# Review: Development of Platinum Electrode for Low Temperature Solid Oxide Fuel Cells

N. A. Rusli, Z. Ibrahim, R. Muhammad, Y. Wahab, S. Sakrani
*Department of Physics, Faculty of Science,*
Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor.
Email : nurhamizah@yahoo.com

***Abstract*—** Platinum thin film for anode and cathode as electrodes in micro-fabrication SOFC is an approach in producing energy power at low temperature by utilizing a combination of balanced electrode-electrolyte nanoscale materials. Solid Oxide Fuel Cell (SOFC) are considered as one of the most feasible generating devices for converting fuel into electricity that operates at temperatures in the range 700-1000 ºC, which is known presents both challenges for the construction and durability. Nevertheless, the ability of SOFC to operate at low temperature has sprung overwhelming interest among researchers to extend its application by operating temperatures down to 600 °C. Among many types of anode and cathode materials, platinum (Pt) exhibits large potential as catalytic activity towards the electrochemical oxidation and reduction. This paper reviews platinum anode-cathode thin film materials coated on micro-scale SOFC device and focuses on the effect of fabrications and electrolyte materials on the characteristic of cell performance.

***Keywords—electrode, platinum, SOFC, YSZ, cell performance***

## I. INTRODUCTION

A SOFC is a high-temperature fuel cell (ranging between 500 to 1000 °C) that contained of porous anode and cathode sandwiched with a dense electrolyte. Basically, in solid oxide fuel cells the oxygen ion ($O^{2-}$) from the cathode (platinum) side move through an ion conducting electrolyte (YSZ) to the anode (platinum) side. The process then combines with hydrogen creating electricity, water and heat, which is referred as an electrochemical mechanism where developed chemical reaction to electrical energy conversion. At the anode side, platinum catalyst causes the hydrogen gas to split into positive ions (protons) and negative electrons. To meet a good electronic and ionic conductivity, a sufficient porosity (>30 vol %) is required to allow gas diffusion to the triple phase boundary (TRB) [1]. Meanwhile, at low operating temperature, the sluggish oxygen reduction reaction (ORR) at the cathode side causes the drawback performance of SOFC. Therefore, to improve the active site of the cathode thin film, the development of mixed ionic electronic cathode (MIEC) and electron conducting cathodes were developed [1]. Platinum porous anode and cathode can be defined as a permeable to gasses with the excellent electronic conductor at low operating temperatures of SOFC (300-500 °C). Hence, to extend the ability of the platinum, reviewing with researchers worldwide can increase the innovative approach towards platinum-YSZ performance; hence prolong the uses of platinum as electrode material in low temperature of SOFC.

## II. FABRICATION OF PLATINUM ELECTRODES

### *A. Fabrication of Platinum Electrodes*

Thin film fabrication of platinum as electrode offers various techniques such as using micro-electro-mechanical system (MEMS) and machining techniques as reviewed by Anna *et al.* [2]. The combination of micromachining technique and thin film deposition plays a significant role in producing mechanically stable platinum electrode-electrolyte materials. Thus, the thin film fabrication such as chemical and physical deposition can be used to produce SOFC cell as freestanding membrane [3-5] or on porous substrates [6-8] as shown in Fig. 1.

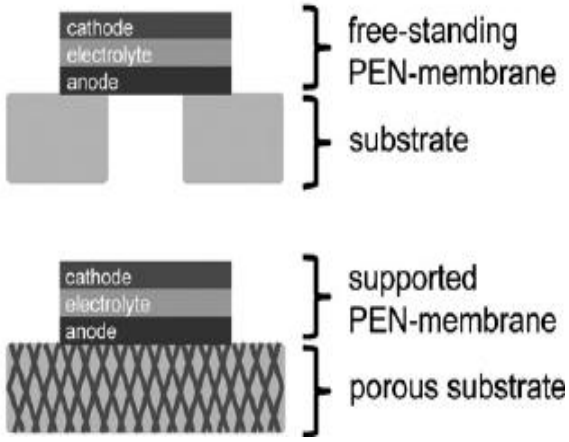


**Fig. 1.** Thin film fabrication of free-standing membrane and membrane on porous substrate. [2]

Generally, chemical deposition by atomic layer deposition (ALD) technique involves a vaporized source precursor to a reaction chamber and the deposition was carried out onto substrate surface. 150 nm thick Ag as cathode and Pt as anode were sputtered onto GDC and the different layers (7 and 15 cycles) of YSZ on Ag. The deposition of YSZ at

temperature 250 °C with 7 cycles produced peak power of 14.7 mW/cm$^2$ compared 15 layers with 9.5 mW/cm$^2$ because YSZ layer forms a conformal and dense layer that can passivity the Ag electrode by capping the surface where decrease the TRB-ORR sites with increase in ALD YSZ on the surface of Ag [9].

Beck *et al.* [10] study the effect of substrates (single, polycrystalline, amorphous) on the characteristic of platinum thin film onto YSZ microstructure with the electrode kinetics by using pulse laser deposition (PLD). The prepared thin film achieved at pulse number of 36,000 with thickness about 500 nm. The deposition temperature and annealed were utilized at 400 °C and 750 °C, respectively. Based on the morphology results of platinum thin film on (100) YSZ, largest grain size was detected at value 500-10,000 nm. Meanwhile, polycrystalline YSZ and amorphous quartz glass consists of 400-2000 nm and 300-900 nm, respectively.

In addition, physical deposition requires expensive tools and vacuum environment to produce high crystallinity of nanofilm (<100nm), thin film (~1000nm) and film coating (>1µm). Mainly the principle technique of sputtering was conducted by the solid surface is subjected to energetic ion bombardment where the target-material atoms are sputtered away. According to Jolita *et al.* [11], the reaction between silica substrate and platinum tend to produce platinum silicide at temperature 200-450 °C during sputtering deposition. Therefore, the deposition of thin Ti as interlayer between Si substrate and platinum thin film is utilized. The deposition of YSZ on low surface roughness produce uniform and dense morphology created by using low Ar pressure using RF magnetron sputtering. Ar pressure at 0.67-5.33 Pa allows the dense platinum surface and high Ar pressure allows porous surface of platinum due to melting, coarsening and coalescence of grains of Pt/Ti thin film. In addition, the utilized 8 rotation during PVD with high sputtering pressure and low sputtering power will cause high large surface area and improve electrochemical activity.

Topalov *et al.* [12] study the Pt alloy with Ir (Iridium) to improve the efficiency but also stability of the composite catalyst. Bi metallic thin Pt-Ir films were simultaneously co-sputtering from two pure metal targets. The increase in Ir content because of sputtering power applied to the Ir target consist more toughly packed layer. The increases in alloying amount with Ir causes shrinkage of the metal lattice and decrease of the Pt -Pt nearest neighbor bond, thus inducing low energy Pt surface sites and enhanced adsorption of oxygen.

### *B. Electrolyte Materials use with Platinum Electrodes for Low Temperature SOFC*

Zirconia -based materials (YSZ and SSZ). Yttria stabilized Zirconia with a chemical formula of YSZ known as oxide ion conductor. YSZ have been used as electrolyte material in high to low temperature of SOFC to conduct $O^{2-}$ ions from cathode to anode. *Joong et al.* [13] indicated that the high grain boundary densities and the degree of crystallinity seems to promote faster proton transport pathways into the lattice of YSZ at low temperature regime of 300-450 °C. Densification and crystallization of YSZ prepared from powder form occurred at temperature above 1200 °C for 2 hours [14]. On the other side, crystallization of YSZ by thin film also can be carried out in low temperature by utilizing two metallic Zr-Y (86:14 at. %) through RF magnetron sputtering at 500 °C as studied by Sonderby *et al.* [15]. Chen *et. al* [16] study the 150 nm Pt/70 nm YSZ interface through SEM images after the post annealing at 300-600 °C. Results showed the intermediate temperature (500 °C) produced better cell performance effects because it has high density of nanoscale triple phase boundary (TRB) where cracks have merged completely. Hojean *et al.* [17] reported under 400 °C test cell performance, the porous Pt have lowest ohmic and polarization value compared to Ni and LSC electrodes because of the disconnected neighboring between Ni-YSZ surface and lower catalytic reaction of LSC at this temperature, respectively. In addition some researchers implemented the different of YSZ thickness as an electrolyte in the application of the experimentation. The YSZ were prepared at thickness of 35 nm, 70 nm, 140 nm and 210 nm deposited using atomic layer deposition. Electrochemical analysis shows that YSZ with moderate thickness of 70 nm produce the most gastight with pinhole free structure, high power density (170 mW/cm$^2$) with 1.17 V of open circuit voltage (OCV) as reported by Sanghoon *et al.* [18].

Sc-doped $ZrO_2$ (ScSz) is the alternative materials of oxide-ion conducting materials for electrolyte. It was used by researchers in order to improve the ionic conductivity at intermediate temperature. Crina *et al.* [19] reported that, the low content of $Sc_2O_3$ (7-15 mol %) influenced the crystallinity with cubic structure hence improve the electrical conductivity of ScSz because due to the open structure thus, enhanced the mobility of charge carriers.

However, ultra-low operating temperature (319 °C) studied by Ikwhang *et al.* [20] indicated abrupt voltage drop from 1.6 to 1.0 V since electrical short-circuiting form during the start up at room temperature to 319 °C. This condition can be related by the metal migration via nano-defects and the internal resistance imbalance because of the increasing temperature. In addition, the defects in the AAO template may lead to decrease in OCV value. Yan *et al.* [5] also reported low OCV and power density 0.68 V and 4.22 mW/cm$^2$, respectively. The low value can be explained from the porous platinum thin film recrystallizes and is de-wetting from the surface of YSZ electrolyte layer after operating at 500 °C. Fig. 2 shows SEM images (surface morphology) of Pt grains above a matrix of YSZ before and after annealing at 500 °C. Images show that the composite coating consist of smooth nano-structured film before and after annealing process (large Pt grains above a matrix of YSZ).

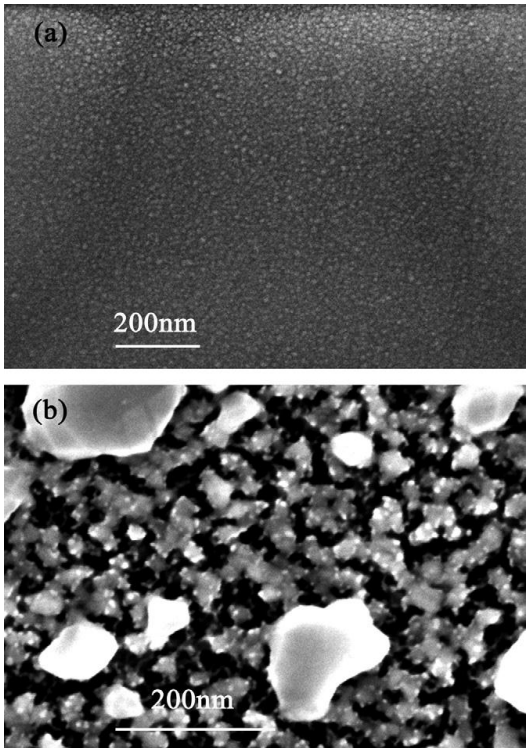


**Fig. 2.** SEM images (surface morphology) of Pt grains above a matrix of YSZ (a) before and (b) after annealing at 500 °C [5]

Ceria-based material (GDC and SDC). Gadollinium and Samaria doped Ceria ($CeO_2$) are another fluorite-type oxide ion conductor that most promising electrolyte for low temperature. The deposition bi-layer electrolyte of YSZ on anode side and GDC on cathode side of platinum (produced from atomic layer deposition) was carried out using 20 nm and 80 nm pore diameter AAO as substrates. Simultaneously, as the number of pore diameter increases, the less cathode-electrolyte interfacial resistance as well as the triple phase boundary (TPB) length will also increase. In addition, the power density performance of the cell at 450 °C will also be affected by the increment in rough substrate surface as reported by Sangoon *et al.* [21].

It was observed that the performance of low temperature SOFC have increased with few tens of nanometers thickness gadolinium-doped ceria (GDC) interlayer between metal anode and nanothin zirconia electrolyte. Based on the work conducted from researchers in Table 1, the OCV value (>1.0 ) means direct indicator of electrolyte ability in terms of gas tightness and electron blockage proves the GDC acts as barrier layer between YSZ and electrode.

Table 1: Effect of GDC barrier layer between YSZ electrodes on the OCV value

| | GDC | YSZ | Cathode | Test temperature (°C) | Power density ($mW/cm^2$) | Open current voltage, OCV |
|---|---|---|---|---|---|---|
| [21] | 200 nm | 100 nm | 50 nm Pt | 450 | 60-80 | 1.13-1.16V |
| [22] | 420 nm | 40 nm | 200 nm Pt | 450 | 35 | 1.07 V |
| [23] | 400 nm | 120 nm | 200 nm Pt | 400<br>450 | 63<br>110 | 1.03 V<br>1.028 V |
| [24] | *GDC | 70 nm<br>210 nm | 150 nm Pt | 500 | 170<br>130 | 1.17 V |
| [25] | *GDC<br>5 nm<br>10 nm | 500 µm | 150 nm Pt | 500 | 3.37<br>6.35<br>6.60 | - |
| [6] | *GDC<br>20 nm | 500 nm | 200 nm Pt | 500 | 90<br>120 | 0.86 V<br>1.15 V |

*-without GDC

Yoon *et al.* [25] study the mixed ionic electronic conductor (MIEC) composite structure of Pt and GDC properties using dispersion hardening method deposited by PVD sputtering. Variation of the amount of GDC to platinum from (0, 5, 10 and 20 vol %) were used to identify optimize nano-porous platinum electrode based on the characterization towards surface morphology and electrochemical analysis (resistivity and power density). Based on the result, researcher claimed that 5 % of GDC content leads to improve power density and surface morphology of nanoporous metal electrode with degradation of 7.7 %/h followed by pure (43.1 %/h), 10 % (11.6 %/h) and 20 % (7.7 %/h). In addition, larger pores and higher porosity leads to increase in TPB density and gas supply with less percentage of resistance increments.

Kulkarni *et al.* [26] systematically studied ceria co-doped by samarium as thin nanofilm onto YSZ electrolyte and platinum as a model of electrode. It was found that cell with the SDC had low cathode polarization resistance with enhance power density (163 $mW/cm^2$) compared cell without SDC (121 $mW/cm^2$). The increase in cell performance through nano-thin film was attributed to the increases active area between electrode-electrolyte, which suggests that the very fine ceria nanoparticles penetrated inside the surface irregularities of the electrolyte.

Moreover, review from this paper will be able to contribute toward enhanced deposition of platinum thin films by identifying the suitable electrode, processing technique, material selections of electrolyte that can reduce Ohmic resistance and improve cell performance. Materials science studies on electrolytes and electrode materials that can lead to high performance fuel cells will contribute to the development of low temperature SOFC.

## III. CONCLUSIONS

As conclusion, this paper reviews several methods of platinum electrode that have been produced and materials used to describe the development of low temperature SOFC in their

research. This review shows the feasibility of using platinum as anode and cathode for SOFC operating at temperature below 500 °C that can potentially fulfill the basic requirements on the anodic and cathodic sides.

## V. ACKNOWLEDGEMENTS

This research has been supported by the LRGS: R.K 130000.7340.4L825 (Long Term Research Grant Scheme) Razak School of Universiti Teknologi Malaysia, UTM

## REFERENCES

[1] T.S. Zhao and N. Meng, "Solid Oxide Fuel Cells", RSC Publishing, 2013.

[2] E. Anna, B. Anja, L. M. Jennifer, J. G. Ludwid, " Review on Microfabricated Micro-Solid Oxide Fuel Cells Membranes", J. Power Sources., vol 194, pp. 119-129, 2009.

[3] W. K. Chang, W. S. Ji, H. L. Jong, M. K. Hyun, W. L. Hae, B. K. Ki, "High Performance Micro-Solid Oxide Fuel Cells Fabricated on Nanporous Anodic Aluminum Oxide Templates", Adv. Funct. Mater., vol 21, pp. 1154-1159, 2011.

[4] H. S. Joon, C. C. Cheng, H. Hong, B. P. Fritz, "Atomic Layer Deposition of Yttria-Stabilized Zirconia for Solid Oxide Fuel Cells", Chem. Mater., vol. 19, pp. 3850-3854.

[5] Y. Yan, C. S. Silviu, C. Janine and M. Paul, " Experimental Study of Single Triple-Phase-Boundary and Platinum- Yttria Stabilized Zirconia Composite as Cathodes for Micro-Solid Oxide Fuel Cells", J. Power Sources., vol 206, pp. 84-90, 2012.

[6] J.Sanghoon, H.T. Waqas, Y. Wonjung, Y. Wonjung, K. Sungmin, Y. C. Gu, H. K. Sung, A. Jihwan, W. C. Suk, "Surface Engineering of Nanoporous Substrate for Solid Oxide Fuel Cells with Atomic Layer Deposition Electrolyte", J. Nanotechnology., vol. 6, pp. 1805-1810, 2015.

[7] T. L. Yun, Y.S. Jong, " Micro- Solid Oxide Fuel Cells with Yttria-Stabilized Zirconia and Nanoporous Pt Electrodes", Bull. Korean Chem. Soc., vol 34 (9), pp. 2822-2824, 2013.

[8] R. Tolke, A. Bieberle-Hutter, A. Evans, J. L. M. Rupp, L. J. Gauckler, " Processing of Foturan Glass Ceramic Substrates for Micro-Solid Oxide Fuel Cells", J. Eur. Cer. Soc., vol 32, pp. 3229-3238, 2012.

[9] K. L. You, J. C. Hyung, K. K. Ho, K. C. Neoh, K. Manjin, K. Junmo, J. J. Heon, Y. J. Dong, H. S. Joon, "Nanoporous Silver Cathodes Surface-Treated by Atomic Layer Deposition of Y:$ZrO_2$", J. Power Sources., vol. 295, pp. 175-181, 2015.

[10] G. Beck, H. Popke, B. Luerben, J. Janek, "Microstructure of Platinum Films on YSZ Prepared by Pulsed Laser Deposition", J. Cryst. Growth., vol. 322, pp. 95-102, 2011.

[11] S. Jolita, A. Brigita, S. Kestutis, T. Sigitas, "Influence of Magnetron Sputtering Deposition Conditions and Thermal Treatment on Properties of Platinum Thin Films for Positive Electrode-Electrolyte Negative Electrode Structure", Thin Solid Films., vol. 594, pp. 101-108, 2015.

[12] G. Topalov, G. Ganske, E. Lefterova, U. Schnakenberg, E. Slavcheva, "Preparation and Properties of Thin Pt-Ir Films Deposited by DC Magnetron Co-sputtering", Int. J. Hydrogen Energy., vol. 36, pp. 15437-15445, 2011.

[13] S.P. Joong, P.H. Timothy, H.S. Joon, B.P. Fritz, "Improved Oxygen Surface Exchange Kinetics at Grain Boundaries in Nanocrystalline Yttria-Stabilized Zirconia", Mater. Res. Society., vol. 2, pp. 107-111, 2012.

[14] S. Promsuy, A. Tangtrakarn, C. Mongkolkachit, S. Wanakitti, V. Amornkitbamrung, "A New Sol-Gel Precursor for Preparation of $La_{0.56}Sr_{0.42}Co_{0.2}Fe_{0.8}O_{3-\delta}$ Film", J. Sol-Gel Sci. Technol., vol. 78, pp. 187-194, 2016.

[15] S. Sonderby, A.J. Nielsen, B.H.Christensen, K.P. Almtoft, J. Lu, J. Jensen, L.P. Nielsen, P. Eklund, "Reactive Magnetron Sputtering of Uniform Yttria-Stabilized Zirconia Coatings in an Industrial Setup", Surf. Coat. Technol., vol. 206, pp. 4126-4131, 2012.

[16] C.Y. Chen, K. Sanwi, D.B. Jong, L. Yong, C.S. Pei, S.K. Taek, "Direct Observation of Nanoscale Pt Electrode Agglomeration at the Triple Phase Boundary", ASC Appl. Mater. Interface., vol. 7, pp. 6036-6040, 2015.

[17] J. Hojean, B. Kiho, Y.J. Dong, H.L. Yoon, W.C. Suk, H.S. Joon," Evaluation of Porous Platinum, Nickel, and Lanthanum Strontium Cobaltite as Electrode Materials for Low-Temperature Solid Oxide Fuel Cells", Int. J. Hydrogen Energy., vol. 39, pp. 17828-17835, 2014.

[18] J. Sanghoon, Y. C. Gu, Y. Wonjong, C. S. Pei, H. L. Min, W. C. Suk, " Plasma-Enhanced Atomic Layer Deposition of Nanoscale Yttria-Stabilized Zirconia Electrolyte for Solid Oxide Fuel Cells with Porous Substrate", ACS Appl. Mater. Interfaces., vol 7(5), pp. 2998–3002, 2015.

[19] S. Crina, S.E. Egil, C.H. Alex, D. Eugen, T. Romulus, "Modified Sol-Gel Method Used for Obtaining SOFC Electrolyte Materials", J. Electrochem. Soc., vol. 25(2), pp. 1679-1686, 2009.C.

[20] Ikwhang, B. Jiwoong, P. Joonho, L. Sunho, B. Myeongseok, P. Taehyun, H. L. Yoon, H. S. Han, B. K. Young, W. C. Suk, "A Thermally Self-Sustaining Solid Oxide Fuel Cell System at Ultra-Low Operating Temperature (319 °C)", Energy., vol. 104, pp. 107-113, 2016.

[21] J. Sanghoon, H. Jinsu, P. Taehyun, K. Yusung, K. Bongjun, B. K. Young, A. Jihwan, W. C. Suk, "Substrate- Dependent Growth of Nanothin Film Solid Oxide Fuel Cells towards Cost-Effective Nanostructuring", Int. J. Precis. Eng. Manuf., vol. 3(1), pp. 35-39, 2016

[22] J. Sanghoon, C. Ikwhang, H. L. Yoon, P. Joonho, Y. P. Jun, H. L. Min, W. C. Suk, "Fabrication of Low-Temperature Solid Oxide Fuel Cells with a Nanothin Protective Layer by Atomic Layer Deposition", Nanoscale Res. Lett., 8:48, 2013.

[23] J. Sanghoon, C. Ikwhang, Y. C. Gu, H. L. Yoon, H. S. Joon, W. C. Suk, " Application of Dense Nano-Thin Platinum Films for Low-Temperature Solid Oxide Fuel Cells by Atomic Layer Deposition", Int. J. Hydrogen Energy., vol. 39, pp. 12402-12408, 2014.

[24] J. Sanghoon, H.L. Yoon, P. Taehyun, Y. C. Gu, N. Seungtak, L. Yeageun, K. Minwoo, H. Seungbum, A. Jihwan, W.C. Suk, "Doped Ceria Anode Interlayer for Low-Temperature Solid Oxide Fuel Cells with Nanothin Electrolyte", Thin Solid Films., vol. 591, pp. 250-254, 2015.

[25] H. L. Yoon, Y. C. Gu, C. Ikwhang, Ji. Sanghoon, B.K. Young, "Platinum-based Nanocomposite Electrodes for Low-Temperature Solid Oxide Fuel Cells with Extended Lifetime", J. Power Source., vol. 307, pp. 289-296, 2016.

[26] A. P. Kulkarni, S. Giddey, and S.P.S. Badwal, "Enhancing Oxygen Reduction Reactions in Solid Oxide Fuel Cells with Ultrathin Nanofilm Electrode−Electrolyte Interfacial Layers", J. Phys. Chem. C., 2016.