Role of the diffuse layer in acidic and alkaline fuel cells

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ABSTRACT

A numerical model is developed to study electrolyte dependent kinetics in fuel cells. The model is based on the Poisson–Nernst–Planck (PNP) and generalized-Frumkin–Butler–Volmer (gFBV) equations, and is used to understand how the diffuse layer and ionic transport play a role in the performance difference between acidic and alkaline systems. The laminar flow fuel cell (LFFC) is used as the model fuel cell architecture to allow for the appropriate comparison of equivalent acidic and alkaline systems. We study the overall cell performance and individual electrode polarizations of acidic and alkaline fuel cells for both balanced and unbalanced electrode kinetics as well as in the presence of transport limitations. The results predict cell behavior based on electrolyte composition that strongly correlates with observed experimental results from literature and provides insight into the fundamental cause of these results. *Specifically, it is found that the working ion concentration at the reaction plane plays a significant role in fuel cell performance including activation losses and the response to different kinetic rates at an individual electrode.* The working ion and the electrode where its consumed are different for acidic and alkaline fuel cells. Therefore, we compare the role of the diffuse region in both acidic and alkaline fuel cells. *From this we conclude that oxidant reduction at the cathode and slow fuel oxidation (such as alcohol oxidation) can be improved with an alkaline electrolyte.*

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1. Introduction

The basic principle of fuel cell technology has been known since the late 1830s but it was not until the mid twentieth century that it was proven to be a viable option for power generation with the introduction of the alkaline fuel cell. During that time, alkaline fuel cells were the prevalent fuel cell technology and as such were given substantial research interest. The most common alkaline fuel cell is the mobile electrolyte fuel cell whose basic physical structure consists of an anode and a cathode separated by a flowing alkaline electrolyte solution [1]. However, despite several advantages over their acidic counter parts, including superior oxidant reduction and alcohol oxidation, alkaline fuel cells suffer some major limitations at the device level that lead to significant reduction in interest in alkaline fuel cells [2].

In recent years, acidic fuel cells (i.e. proton exchange membrane fuel cells (PEMFC)) have risen to prominence in the fuel cell community as the preferred low temperature solution. The PEMFC uses a solid acidic membrane to separate the anode and cathode [1] and has been studied extensively both experimentally and numerically [3–6]. There have also been mathematical models presented in literature for alkaline fuel cells [7–13] although they are significantly less abundant. These models tend to focus on the system level description of fuel cells (especially for alkaline fuel cells), and to our knowledge there are no theoretical works for comparing fundamental differences in acidic and alkaline fuel cells.

At the basal level, the primary differences between and acidic and alkaline fuel cell are the electrolyte and the working ion. Here we are using "working ion" to mean the ion that is produced at one electrode and migrates across the electrolyte to be consumed at the other electrode, thus completing the circuit. To study how the electrolyte and working ion affect fuel cell operation, the ionic transport within the electrolyte must be modeled explicitly. Additionally, it is essential to include electric double layer (EDL) effects due to the strong influence the diffuse layer has on ionic concentrations at the reaction plane of an electrode [14]. These phenomena can be modeled using the Poisson–Nernst–Planck (PNP) equations. The PNP equations have successfully been applied to galvanic cells [15,16] and fuel cells [17–20] in the literature.

At the functional level one of the primary differences between acidic and alkaline fuel cells is that oxygen reduction and simple alcohol oxidation kinetics are superior in alkaline fuel cells than in acidic fuel cells [2]. The fundamental cause of the improved kinetics in alkaline cells is of paramount interest [21–24]. One general explanation was offered by Spendlow and Wieckowski [21], who suggested that the working potential range of an electrochemical process is often limited to a range in which water is stable. This range shifts with increasing pH according to the Nernst equation, which can affect the local double layer structure at the electrode thus impacting the kinetics. However, despite all the research there

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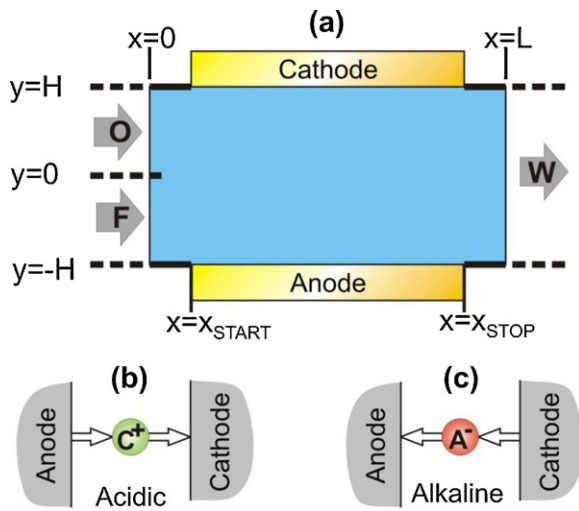*E-mail address:* dutta@mail.wsu.edu (P. Dutta).

Fig. 1. (a) Schematic of the computational domain for a LFFC depicting two inlets (fuel and oxidant) and a single outlet (waste). The walls are located at $Y=\pm H$ with the electrodes in the domain $x_{Start} \leq x \leq x_{Stop}$. The working ion type and flux direction within the electrolyte are depicted for both (b) acidic and (c) alkaline media. In the case of an acidic fuel cell, cations (C^+) migrate from the anode to the cathode while in an alkaline fuel cell, anions (A^-) migrate from the cathode to the anode.

does not seem to be an axiomatic justification for the altered electrode kinetics between acidic and alkaline media. *In this work we offer a unique explanation of altered electrode kinetics by studying how the diffuse layer and ionic transport play a significant role in the performance differences of acidic and alkaline systems.*

For direct comparison between acidic and alkaline fuel cells, a fuel cell architecture that is compatible with both acidic and alkaline fuel cells must be selected to isolate the electrolyte and ionic transport effects from the physical system differences. One such architecture is the laminar flow fuel cell (LFFC) which has been studied in acidic [25–27] and alkaline [28,29] media due to their excellent fuel and electrolyte flexibility. Another benefit of selecting a LFFC for our comparison is their relatively simplistic design and operation, which is ideal for mathematical analysis. Several models of LFFCs have been presented in the literature [30–34].

In our previous works we presented a mathematical model for a LFFC based on the PNP equations for ionic transport and a generalized Frumkin–Butler–Volmer (gFBV) equation for electrode kinetics [19,20]. The focus of this work is to study a LFFC using the gFBV-PNP model adapted for acidic and alkaline media. We studied overall device performance, the anode and cathode polarizations for each case, and the performance response to changing reaction kinetics as well as reactant concentrations in both acidic and alkaline fuel cells.
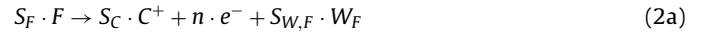
2. Model development

Fig. 1a shows the schematic of the laminar flow fuel cell system with separate fuel and oxidant inlets and a single waste outlet. For simplicity, the computational domain is selected from just upstream of the electrodes at $x=0$ to just downstream of the electrodes at $x=L$. The channel walls are located at $y=\pm H$ with the anode defined at $y=-H$ and the cathode at $y=H$. The anode and cathode electrodes are located between $x=x_{Start}$ and $x=x_{Stop}$ where $0 < x_{Start} < x_{Stop} < L$. A simple redox reaction of fuel (F) and oxidant (O) producing waste (W) is considered for both the acidic and alkaline systems. The overall stoichiometric equation is:

$$S_F \cdot F + S_O \cdot O \rightarrow S_{W,F} \cdot W_F + S_{W,O} \cdot W_O \tag{1}$$
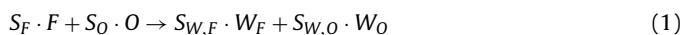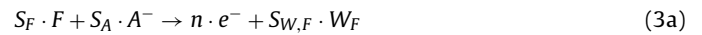
where W_F is the waste produced by fuel oxidation and W_O is the waste produced by oxidant reduction. These terms may be

neglected if there is no waste (e.g. hydrogen oxidation) or if the waste is water which is adsorbed into an aqueous solution at a constant chemical potential (as is the case for oxygen reduction). For methanol oxidation, however, the waste W_F is CO_2 which is a gas but present in concentrations far below its solubility limit and remains dissolved in the aqueous bulk electrolyte.

For ease of analysis, the reaction is considered to proceed in the presence of a simple binary electrolyte consisting of an anion (A^-) and a cation (C^+) each of unit charge, $z_c = -z_A = 1$. The working ion and half reactions of fuel oxidation and oxidant reduction depend on the type of system considered, acidic or alkaline. For an acidic electrolyte the cation is the working ion, being produced at the anode and consumed at the cathode, Fig. 1b. Therefore, in the acidic case the half reactions become:

$$S_F \cdot F \rightarrow S_C \cdot C^+ + n \cdot e^- + S_{W,F} \cdot W_F \tag{2a}$$

$$S_C \cdot C^+ + n \cdot e^- + S_O \cdot O \rightarrow S_{W,O} \cdot W_O \tag{2b}$$

where n is the number of electrons involved in the reaction and depends on the specific reactants in the overall reaction. On the other hand, for an alkaline electrolyte the anion is the working ion which is produced at the cathode and consumed by the anode, Fig. 1c. Therefore, the half reactions for the alkaline case become:

$$S_F \cdot F + S_A \cdot A^- \rightarrow n \cdot e^- + S_{W,F} \cdot W_F \tag{3a}$$

$$S_O \cdot O + n \cdot e^- \rightarrow S_A \cdot A^- + S_{W,O} \cdot W_O \tag{3b}$$

It is assumed that in an acidic fuel cell the anion is inert, while in an alkaline fuel cell the cation is the inert ion.

2.1. Electrode kinetics

The rate at which the above half reactions proceed is determined by the electrode kinetics at the electrolyte–electrode interface located at the anode and cathode in the presence of the EDL. The electrode kinetics are governed by the generalized Frumkin–Butler–Volmer equation (gFBV), which gives the net current for a specific half reaction as a function of the potential drop across the inner region of the EDL and the concentration of the reactants at interface (reaction plane) of the inner and outer regions. The Stern model of the electric double layer assumes a linear potential drop across the inner region, called the Stern layer, that is continuous with the potential in the outer region, called the diffuse layer [35]. The gFBV equations for the fuel and oxidant reactions in an acidic fuel cell are respectively:

$$J_{F,Net} = J_{F,O} - J_{F,R} = Fn[(K_{F,O}^{Acidic} C_F e^{((1-\beta)\Delta\phi_S F/RT)})$$
$$- (K_{F,R}^{Acidic} C_{C^+} C_W e^{-(\beta\Delta\phi_S F/RT)})] \tag{4a}$$

$$J_{O,Net} = J_{O,O} - J_{O,R} = Fn[(K_{O,O}^{Acidic} C_W e^{((1-\beta)\Delta\phi_S F/RT)})$$
$$- (K_{O,R}^{Acidic} C_O C_{C^+} e^{-(\beta\Delta\phi_S F/RT)})] \tag{4b}$$

where $\Delta\phi_S$ is the potential difference across the Stern layer. From this equation it is clear that the net current from a specific half reaction is the difference between the oxidation (forward) and reduction (reverse) currents. Similarly, the gFBV equations for the fuel and oxidant reactions in an alkaline fuel cell are respectively:

$$J_{F,Net} = J_{F,O} - J_{F,R} = Fn[(K_{F,O}^{Alkaline} C_F C_{A^-} e^{((1-\beta)\Delta\phi_S F/RT)})$$
$$- (K_{F,R}^{Alkaline} C_W e^{-(\beta\Delta\phi_S F/RT)})] \tag{5a}$$

$$J_{O,Net} = J_{O,O} - J_{O,R} = Fn[(K_{O,O}^{Alkaline} C_W C_{A^-} e^{((1-\beta)\Delta\phi_S F/RT)})$$
$$- (K_{O,R}^{Alkaline} C_O e^{-(\beta\Delta\phi_S F/RT)})] \tag{5b}$$