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Investigation of perovskite oxide $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ as cathode for a room temperature direct ammonia fuel cell

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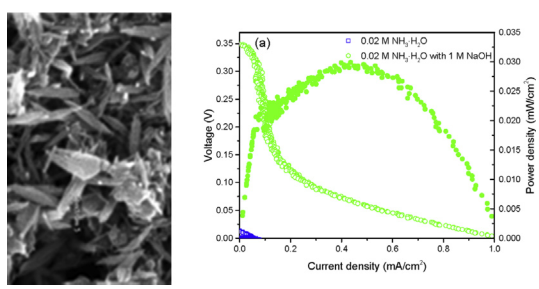
HIGHLIGHTS

- Shuttle shaped $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ was synthesised by a Pechini method.
- $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ is a potential cathode for direct ammonia fuel cells.
- Fuel cell performance using different concentration of NH_3H_2O as a fuel was investigated.
- Open circuit voltage and power density of fuel cells were improved by adding 1 M NaOH.

GRAPHICAL ABSTRACT



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ABSTRACT

Through Pechini method, a single phase shuttle-shaped perovskite oxide $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ was successfully synthesised at 1000 °C. It was combined with active carbon, forming a composite electrode to be used as cathode in a room temperature ammonia fuel cell based on an alkaline membrane electrolyte and Pt/C anode. Reasonable OCV and power density were observed for an ammonia fuel cell using $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$/C composite cathode. Although the power density is not high enough for conventional portable or transport applications, it has the potential for stationary application in removal of ammonia from wastewater because the requirements on power density is relatively low. When a dilute 0.02 M ammonia solution (340 ppm) was used as the fuel, the fuel cell using this perovskite oxide can obtain an open circuit voltage of 0.35 V and a power density of 0.03 mW/cm^2. In order to obtain higher OCV, NaOH is necessary to be added in the fuel, especially when the fuel contains a low concentration of ammonia.

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This study indicates that perovskite oxides are potential good cathode for low temperature direct ammonia or alkaline membrane fuel cells.

Introduction

A fuel cell is an energy conversion device that converts the chemical energy in fuels directly into electricity at high efficiency [1]. There are different types of fuel cells such as solid oxide fuel cells, molten carbonate fuel cells, phosphoric acid fuel cells, alkaline fuel cells, and polymeric electrolyte membrane fuel cells [1]. For low temperature fuel cells, depending on the types of charge carriers, they can be divided into proton exchange membrane fuel cells (PEMFCs) using H^+ ions as the charge carriers whilst those rely on negative OH^- ions as the charge carrier in the electrolyte is called alkaline membrane fuel cells (AMFCs). The electrolyte and electrode materials used for different types of fuel cells are very different in order to meet their specific requirements. Among these fuel cells, AMFCs are of particular interest because theoretically low-cost non-precious metal catalysts can be used in both anode and cathode thus the overall cost for materials will be lower compared with the PEMFCs, which require precious metals, such as Pt, Pd, Ag as the catalysts in electrodes [2,3]. However, in real AMFCs, those with electrodes based on precious-metal catalysts still exhibit better performance than non-precious metal catalysts [4–7]. The Pt/C and Pd/C based electrocatalysts in AMFCs are also unstable and degradation of these catalysts has been observed [8]. Therefore, it is desired to develop new catalysts, particularly new non-precious catalysts for AMFCs. Non precious metals, metal oxides and non-metals have been investigated as low-cost catalysts for AMFCs [2]. As the anode activity is related to the fuels used in the fuel cells, therefore, different anode will be applied according to various fuels. In our research, we pay more attention in the cathode catalysts for AMFCs. The reaction at the AMFC cathode is [9,10]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad E^0 = +0.40V \tag{1}$$

This reaction is also called oxygen reduction reaction (ORR) under alkaline conditions. At present, platinum group metal (PGM) catalysts are regarded as one of the most active electrocatalysts for ORR due to their high activity and low overpotential [11–13]. However, because Pt resources are expensive, scarce and poorly stable [14], they are unable to be applied at a large scale [15,16]. In recent years, there are many optimization researches on finding higher activity and cheaper catalyst for ORR. According to laboratory test, in alkaline electrolyte, the ORR performance of those materials can be even better than that for Pt/C. For example, carbonaceous materials containing nitrogen and transition metals (Me–N–C, where Me = Fe, Co, Mn) have been synthesised through pyrolysis to control the porosity and structure, which exhibited significantly higher ORR activity under alkaline conditions than under acidic conditions [17]. In addition, the ORR activity can also be significantly increased by doping the aqueous electrolyte with heteroatoms (such as N, P, S) and transition metals (such as Fe, Co, Ni) [18,19]. This is because the activity of catalysts can be improved through porous morphology and larger electrochemical surface area [20,21]. On the other hand, perovskite oxides are mixed metal oxides with a general formula of ABO_3, first discovered in Russia in 1830 [22–24]. Compared with other types of non-noble metal oxides, perovskite oxides have a good flexibility in composition and structure [14]. Perovskite oxides have excellent properties in rechargeable metal-air batteries and regenerative fuel cells, especially in solid oxide fuel cells [25–28]. Perovskite oxides have been widely used as both cathode and anode in solid oxide fuel cells and solid oxide electrolysis cells [1,29] and catalysts for ammonia synthesis [30–32]. Due to the low cost and high activity of the perovskite oxides in alkaline media and the ability to form a large number of potential chemicals, it has become a popular inexpensive alternative to precious metal catalysts, measured by three electrode set-up [14,33]. However, to the best of our knowledge, research on perovskite oxide catalyst for low temperature fuel cells or electrolysers focus on three electrode set-up whilst reports on using perovskite oxide as the cathode in a two electrode are scarce. In a previous report, we proved that the perovskite oxides Cu- and Nb- co-doped $SrCoO_{3-\delta}$, $SrCo_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ is a good cathode catalyst for direct room temperature ammonia fuel cell [34]. On the other hand, we also investigated Cu- and Nb- co-doped $SrFeO_{3-\delta}$ with various Cu molar ratio from x = 0 to 0.4, and it was found that, in $SrFe_{1-2x}Cu_xNb_xO_{3-\delta}$, sample $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ with x = 0.1 exhibits the highest conductivity in both air and 5% H_2/Ar thus suitable for use as electrodes in solid oxide fuel cells [35]. Therefore, we believe $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ could be a potential cathode material for low temperature alkaline membrane fuel cells.

In term of various fuel for fuel cells, ammonia is unique in terms of wastewater treatment and indirect on-board hydrogen storage [36–39]. Although there are various types of high temperature ammonia fuel cells, the high operating temperature of ammonia solid oxide fuel cells (SOFCs) or ammonia alkaline fuel cells (AFCs) makes them very difficult to be directly used for ammonia-containing wastewater treatment due to the high thermal capacity of water [34,38,40–42]. Fortunately, we reported the first low temperature ammonia fuel cells based on either alkaline membrane or acidic Nafion membranes although the power density is quite low [10,34,43]. There are several reports on ammonia fuel cells based on alkaline membrane fuel cells [44–47]. If the power density is high enough, direct ammonia fuel cells have the potential to power electric vehicles [38]. It has been proposed to use direct ammonia fuel cell to convert low grade waste heat into electricity [48]. On the other hand, high concentration of ammonia is normally present in wastewater such as landfill leachate and sewage water. In most cases, there are free ammonia (NH_3) or ammonium (NH_4^+) existing in wastewater [10,21,49–51], which may come from natural hydrolysis of urea in urine [52]. Therefore, instead of consuming energy to remove ammonia, electricity will be generated from ammonia-containing wastewater with the application of ammonia fuel cells.

In this work, for the first time, perovskite oxide $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ was investigated as the cathode for directly ammonia fuel cells. It has been reported that Pt/C is a good catalyst for electrochemical oxidation of ammonia thus would be a good anode for direct ammonia fuel cells [53,54]. The performances of a room temperature ammonia fuel cell with Pt/C as the anode, $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ as the cathode and alkaline membrane as the electrolyte were investigated in detail.

Experimental methods

Synthesis of $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$

The perovskite oxide sample of $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ was synthesised by a Pechini method [25,34]. Firstly, dissolve all the chemical precursors, ammonium niobate(V) oxalate hydrate, $C_4H_4NNbO_9 \cdot xH_2O$ (99.99%, Sigma Aldrich, x = 6.7), $Sr(NO_3)_2$ (98%, Alfa Aesar), $Fe(NO_3)_3 \cdot 9H_2O$ (98+%, Alfa Aesar), and $Cu(NO_3)_2 \cdot 2.5H_2O$ (98%, Alfa Aesar), in deionized water with the stoichiometric molar ratio of 0.1:1.0:0.8:0.1 to prepare a mixed solution. Secondly, citric acid (99+%, Alfa Aesar) and ethylene glycol (Fisher Scientific) were added into the mixed solution. The molar ratio of citric acid, ethylene glycol and total metal ions was 1.2:1.2:1. Thirdly, the mixed solution was magnetically stirred at 125 °C for over 10 h on a hot plate (IKA C-MAG HS7). While stirring, the gel was formed as poly resin. The gel was then dried at a constant temperature of 350 °C to remove the extra solvent from the mixture. After cooling down, the mixture was ground in an agate mortar and pestle to form powders. Finally, the prepared powders were calcined in a muffle furnace (Carbolite RHF1600) at 400 °C for 2 h then 1000 °C for 4 h at a heating/cooling rate of 5 °C/min. The as-prepared $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ was used for materials characterisation and fuel cell measurements.

Materials characterisation

The X-ray diffraction (XRD) data was collected on a PAN analytical X'Pert Pro in the Bragg-Brentano reflection geometry with a Ni-filtered Cu Kα source (1.5405 Å), fitted with the X'Celerator detector and an Empyrean CuLFF XRD tube. Absolute scans in the 2θ range of 10–90° with step sizes of 0.0167° were used during data collection [34]. Scanning electron microscopy (SEM) measurements were carried out on a ZEISS SUPRA 55-VP Field Emission Scanning Electron Microscope equipped with an energy dispersive X-ray (EDX) spectrometer that allows elemental composition analysis [55]. Brunauer, Emmett and Teller (B.E.T.) surface area analyses was carried out using a QUADRASORB SI surface area analyser with nitrogen as the adsorbate gas, all catalysts were degassed at 150 °C with measurements carried out at liquid nitrogen temperature (77 K).

Electrode fabrication

The preparation of the $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ cathode ink consists of three steps [34,56,57]. The first step was to mix 1 g as-prepared $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$, 0.2 g carbon black (Cabot Vulcan XC-72) and 0.2 g Amberlite IRA-402(OH) resin (Alfa Aesar). The mixed powder was ball-milled at 200 rpm for 24 h on an Ortoalresa OABM 255 miller. Then a suspension of polytetrafluoroethylene (PTFE) containing 0.2 g of PTFE was added into the milled mixture using 5 ml water and 5 ml isopropanol as the solvent. The mixture above was stirred at room temperature for at least 24 h to prepare the ink for use as cathode of an ammonia fuel cell.

The substrate for the catalysts in this work is plain carbon fibre cloth (0.35 mm thickness, E-TEK). Clean and pre-treat the carbon cloth electrode (1 × 2 cm^2) was firstly sonicated in dilute hydrochloric acid, water and isopropanol for 1 min respectively. The as-prepared ink was then brushed onto the pre-treated carbon cloth. Finally, the electrode was put in a fume cupboard and naturally dried for overnight. The loading of catalyst $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ is approximately 14 mg/cm^2.

Electrochemical measurements

The fuel cell was assembled in a home-made fuel cell testing jig with prepared anode, cathode and electrolyte membrane. The cathode was perovskite oxide $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ with carbon black and Amberlite resin. Co-impregnated ARE-PVA membrane prepared according to a previous report [58] was used as electrolyte. The Pt/C anode was prepared according the method described in a previous paper whilst commercial Pt/C (20 wt% of Pt, Alfa Aesar) was used as the Pt source and the same plain carbon cloth was used as the substrate [59]. The loading of Pt was 0.8 mg/cm^2. The effective area of cell was 1 × 1 cm^2. The ammonia solution and compressed air were pumped and flowed into the anode and cathode chamber respectively. The flow rate of ammonia solution is controlled by a small pump rotated at 20 rpm, and the flow rate of air is controlled at 10 mL/min by a mass flow controller. The fuel cell performance was measured by a Solartron 1287A Electrochemical Interface coupled with a Solartron 1250 controlled by electrochemical software CorrWare/CorrView and Z-Plot/Z-view. The a.c. impedance was measured in the frequency range between 65 kHz and 0.01 Hz at the amplitude of the a.c. signal 20 mV [10].

The fuel was prepared by the ammonia hydrolyte solution (35 wt%, 0.88 g/mL, Fisher Chemical) and sodium hydroxide (98%, Alfa Aesar). At the beginning, the performance of fuel cell in different concentrations of ammonia solutions was tested at room temperature. Then ammonia solutions with 1 M NaOH were used as the fuel. In most cases, the ammonia concentration in the wastewater is between 200 ppm and 2000 ppm, so it is important to test the performance for fuels with low concentration of ammonia to determine if this

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technology is suitable for power generation from ammonia-containing wastewater.

Results and discussion

XRD and SEM/EDS analyses of synthesised $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$

Pechini method was used to prepare the $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ cathode catalyst in order to obtain the single phase materials to relatively low temperature with smaller particle size and higher specific surface area. The XRD pattern of $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ after firing at 1000 °C for 4 h is shown in Fig. 1. It can be seen that a single phase perovskite oxide $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ was successfully obtained. It can be indexed as cubic structure with a = 3.8866 (1) Å, which is comparable to the a = 3.8817 (1) Å in our previous report for pure $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$when the sample was prepared by a sol-gel process [35]. In this study, the firing temperature was 1000 °C which is 300 °C lower than that in the previous study when $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ was synthesised by a sol-gel process. The specific surface area of the as-synthesised $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ is 2.913 m^2 g^{-1} when measured by a BET method (Table 1). This is reasonable because the sample was fired at 1000 °C.

The SEM picture of the synthesised $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ is shown in Fig. 2a. The majority of the powder is composed of shuttle-shaped nano-rods. The picture with a magnification factor of 50000 is shown in Fig. 2b. The shuttle-shaped nano-rods have a length of 200–400 nm and a diameter of 30–60 nm. Some thinner nano-rods has a diameter of 10 nm. A small number of large particles with secondary particle size ~500 nm was also observed. EDS point analysis indicate that both the shuttle-shaped nanorods and the large particles are composed of element Sr, Fe, Cu, Nb and O indicating they are both $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ but with different shapes (Fig. 2c–g). To the best of our knowledge, this is the first time, that shuttle-shaped perovskite oxide was prepared. It has been reported that shuttle-shaped α-Fe_2O_3 was prepared by a

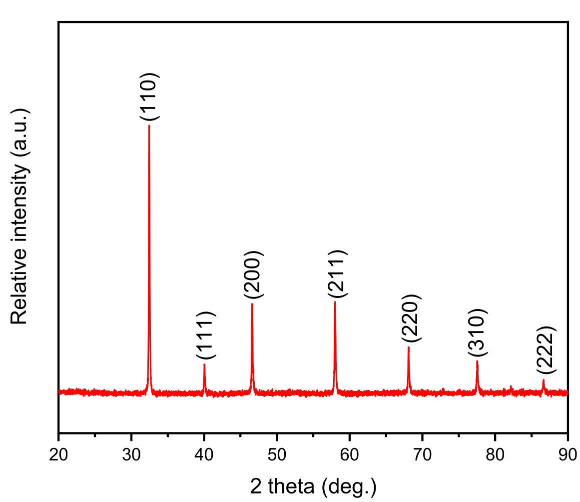

Fig. 1 – XRD pattern of the prepared $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ collected at room temperature.

Table 1 – Comparison of specific surface area of different samples.

Sample	Specific surface area (m^2 g^{-1})
carbon black (Cabot Vulcan XC-72)	148.221
$SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ powder	2.913
$SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$/carbon black	37.302
$SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$/carbon black/carbon cloth	13.465

supramolecular template [60]. Shuttle-shaped ceria was synthesised via a surfactant octadecyl amine and urea assisted solvothermal process for use as catalyst for CO oxidation [61]. Supramolecular template or surfactant was required in order to obtain shuttle-shaped oxides Fe_2O_3 and CeO_2 whilst neither was used in the synthesis process of $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ in this study. Recently halide perovskite $CsPbX_3$ (X = Br, or/and I) was prepared by dissolving the Cs, Pb salts in octane at 90 °C [62]. In general, this low temperature synthesis method is not suitable for preparation of perovskite oxides. Shuttle-shaped materials may have special catalytical, magnetic or mechanical properties. In this study, it happens that shuttle-shaped perovskite oxide $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ was prepared by a conventional Pechini method. The mechanism of the formation process is not clear which needs further investigation. However, in this study, it has been demonstrated that this material is a good cathode material for ammonia fuel cells based on alkaline membrane electrolytes.

Ammonia fuel cell performance without the addition of NaOH

An alkaline fuel cell based on Co-AER-PVA membrane, Pt/C anode and $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$/C cathode was fabricated to test the performance when ammonia was used as the fuel. Although pure $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ is quite conductive, the contact between rigid $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ and the carbon cloth current collector would not be good, therefore black carbon Cabot Vulcan XC-72 was mixed with perovskite oxide $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ to form a composite electrode in order to improve the contact between $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ catalyst and carbon cloth current collector. The specific surface area of the $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ and black carbon mixture is 37.302 m^2g^{-1} which is between that for pure $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ and pure carbon black (Table 1). Introduction of carbon black not only improve the contact between the hard $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ and soft carbon cloth substrate but also increase the overall specific surface area which will benefit the catalytic activity of this composite cathode. However, the overall specific surface area of the cathode including carbon cloth is only 1/3 of that for $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$/carbon black composite because of the low surface area of carbon cloth (Table 1).

Fig. 3a shows the I–V curves of the fuel cell at room temperature when different concentration of ammonia aqueous solutions were used as the fuel. It was found that the open circuit voltage (OCV) was quite low when the ammonia fuel concentration is below 1 M. This indicates that it is difficult to generate electricity from low concentration of ammonia which normally exists in wastewater. The OCV increased to

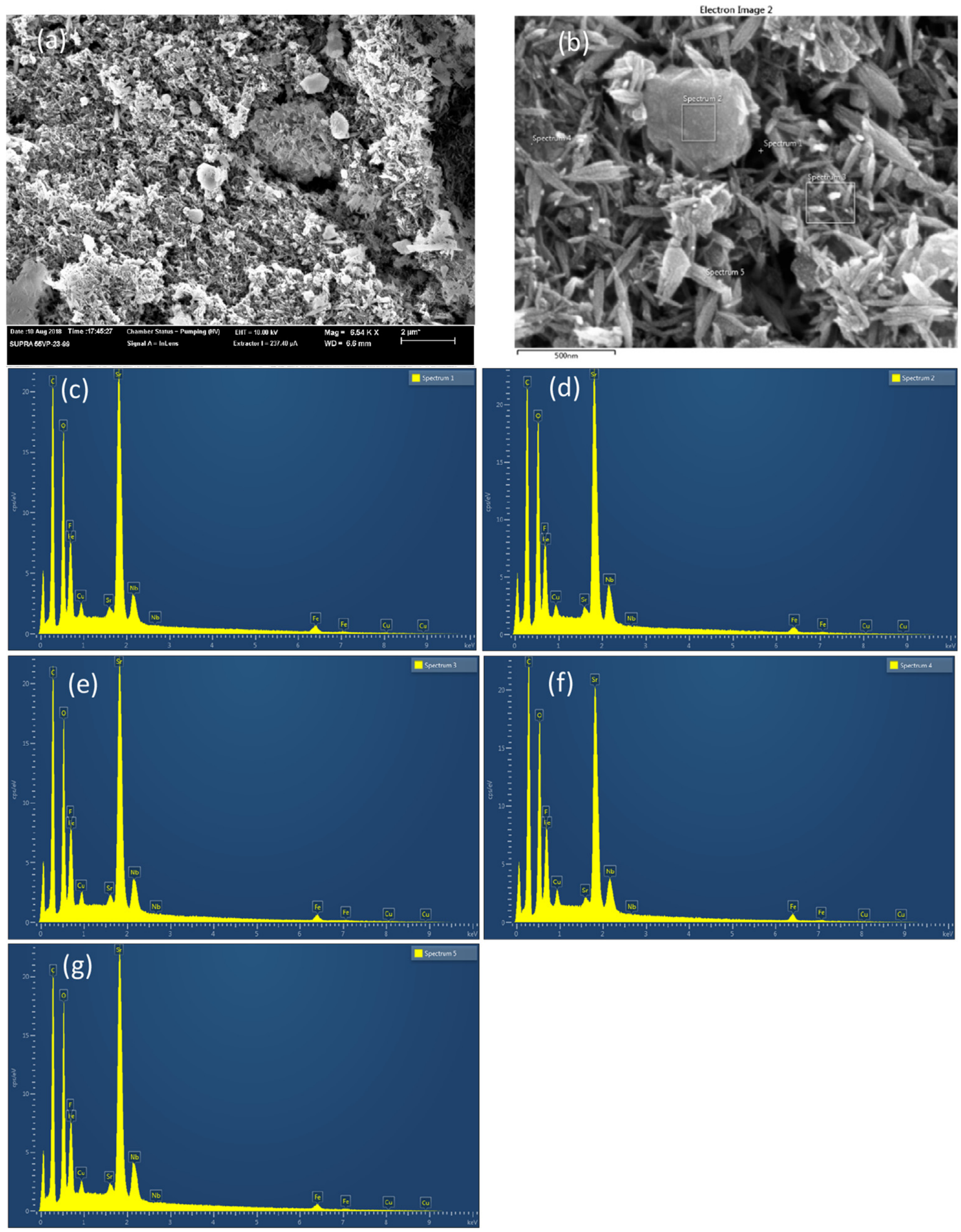

Fig. 2 – SEM pictures of $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ powder. (a) 6500X; (b) 50000X; (c)–(g) point analysis of elements.

0.075 V when 3 M ammonia was used as the fuel and further increased to 0.25 V when 5 M ammonia was input in the fuel cells (Fig. 3b). This experiment indicates that both anode and cathode catalysts have some activity to oxidation of ammonia at anode and reduction of oxygen at the cathode. Pt/C is a good anode catalyst for ammonia fuel cell but the reaction kinetics on Pt is slow, which is reflected on the low OCV of the cell, particularly at low concentration of fuels [9,63]. A maximum current and power density of 0.6 mA/cm^2 and 0.038 mW/cm^2 was achieved when 35 wt% concentrated ammonia was used as the fuel.

What should be noted is that it is very common to add strong base such as KOH or NaOH to increase pH value when investigating the activities of perovskite oxides on oxygen reduction reaction in alkaline conditions [14]. In this work, to investigate the activity of $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ cathode in the presence of strong alkaline condition, some NaOH was added to the ammonia fuel to investigate the performance.

Ammonia fuel cell performance with the addition of NaOH to a concentration of 1 M

Fig. 4a shows the fuel cell performance when NaOH was added to the ammonia fuel at a concentration of 1 M. When the ammonia concentration was as low as 0.02 M, the OCV was 0.35 V whilst the maximum current density was 1 mA/cm^2,

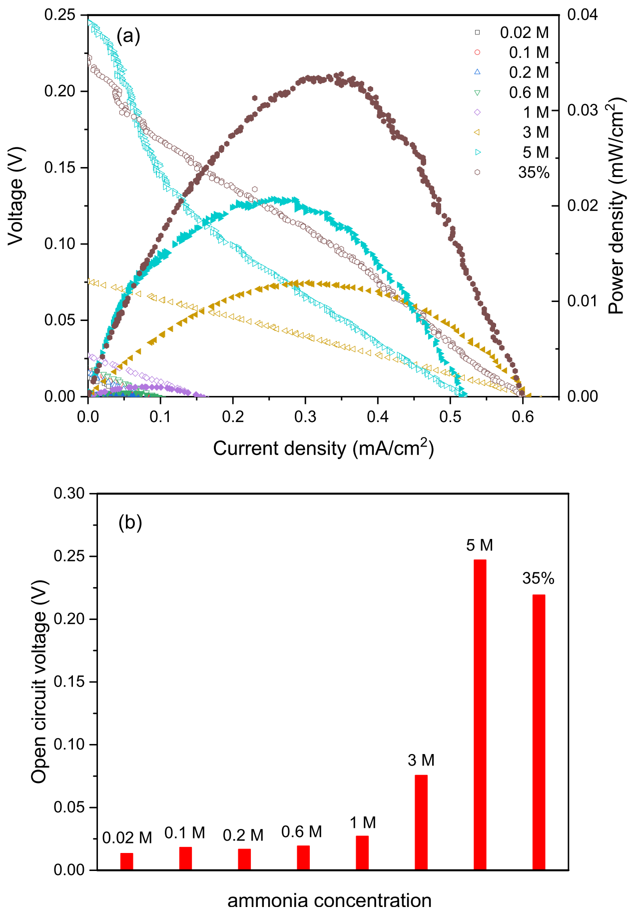

Fig. 3 – The I–V curve (a) and OCV (b) of a room temperature ammonia fuel cell at different ammonia concentrations using $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ electrode as the cathode.

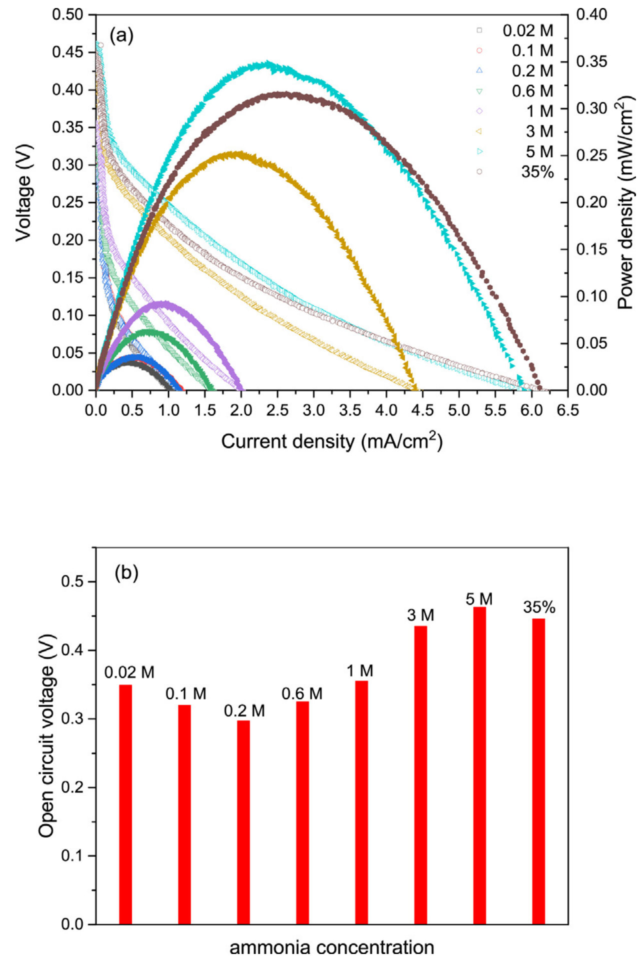

Fig. 4 – The I–V curve (a) and OCV (b) of a room temperature ammonia fuel cell at different ammonia concentrations with 1 M NaOH using $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ electrode as the cathode.

which is higher than that when 35 wt% ammonia was used as the fuel without the addition of NaOH (Fig. 3). Even the ammonia concentration was only 0.02 M, the maximum power density was 0.03 mW/cm^2, which is comparable to that when using 35 wt% ammonia as the fuel without the addition of NaOH (Fig. 3a). This experiment indicates that this type of fuel cell has the potential to generate electricity from low concentration of ammonia from wastewater with the presence of base such as NaOH. In case the pH value of the ammonia-containing wastewater is not high enough, some alkaline waste such as coal fly ash which contains a significant amount of CaO can be added into the ammonia-containing wastewater to increase the pH value, making the fuel suitable for ammonia fuel cell performance [64]. When concentrated 35 wt% ammonia solution with 1 M NaOH was used as the fuel, the OCV was 0.46 V (Fig. 4b), which is higher than the 0.3 V for an ammonia fuel cell using NH_4^+-form Nafion membrane as the electrolyte and Pt/C as both as the anode and cathode [10]. The theoretical OCV of ammonia fuel cell is the same as long as the fuel concentration at the anode and oxidant (air or O_2) at the cathode are identical, disregarding the charge carriers in the electrolyte. However, the real overpotential at either electrode is related to the charge carrier and the activity of the catalysts. The difference in observed OCV could be related to the membrane or/and the cathode materials as the anode is the same although Pt was 0.6 mg/cm^2 in previous study, slightly lower than the 0.8 mg/cm^2 in this study [10]. The maximum current density was 6.2 mA/cm^2 which is comparable to the 8.0 mA/cm^2 for an ammonia fuel cell at room temperature when Pt/C was used as both anode and cathode [10]. Compared with our previous fuel cell work using Cu-doped $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ perovskite oxides as the cathode [34], in the presence of NaOH, the OCV is same, approximately 0.45 V, but the power density generated from $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ cathode is higher. Especially when the ammonia concentration is higher than 1 M, the fuel cell with $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ cathode exhibits higher current and power densities. For example, the maximum current density and power density generated from Cu-doped $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ cathode was 5 mA/cm^2 and 0.25 mW/cm^2, lower than 6.2 mA/cm^2 and 0.35 mW/cm^2 for Cu-doped $SrFe_{0.9}Nb_{0.1}O_{3-\delta}$ cathode in this work. These results indicate that the perovskite oxide $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ is a reasonably good cathode in the presence of NaOH.

In a direct ammonia fuel cell based on alkaline membrane, the anode reaction is [10]:

$$2NH_3 + 6OH^- \rightarrow N_2 + 6H_2O + 6e^- \quad E^0 = -0.77V \qquad (2)$$

The introduction of NaOH will increase the concentration of OH^- ions, making reaction (2) shift to the right. Therefore, the kinetics of ammonia oxidation is improved thus the overpotential at the anode decreases leading to higher OCV. As for the cathode, most perovskite oxides are active for ORR reaction in strong alkaline condition. It is believed that adding NaOH will increase the activity of $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ therefore the fuel cell performance is much better in the presence of NaOH, compared to the results shown in Fig. 3.

For comparison, the performance of the fuel cell with 0.02 M and 5 M ammonia solution as the fuel when with and without addition of NaOH to a concentration of 1 M is plotted together in Fig. 5. The effect of NaOH is significant on the fuel cell performance. In order to generate electricity from wastewater with low concentration of ammonia, such as 0.02 M or 340 ppm, it is important that the pH value of the wastewater must be very high. Although significant progress has been made on low temperature direct ammonia fuel cells, the catalytic activities of both anode and cathode are still not high enough to achieve high power density. It is therefore desired to develop new catalysts for electrochemical oxidation of ammonia at weak alkaline or neutral condition to be used as anode for ammonia fuel cells for this particular application.

XRD and SEM/EDS analysis of the $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$/C cathode after ammonia fuel cell measurements

In order to investigate the stability of perovskite oxide $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ in ammonia fuel cells, XRD and SEM/EDS analysis were carried out for the cathode after the fuel cell measurements. The XRD patterns of the $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$/C composite cathode before and after the fuel cell measurements are shown in Fig. 6. As expected, before the fuel cell measurements, the cathode is composed of $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ and carbon. The small peak at 2θ of ~37° belongs to the PTFE binder [65]. However, after the fuel cell measurements, the peaks for $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ became very weak whilst carbon and PTFE were present (Fig. 6b). This

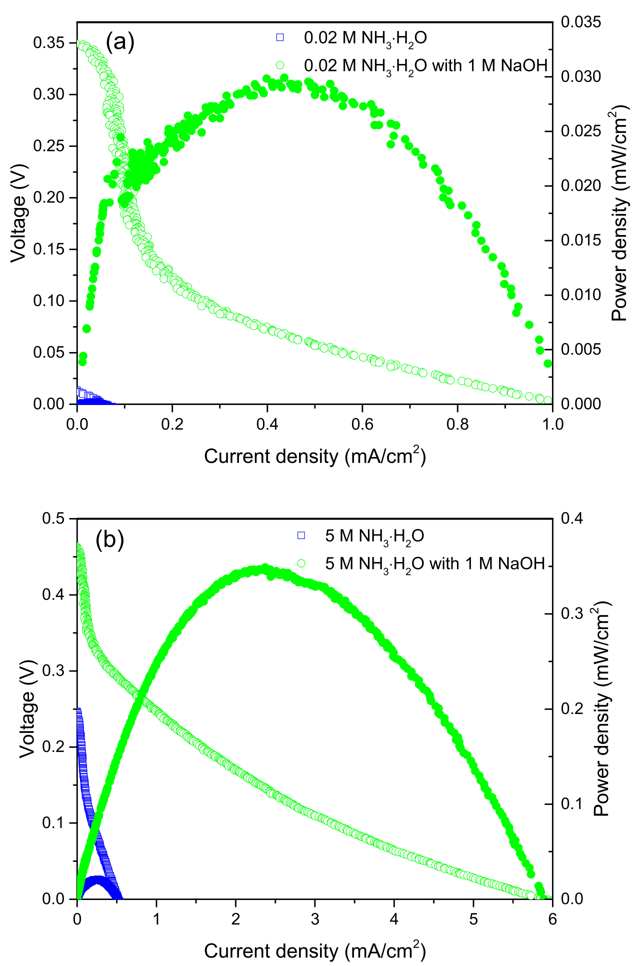

Fig. 5 – The I–V curve of ammonia fuel cell in (a) 0.02 M and (b) 5 M ammonia with and without 1 M NaOH.

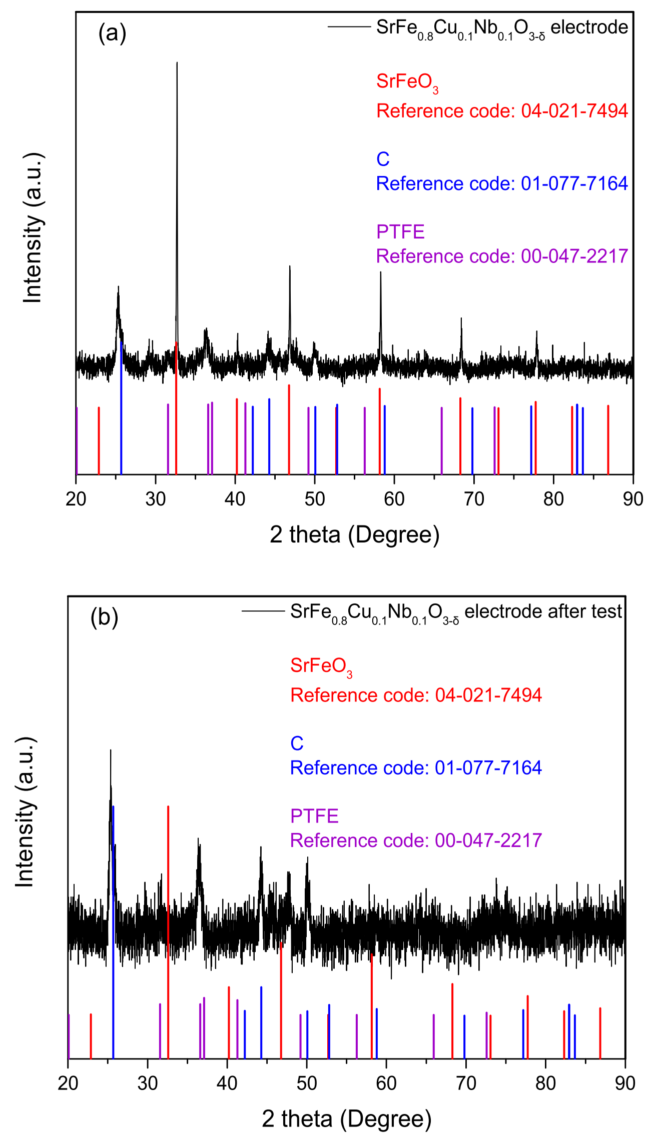

Fig. 6 – XRD data of the $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ cathode (a) before and (b) after the fuel cell measurements.

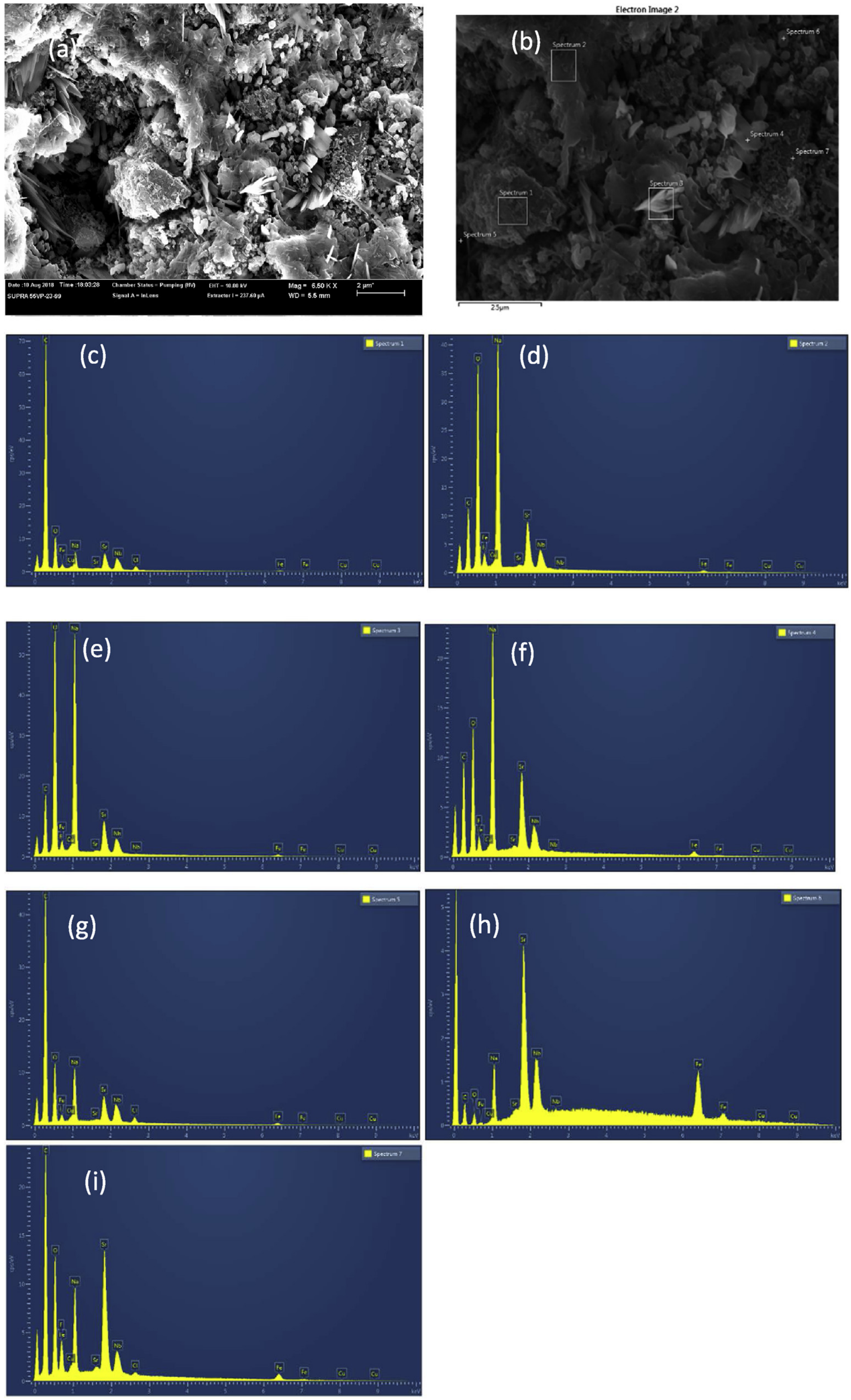

Fig. 7 — SEM pictures of $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ cathode after the fuel cell measurement. (a) 6500X; (b) 10000X; (c)–(i) EDS point analysis.

indicates $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ was poorly crystallised or it decomposed during the fuel cell measurements.

Fig. 7 shows the SEM & EDS analysis of the electrode after fuel cell test. Although the XRD result after test is confusing, the EDS results has proved the elements of catalyst including Sr, Fe, Cu, Nb & O. This means the perovskite oxide are still there, but they are in poorly crystallised state. It cannot be ruled out that it decomposed to other oxides but still stayed in the cathode current collector. However, during the fuel cell measurement, there is no sudden drop in the performance. The performance of the cell is consistent with the fuel concentration. This implied that the stability of the $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ is relatively good. The reason for decreased crystallinity of $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ is not clear yet. Some of the beautiful shuttle-shaped $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ still present at the cathode after the fuel cell measurements (Fig. 7b). Element Na was also picked up by EDS indicating the cross-diffusion of the fuel from anode to the cathode during the fuel cell measurements. Therefore better alkaline membrane with low ammonia crossover is desired for low temperature ammonia fuel cells.

Conclusions

Shuttle-shaped perovskite oxide $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ was synthesised without the use of template or surfactant. It was used as cathode for a room temperature ammonia fuel cell. This study indicates that the perovskite oxide $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ not only can be used as electrodes in solid oxide fuel cell, but also has the potential to be used as cathode for low temperature alkaline membrane fuel cells, which can avoid unnecessary by-reactions happened in high temperatures. Reasonable OCV and power density were observed for an ammonia fuel cell using $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$/C composite cathode. Although the power density is not high enough for conventional portable or transport applications, it has the potential for stationary application in removal of low concentration ammonia from wastewater. This is because the requirements on power density is relatively low, not alone the generated electricity is a bonus whilst wastewater is treated. When ammonia concentration is as low as 340 ppm (0.02 M), the fuel cell with Pt/C anode and $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$/C cathode can generate OCV of 0.35 V and power density of 0.03 mW/cm^2. In order to obtain reasonable OCV for fuel cell in wastewater containing low concentration of ammonia, it is necessary to add base such as NaOH to create a strong alkaline condition. This can be achieved through the addition of alkaline waste, such as coal fly ash which contains a significant amount of CaO. On the other hand, the power density of this device still can be improved. In addition, if the Pt/C anode is replaced with non-precious metal catalysts, which have good activity on electrochemical oxidation of ammonia, the ammonia fuel cell can be good economic way to simultaneously treat ammonia-containing wastewater and generate electricity from waste.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2019.08.097.

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