DUAL LAYER HOLLOW FIBRE AS MAIN COMPONENT OF METHANE FUELLED SOLID OXIDE FUEL CELL

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ABSTRACT

Solid oxide fuel cell (SOFC) has been regarded as one of the most amazing technologies in energy production that could directly convert hydrocarbon fuel into electricity without reforming procedure. This study was conducted to analyse the micro-tubular solid oxide fuel cell (MT-SOFC) with different electrolyte thicknesses in terms of its performance by utilising methane (CH_4) as the fuel. MT-SOFCs investigated in this work consisted of thin cathode layer, coated onto co-extruded anode/electrolyte dual-layer hollow fibre (DLHF). A DLHFs with different electrolyte thicknesses had been developed in this study by adjusting the extrusion rate upon a single-step phase inversion-based co-extrusion and co-sintering process. Uniform outer electrolyte layer from 18 to 34 µm were achieved when the extrusion rate of outer layer was increased from 1 to 5 ml min^{-1}. The fabricated DLHFs were then co-sintered at various temperatures (1350, 1400 and 1450 °C) prior to reduction process at 550 °C for 3 h. In evaluating the performance of DLHFs fuelled by CH_4 gas, current-voltage (I-V) measurement, impedance spectra, as well as stability test were performed at various temperatures ranging from 750 to 850 °C. Although the bending strength and gas-tightness properties were reduced with the decrease in electrolyte layer thickness, significant improvement in power output of the cell was achieved. Power density as high as 0.32 W cm^{-2} was obtained on the cell with the electrolyte layer of 18 µm in thickness, which is 20 % higher than the cell with an electrolyte layer of 34 µm, which was only 0.12 W cm^{-2} when operated at 850 °C. Stability test has shown that the cell with thinnest electrolyte (18 µm) can only survived for 8 h while the thickest cell (34 µm) can operate up to 15 h at 750 °C. The results show that there was a significant reduction in cell performance when CH_4 was used as the fuel, due to the carbon deposition as proven by Raman spectroscopy and carbon, hydrogen, nitrogen and sulphur (CHNS) analyzer as qualitative and quantitative analyses, respectively. The study also shows that the optimum electrolyte thickness has to be around 23 to 24.5 µm in order to produce a high quality DLHF to withstand carbon deposition.

ABSTRAK

Sel bahan api pepejal oksida (SOFC) telah dianggap sebagai salah satu teknologi yang menakjubkan dalam pengeluaran tenaga yang boleh menukar hidrokarbon menjadi elektrik secara langsung tanpa prosedur pembentukan semula. Kajian ini dijalankan untuk menganalisis sel bahan api pepejal oksida-mikro-tiub (MT-SOFC) dengan ketebalan elektrolit yang berbeza daripada segi prestasi dengan menggunakan metana (CH_4) sebagai bahan api. MT-SOFC yang disiasat dalam kajian ini terdiri daripada lapisan nipis katod, disalut ke atas anod / elektrolit dwi-lapisan serat berongga (DLHF). DLHF dengan ketebalan elektrolit berbeza telah dibangunkan dalam kajian ini dengan mengubahsuai kadar penyemperitan terhadap songsangan fasa langkah tunggal berasaskan proses sepenyemperitan dan sepensinteran. Lapisan elektrolit luaran seragam dari 18 hingga 34 μm telah dicapai apabila kadar penyemperitan lapisan luaran meningkat dari 1 hingga 5 ml min^{-1}. DLHF yang dihasilkan kemudian melalui sepensinteran bersama pada pelbagai suhu (1400 °C, 1425 °C dan 1450 °C) sebelum proses penurunan pada 550 °C selama 3 jam. Dalam menilai prestasi DLHF yang didorong oleh gas CH_4, pengukuran voltan semasa (I-V), spektra impedans, serta ujian kestabilan dilakukan pada pelbagai suhu antara 750 °C hingga 850 °C. Walaupun kekuatan lenturan dan sifat kekedapan gas dikurangkan dengan penurunan ketebalan lapisan elektrolit, peningkatan ketara dalam keluaran kuasa sel telah dicapai. Ketumpatan kuasa setinggi 0.32 W cm^{-2} diperolehi pada sel dengan lapisan elektrolit dengan ketebalan 18 μm, iaitu 20 % lebih tinggi daripada sel dengan lapisan elektrolit 34 μm, yang hanya 0.12 W cm^{-2} apabila dikendalikan pada 850 °C. Ujian kestabilan menunjukkan bahawa sel dengan elektrolit nipis (18 μm) hanya dapat bertahan selama 8 jam manakala sel tebal (34 μm) boleh beroperasi sehingga 15 jam pada 750 °C. Terdapat pengurangan yang signifikan dalam prestasi sel ketika CH4 digunakan sebagai bahan api, disebabkan oleh pemendapan karbon yang dibuktikan oleh spektroskopi Raman dan analisa karbon, hidrogen, nitrogen dan sulfur (CHNS) masing-masing sebagai analisis kualitatif dan kuantitatif. Kajian ini juga menunjukkan bahawa ketebalan elektrolit optimum adalah sekitar 23 μm hingga 24.5 μm untuk menghasilkan DLHF yang berkualiti untuk menahan pemendapan karbon.

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LIST OF ABBREVIATIONS

DLHF	-	Dual-Layer Hollow Fibre
SOFC	-	Solid Oxide Fuel Cell
MT-SOFC	-	Micro-Tubular Solid Oxide Fuel Cell
CH_4	-	Methane
H_2	-	Hydrogen
O_2	-	Oxygen
N_2	-	Nitrogen
YSZ	-	Yttria-stabilized zirconia
NiO	-	Nickel oxide
LSM	-	Lanthanum strontium manganite
SEM	-	Scanning Electron Microscopy
OCV	-	Open-circuit voltages
I-V	-	Current-Voltage
ASR	-	Area specific resistance

LIST OF SYMBOLS

^{o}C	-	degree celcius
%	-	percentage
mm	-	millimetre
µm	-	micrometre
g	-	gram
wt.%	-	weight percentage
D_o	-	outer diameter
D_i	-	inner diameter
min	-	minute
h	-	hour
MPa	-	Mega Pascal
W cm^{-2}	-	Watt per centimetre squared
V	-	volts
Ω cm^2	-	Ohm centimetre squared

CHAPTER 1

INTRODUCTION

1.1 Research Background

The world population has experienced continuous growth since the last 50 years, which directly resulted in a large increase in primary energy consumption (Chen et al. 2019). The utilisation of energy is growing as of more prominent demands in almost every human activity including: stationary applications such as power production plants, transportation, household uses, agriculture, industry and manufacturing, service, buildings, and more (Brouwer 2010). Fossil fuel is currently the primary source for this energy. The products are distributed globally and thus greatly available, easily accessible and the overall production costs are low. A rough estimation is that the worldwide energy consumption will rise more than 50 % until 2030 and fossil fuel will cover over 80 % of the energy demand (Milano et al. 2016).

Nevertheless, the total resources of non-renewable fossil fuel are not endless and the costs of its uses are a high emission of harmful products such as carbon dioxide (CO2) and sulphur (S) (Bridges et al. 2015). Hence, the world is currently facing two detrimental challenges, which is energy crisis and environmental pollution. To confront this issue, most of the scholars around the globe are focusing to create the innovation for environmental-friendly energy converter. Fuel cell innovation demonstrates promising characteristics and qualities to solve these problems as it consumes fuels at high efficiency with less impact on environment and yield more electricity from a similar amount of fuel particularly when compared to interior combustion engines (Brouwer 2010).

Fuel cell is an electrochemical device which converts chemical energy resulting from chemical reaction into electrical energy and heat. It produces electricity through a chemical reaction, without combustion. This energy conversion system is

used for primary and backup power for commercial, industrial and residential buildings and in remote or inaccessible areas. They are also used for transportation purposes such as fuel cell vehicles, including forklifts, automobiles, buses, boats, motorcycles and submarines (Ellamla et al. 2015). Besides that, this device is a potential and promising system to be in the power generation field due to its direct conversion from wide variety of fuels to electricity.

Fuel cells operates much like a battery, except they do not require electrical recharging. A battery stores all of its chemicals inside and coverts the chemicals into electricity. Once those chemicals run out, the battery dies. A fuel cell, on the other hand, receives the chemicals it uses from the outside; therefore, it will not run out. Fuel cells can generate power almost indefinitely, as long as they have fuel to use. In addition to that, fuel cell is also mechanically ideal as it does not involve any moving parts during the operation, thus making them quiet and reliable sources of power (Hardman, Chandan, and Steinberger-Wilckens 2015). Therefore, fuel cell should be marketed and would replacing the conventional energy in future as it provides so much potentials.

Figure 1.1 illustrates the general operating principle of fuel cell. Every fuel cell is comprised of an electrolyte layer and two electrodes layer, one positive and one negative, called respectively, the anode and the cathode. In electrodes, the operation of fuel cells involves a combined oxidation-reduction reaction (Saribo͡ga and Öksüzömer 2012). Oxidant is reduced in cathode while fuel is oxidised in anode. A presence of catalyst will accelerate the reactions take place in the electrodes (Goodenough and Huang 2007). While electrolyte will carry electrically charged particles from one electrode to the other via external load, by which the energy is produced.

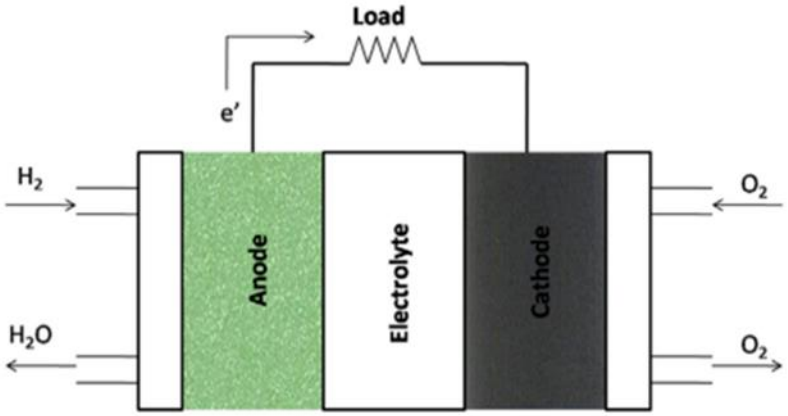

Figure 1.1 Operating principle of fuel cell (Sariboĝa and Öksüzömer 2012)

The amount of power produced by a fuel cell depends upon several factors, such as fuel cell type, cell size, the temperature at which it operates, and the pressure at which the gases are supplied to the cell. Fuel cells are classified primarily by the kind of electrolyte they employ. This determines the kind of chemical reactions that take place in the cell, the kind of catalysts required, the temperature range in which the cell operates, the fuel required, and other factors (Ellamla et al. 2015). Most importantly, these properties ultimately decide the applications for which these fuel cells are most suitable.

There are several types of fuel cells currently under development, each with its own advantages, limitations, and potential applications such as solid oxide fuel cell (SOFC), proton exchange membrane fuel cell (PEMFC), alkaline fuel cell (AFC), direct methanol fuel cell (DMFC), phosphoric fuel cell (PAFC) and molten carbonate fuel cell (MCFC) (Wang et al. 2017). SOFC, MCFC and AFC are classified as anion-conducting electrolyte because they transfer anion from cathode to anode. Whereas, PAFC, DMFC and PEMFC are considered as proton-conducting electrolyte because they are cation charge carriers. Table 1.1 summaries the properties of different types of fuel cell in term of their operating temperature, electrolyte materials and applications.

Table 1.1 Different between fuel cells (Bernay, Marchand, and Cassir 2002)

Fuel cell	Type of electrolyte	Electrolyte material	Charge carrier	Operating temperature °C	Applications
AFC	Liquid: circulating or in matrix	Potash KOH generally in aqueous solution at 35% in weight	OH^-	60-100	Vehicle, spatial
DMFC	Solid: polymer which has been moistened	Proton exchange membrane	H^+	60-120	Vehicle, portable
MCFC	Liquid: in porous matrix of lithium aluminate	Old generation Li_2CO_3/K_2CO_3 Old generation Li_2CO_3/Na_2CO_3	CO_3^{2-}	600-700	Stationary
PAFC	Liquid: in a porous matrix of silicon carbide	Pure phosphoric acid	H^+	160-200	Stationary
PEMFC	Solid: polymer which has been moistened	Proton exchange membrane	H^+	60-90	Vehicle, stationary, portable
SOFC	Solid oxide (ceramic)	Yttrium stabilized zirconia Cerium-gadolinium oxide	O^{2-}	800-1000 500-700	Vehicle, stationary

Nevertheless, this study is focuses on SOFC based on solid oxide electrolyte. SOFC is one of the most exciting technologies in the power generation field because of its great flexibility of fuel especially with regards to fuels derived from biomass, instead of hydrogen (H_2) (Lo Faro et al. 2012). SOFC operates at wide operating temperatures, from 500 °C to 1000 °C. Operation at such temperature allows an internal reforming reaction and high enough to initiate fuel conversion reactions. Besides that, no fuel pre-treatment is applied since the reforming reactions (conversion of H_2 from hydrocarbon) could directly promote within anode cell due to the high operative temperature (Assabumrungrat, Pavarajarn, and Charojrochkul 2004).

There are two structural designs of the SOFC that have been commercialized; planar and tubular SOFCs. The tubular design has been introduced by extrusion method in order to prevent the thermal shock problem facing by conventional planar design. Since the power density is inversely proportional to the tubular cell diameter, there was an effort developed by scholars by introducing a smaller cell diameter known as micro-tubular SOFCs (MT-SOFCs) to boost the performance. In fact, the development of this advanced cell design, i.e. MT-SOFC promotes an excellent thermal stability during rapid heat cycling, quick start-up capability, high power output density, low capital cost and portable characteristics compared to the conventional planar and tubular SOFCs (Jamil et al. 2015).

First generation of MT-SOFC developed was designed in an electrolyte-supported SOFC system with yttria stabilized zirconia (YSZ) electrolyte tubes up to 5 mm in diameter. Thick electrolyte layer was first developed to serve as “cell backbone”, that is responsible to provide mechanical strength to the entire cell for deposition of the remaining cell layers (Wei et al. 2008). Other promising designs are electrode-supported SOFC which use thick anode or cathode as the supporting layer. Table 1.2 shows the difference of three supported systems. Anode-supported MT-SOFC is more favourable because it allows the application of thin electrolyte layer, which results to the reduction in ohmic lose and consequently, enhance cell’s power density (Zhou et al. 2012).

Current method of fabricating multi-layer hollow fibre for high temperature SOFC system using YSZ as the ceramic material is very challenging. It involves many steps of extrusion, layer of depositions and sintering processes. Each step needs to undergo sintering process and these repetition steps lead to high manufacturing cost. Fortunately, the cost can be reduced by using an economical fabrication technique, i.e. single-step phase inversion-based co-extrusion and co-sintering technique (Jamil et al. 2017). The single-step fabrication offers a time-consume and flexible method because it fabricates a dual-layer hollow fibre (DLHF) simultaneously with smaller diameter and better adhesion. In addition, the phase-inversion technique offers major influence on creating porous structure which leads to the formation of asymmetric structure on the prepared fibre.

Nevertheless, limited knowledge and study on the fabrication of DLHF via phase inversion based-co-extrusion and co-sintering technique is realized. The most challenging issue that need to be tackled is during co-sintering. The DLHF needs to be co-sintered at high temperature to fully densify the electrolyte but at the same time, has reduced the porosity of anode. A dense electrolyte layer is compulsory since it will act as a barrier between electrodes, preventing direct flow of fuel and oxidant. While, the anode should be porous in order to provide many active sites reactions to the structures (Othman, Droushiotis, Wu, Kelsall, and K. Li 2011).

Table 1.2 Difference of MT-SOFC supported systems (Droushiotis et al. 2014)

MT-SOFC Configuration	**Electrolyte-supported SOFC**	**Electrode-Supported SOFC**	
		Anode-supported SOFC	**Cathode-supported SOFC**
Advantages	• High mechanical robustness due to dense structures and good stability for RedOx cycles.	• Low operating temperature (about 750 °C) and ohmic resistance due thin electrolyte layer. • High the electrical output due to low ohmic resistance. • Low materials cost since nickel (Ni) or nickel oxide (NiO) is relatively cheap. • Easy to fabricate.	• Good stability under RedOx condition and low carbon deposition due thin anode.
Disadvantages	• High ohmic losses resulting from thick electrolyte layer.	• Low mechanical reliability due to porous structures and low RedOx stability.	• Lack of study and research based on cathode-supported. • Induce chemical reaction between cathode and electrolyte at high sintering temperature. • High polarisation resistance.

1.2 Problem Statement

On the off chance that the hydrocarbons can be utilised directly as a fuel, the whole expenses would be significantly decreased. Moreover, hydrocarbon such as methane (CH_4) produce energy in a more efficient manner, given the presence of extra electrons in one molecule. H_2 can only produce two electrons, whereas the CH_4 is comprised of eight electrons in each molecule. Utilisation of hydrocarbon for SOFC frameworks is a splendid thought. However, hydrocarbon-based fuel can also cause carbon deposition; as a matter of fact, the presence of nickel (Ni) catalyst in anode promotes this reaction when utilising CH_4 (Omar et al. 2018) but Ni is still be used since it offers the best conductivity and catalytic performance (Stoeckl et al. 2017).

Carbon deposition is not only lead to the catalyst poisoning, but can cause the cell damage/crack as well (fracture of the thin film electrolyte layer) which is initiated by decomposition of the hydrocarbons on the Ni catalyst surface (Ivers-Tiffée et al. 2010). Thus, this study is focusing on how to reduce the cell damage/crack. There are several strategies have been introduced in order to tackle this problem, but most of them are focusing on the modification of anode layer compared to the electrolyte layer (Subotić, Schluckner, Schroettner, et al. 2016). The electrolyte layer also plays important role in fabrication of DLHF which provide the durability needed for CH_4-based MT-SOFC. The strategy on modifying the electrolyte layer is also an efficient way to further improve the performance of MT-SOFC by reducing thickness of the electrolyte layer, the ohmic losses in the electrolyte layer can be minimised.

In additional, electrolyte thickness modification is also important as the optimum thickness can avoid/prevent crack on the cell after carbon deposition take place. This can be done by adjusting the co-extrusion parameters such as the extrusion rate of the electrolyte layer suspension (Othman, Droushiotis, et al. 2010). MT-SOFC is operated at high temperatures (600 to 1000 °C) by having a constant supply of fuel and oxidant at the anode and cathode side, respectively. Obviously, the two gases should not be intermixed to i) obtain high open circuit voltage and ii) avoid violent burn out (Sındıraç et al. 2019). This can be achieved by having a dense gas tight ceramic electrolyte. In order to be gas leak-free cell, the DLHFs must be sintered at

high co-sintering temperatures ranges from 1350 to 1450 °C (Yang, Tan, and Ma 2008).

1.3 Objectives of Study

The main aim of this study is to fabricate YSZ-based DLHFs with desired structure for CH_4-fuelled MT-SOFC. The specific objectives are as follow:

(a) To examine the effect of different electrolyte thicknesses of DLHF in term of morphology and physical property for CH_4-fuelled MT-SOFC.

(b) To investigate the effect of co-sintering temperature toward the properties of DLHFs with different electrolyte thicknesses.

(c) To study the performance of DLHFs as a complete MT-SOFC with different electrolyte thicknesses in term of I-V measurement, impedance spectra and stability test by using CH_4 as fuel.

1.4 Scopes of Study

In order to achieve the objectives of this study, the following scopes are outlined:

(a) Fabricating DLHF precursors by phase inversion-based co-extrusion method.

1. Preparing anode and electrolyte spinning suspensions based on the composition reported in literature.

2. Extrude the spinning suspension into DLHF by controlling the extrusion rate of the electrolyte outer layer from 1 to 5 ml min^{-1}.

3. Co-sintering the DLHF precursors at different temperatures (1350, 1400 and 1450 °C)

(b) Characterizing the properties of DLHF with different electrolyte thicknesses and co-sintering temperature in term of morphology, mechanical strength, gas-tightness and gas-permeability properties by performing scanning electron microscope (SEM), three-point bending test gas-tightness test and gas permeability test.

(c) Performing MT-SOFC by potentiostat/galvanostate.

1. Utilising CH_4 as fuel and oxygen (O_2) as oxidant at various temperatures (750, 800 and 850 °C). For comparison, H_2 has been used as the control sample.

2. Conducting I-V measurement, impedance spectra and stability test.

3. Analysing carbon deposition in DLHFs by conducting Raman spectroscopy and Carbon, Hydrogen, Nitrogen and Sulphur (CHNS) analysis.

1.5 Significance of Study

This study is expected to provide a better understanding on the fundamental principle for the fabrication of anode/electrolyte DLHF for CH_4-fuelled MT-SOFC, which consists of the modifications of electrolyte thickness by considering the morphological, mechanical strength and gas-tightness properties. It is acknowledged that there are various methods have been introduced in order to prevent carbon deposition on the MT-SOFC when using CH_4 by modifying the anode side, but little attention has been given on the electrolyte side. Therefore, attempts are made to investigate the potential of electrolyte thickness modification to be used to fabricate a complete MT-SOFC powered by CH_4 fuel.

To the best of author's knowledge, no study has been conducted so far to be power the MT-SOFC with CH_4 fuel by controlling the electrolyte thickness. This study could be beneficial to the researchers in this area regarding to the knowledge

REFERENCES

Ahmad, S. H., Jamil, S. M., Othman, M. H. D., Rahman, M. A., Jaafar, J., & Ismail, A. F. (2017). Co-extruded dual-layer hollow fiber with different electrolyte structure for a high temperature micro-tubular solid oxide fuel cell. International Journal of Hydrogen Energy, 42(14), 9116–9124. https://doi.org/10.1016/j.ijhydene.2016.06.044

Aslannejad, H., Barelli, L., Babaie, A., & Bozorgmehri, S. (2016). Effect of air addition to methane on performance stability and coking over NiO-YSZ anodes of SOFC. Applied Energy, 177, 179–186. https://doi.org/10.1016/j.apenergy.2016.05.127

Assabumrungrat, S., Pavarajarn, V., & Charojrochkul, S. (2004). Thermodynamic analysis for a solid oxide fuel cell with direct internal reforming fueled by ethanol. 59, 6015–6020. https://doi.org/10.1016/j.ces.2004.07.039

Atkinson, A., Barnett, S., Gorte, R. J., Irvine, J. T. S., Mcevoy, A. J., Mogenson, M., … Vohs, J. (2004). Advanced anodes for high-temperature fuel cells. Nature Materials, 3, 17–27.

Barbir, F. (2013). Future of Fuel Cells and Hydrogen. In PEM Fuel Cells. https://doi.org/10.1016/B978-0-12-387710-9.00012-6

Bernay, C., Marchand, M., & Cassir, M. (2002). Prospects of different fuel cell technologies for vehicle applications. Journal of Power Sources, 108(1–2), 139–152. https://doi.org/10.1016/S0378-7753(02)00029-0

Bridges, A., Felder, F. A., McKelvey, K., & Niyogi, I. (2015). Uncertainty in energy planning: Estimating the health impacts of air pollution from fossil fuel electricity generation. Energy Research and Social Science, 6, 74–77. https://doi.org/10.1016/j.erss.2014.12.002

Brouwer, J. (2010). On the role of fuel cells and hydrogen in a more sustainable and renewable energy future. Current Applied Physics, 10(2 SUPPL.), S9–S17. https://doi.org/10.1016/j.cap.2009.11.002

Chen, G. Q., Wu, X. D., Guo, J., Meng, J., & Li, C. (2019). Global overview for energy use of the world economy: Household-consumption-based accounting based

on the world input-output database (WIOD). Energy Economics, 81, 835–847. https://doi.org/10.1016/j.eneco.2019.05.019

Chen, T., Wang, W. G., Miao, H., Li, T., & Xu, C. (2011). Evaluation of carbon deposition behavior on the nickel/yttrium-stabilized zirconia anode-supported fuel cell fueled with simulated syngas. Journal of Power Sources, 196(5), 2461–2468. https://doi.org/10.1016/j.jpowsour.2010.11.095

Chen, Z., Bian, L., Wang, L., Chen, N., Zhao, H., Li, F., & Chou, K. (2016). Effect of hydrogen and carbon dioxide on the performance of methane fueled solid oxide fuel cell. International Journal of Hydrogen Energy, 41(18), 7453–7463. https://doi.org/10.1016/j.ijhydene.2016.03.090

Cheng, Z., Zha, S., & Liu, M. (2007). Influence of cell voltage and current on sulfur poisoning behavior of solid oxide fuel cells. Journal of Power Sources, 172(2), 688–693. https://doi.org/10.1016/j.jpowsour.2007.07.052

Clarke, S. H., Dicks, A. L., Pointon, K., Smith, T. A., & Swann, A. (1997). Catalytic aspects of the steam reforming of hydrocarbons in internal reforming fuel cells. Catalysis Today, 38(4), 411–423. https://doi.org/10.1016/S0920-5861(97)00052-7

Dhir, A., & Kendall, K. (2008). Microtubular SOFC anode optimisation for direct use on methane. Journal of Power Sources, 181(2), 297–303. https://doi.org/10.1016/j.jpowsour.2007.11.005

Droushiotis, N., Grande, F. D., Dzarfan Othman, M. H., Kanawka, K., Doraswami, U., Metcalfe, I. S., … Kelsall, G. (2014). Comparison between anode-supported and electrolyte-supported Ni-CGO-LSCF micro-tubular solid oxide fuel cells. Fuel Cells, 14(2), 200–211. https://doi.org/10.1002/fuce.201300024

Droushiotis, Nicolas, Doraswami, U., Ivey, D., Othman, M. H. D., Li, K., & Kelsall, G. (2010). Fabrication by Co-extrusion and electrochemical characterization of micro-tubular hollow fibre solid oxide fuel cells. Electrochemistry Communications, 12(6), 792–795. https://doi.org/10.1016/j.elecom.2010.03.035

Droushiotis, Nicolas, Othman, M. H. D., Doraswami, U., Wu, Z., Kelsall, G., & Li, K. (2009a). Novel co-extruded electrolyte-anode hollow fibres for solid oxide fuel cells. Electrochemistry Communications, 11(9), 1799–1802. https://doi.org/10.1016/j.elecom.2009.07.022

Droushiotis, Nicolas, Othman, M. H. D., Doraswami, U., Wu, Z., Kelsall, G., & Li, K. (2009b). Novel co-extruded electrolyte-anode hollow fibres for solid oxide fuel cells. Electrochemistry Communications, 11(9), 1799–1802. https://doi.org/10.1016/j.elecom.2009.07.022

Ellamla, H. R., Staffell, I., Bujlo, P., Pollet, B. G., & Pasupathi, S. (2015). Current status of fuel cell based combined heat and power systems for residential sector. Journal of Power Sources, 293, 312–328. https://doi.org/10.1016/j.jpowsour.2015.05.050

Goodenough, J. B., & Huang, Y. (2007). Alternative anode materials for solid oxide fuel cells. 173, 1–10. https://doi.org/10.1016/j.jpowsour.2007.08.011

Han, M. F., Yang, Z., Liu, Z., & Le, H. R. (2010). Fabrication and characterizations of YSZ electrolyte films for SOFC. Key Engineering Materials, 434–435, 705–709. https://doi.org/10.4028/www.scientific.net/KEM.434-435.705

Hardman, S., Chandan, A., & Steinberger-Wilckens, R. (2015). Fuel cell added value for early market applications. Journal of Power Sources, 287, 297–306. https://doi.org/10.1016/j.jpowsour.2015.04.056

Haslam, J. J., Pham, A. Q., Chung, B. W., DiCarlo, J. F., & Glass, R. S. (2005). Effects of the use of pore formers on performance of an anode supported solid oxide fuel cell. Journal of the American Ceramic Society, 88(3), 513–518. https://doi.org/10.1111/j.1551-2916.2005.00097.x

Hayre, R. O. (2016). PART I.

Ideris, A., Croiset, E., Pritzker, M., & Amin, A. (2017). Direct-methane solid oxide fuel cell (SOFC) with Ni-SDC anode-supported cell. International Journal of Hydrogen Energy, 42(36), 23118–23129. https://doi.org/10.1016/j.ijhydene.2017.07.117

Irshad, M., Siraj, K., Raza, R., Ali, A., Tiwari, P., Zhu, B., … Usman, A. (2016). A Brief Description of High Temperature Solid Oxide Fuel Cell's Operation, Materials, Design, Fabrication Technologies and Performance. Applied Sciences, 6(3), 75. https://doi.org/10.3390/app6030075

Ivers-Tiffée, E., Timmermann, H., Leonide, A., Menzler, N. H., & Malzbender, J. (2010). Methane reforming kinetics, carbon deposition, and redox durability of Ni/8 yttria-stabilized zirconia (YSZ) anodes. Handbook of Fuel Cells, 1–24. https://doi.org/10.1002/9780470974001.f500063

Jamil, S. M., Othman, M. H. D., Rahman, M. A., Jaafar, J., & Ismail, A. F. (2017). Anode supported micro-tubular SOFC fabricated with mixed particle size electrolyte via phase-inversion technique. International Journal of Hydrogen Energy, 42(14), 9188–9201. https://doi.org/10.1016/j.ijhydene.2016.05.016

Jamil, S. M., Othman, M. H. D., Rahman, M. A., Jaafar, J., Ismail, A. F., & Li, K. (2015). Recent fabrication techniques for micro-tubular solid oxide fuel cell support: A review. Journal of the European Ceramic Society, 35(1), 1–22. https://doi.org/10.1016/j.jeurceramsoc.2014.08.034

Jang, J. H., Ryu, J. H., & Oh, S. M. (2000). Microstructure of Ni/YSZ cermets according to particle size of precursor powders and their anodic performances in SOFC. Ionics, 6(1–2), 86–91. https://doi.org/10.1007/BF02375551

Jin, C., Liu, J., Li, L., & Bai, Y. (2009). Electrochemical properties analysis of tubular NiO-YSZ anode-supported SOFCs fabricated by the phase-inversion method. Journal of Membrane Science, 341(1–2), 233–237. https://doi.org/10.1016/j.memsci.2009.06.012

Kingsbury, B. F. K., & Li, K. (2009). A morphological study of ceramic hollow fibre membranes. Journal of Membrane Science, 328(1–2), 134–140. https://doi.org/10.1016/j.memsci.2008.11.050

Laosiripojana, N., & Assabumrungrat, S. (2007). Catalytic steam reforming of methane, methanol, and ethanol over Ni/YSZ: The possible use of these fuels in internal reforming SOFC. Journal of Power Sources, 163(2), 943–951. https://doi.org/10.1016/j.jpowsour.2006.10.006

Lee, J. H., Heo, J. W., Lee, D. S., Kim, J., Kim, G. H., Lee, H. W., … Moon, J. H. (2003). The impact of anode microstructure on the power generating characteristics of SOFC. Solid State Ionics, 158(3–4), 225–232. https://doi.org/10.1016/S0167-2738(02)00915-3

Li, K. (2007). Ceramic Membranes for Separation and Reaction. John Wiley & Sons.

Liu, J., & Barnett, S. A. (2003). Operation of anode-supported solid oxide fuel cells on methane and natural gas. Solid State Ionics, 158(1–2), 11–16. https://doi.org/10.1016/S0167-2738(02)00769-5

Liu, L., Tan, X., & Liu, S. (2006). Yttria stabilized zirconia hollow fiber membranes. Journal of the American Ceramic Society, 89(3), 1156–1159. https://doi.org/10.1111/j.1551-2916.2005.00901.x

Lo Faro, M., Antonucci, V., Antonucci, P. L., & Aricó, A. S. (2012). Fuel flexibility: A key challenge for SOFC technology. Fuel, 102, 554–559. https://doi.org/10.1016/j.fuel.2012.07.031

Lu, K., & Shen, F. (2014). Long term behaviors of La0.8Sr0.2MnO3 and La0.6Sr0.4Co0.2Fe0.8O3 as cathodes for solid oxide fuel cells. International Journal of Hydrogen Energy, 39(15), 7963–7971. https://doi.org/10.1016/j.ijhydene.2014.03.046

Meng, X., Gong, X., Yang, N., Yin, Y., Tan, X., & Ma, Z. F. (2014). Carbon-resistant Ni-YSZ/Cu-CeO2-YSZ dual-layer hollow fiber anode for micro tubular solid oxide fuel cell. International Journal of Hydrogen Energy, 39(8), 3879–3886. https://doi.org/10.1016/j.ijhydene.2013.12.168

Meng, X., Gong, X., Yin, Y., Yang, N., Tan, X., & Ma, Z. F. (2014). Effect of the co-spun anode functional layer on the performance of the direct-methane microtubular solid oxide fuel cells. Journal of Power Sources, 247, 587–593. https://doi.org/10.1016/j.jpowsour.2013.08.133

Milano, J., Ong, H. C., Masjuki, H. H., Chong, W. T., Lam, M. K., Loh, P. K., & Vellayan, V. (2016). Microalgae biofuels as an alternative to fossil fuel for power generation. Renewable and Sustainable Energy Reviews, 58, 180–197. https://doi.org/10.1016/j.rser.2015.12.150

Mohamed, M. H., Othman, M. H. D., Hubadillah, S. K., Rahman, M. A., Jaafar, J., & Ismail, A. F. (2019). Comparative study on the performance of co-extruded hollow fiber solid oxide fuel cell fuelled with hydrogen and methane. Journal of Solid State Electrochemistry, 23(7), 2195–2203. https://doi.org/10.1007/s10008-019-04314-5

Mohanta, V., Das, S. K., & Roul, B. K. (2017). Development of Ni-doped Yttria stabilized Zirconia composite for SOFC applications as Anodic material. IOSR Journal of Applied Physics, 09(01), 15–23. https://doi.org/10.9790/4861-0901021523

Omar, A. F., Othman, M. H. D., Gunaedi, C. N., Jamil, S. M., Mohamed, M. H., Jaafar, J., … Ismail, A. F. (2018). Performance analysis of hollow fibre-based micro-tubular solid oxide fuel cell utilising methane fuel. International Journal of Hydrogen Energy, 1–9. https://doi.org/10.1016/j.ijhydene.2018.03.107

Othman, M. H. D. (2011). High performance micro-tubular solid oxide fuel cell. Retrieved from http://ethos.bl.uk/OrderDetails.do?uin=uk.bl.ethos.555892

Othman, Mohd Hafiz Dzarfan, Droushiotis, N., Wu, Z., Kanawka, K., Kelsall, G., & Li, K. (2010). Electrolyte thickness control and its effect on electrolyte/anode dual-layer hollow fibres for micro-tubular solid oxide fuel cells. Journal of Membrane Science, 365(1–2), 382–388. https://doi.org/10.1016/j.memsci.2010.09.036

Othman, Mohd Hafiz Dzarfan, Droushiotis, N., Wu, Z., Kelsall, G., & Li, K. (2011a). High-performance, anode-supported, microtubular sofc prepared from single-step-fabricated, dual-layer hollow fibers. Advanced Materials, 23(21), 2480–2483. https://doi.org/10.1002/adma.201100194

Othman, Mohd Hafiz Dzarfan, Droushiotis, N., Wu, Z., Kelsall, G., & Li, K. (2011b). Novel fabrication technique of hollow fibre support for micro-tubular solid oxide fuel cells. Journal of Power Sources, 196(11), 5035–5044. https://doi.org/10.1016/j.jpowsour.2011.02.006

Othman, Mohd Hafiz Dzarfan, Droushiotis, N., Wu, Z., Kelsall, G., & Li, K. (2012). Dual-layer hollow fibres with different anode structures for micro-tubular solid oxide fuel cells. Journal of Power Sources, 205, 272–280. https://doi.org/10.1016/j.jpowsour.2012.01.002

Othman, Mohd Hafiz Dzarfan, Wu, Z., Droushiotis, N., Doraswami, U., Kelsall, G., & Li, K. (2010). Single-step fabrication and characterisations of electrolyte/anode dual-layer hollow fibres for micro-tubular solid oxide fuel cells. Journal of Membrane Science, 351(1–2), 196–204. https://doi.org/10.1016/j.memsci.2010.01.050

Othman, Mohd Hafiz Dzarfan, Wu, Z., Droushiotis, N., Kelsall, G., & Li, K. (2010). Morphological studies of macrostructure of Ni-CGO anode hollow fibres for intermediate temperature solid oxide fuel cells. Journal of Membrane Science, 360(1–2), 410–417. https://doi.org/10.1016/j.memsci.2010.05.040

Panthi, D., & Tsutsumi, A. (2014). Micro-tubular solid oxide fuel cell based on a porous yttria-stabilized zirconia support. Scientific Reports, 4, 1–6. https://doi.org/10.1038/srep05754

Primdahl, S., Sørensen, B. F., & Mogensen, M. (2004). Effect of Nickel Oxide/Yttria-Stabilized Zirconia Anode Precursor Sintering Temperature on the Properties of Solid Oxide Fuel Cells. Journal of the American Ceramic Society, 83(3), 489–494. https://doi.org/10.1111/j.1151-2916.2000.tb01222.x

Rabuni, M. F., Li, T., Punmeechao, P., & Li, K. (2018). Electrode design for direct-methane micro-tubular solid oxide fuel cell (MT-SOFC). Journal of Power Sources, 384(December 2017), 287–294. https://doi.org/10.1016/j.jpowsour.2018.03.002

Rautenbach, R. & Albert, R. (1989). Membrane Process. John Wiley & Sons Ltd. New York. Retrieved from https://www.academia.edu/31551491/Modul_F_Reverse_Osmosis

Sammes, N. M., Du, Y., & Bove, R. (2005). Design and fabrication of a 100 W anode supported micro-tubular SOFC stack. Journal of Power Sources, 145(2), 428–434. https://doi.org/10.1016/j.jpowsour.2005.01.079

Saribo̧a, V., & Öksüzömer, F. (2012). The investigation of active Ni/YSZ interlayer for Cu-based direct-methane solid oxide fuel cells. Applied Energy, 93, 707–721. https://doi.org/10.1016/j.apenergy.2012.01.003

Sarikaya, A., Petrovsky, V., & Dogan, F. (2012). Effect of the anode microstructure on the enhanced performance of solid oxide fuel cells. International Journal of Hydrogen Energy, 37(15), 11370–11377. https://doi.org/10.1016/j.ijhydene.2012.05.007

Schoenbein, C. F. (1839). On the voltaic polarization of certain solid and fluid substances. Phil. Mag. (III), 14, 43–45.

Shri Prakash, B., Senthil Kumar, S., & Aruna, S. T. (2014). Properties and development of Ni/YSZ as an anode material in solid oxide fuel cell: A review. Renewable and Sustainable Energy Reviews, 36, 149–179. https://doi.org/10.1016/j.rser.2014.04.043

Sındıraç, C., Çakırlar, S., Büyükaksoy, A., & Akkurt, S. (2019). Lowering the sintering temperature of solid oxide fuel cell electrolytes by infiltration. Journal of the European Ceramic Society, 39(2–3), 409–417. https://doi.org/10.1016/j.jeurceramsoc.2018.09.029

Stoeckl, B., Subotić, V., Reichholf, D., Schroettner, H., & Hochenauer, C. (2017). Extensive analysis of large planar SOFC: Operation with humidified methane and carbon monoxide to examine carbon deposition based degradation. Electrochimica Acta, 256, 325–336. https://doi.org/10.1016/j.electacta.2017.09.026

Subotić, V., Schluckner, C., Schroettner, H., & Hochenauer, C. (2016). Analysis of possibilities for carbon removal from porous anode of solid oxide fuel cells

after different failure modes. Journal of Power Sources, 302, 378–386. https://doi.org/10.1016/j.jpowsour.2015.10.071

Subotić, V., Schluckner, C., Stöckl, B., Lawlor, V., Schroettner, H., & Hochenauer, C. (2016). Strategy for carbon gasification from porous Ni-YSZ anodes of industrial-sized ASC-SOFCs and effects of carbon growth. Journal of the Electrochemical Society, 163(14), F1515–F1522. https://doi.org/10.1149/2.0521614jes

Sun, C., Hui, R., & Roller, J. (2010). Cathode materials for solid oxide fuel cells: A review. Journal of Solid State Electrochemistry, 14(7), 1125–1144. https://doi.org/10.1007/s10008-009-0932-0

Sun, C., & Stimming, U. (2007). Recent anode advances in solid oxide fuel cells. Journal of Power Sources, 171(2), 247–260. https://doi.org/10.1016/j.jpowsour.2007.06.086

Suzuki, T., Yamaguchi, T., Fujishiro, Y., & Awano, M. (2006). Fabrication and characterization of micro tubular SOFCs for operation in the intermediate temperature. Journal of Power Sources, 160(1), 73–77. https://doi.org/10.1016/j.jpowsour.2006.01.037

Tan, X., Liu, S., & Li, K. (2001). Preparation and characterization of inorganic hollow fiber membranes. Journal of Membrane Science, 188(1), 87–95. https://doi.org/10.1016/S0376-7388(01)00369-6

Tarancón, A. (2009). Strategies for lowering solid oxide fuel cells operating temperature. Energies, 2(4), 1130–1150. https://doi.org/10.3390/en20401130

Tompsett, G. A., Finnerty, C., Kendall, K., Alston, T., & Sammes, N. M. (2000). Novel applications for micro-SOFCs. Journal of Power Sources, 86(1), 376–382. https://doi.org/10.1016/S0378-7753(99)00418-8

Wang, Y., Leung, D. Y. C., Xuan, J., & Wang, H. (2017). A review on unitized regenerative fuel cell technologies, part B: Unitized regenerative alkaline fuel cell, solid oxide fuel cell, and microfluidic fuel cell. Renewable and Sustainable Energy Reviews, 75(January 2016), 775–795. https://doi.org/10.1016/j.rser.2016.11.054

Wei, C. C., Chen, O. Y., Liu, Y., & Li, K. (2008). Ceramic asymmetric hollow fibre membranes-One step fabrication process. Journal of Membrane Science, 320(1–2), 191–197. https://doi.org/10.1016/j.memsci.2008.04.003

Xu, N., Chen, M., & Han, M. (2018). Oxidation behavior of a Ni-Fe support in SOFC anode atmosphere. Journal of Alloys and Compounds, 765, 757–763. https://doi.org/10.1016/j.jallcom.2018.04.326

Yang, C., Jin, C., & Chen, F. (2010). Micro-tubular solid oxide fuel cells fabricated by phase-inversion method. Electrochemistry Communications, 12(5), 657–660. https://doi.org/10.1016/j.elecom.2010.02.024

Yang, N., Tan, X., & Ma, Z. (2008). A phase inversion/sintering process to fabricate nickel/yttria-stabilized zirconia hollow fibers as the anode support for micro-tubular solid oxide fuel cells. Journal of Power Sources, 183(1), 14–19. https://doi.org/10.1016/j.jpowsour.2008.05.006

Zhou, D., Peng, S., Wei, Y., Li, Z., & Wang, H. (2012). Novel asymmetric anode-supported hollow fiber solid oxide fuel cell. Journal of Alloys and Compounds, 523, 134–138. https://doi.org/10.1016/j.jallcom.2012.01.120

LIST OF PUBLICATIONS

Omar, A. F., Othman, M. H. D., Gunaedi, C. N., Jamil, S. M., Mohamed, M. H., Jaafar, J., Ismail, A. F. (2018). Performance analysis of hollow fibre-based micro-tubular solid oxide fuel cell utilising methane fuel. *International Journal of Hydrogen Energy*, 1–9. https://doi.org/10.1016/j.ijhydene.2018.03.107 **(IF 2017 = 4.229)**