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Review

Gas transport in porous electrodes of solid oxide fuel cells: A review on diffusion and diffusivity measurement

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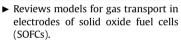
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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

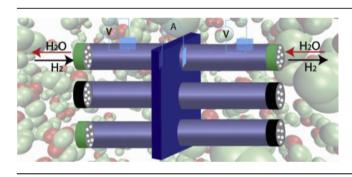


- Discusses recently-developed devices for direct diffusivity measurement in SOFCs.
- Shows that diffusivity measurement facilitates the research on SOFC electrodes.

A R T I C L E I N F O

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ABSTRACT

A reduction in Ohmic, activation and concentration-polarization losses is of paramount importance in improving the efficiency of solid oxide fuel cells, proton-exchange-membrane fuel cells, and moltencarbonate fuel cells. Efficient measurements of gas diffusivities at the operating conditions of fuel cells allow concentration polarization losses of these fuel cells to be reliably evaluated. To enhance the applicability of solid oxide fuel cells, tremendous work on the development of gas diffusion models and gas diffusivity measurement techniques have been done to pre-evaluate the concentration polarization losses of the recent advancement of gas diffusion models and diffusivity measurement techniques of solid oxide fuel cells. The review seeks to provide an insightful guidance for designing high-performance solid oxide fuel cell cell electrodes with efficient thickness, porosity, among other parameters.

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1. Introduction

As the global population and economy continue to expand, a lot of attention is focused on improving the performance of existing

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energy systems as well as exploring new forms of sustainable energy sources [1–13]. One of the main proposed strategies toward sustainable energy sources is hydrogen-fuel based fuel cells, such as proton exchange membrane fuel cells (PEMFCs), molten carbonate fuel cells (MCFCs), and solid oxide fuel cells (SOFCs). Fuel cells directly convert stored chemical energy of fuels into electrical energy without combustion, and are capable of overcoming the combustion efficiency limitation as imposed by the Carnot cycle. Moreover, fuel cells reduce the emission of pollutants like nitrogen oxides (N_xO_y) and hence are environmentally friendly. Compared with other types of fuel cells, solid oxide fuel cells exhibit excellent fuel flexibility, and many chemicals including hydrogen, hydrocarbons, carbon monoxide and carbon, can be utilized as fuels [14–30].

There are mainly three types of energy losses associated with a fuel cell, i.e., activation loss (AL), concentration polarization (CP), and Ohmic loss (OL). Research has gained remarkable success in increasing the efficiency of SOFCs, the energy losses can be controlled well below 30%. The main drawback of SOFCs is their high operating temperatures, which are typically above 500 °C. At these temperatures, only a few materials can be employed as electrolytes and electrodes. This leads to an increase in cost, and hinders potential applications in portable and automobile power source. On the other hand, the concentration polarization of SOFCs typically increases as the operating temperature decreases [31,32]. Lowering the operation temperatures of SOFCs while maintaining a high efficiency has become the key focus in the SOFC field [33–40]. Toward this direction, new nanostructured electrodes composed of existing electrode materials, have been studied for potential applications in SOFCs [28,41–49]. In addition to materials development, efficient methods are required to pre-evaluate an electrode before it is assembled into a fuel cell. In particular, measuring the gas diffusivity in an electrode is considered to be an important aspect in facilitating such an evaluation since gas diffusivity correlates with both polarization loss and electrode parameters including porosity, thickness and tortuosity. Recently, gas diffusivity measurement techniques have undergone significant improvement, which has facilitated the efficient pre-evaluation of the polarization loss of SOFC electrodes in an out-of-cell fashion [50-53].

In this review, an overview on existing mechanisms and mathematical models of fuel gas transport through porous electrodes is presented, followed by a discussion on gas diffusivity. We then systematically investigate the efficiency of recently-developed electrochemical devices for direct diffusivity measurements and concentration polarization evaluation. We conclude by providing prospectives on possible future developments of gas transport models and further improvement of gas diffusivity measurements. The review and prospectives aim to enhance the performance of SOFCs by improving diffusivity measurement techniques and by pre-evaluating the parameters associated with micro/nano-porous electrodes.

2. Fuel gas diffusion models

In a fuel cell, oxygen molecules diffuse in the cathode, and are reduced to oxygen ions at the cathode active layer. These oxygen ions then transport through the electrolyte and react with the fuel gas at the anode/electrolyte interface to produce electricity. The driving force of a fuel cell is provided by the anode/cathode reaction. For a gas-based solid oxide fuel cell to operate, the activation energy of the anode/cathode reaction has to be overcome [54–57]. The pressure gradient of anode/cathode gas and the concentration gradient of oxygen ions across the anode/cathode and the electrolyte are determined by the transport rates of these gaseous and ionic species. While providing electricity, electrical resistance is

also present in all operating components of the fuel cell [58–60]. Despite the high efficiency of existing SOFCs, there is still room for efficiency improvement. Moreover, an improvement of the cost effectiveness, even by a small amount, is crucial to the implementation of SOFCs in applications [1,61–64]. Fig. 1 shows a demonstration of concentration polarization loss, Ohmic loss, and activation loss associated with different components of a fuel cell. Ohmic loss due to electrical resistance is present across all fuel cell components whereas activation loss is induced by offsetting energy barrier for catalytic reactions at electrode/electrolyte interfaces. Concentration polarization is induced by the pressure gradient due to limited transport rates of gaseous reactant and/or product species through SOFC electrodes [31,50,51,61]. The chemical potential of a mass system is the function of the concentration/density of the mass species, and can be expressed by Eq. (1),

$$\mu_i = \mu_0 + RT \ln n_i \tag{1}$$

where μ_i is the chemical potential of species *i* at a given state, *R* is gas constant, *T* is temperature, and n_i is the concentration of species *i*. CP is induced by the chemical potential gradient due to diffusion-limited gas transport through electrodes.

A thorough understanding of the gas transport mechanism along with an accurate calculation or measurement of CP at operating conditions is important for reducing polarization losses in SOFCs. The one-dimensional diffusion of gas fuel molecules in porous media involves molecular interactions between gas molecules as well as collisions between gas molecules and the porous media [65-67]. As gas fuel molecules, such as H₂, and CH₄, transport through the porous anode of an SOFC, one of three mechanisms can occur, depending on the characteristic of the diffusing gas species and the intrinsic microstructure of the anode [67]. The three mechanisms are molecular diffusion, viscous diffusion, and Knudsen diffusion. To distinguish the three mechanisms, Knudsen number (K_n) , the ratio of the gas mean free path to the size of pores of an electrode, is typically used [66–68]. If K_n is much greater than 10, collisions between gas molecules and a porous electrode are more dominant than the collisions between gas molecules resulting in negligible molecular diffusion as well as viscous diffusion. If K_n is much smaller than 0.1, collisions and interactions between gas molecules become dominant and Knudsen diffusion becomes negligible compared with molecular diffusion and viscous diffusion. When the K_n of a system ranges between 0.1 and 10, all the

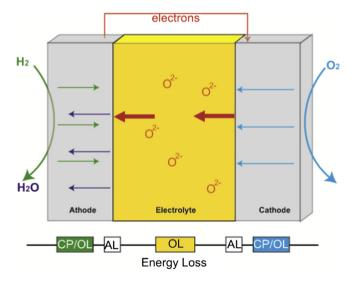


Fig. 1. Polarization losses and mass transfer associated with SOFC components.

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