Thermal stability and performance enhancement of nano-porous platinum cathode in solid oxide fuel cells by nanoscale ZrO₂ capping

Liu, Kang-Yu; Fan, Liangdong; Yu, Chen-Chiang; Su, Pei-Chen

2015

Liu, K.-Y., Fan, L., Yu, C.-C., & Su, P.-C. (2015). Thermal stability and performance enhancement of nano-porous platinum cathode in solid oxide fuel cells by nanoscale ZrO₂ capping. *Electrochemistry Communications*, 56, 65-69.

<https://hdl.handle.net/10356/85503>

<https://doi.org/10.1016/j.elecom.2015.04.008>

© 2015 Elsevier. This is the author created version of a work that has been peer reviewed and accepted for publication by *Electrochemistry Communications*, Elsevier. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1016/j.elecom.2015.04.008>].

Downloaded on 26 Apr 2023 20:05:10 SGT

Thermal stability and performance enhancement of nano-porous platinum cathode in solid oxide fuel cells by nanoscale ZrO₂ capping

Kang-Yu Liu^a, Liangdong Fan^a, Chen-Chiang Yu^b and Pei-Chen Su^{a,*}

^a School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

^b Energy Research Institute@NTU, Interdisciplinary Graduate School, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

*Corresponding author

Tel.: +65 6790 5586

E-mail address: peichensu@ntu.edu.sg

Abstract

This work demonstrates a nanoscale zirconia layer coated by atomic layer deposition (ALD) with only a few coating cycles on a nano-porous platinum cathode surface to serve as a physical confinement to prevent the electrode agglomeration under high temperature operation, and at the same time to enhance the cathode oxygen reduction activity. The resulted enhancement in cathode electrochemical performance can arise from the discontinuous ZrO_2 film that facilitates the oxygen adsorption on cathode surface and decrease the oxygen adsorption-desorption resistance.

Keyword: micro-SOFCs; atomic layer deposition (ALD); zirconia; nano-porous platinum cathode; thermal stability; oxygen reduction activity

1 Introduction

Recent advances in ultra-low temperature solid oxide fuel cells (SOFCs), also referred as micro-SOFCs in some literature, operating at temperature below 500°C with superior performance have been demonstrated using nanoscale thin film electrolytes[1–3]. The highest power density reported to date was 1.3W/cm² at 450°C[4], and the lowest temperature demonstrated was at 265°C with a power density of 28mW/cm²[5], both of which have shown great potential for the extension of SOFC applications from conventional stationary to portable power sources. Since the operating temperature is much lower than conventional SOFCs, the cathode oxygen reduction process becomes the most rate-limiting among all polarization processes. Currently, noble metal cathodes with high activities such as platinum[1,6] or its alloys[7–9] with high density of nanoscale pores are still common choices for demonstration of such high performance.

One major issue of using nano-porous metal as electrode is the poor thermal stability which often causes irreversible deterioration to cell performance. Among the reported observation of thermally-driven agglomeration in nano-porous platinum[10] and its alloy with nickel[9], severe losses in effective triple phase boundary (TPB) densities with increasing temperature were consistently observed. Using oxide materials as cathodes can have superior thermal stability over metal, but the cell performance is still far from satisfactory at temperature below 500°C[11,12]. Therefore, maintaining the thermal stability of the nano-porous electrode is critical for practical application of micro-SOFCs.

Earlier literature have proposed the capping of electrodes using atomic layer deposition (ALD) with zirconia (ZrO₂) films on oxide or metal electrodes of electrochemical devices, with the purpose either to maintain the electrode chemical stability or to introduce additional reaction

sites between the backbone electrode and the ZrO_2 [13–15]. In this work, we applied only a few cycles of ALD- ZrO_2 capping on nano-porous metal to serve as a geometrical confinement against thermal agglomeration, while an unexpected decrease in cathode polarization resistance was also observed. The thermal stability of the confined nano-porous platinum cathode, the origin of the cathode enhancement, and the cell durability testing up to 120 hours were presented and discussed.

2 Experimental

2.1 ZrO_2 capping on nano-porous platinum

Nano-porous platinum cathodes (100nm-thick) were deposited on yttria-stabilized zirconia (YSZ) substrates using radio frequency sputtering[16]. ZrO_2 capping layer was then deposited by ALD (CN1 Co., Ltd.) onto the platinum cathode for 0, 10, 15, 30, and 60 cycles, with tetrakis(dimethylamino)zirconium(IV) (99.99%) (Strem Chemicals Inc.) as ZrO_2 precursor, oxygen (99.999%) as oxidant at the substrate temperature of 250°C. Here one ALD cycle refers to the combination of one pulse of precursor followed by one pulse of oxygen oxidant.

2.2 Thermal stability and cathode performance characterization

The uncapped and ZrO_2 -capped platinum were annealed at 450 and 600°C for 12 hours to test the effectiveness of capping on the thermal stability of cathode, and their microstructures were observed by field emission scanning electron microscopy (FESEM).

Fuel cells with uncapped and ZrO_2 -capped cathodes were fabricated on (100) single crystalline YSZ substrates, and uncapped platinum were used as the anodes. The polarization and electrochemical impedance spectroscopy (EIS) curves were retrieved at 450°C using an electrochemical potentiostat (Solartron analytical) with 99.99% hydrogen as fuel and air as oxidant.

3 Results and discussion

3.1 Morphological evolution of ALD-ZrO₂ on Pt

Since the growth of ALD films will undergo the nucleation and crystalline growth process, depending on the substrate material and deposition temperature[17], surface morphologies were firstly examined approximately when the film became continuous over platinum surface. Figure 1a shows the experiment to grow ALD-ZrO₂ on “dense” platinum film instead of a nano-porous film in order to avoid geometrical confusion when identifying the ALD-ZrO₂ by FESEM imaging. A bare platinum surface or platinum capped with non-continuous ZrO₂ film will give minimized electron charging during FESEM imaging, while the charging will appear with continuous ZrO₂ film. The platinum surface without capping showed a high density of grain boundaries (Figure 1b), and similar morphologies after 10-and 15-cycle of ALD-ZrO₂ capping were observed with insignificant charging effect. However, the 30-cycle ZrO₂ capping appeared to block the platinum surface since the surface grain boundaries and grooves became invisible, while the electron charging was severe. Same observation became more obvious with 60-cycle capping. Therefore, we expect the ALD-ZrO₂ capping on nano-porous platinum to show similar behavior, forming a discontinuous film at 10- and 15-cycle and a continuous blocking film over 30-cycle.

3.2 Morphological stability under high temperature annealing

Figure 2 shows the surface morphologies of cathodes with/without ZrO₂ capping and before/after thermal annealing. The uncapped platinum electrode (figure 2a) showed the expected nano-porous structure with columnar grains and high TPB density, and agglomerated significantly after annealed at 450 and 600°C (figure 2b-2c), which is consistent with literature[10]. With only 10-cycle ZrO₂ capping (approximately 1.6 nm in thickness) (figure 2d-

2f), the agglomeration was effectively hindered. With 60-cycle capping (figure 2g-2i), the cracks between platinum clusters were narrower by thicker ZrO₂ deposition, but stable nano-porous morphologies after annealing was still maintained. .

3.3 ORR enhancement of ALD-ZrO₂ capping

The I-V curves (Figure 3a) showed that the cell with 10-cycle capped cathode had the highest performance, followed by cell with 15-cycle capping. With thicker capping of 30- and 60-cycle, the performance dropped below the cell of uncapped cathode.

The EIS curves (Figure 3b) were retrieved at 0.9V of cell voltage and showed parallel trend with I-V curves. The Ohmic contribution due to variation of thickness among YSZ substrates was subtracted and re-drawn in the insert to compare only the polarization resistance values (R_p) among cells. We ascribe R_p to mainly the resistance of cathode reactions due to the sluggish ORR over anode reactions at 450°C. The R_p was 50.3 Ωcm^2 for uncapped cathode, and dropped to 5.3 Ωcm^2 at 10-cycle capping. But after 15-cycle, R_p increased and became higher than the uncapped cathode at 30-cycle. At 60-cycle, huge polarization resistance of up to 640 Ωcm^2 was observed. In other words, the improved ORR activity was only observed in cathodes with low capping cycles (10- and 15-cycle).

Bode plots were further analyzed to identify the rate-limiting processes affected by the ALD-ZrO₂ capping (Figure 3c). Two overlapped peaks of phase angles were observed, where a higher and obvious peak dominates at low frequency and a suppressed peak at high frequency. The phase angle at high frequency range (10^5 - 10^3 Hz) is ascribed to the charge transfer process, while the phase angles at low frequency range (10^2 -0.1Hz) relates to the non-charge transfer processes, including gas diffusion and dissociative adsorption[18,19]. The high frequency peak had no significant change with capping, while the low frequency peak remarkably decreased with only

10-cycle ZrO_2 capping, indicating the promotion of oxygen gas adsorption and dissociation process. With 15-cycle capping, the low frequency phase angle increased back, but still smaller than that of uncapped platinum. At 30- and 60-cycle capping, the continuous coverage of ALD- ZrO_2 had fully blocked the platinum surface, and both a increased magnitude of phase angle and its shift to lower frequencies were observed, meaning the oxygen gas adsorption and dissociation process was blocked by thicker ZrO_2 . Especially, the 60-cycle capped cathode showed a clear gas diffusion resistance as evidenced by a large phase angle at the characteristic relaxation frequency of 0.1-1 Hz[19].

The origin of the observed enhancement in oxygen gas adsorption and dissociation can be explained as follows. At low ALD-capping cycles, the ZrO_2 film was not continuous and may be only scattered nanoparticles or connected particle networks, where a majority of platinum surface remained exposed to oxygen atmosphere. Thus, the surface diffusion pathways for adsorbed oxygen are still available. The existence of ALD- ZrO_2 on platinum surface may either provide a facile oxygen diffusion pathway[20–22] or assist the oxygen adsorption onto the oxygen-adsorbing favourable ZrO_2 surface, thus facilitated the ORR process. When the surface of platinum is completely covered by ZrO_2 with higher ALD cycles, both the diffusion of gaseous oxygen onto platinum surface and the transfer of adsorbed oxygen along platinum active surface become difficult, resulting in a slower ORR. A recent study by Chang et al also observed the cathode enhancement with thicker ALD-YSZ capping, but only when the initially dense YSZ broke into interconnected networks after heating. No enhancement was shown with the initially dense capping film[23]. However, unlike what Chang claimed, where the origin of enhancement was from an enhanced triple phase boundary area at the vicinity of the Pt/electrolyte interface, our results showed the enhancement is more likely from the non-charge transfer process of

surface adsorption/dissociation, as evidenced by the suppressed low frequency phase angles with 10- and 15-cycle capping.

3.4 Performance stability with time

The stability of output current between cells with 10-cycle ZrO_2 -capped and uncapped cathode were compared at 450°C for 120 hours (Figure 4), which is the longest test among literature for metallic electrode based micro-SOFCs. The current was drained at 0.5V around the voltage of the peak power density to accelerate the agglomeration. Both cells went through a continuous current drop and then stabilized. The cell with capped cathode dropped 29.5% upon stabilization and the cell with uncapped cathode dropped 86.2%. After test, the capped cathode remained similar to its initial morphology (FESEM insert in figure 4). The low 10-cycle capping had effectively hindered the agglomeration of the nano-porous platinum cathode during fuel cell operation by more than 50%. The remaining 29.5% degradation could come from the agglomeration of uncapped nanoscopic features[16,24] that resided within the platinum clusters which were unreachable by ZrO_2 precursors with our deposition parameters. Since we purposefully chose pure platinum as the backbone cathode, which is more vulnerable to agglomeration, to demonstrate the effectiveness of ALD- ZrO_2 capping, less degradation of output current over time can be expected if Pt alloys such as Pt-Ni were used as the backbone electrode.

4 Conclusion

By low cycles of ALD- ZrO_2 capping on nano-porous platinum cathode, the thermally-driven agglomeration was effectively hindered. An improved cathode ORR was also observed, which may originate from the non-continuous ALD- ZrO_2 film attached on platinum surface that

promoted the oxygen adsorption and dissociation. The benefit brought by ALD-ZrO₂ capping on cathode ORR can be optimized by carefully control the ZrO₂ coverage on platinum to maximize the oxygen adsorption/desorption without sacrificing the gas diffusion and oxygen surface migration.

Acknowledgements

The authors thank the financial support from Tier 1 (RG92/13) and Tier 2 (ARC20/14) grants, both from Singapore Ministry of Education.

References

- [1] P.-C. Su, C.-C. Chao, J.H. Shim, R. Fasching, F.B. Prinz, Solid Oxide Fuel Cell with Corrugated Thin Film Electrolyte, *Nano Lett.* 8 (2008) 2289–2292. doi:10.1021/nl800977z.
- [2] M. Tsuchiya, B.-K. Lai, S. Ramanathan, Scalable nanostructured membranes for solid-oxide fuel cells, *Nat. Nanotechnol.* 6 (2011) 282–286. doi:10.1038/nnano.2011.43.
- [3] S. Ha, P.-C. Su, S.-W. Cha, Combinatorial deposition of a dense nano-thin film YSZ electrolyte for low temperature solid oxide fuel cells, *J. Mater. Chem. A.* 1 (2013) 9645–9649. doi:10.1039/C3TA11758H.
- [4] J. An, Y.-B. Kim, J. Park, T.M. Gür, F.B. Prinz, Three-Dimensional Nanostructured Bilayer Solid Oxide Fuel Cell with 1.3 W/cm² at 450 °C, *Nano Lett.* 13 (2013) 4551–4555. doi:10.1021/nl402661p.
- [5] J.H. Shim, C.-C. Chao, H. Huang, F.B. Prinz, Atomic Layer Deposition of Ytria-Stabilized Zirconia for Solid Oxide Fuel Cells, *Chem. Mater.* 19 (2007) 3850–3854. doi:10.1021/cm070913t.
- [6] J.H. Shim, J.S. Park, J. An, T.M. Gür, S. Kang, F.B. Prinz, Intermediate-Temperature Ceramic Fuel Cells with Thin Film Yttrium-Doped Barium Zirconate Electrolytes, *Chem. Mater.* 21 (2009) 3290–3296. doi:10.1021/cm900820p.
- [7] S. Kang, P.C. Su, Y.I. Park, Y. Saito, F.B. Prinz, Thin-Film Solid Oxide Fuel Cells on Porous Nickel Substrates with Multistage Nanohole Array, *J. Electrochem. Soc.* 153 (2006) A554–A559. doi:10.1149/1.2164769.
- [8] S. Rey-Mermet, P. Muralt, Solid oxide fuel cell membranes supported by nickel grid anode, *Solid State Ion.* 179 (2008) 1497–1500. doi:10.1016/j.ssi.2008.01.007.
- [9] X. Wang, H. Huang, T. Holme, X. Tian, F.B. Prinz, Thermal stabilities of nanoporous metallic electrodes at elevated temperatures, *J. Power Sources.* 175 (2008) 75–81. doi:10.1016/j.jpowsour.2007.09.066.

- [10] K. Kerman, B.-K. Lai, S. Ramanathan, Pt/Y_{0.16}Zr_{0.84}O_{1.92}/Pt thin film solid oxide fuel cells: Electrode microstructure and stability considerations, *J. Power Sources*. 196 (2011) 2608–2614. doi:10.1016/j.jpowsour.2010.10.068.
- [11] A. Evans, S. Karalić, J. Martynczuk, M. Prestat, R. Tölke, Z. Yáng, et al., La_{0.6}Sr_{0.4}CoO_{3-δ} Thin Films Prepared by Pulsed Laser Deposition as Cathodes for Micro-Solid Oxide Fuel Cells, *ECS Trans.* 45 (2012) 333–336. doi:10.1149/1.3701323.
- [12] H.-S. Noh, K.J. Yoon, B.-K. Kim, H.-J. Je, H.-W. Lee, J.-H. Lee, et al., The potential and challenges of thin-film electrolyte and nanostructured electrode for yttria-stabilized zirconia-base anode-supported solid oxide fuel cells, *J. Power Sources*. 247 (2014) 105–111. doi:10.1016/j.jpowsour.2013.08.072.
- [13] Y. Gong, D. Palacio, X. Song, R.L. Patel, X. Liang, X. Zhao, et al., Stabilizing Nanostructured Solid Oxide Fuel Cell Cathode with Atomic Layer Deposition, *Nano Lett.* 13 (2013) 4340–4345. doi:10.1021/nl402138w.
- [14] Y. Gong, R.L. Patel, X. Liang, D. Palacio, X. Song, J.B. Goodenough, et al., Atomic Layer Deposition Functionalized Composite SOFC Cathode La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-δ} - Gd_{0.2}Ce_{0.8}O_{1.9}: Enhanced Long-Term Stability, *Chem. Mater.* 25 (2013) 4224–4231. doi:10.1021/cm402879r.
- [15] J. Liu, X. Li, M. Cai, R. Li, X. Sun, Ultrathin atomic layer deposited ZrO₂ coating to enhance the electrochemical performance of Li₄Ti₅O₁₂ as an anode material, *Electrochimica Acta*. 93 (2013) 195–201. doi:10.1016/j.electacta.2012.12.141.
- [16] C.-C. Yu, S. Kim, J.D. Baek, Y. Li, P.-C. Su, T.-S. Kim, Direct Observation of Nanoscale Pt Electrode Agglomeration at the Triple Phase Boundary, *ACS Appl. Mater. Interfaces*. 7 (2015) 6036–6040. doi:10.1021/acsami.5b00134.
- [17] D.M. Hausmann, R.G. Gordon, Surface morphology and crystallinity control in the atomic layer deposition (ALD) of hafnium and zirconium oxide thin films, *J. Cryst. Growth*. 249 (2003) 251–261. doi:10.1016/S0022-0248(02)02133-4.
- [18] T.Z. Sholklapper, H. Kurokawa, C.P. Jacobson, S.J. Visco, L.C. De Jonghe, Nanostructured Solid Oxide Fuel Cell Electrodes, *Nano Lett.* 7 (2007) 2136–2141. doi:10.1021/nl071007i.
- [19] S. Lee, N. Miller, M. Staruch, K. Gerdes, M. Jain, A. Manivannan, Pr_{0.6}Sr_{0.4}CoO_{3-δ} electrocatalyst for solid oxide fuel cell cathode introduced via infiltration, *Electrochimica Acta*. 56 (2011) 9904–9909. doi:10.1016/j.electacta.2011.08.060.
- [20] C.E. Hori, H. Permana, K.Y.S. Ng, A. Brenner, K. More, K.M. Rahmoeller, et al., Thermal stability of oxygen storage properties in a mixed CeO₂-ZrO₂ system, *Appl. Catal. B Environ.* 16 (1998) 105–117. doi:10.1016/S0926-3373(97)00060-X.
- [21] U. Brossmann, R. Würschum, U. Södervall, H.-E. Schaefer, Oxygen diffusion in ultrafine grained monoclinic ZrO₂, *J. Appl. Phys.* 85 (1999) 7646–7654. doi:10.1063/1.370567.
- [22] C. Ko, K. Kerman, S. Ramanathan, Ultra-thin film solid oxide fuel cells utilizing un-doped nanostructured zirconia electrolytes, *J. Power Sources*. 213 (2012) 343–349. doi:10.1016/j.jpowsour.2012.04.034.
- [23] I. Chang, S. Ji, J. Park, M.H. Lee, S.W. Cha, Ultrathin YSZ Coating on Pt Cathode for High Thermal Stability and Enhanced Oxygen Reduction Reaction Activity, *Adv. Energy Mater.* (2015) n/a–n/a. doi:10.1002/aenm.201402251.
- [24] T. Ryll, H. Galinski, L. Schlagenhauf, P. Elser, J.L.M. Rupp, A. Bieberle-Hutter, et al., Microscopic and Nanoscopic Three-Phase-Boundaries of Platinum Thin-Film Electrodes on YSZ Electrolyte, *Adv. Funct. Mater.* 21 (2011) 565–572. doi:10.1002/adfm.201001729.

Figure captions

Figure 1. (a) Schematic and (b) FESEM with 0, 10, 15, 30, and 60 cycles ALD-ZrO₂ capping on dense platinum.

Figure 2. FESEM images of uncapped (a~c), 10-cycle (d~f) and 60-cycle (g~i) ZrO₂-capped platinum electrodes on YSZ substrate before/after annealing.

Figure 3. (a) IV curves the platinum cathodes with 0, 10, 15, 30, 60 cycles ZrO₂ capping at 450°C. (b) Nyquist plot (from 0.1 to 20,000Hz) and; (c) Bode plots of the platinum cathodes with 0, 10, 15, 30, 60 cycles ZrO₂ capping at 0.9V and 450°C.

Figure 4. Current output with time of fuel cells using uncapped and 10-cycle ALD-ZrO₂ capped platinum cathodes. The inserts are cathode morphologies after test.

Figure1

Figure2

Figure3

Figure 4