEM	cation exchange membrane
sol	aqueous solution

theory was used to account for the membrane structure, and the Brunauer-Emmett-Teller equation for the effect of the water content. Even when these methods acceptably predict the membrane ionic conductivity, they utilize fitted constants—only valid for particular conditions—and employ relatively complex mathematical relations that highly limit their application.

The aim of this study was to develop a simple but accurate analytic method to determine, from the solution concentration and temperature, the conductivity of cationic exchange membranes CEMs (with mobile Na^+ ions) and anionic exchange membranes AEMs (with mobile OH^- ions) immersed in alkaline media. We asked whether the ionic conductivity of these membranes can be accounted for in a similar fashion to the method proposed by Springer et al. [9] for proton exchange membranes, which has been extensively used for the simulation of proton exchange membrane fuel cells.

2. Model development

An anion exchange membrane (AEM) is a solid polymer electrolyte matrix composed of positive functional groups e.g. quaternary ammonium (poly-N^+ CH3) that electrostatically attract negative ions [10]. In real operation, a diffusional transport of neutral species occurs through the opening areas of the matrix [11]. Water is dragged by OH^- ions [12]. The main advantages are: (i) elimination of carbonate precipitation due to null interaction between Na^+ and CO_2 in the cathodic chamber [13], and (ii) superior conductivity due to high OH^- mobility. The major drawback is that its functionality decays in alkaline media at elevated temperatures due to poor chemical stability of the quaternary cations [14]. Moreover, studies reveal that an AEM is a heterogeneous structure with regions of minimal or no conductive groups which potentially lower the ionic conductivity [11]. A cation exchange membrane (CEM) is composed of negatively charged functional groups e.g. $-SO_3^-$ which electrostatically attract positive ions. The CEM transports water molecules by electroosmotic drag [15]. Due to membrane pretreatment in an alkaline solution, alkali doped free volumes may form in the CEM which could conduct hydroxide ions [16]. Anions and cations of neutral compounds separately pass through a CEM, alkali doped free volumes attract the anions and sulfonic groups attract the cations [17,18]. A CEM has good chemical, thermal, and mechanical stability [2]. In comparison to an AEM, the CEM has lower conductivity mainly due to the low Na^+ mobility. However, the homogeneous structure of the CEM offers a more facile ion transport, which compensates the low Na^+ ion mobility [11].

The present work describes a methodology that captures the ionic conductivity of an AEM and a CEM immersed in alkaline media. The work developed by An et al. [4] is used as the basis for the methodology. An et al. experimentally characterized the conductivity of both an AEM (A201 provided by Tokuyama) and a CEM (Nafion 211), each of which has been employed in alkaline media fuel cells. In their work, the AEM and CEM were pretreated to activate the membranes for OH^- and Na^+ conduction, respectively. The membranes were then immersed in NaOH solutions, and their resistance was measured by electrochemical impedance spectra. The analyzed parameters were the NaOH solution concentration (varied in a 0–10 M range), and the temperature (23, 40 and 60 °C). The authors found that, as the concentration increases, the conductivity initially increases, passes through a maximum and then decreases. A similar behavior was noted in other studies [5,6]. For the temperature dependence, the authors reported a linear increment of the conductivity with an increase in temperature.

It is important to mention the similarity of the results from An et al. to other experimental studies. For the CEM, An et al. reported a membrane ionic conductivity of 5–10 mS cm^{-1} at room temperature, whereas Ma et al. [19] recorded a value of 7.4 mS cm^{-1} for a Nafion 212 immersed in a 10 wt.% (2.8 M) NaOH solution at room temperature, and Chandran et al. [6] reported a conductivity between 2 and 6 mS cm^{-1} for a Nafion 901 immersed in a 2–10 M NaOH solution at room temperature. Similarly, for the AEM, An et al. measured an ionic conductivity in the range of 5–30 mS cm^{-1}, whereas Unlu et al. [20] reported a conductivity of 21.1 mS cm^{-1} for an AEM immersed in a 1 M potassium hydroxide solution, and Agel et al. [21] reported OH^- conductivities in the range of 10–40 mS cm^{-1} for 0.5–8 M KaOH concentrations.

Similar to the model of Springer et al. [9], the model proposed in the present work captures the relationship between the membrane conductivity, NaOH concentration, and temperature, by the product of two terms: one term that determines the conductivity as a function of the concentration but at a specific temperature, and a second term —an exponential term— that accounts for the effect of the temperature, see Eq. (1).

$$\sigma^{\xi}(C_{NaOH}, T) = \sigma^{\xi}_{23C}(C_{NaOH}) exp\left[C_{\xi}\left(\frac{1}{296} - \frac{1}{T}\right)\right] \quad (1)$$

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