Journal of Power Sources 330 (2016) 285–291

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Investigation of the electrochemical reactions at a limited-contact $La_{1-x}Sr_xMnO_3$/Y-doped ZrO_2 interface with a rod-type ionic-probe

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HIGHLIGHTS

- Geometrically well-defined ionic probe is used for the characterization of electrode polarization.
- A more quantitatively controllable TPB of LSM/YSZ interface can be constructed.
- ORR is limited by the diffusion of adsorbed oxygen along the LSM bulk surface.

ARTICLE INFO

Article history:
Received 7 May 2016
Received in revised form
18 August 2016
Accepted 1 September 2016
Available online 13 September 2016

Keywords:
LSM
Polarization resistance
Oxygen reduction reaction
Surface diffusion
Triple phase boundary

ABSTRACT

A more quantitatively controllable triple phase boundary (TPB) of a lanthanum strontium manganite/yttria-stabilized zirconia (LSM/YSZ) interface was constructed by using an YSZ ionic probe with well-defined dimensions. A bar-shaped, dense YSZ sintered body was employed as an ionic probe and embedded in the pellet-shaped, dense LSM bulk. The TPB length of the LSM/YSZ interface can be simply determined from the circumference of the YSZ bars. To identify the reaction mechanism of the oxygen reduction reaction (ORR) at the TPB of the LSM/YSZ interface, limited-contact AC impedance spectroscopy was used; this distinguished the LSM/YSZ interface related polarization from other polarizations present in the Pt/LSM/YSZ/Pt electrochemical cell. By analyzing the electrode-related polarizations in the electrochemical cell with the geometrically quantified YSZ ionic probe, the rate determining step of the ORR was the diffusion of adsorbed oxygen along the LSM bulk surface. In this paper, emphasis is placed on the experimental versatility and the limitations of our designed electrochemical analysis with bar-shaped ionic probes.

1. Introduction

Solid oxide fuel cells (SOFCs) offer the possibility of clean and highly efficient power generation. However, regarding cost and durability, SOFCs cannot yet compete with conventional power generating systems. In recent years, significant efforts have been made to develop low or intermediate temperature SOFCs (LT- or IT-SOFCs). Operation at temperatures below 800 °C eliminates cost and durability problems arising from the high operating temperature of conventional SOFCs. However, while operating SOFCs at intermediate or low temperatures has advantages, a reduced operating temperature decreases electrode reaction kinetics, resulting in substantial interfacial polarization resistance [1]. Numerous studies have shown that cathode polarization is the major source of the overall performance losses in SOFCs, especially for LT- or IT-SOFCs [2–4]. A good example of this type of performance loss is seen in $La_{1-x}Sr_xMnO_3$ (LSM) composite cathodes [5]. According to Ref. [5], cathodic polarization reached up to 45% of the overall performance losses of the SOFCs; thus, suppression of possible cathodic polarization loss is a key issues for the development of high-performance SOFCs. In this context, a proper understanding of the cathode reaction mechanism is a good starting point to find an effective design for a high-performance cathode.

Large performance losses from the cathode reaction originate from electrochemical impedance related to the oxygen reduction reaction (ORR) at the cathode [2–4]. Despite extensive

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http://dx.doi.org/10.1016/j.jpowsour.2016.09.004
0378-7753/

investigation into the ORR at SOFC cathodes, significant uncertainty remains because of the complex ORR mechanism at the cathode/electrolyte interface [6]. Furthermore, high-temperature electrochemical measurements are easily affected by various experimental variables such as microstructure and the spatial configuration of electrode/electrolyte interface, malfunction of the reference electrode, and non-ideal cell geometry, which can all hinder accurate ORR analysis [7–11].

There are many interpretations, some of which are controversial or ambiguous, of the electrode reaction mechanism at the SOFC cathode; ambiguity arises because of the technical difficulty in controlling and quantifying the exact electrode reaction sites [6,7,12–14]. In particular, for the LSM cathode, which has lower ionic conductivity compared to other mixed ionic-electronic conducting (MIEC) cathodes [6], the exact configuration of the triple-phase boundary (TPB) of cathode/electrolyte interface and its role in controlling cathodic reactions must be identified.

Recently, a microelectrode technique has been used in a model experiment for the mechanistic analysis of the ORR in SOFC cathodes [9,10,15–18]. In general, this technique employs thin, dense cathode films, where the TPB length and electrode area are better defined than those of conventional porous cathodes; thus, more quantitative analysis on the ORR mechanism is possible [9,10,15,16]. However, the following limitations must be considered when using this thin-film microelectrode technique: a thin-film cathode may have different thermochemical phase stability and induce unusual electrocatalytic properties compared to a bulk cathode due to divergence of a surface morphologies and/or oxygen non-stoichiometry [19–24].

Three-point AC impedance spectroscopy is generally used for mechanistic studies of the electrode reactions of electrochemical cells because it can separate the electrochemical responses of the electrode from other components such as the electrical/dielectric features of the electrode bulk and electrolyte [25–28]. However, this conventional electrochemical cell design with a three probe configuration can separate the authentic electrochemical response of the electrode reaction only when the following two conditions are met: the parallel equipotential lines across the solid electrolyte are maintained and the impedance of the reference electrode is smaller than the internal impedance of the frequency response analyzer during the measurement. In some studies, a technical problem often arises, i.e., limited resistance at the reference electrode [29–35]. Therefore, an alternative for conventional AC three-point impedance spectroscopy is a limited-contact, AC, two-point configuration; this resolves the electrochemical response of the electrode without the use of a reference electrode by relatively amplifying the resistive part of the relevant electrochemical responses associated with the electrode of interest [36–39].

Consequently, in this study, we propose a more practical way of quantifying TPB length and assessing its effect on the electrode reaction by using a bulk electrode and electrolyte materials that are conventionally heat treated and expected to more realistically represent the SOFC reactions than that of a thin-film based microelectrode. Furthermore, in this study, to obtain amplified electrical signals relative to the electrical interference, a limited contact situation is made where a small, bar-shaped YSZ probe is placed in close contact with a dense LSM bulk pellet. In this configuration, because transport through bulk LSM is minimized, TPB length can be simply defined as the circumference of the YSZ bar, and the correlation between the TPB length and any reaction steps affected by the TPB length can be more clearly investigated. Accompanying a thorough analysis on the electrode-related polarization in the LSM/YSZ electrochemical cell with the geometrically quantified YSZ ionic probe, we also emphasize the experimental versatility as well as the limitation of our electrochemical analysis with bar-shaped ionic probes.

2. Experimental

Commercial LSM ($(La_{0.7}Sr_{0.3})_{0.95}MnO_{3-\delta}$, Seimi, Japan) powder was compacted into disk-shaped samples using uniaxial die-pressing. To secure the appropriate handling for the subsequent electrochemical cell fabrication, the powder compact was pre-sintered at 900 °C for 3 h in air. Full dense YSZ (TZ8Y, Tosoh, Japan) samples were fabricated via conventional ceramic processing methods involving uniaxial die-pressing of YSZ powder, followed by sintering at 1500 °C for 5 h (Fig. S1). The sintered YSZ was cut into small sized rectangular parallelepipeds and embedded into relatively large sized pre-sintered LSM disk (5 mm in diameters) to amplify the signal from LSM/YSZ interface by the limited contact effect [39–41]. To construct a counter electrode, Pt paste and a Pt-mesh were applied to the opposite end of the YSZ bar (Fig. S1). As a final step, the specimen was heat-treated at 1200 °C for 3 h under a uniaxial load to ensure intimate contact between full dense YSZ and LSM body without any chemical reaction in between. To explore any other possible impedance contributions to the LSM/YSZ interfacial reaction during the two-probe AC impedance analysis, a pre-test electrochemical cell (RE-cell) was constructed as a reference by placing a Pt wire, used as a reference electrode, around the middle of YSZ bar, i.e., where the parallel equipotential lines across the solid electrolyte can be maintained (Fig. 1(a), Fig. S1).

To identify clearly the correlation between electrode impedance and TPB of the LSM/YSZ interface, we prepared two kinds of electrochemical cells that had different TPB lengths but the same LSM/

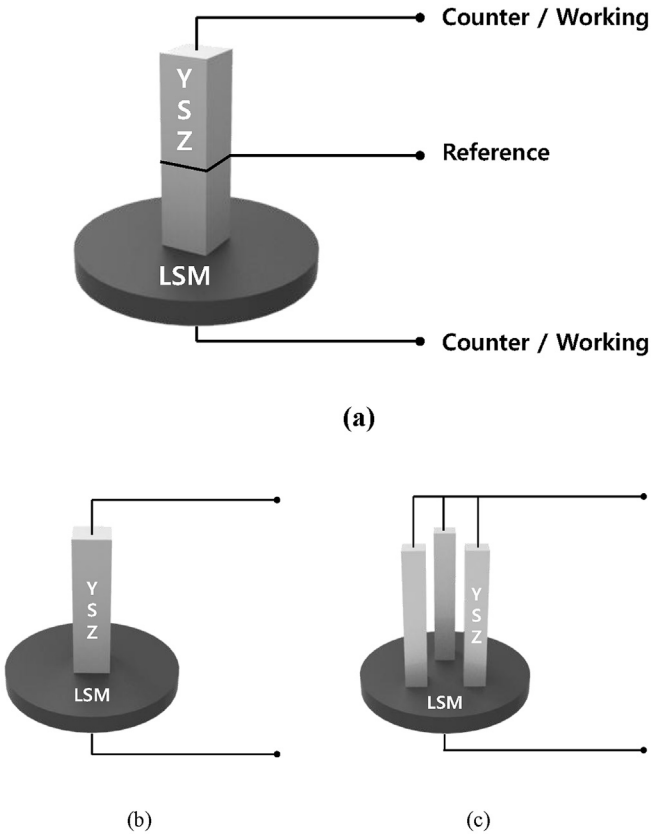

Fig. 1. Configuration of (a) reference electrochemical cell: Pt (counter/working electrode) | YSZ | LSM | Pt (working/counter electrode) and two electrochemical cells, (b) cell #1 (A_{cross} = 3.625 mm^2, l_{TPB} = 7.62 mm) and (c) cell #2 (A_{cross} = 3.624 mm^2, l_{TPB} = 13.20 mm).