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Effects of surface chemistry and microstructure of electrolyte on oxygen reduction kinetics of solid oxide fuel cells



Joong Sun Park ^{a, b}, Jihwan An ^{b, c}, Min Hwan Lee ^d, Fritz B. Prinz ^{b, e}, Wonyoung Lee ^{b, f, *}

^a Chemical Sciences and Engineering Division, Argonne National Laboratory, USA

^b Department of Mechanical Engineering, Stanford University, USA

^c Manufacturing Systems and Design Engineering Program, Seoul National University of Science and Technology, Republic of Korea

^d Department of Mechanical Engineering, University of California, Merced, USA

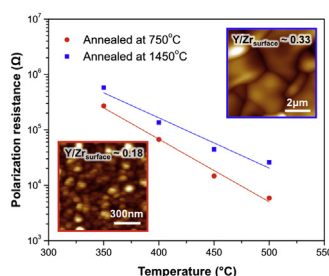
^e Department of Materials and Science Engineering, Stanford University, USA

^f School of Mechanical Engineering, Sungkyunkwan University, Republic of Korea

HIGHLIGHTS

- Enhanced surface kinetics with increase in grain boundary density.
- Mobile oxygen vacancies populated at grain boundaries.
- Oxygen vacancies induced by Y^{3+} surface segregation were found to be inactive.
- Our results provide guidelines to engineer the electrolyte–electrode interfaces.

GRAPHICAL ABSTRACT



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ABSTRACT

We report systematic investigation of the surface properties of yttria-stabilized zirconia (YSZ) electrolytes with the control of the grain boundary (GB) density at the surface, and its effects on electrochemical activities. The GB density of thin surface layers deposited on single crystal YSZ substrates is controlled by changing the annealing temperature (750–1450 °C). Higher oxygen reduction reactions (ORR) kinetics is observed in samples annealed at lower temperatures. The higher ORR activity is ascribed to the higher GB density at the YSZ surface where ‘mobile’ oxide ion vacancies are more populated. Meanwhile, oxide ion vacancies concurrently created with yttrium segregation at the surface at the higher annealing temperature are considered inactive to oxygen incorporation reactions. Our results provide additional insight into the interplay between the surface chemistry, microstructures, and electrochemical activity. They potentially provide important guidelines for engineering the electrolyte–electrode interfaces of solid oxide fuel cells for higher electrochemical performance.

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1. Introduction

Fluorite-structured oxides, such as yttria-stabilized zirconia (YSZ) and gadolinia-doped ceria (GDC), are widely used as solid-

state electrolytes for electrochemical energy conversion devices. Among them, YSZ is one of the most commonly used electrolyte materials, due to its chemical stability with reasonably high ionic conductivity for solid oxide fuel cells (SOFCs) [1–3]. In this material, interfacial properties often dominate the electrochemical performances at low temperature operation. First, the properties of surface, the interface between the material and the atmosphere, are often the determining factor for the overall device performance,

* Corresponding author. School of Mechanical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea.

E-mail address: leewy@skku.edu (W. Lee).

especially in the thin film devices. For example, Chao et al. showed that the 1 nm thick YSZ surface modification layer, in which the concentration of oxide ion vacancies was controlled to be higher than that of bulk YSZ, significantly enhanced the surface exchange coefficient [4]. Second, the grain boundary (GB; i.e. inter-granular interface) plays a crucial role in the ionic transport and exchange reactions. Ionic transport across GBs is known to be hindered due to an electrical potential barrier built up by defect segregation [5,6], while exchange reaction is enhanced near the GBs, due to the higher concentration of oxide ion vacancies [7–11].

Several studies have been reported on the systematic control of GB density near the surface by thermal annealing processes to enhance the surface exchange rate and electrochemical performance in various fluorite-based materials [8–11]. The surface exchange rate increased with the GB density at the surface. However, thermal annealing may affect not only the GB density, but also the chemical composition due to segregation of defects and ions [12–14]. Dopant segregation at the surface is important in cathode reactions in SOFCs since it can affect the near-surface chemical reactions and ionic transport of the electrolytes [15–18]. The correlation between the observed surface exchange rate and the surface defect segregation level has not yet been elucidated, even though those two factors are highly likely to be correlated each other.

In this study, we present a systematic investigation of the YSZ surface properties with the control of GB density at the surface, and its effects on electrochemical activities. The GB density in the thin surface layers deposited on polycrystalline YSZ substrates was controlled by the temperature of annealing process (750–1450 °C). With the higher annealing temperature, the grain size became larger resulting in a lower GB density, and the oxide ion vacancies at the surface became more populated by enhanced dopant segregation. The reduction of GB density at the surface may decrease the oxygen reduction reaction (ORR) rates while a higher concentration of oxide ion vacancies may increase the reaction sites for ORR. We present a comprehensive discussion through various characterizations on the material and electrochemical properties with the aid of atomic force microscopy (AFM), X-ray diffraction (XRD), angle-resolved X-ray photoemission spectroscopy (AR-XPS), and electrochemical impedance spectroscopy (EIS). Such a systematic quantification of the temperature-induced changes in the electrolyte surfaces provides enhanced understanding on the interplay between the surface chemistry, microstructures, and electrochemical activity, which may lead to the capability to further engineer functional materials for higher performance.

2. Experimental

Thin film YSZ with a thickness of ~500 nm was deposited on 500 μm thick polycrystalline YSZ substrates (Ceraflex 8YSZ) by pulsed laser deposition (PLD), using a Lambda Physik 248 nm KrF excimer laser with a fluence of 1.5 J/cm² per pulse. The substrate temperature was kept at 750 °C during deposition. The oxygen pressure was 100 mTorr and 200 Torr for deposition and cooling, respectively. The samples were annealed in air at a temperature between 750 and 1450 °C for 10 h to control the surface microstructures. Porous Pt with a thickness of ~80 nm was deposited on both sides of the samples by DC sputtering at an Ar pressure of 10 Pa.

A commercial AFM system (JSPM5200, JEOL) was used to characterize the surface morphology in the tapping mode. XRD patterns were obtained with Bruker D2 phaser instrument (Cu K α with $\lambda = 1.5406 \text{ \AA}$) with a scan rate of 1°/min and 0.05° step size. AR-XPS was used to identify the cation chemistries of YSZ film surfaces. Phi Versa Probe XPS microscope was operated with Al K α X-ray

(1486 eV) at 200 W for spectral analysis and compositional quantification. Spectra were acquired with emission angles from 15° to 75°, as defined relative to the surface normal. For the excitation energy of 1486 eV, the sampling depths of these photoelectrons at the emission angle of 15° are ~6.8 nm for both Zr 3d and Y 3d, considering the inelastic mean free path of photoelectrons. At the emission angle of 75°, on the other hand, the sampling depths of both elements are ~1.8 nm, making the measurements significantly more surface sensitive [17,19]. Spectra were acquired twice, to reveal the distribution of chemical composition in the thickness direction. This was done by subsequent acquisition; first, from the as-annealed surfaces; and second, after Ar etching to remove the surface layer of approximately 2–3 nm. Y 3d_{3/2}/3d_{5/2} and Zr 3d_{3/2}/3d_{5/2} peaks were used for the peak integration. Conditions for Ar etching in XPS were 5 kV, 1 μA and $2 \times 2 \text{ mm}^2$ of area. Etching rate of the films was back calculated by depth profiling. EIS measurements were performed using a Gamry FAS2 Femtostat system at 350, 400, 450, and 500 °C in the frequency range of 300 kHz–0.1 Hz with an AC signal amplitude of 50 mV. Hydrogen was fed at the anode with 10 sccm while the cathode was exposed to atmospheric air. The EIS results were analyzed and fitted to the spectra based on a complex nonlinear least squares fitting method. Details of sample setups including gas feedings and substrate heating, was previously described [20–22].

3. Results and discussion

First, we performed a structural analysis with AFM and XRD, to explore the effects of thermal annealing on the surface microstructures. The change of thermal annealing temperature was intended to control the GB density in the surface layers. Fig. 1 shows the surface morphology of YSZ samples annealed at different temperatures. The grain sizes varied from ~50 nm to ~5 μm , depending on the annealing temperature from 750 °C to 1450 °C. Assuming a constant GB width regardless of annealing temperature, the GB density decreased by a factor of 20–100, with the increase of the annealing temperature from 750 °C to 1450 °C. As was found in our earlier observations, the grain growth induced by thermal annealing enabled us to control the GB density at the surface [8–11]. Fig. 2 shows X-ray diffraction patterns from the YSZ samples annealed at 750 °C and 1450 °C. The patterns showed no noticeable difference between samples, indicating that no significant secondary phases or impurities were evolved during the thermal annealing within a resolution of XRD used here. These results substantiate that the thermal annealing enabled the control of the GB density in the surface layers without generating undesired phases.

To find the correlation between the GB density near the YSZ surface and electrochemical activity, we performed a series of EIS measurements at 350–500 °C. Fig. 3 shows representative Nyquist plots measured at 500 °C from the YSZ samples annealed at 750 °C and 1450 °C under $V_{\text{DC}} = 0.5 \text{ V}$ with respect to the reference electrode connected to the anode. The anode and cathode were exposed to pure dry hydrogen and ambient air, respectively. The impedance spectra with porous Pt electrodes showed two distinct arcs. The arc at the high frequencies is known to describe charge transport through the electrolyte, associated with oxide ion diffusion through the grains and the grain boundaries in the bulk electrolyte [23–25]. The magnitude of arc at the high frequencies showed no appreciable distinction between samples and the calculated oxide ion conductivities matched well with reported values (see Fig. S1) [2,21,22,26]. Although the oxide ion diffusivity across GBs is known to be several orders lower than that through grains [5,27–29], the obtained high frequency arc shows no discernible difference between the samples. (Note that two

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