A novel micro-solid oxide fuel cell (μ -SOFC) for detecting methane content in biogas

S PHAJIT¹, M SUKLUENG^{2,*}, S MARTHOSA³, S NIYOMWAS⁴, N Y VOO⁵ and A KUMAR⁶

¹Energy Technology Program, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla 90110, Thailand

²PSU Energy Systems Research Institute (PERIN), Interdisciplinary Graduate School of Energy Systems, Prince of Songkla University, HatYai, Songkhla 90110, Thailand

³Faculty of Science and Industrial Technology, Prince of Songkla University, Suratthani Campus, Surat Thani 84000, Thailand

⁴Department of Mechanical Engineering, Faculty of Engineering, Prince of Songkla University, HatYai, Songkhla 90110, Thailand

⁵Centre for Advanced Material and Energy Sciences (CAMES), Universiti Brunei Darussalam, Jalan Tungku Link, Gadong BE1410, Brunei Darussalam

⁶Department of Mechanical Engineering, Delhi Technological University, Delhi 110042, India

*Author for correspondence (montri.su@psu.ac.th)

MS received 10 May 2018; accepted 19 December 2018; published online 25 April 2019

Abstract. A novel micro-solid oxide fuel cell (μ -SOFC), with a rectangular saw-tooth shape, was designed with a 50 wt% BYCF + 50 wt% GDC₁₀ cathode and a 60 wt% NiO + 40 wt% GDC₁₀ anode deposited on a GDC₁₀ electrolyte substrate by the spray pyrolysis technique. μ -SOFC receives methane only (CH₄) as fuel gas from one side. The fuel gas was applied at a flow rate of 0.2 l min⁻¹. The power density obtained was 1.0 μ W at 800°C. Voltage levels generated by the μ -SOFC at 40–99.99% CH₄ was highly accurate representing the quantity of CH₄. Low accuracy was observed at 10–30% of CH₄. Therefore, μ -SOFC is an application of SOFC technology to be a sensor for economically detecting CH₄ in a biogas system, while being capable of operating in humid conditions at high temperatures.

Keyword. μ -SOFCs; BYCF cathode; methane; biogas; sensor.

1. Introduction

A methane (CH₄) concentration in biogas of ~60–70% [1,2] enables us to convert H₂ by a reforming process which further can be converted into electricity by a fuel cell. Thailand is the world's largest producer of dry natural rubber [3]. The waste water from oil palm, and rubber can be used to produce biogas [4]. CH₄ is one of such biogases produced which could be used as a possible alternative fuel in the drying process. The direct methane use is challenging as the fuel processing system needs to convert hydrocarbons into hydrogen for the fuel cells [5]. The gaseous components and composition of biogas depend on the operating conditions, raw materials, retention time and temperature [1]. Hence, the quality and quantity of biogas vary widely [3]. Particularly, the biogas steam reform technique is operated at temperatures 700–900°C with a CH₄/CO₂ molar ratio of 1–1.5 with a yield of around 50% H₂ [6]. Steam reform uses high temperatures of equal to or greater than 850°C to excite the chemical reaction in the presence of a Ni catalyst. At lower temperatures, this catalyst which proved efficient in steam

reforming reactions is not sufficient to activate the chemical reaction [6]. This gas reform needs a sensor which can sustain at high temperatures. Micro-solid oxide fuel cells (μ -SOFCs) are electrochemical conversion devices that could support portable equipment such as laptop computers and mobile phones [7–9].

The high power density and the ability of continuous operation for long time periods without recharge is the speciality of this device [10,11]. Thus, μ -SOFCs are of particular interest, and more attractive due to their improved reliability and robustness with a ceramic structure [12]. They can operate at temperatures between 300 and 700°C, which is below the range of large-scale conventional SOFCs [13]. The decrease in overall thickness of SOFCs in order to increase the activation levels of ion oxide is required to lower temperatures [14]. Electrolytes, such as gadolinium-doped ceria (GDC), have also been improved in terms of their higher ionic conductivity [15]. Cathode and anode sides of the fuel cells have also evolved with decrease in resistivity, low thermal expansion, high porosity and the ability to operate at lower temperature [16–19]. The key reaction takes place between electrons, ions and gas molecules which occurs in the interfacial layer with

Figure 1. A novel μ -SOFC for detecting CH_4 in biogas.

anode/electrolyte/cathode interactions on the SOFC. Hence, the length of this triple phase boundary (TPB) should be maximized [20,21].

Suitable sensors could be used to monitor the multiple trace gases dissolved in transformer oil. The SOFC-based gas sensor is an alternative to detect H_2 , CO , CH_4 , C_2H_6 , C_2H_4 and N_2 [22]. CH_4 is a very important and dangerous flammable gas used in domestic and industrial applications. High-performance methane gas sensors have been developed from nickel oxide (Ni_2O_3), decorated tin oxide (SnO_2) semi-conducting films [23] and copper electrodes. Graphene oxide can be used to detect methane [24]. These sensors are based on materials with a high sensitivity to CH_4 .

This investigation aims to design a novel gas sensor using a SOFC system to detect CH_4 in biogas for a reforming system. The sensor was constructed using GDC_{10} electrolyte as the substrate with a BYCF cathode and a nickel oxide (NiO) anode deposited on it, as shown in figure 1. The spray pyrolysis (SP) technique was used to deposit the cathode and anode layers on the electrolyte, in a rectangular saw-tooth shape, with a narrow space left between the cathode and the anode.

2. Experimental

A cathode composite BYCF ($\text{Ba}_{0.054}\text{Y}_{0.029}\text{Co}_{1.8}\text{Fe}_{0.062}\text{O}_{2.89}$) [25] was prepared using re-agent grade metal oxide powders from Sigma Aldrich, Germany. A mixture of 5 wt% BaO , 3 wt% Fe_2O_3 , 2 wt% Y_2O_3 and 90 wt% Co_3O_4 was obtained by conventional ceramic powder processing. Commercial GDC_{10} (10% gadolinium-doped ceria, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$) electrolyte powder with a surface area of $10\text{--}14\text{ m}^2\text{ g}^{-1}$ and particle size of $0.1\text{--}0.4\text{ }\mu\text{m}$ was obtained from Fuel Cell Materials, USA. The NiO anode powder with a surface area of $2.9\text{ m}^2\text{ g}^{-1}$ and particle size of $0.5\text{--}1.5\text{ }\mu\text{m}$ was also sourced from Fuel Cell Materials, USA.

The cathode was a 50:50 mixture of BYCF and GDC_{10} , while the anode was a 60:40 mixture of NiO and GDC_{10} . These compositions were used to control and maintain the thermal expansion coefficient close to that of GDC_{10} , which is $13.08 \times 10^{-6}\text{ }^\circ\text{C}^{-1}$ at 900°C [26].

The electrolyte powders were ground for 1 h and mixed with distilled water, including 10% polyvinyl alcohol as a binder, by weight. The binder-added powder was pelletized

Figure 2. (a) GDC_{10} electrolyte. A uniaxial press was used to produce a pellet of 15 mm in diameter and 2 mm in thickness. (b) The SP technique was used to deposit a 50:50 BYCF + GDC_{10} cathode on the electrolyte substrate. (c) The μ -SOFC was completed by SP to deposit a 60:40 NiO + GDC_{10} anode with rectangular 'teeth' on the electrolyte substrate.

with the help of hydraulic press machine. The cathode and anode mixtures were milled for 12 h in a cylindrical-capped container with alumina balls as filling with the help of a horizontal rotary ball mill and dried in an oven at 150°C . The powders were ground again for 4 h in our in-house-made grinding machine and sieved through a 150 mesh.

In the SP technique, the spray gun was operated at 120 psi air pressure and the nozzle was set up at a height of 20 cm with a 16 cm spraying diameter. The pellet was placed on a stainless steel substrate and temperature was increased to 450°C . In order to use this technique, cathode and anode mixtures were needed in the form of slurries. The mixtures were mixed with distilled water in the ratio 30:70 vol%. All slurries were milled for 12 h in a horizontal rotary ball mill for obtaining highly homogeneous slurries.

In order to prepare a μ -SOFC sensor, the full fuel cell was fabricated with a 50:50 BYCF + GDC_{10} cathode and 60:40 NiO + GDC_{10} anode deposited on the GDC_{10} electrolyte pellet (50:50 BYCF + GDC_{10} |60:40 NiO + GDC_{10} | GDC_{10}) as shown in figure 1. The GDC_{10} powder was pressed to form pellets of 15 mm diameter and 2 mm thickness by using a uniaxial press under 3000 psi pressure. The GDC_{10} pellet, as seen in figure 2a, was sintered at 1400°C with a heating rate of $10^\circ\text{C min}^{-1}$ for 10 h. This GDC_{10} pellet shows high density for ion conduction at high temperatures [27]. The 50:50 BYCF + GDC_{10} cathode was deposited on the GDC_{10} electrolyte pellet by SP in which the rectangular saw-tooth shape sticker covered the surface to control the shape of the cathode layer. After spraying the cathode, this pellet was co-sintered at 1100°C with a heating rate of $10^\circ\text{C min}^{-1}$ for 10 h as shown in figure 2b. Meanwhile a 60:40 NiO + GDC_{10} anode was also deposited on the GDC_{10} electrolyte pellet, opposite to the cathode area, by SP, where the rectangular saw-tooth shape sticker covered the cathode layer to control the shape of the anode, and provided a space between the anode and cathode area. In order to obtain high porosity for the adsorption of gas and increase the electrochemical power density [28,29], this pellet was co-sintered at 1100°C with a heating rate of $10^\circ\text{C min}^{-1}$ for 10 h under an atmosphere as shown in figure 2c. The symmetrical μ -SOFC

with a 50:50 BYCF+GDC₁₀|50:50 NiO+GDC₁₀|GDC₁₀ was fabricated using the same process as the full μ -SOFC for measuring impedance spectra.

Figure 3 shows platinum electrodes as probes which were primed with platinum paste and pressed to ensure good contact. In the real experiment, the pellet with the platinum probes

Figure 3. (a) The μ -SOFC with an alumina tube and platinum wire. (b) Diagram showing the μ -SOFC set-up for gas flow measurements.

was placed in an in-house designed furnace. Microstructures were observed using a scanning electron microscope (SEM) (Gemini SEM, FE-SEM, and Zeiss). The ohmic and the interfacial resistance were determined by impedance spectroscopy using a Solartron 1286 electrochemical interface and a Solartron 1255 HF frequency response analyser. These were interfaced with a computer in the frequency range from 0.01 Hz to 1 MHz. A PROVA 200A PV analyser was used to measure power density. The biogas composition (H_2 , CO_2 , CH_4 , N_2 and H_2S) was determined by gas chromatography with a flame thermal conductivity and photometric detector by using an Agilent GC7890. The mixture of gases used was 99.99% methane (CH_4) and 99.99% nitrogen (N_2), each at 60 psi pressure and mixed by a metreing valve from Swagelok as shown in figure 8b. The biogas was collected from a palm oil factory in the south of Thailand.

3. Results and discussion

The μ -SOFC surface was examined using a SEM. Figure 4a shows the structure of the μ -SOFC surface with anode and cathode deposited on the electrolyte. The space (electrolyte) separating the anode and cathode was a rectangular saw-tooth shape on the 15 mm diameter electrolyte substrate. Figure 4b shows the microstructure of the anode with $\sim 1 \mu\text{m}$ pin-holes. Figure 4c shows the microstructure of the cathode

Figure 4. (a) The used μ -SOFC after gas sensing. (b) Microstructure of the 60:40 NiO + GDC₁₀ anode. (c) Microstructure of the 50:50 BYCF + GDC₁₀ cathode. (d) Microstructure of the GDC₁₀ electrolyte.

Figure 5. (a) The used μ -SOFC after gas sensing. (b) Cross-section of the microstructure between the 60:40 NiO + GDC₁₀ anode and GDC₁₀ electrolyte. (c) Cross-section showing the interface of the 50:50 BYCF + GDC₁₀ cathode and the GDC₁₀ electrolyte. (d) The free space separating the anode and cathode layers.

Figure 6. (a) Nyquist plots of the μ -SOFC impedance spectra at various temperatures in the range of 550–800°C. (b) Bode plots of the μ -SOFC at various temperatures.

with $\sim 10 \mu\text{m}$ pin-holes. High porosity was observed from the microstructure of the cathode and anode [27]. Figure 4d shows the microstructure of the electrolyte with no pin-holes. This microstructure indicated that the electrolyte is highly dense. The deposited anode was $40 \mu\text{m}$ in thickness on the electrolyte substrate (figure 5b). The deposited cathode was $80 \mu\text{m}$ in thickness on the electrolyte substrate (figure 5c). SEM images clearly shows that the surfaces are well-connected to cathode–electrolyte and anode–electrolyte interfaces (figure 5b and c).

The free space on the electrolyte surface was $900 \mu\text{m}$ wide between the anode and the cathode (figure 5d).

Impedance spectroscopy was utilized to assess the electrochemical properties and characteristics at different temperatures of the μ -SOFC. The impedance spectra of BYCF–GDC₁₀–NiO are fitted using Zview software with a proper equivalent circuit model as shown in figure 6a. In these models, L_o represents the inductance arising from equipment and cables during the measurements [28]. While R_s exhibits

Figure 8. (a) The μ -SOFC sensor was set-up in the furnace for application of the gas sensing. (b) The conventional gas mixing technology by using metering valve to mix the CH_4 and N_2 gas.

in the complex impedance corresponding to the cathode–electrolyte and electrolyte–anode interfacial impedance contributions to the total impedance of the system. The total impedance decreases with frequency and temperature as shown in figure 6b. It is affected by porous-media transport, elementary heterogeneous chemical reaction, ion conduction and electrochemical charge transfer, as shown in equation (1):

$$Z_{\text{tot}} = Z_{\text{rd}} + \frac{R_{\text{ct},a}}{i + j\omega R_{\text{ct},a} C_{\text{dl},a}} + R_{\text{ele}} + \frac{R_{\text{ct},c}}{i + j\omega R_{\text{ct},c} C_{\text{dl},c}} \quad (1)$$

Here, $C_{\text{dl},a}$ and $C_{\text{dl},c}$ are the double layer capacitances at the anode–electrolyte and cathode–electrolyte interfaces respectively; $R_{\text{ct},a}$ and $R_{\text{ct},c}$ are the charge transfer resistances at the anode and cathode respectively; R_{ele} is the ohmic resistance of the electrolyte; Z_{rd} is the effective reaction-diffusion resistance and $\omega = 2\pi f$ is the angular frequency [34].

Figure 9. Current–voltage characteristics of biogas from the palm oil factory in the south of Thailand and the corresponding power densities for the μ -SOFC with a flow rate of $\text{CH}_4 = 0.2 \text{ l min}^{-1}$ at 700–800°C.

Therefore, the frequency also affects the total impedance through capacitances.

The biogas, as the fuel for the sensor was collected from a palm oil factory in the south of Thailand. Table 2 indicates that the biogas was measured three times by GC machine which contains N_2 , CH_4 , CO_2 and H_2S . The average biogas composition was 5% N_2 , 60% CH_4 and 35% CO_2 by % volume. Hydrogen sulphide (H_2S) was obtained in biogas in the small amount of 944.437 ppm due to the palm wood materials. Lau *et al* [35] reported that biogas produced by palm oil mill effluent anaerobic digestion contains small amounts of H_2S . Figure 8a shows the set-up for measuring the voltage generated by the μ -SOFC sensor at 700–800°C temperature of the furnace. The calibration on the μ -SOFC sensor needs various percentages of CH_4 to generate the voltage because biogas from the factory contains 60% CH_4 . Therefore, calibration of the sensor was conducted at various percentage levels of methane gas as shown in figure 8b. Figure 9 exhibits power density and voltage as a function of biogas, the palm factory, fed to the sensor at 700 and 800°C. The maximum power density of the μ -SOFC sensor was $1.00 \mu\text{W cm}^{-2}$ at 700 and 800°C. This means almost the same power density generated at both temperatures. Therefore, the μ -SOFC sensor can be operated at 700°C to save on energy consumption as well as thermal stress relief. Le *et al* [36] observed

Figure 10. Measured voltage levels for different gas mixtures fed to the μ -SOFC at 800°C with the gas flow rate of 0.2 l min^{-1} .

Figure 11. Comparison of voltage levels of biogas from the palm oil factory in the south of Thailand and the mixture of gases measured by the μ -SOFC at 800°C, with a flow rate of 0.2 l min⁻¹.

a power density of 0.26 W cm⁻² from the full fuel cell fabricated from Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃ (BSCF) + GDC cathode, La_{1.8}Dy_{0.2}Mo_{0.2}O₉ (LDM) electrolyte and GDC + NiO + LDM anode which operated in an atmospheric reactant with a 1.5:1 (CH₄:O₂) ratio. At high temperatures, the composition of the BSCF + GDC cathode reacted to thermal expansions; however, it performed steadily in the temperature range of 652–700°C.

The measured voltage levels correspond to the amount of methane gas fed to the sensor. Experiments used mixture of gases which involves percentages of CH₄ and N₂ varying from 10 to 99.99%. The voltage levels of 50% CH₄ to 99.99% CH₄ were highly stable and can be used for reference. Meanwhile the voltage levels of 30% CH₄ to 40% CH₄ were unstable and had high error levels. For 10% CH₄ to 20% CH₄, it was not possible to separate the exact voltage level as shown in figure 10. There are three-layer fuel cells of BSCF/GDC/NiO which have a current level of around 0.55 A cm² spending 200 h, based on a 700 mV voltage level at 550°C [37]. Therefore, the μ -SOFC is a potential option for CH₄ gas detectors at high temperature.

There is insufficient methane to react in the reforming to convert CH₄ to hydrogen when the CH₄ concentration was below 40% (equation (2)). Hence, a low voltage level was detected with high error levels. CH₄ quantity should be sufficient to produce a typical endothermic reaction at high temperatures of 700–900°C. High catalysts are required to promote the conversion of syngas when the NiO-based material is used. Other reactions also occur concurrently during the dry reforming process. One typical side chemical reaction is a reverse water gas shift which can reduce the H₂/CO ratio

in the syngas product. This chemical reaction contributes to proper adjustment of the H₂/CO ratio for production of higher hydrocarbons [38].

Biogas was compared with the mixture of gases as shown in figure 11. Biogas-generated voltage level is 20.90 mV while the mixture was reported at 18.84 mV (figure 11). All gas samples were measured under the same conditions. The biogas from the factory was higher than the mixture of gas by around 10.93%, because H₂ was reformed from CH₄ gas on the anode side and mixed with the air in the alumina tube chamber. The NiO composition included in the anode side of the μ -SOFC, activated and contributed to CH₄-dry reforming as shown in equation (2) [5]. The biogas from the factory contained higher CO₂ levels than the mixture of gas, and H₂S was also detected in biogas. It may also be the case that H₂S causes the generation of the H₂ which is used by CH₄ dry reforming to produce the voltage, but it has a very small effect. Normally, the SOFC technology can produce the electricity (voltage level; e⁻) by H₂ and O₂, following H₂ + O₂²⁻ → H₂O + 2e⁻ and 1/2O₂ + e⁻ → O²⁻. Therefore, the biogas from factory can produce high voltage levels that occurred in the chemical reaction following equation (2):

Therefore, CH₄ is used to generate electricity using the μ -SOFC. A μ -SOFC with small-sized pellets cannot produce enough electricity to act as a power source. However, μ -SOFC can still be used as a low-cost sensor for CH₄ in biogas.

4. Conclusions

A novel μ -SOFC, consisted of a 50:50 BYCF + GDC₁₀ cathode and 60:40 NiO + a GDC₁₀ anode deposited on a GDC₁₀ electrolyte substrate in rectangular saw-tooth shapes, was fabricated. This μ -SOFC only allowed the fuel gas to be fed on one side and produced microwatt power density. CH₄ gas generated with 1 μ W cm⁻² of power density and the device can be adapted to a low-cost sensor for detecting methane in the biogas which contains H₂S, CO₂, N₂ and CH₄ with CH₄ the major component at 60% (based on biogas from oil palm wood). The sensor was monitored in terms of voltage level corresponding to the quantity of CH₄ in the biogas. This sensor cannot represent accurate voltage levels for 10–40% CH₄. The μ -SOFC sensor can be usefully operated at high temperatures which would be suitable in gas forming systems and biogas power plants. The electronic sensors are sensitive to humidity, which affects both metals and semiconductors. In contrast, the μ -SOFC can be operated at comparatively high temperatures and is mainly ceramic. Therefore, the novel μ -SOFC has potential for use as a low-cost sensor to detect biogas composition.

Acknowledgements

This research was supported by the Innovation Fund (RDO590769S), Prince of Songkla University. We thank our colleagues from the Faculty of Engineering; PSU Energy Systems Research Institute (PERIN), Centre of Excellence in Materials Engineering (CEME) and Centre for Advanced Material and Energy Sciences (CAMES, Universiti Brunei Darussalam) and all those who provided their insight and expertise that greatly assisted this research.

References

- [1] Charnnok B, Suksaroj T, Boonswang P and Chaiprapat S 2013 *Bioresour. Technol.* **131** 492
- [2] Chaiprapat S, Wongchana S, Loykulnant S, Kongkaew C and Charnnok B 2015 *Process Saf. Environ. Prot.* **94** 420
- [3] Choosong T, Phakthongsuk P, Tekasakul S and Tekasakul P 2014 *Saf. Health Work* **5** 86
- [4] Chaikitkaew S, Kongjan P and Thong S O 2015 *Energy Procedia* **79** 838
- [5] González-Gil R, Herrera C, Larrubia M Á, Kowalik P, Pieta I S and Alemany L J 2016 *Int. J. Hydrog. Energy* **41** 19781
- [6] Tuna C E, Silveira J L, da Silva M E, Boloy R M, Braga L B and Pérez N P 2018 *Int. J. Hydrog. Energy* **43** 2108
- [7] Bornapour M, Hooshmand R-A, Khodabakhshian A and Parastegari M 2016 *Energy* **117** 176
- [8] Rottmayer M, Singh R and Huang H 2016 *J. Power Sources* **332** 139
- [9] Timurkutluk B, Timurkutluk C, Mat M D and Kaplan Y 2016 *Renew. Sustain. Energy Rev.* **56** 1101
- [10] Patil T C and Duttagupta S P 2016 *Appl. Energy* **168** 534
- [11] Pla D, Sánchez-González A, Garbayo I, Salleras M, Morata A and Tarancón A 2015 *J. Power Sources* **293** 264
- [12] Wang J 2015 *Energy* **80** 509
- [13] Sohn S, Baek S M, Nam J H and Kim C-J 2016 *Int. J. Hydrog. Energy* **41** 5582
- [14] Kim K-J, Choi S-W, Kim M-Y, Lee M-S, Kim Y-S and Kim H-S 2016 *J. Ind. Eng. Chem.* **42** 69
- [15] Yao C, Meng J, Liu X, Zhang X, Liu X, Meng F *et al* 2015 *Solid State Sci.* **49** 90
- [16] Jin F, Liu J, Shen Y and He T 2016 *J. Alloys Compd.* **685** 483
- [17] Yi S, Shen Y, Zhao H, Du Z, Chen N and Huang B 2016 *Electrochim. Acta* **219** 394
- [18] Patro P K, Delahaye T and Bouyer E 2010 *Solid State Ion.* **181** 1378
- [19] Handal H T and Thangadurai V 2014 *Solid State Ion.* **262** 359
- [20] Doraswami U, Shearing P, Droushiotis N, Li K, Brandon N P and Kelsall G H 2011 *Solid State Ion.* **192** 494
- [21] Mukhopadhyay M, Mukhopadhyay J, Sharma A D and Basu R N 2011 *Int. J. Hydrog. Energy* **36** 7677
- [22] Ding J, Li X, Cao J, Sheng L, Yin L and Xu X 2014 *Sens. Actuators B* **202** 232
- [23] Vuong N M, Hieu N M, Hieu H N, Yi H, Kim D, Han Y-S *et al* 2014 *Sens. Actuators B* **192** 327
- [24] Assar M and Karimzadeh R 2016 *J. Colloid Interface Sci.* **483** 275
- [25] Hing P 2015 *ECS Conference on Electrochemical Energy Conversion & Storage with SOFC-XIV (July 26–31, 2015)*, ECS
- [26] Wongthong P, Nakason C, Pan Q, Rempel G L and Kiatkamjornwong S 2015 *J. Appl. Polym. Sci.* **132** 42520
- [27] Hanifi A R, Laguna-Bercero M A, Sandhu N K, Etsell T H and Sarkar P 2016 *Sci. Rep.* **6** 27359
- [28] Pang S, Jiang X, Li X, Wang Q and Su Z 2012 *J. Power Sources* **204** 53
- [29] Çelikbilek Ö, Siebert E, Jauffrès D, Martin C L and Djurado E 2017 *Electrochim. Acta* **246** 1248
- [30] Li R, Ge L, Chen H and Guo L 2012 *Electrochim. Acta* **85** 273
- [31] Suklueng M, Yoong V N, Hing P and Ming L C 2014 *Walailak J. Sci. Technol. (WJST)* **12** 373
- [32] Chourashiya M G and Jadhav L D 2011 *Int. J. Hydrog. Energy* **36** 14984
- [33] Pang S, Jiang X, Li X, Wang Q and Su Z 2012 *Int. J. Hydrog. Energy* **37** 2157
- [34] Huang Q-A, Hui R, Wang B and Zhang J 2007 *Electrochim. Acta* **52** 8144
- [35] Ohimain E I and Izah S C 2017 *Renew. Sustain. Energy Rev.* **70** 242
- [36] Le M-V, Tsai D-S and Nguyen T-A 2018 *Ceram. Int.* **44** 1726
- [37] Kim C, Park H, Jang I, Kim S, Kim K, Yoon H *et al* 2018 *J. Power Sources* **378** 404
- [38] Gao Y, Jiang J, Meng Y, Yan F and Aihemaiti A 2018 *Energy Convers. Manage* **171** 133