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Sputtered Nanoporous PtNi Thin Film Cathodes with Improved Thermal Stability for Low Temperature Solid Oxide Fuel Cells

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ABSTRACT

Nanoporous PtNi alloy thin film was demonstrated to effectively improve the thermal stability of cathode under high temperature fuel cell operation. The grain growth, which indicates the agglomeration of the nanoparticles, were constrained, as observed by comparing the surface morphologies and grain sizes in bulk of film between pure Pt and PtNi alloy cathodes. The constrained grain growth by alloying with Ni maintained the porosity in bulk of cathode film for sufficient cathode oxygen diffusion and adsorption/dissociation processes. Fuel cell using Pt_{67}-Ni_{33} cathode better maintained the output current density than the cell using pure Pt cathode by 26% after 48 hours of continuous operation.

1. Introduction

Nanoporous platinum (Pt) thin film is one common choice of cathode for micro-solid oxide fuel cells (micro-SOFCs) operating at temperatures below 500 °C [1–4]. The superior catalytic activity of Pt is necessary to compensate for the sluggish cathode oxygen reduction reaction (ORR) kinetics when operating at such low temperatures [5,6]. The nanoporous Pt cathode films are often fabricated by direct current (DC) magnetron sputtering or radio frequency (RF) sputtering at a high argon gas pressure to generate a high density of nanoscale pores or cracks within the film, and the resulting pore size is in the range of tens to a few nanometers. The high density of reaction sites allows a high energy conversion rate with low electrode polarization so that a high power output of the fuel cell is promised [7–9].

One chronical issue of using nanoporous Pt cathode for micro-SOFCs is its poor thermal stability under high temperature operation. Despite the high density of nanopores and cracks that can maximize the electrochemically active sites, or the triple phase boundaries (TPBs), the nanoscale features are subjected to thermally-driven agglomeration to lower its high surface free energy to a thermodynamic balance, which inevitably resulted in a rapid loss of the effective surface area and hence the lower cell current output. The thermal agglomeration of a sputtered nanoporous Pt film was reported to initiate at around 300 °C [6,10], which is way below the typical operating temperature of micro-SOFCs between 350 to 500 °C. The irreversible deterioration to fuel cell performance caused by the cathode agglomeration was reported to be about 50% after 12 hours of operation at 400 °C [11], and our earlier report also showed an 86.2% of performance loss at 450 °C after 75 hours [12]. These results are far from the U.S. Department of Energy target in 2015 that 20% loss within 1,500 hours was set for fuel cells as portable power sources [13]. Although replacing Pt with conventional oxide cathodes materials for SOFCs, such as LSCF, was reported, it requires the operating temperature to be higher than 500 °C to obtain satisfactory performance [14,15]. Therefore, it is worthwhile to search for solutions to improve the thermal stability of nanoporous Pt cathodes.

Reported methods to maintain the high density of nanoporous features of pure Pt electrode include electrode surface-capping by a thin layer of oxide [12,16,17], employing the core-shell structure of the nanoparticles [18], or alloying with another catalytically active element such as nickel [19]. In particular, alloying Pt with nickel (Ni) can be a simple solution to effectively hinder thermal agglomeration since the melting temperature of PtNi nanoalloys is higher than Pt [20]. The high loading of Pt in micro-SOFCs can also be reduced by alloying with the significantly cheaper Ni. An initial study on the agglomeration behavior of Pt and PtNi alloy was reported by Wang et al. [19], showing the nanoscale pores and cracks in the sputtered PtNi film are indeed more resistive to Ostwald ripening under thermal annealing. However, the work

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only addressed the morphological stability, and no *in-situ* fuel cell test to characterize the performance of the cathodes was done to verify the effectiveness in maintaining the fuel cell performance in micro-SOFCs operating temperature range.

In this work, the effectiveness of Ni alloyed Pt on hindering thermal agglomeration of nanoporous thin film cathode was examined and compared with nanoporous pure Pt cathode. The thermally-driven morphological evolution on the film surface and the grain growth in the bulk of film were compared between PtNi and pure Pt. The thermal stability and cathode electrochemical performance over time were examined. The nanostructure observation, crystallinity, and grain size evolution were also investigated to confirm the origin of the improved thermal stability in nanoporous PtNi cathode.

2. Experimental

Pt and PtNi thin films were deposited on silicon substrates and yttria-stabilized zirconia (YSZ) substrates accordingly using radio frequency (RF) sputtering at 100 W and 30 mTorr of argon pressure at room temperature. The thickness for all films was 100 nm. Three different compositions of PtNi were deposited, with the Ni content being varied by placing 2, 4, and 6 of Ni rods (6 mm tall and 6 mm in diameter) on Pt target. The compositions of the as-deposited Pt and

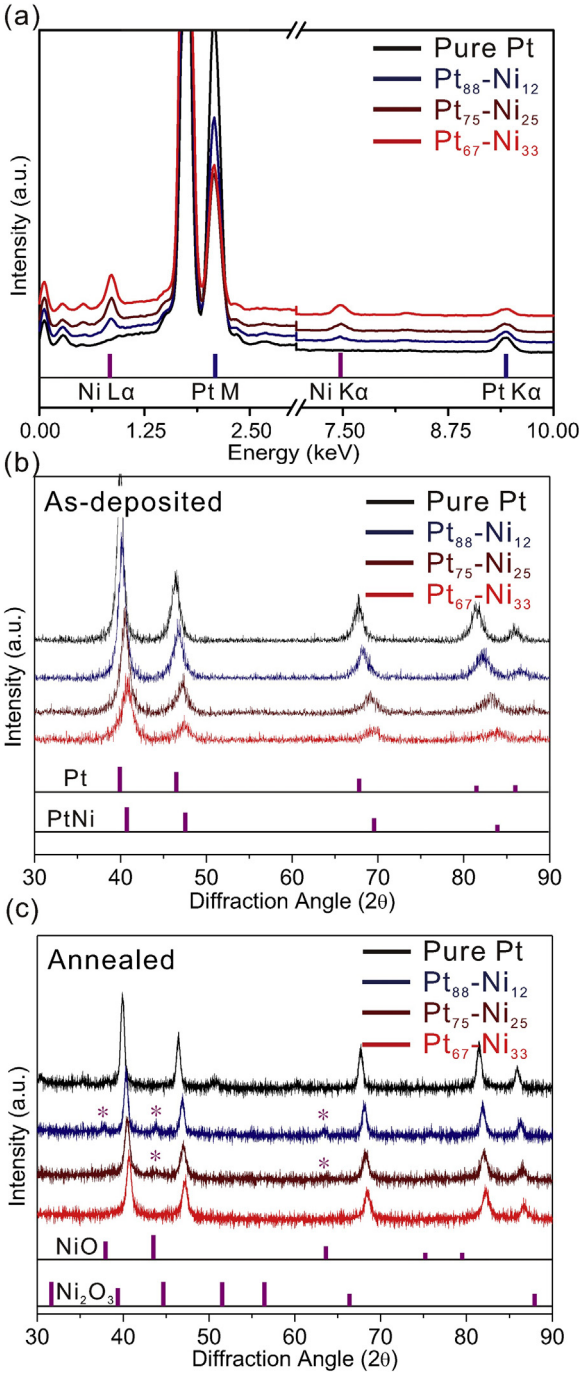

Fig. 1. (a) EDX, (b) XRD patterns of the as-deposited, and (c) the 800 °C-annealed nanoporous pure Pt, Pt_{88}-Ni_{12}, Pt_{75}-Ni_{25}, and Pt_{67}-Ni_{33} films.