Short communication

Membrane water-flow rate in electrolyzer cells with a solid polymer electrolyte (SPE)

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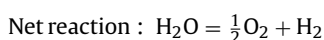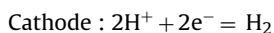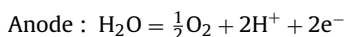
ABSTRACT

Water-flow rate across Nafion membrane in SPE electrolyzer cells was measured and modelled. From the analysis of water transport mechanisms in SPE water electrolysis, the water-flow rate through membrane can be described by the electro-osmotic drag. The calculated electro-osmotic drag coefficients, n_d, for the membrane in SPE electrolysis cells at different temperatures were compared with literature and in good agreement with those of Ge et al. and Ise et al. To describe the water-flow rate through membrane more accurately, a linear fit of n_d as a function of temperature for the membrane in SPE water electrolysis was proposed in this paper. This paper studied the membrane water-flow rate experimentally and mathematically, which is of importance in the designing and optimization of the process of SPE water electrolysis. This paper also provided a novel method for measuring the electro-osmotic drag coefficient of Nafion membrane in contact with liquid water, acid and methanol solutions, etc.

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1. Introduction

The solid polymer electrolyte water electrolysis, developed by the General Electric Company, is now considered as one of the most promising methodology for generating hydrogen/oxygen from nuclear, solar or other non-fossil fuel sources [1]. As an alternative to the conventional alkaline water electrolysis, SPE water electrolysis is unique in that it uses solid polymer electrolyte instead of liquid electrolytes. So there is no leakage, corrosion or possible hazard of electrolyte to deal with in SPE electrochemical cell.

The SPE water electrolysis consists of an anode, cathode and a solid polymer membrane. The electrolyte membrane, usually Nafion®, is sandwiched in between anode and cathode. On the anode side, water is dissociated to produce gaseous oxygen, protons (H^+), and electrons (e^-). On the cathode side, hydrogen ions combine with electrons to form gaseous hydrogen. The electrochemical reactions for the SPE water electrolysis are as follows:

$$\text{Anode}: H_2O = \frac{1}{2}O_2 + 2H^+ + 2e^-$$

$$\text{Cathode}: 2H^+ + 2e^- = H_2$$

$$\text{Net reaction}: H_2O = \frac{1}{2}O_2 + H_2$$

The feed water for the electrolysis process can be supplied on either side of the electrolyzer cell. For the case of water supplied at the anode side, due to the electro-osmotic drag and diffusion, the water migrates from the anode to the cathode through Nafion membrane. So the feed water on the anode side is required to offset not only the process water for electrolysis but also water-flow across membrane. It is of importance to investigate the membrane water-flow rate in electrolyzers with SPE for the design and optimization of the process. Over the last two decades, there has been growing interests in studying SPE electrolyzer experimentally and numerically [2–6]. For example, Millet [2,3] has computed the electrical potential distribution and the temperature profiles across a Nafion membrane during SPE water electrolysis. Onda et al. [4] made a performance analysis for the polymer electrolyte electrolysis cell (PEEC) and found the constant profiles of current density and temperature along the water-flow direction. Harrison et al. [5] used a semiempirical equation to represent the performance characteristics of a 20-cell SPE electrolyzer stack. Goldberg et al. [6] proposed a hydrodynamic model for two-phase water electrolysis filtration in porous electrocatalysts and current collectors using a SPE. However, to our knowledge, no study concerning on the membrane water-flow rate in electrolyzers with SPE was reported.

Fortunately, many papers have been concerned on the water transport through membrane in polymer electrolyte fuel cell, which is beneficial for predicting the water-flow rate in electrolyzer cells. To predict the water-flow rate across membrane in SPE water electrolysis, an accurate description of the diffusion flux and the flux due to electro-osmotic drag is required. Using nuclear mag-

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netic resonance (NMR) techniques, Zawodzinski et al. measured the diffusion coefficient of Nafion membrane [7]. Motupally et al. found that the diffusion flux across Nafion membrane can be accurately predicted by using the self-diffusion coefficient expression for water [8]. However, for the flux due to electro-osmotic drag, electro-osmotic drag coefficients and their dependence on the water content in Nafion membrane varied significantly in the literature [6,9–11]. As far as the drag coefficient for membrane in contact with liquid water is concerned, there also exist arguments [6,9,12–16]. For example, an electro-osmotic drag coefficient, $n_d = 2$, was adopted in the hydrodynamic model for PEEC [6]. Whereas, Zawodzinski et al. reported $n_d = 2.5$ for membranes in contact with liquid water [12]. In addition, the electro-osmotic drag coefficients in Nafion membrane in contact with acid and methanol solutions was also investigated [17–21], which are higher than that in liquid water. For example, the n_d value given by Pivovar et al. [19] is up to 6 for the membrane in contact with aqueous sulfuric acid solution.

The objective of this paper is to investigate the water-flow rate across membrane, as well as to quantify the electro-osmotic drag coefficient of Nafion membrane in SPE water electrolysis. For this purpose, the water-flow rate across Nafion in electrolyzer cells was measured at different operating currents and temperatures. Finally, the electro-osmotic drag coefficient was calculated as a function of temperature and also compared with the literature.

2. Experimental

The schematic illustration of SPE water electrolysis in present study is shown in Fig. 1. A 35-cell SPE electrolyzer stack is used in the experiment with an active area of 162 cm^2. In this paper, the electrolyte membrane is Nafion® (N-115, DuPont) and the preparation of the catalyst-coated membrane (CCM) can be referred to Ref. [22].
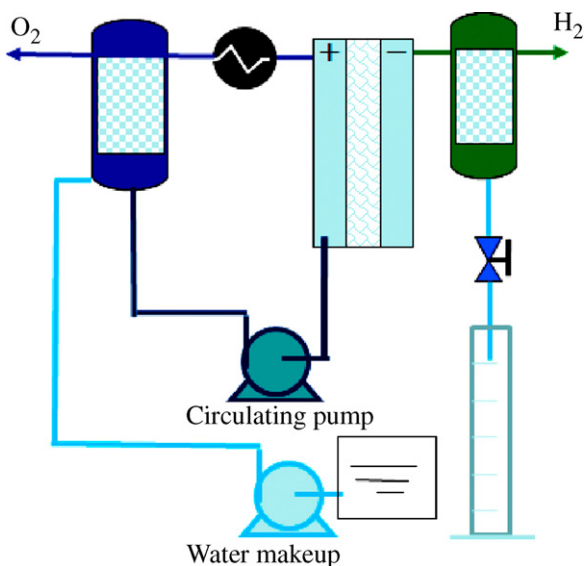
The feed water for the electrolysis is supplied at the anode side, which is circulated to perform the thermal management, as well to provide the process water for the electrolysis stack. Due to electro-osmotic migration of water with the proton, the hydrogen generated at the cathode side also contains liquid water and needs to be separated before usage or storage. The water exiting the cell on cathode side is collected in a water-separator and the gas leaves the separator with water-saturated pressure. The amount of water-flow across the membrane is the sum of water in the water-separator plus the amount of water vapor leaving the separator. In this study, the temperature of the electrolysis cell and the existing gases is kept equal in the range of 330–340 K. And the pressure in both sides of anode and cathode is also kept in equal of atmosphere. The time interval for water collection is about 0.2–1 h, due to the difference of the cell operating current.

3. Model development

Assumptions—Fig. 2 shows the schematic diagram of water transport in SPE electrolysis cell. For the water transport process for a membrane in contact with liquid water, the assumptions and simplifications adopted in the present model are as follows: The membrane is in contact and in equilibrium with liquid water on both sides of the cell. The gas mixture is assumed ideal. In the flow channel, a plug flow is assumed and the gas and liquid water are perfectly well mixed in the x direction. The pressure in both sides of anode and cathode is in equal. The membrane is considered impervious for product gases. The whole cell operates under uniform current density and temperature [2,3].

Water flux across the membrane—In the membrane, water is transported by electro-osmotic drag, back-diffusion, and convection generated by pressure gradient. In this work, there is no pressure drop between anode and cathode, so the convection of water is neglected. As the thickness of the membrane is much less than its length, the diffusion of water in the y direction is neglected. Due to the equilibrium of the membrane with liquid water in both sides of the cell, the diffusion of water in x direction is also neglected. So the local flux of water-flow through the

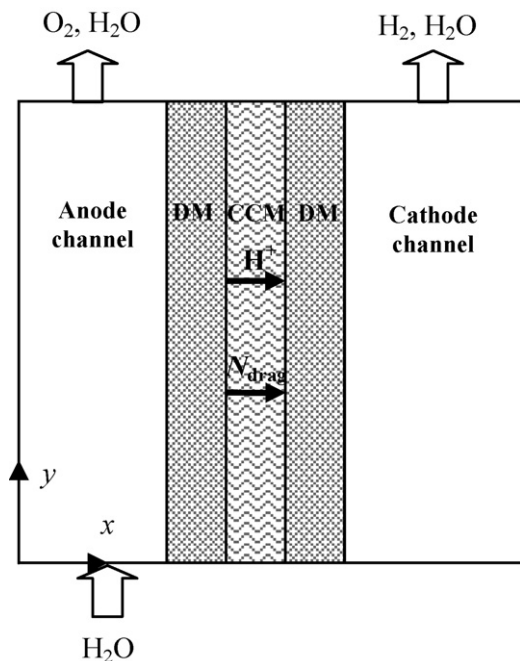**Fig. 1.** The schematic diagram of experimental setup for SPE water electrolysis.

Fig. 2. The schematic diagram of water transport in SPE electrolysis cell.

membrane, $N_{w,x}$, can be simplified as follows

$$\dot{N}_{w,x} = n_d \frac{j}{F} \tag{1}$$

where j is the local current density, F is Faraday constant and n_d is the electro-osmotic drag coefficient of water in membrane. The total flux of water-flow across membrane can be expressed as follows:

$$\dot{N}_w = n_d \frac{j}{F} A = n_d \frac{I}{F} \tag{2}$$

where A is the catalyst-coated membrane area, I, the operating current of electrolysis cell.

Parameters—It can be clearly seen that the membrane water flux in SPE electrolysis cells is a function of electro-osmotic drag coefficient and cell operating current. However, the electro-osmotic drag coefficient of Nafion membrane in contact with liquid water is varied significantly in the literature [6,9,12–15,23]. In Ref. [6], electro-osmotic drag coefficient, $n_d = 2$, was adopted in their hydrodynamic model in PEEC. The drag coefficient was measured by Zawodzinski et al. for membranes immersed in liquid water ($n_d = 2.5$) [23] and for membranes at equilibrium with water vapor over a wide range of activities ($n_d = 1$) [9]. Ise et al. [14] showed that n_d increases with increasing temperature and water content ($\lambda = 11$–20) and the n_d value for the membrane with water content of 13 at temperature of 22 and 79 °C are 1.7 and 2.5. Ge et al. [15] investigated the electro-osmotic drag coefficient of water in the Nafion 117 membrane in contact with liquid water at different temperatures and their results are slightly higher than those of Ise et al. [14].

Besides, the electro-osmotic drag coefficient has also been related to the membrane water content [9,10]. Measuring the water content, λ, of membrane in contact with liquid water, Zawodzinski et al. [12] reported λ values of 17 and 22 of Nafion membrane in contact with liquid water at 30 and 80 °C, respectively. However, Ise et al. [14] reported the λ value of 20 for the fully hydrated Nafion membrane at 79 °C. The difference of water content between Ref. [12] and Ref. [14] was probably due to the measurement errors. In conclusion, the values/expressions of electro-osmotic drag coefficient for membranes equilibrated with liquid water, are listed as follows.

$$n_d = \begin{cases} 2 & [6] \\ 2.5 & [12-14,23] \\ -1.834 + 0.0126T & [15] \quad (3) \\ 0.1875\lambda - 1.625 & [9] \quad \lambda > 14 \quad (4) \end{cases}$$

4. Result and discussion

The fluxes of water through the membrane in contact with liquid water were investigated at different cell currents and temperatures. In this work, the operating current of electrolysis cell at 330, 332, 336, 340 K is in the range of 5–20 A. The measured membrane water-flow rate per cell at 340 K is shown in Fig. 3. The simulated water flux through Nafion membrane in contact with liquid water is also shown in Fig. 3 from the literature. In Fig. 3, the experimental values increase linearly with the cell operating current and are in agreement with the simulated results with $n_d = 2.5$. Therefore, it is verified that the water flux of membrane in electrolysis cells with SPE can be modeled by Eq. (2) and the corresponding electro-osmotic drag coefficient for Eq. (2) is 2.5 for currents in the range of 5–20 A.

Fig. 4 shows the effect of temperature on the electro-osmotic drag coefficient. The results from Ise et al. and Ge et al. are also shown in Fig. 4. Our results show that the electro-osmotic drag coef-
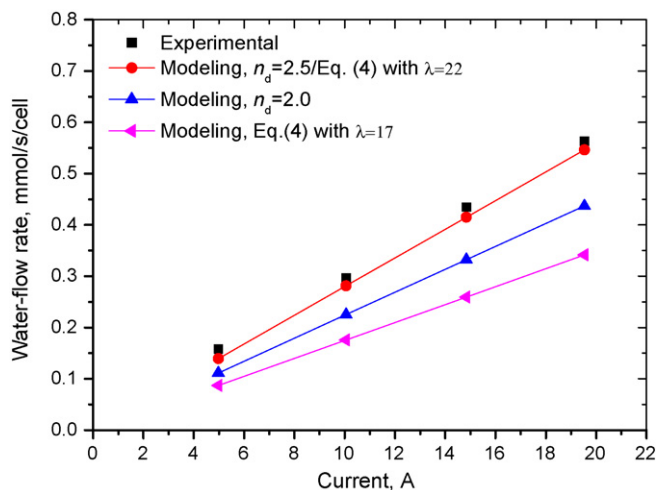

Fig. 3. Water flux across the membrane at different current density ($T = 340$ K).
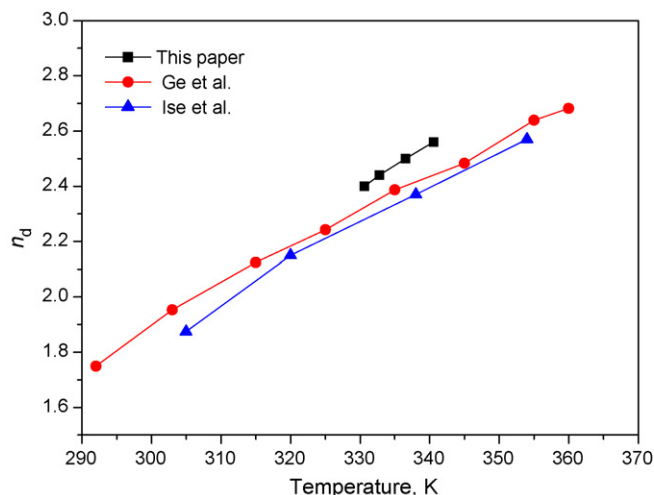

Fig. 4. Effect of temperature on the electro-osmotic drag coefficient of Nafion membrane.

ficient increase linearly from 2.4 at the temperature of 330 K to 2.56 at 340 K, which is in agreement with those reported. Our n_d value is very close to but slightly higher than those of Ise et al. and Ge et al. This is probably due to the difference of membrane water content in ours, Ise's and Ge's experiments. In their tests, polymer electrolyte membrane fuel cell was used. But the electrolysis cell with SPE was used in our experiments and the catalyst-coated membrane of electrolysis cell was completely immersed in liquid water. The water content of Ise's and Ge's is reported of 13 and 16.8 in their tests, but 19 and 20.1 at 330 and 340 K in our experiments. Using the data shown in Fig. 4, a fit of n_d as a function of temperature for the membrane in SPE electrolysis cell is as follows.

$$n_d = -2.89556 + 0.016T \tag{5}$$

5. Conclusions

In this paper, the water-flow rate across Nafion membrane of electrolysis cells was investigated at different current densities and temperatures. From the modeling of water transport mechanisms, the water-flow rate through membrane in SPE electrolysis cell is mainly due to the electro-osmotic drag. The measured electro-osmotic drag coefficient of Nafion membrane in SPE electrolysis cell was investigated as a function of temperature and also com-

pared with those of Nafion membrane in contact with liquid water. The measured electro-osmotic drag coefficients, n_d, in this work is very close to but slightly higher than those of Ise et al. and Ge et al. Therefore, a linear fit of n_d as a function of temperature for the membrane in SPE water electrolysis cell was proposed in this paper. This paper studied the membrane water-flow rate experimentally and mathematically, which is of importance in the designing and optimization of the process of SPE water electrolysis. This paper also provided a novel method for measuring the electro-osmotic drag coefficient of Nafion membrane in contact with liquid water, acid and methanol solutions, etc.

Acknowledgements

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