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ScienceDirect
Solid State Ionics 178 (2007) 915–923
SOLID STATE IONICS
www.elsevier.com/locate/ssi

Measurement and finite element modeling of triple phase boundary-related current constriction in YSZ

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Received 21 December 2006; received in revised form 3 April 2007; accepted 5 April 2007

Abstract

Dense, photolithographically patterned platinum microelectrodes were created on yttria-stabilized zirconia (YSZ). The electrodes, typically tens of microns across, were orders of magnitude greater in width than that reported for the triple phase boundary width. Impedance spectra exhibited an additional feature at low frequencies that was believed to be due to a constriction resistance, where all of the current had to pass through a narrow triple phase boundary. The resistance of this feature had a similar activation energy to the conductivity of the electrolyte and was as large as nearly 100 times the high frequency resistance. Finite element models describing constricted and unconstricted resistances achieved qualitative agreement with the experimental results but consistently underestimated the constricted resistance. The implications of constriction upon the performance of micro-ionic devices and the potential for future similar measurements to quantify triple phase boundary widths are discussed.

Keywords: Platinum; Yttria stabilized zirconia (YSZ); Microelectrodes; Impedance spectroscopy; Triple phase boundary; Constriction resistance

1. Introduction

Photolithographically patterned microelectrodes are increasingly being used for fundamental studies of electrode kinetics in solid state electrochemical systems. When dense, ionically-blocking materials like platinum are used as the electrodes, the electrode half-reactions are expected to be localized to the triple phase boundary (TPB). Recent papers have measured the kinetics of micropatterned platinum, nickel, and lanthanum–strontium manganite electrodes and verified this localization [1–4]. Electrodes formed in this manner may be of practical importance in microdevices, such as micro-fuel cells [5].

These electrodes, given the manner in which they are fabricated (e.g., as interdigitated electrodes with widths typically in the tens of microns), exhibit a large ratio between electrode area and TPB length. Though this geometry is beneficial in gaining an understanding of electrode kinetics, it leads to a degradation in electrode performance and an effective increase in electrolytic resistance. The latter occurs because, under DC bias, the current is constricted to flow through the local neighborhood of the TPB, commonly referred to as the TPB width. At elevated frequencies, on the other hand, displacement current may flow over the entire electrode–electrolyte interfacial area, given the ability of the interface to store a finite amount of charged defects as illustrated in Fig. 1.

Experimentally, impedance spectroscopy may be used to separate the low frequency, constricted microelectrode resistance from the high frequency, unconstricted resistance. Since only the constricted resistance depends on the TPB width, this technique offers, in principle, the opportunity to extract this important geometric parameter. Though the TPB width is a factor in numerical modeling of fuel cells, its value has only been estimated in the past [6]. The power output of a fuel cell utilizing largely electronically conducting electrodes such as $(La,Sr)MnO_3$ (LSM) is believed to depend upon the TPB width [7], however the factors that control its width can currently only be presumed and not directly measured.

The technique described here to measure the TPB width relies upon the use of electrode geometries with a large ratio between TPB length and electrode contact area in order to create

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doi:10.1016/j.ssi.2007.04.003

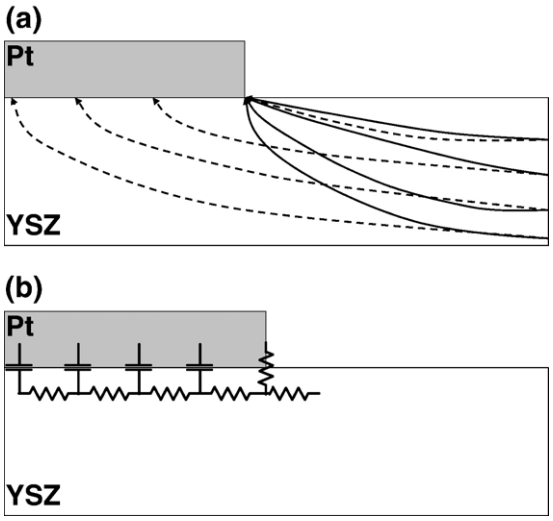

Fig. 1. Schematic picture of the constriction resistance. (a) The unconstricted current path is shown with dashed lines; the constricted current path is shown with solid lines. (b) The electrode–electrolyte interface modeled as a transmission line.

a constriction resistance measurably larger than the unconstricted resistance. Typical porous and/or composite electrodes do not satisfy this requirement, so constriction resistances are not normally observed. This technique also relies upon knowledge of the relationship between the measured resistance and the geometry of the current path. Typical samples used to measure the conductivity of a solid material have a parallel plate or bar geometry. Either of these situations yields a simple, analytic relationship between the resistance and geometry:

$$R = \frac{l}{\sigma \cdot A} \tag{1}$$

where R is the resistance, l is the path length of the current, σ is the conductivity, and A is the cross-sectional area of the current path. Similar expressions can be derived for other geometries, especially when symmetry arguments reduce the geometry to a simple form [8]. Samples with less symmetric geometries and/or heterogeneous material properties are often incapable of yielding an analytic expression similar to Eq. (1). In these situations, numerical methods must be used. One such method is finite element analysis and its application to this problem is outlined below.

We begin by considering Poisson's equation in partial differential form:

$$-\nabla \cdot \sigma \nabla \phi = 0 \tag{2}$$

where ϕ is the spatially-varying potential. To determine a structure's electrical resistance, Eq. (2) is solved with the relevant geometry and boundary conditions to determine the electrical potential as a function of position within the structure. The spatially-varying current density is found by multiplying the gradient of the voltage by the conductivity. The total current flow is determined by integrating the current density over an equipotential surface. Thus, the voltage and current through the structure is found and the resistance is calculated from their ratio.

This method has been used by Fleig to understand the effects of electrode porosity upon the measured electrolytic resistance [9–12]. These studies introduced the use of finite element analysis to predict a constriction resistance that develops in those situations and concluded that impedance spectroscopy could be used to measure the amount of constriction. Later work discussed a circular microfabricated electrode geometry and mentioned the potential use of a constriction resistance measurement as a metric for the TPB width [13]. Impedance spectra were calculated in reference [10,12] to show the possibility of this measurement technique. Experimental data to compare with the models was not presented, however, so that an estimate of the TPB width could not be made.

In this work, we have created interdigitated electrodes of dense platinum on the surface of thin film and bulk YSZ. Using impedance spectroscopy, we found resistance features that were ascribed to constricted and unconstricted resistances within the electrolyte. Finite element analysis was then used to try to describe the ratio of these two resistances in terms of the dependence on geometric factors including the TPB width. Ultimately, a lack of quantitative agreement between the experimentation and the numerical modeling prevented an estimation of the TPB width, suggesting more complex constriction effects than initially assumed. Proposed refinements to the experimentation and numerical modeling may enable such an estimation in the future.

2. Experimentation

2.1. Physical measurements

Dense platinum electrodes were microfabricated on the surfaces of single crystal YSZ substrates; tapecast, polycrystalline YSZ substrates; and sputtered YSZ thin films deposited on insulating fused silica substrates. Wideband ultraviolet photolithography was used to form the electrodes in interdigitated patterns. The fabrication and photolithographic patterning of these structures are described elsewhere [14].

A few different interdigitated electrode geometries were used. Each geometry had a set of fingers approximately 7.8 mm long and of varying width (see Fig. 2(a)). The separation between neighboring fingers was always equal to the finger width. Each design was about 8 mm × 8 mm, designed to fit on a 10 mm × 10 mm die. The electrodes were roughly 150 nm thick and did not appear, by scanning electron microscopy, to have pinholes before or after testing. Two devices produced by this method are pictured in Fig. 2(b).

Samples were electrically characterized in a Suss MicroTec (Waterbury Center, VT) model SOM4 probe station modified by the addition of a small hot stage, the Linkam Scientific Instruments (Tadworth, UK) model TS1500. Samples were contacted with 250 μm diameter, 99.99% pure platinum wire. The wires were formed into a loop and mounted in a Suss MicroTec PH150 manual XYZ positioner. The wires then made pressure contact to the electrodes, as determined by visual