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Short communication

A current-sensor electrochemical device for accurate gas diffusivity measurement in fuel cells

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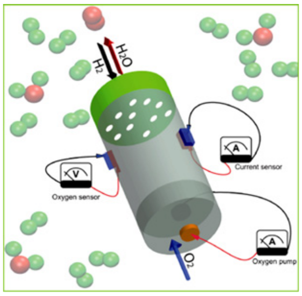
HIGHLIGHTS

- ► Designs a current-sensor device for accurate fuel cell diffusivity measurement.
- ► Improves evaluation accuracy of concentration polarization & limiting current.
- ► Shows that the proposed device is reliable for fuel cell electrode pre-evaluation.

GRAPHICAL ABSTRACT



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ABSTRACT

In the previous diffusivity measurements via the electrochemical devices designed by the authors, the electronic conduction contribution of electrolyte materials was neglected, and an error in the subsequent evaluations of limiting current density and concentration polarization was consequently induced. In this report, a current-sensor and oxygen-sensor based electrochemical cell was designed for accurate diffusivity measurements in fuel cells. Our analytical investigation shows that diffusivity measurements via the new device lead to accurate analytical evaluations of limiting current density and concentration polarization in fuel cells. With the improved accuracy, one can reliably pre-evaluate the limiting current density and concentration polarization of fuel cell electrodes with different thicknesses ranging from several nanometers to a few millimeters at different operating temperatures.

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1. Introduction

To facilitate the sustainable advancement of our society, reducing energy crisis has become more urgent than ever. Hydrogen-based fuel cells have emerged into an efficient component in current renewable energy policy. Many novel materials and structures have been developed to improve the energy conversion efficiency and lifetime of the existing fuel cell devices, including solid oxide fuel cells (SOFCs), proton exchange membrane fuel cells (PEMFCs), and molten carbonate fuel cells (MCFCs) [1–5]. In particular, highly-porous nanostructured electrodes have drawn tremendous research interest in the past decade due to their promising features, such as pronounced mechanical strength, and low polarization loss [6–9]. Among the polarization losses of fuel cells, including concentration polarization (*CP*), Ohmic loss (*OL*) and activation loss (*AL*), *CP* is a function of gas diffusivity in fuel cells,

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and reliable gas diffusivity measurements can help one to make efficient strategies to reduce the *CP* of a fuel cell system [10–13]. *CP* is a function of gas diffusivity, which correlates with the important parameters associated with an electrode, such as porosity and tortuosity, as shown in Eqs. (1)–(4),

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

$$\eta_c = -\frac{RT}{4F}\ln\left(1-\frac{i}{i_c}\right) \tag{2}$$

$$D^{\mathrm{eff}}_{H_2-H_2O} = \frac{\varphi_q}{\tau_a}D_{H_2-H_2O} \tag{3}$$

$$D^{\mathrm{eff}}_{O_2-N_2} = \frac{\varphi_c}{\tau_c}D_{O_2-N_2} \tag{4}$$

where $\eta_a(\eta_c)$ is the anode (cathode) concentration polarization, $p^{o}_{H_2}(p^{o}_{H_2O})$ is the pressure of anode H_2 (H_2O) gas, i is the operating current, $i_a(i_c)$ is the diffusivity-dependent anode (cathode) limiting current density (*LCD*), *F* is the Faraday constant, *R* is the gas constant, *T* is the operating temperature, $D^{\mathrm{eff}}_{H_2-H_2O}(D^{\mathrm{eff}}_{O_2-N_2})$ is the effective binary anode (cathode) gas diffusivity, $\tau_a(\tau_c)$ is the anode (cathode) tortuosity factor, $\varphi_a(\varphi_c)$ is the volumetric porosity of the anode (cathode), and $D_{H_2-H_2O}(D_{O_2-N_2})$ is the bulk binary anode (cathode) diffusivity defined by Chapman–Enskog relation [13–15]. Unlike the measurement techniques of ionic conduction, such as electrochemical impedance spectroscopy, and nuclear magnetic resonance spectroscopy, which have been developed since decades ago, a traditional evaluation of gas diffusivity is typically done through mathematical fittings on the data of multiple voltage–current measurements on intact fuel cells [16–19]. Techniques of directly measuring effective binary gas diffusivities of electrodes in fuel cells in an out-of-cell fashion have only been developed in recent years [20–23]. Although the electrochemical devices allowed one to measure the gas diffusivity and evaluate the polarization loss as well as limiting current density in fuel cells, the accuracy of the measurement is still in debate; the measurement is based on the assumption that little electronic conduction through the electrolyte disc contributes to the current provided through the oxygen pump [21]. In the actual operation of an SOFC system, both ionic and electronic conductions can contribute to the electrical conduction of an electrolyte and thus, ignoring electronic contribution can cause inaccuracy in the gas diffusivity measurement and in the subsequent evaluation of limiting current density and concentration polarization loss [1].

In this Communication, an electrochemical cell with a current meter that reads the current only induced by ionic conduction, is proposed and analyzed. The correlation between the measurement uncertainty of the applied current and the evaluation errors of different parameters, such as diffusivity *CP*, and *LCD*, is investigated. The analysis shows that the proposed electrochemical device is highly favorable for accurate gas diffusivity measurements in fuel cells. The accurate diffusivity measurements lead to the accurate evaluation of concentration polarization loss and limiting current density in fuel cells, which is practically significant for the reliable and efficient pre-evaluation of electrodes before their assembly in intact fuel cells.

2. Materials and methods

2.1. Current-sensor based electrochemical cell device

The device can be employed to measure the gas diffusivity in any type of fuel cells, and for each type of fuel cells, specific electrolyte and electrode materials should be selected to measure the gas diffusivity in the operating conductions of fuel cells. Fig. 1 shows a schematic of the proposed electrochemical device for anode gas diffusivity measurements in solid oxide fuel cells. A yttria-stablized-zirconia (YSZ) tube is employed to create an isolated electrochemical cell system. A YSZ disc is attached to one end of the YSZ tube, and an anode sample to be measured is attached to the other end of the tube. A current provider is attached across the YSZ disc to be employed as an oxygen pump, and a voltage meter is attached to the YSZ tube to be used as an oxygen sensor. Previously, the applied current provided by the oxygen pump, the current measured with the oxygen sensor, and the equilibrium equation for H_2O, H_2 and O_2 phases were combined to measure the effective binary diffusivity of H_2 in porous anodes [20,21]. The electrical conduction in a ceramic fuel cell electrolyte can be contributed by both electronic and ionic species and thus, the applied current provided the oxygen pump is caused by the electronic and ionic conduction in the YSZ electrolyte [1,16]. This can introduce an inaccuracy in the subsequent calculation of effective binary diffusivities in fuel cells. Therefore, we need to improve the devices such that the ionic current induced by O^{2-} ions can be accurately measured. Differently from the reported gas diffusivity measurement devices, in this report a current meter is attached across the YSZ tube to measure the current only induced by O^{2-} conduction during the gas diffusivity measurement, as shown in Fig. 1.

2.2. Theoretical analysis

In anode diffusivity measurements, a H_2/H_2O gas mixture can be used. Upon the supply of a current via the oxygen pump, H_2/H_2O fluxes will be induced through the anode sample, according to Eq. (5),

$$J_{H_2} = -J_{H_2O} = \frac{i}{4F} \tag{5}$$

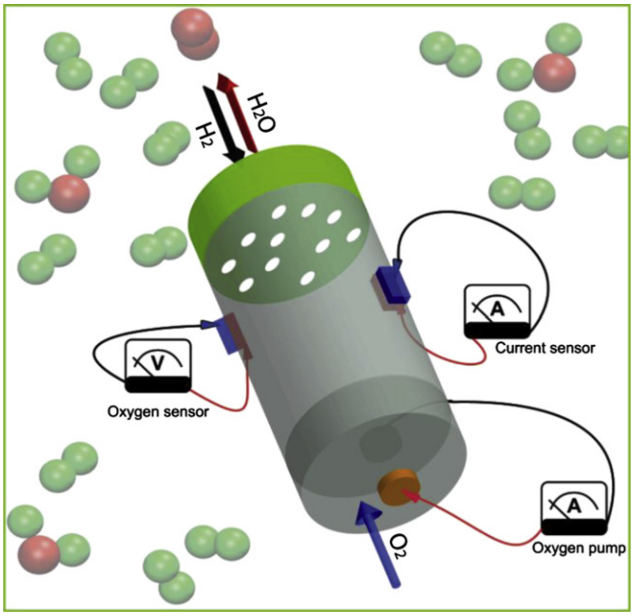

Fig. 1. A modified electrochemical device with a current sensor for accurate gas diffusivity measurement in solid oxide fuel cells. The device is placed inside a sealed tube furnace, H_2/H_2O or O_2/N_2 gas is driven into the tube furnace with a certain flow rate, and the system is then heated to the temperature at which diffusivity measurement is conducted. The directions of H_2/H_2O fluxes induced by the current provided via the oxygen pump, are demarcated by black/red arrows. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)