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Oxygen transport through LSM/YSZ/LaAlO system for use of fuel cell type reactor

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Abstract

Oxygen transport in an LSM/YSZ/LaAlO solid oxide fuel cell type reactor was studied. The oxygen permeation flux was 8.90×10^{-8} mol m^{-2} s^{-1} at 1173 K with an activation energy of 170 kJ mol^{-1}. By applying an external potential, the oxygen permeation flux increased while the activation energy of oxygen permeation decreased. The oxygen permeation fluxes under methane feed in the anode side are 1–2 orders of magnitude higher than those under helium feed. A model of oxygen permeation was presented and the permeation parameters were proposed. In the case of helium feed, the oxygen permeation at the LaAlO anode was the rate-limiting step. However, changing helium to methane as a reactive gas, the resistances for the oxygen permeation in the three parts (LSM/YSZ/LaAlO) were comparable.

Keywords: Solid oxide fuel cell; SOFC reactor; Oxygen permeation; Modeling; Methane

1. Introduction

Solid oxide fuel cell (SOFC) is a promising energy conversion technology for future applications [1,2]. In our previous papers, the SOFC system was applied as a selective oxidation reactor for chemical energy co-generation. Particular focuses were on catalyst preparation method [3–5] and reactor performance test [6–8]. In these studies, the oxidative coupling of methane to ethane and ethylene (C2) was studied. The solid electrolyte was used as an oxygen separator and an oxygen distributor to achieve high C2 selectivity. In these electrocatalytic systems, combined effects of activation of oxygen on an anode and permeation of oxygen through an yttria stabilized zirconia (YSZ) controlled the reactor performance.

Therefore, the oxygen transport through the electrochemical system should be studied. Several research groups have published their experimental results on the overall oxygen permeation through many oxygen-permeable electrolyte membranes such as YSZ [9], calcia stabilized zirconia (CSZ) [10], mixed ion-electronic conducting materials such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) [11,12] and other perovskite-type ceramics, for example, $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS) [13,14], $BaBi_xCo_{0.2}Fe_{0.8-x}O_{3-\delta}$ [15], $BaCo_{0.4}Fe_{0.6-x}Zr_xO_{3-\delta}$ [16].

Several studies focused on the steady-state oxygen permeation in membrane reactors for oxidation reactions, for example, partial oxidation of methane [17] and oxidative coupling of methane [14,18]. However, very limited studies on oxygen permeation in the SOFC reactors have been reported. The conventional YSZ electrolyte has been widely used to provide the electrochemical permeation of oxygen for the oxidative coupling of methane [3–8]. The use of external potential as well as the effect of non-Faradaic electrochemical modification of catalytic activity (NEMCA) are of recent interest.

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Nomenclature

A_j	pre-exponential factor of conductivity ($S\,K\,m^{-1}$)
A_{Per}	pre-exponential factor of oxygen permeation ($mol\,m^{-2}\,s^{-1}$)
E	electromotive force (V)
E_j	activation energy of conductivity ($J\,mol^{-1}$)
E_{Per}	activation energy of oxygen permeation ($J\,mol^{-1}$)
F	Faraday's constant, 96487 ($C\,mol^{-1}$)
J_{O_2}	oxygen permeation flux ($mol\,m^{-2}\,s^{-1}$)
$k_{O_2\text{-perm}}$	overall oxygen ions recombination and diffusion coefficient ($mol\,m^{-2}\,s^{-1}$)
$k_{O_2\text{-Rxn}}$	oxygen surface reaction coefficient ($mol\,m^{-2}\,s^{-1}\,Pa^{-1}$)
k_V	proportional constant ($mol\,m^{-2}\,s^{-1}\,V^{-1}$)
L	thickness of material (m)
Per, O	specific oxygen permeability ($mol\,m^{-1}\,s^{-1}$)
P_{feed}	oxygen partial pressure at feed side (cathode side) (Pa)
P_{lean}	oxygen partial pressure at lean side of materials (Pa)
$P_{O_2(I)}$	oxygen partial pressure at the gas–membrane interface (Pa)
$P_{O_2(II)}$	oxygen partial pressure at membrane–gas interface (Pa)
P_{perm}	oxygen partial pressure at permeate side (anode side) (Pa)
P_{rich}	oxygen partial pressure at rich side of materials (Pa)
R_g	gas constant, 8.314 ($J\,mol^{-1}\,K^{-1}$)
T	temperature (K)
V_{Per}	applied external potential during steady-state permeation (V)

Greek letters

α	permeation rate constants in interface diffusion step ($mol\,m^{-2}\,s^{-1}\,Pa^{-1/2}$)
β	permeation rate constants in bulk diffusion step ($mol\,m^{-1}\,s^{-1}\,Pa^{-1/4}$)
σ	conductivities ($S\,m^{-1}$)

Subscripts

e	electronic
i	ionic

In the previous paper [8], the fuel cell type temperature-programmed desorption (FC-TPD) was studied on the LSM/YSZ/LaAlO system. Increasing the applied potential increased the amount of adsorbed oxygen. The change in the selectivity of active sites gave a new aspect to the NEMCA phenomena in the oxidative coupling of methane in the SOFC reactor. The applied potential also decreased the activation energy of desorption of oxygen at the anode catalyst [19]. In addition, the FC-TPD analysis could correlate the behavior of adsorbed oxygen species to the NEMCA effect.

In this study, the steady-state oxygen permeation using helium or methane as an anode gas was investigated. The effect of applied potential on the oxygen permeation through the LSM/YSZ/LaAlO in the SOFC reactor was studied. In addition, a model of oxygen permeation was proposed.

2. Experimental

2.1. Apparatus

The schematic diagram of the solid oxide fuel cell type reactor is illustrated in Fig. 1. A tube-type YSZ membrane (8 mol% Y_2O_3, thickness = 1.5 mm, inside diameter = 18 mm, outside diameter = 21 mm, length = 500 mm, effective surface area = 0.0148 m^2) was used as an electrolyte. $La_{1.8}Al_{0.2}O_3$ (abbreviated as LaAlO) prepared by a mist decomposition method was used as an anode catalyst on the inner surface of the tube while $La_{0.85}Sr_{0.15}MnO_3$ (abbreviated as LSM) prepared by paste method was used as the cathode on the outer surface [7,8]. Details of the electrode preparation methods were described elsewhere [3,4,7].

Platinum wire was connected to platinum meshes placed on both electrode surfaces to serve as current collectors. The outlet gas from the anode side was directly connected to a gas chromatograph for analysis of gas composition. A potentiostat was used to supply an external electrical potential to the system. Oxygen transport from the cathode side to the anode side was promoted under the applied positive potential.

2.2. Steady-state oxygen permeation

Steady-state oxygen permeation measurements were performed at various temperature levels: i.e., T = 1073, 1123, 1173, 1223 and 1273 K. Helium (1.36×10^{-5} mol s^{-1}) and oxygen (1.02×10^{-5} mol s^{-1}) were fed to the anode and the cathode, respectively. The oxygen permeation flux was calculated from the flow rate and composition of the anode exit gas. The flow rate and its composition was measured and analyzed by a bubble flow meter and a gas chromatograph with a TCD detector, respectively. Sampling was conducted every 5 min until reaching a steady-state condition (approximately 0.5 h). Another set of steady-state oxygen permeation was carried out by using methane (6.8×10^{-6} mol s^{-1}) as an anode reactant gas at various temperature levels: i.e. T = 1073, 1123, 1173, 1223 and 1273 K. In this case, permeated oxygen has reacted with methane to produce oxygen, containing species such as CO, CO_2, H_2O. Thus, the oxygen permeation flux was estimated by analyzing these oxygen-containing products. The steady-state measurements for both sets of experiments were carried out at various levels of the applied potential.