Mechanism of Cathodic Performance Enhancement by a Few-Nanometer-Thick Oxide Overcoat on Porous Pt Cathodes of Solid Oxide Fuel Cells

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Supporting Information

ABSTRACT: In a recent report, we demonstrated that few-nanometer-thick yttria-stabilized zirconia (YSZ) coating on a porous Pt cathode of a solid oxide fuel cell is an excellent facilitator of oxygen reduction reaction (ORR) kinetics and an effective suppressor of Pt agglomeration. In this article, we reveal the actual role of the YSZ overcoat in the ORR process through a series of electrochemical analyses. Without the overcoat, the nanoporous Pt is significantly agglomerated during a high-temperature operation and the ORR becomes limited by the availability of triple phase boundaries (TPBs). An ultrathin YSZ overcoat prevents the ORR process from being limited by TPB area by preserving the morphology of its underlying Pt layer. More importantly, the overcoat acts as an excellent facilitator of the atomic-oxygen-species-mediated chemical process(es) that used to be rate-limiting in the ORR of a noncoated Pt/YSZ system.

INTRODUCTION

Solid oxide fuel cells (SOFCs) have been widely studied as an alternative clean power source because of their advantages in terms of fuel flexibility, system simplicity, and efficiency. Despite these advantages, their high operating temperature (>800 °C) has limited their lifetime, cost competitiveness, start-up/shut-down speed, and applicability to small-scale devices.5−9 However, reduction of operating temperature down to an intermediate (600−800 °C) or a low (<600 °C) temperature regime results in a dramatic loss of kinetics in both ionic transport and electrode reaction.6−9 Recently, researchers have addressed the issue of sluggish ionic transport kinetics of low-temperature SOFCs by thinning conventional electrolytes down to a few hundreds of nanometers.20,21 For the cathode, porous Pt is still the material of choice due to its superb catalytic performance despite its high cost and limited availability.10,11

For catalysis per mass and volume, catalysts with a maximized surface area are preferred. As the size of catalysts becomes smaller, the surface area to volume ratio and thus the proportion of catalytically active low-coordination sites become larger. However, these high-surface catalysts are prone to agglomeration, degrading their overall catalytic activity during operation. One of the most widely used methods to suppress the agglomeration is to interface the metal catalyst with an oxide.12−19 Usual approaches include coating metal catalysts by a gas-permeable oxide film through chemical vapor deposition and wet chemistry.19−21 However, these approaches do not provide a precise control over the thickness and uniformity of the oxides, let alone the location and area of oxide−metal interfaces newly formed by the coating, making a reproducible and maximized catalytic performance difficult to achieve. Recently, atomic layer deposition (ALD) has emerged as a promising tool to overcome these issues with its fascinating capabilities. The self-limiting nature of ALD offers atomic-scale thickness control and enables highly uniform and conformal films with excellent reproducibility.22

In our recent study, an ultrathin layer of yttrium-stabilized zirconia (YSZ) was coated on a highly porous Pt cathode by ALD to suppress Pt agglomeration for a low-temperature SOFC.23 Even a few-nanometer-thick coating was found to suppress the morphological degradation of nanoporous Pt, which was confirmed by other researchers as well.24,25 To our surprise, it was also found that the oxide coating enhanced the catalytic activity toward the oxygen reduction reaction (ORR) even if the oxide is expected to cover (and thus deactivate) part of catalytically active Pt surface. In this article, a mechanistic study was performed to understand the impact of ultrathin...
ALD coating on catalytic kinetics, especially for ORR on a Pt/YSZ system.

RESULTS AND DISCUSSION

Figure 1 shows schematic diagrams of two different kinds of cells examined in this study. One is a Pt/YSZ/Pt cell in which porous Pt was sputter-deposited on both sides of a 270 μm thick YSZ substrate. The other cell is based upon the same Pt/YSZ/Pt cell, but an ultrathin layer of YSZ is coated on one of the two Pt electrodes by ALD (see the Experimental Section). We call them BP (bare Pt-based) and CP (coated Pt-based) cells, respectively. Figure 2 includes time-dependent power densities of a BP and a CP cell and the corresponding polarization curves obtained at $t = 1, 3,$ and $14$ h at $600^\circ$C. Before the measurement, the cells were heated to $600^\circ$C at a rate of $10^\circ$C min$^{-1}$, and the aging clock started as soon as the temperature of the furnace enclosing the cell reached $600^\circ$C. A continuous cell bias of $0.2$ V was applied throughout the aging test except for the duration of intermittent impedance and polarization measurements. The trend of power density with time is very similar to that in our recent study, in which a significantly enhanced thermal stability was achieved by an ultrathin YSZ overcoat on a Pt-based cathode.$^{23}$ The BP cell degraded very fast from the initial power density of $1.57$ W cm$^{-2}$ measured at $t = 1$ h to $0.26$ W cm$^{-2}$ at $t = 14$ h under high-temperature polarization. On the other hand, the CP cell maintained its powering capability with a relatively insignificant change from $8.66$ to $7.11$ W cm$^{-2}$. Most of its degradation occurred in the first few hours, and the power density at $t = 14$ h was $98.7\%$ of the value at $t = 5$ h. Scanning electron microscopy (SEM) images of cathodes before and after the 14 h long operation are presented in Figure 3. As reported earlier,$^{23}$ an ultrathin ALD-based YSZ coating preserved the nanogranular microstructure during the high-temperature operation, whereas the noncoated Pt suffered from a severe agglomeration. In addition, the initially uniform YSZ overcoat is conjectured to have agglomerated into nanoscale islands or an interconnected network after being exposed to a high temperature,$^{23}$ making room for O$_2$ access to the Pt surface, as depicted in the insets of Figure 3.

The ORR process comprises smaller steps. In a Pt/YSZ system, these steps are as follows: (1) adsorption of molecular
oxygen on the catalyst surface, (2) dissociation of molecular oxygen into atomic species, (3) surface diffusion of atomic oxygen to the triple phase boundary (TPB), (4) charge transfer reaction, and (5) incorporation of oxygen ions into electrolyte.
To better understand the main factors affecting the discrepancy in the performance between the two cells presented above, we first studied ORR kinetics under different oxygen partial pressures \( p(O_2) \) ranging from 0.04 to 1.0 atm. The reaction order, \( m \), defined in relation \( R_p^{-1} \propto p(O_2)^m \) (\( R_p \) electrode polarization resistance), provides abundant clues about the rate-limiting step.\(^{26}\) For example, reaction order of \( m = 1 \) indicates that the rate-determining step is likely related to a molecular-oxygen-mediated process, such as \( O_2 \) adsorption and diffusion. A square root \( p(O_2) \) dependence (\( m = 1/2 \)) corresponds to an atomic-oxygen-related process, including dissociation into atomic oxygen species and their surface transport, and the \( m = 1/4 \) dependence can be ascribed to a process related to the charge transfer reaction.\(^{27}\)

Electrochemical impedance spectroscopy (EIS) was performed on a BP and a CP cell, and the resulting spectra are presented in Figures 4 and 5, respectively. Each cell was continuously exposed to the operational condition of choice (cell bias of 0.2 V at 600 °C), and the \( p(O_2) \) dependence of ORR kinetics was measured at \( t = 1 \) and 14 h. Each EIS was performed only when the electrical current measured at the cell bias of 0.2 V had not changed by more than \( \sim 3\% \) for 1 min after each \( p(O_2) \) change, which usually corresponds to \( 2\sim7 \) min after \( p(O_2) \) changes. For both BP and CP cells, the shape of the

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**Figure 5.** Nyquist (a, c) and Bode plots (b, d) of the CP cell with various \( p(O_2) \)'s at \( t = 1 \) and 14 h under \( \eta = 0.2 \) V at 600 °C.

**Figure 6.** (a) Equivalent circuits used to fit the EIS data. For both the BP and CP cells, equivalent circuits 1 and 2 were used for the data obtained at \( t = 1 \) and 14 h, respectively. (b, c) The resulting area-specific electrode polarization resistances of the BP and CP cells as a function of \( p(O_2) \). The resulting reaction order, \( m \), was obtained by the least-squares fitting of each dataset.
spectra obtained at $t = 1$ h hints that at least two R/CPE components can fit in there, whereas it is hard to resolve multiple R/CPE components from those measured at $t = 14$ h with reasonable accuracy. Therefore, for data fitting, two different equivalent circuits (Figure 6a) were used accordingly to extract each characteristic electrode resistance. The resulting electrode resistances are presented in Figure 6b (BP) and Figure 6c (CP) (see Table S1 in Supporting Information for the EIS fitting parameters). $R_1$ is the ohmic resistance originated mainly from ionic transport through the electrolyte, which approximately corresponds to the high-frequency intercept on the real axis of the Nyquist plot. $R_2$ and $R_3$ are assigned to the electrode resistances. It is postulated that both $R_2$ and $R_3$ correspond to cathodic polarization resistances because little meaningful change in these resistances was found by the change of H$_2$ flow rate ranging from 30 to 80 sccm. Cathodic overpotential is also widely accepted to dominate electrode loss in low-/intermediate-temperature SOFCs. It is also noted that all of the resistance values presented in this report are normalized by the cell area of 0.37 cm$^2$. The 1 h data fitted to equivalent circuit 1 shows that there are two distinct electrode processes that follow relation $R_p^{-1} \propto p(O_2)^m$. First, for the BP cell, $R_2$ shows a trend of $m = 1.107$ (close to 1), which is likely to indicate a molecular-oxygen-mediated process. The $m$ value of $R_3$ is 0.463 (close to 0.5) and is ascribed to an atomic-oxygen-mediated process such as dissociation of oxygen into atomic oxygen species and their adsorption onto the electrode. After $t \geq 14$ h, under a continuous cell bias of 0.2 V at 600 °C, the overall electrode resistance increased by more than 2 orders of magnitude and its $p(O_2)$ dependency became $m = 0.15$, implying a charge-transfer-limited ORR process. As the charge transfer process is known to be much faster than chemically driven processes such as dissociative adsorption and atomic surface diffusion, the interpretation of $m$ above is well-aligned with the fact that the peak frequency at $t = 14$ h is found to be higher than that at $t = 1$ h approximately by an order of magnitude, as can be compared in Figure 4b,d.

This inference is corroborated by dc-bias-dependent impedance measurements compiled in Figure 7. The total electrode resistances ($R_2 + R_3$ for 1 h cells and $R_2$ for 14 h cells) were extracted from impedance data obtained with different cell biases ranging from 0 to 0.4 V. If an ORR rate is limited by a charge transfer reaction, the electrode resistance would follow the Tafel behavior. Then, the area-specific electrode resistance (ASR) for ORR from an impedance measurement is expressed as

$$\text{ASR}_{\text{ORR}} = \frac{\partial \eta}{\partial F} = \frac{RT}{nFj} = \frac{RT}{nFj_0} \frac{1}{e^{\alpha nFj/R}\eta}$$

where $\alpha$ is the electron transfer coefficient, $n$ is the number of electrons per species, $F$ is the Faraday constant, $R$ is the gas constant, $T$ is the temperature, $j$ is the current density, $j_0$ is the exchange current density, and $\eta$ is the ORR overpotential.

According to this equation, the slope of the logarithmic ASR versus overpotential graph can be used to quantify $\alpha n$. As for the BP cell at $t = 1$ h, not only the logarithmic ASR versus $\eta$ deviates from the linear behavior significantly but also $\alpha n$ is calculated to be $<$0.4, indicating that the charge transfer reaction is unlikely to be the rate-limiting factor. (Note that the usual $\alpha$ is in the vicinity of 0.5.) At $t = 14$ h, the $\alpha n$ value becomes $\sim$0.8, making it reasonable to consider that the measured quantities correspond to the charge transfer process. Here, the change in the rate-determining step of ORR after 14 h is ascribed solely to the geometric agglomeration of Pt, not to
other factors such as oxidation of Pt surface, because, whereas a very thin layer of PtO2 would reside on its surface, this oxide is known to decompose into Pt and O2 at \( \sim 450 \) °C in 1 atm of oxygen.

On the other hand, the CP cell showed the overall electrode resistances and power densities much smaller than those of the BP cell, as shown in Figures 6 and 2, respectively. Interestingly, this is the case from a very early stage of operation when the nanoporous Pt of the BP cell is not expected to have developed significant agglomeration. This indicates that the effect of suppressed agglomeration only cannot fully explain the oxide-overcoat-induced enhancement of ORR kinetics. In Figure 6c, the two electrode resistances of the CP cell at \( t = 1 \) h exhibit different \( p(O_2) \) dependences as those of the BP cell did. The processes characterized by \( R_3/CPE_3 \) and \( R_4/CPE_4 \) have reaction orders of \( m = 0.034 \) (close to 0) and 0.034 (close to 0), respectively. Overall, the \( R_3/CPE_3 \) process dominates \( R_4/CPE_4 \), especially above 0.2 atm of oxygen. First, the \( R_3/CPE_3 \) process is likely to correspond to a process involving molecular O2 species such as O2 adsorption as reported in a recent ORR mechanism study for ultrathin ZrO2-coated Pt by Liu et al.25 On the other hand, the very small \( m \) value of the \( R_3/CPE_3 \) process can be ascribed to the incorporation of oxide ions (O\(^2^-\)) into the vacancies of electrolyte or gaseous O2 diffusion on the surface of Pt.1,26 If the ORR rate is governed by O2 diffusion, \( R_4 \) is not expected to show an explicit temperature dependency. As the CP cell shows an Arrhenius behavior with temperature dependence much facilitated. This explanation is also well-aligned with the disappearance of the process with \( m = \sim 0.5 \) that used to be dominant in the BP cell. The \( m \) value quantified even from the steepest slope of Figure 7c,d (between \( \eta = 0 \) and 0.2 V) was \( \sim 0.15 \) for both 1 and 14 h data. Given the usual \( \alpha \) value of \( \sim 0.5 \), the resulting \( n \) is too small to correspond to the charge transfer process of ORR. It is noted that Figure 7 is based upon the cell overpotential, not the activation overpotential.

The aforementioned observations can be summarized as follows. First, in our BP cell, a chemical process mediated by atomic oxygen species is the limiting process in ORR when the Pt electrode is relatively intact (at \( t = 1 \) h). As agglomeration continues during the operation at 600 °C, the site for charge transfer reaction (i.e., TPB) will become significantly smaller, which is further supported by the morphology images shown in Figure 3, making the overall ORR kinetics limited by the charge transfer step. As for the CP cell, the ORR is governed by either O2 incorporation into the electrolyte or O2\(^2^-\) transport through the newly formed Pt/YSZ interfaces, whereas molecular O2 adsorption also becomes a considerable rate-limiting process at low oxygen pressures (\( p(O_2) \) < 0.1 atm). It is also noted that the process with \( m = 0.463 \) visible in the BP cell disappears in the CP cell. This suggests that the rate-limiting step in the BP cell (atomic-oxygen-mediated processes) becomes highly facilitated by an ultrathin YSZ overcoat and does not function as the rate-limiting step in the CP cell.

### CONCLUSIONS

It was reported earlier that a highly uniform atomic-/nanoscale YSZ overcoat on a Pt catalyst enabled by ALD preserves the underlying Pt nanostructure and even enhanced the ORR kinetics significantly.23 Although the impact of overcoat on the Pt agglomeration seems obvious, it stayed mysterious that the CP cell shows higher ORR activity than the BP cell even when the bare Pt was not agglomerated. In this article, the mechanism of catalysis enhancement is presented through a series of electrochemical measurements. First, the ORR kinetics on a fresh nanoporous Pt/YSZ system is mainly governed by an atomic-oxygen-mediated chemical process. After Pt becomes highly agglomerated during the high-temperature operation, the rate-limiting step shifted to the charge transfer reaction due to a much smaller TPB area. On the other hand, a nanoporous Pt catalyst with a well-dispersed nanoscale YSZ overcoat seems to exhibit an ORR process mainly limited by the O2\(^2^-\) incorporation or O2\(^2^-\) transport through the new Pt/YSZ.
interfaces formed by the YSZ overcoat, whereas the molecular O₂ adsorption process also plays a considerable rate-determining role especially at a low p(O₂) regime (<0.1 atm). With these observations, the YSZ overcoat on Pt can be regarded as a significant facilitator of chemical processes related to atomic oxygen species during ORR in addition to an effective suppressor of Pt agglomeration.

■ EXPERIMENTAL SECTION

Electrolyte-supported Pt/YSZ/Pt cells were fabricated for electrochemical characterization. Pt layers of ~100 nm were deposited on both sides of a ~270 μm thick commercial electrolyte (Fuel Cell Materials) with an ac magnetron sputter at 30 W with an Ar pressure of 55 mtorr. The Pt electrodes with the active area of 0.37 cm² were placed between two current-collecting Pt meshes made solid oxide cell test setup. Cells with the active area of 0.37 cm² were placed between two current-collecting Pt meshes made solid oxide cell test setup. Cells with the active area of ~100 nm were deposited on both sides of a ~270 μm thick commercial electrolyte (Fuel Cell Materials) with an ac magnetron sputter at 30 W with an Ar pressure of 55 mtorr. The Pt electrodes were used as the precursors of Zr and Y, respectively. Ar (99.999%) and distilled water were used as the purging gas and oxidant, respectively. The ratio of cycles between ZrO₂ and Y₂O₃ deposition was 4:1 to render ~7.5 mol % YSZ as quantified by an X-ray photoelectron spectroscopy system (PHI XPS; see Figure S1 for the spectrum).

The canister temperatures for ZrO₂ and Y₂O₃ were 85 and 160 °C, respectively, and the line temperature was 180 °C. The chamber temperature was set at 250 °C. The ALD supercycles were performed on the porous cathode 6 times to make a ~3 nm thick YSZ coating. The microstructures of thin films were characterized by a field-emission SEM (Zeiss GeminiSEM) at the operating voltage of 3–5 kV.

Electrochemical characterization was performed in a homemade solid oxide cell test setup. Cells with the active area of 0.37 cm² were placed between two current-collecting Pt meshes (Goodfellow Co.). The cell was enclosed in a furnace in which the operating temperature is controlled at a set point through a feedback loop. Polarization curves and EIS spectra were obtained using a potentiostat and impedance analyzer (Bio-Logic SP-240). The EIS was performed with a 20 mV perturbation and a dc bias ranging from OCV to the cathode side to control the O₂ partial pressure ranging to the cathode side to control the O₂ partial pressure ranging.

The resulting EIS spectra were fitted to the equivalent circuit using commercial software (EC-Lab, Bio-Logic Science Instruments).

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00433.

Parameters extracted from the EIS measurements by fitting to equivalent circuits, and an XPS spectrum of YSZ film (PDF)

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Notes
The authors declare no competing financial interest.

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