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Improving thermal stability of nanoporous platinum cathode at platinum/yttria-stabilized zirconia interface by oxygen plasma treatment

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HIGHLIGHTS

- Enhanced Pt/YSZ adhesion by O_2 plasma has suppressed Pt agglomeration at high temperatures.
- The cell of OH^--rich YSZ has stronger adhesion to Pt nanoporous thin film.
- Pt nanoporous features at YSZ contact interface was delaminated for morphology observation.
- Enhanced adhesion force in the cell of O_2 plasma treated YSZ was measured by AFM.
- O_2 plasma treated cell has retained 88.2% of power output under operating at 450 °C for 10 h.

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ABSTRACT

A short oxygen plasma treatment applied on yttria-stabilized zirconia (YSZ) electrolyte of a solid oxide fuel cell has effectively improved the adhesion between the nanoporous Pt thin film cathode and the YSZ electrolyte, which stabilizes the electrochemically active nanoscale features of Pt at YSZ contact interface. After operating at 450 °C for 10 h, the cell with YSZ surface treated by oxygen plasma has retained 88.2% of the fuel cell current output, and the increase of R_{ohm} is approximately 20% lower in the cell with YSZ than the non-treated YSZ. This is because the ion incorporation reaction sites which usually occurs at Pt/YSZ interface is retained by the preservation of nanoporous Pt features at YSZ contact interface.

1. Introduction

Nanoporous platinum (Pt) thin film is a common cathode used for micro-solid oxide fuel cells (micro-SOFCs) due to its superior catalytic activity towards sluggish cathode oxygen reduction reactions (ORR) at very low temperatures (< 500 °C) [1–5]. The nanoporous Pt cathode thin films are usually deposited by direct current (DC) magnetron sputtering [2] or radio frequency (RF) sputtering [5] at a high argon gas pressure to create a nanoporous microstructure with high density of nanoscale features, which not only facilitates gas diffusion through the electrode but also maximizes the density of triple phase boundary (TPB) (the electrolyte/electrode/gas junctions). Micro-SOFCs using sputtered nanoporous Pt thin film as a catalytic cathode have shown impressive peak power densities up to 1.3 W/cm^2 at 450 °C [6].

One critical issue of using sputtered nanoporous Pt cathode is its poor thermal stability under high temperature operation. The thermodynamically unstable nanoscale features agglomerate very rapidly to lower its surface energy, which results in loss of TPBs, and less electrochemical reaction sites for energy conversion become available. The degradation of fuel cell performance was very fast, which was about 25% loss in output current within the first hour, and more than 50% after 12 h of operation at 400 °C [7,8].

The thermal stability of the nanoscale features in sputtered nanoporous Pt thin films can be improved by methods involving surface oxide capping or compositing with an ionic conducting oxide such as YSZ or by alloying. In earlier reported works, the concept of using an oxide-capping through a vapor deposited process on the nanoporous metallic electrode has been demonstrated, which play a role in preventing the nanoporous features from the thermally-driven agglomeration for the current output stability. Our previous work [9] found that a few nanometer-thin zirconia capping on top of nanoporous Pt cathode by atomic layer deposition (ALD) has confined the nanoporous Pt features at 450 °C and simultaneously facilitated the oxygen adsorption-dissociation process on Pt cathode surface. Chang et al. [10] also reported that an ALD-YSZ coating on a porous Pt electrode showed an improved thermal stability of the Pt electrode, and the partially agglomerated YSZ at a high temperature of 500 °C has formed a favorable structure for a maximized reaction area. Hong et al. [11]

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suggested a gadolinia-doped ceria capped Pt cathode by sputtering can function as a thermal barrier to enable the production of passive layers for the top surface morphology of the Pt cathode. Choi et al. [12] evaluated silver (Ag) cathodes surface-coated with scandia-stabilized zirconia (ScSZ) nanoparticles by sputtering for the thermal stability against silver agglomeration, and then increased the triple boundary area where the Ag electrode, ScSZ electrolyte and oxygen gas meet.

Making Pt-based nanocomposites or alloying Pt with another catalytically active metal were also reported for the morphological stability in the interior of the electrode. Our previous work [13] found the alloying Pt with 12 at% Ni by co-sputtering constrained the thermally-driven grain growth and maintained the porosity in the bulk of cathode film for sufficient cathode oxygen diffusion. A significant grain growth of pure Pt film occurred from 300 to 450 °C, while PtNi alloy films had consistent grain sizes of few nanometers at temperatures below 450 °C. Wang et al. [7] presented the nanoscale pores and cracks in the sputtered PtNi films are more resistive to thermal agglomeration due to lower surface energy by *ab initio* calculations. Lee et al. [14] fabricated Pt-based nanocomposites with 5 vol% gadolinium doped ceria (GDC) as a dispersant by dispersion hardening process, and the Pt/GDC electrode retained the higher ratio of pores after the operation at 500 °C for 1 h. Rottmayer et al. [15] explored the functional-grading Pt/YSZ nanocomposites as a morphologically stable cathode over 250–400 °C, and the increased porosity in Pt/YSZ film led to more efficient oxygen diffusion which is determined to be the rate-limiting process.

Although the thermal stability against the Pt agglomeration was improved through oxide-capped Pt surface and oxide-composited Pt interior, there was still a significant amount of performance degradation being observed. This is because the thermally-driven agglomeration at the interface of Pt cathode and YSZ electrolyte at high temperatures can still affect the fuel cell performance stability. It is reported that the adhesion of Pt on single crystal YSZ substrate is thermally unstable, which causes the hillock growth [16], hole formation [17] or delamination of the Pt thin film. The nanoporous Pt thin film annealed or operated as a fuel cell in high temperature after a short time of operation can either result in delamination from the YSZ substrate or agglomeration, which the former makes the Pt lose contact with YSZ, and the latter makes the Pt to form disconnected islands instead of a continuous film and loses its electrical conductivity. The poor interfacial adhesion between nanoporous Pt thin film cathode and YSZ electrolyte that affected the fuel cell performance was observed in a few works. Rottmayer et al. [15] reported the coarsening and delamination of 120 nm-thick sputtered Pt thin film from the 100 μm-thick YSZ electrolyte and resulted in the cell to fail within 15 min of operation at 400 °C. Ryll et al. [18] observed the voids to form near the interface of Pt/YSZ after annealing at 450 °C for 2 h, and the annealed Pt films have formed disconnected islands under different sputtering parameters. Yan et al. [19] reported the significantly increased area specific resistance (ASR) after annealing at 500 °C for 10 h due to disconnected Pt that resulted in poor electrical conduction and adhesion to YSZ substrate. In our previous work [20], the 150 nm-thin Pt thin film was peeled off from the YSZ substrate, and the agglomeration of the sputtered nanoporous Pt at YSZ contact interface was directly observed with SEM imaging. Although the agglomeration of Pt bonded at the YSZ contact interface requires higher temperature to occur than the agglomeration at the unbonded top surface of the Pt film, significant agglomeration of Pt at the YSZ contact interface still occur at temperatures higher than 500 °C.

Oxygen plasma treatment, a common process in the semiconductor industry, has been previously used successfully to control hydrophilicity of substrates [21–24] with high efficiency, and reproductivity as well as being a fast, easy-to-scale-up, and clean process. Choi et al. [21] showed that oxygen-plasma-induced distinctive high-polar characteristics caused the increased total surface energy for both silicon and glass substrates even at low power or short plasma exposure times. Bhattacharya et al. [22] found the change in wettability of surface owing to various dosages of oxygen plasma exposure can be a useful parameter to gauge the bond strength between glass and poly(dimethyl siloxane)(PDMS). Nakamura et al. [24] used oxygen plasma treatment to improve the adhesive strength between the polyimide and metal, which was dominated by the chemical state of bonding on the surface of polyimide films rather than surface morphology. In addition to the various material in the semiconductor industry, Wu et al. [25] and Watanabe et al. [26] also employed oxygen plasma to retain stable hydrophilicity on zirconia dental ceramic, and the improved wettability did actively promote the attachment and biocompatibility of osteoblast-like cells by the effect of hydroxylation.

In this work, we proposed to improve the bonding between Pt and YSZ substrate by using an oxygen plasma treatment on the YSZ substrate prior to the deposition of nanoporous Pt cathode. The oxygen plasma treatment facilitated a more chemically active YSZ surface via hydroxylation, and the free radical on hydroxyl groups provides the extra electrostatic interaction towards the sputtered Pt thin film. Therefore, the adhesion between Pt and YSZ was expected to improve. The current stability at 450 °C of the fuel cell with and without the YSZ surface plasma treatment was compared. The plasma-treated YSZ surface showed better adhesion to the sputtered Pt thin film cathode, and the thermal stability of the fuel cell was noticeably improved.

2. Experimental

2.1. O_2 plasma treatment on YSZ

A 200 μm-thick (100) single crystal and polished YSZ substrate (Latech Scientific Supply Pte. Ltd.) was used. O_2 plasma at 600 W of power and pure O_2 pressure of 300 mTorr (PX-500 Plasma Treatment System, Nordson MARCH) was applied on the YSZ surface at room temperature for 1, 3 and 5 min accordingly.

A simple contact angle test was done to verify the effect of plasma treatment on YSZ surface. A 1 μL of deionized water droplet was put on the YSZ surfaces under ambient conditions and observed with a static contact angle goniometer (DataPhysics, OCA 15 EC).

The chemical state of YSZ surfaces before and after plasma treatment was identified by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra). The detail spectra of C_{1s} and O_{1s} were obtained by irradiating the YSZ surface with a beam of X-rays while simultaneously measuring the binding energy and number of electrons that escape from the YSZ top surface. The samples were always stored in the desiccator to avoid the adsorption of ambient moisture.

The adhesion force between Pt and YSZ surface was determined by an atomic force spectroscopy (AFM, Asylum Research MFP-3D) [27]. A Pt-coated silicon tip was used to probe on the YSZ surfaces before and after plasma treatment. The interaction between Pt tip and YSZ substrates delivered different magnitude of forces acting on the probe cantilever, causing the deflections on the cantilever. The Pt tip in contact with YSZ surface is withdrawn until the tip break contact with the surface. The breaking point occurred when the spring force of cantilever exceeded the adhesion force between Pt and YSZ, and the resulting deflection of the cantilever multiplied by the known spring constant (0.2 N/m) of the Pt-coated tip (NANOSENSORS, PPP-CONTPt-10) represented the Pt/YSZ adhesion, following Hooke's law.

2.2. Direct morphology observation of nanoporous Pt at the YSZ contact interface

A delamination method based on double cantilever beam (DCB) technique [20,28,29] is applied to neatly delaminate the nanoporous Pt thin film from YSZ substrate in order to reveal the morphology of nanoporous Pt at the YSZ contact interface. DCB technique allows the precise control of delamination up to atomic monolayer along the targeted interface. A dummy silicon strip with the same dimension as the Pt/YSZ substrate was diced and coated with a thick layer of epoxy

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