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Mathematical modeling of gas evolution from flowing electrolytes on stable porous anodes of finite matrix phase conductivity

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Abstract

A mathematical model was developed to simulate the effects of the matrix phase conductivity on the behavior of flow-through porous anode operating for gas evolution reaction. The anode material was assumed to be stable and has a finite conductivity. The model accounts for the conductivities of the solution and the matrix phases, the electrode kinetics, hydrodynamics and gas bubble formation. The different ratios and values of the matrix conductivity group, K_σ (a measure of the matrix conductivity) and the electrolyte conductivity group, K_κ (a measure of the electrolyte conductivity) were found to have significant effects on the distributions of current, potential and gas void fraction. When K_σ was a finite value the reaction was pushed towards the back of the electrode and when K_κ was finite the reaction was pushed towards the front face. The effects of the bubble group, χ on the potential and current distributions were investigated under different impacts of K_σ and K_κ. When K_σ was limited the gas bubbles formed at the back of the electrode were forced to travel within the whole bed with the electrolyte streams, causing larger accumulation of the bubbles and hence higher polarization within the bed. The gas bubble formation limited the conductivity of the pore electrolyte resulting in potential and current distributions similar to the case of finite electrolyte conductivity.

Keywords: Mathematical modeling; Gas bubbles; Porous; Conductivity; Anode

1. Introduction

Mathematical modeling of porous electrodes has always been an important way to understand the behavior of such systems for different applications [1–3]. This could not be a surprise if we considered that porous electrode is the heart of many technological and industrial processes. For instance, fuel cells, water treatment and electrolysis cells [4–6] are important examples. The modeling of three-phase (gas–liquid–solid) porous electrodes is of special importance from academic and practical point of view. While measurements on such systems and optimization could face physical limitations, mathematical modeling of such systems can introduce insight and guidelines for optimization and design of such systems [7,8]. The gas evolution reaction on flow-through porous electrodes can introduce a reasonable method to produce high purity gas such as hydrogen [9,10]. Porous electrodes are typically made with conductive materials, but these may degrade under high temperatures or anodic potential conditions. This problem is of less importance for fuel-cell anode catalysts, which operate at relatively low potentials but it can be quite significant for electrolyzers [11]. In previous modeling of gas evolving flow-through porous cathode, the effect of the matrix phase conductivity was considered to be negligible with respect to the electrolyte phase conductivity [12,13]. In other applications such as anodic oxygen, ozone or chlorine generation, there is a growing trend to use so-called dimensionally stable anodes (DSA), which contain oxides in its structures and hence its conductivity may not be considered as negligible [14,15]. While theoretical and experimental works have been conducted extensively for the anodic gas evolution on planar electrodes, a few studies have been reported on porous electrodes [16–20]. Flow-through porous electrodes can introduce a good candidate for such anodic reaction with a proper design and understanding of the behavior of such systems. A special extra advantage of flow-through porous electrode for the purpose of the present work is the continuous feed of a solution

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saturated with a desired gas, e.g. ozone. The theory and applications of porous electrode have been reviewed in several articles [21–24]. The effects of the matrix conductivity on the behavior of the flow-through porous electrodes have been studied but in the absence of gas bubbles [25,26].

It is the purpose of the present study to introduce a general model to account for the effects of the matrix phase conductivity on the behavior of flow-through porous electrode operating for anodic evolution of gaseous phase products. A system of governing equations is introduced and solved numerically. It includes the effects of electrode kinetics, hydrodynamics and matrix phase and electrolyte phase conductivities on the current, potential and gas void fraction distributions within the porous electrode. Those effects will be discussed in the light of the present theory of porous electrodes.

2. Mathematical model

Fig. 1 shows the porous electrode arrangement and direction of flow. The mathematical model was developed under the following conditions. The model is one-dimensional and hence the variables are functions only of the x-direction. The porous electrode is considered to consist of a continuum of two phases, each phase is either pure ionic or electronic conductor [27]. Butler–Volmer equation governs the kinetic charge transfer rate of the electrochemical reaction. The reaction is of zero order in the reactant and involves one electron rate-determining step and is only charge transfer controlled. It is assumed that the porous matrix has a uniform porosity, θ and does not undergo anodic dissolution.

The electrochemical reaction at the porous anode can be represented as:

$$A^{-z} \rightarrow \tfrac{1}{2}A_2 + ze^- \tag{1}$$

where the evolved gas, A_2 is of limited solubility in the electrolyte. Defining current as positive and using Butler–Volmer equation along with the above assumptions, the gradient of the ionic current i_2 which enters the pore solution is given by [28]:

$$\frac{\mathrm{d}i_2(x)}{\mathrm{d}x} = i_0 a[\mathrm{e}^{nf(1-\alpha)(\Phi_1-\Phi_2-E^0)} - \mathrm{e}^{-nf\alpha(\Phi_1-\Phi_2-E^0)}] \tag{2}$$

where Φ_1 and Φ_2 are the potentials of the solid phase and the solution phase, respectively. Note that the difference $(\Phi_1 - \Phi_2 - E^0)$ is the polarization, η at specific solution current density, i_2. The gradient of potential inside the matrix phase is related to the electronic current by ohm's law:

$$i_1(x) = -\sigma\frac{\mathrm{d}\Phi_1}{\mathrm{d}x} \tag{3}$$

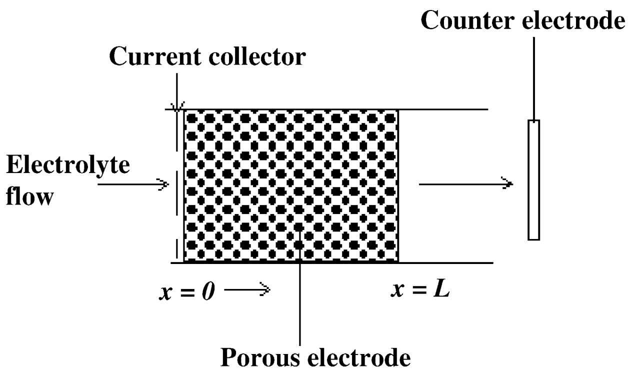

Fig. 1. Schematic of the cell arrangement and flow direction.

where σ is the matrix conductivity and it is assumed to be constant within the bed. The ionic current in the solution phase, i_2 is correlated to the gradient of the potential in the solution phase by

$$i_2(x) = -\kappa(x)\frac{\mathrm{d}\Phi_2}{\mathrm{d}x} \tag{4}$$

where $\kappa(x)$ is the pore electrolyte conductivity and it varies with the distance inside the bed. It depends on the composition and extent of bubble generation within the pore electrolyte (see Eq. (7)). Combining Eqs. (3) and (4) yields

$$\frac{\mathrm{d}\eta(x)}{\mathrm{d}x} = \frac{i_2(x)}{\kappa(x)} - \frac{i_1(x)}{\sigma} \tag{5}$$

The sum of the divergences of the solution and matrix current densities equals zero as a consequence of the electroneutrality. Mathematically, this can be expressed by [27]:

$$\frac{\mathrm{d}i_1(x)}{\mathrm{d}x} + \frac{\mathrm{d}i_2(x)}{\mathrm{d}x} = 0 \tag{6}$$

The pore electrolyte conductivity, $\kappa(x)$ is correlated to the electrolyte conductivity in the bulk outside the pores, κ^0 by Bruggeman's equation [29,30]:

$$\kappa(x) = \kappa^0[\theta - \varepsilon(x)]^{1.5} \tag{7}$$

where $\varepsilon(x)$ is the gas void fraction and is proportional to the current which is producing it. The latter can be given by (see Appendix B for derivation of Eq. (8)):

$$\varepsilon(x) = \frac{\theta i_2(x)}{\upsilon\gamma + i_2(x)} \tag{8}$$

where υ is the superficial flow rate and γ is the coefficient of Faradaic gas generation which is a factor converting the solution current to volume of the generating gas bubbles, such that [30]:

$$\gamma = \frac{2PF}{RT} \tag{9}$$

Assuming ideal gas behavior, and assuming two Faradaic electrons per one mole of the evolved gas (as 2 appears in Eq. (9)), γ equals 7.9 C cm^{-3} at standard temperature and pressure.

Eqs. (2), (5)–(8) describe the behavior of the system and give the distributions of the variables, i_1, i_2, η, κ and ε within the porous electrode. Substituting dimensionless variables: $\bar{i} = (i/I_0)$, $\bar{\eta} = \eta f$, $\bar{\kappa} = (\kappa/\kappa^0)$ and $y = x/L$ one can obtain the system of equations in dimensionless form as follows:

$$\frac{\mathrm{d}\bar{i}_2(y)}{\mathrm{d}y} = [\mathrm{e}^{(1-\alpha)\bar{\eta}} - \mathrm{e}^{-\alpha\bar{\eta}}] \tag{10}$$

$$\frac{\mathrm{d}\bar{\eta}(y)}{\mathrm{d}y} = \frac{\bar{i}_2(y)}{K_\kappa\bar{\kappa}(y)} - \frac{\bar{i}_1(y)}{K_\sigma} \tag{11}$$