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Characterization of electrode polarization losses in solid oxide fuel cells: Impedance spectroscopy involving spatially-limited electrode geometry

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ABSTRACT

The concept of "spatially-limited geometry" in an ionic conductor is incorporated into AC two-probe impedance spectroscopy in order to investigate the electrode-related responses of solid oxide fuel cells (SOFCs). A semispherical cylinder-shaped ionic conductor made of yttria–stabilized zirconia (YSZ) is applied to the planar electrode, and the electrical and electrochemical losses in the electrolyte and electrode are characterized. According to our study, the spatial constriction of the contact interface amplifies the electrode-related impedances, and can more efficiently separate the bulk-related impedance from the electrode polarization that is very sensitive to the microstructural features of the electrode such as size and distribution of constituent phases. In this study, the resolved bulk resistances are analyzed using the concept of "spreading resistance," whereas the resulting polarization losses in the electrolyte/electrode interface are analyzed in combination with an equivalent circuit model as a function of the resistances and constant phase elements. The present approach with spatially-limited contact impedance spectroscopy is fully explored for various electrode materials in order to confirm the validity of current methodology.

1. Introduction

Over the last two decades, solid oxide fuel cells (SOFCs) have attracted widespread attention due to the increased petroleum price and various environmental issues associated with air pollution [1–5]. SOFCs are highly efficient electrochemical conversion systems which are usually operated at high temperatures near 1000 °C, in which oxygen and hydrogen are electrochemically reacted to generate electric power. In general, the high operating temperatures of SOFCs can introduce numerous undesired technical problems due to the chemical instability and mechanical discordance between dissimilar materials in the SOFC components, including the electrolytes, electrodes, interconnects, and sealing materials. Hence to overcome these problems, most research and development activities have focused on the development of intermediate-temperature solid oxide fuel cells IT-SOFCs that can be operated at a temperature range of 600–800 °C [2–5]. However, as the operating temperature is lowered, the polarization loss of a cell also greatly increases, mainly due to the electrode overpotential, especially at the cathode. In order to prevent significant electrodic polarization loss at lower temperature, electrode has to be carefully designed to keep their electrochemical activity as high as possible by maximizing the number of electrode reaction sites as well as promoting the supplying of reactants or removal of products from the electrode reaction. Hence in order to optimize SOFC electrode, it should be thoroughly exploited in terms of its physicochemical properties and corresponding electrochemical functions.

There have been substantial efforts in the research and development of high performance electrode. Nevertheless, still some unsolved issues are remained [6–10]. These issues are closely ascribed to the lower electrochemical efficiency of the electrodes, such as activation polarization loss or concentration polarization loss at the electrode. In general, most of the challenging issues are strongly dependent on the microstructural factors of the electrode, such as the volume fraction, interconnectivity, and size distribution of the constituent components, i.e., solid phases and pores. In particular, optimization of the triple phase boundary (TPB) configuration, which has been recognized as a critical issue in achieving high electrochemical conversion efficiencies for the electrode reaction, is strongly influenced by the constitutional forms of the solid electrolyte, electrode, and pore phase. In addition to the extensive research and development regarding the overall cell performance of SOFCs, there have been many studies intended to provide an exhaustive understanding of the correlation between the microstructure and its related electrodic functions, either at the anodes or cathodes [6–10].

Impedance spectroscopy has been an exceedingly powerful technique to separate the bulk responses from the grain boundary

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features in electroceramics, such as ZnO varistors, $BaTiO_3$ PTCRs, and magnetic ferrites [11–14]. Impedance spectroscopy allows the simultaneous monitoring of electrical and dielectric phenomena given an arc or semicircle in a Nyquist plot (an imaginary part of measured impedance (-Im(Z)) versus a real impedance part (Re(Z))). The conductivity and dielectric constants can be estimated simultaneously using an equivalent circuit model. The degree of depression in the impedance arcs is evaluated in order to find the homogeneity of the relevant mechanisms. Impedance spectroscopy is also useful for the study of the cement-based materials, and batteries, and to monitor the corrosion behavior of metals in aqueous environments [15–17].

Impedance spectroscopy is now becoming a main tool to characterize the electrolyte/electrode properties in fuel cells, especially SOFCs [18–20]. A detailed understanding of the rate-limiting steps in SOFC electrode reactions is highly desirable from an optimization point of view. In general electrode reaction comprises multiple electrochemical as well as physical or chemical transport steps [6–8,18–20]. It is important to find out the major limiting process among various reaction steps which are normally related to the microstructure of electrode and surroundings, such as contacting state and gas supplying condition. In that sense, impedance spectroscopy is very efficient to analyze this complex system.

Until now, AC three-probe impedance spectroscopy has generally been applied to SOFCs in order to separate the electrical/dielectric features of the bulk from the electrochemical response from the electrodes. In the sophisticated three-probe cell design, which guarantees parallel equi-potential lines across the solid electrolyte, it is possible to separate the electrochemical responses originating from the electrode as long as the impedance of the reference electrode is smaller than the inherent impedance of the frequency response analyzer [20,21]. However, if the appropriate configuration in three-point impedance spectroscopy is not guaranteed, the obtained electrode information can exhibit erroneous arc features in electrode-based responses due to the undesired distortion in equi-potential lines [22]. The electrode placement similar to the Luggin capillary probe is preferred in terms of the measurement accuracy in estimating the electrolyte and electrode parameters [23].

Recently, the spatially-limited contact AC two-probe configuration was introduced that is expected to substitute conventional AC three-probe impedance spectroscopy to resolve the electrical responses of one electrode from the bulk electrolyte by amplifying the resistive part of the relevant electrochemical responses associated with that electrode along with the bulk response. One of the main advantage of this spatially-limited contact electrode with AC two-probe impedance spectroscopy is that it does not suffer from the limited impedance magnitude of reference electrodes encountered in AC three-probe impedance spectroscopy [20,21], thereby enabling a proper investigation of the electrode responses in SOFCs with a two-probe configuration. The concept of this limited-contact method is very useful to separate the information from the electrolyte/electrode interface near the point-contact between the electrolyte and electrode, which is believed to be qualitatively equivalent to the information obtained from AC three-probe impedance spectroscopy. The spatially-limited contact geometry can be formed into either a semispherical YSZ probe onto the cathode materials or a semispherical electrode probe onto the electrolytes [18,19,24]. The latter case was reported by Baker et. al. 18 and Fleig [24], where a limited contact was constructed based on the electrode materials. However, since the cathode materials are normally porous and not so robust, the elaborate machining of cathode into the spherical shape is not straightforward, which may lead to mechanical failure. On the other hand, spatially-limited contact based on a robust electrolyte such as YSZ electrolyte is expected to give more reliable measurement setup.

In this study, we report on a unique characterization method for the electrode reactions of SOFCs via impedance spectroscopy combined with a spatially-limited contact AC two-probe configuration using a semispherical cylinder-shaped ionic conductor. With this spatially-limited configurations based on semispherical cylinder-shaped electrolyte, we can intentionally amplify the electrode and bulk impedances, expecting to obtaining a universal parameter which allows a straightforward comparison between the electrodes. In order to validate the current spatially-limited contact method, various materials were chosen for the testing electrode, Unlike a preliminary study [19] incorporating composite cathode materials, the current approach was applied to three types of cathode systems found in cathodes of SOFCs, i.e., electronically-conducting metallic, electronically-conducting ceramic, and mixed-conducting electrodes. The ramifications of "limited-contact" impedance spectroscopy are discussed for an exhaustive understanding of electrode-related polarizations in SOFCs.

2. Experiment

In order to avoid the vulnerability in shaping the electrode into the pointed configuration, we devised the limited contact in the electrolyte by machining the dense sintered body of YSZ (Tosoh, TZ-8Y) into a semispherical cylinder. One side of the YSZ specimen had a semispherical shape and the other side maintained a cylindrical form. The hemispherical YSZ probe was fabricated so that the diameter of the YSZ probe is approximately 8 mm and the lateral portion of the circular column is approximately 2 mm long. The upper portion of the electrolyte was connected to the platinum lead wires using platinum paste and platinum mesh, in order to guarantee close contact between the YSZ and the Pt wire electrode. The mechanical contact between the Pt mesh and the Pt-painted surface was treated at 800 °C for 1 h in an electric furnace.

After the complete electroding of the semispherical YSZ electrolyte, the lower spherical portion was placed on the planar top portion of the electrode material. Pure electronic conducting gold (Au) was employed as a reference material in order to verify the current "limited-contact" impedance spectroscopy. LSM ($(La_{0.7}Sr_{0.3})_{0.95}MnO_3$) and LSCo ($La_{0.6}Sr_{0.4}CoO_3$) which are the typical electronic conducting and mixed ionic–electronic conducting cathode materials, respectively, were also incorporated into current configuration for checking the viability of this methodology. Au was employed in the form of thin foil whereas the ceramic electrode was employed in the form of disk-shaped bulk. The synthesized LSM powder using a glycine nitrate process [19] and commercial LSCo (AGC SEIMI CHEM, Japan) powder were compacted into disks using uniaxial pressing and heat-treated in a furnace at 600 °C after binder removal at 400 °C. The pre-sintered specimen was placed into a furnace and then heated to 800 °C to create a complete contact between the electrode materials and the Pt-pasted counter electrode. As a final step, the specimens were contacted with the semispherical part of YSZ electrolyte and then heat-treated at high temperature around 1200 °C for 1 h, in order to mimic actual cathode fabrication conditions of SOFCs. The final configuration of our spatially-limited contact electrode for AC two-probe impedance spectroscopy was shown in Fig. 1.

Impedance spectra were collected as a function of temperature and oxygen partial pressure using a frequency response analyzer (SI 1260, Solatron, Berkshire, UK). Since the electrolyte/electrode interface is sensitive to the oscillating amplitude, an oscillating voltage was fixed at 25 mV in order to minimize the effects induced by the high oscillating voltage. The impedance spectra were acquired in a logarithmic manner between 1 MHz and 0.01 Hz with 10 points per decade. Impedance measurements were collected between 600 °C and 800 °C in an electric furnace which