Short Communication

A novel method to determine the I–V curve and polarization resistance at the three-phase boundary of composite cathode

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ABSTRACT

The oxygen incorporation process is investigated in a new insight based on the electrical conductivity relaxation (ECR) technique. A theoretical method is proposed to qualitatively evaluate the electrochemical performance for the oxygen reduction reaction on the electrocatalyst for solid oxide fuel cells (SOFCs). In this method, the change in oxygen partial pressure to conduct the ECR process corresponds to an electromotive force while the surface reaction rate to a current density. Accordingly, the polarization resistance as well as the current–voltage relation can be derived for the oxygen reduction reaction occurred on the electrocatalyst-gas two-phase interface and at the electrocatslyst-electrolyte-gas three-phase boundary. The method is demonstrated with our previously experimental results on the composite system consisting of lanthanum strontium cobalt ferrite and samaria-doped ceria, which is a typical composite cathode for intermediate-temperature SOFCs.

Introduction

In present, further understanding of the cathode reaction or rather the oxygen reduction reaction (ORR) mechanism is necessary and significant for the development of intermediate-temperature SOFCs (IT-SOFCs) [1,2]. It is widely accepted that the ORR mainly occurs at the electrocatalyst-electrolyte-gas three-phase boundary (3PB) for an electrocatalyst with pure electronic conductivity such as strontium-doped lanthanum manganite. And the reaction site can spread to the electrocatalyst-gas two-phase interface (2PB) when a mixed electronic-ionic conductor is employed as the electrocatalyst like $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF). Therefore, it is significant to quantitatively determine the polarization resistance as well as the current–voltage relation for ORR over 2PB and 3PB. Usually, the ORR on 2PB is determined by the AC impedance spectroscopy using the dense electrodes with current collecting materials such as Pt and Au [3,4]. The performance at 3PB can be measured using patterned electrodes [5–7]. In addition, the electrochemical property at 3PB can be

obtained through the corrosion of a cathode material to quantitatively character the 3PB length. Nevertheless, only a few materials have been investigated due to the difficulty in preparing the patterned electrodes and precisely determining the 3PB length in the corrosion process.

The electrical conductivity relaxation (ECR) method is developed to determine the ORR kinetic on an electrocatalyst, precisely, the chemical oxygen surface exchange coefficient k (m s^{-1}) and the chemical oxygen diffusion coefficient D (m^2 s^{-1}) [8,9]. In the measurement, a step change in oxygen partial pressure (P) causes oxygen migration between the oxide electrocatalyst and gas, and in turn changes the oxide conductivity. Then, k and D can be estimated by fitting the conductivity data through solving the Fick's diffusion equation with linear absorbing boundary conditions. The ECR technique is widely employed for simple testing device, low cost and convenient measurement of the conductivity. However, the obtained parameters, D and k, are in some way difficult to be connected to the factors in usual electrochemical characterization. Adler et al. [10,11] have developed a quantitative analytical model, which determines the steady-state DC area specific resistance of a oxide cathode based on the thermodynamic oxygen exchange parameters obtained from isotope exchange measurement. Nevertheless, the relation between electrochemical characterization and the parameters from ECR method is still uncertain. In this communication, a method is proposed to determine the electrochemical performance for ORR over 2PB and 3PB using the ECR technique. It is noted that the step change in P can be treated as electromotive force while k can be transferred to current density. Consequently, the I–V curve as well as the polarization resistance can be derived. The method is demonstrated with previously reported data for LSCF-SDC (Sm$_{0.2}$Ce$_{0.8}$O$_{1.9}$) composites to calculate the electromotive force, current density, and polarization resistance over 2PB and 3PB [12].

Theoretical approach

Electrochemical performance on 2PB

Electromotive force from ECR
In the ECR measurement, LSCF is subjected to a step change in the oxygen partial pressure increasing from P_0 to P_∞ (atm) at a constant temperature, T (K). The associated change in the conductivity is monitored as a function of elapsed time, t (s). When $P_\infty/P_0 \leq 10$, a linear relationship is assumed between the normalized electrical conductivity and oxygen concentration [8,9,13].

$$n(t) = \frac{c(t) - c(0)}{c(\infty) - c(0)} = \frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} \quad (1)$$

where $n(t)$ is the dimensionless, normalized change in the conductivity/concentration, $c(t)$ (mol m^{-3}) and $\sigma(t)$ (S m^{-1}) are, respectively, the concentration and conductivity at time t, $c(0)$ and $\sigma(0)$ the corresponding initial values, $c(\infty)$ and $\sigma(\infty)$ those at infinite time (i.e. equilibrium/relaxation time) when the new thermodynamic equilibrium state is achieved at P_∞.

At $t = 0$, the oxygen in solid LSCF equilibrates with the gaseous oxygen. That is, the oxygen chemical potential of LSCF, μ_0 (J mol^{-1}), is

$$\mu_0 = \mu^\Theta + \frac{1}{2}RT\ln(P_0/P^\Theta) \quad (2a)$$

where μ^Θ is the chemical potential under standard state, R (J k^{-1} mol^{-1}) is the molar gas constant, and $P^\Theta = 1$ atm.

At $t = \infty$, LSCF achieves a new equilibrium state at P_∞, so

$$\mu_\infty = \mu^\Theta + \frac{1}{2}RT\ln(P_\infty/P^\Theta) \quad (2b)$$

Once the oxygen partial pressure is increased from P_0 to P_∞, oxygen incorporation begins. At elapsed time t ($0 < t < t_\infty$), the chemical equilibrium state is not achieved between LSCF and the gas with P_∞. ORR continues until $t = t_\infty$. The reaction is controlled by the surface exchange process while the bulk transportation is fast enough to obtain instant uniform oxygen concentration, $c(t)$, throughout LSCF when the sample thickness is much smaller than D/k [14,15]. Accordingly, the oxygen chemical potential, μ_t, is uniform in LSCF.

$$\mu_t = \mu^\Theta + \frac{1}{2}RT\ln(P_t/P^\Theta) \quad (2c)$$

where P_t is a hypothetic oxygen partial pressure that equilibrates with LSCF at elapsed time t.

ORR is actually an oxygen incorporation process driven by the difference in the chemical potential between oxygen in the gas and LSCF. The difference can be considered as an electromotive force applied to the LSCF-gas two-phase interface. The corresponding electromotive force on 2PB, $\eta_{2PB}(t)$ (V), can be obtained via Nernst Equation.

$$\eta_{2PB}(t) = \frac{\mu_{gas} - \mu_{LSCF}}{NF} = \frac{RT}{2NF}\ln(P_\infty/P_t) \quad (3)$$

where F (C mol^{-1}) is the Faraday constant and N is the charge number of the carriers, $N = 2$.

When oxygen is incorporated to LSCF, the conductivity increases as a function of P [16]:

$$\sigma = euP^{1/4}\sqrt{\frac{x_{Sr}}{2K}} \quad (4)$$

where e is the electron charge, u is the mobility, x_{Sr} is the Sr doping content, and K is the equilibrium constant of the defect reaction. The normalized conductivity can be expressed with P from Eqs. (1) and (4).

$$n(t) = \frac{P_t^{1/4} - P_0^{1/4}}{P_\infty^{1/4} - P_0^{1/4}} \quad (5)$$

Substituting Eq. (5) into Eq. (3), the electromotive force can be obtained from the normalized conductivity $n(t)$, which is recorded in the ECR measurement.

$$\eta_{2PB}(t) = \frac{RT}{2NF}\ln\frac{P_\infty}{P_0}\left[1 + \left(\frac{P_\infty^{1/4}}{P_0^{1/4}} - 1\right)n(t)\right]^{-4} \quad (6a)$$

In the previous experimental work, the atmosphere step change was from $P_0 = 0.01$ atm to $P_\infty = 0.1$ atm using O$_2$–N$_2$ gas mixtures [12]. Thus, Eq. (6a) can be written as: