Short communication

Direct liquid methanol-fueled solid oxide fuel cell

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ABSTRACT

Anode coking problem of solid oxide fuel cell (SOFC) when using hydrocarbon fuels has been the major barrier for the practice and commercialization of well-developed high performance SOFC. In this work, based on fuels consideration, we chose liquid methanol as the candidate fuel for SOFC with the configuration of NiO/SDC–SDC–SSC/SDC. For comparison, traditional fuels, hydrogen and ammonia, were tested. With methanol as fuel, the maximum power densities were 698, 430 and 223 mW cm^{-2} at 650, 600 and 550 °C, respectively, which were higher than that with ammonia and lower than that of hydrogen. The electrochemical properties of the cells with the three fuels were investigated by AC impedance spectroscopy. The long-term stability of the cell with methanol, methane and ethanol were also studied at a constant output voltage of 0.5 V.

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1. Introduction

Solid oxide fuel cell (SOFC), with outstanding advantages of fuel flexibility and module integrity, has been expected to be an excellent green energy sources that be used as portable applications [1]. As countries develop, the exponential increase in the demand for energy has brought SOFC to a commercial stage.

Nowadays the crucial issue for the developments of SOFC is to explore proper fuels. Though hydrogen is the most optimal fuel for being directly used in SOFC, the requirement of storage and transportation for hydrogen is not only too expensive but also very severe. The intrinsic advantage of SOFC is that hydrocarbon fuels can be utilized directly with little or minimal fuel processing. However, the conventional Ni-based anodes suffers a number of drawbacks while using hydrocarbon fuels due to the propensity of Ni to catalyze carbon formation, resulting in the rapid degradation of the cell performance, which hindered SOFC from its commercialization. In order to overcome the carbon deposition problem at the anode, several solutions have been investigated: (1) using SDC coated Ni anode [2] or making anode protection with a composite layer of Ru–SDC [3] to block hydrocarbon from approaching the Ni; (2) exploring other appropriate active anodes, such as copper anodes [4], single phase redox-stable La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_3$ (LSCM) anodes [5], and Cu, Cu–Pd or GDC-impregnated La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_3$ (LSCM) anodes [6,7], to supersede the traditional Ni-based anode. Though coking problems were suppressed effectively and positive results were obtained partially in all these cases, neither was the right solution due to their shortcomings, such as insufficient catalysis activity or high cost. In addition, even if the new anodes are applied in SOFC, they are difficult to achieve a universal fuel cell to satisfy all the fuels. Therefore, from the viewpoint of practical considerations, the well-developed Ni-based anodes would be the best choice. The problem is how to overcome the coking problems.

In the authors' lab, we have focused mostly on the fuel consideration to solve the carbon deposition in recent years. Firstly, industrial liquid ammonia was taken as the right source of H$_2$ fuel as it can decomposes into H$_2$ and N$_2$ under the operation temperature and Ni-based anode condition of SOFC. And the experimental results have well met the expectation [8–12]. Tough ammonia has demonstrated as an excellent green fuel for SOFC. However, we cannot evade carbon-containing fuels as hydrocarbons spread everywhere and are the major energy carriers in the nature. Among the various fuels, methanol might be an ideal alternative green fuel for the following reasons. Firstly, methanol is the simplest hydrocarbon fuel except methane, and the liquid state of methanol at ambient conditions makes it ease of handling, transportation and storage. Secondly, methanol has a volumetric energy density of 15,800 kJ m^{-3} [13], which is even higher than that of liquid hydrogen. Thirdly, methanol is a clear and renewable source (say "it is a way of storing energy" maybe more exactly) that can be derived from all fossil resource, agricultural byproducts and biomass [14]. Fourthly, methanol can be also easily reformed back to CO and

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H$_2$ at relatively mild temperatures [15,16]. All of above imply that methanol could be an optimal candidate for a liquid fuel for SOFC. And methanol is much different from other hydrocarbon fuels, which carries sufficient oxygen to avoid entering into the thermodynamically unstable, carbon-forming regime [17,18]. Hence, methanol has been extensively researched in SOFC [14,19–22], even with Ni-based anodes, but there were some arguments on the long-term stability. Saunders et al. [20] found that carbon formed on Ni anodes when operated on methanol and the amount of carbon deposition was increased with decreasing temperature over the range of 700–850 °C. In contrast, Jiang and Virkar [14] reported that there was no carbon deposition when SOFC operated on direct methanol at temperatures as low as 550 °C. Another investigation, reported by Bi et al. [21], has also achieved pretty good results by using Ni-GDC anodes, but there was no evidence of the long-term stability to check whether the coking appeared or not on the anodes. Hence, it is necessary for us to study the stability of direct methanol-fueled SOFC.

In the present work, we tried to feed SOFC with liquid methanol at 550–650 °C. The cell is consisted of conventional Ni/SDC anode, SDC electrolyte and Sm$_{0.5}$Sr$_{0.5}$CoO$_3$ (SSC)/SDC cathode. The cell performance of the cell with methanol as fuel was investigated, and the characteristics of the cell with methane, ethanol, hydrogen and ammonia as the fuels were studied.

2. Experimental

2.1. Fabrication of NiO/SDC anode support

Commercial NiO and SDC powders prepared by citric acid–nitric auto ignition process were mixed in a weight ratio of 6:4, and the mixture with a proper amount of starch was ball-milled in an ethanol medium for 24 h and dried subsequently. Starch was used as a pore former to enhance the porosity of anode. NiO/SDC anode supports were made by uniaxially pressing the mixed powders under a pressure of 250 MPa and then pre-calcined at 600 °C for 2 h.

2.2. Fabricating SDC membrane on anode substrates

Thin electrolyte membrane of SDC was processed by a refined particles suspension coating technique [23,24]. SDC powders, synthesized via carbonate co-precipitation process [25], were employed to make a suspension. The suspension was drop-coated on the porous NiO/SDC anode supports surface to make SDC layers. Finally, the anode supports with SDC coats were co-sintered at 1400 °C for 5 h.

2.3. Preparation of cathode

Sm$_{0.5}$Sr$_{0.5}$CoO$_3$ (SSC)/SDC was applied as the cathode. The SSC and SDC powders were synthesized by glycine–nitrate process (GNP) [26]. The preparing process of cathode was similar to the previous studies [23,27]. The cells coated with cathode layer were finally sintered at 950 °C for 2 h in air.

2.4. Evaluation of cell performance

To avoid the possible catalysis decomposition of methanol to form carbon, the cell support and the gas tubing in our home-developed-cell-testing systems (see Fig. 1) are all made of alumina instead of stainless. The single cell was sealed on alumina tube with silver paste and tested at 500–650 °C. Liquid methanol in a glass was directly injected into the anode compartment at a feeding rate of 0.013 ml min^{-1} (roughly calculated from the result, about 120 ml of methanol has been used up in 160 h) by a peristaltic pump and
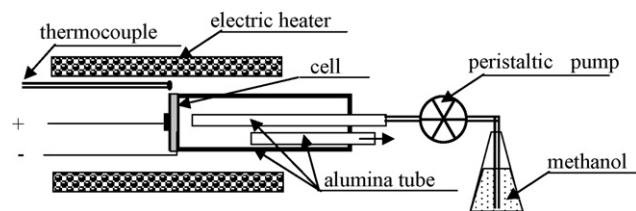

Fig. 1. A schematic diagram of the home-developed-cell-testing system.

then vaporized into gas at anode side. NiO in anode was directly reduced to form metal Ni in situ by methanol gas at 650 °C before the electrochemical measuring. The cell voltages and output currents of the cell were measured and recorded using an electronic load (IT8500, ITECH Electronic Co., Ltd.). AC impedance of the cells was conducted via a two-probe impedance spectroscopy (Chenhua Chi604c, Shanghai) under open circuit conditions in the frequency range of 0.01 Hz to 100 kHz with 10 mV as the excitation ac amplitude. The microstructure and the morphology of the tested cell was observed using scanning electron microscopy (SEM, model KYKY 1010).

3. Results and discussion

Fig. 2 shows the SEM image of the fractured Ni/SDC–SDC–SSC/SDC fuel cell after electrochemical testing. It can be seen that the SDC membrane about 24 μm seems uniformly continuous and is well adhered to both the porous Ni/SDC anode substrate and the cathode, almost without any cracks or noticeable pores.

Fig. 3 presents current–voltage (I–V) and current–power density (I–P) curves of the as-fabricated cell using liquid methanol and ambient air as fuel and oxidant, respectively. The maximum power density of 698 mW cm^{-2} is obtained at 650 °C, which is much higher than the highest record at 650 °C known to date (about 560 mW cm^{-2}) reported by Jiang and Virkar [14] for a cell with Ni/YSZ anode support, Ni/YSZ anode interlayer, 10-μm thick YSZ electrolyte, LSM/YSZ cathode interlayer and LSM cathode. The higher performance achieved in our case may result from the higher conductivity of SDC than that of YSZ at intermediate temperatures. As the temperature reduced to 600 and 550 °C, the maximum power
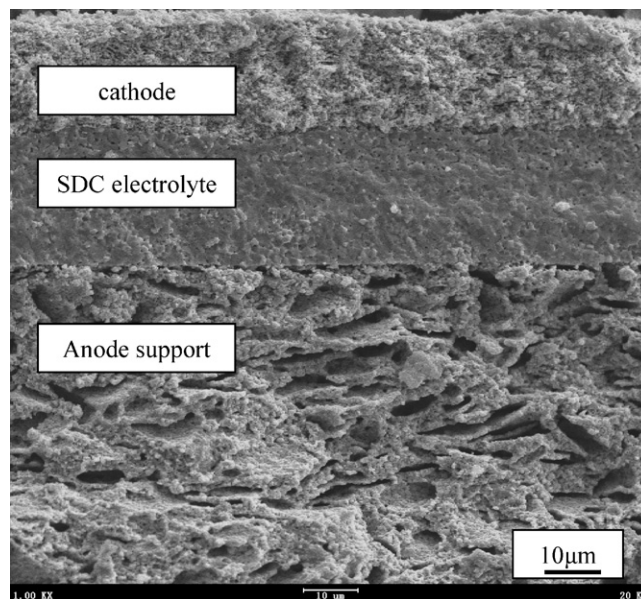

Fig. 2. Cross-sectional image of the tested cell with Ni/SDC, SDC and SSC/SDC.
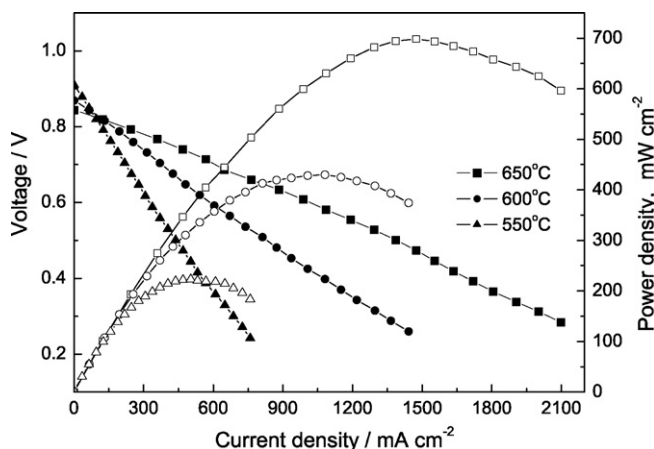
Fig. 3. Cell performance with methanol at various temperatures. The solid symbols correspond to the cell voltage and open symbols to power density.

densities are 430 and 223 mW cm^{-2}, respectively. Although there is a significant decrease in cell performance at lower temperatures, power densities of practical interest can be realized at temperatures as low as 550 °C.

To investigate the endurance of the cell with methanol as fuel, the cell was operated at a voltage of 0.5 V at 550 and 650 °C for several days. As can be seen from Fig. 4, no detectable decay in the cell current is observed within the operating duration. The fluctuation in the current densities of the cell was due to that the liquid methanol was directly injected into the anode compartment by a peristaltic pump which works in a disconnected way and the evaporation of the methanol needs time. Though the current fluctuated around 200 mA cm^{-2}, the highest and the average current values are always kept almost constant at a certain temperature. This result surely demonstrates no degradation of the cell performance, indicating no coking on anode. After running about 160 h, the methanol in the glass was exhaust, so the current density attenuated to zero, as well as the voltage.

As a comparison, the long-term stability of the cell with methane and ethanol as fuels at 650 °C are shown in Fig. 5. However, the current densities of the cell with methane and ethanol as fuels exhibit severe degradation at a voltage of 0.5 V. The very encouraged results from methanol-fueled SOFC compared with that fueled with other hydrocarbons can be surely attributed to methanol itself. Originally, we tried to explain this nice expected result from the thermodynamic viewpoint. The so-called Gibbs free energy
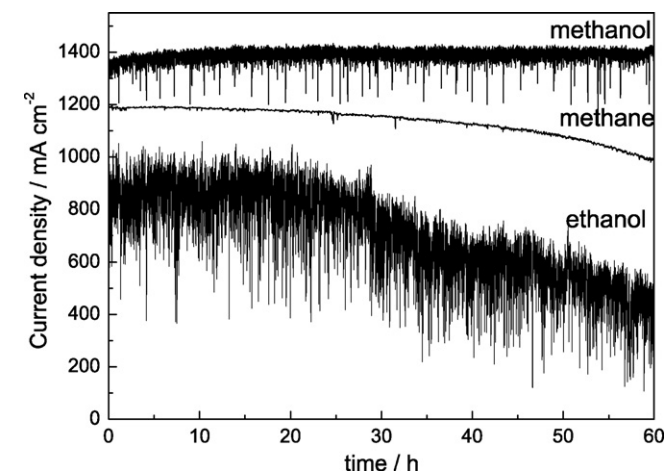

Fig. 5. Long-term stability of the cell *t* with methanol, methane and ethanol as fuel tested at 650 °C.

minimization method [28] is used to calculate the equilibrium compositions. In order to simplify the calculation, we assume that methanol decomposes completely at anode side and the species of H$_2$, CO$_2$, H$_2$O, CO, CH$_4$ [22], as well as solid carbon in the form of graphite are considered in the equilibrium composition. As shown in Fig. 6, the thermodynamic equilibrium analysis of methanol vapor in the temperature range of 500–1000 °C indicates a rather high carbon formation at below 900 °C, even assuming existence of a quite high O^{2-} current come from cathode side. Brett et al. [29] also reported a similar conclusion. This means that the behavior of methanol at anode surface is not controlled by thermodynamic. Hence, we have to consider it based on the kinetic factors. The molecule structures of these three substances possess quite different characteristics as shown in Fig. 7. The C–O bond in methanol
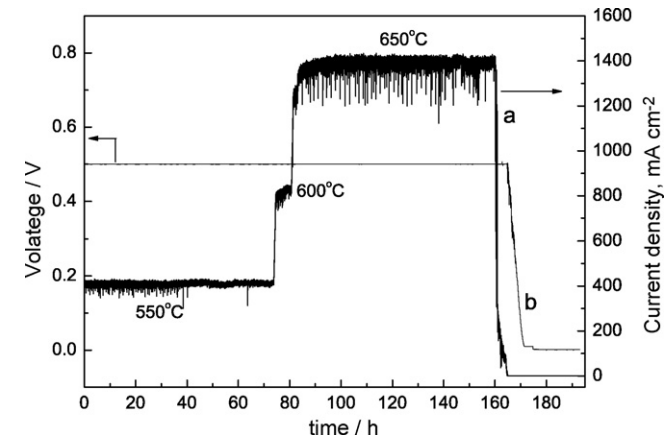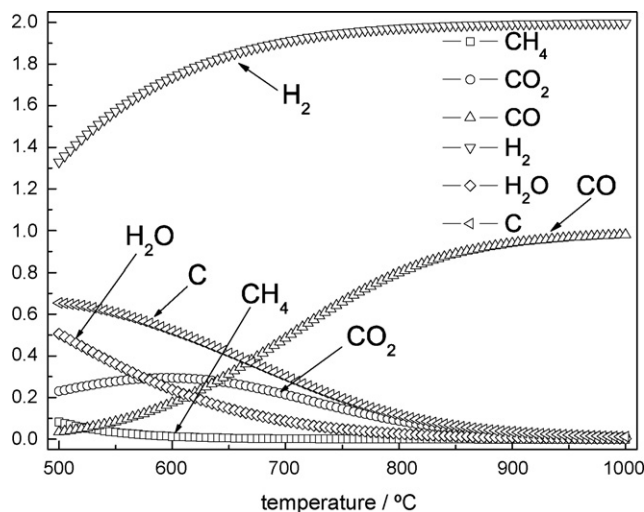

Fig. 6. The equilibrium partial pressures of the chemical species from methanol gas in the temperature range of 500–1000 °C.
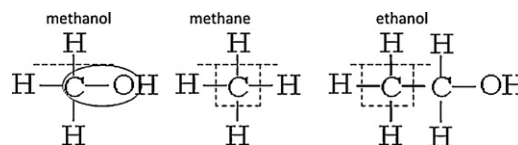

Fig. 7. The chemical bonds in methanol, methane and ethanol.

Fig. 4. Long-term stability of the cell tested at 550–650 °C with methanol as fuel.
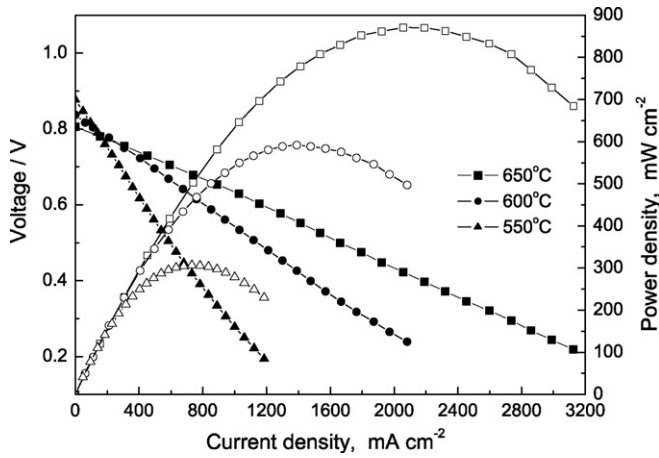
Fig. 8. Cell performance with humidified hydrogen at various temperatures. The solid symbols correspond to the cell voltage and open symbols to power density.

easily reacts with oxygen ions from cathode to form CO_2. In another hand, the H_2O and CO_2 formed from the anode reactions during the cell operation can suppress the carbon formation. Besides, Ni-based anode is a good catalyst to break CH_3OH directly into CO and H_2, which are the right fuels for SOFC. In CH_4, however, there is only C–H bonds that coking is possible if C–H bonds break into C and H_2 on the Ni catalysis but no sufficient O^{2-} to react with. While in the case of ethanol molecule, the situation would be surely more severe due to the existence of C–C bonds. The above predictions have been confirmed by the cell performance of the long-term stability (Fig. 5).

Finally, the cell performance with humidified H_2 and ammonia as fuels at the same temperatures are also tested. Figs. 8 and 9, respectively, show the performance of the cell with humidified hydrogen and ammonia at different temperatures. With H_2 (Fig. 8), the maximum power densities are obviously higher than that for methanol cell, 870, 591 and 306 mW cm^{-2}, at 650, 600 and 550 °C, respectively. These results are quite reasonable according to thermodynamic prediction and mass transfer consideration. However, with ammonia (Fig. 9), the maximum power densities are 467, 291 and 167 mW cm^{-2}, correspondingly, which are much lower than that with methanol.

As we know, the cell performance is governed by interfacial resistances (R_p) as well as ohmic resistances (R_o). Fig. 10 gives the comparisons of impedance spectra of the single cells fuelled by methanol, humidified hydrogen and ammonia under open-current
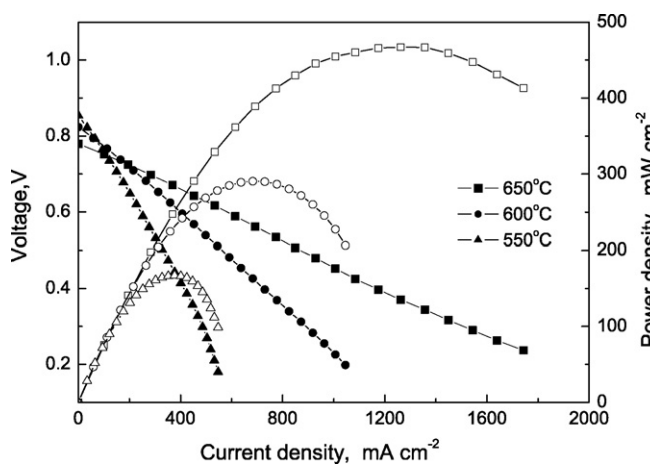

Fig. 9. Cell performance with ammonia at various temperatures. The solid symbols correspond to the cell voltage and open symbols to power density.
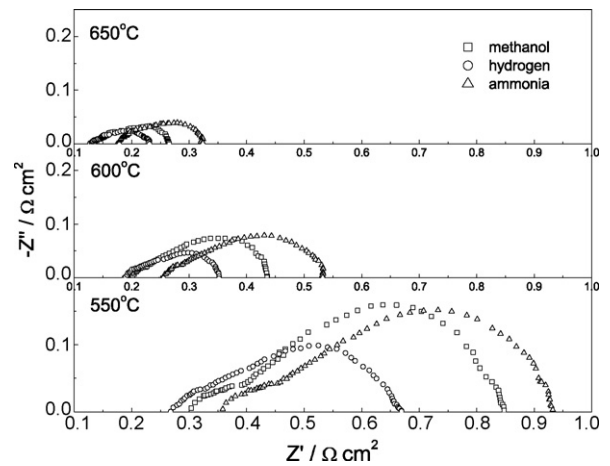

Fig. 10. Impedance spectra of the cell with methanol (squares symbol), humidified hydrogen (circle symbol) and NH_3 (up triangle symbol) as fuel under open-circuit conditions.

conditions at different temperatures. The value of R_o and R_p can be obtained from the left intercept with the real axis at high frequency range and the difference between low frequency and high frequency intercept with the real axis, respectively. As listed in Table 1, the R_o and R_p values in methanol and ammonia fuel cell are higher than that in hydrogen fuel cell at the operating temperatures, and the difference increased with the temperature decreased, which led to lower cell performance compared to H_2 fuel cell. The difference might be related to the different process of the three fuels involved at anode side.

When be used as fuels, methanol and ammonia are thermally decomposed at anode:

$$CH_3OH = CO + 2H_2 \qquad (1)$$

$$NH_3 = 1/2N_2 + 3/2H_2 \qquad (2)$$

And then, the resulting fuel compositions, H_2 and CO for methanol or H_2 for ammonia, react with the oxygen ions (O^{2-}) transported through electrolyte, thereby it generates useful power from the combustion of the fuels:

$$H_2 + O^{2-} = H_2O + 2e^- \qquad (3)$$

$$CO + O^{2-} = CO_2 + 2e^- \qquad (4)$$
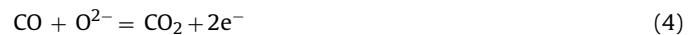
The decomposition of methanol (Eq. (1)) and ammonia (Eq. (2)) are certainly endothermic. Therefore, the temperature at the anode surface actually is lower than the system temperature controlled by the thermocouple (see Fig. 1). This means that the temperatures of anode surface with methanol and ammonia as fuels are lower than that with hydrogen. This might be the major factor for the higher R_o values of methanol and ammonia fuel cell compared with H_2 fuel cell. In the previous work [10], it was found that the decomposition of NH_3 (Eq. (2)) was the most important step for ammonia fuel cell and the converting percent of ammonia was influenced much by the temperature. As seem from the V–I curves in Fig. 9, obviously bending down is observed at 550 °C. That implies the existence of concentration polarization, which might be attributed to the incomplete decomposition of NH_3 at 550 °C (the real temperature was lower than 550 °C).

However, as seen from Table 1, methanol is much different from ammonia. Under cell working conditions (with current being drawn from the fuel cell), methanol at anode surface would be partially oxidized (Eq. (5)) or direct oxidated (Eq. (6)) by the oxygen ionic

Table 1
Ohmic resistances (R_e) and interfacial resistances resistance (R_p) of the cell with methanol, humidified hydrogen and ammonia as the fuel, obtained from AC impedance spectra

Cell (°C)	Methanol		Humidified hydrogen		Ammonia	
	R_e ($\Omega\,cm^{-2}$)	R_p ($\Omega\,cm^{-2}$)	R_e ($\Omega\,cm^{-2}$)	R_p ($\Omega\,cm^{-2}$)	R_e ($\Omega\,cm^{-2}$)	R_p ($\Omega\,cm^{-2}$)
650	0.133	0.132	0.127	0.103	0.178	0.146
600	0.200	0.236	0.187	0.165	0.255	0.278
550	0.299	0.549	0.267	0.403	0.355	0.575

passing through the electrolyte to the anode:

$$CH_3OH + O^{2-} = CO_2 + 2H_2 + 2e^- \tag{5}$$

$$CH_3OH + 3O^{2-} = CO_2 + 2H_2O + 6e^- \tag{6}$$
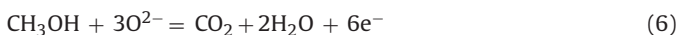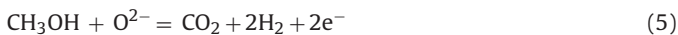
The electrochemical oxidation processes of Eqs. (5) and (6) are exothermic, and it will partially provide the heat energy required for methanol decomposition (Eq. (1)). Hence, R_o values for methanol are little higher than hydrogen but much lower than ammonia. It should be pointed out that if more oxygen ionic supplied at anode, the electrochemical oxidation of methanol can be performed exclusively and carbon deposition can be avoided.

SDC electrolyte has a partial electronic conduction, even under OCV conditions (with no current being drawn from the fuel cell), there should be negligible supply of oxygen through the electrolyte to maintain charge balance. Though it reduces efficiency of power generation, the oxygen ionic (O^{2-}) permeation across the electrolyte will lead to electro-catalytic oxidation reactions of methanol at the anode side. Meanwhile, other process, such as steam reforming (Eq. (7)) and water gas shift reaction (Eq. (8)) will take place at anode to produce more H_2, which would suppress carbon deposition:

$$CH_3OH + H_2O = CO_2 + 3H_2 \tag{7}$$

$$CO + H_2O = CO_2 + H_2 \tag{8}$$

Further analysis of the interfacial resistances (R_p) with the three fuels, the activation energies are 90.2, 86.6 and 86.6 kJ mol^{-1} for methanol, hydrogen and ammonia, respectively. Same activation energy for hydrogen and ammonia indicates that the electrode process mechanisms are similar, where the essential fuels are H_2. The higher activation energy for methanol may result from the more complex electrochemical process taken place in the cell.

4. Conclusions

SDC thin membrane (24 μm) based SOFC with the structure of Ni/SDC–SDC–SSC/SDC is successfully fabricated via suspension coating/co-firing processes.

With liquid methanol as fuel, the maximum power densities at 650, 600 and 550 °C are 698, 430 and 223 mW cm^{-2}, respectively, while the maximum power densities of 870 and 467 mW cm^{-2} are obtained respectively with H_2 and ammonia as fuels at 650 °C. The differences in performance of the cells are related to the different process of the three fuels involved at anode side, which can be explained by the AC impedance spectroscopy.

Direct methanol-fueled SOFC exhibits high performance without notable degradation during long-term testing, indicating no coking on the anode. While the cell with methane or ethanol as fuel show severe performance degradation with obvious coking on anode surface.

Though the performance of the cell with methanol is lower than that with H_2, the abundance resource, the ease of handling liquid methanol and the high performance produced at intermediate temperatures may lead to widespread applications of the direct methanol-fueled SOFC in the future.

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