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Short communication

An electrochemical device with a multifunctional sensor for gas diffusivity measurement in fuel cells

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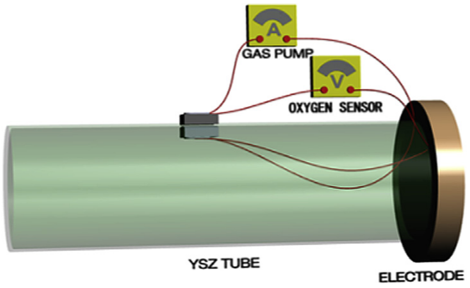
HIGHLIGHTS

- Designs a multifunctional sensor device for accurate diffusivity measurement.
- Eliminates temperature uncertainty in the diffusivity measurement.
- Improves efficiency of evaluating concentration polarization & limiting current.

GRAPHICAL ABSTRACT



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ABSTRACT

Mass transport is of paramount importance to the electrochemical performance of fuel cells. The high performance of fuel cells requires a large diffusion coefficient, *i.e.* the diffusivity, of the gas transport in electrodes and efficient gas diffusion can lead to large limiting currents and controlled concentration polarization. Recently-designed electrochemical devices allow for the direct evaluation of gas diffusivity in fuel cells. To realize these devices, a gas pump and an oxygen sensor are typically attached to two different spots of the inside wall of an electrolyte tube, which inevitably induces the uncertainty in measurement temperature. To eliminate temperature uncertainty in the diffusivity measurement, an electrochemical device with a multifunctional sensor is designed in this report. Quantitative analysis shows that temperature uncertainty can indeed induce substantial evaluation errors of gas diffusivity, limiting current density and concentration polarization, which in turn verifies the necessity of the multifunctional sensor device for the accurate diffusivity measurement in fuel cells.

1. Introduction

The high performance of fuel cells requires efficient mass transport in the electrolytes and the porous electrodes. To acquire efficient mass transport, the conduction of ionic species and the diffusion of gaseous fuel species must be fast [1–3]. In recent years, it has become the key focus in the fuel cell field, especially in the solid oxide fuel cell (SOFC) area, to develop fuel cell materials that exhibit improved conduction and diffusion properties at relatively low operation temperatures [4,5]. Such efforts have resulted in tremendous scientific findings in the fuel cell area and have brought about insightful implications in the general energy area. For instance, Santamaria et al. reported the colossal conductivity at the interfaces of crystalline ZrO_2:Y_2O_3/$SrTiO_3$ heterostructures [6]. Vertically-aligned nanocomposite material $(Ce_{0.9}Gd_{0.1}O_{1.95})_{0.5}$/$(Zr_{0.92}Y_{0.08}O_{1.96})_{0.5}$(GDC/YSZ) with pronounced ionic conductivity was realized via a PLD method by Wang et al [7]. To achieve fast

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diffusion at a low operating temperature, Hussain et al. prepared nickel-ceria infiltrated Nb-doped $SrTiO_3$ anodes with highly-efficient diffusion properties [8]. Park et al. employed a screen-printing method to synthesize (La, Sr)CoO_3-based multilayered composite cathode materials that exhibit pronounced transport properties [9]. In parallel, the techniques for the measurement of mass transport in fuel cells have also been well advanced in recent years [10–12]. In particular, the authors have designed sensor-based electrochemical devices for the direct measurement of gas diffusivity in fuel cells [13–18]. The measured gas diffusivity provides the quantitative basis for the efficient evaluation of limiting current density and concentration polarization, which are two key performance parameters in fuel cells. However, all the previous electrochemical devices designed by the authors neglected the temperature uncertainty caused by the different positions of the oxygen pump and the oxygen sensor across the electrolyte tube. As a consequence, errors in the gas diffusivity measurement and the subsequent evaluations of limiting current and concentration polarization were inevitably induced according to Eqs. 1–6,

$$\Delta D^{\mathrm{eff}}_{\mathrm{H_2-H_2O}} = \frac{RTl_a i}{4F\left(p^{\mathrm{o}}_{\mathrm{H_2}} - \Delta p^{\mathrm{i}}_{\mathrm{H_2}}\right)} \tag{1}$$

$$\Delta D^{\mathrm{eff}}_{\mathrm{O_2-N_2}} = \frac{RTl_c i}{8F\left(\Delta p^{\mathrm{i}}_{\mathrm{O_2}} - p^{\mathrm{o}}_{\mathrm{O_2}}\right)} \tag{2}$$

where T is the measurement temperature, F is the Faraday constant, R is the gas constant, i is the applied current density, l_a (l_c) is the anode (cathode) thickness, $D^{\mathrm{eff}}_{\mathrm{H_2-H_2O}}$($D^{\mathrm{eff}}_{\mathrm{O_2-N_2}}$) is the effective binary gas diffusivity of the anode (cathode), $p^{\mathrm{o}}_{\mathrm{H_2}}$($p^{\mathrm{o}}_{\mathrm{O_2}}$) is the H_2 (O_2) pressure out of the measurement device, and $p^{\mathrm{i}}_{\mathrm{H_2}}a(p^{\mathrm{i}}_{\mathrm{O_2}})$ is the H_2 (O_2) pressure in the YSZ tube of the device [13–18].

$$i_a \approx \frac{4Fp^{\mathrm{o}}_{\mathrm{H_2}}D^{\mathrm{eff}}_{\mathrm{H_2-H_2O}}}{RTl_a} \tag{3}$$

$$i_c \approx \frac{8Fp^{\mathrm{o}}_{\mathrm{O_2}}D^{\mathrm{eff}}_{\mathrm{O_2-N_2}}}{RTl_c}\left(\frac{p_t}{p_t - p^{\mathrm{o}}_{\mathrm{O_2}}}\right) \tag{4}$$

where i_a (i_c) is the anode (cathode) limiting current density, and p_t ($\sim$1 atm) is the total pressure of gaseous species in the measurement system.

$$\eta_a = -\frac{RT}{2F}\ln\left(1 - \frac{i}{i_a}\right) + \frac{RT}{2F}\ln\left(1 + \frac{p^{\mathrm{o}}_{\mathrm{H_2}}i}{p^{\mathrm{o}}_{\mathrm{H_2O}}i_a}\right) \tag{5}$$

$$\eta_c = -\frac{RT}{4F}\ln\left(1 - \frac{i}{i_c}\right) \tag{6}$$

where η_a (η_c) is the concentration polarization of the anode (cathode), and $p^{\mathrm{o}}_{\mathrm{H_2}}$ ($p^{\mathrm{o}}_{\mathrm{H_2O}}$) is the pressure of the anode gas (H_2–H_2O) [13–15].

In this report, we eliminate the temperature uncertainty in the gas diffusivity measurement in fuel cells by proposing an electrochemical device with a multifunctional sensor. Our analysis shows that the electrochemical device largely improves the accuracy in the direct gas diffusivity measurement and the evaluations of limiting current and concentration polarization. The device along with the quantitative analysis is expected to facilitate the development of low-temperature fuel cells with reduced energy loss.

2. Materials and methods

2.1. Multifunctional-sensor electrochemical cell device

The electrochemical device proposed for the diffusivity measurement in solid oxide fuel cells is shown in Fig. 1. Without special notes, all the following results and discussions in this report are centered on solid oxide fuel cells. In principle, the device can be employed for the diffusivity measurement in any type of fuel cells upon adjustment of the electrolyte and electrode materials in the device. The proposed device, as shown in Fig. 1, exhibits two obvious advantages over previous electrochemical devices for the gas diffusivity measurement in fuel cells. First, in the previous electrochemical devices, electrolyte discs were attached to the ends of the electrolyte tubes, which could cause gas leak in the diffusivity measurement. Furthermore, the electrolyte discs were typically obtained *via* complex treatments including die pressing, polishing and high-temperature annealing, etc. The employment of the electrolyte disc on one end of the electrolyte tube in the proposed electrochemical device is avoided. The basic frame of the electrochemical device only consists of an electrode to be measured and an electrolyte tube with only one open end and thus, the device is much simplified compared to the previous electrochemical devices. Second, the oxygen sensor and the oxygen pump are located at the same spot across the electrolyte tube. Therefore, the oxygen pump and the oxygen sensor can be operated at the same temperature, and as a result the temperature uncertainty in the diffusivity measurement is eliminated.

2.2. Theoretical analysis for cathode diffusivity measurement

The working mechanisms of anode and cathode diffusivity measurements are similar, and for simplicity we here analyze the working principle of the cathode diffusivity measurement [10]. In the cathode diffusivity measurement, the proposed electrochemical device is placed at the center of a tube furnace and purged with O_2–N_2 gas mixture. With an applied current *via* the oxygen pump (Fig. 1) in an O_2–N_2 flow at a fixed flow rate, a flux of O_2–N_2 gas mixture is induced through the porous cathode sample (Fig. 1) according to the Faraday's law, and the correlation between the flux and the applied current is expressed in Eq. (7),

$$J_{O2} = \frac{i}{4F} \tag{7}$$

where J_{O2} is the O_2 flux induced by the applied current i. Such an induced gas flux results in the pressure difference inside and out of the proposed electrochemical device in the tube furnace. After

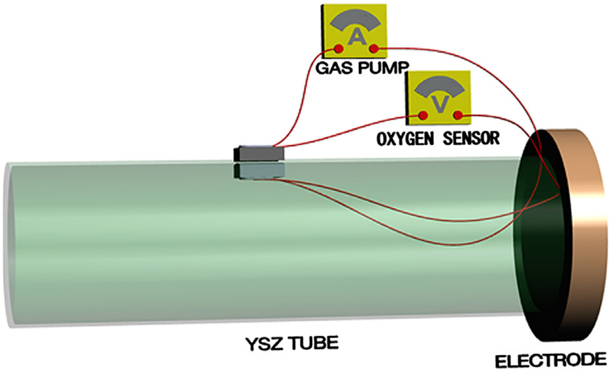

Fig. 1. An electrochemical device with a multifunctional sensor for accurate gas diffusivity measurement in fuel cells. The operation mechanism is based on Eqs. 1–6 and the equilibrium gas reaction of $2H_2O(g) \Leftrightarrow 2H_2(g) + O_2(g)$.