



Study on the 4-channel micro-monolithic design with geometry control for reversible solid oxide cell

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ABSTRACT

Reversible solid oxide cell (R-SOC) has been attracting considerable attention as a technology capable of power generation and CO₂ electrolysis. In addition to new material development, innovation in structural design is also a decisive factor. In this study, a 4-channel micro-monolithic design, in the form of a tear-drop inner channel structure, was successfully developed. The micro-monolith obtained includes plurality of micro-channels growing from multiple directions and spongy active regions near the exterior surface. Uniquely, the irregular tear-drop inner channels further increase the proportion of the electrochemically active region to the overall circumference, achieving more efficient utilization of the geometric surface area. Such micro-structured cells with Ni-YSZ/YSZ/YSZ-LSM materials exhibited effective performance in the reversible operation of R-SOC. A superior performance of 1.20 W·cm⁻² at 800 °C for H₂ fuel cell was demonstrated. Similarly, during the electrolysis of CO₂, current density recorded by the cells reached 1.20 A·cm⁻² at 1.5 V and 800 °C, which is competitive compared with the values of the previous design investigations. Relatively low diffusion polarization shown in electrochemical impedance spectroscopy (EIS) suggests that this is due to the very gas transfer resistance in the fuel electrode. This novel multi-channel micro-monolithic structure shows a potential to substitute the conventional tubular counterpart.

1. Introduction

Under the current trend of decarbonization requirements for various industries, the electrochemical reduction of CO₂ is regarded as a potential technology to reduce carbon emissions [1,2]. Compared with other approaches, electrochemical reduction is more attractive because the process can be controlled by adjusting the applied voltage and reaction temperature [3]. Solid oxide electrolytic cell (SOEC), combined with solid oxide fuel cell (SOFC), can smoothly achieve CO₂ utilization, energy storage, and power generation. Renewable energy needs adequate methods of storage due to its intermittent nature [4], which can be achieved by SOEC via converting renewable energy into stored fuel. While in SOFC mode, fuel can be directly converted into electricity for utilization [5]. This technology is considered unique in the energy field because of its flexible reversible operability [6,7].

Due to the endothermic nature of the CO₂ electrolysis reaction, the high temperature (>600 °C [3]) of SOEC is especially suitable for CO₂

electrolysis, during which the heat required can be provided through the waste heat of various processes [8]. In addition, high operating temperatures usually lead to a higher electrode reaction rate, resulting in a higher current density than electrolytic cells using liquid electrolytes at the same electrolytic voltage. Therefore, CO₂ electrolysis in SOEC will obtain more ideal current density, durability, and energy efficiency compared with other electrolysis technologies [3]. However, to make CO₂ electrolysis in SOEC more practical, a higher gas productivity with a lower energy consumption must be achieved [9,10]. These conditions require the minimization of internal cell loss, which is largely influenced by the selection of cell materials and the design of cell configuration.

The research on R-SOC involving CO₂ electrolysis has been widely studied in traditional planner and tubular structures, but the research on micro-tubular design is relatively scarce [11,12]. In addition, several structural strategies have also been proposed to improve the heat and mass transfer properties in the electrode. An external metal/ceramic porous support has been attempted for R-SOC, which allows thinner

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electrodes and electrolyte layers, thereby reducing ohmic loss and concentration loss of the cell. It is also beneficial to current collection if the support material is conductive [13,14]. Adequate porosity is essential to minimize gas transfer resistance, regardless of external support or electrode support, but it needs to maintain a balance with sufficient mechanical strength [13]. Therefore, the effects of the micro-structure control and tailoring of the electrode needs to be further clarified, including porosity, pore size and distribution. The introduction of asymmetric structure by phase inversion is an effective method to improve the diffusion efficiency of fuel gas in the electrode [15].

Therefore, a novel micro-monolith was developed by combining micro-tubular design and micro-structure manipulation via the phase inversion method in this study. This investigation focuses on a 4-channel micro-monolithic R-SOC with geometry control. The characteristics and electrochemical performances of the resultant electrochemical reactor were then examined to assess its ability of power generation and CO₂ electrolysis. Furthermore, comparisons with state-of-the-art literatures (single-channel, multiple-channel, and planar designs) were made to evaluate the relationship between R-SOC performance obtained and structural design and operational conditions.

2. Materials and methods

2.1. Materials

Commercial nickel oxide (NiO, NexTech Materials Ltd., USA) mixed together with yttria-stabilized zirconia (8 mol% YSZ, NexTech Materials Ltd., USA) in a weight ratio of 3:2 was used to form the basic precursor suspension. N-Methyl-2-pyrrolidone (NMP, VWR), polymethyl methacrylate (PMMA, Mitsubishi Rayon Co. Ltd) and Polyethylene glycol 30-dipolyhydroxystearate (Arlacel P135, Uniquema, UK) were used as solvent, polymer binder and dispersant, respectively. Deionized water was used as external coagulant, while the mixture of deionized water/ethanol (70/30 by weight) was used as internal coagulant. YSZ powder was evenly added in ethanol for electrolyte slurry, where polyethylene glycol (PEG) and polyvinyl butyral (PVB, Butvar) were also added in a certain proportion. The oxygen electrode was composed of two layers, the inner layer is La_{0.8}Sr_{0.2}MnO_{3-δ} (LSM) + YSZ (50–50 wt%), and the outer is pure LSM. Silver wire (0.2 mm diameter and 99.9 % purity) and silver conductive adhesive paste were applied as current collector.

2.2. Fabrication of the 4-channel fibers

The phase inversion-assisted extrusion process was adopted for the fabrication of 4-channel micro-monolith, as described elsewhere [15,16]. The spinning suspension was prepared from NiO, YSZ, Arlacel P135, PMMA and NMP, which were milled using a roll miller for over 72 h. The homogeneous suspension was then moved into a vacuum stirring device to complete the degassing process, in order to remove the bubbles trapped inside the suspension and minimize potential defects and breakages during the preparation of the precursor. A customized spinneret with four separated nozzles was employed to realize the 4-channel micro-monolith design. A mixture of ethanol and deionized water was used as internal coagulant. The external coagulant was deionized water to provide a site for the solidification of the precursor suspension. During the extrusion process, internal coagulant and the prepared suspension were extruded synchronously through the spinneret, with an air gap of 0.5 cm. The solidified precursors obtained were then straightened and dried prior to sintering and coating. To ensure that the defective fibers are not brought forward to further stages, a precautionary check was performed using a microscope.

2.3. Fabrication of a complete single cell

Before dip-coating electrolyte, the NiO-YSZ substrate was first pre-sintered in muffle furnace (600 °C for 2 h and 1200 °C for 5 h) to

obtain essential mechanical strength. The electrolyte was dip-coated on pre-sintered NiO-YSZ substrate, and then sintered at 1350 °C for 5 h to obtain a dense electrolyte layer. The oxygen electrode was covered on the electrolyte surface by brushing, with a length of 1 cm. The active area of the single cell was calculated using the cathode diameter, which is 2.3 mm. After drying, the oxygen electrode was sintered at 1000 °C for 2 h. Silver wire was used for current collection on both electrodes, while silver paste was attached to increase conductivity and fix silver wire.

2.4. Characterizations

The morphology was obtained from a high-resolution scanning electron microscope (SEM, Gemini LEO 1525).

The gas-liquid displacement porometer (PoroluxTM 1000) was used to measure the microscopic pore size distributions and gas permeation performance of different fuel electrode designs. The wetting liquid in the sample pores is discharged by the pressurized N₂, and then pore size distribution and mean pore size are calculated by the relationship between pressure and gas flow. The pressure at the junction of the semi-dry curve (slope is 50% of the dry curve) and the wet curve is used to calculate the mean flow pore size. The pore size is calculated by Eq. (1), where D is the pore size (m), γ is the surface tension of the wetting liquid (N/m), θ is the liquid-solid interface contact angle (°), and P is the pressure (Pa). Before the tests, the samples were treated with H₂ at 650 °C to complete the reduction process.

$$D = \frac{4\gamma\cos\theta}{P} \quad (1)$$

2.5. Performance tests

Before the tests, the reduction process of the complete reactor was first completed, and the cell was heated to 650 °C in a pure H₂ environment for two hours. The furnace temperature was set to the test temperature (700 °C, 750 °C and 800 °C) after NiO inner electrode has been completely reduced to Ni, while the test gases with compositions of CO₂-H₂ (80–20 vol%) and pure H₂ were introduced. The gas flow was fixed at 40 ml/min using automated mass flow controllers, and the oxygen electrode was exposed to the air. The four-terminal method was used to complete the current-voltage measurements and EIS tests, introducing silver wires on both electrodes into a potentiostat/galvanostat (Iviumstat, Netherlands).

3. Results and discussion

3.1. Morphology

The morphology of the micro-monolith was obtained from SEM images, and all of the 4-channel NiO-YSZ substrates after sintering processes exhibited identical morphology. The outer diameter of the substrate is approximately 2.3 mm, so can be considered as a micro-tube, which is important for improving both surface area and power density per unit volume. As can be seen in Fig. 1(a), four identical channels are clearly visible in the tubular substrate, and the most important part is the channels' shape, as the tear-drop design. The optimized structure can be obtained by regulating the parameters of the spinning process on the basis of the traditional circular channel [17]. From Fig. 1, it is distinct that an asymmetric micro-structure can be observed with micro-channels and spongy regions. The formation of this structure can be explained by the Rayleigh-Taylor interfacial instability. Fluid interpenetration occurs at the interface due to the different densities of the spinning suspension and the coagulant [18]. Since the suspension contacts the internal and external coagulants at the same time before solidification, micro-channels were obtained in all parts of the whole cross section, and it is proved that such micro-channels can greatly reduce the resistance of gas transfer [15–17], thereby minimize the concentration

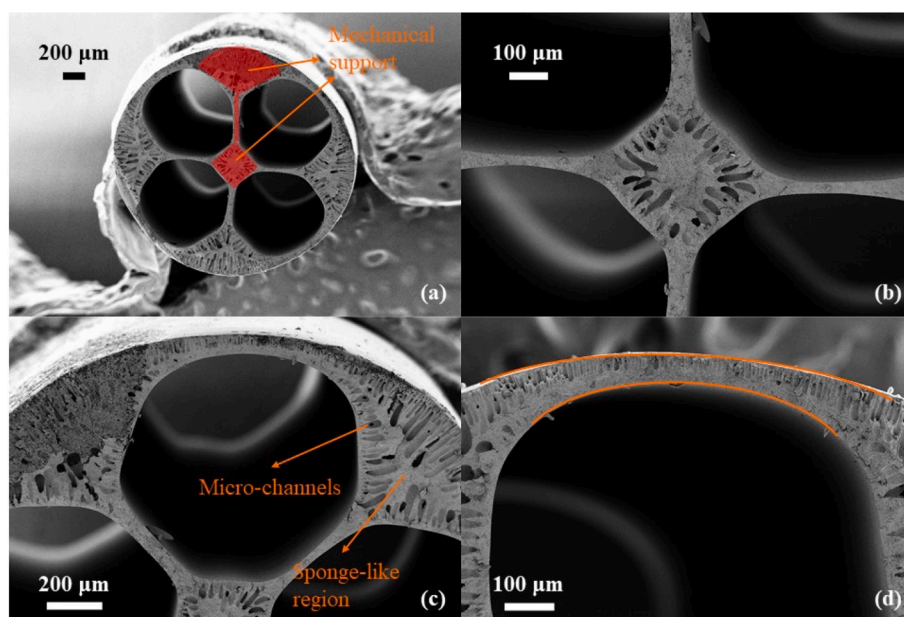


Fig. 1. SEM images of cross-sectional NiO-YSZ fuel electrode with 4-channels: (a) whole view, (b) close up on support between four channels, (c) close up on a single channel, (d) electrochemically active region with relatively uniform thickness.

polarization of the cell. As shown in Fig. 1(c) and Fig. 1(d), the interior surface of the fiber has more sponge regions than the exterior surface, because the internal coagulant is a mixture of ethanol and deionized water, resulting in a decreased solvent/non-solvent exchange rate [10]. Such insufficient exchange is not enough to support the formation of a large number of micro-channels. In addition, the mixture leads to a lower precipitation rate, so the suspension flows longer before solidification, which is conducive to the growth of porous sponge-like region. In contrast, the suspension was exposed to deionized water at the exterior surface, causing a higher precipitation rate and relatively dense skin layer, which is conducive to the dip-coating of electrolyte. The existence of air gap contributes to the smoothness of the exterior surface [19].

In a traditional single-channel hollow fiber membrane, the membrane permeation resistance can be decreased by reducing the thickness

of the separation layer to achieve high permeation [20]. However, excessive reduction of thickness will inevitably lead to weak mechanical strength, and additional structures need to be introduced for reinforcement. In contrast, the tear-drop design can provide this required additional support by the middle parts and other sponge regions as shown in Fig. 1(a) and Fig. 1(b). In our previous study which is the feasibility study of the multi-channel design [15], the three-point bending method was used to test the bending resistance of anode supports with different channel numbers. At different sintering temperatures, the 4-channel micro-monolith outperformed the single-channel design by about three times in terms of bending resistance. Furthermore, Fig. 1(d) shows that the thinnest diffusion thickness is around 50–60 μm , which is relatively thinner compared with other 4-channel design from previous study [18]. The curvature of the outer side of each channel is close to

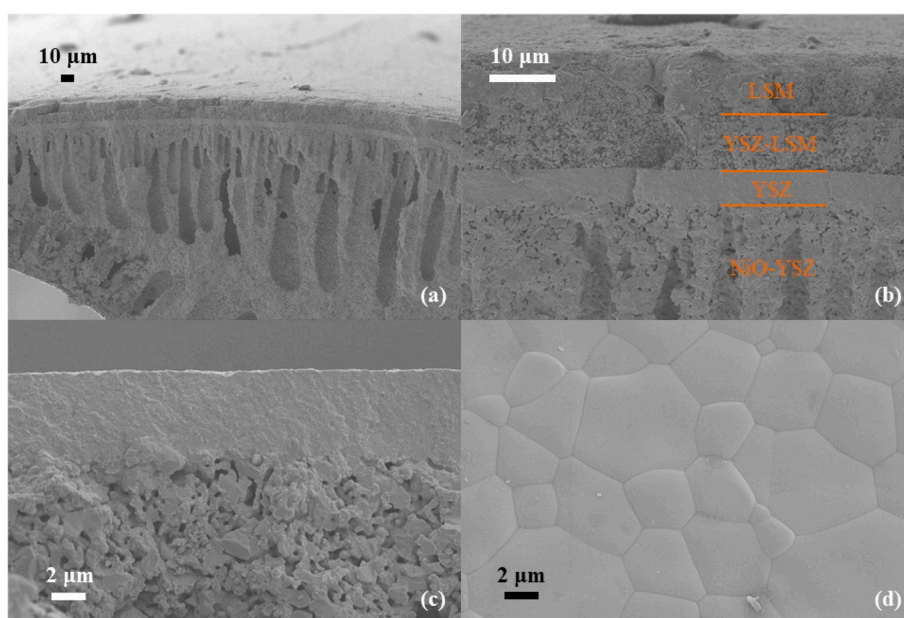


Fig. 2. SEM images of (a) partial cross section of a complete single cell, (b) cross section of three-layer structure, (c) cross section of NiO-YSZ substrate with YSZ electrolyte, (d) outer surface of YSZ electrolyte.

that of the whole NiO-YSZ substrate, as highlighted in Fig. 1(d), which will result in a very high proportion of the electrochemically active region to the overall circumference. These suggest that the design shown in this study exhibited minimum gas transfer resistances.

The SEM images of the cross section of a complete single cell and the electrolyte surface are shown in Fig. 2. Fig. 2(a) and Fig. 2(b) show the three-layer structure. According to the literature, the reaction on the fuel side usually occurs at the interface that extends for 20–40 μm from electrolyte into the electrode [21]. Therefore, the fuel gas needs to diffuse through the inert region before reaching the reactive region. The inert region of the fuel electrode shown in the 4-channel design contains many micro-channels with low gas diffusion resistance, which is helpful to reduce the concentration polarization [10,15]. Fig. 2(c) shows a close-up view of the electrolyte layer. The thickness of the electrolyte is approximately 5 μm , which can reduce the ohmic impedance significantly markedly, thereby improving the overall performance of the cell. From Fig. 2(d), the electrolyte has been fully densified, effectively preventing gas leakage and short circuit. Furthermore, it can be seen from Fig. 2(b) that the porous oxygen electrode has a thickness of about 20 μm , which can provide sufficient reaction sites for oxygen reaction.

The channel of the micro-monolith in this study has a novel tear-drop shape, and its formation mechanism is shown in Fig. 3. In the traditional preparation of hollow fiber, the hydraulic pressure regulation of internal coagulant is crucial, which is related to whether the channel is regular circular shape (Fig. 3(a)). The influence of hydraulic pressure regulation on internal contour can be found elsewhere [22]. As for 4-channel design, under the action of hydraulic pressure, the streams of internal coagulant in each nozzle expand from all directions to the suspension. Its exterior is subject to offset pressure of solidification caused by external coagulant, while its interior is subject to offset pressure caused by adjacent internal coagulant flow. The different offset pressures in each direction cause non-uniform expansion of the channel, which makes it change from a regular circular shape to a tear-drop shape (Fig. 3(b)). In this process, the low solvent power of ethanol/deionized water mixture and long precipitation time are also important factors for the formation of tear-drop like channels. Therefore, the geometry of the support electrode can be controlled to a certain extent by adjusting the hydraulic pressure and solidification speed [17].

3.2. Pore size distribution and gas permeance

The obtained pore size distribution and gas permeance show that in a successful gas penetration test, the mean flow pore size of the 4-channel sample is 365 nm according to the above principle. Further, the mean flow pore size is considered to be the first intersection of the wet and semi-dry curves during permeation. As shown in Fig. 4(a), the mean flow pressure of the 4-channel substrate is about 1.75 bar, which indicates that most of the through pores in the structures are completely filled with gas at this pressure. The N_2 flux of the wet curve suddenly increases after this pressure, and then coincides with the dry curve, showing a proportional trend, which is consistent with the theoretical expectation. Therefore, the characterization results highlight the conformance of the pore size of the prepared 4-channel samples. In contrast, it was observed that the pore sizes of the fibers tested is generally similar or higher than the values reported in the previous studies [4,23].

A conventional single-channel hollow fiber was prepared by a similar method, and a permeance test was carried out to compare it with our design. It should be noted that the 4-channel sample is 1.4 times larger than the single-channel counterpart in terms of diameter, while the lengths are both 2 cm. The comparison was based on the resulting surface area, which is persuasive. The mean flow pore size of the single channel sample is differed slightly from the 4-channel design, with 387 nm. However, the difference is that the 4-channel fiber will show greater permeance when the data is normalized to the membrane area, which illustrates improved gas transfer properties. Similarly, it can also be verified from the magnitude of wet curve that the permeance flux of the 4-channel design is in the order of 10^{-5} ml/min (Fig. 4(a)), while the value of the single channel design is of order of 10^{-6} ml/min (Fig. 4(b)).

3.3. Fuel cell performance

The fuel cell performance of the reduced cell was characterized with pure H_2 fed to the fuel electrode and atmospheric oxygen fed to the oxygen electrode. The cell potential difference (U)-current density (j)-power density (P) data for operating temperatures from 700 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$ are shown in Fig. 5(a). The OCVs of all temperatures are higher than 1.1 V, comparing well with the theoretical value predicted using Nernst equation, indicating that the electrolyte with a thickness of 5 μm has

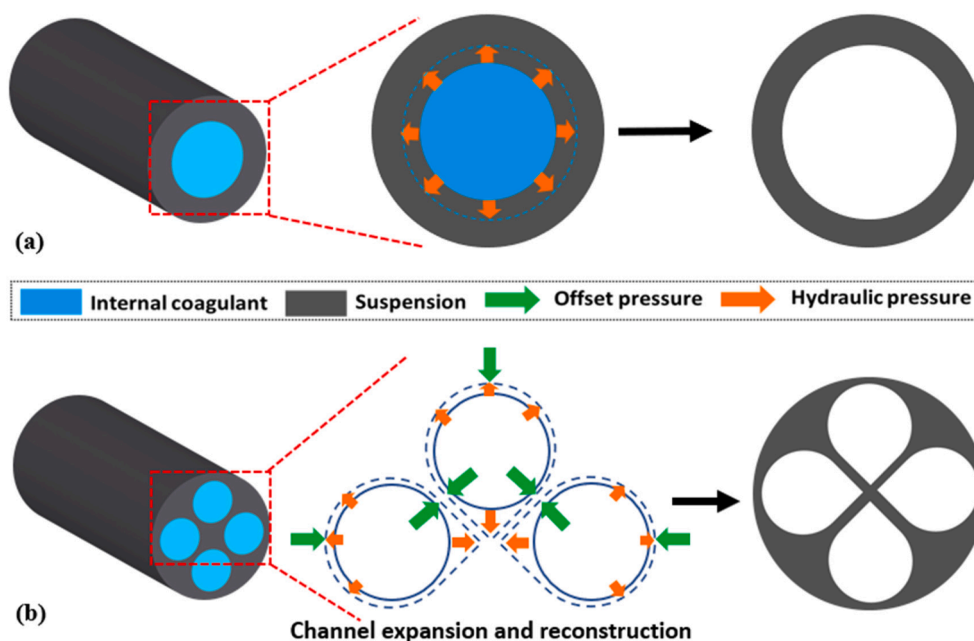


Fig. 3. Schematic diagram of: (a) formation of single-channel hollow fibers, (b) formation of 4-channel hollow fibers with geometry control.

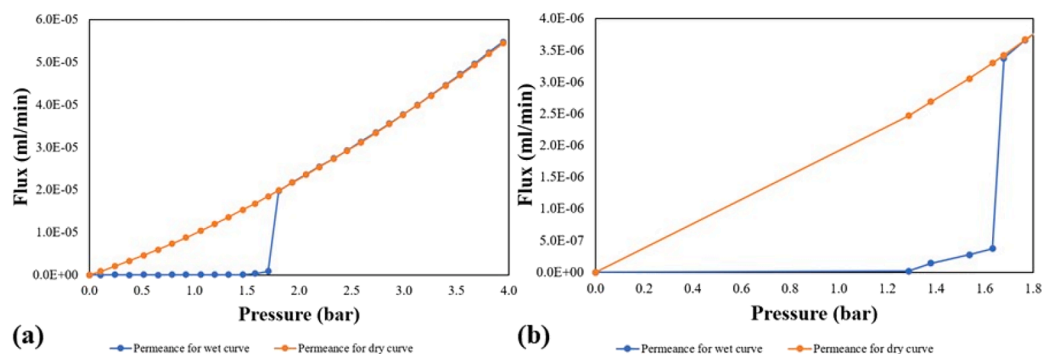


Fig. 4. Wet and dry curve measured in the N_2 permeance test for: (a) 4-channel design, (b) single-channel design.

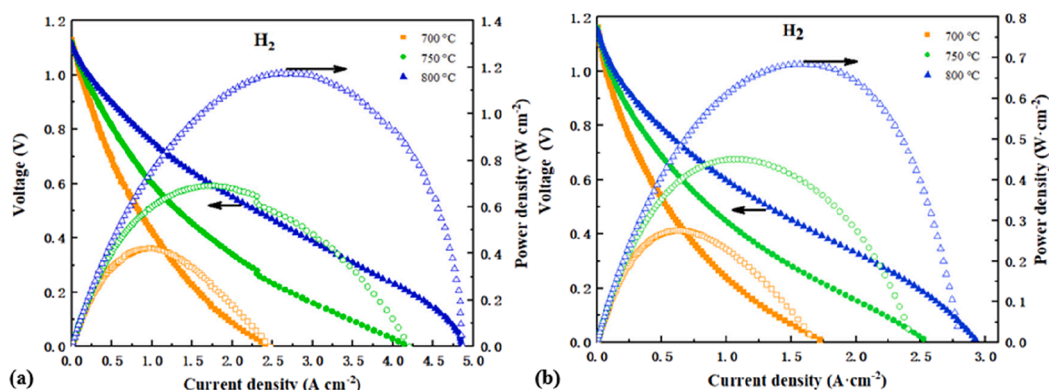


Fig. 5. j-U and j-P curves with pure H_2 as fuel and air as oxidant at different operating temperatures: (a) 4-channel, (b) single channel.

adequate gas-tightness.

The peak power densities of H_2 -SOFC at 700 °C, 750 °C, 800 °C are 0.42, 0.71 and 1.20 $W\cdot cm^{-2}$, respectively. The performance compares well with other tubular and micro-tubular electrochemical reactors. Table 1 shows the peak power densities of H_2 -fuel cell using the same material system, and it can be seen that our cells are also competitive in comparison with similar planar designs. The superior performance is owing to improved structure of the 4-channel micro-monolithic fuel electrode. The fuel electrode shows a unique asymmetric structure, in which the separation of the inert support and the triple phase boundary (TPB) active region drastically shorten the diffusional pathway of the fuel gas to less than 50 μm . Due to the reduction of the additional

resistance from the support, the transport of the fuel has been significantly facilitated. Notably, compared with traditional tubular and planar designs, our 4-channel micro-monolithic design is expected to show better performance according to volumetric power density. This is because the miniaturization and introduction of monolithic structure limit the cell dimension to the ‘micro-tubular’ range, and the superiority of higher active surface area per volume [15]. For comparison, the fuel cell performance with pure H_2 of the single-channel design was tested, as shown in Fig. 5(b). It can be seen that the peak power density of the 4-channel monolith is 50.0 %, 55.5 %, and 71.4 % higher than that of the single-channel design at 700 °C, 750 °C, and 800 °C, respectively. Therefore, the advantages of the 4-channel monolith in gas transfer can be reflected.

The resistance of charge and mass transfer during cell operation can be further analyzed by interpreting the EIS results shown in Fig. 6. EIS tests were carried out under OCV, the frequency range is 10^5 to 0.1 Hz, and the amplitude is 10 mV. The spectrum is composed of a series of semi-circular arcs, from which three main polarization losses of the cell can be obtained: ohmic loss, activation polarization and concentration polarization [10].

Under pure H_2 condition, the nonlinearity of the j-U curves indicates that the main resistance is caused by the activation polarization. The first arc in the region above 100 Hz represents the activation polarization and it drops off sharply with increasing temperature. This is because high temperature can promote charge transfer and molecular diffusion, thereby improving the reaction interface dynamics. Besides, high temperature can also increase the ionic conductivity of the electrolyte. The second arc, corresponding to the low-frequency of 1–100 Hz, is caused by concentration polarization, which remains at 0.40 $\Omega\cdot cm^2$ essentially independent of temperature. The concentration polarization is caused by the rapid consumption of reactants at the electrode interface and cannot be replenished in time. It usually occurs at high current densities and is related to the gas diffusion efficiency. This diffusion restrictions

Table 1

The power density of H_2 -fuel cell with similar cell materials.

Configuration	Materials	Temperature (°C)	P_{max} ($W\cdot cm^{-2}$)	Ref.
Micro-tubular	Ni-YSZ/YSZ (5 μm) /YSZ-LSM	800	1.20	This work
Tubular	Ni-YSZ/YSZ (~16 μm) /YSZ-LSM	750	0.46	[24]
Tubular	Ni-YSZ/YSZ (15 μm) /YSZ-LSM	850	0.52	[25]
Micro-tubular	Ni-YSZ/YSZ (15 μm) /YSZ-LSM	850	0.60	[26]
Micro-tubular	Ni-YSZ/YSZ (5 μm) /YSZ-LSM	800	0.97	[27]
Micro-tubular	Ni-YSZ/YSZ (15 μm) /YSZ-LSM-SDC	900	1.25	[28]
Micro-tubular	Ni-YSZ/YSZ (5 μm) /YSZ-LSM	800	1.62	[10]
Planar	Ni-YSZ/YSZ (23 μm) /YSZ-LSM	788	0.69	[29]
Planar	Ni-YSZ/YSZ (10 μm) /YSZ-LSM	800	1.20	[30]

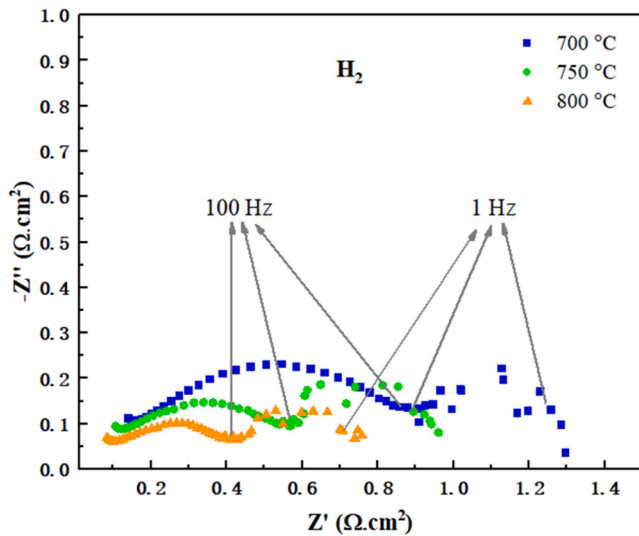


Fig. 6. Electrochemical impedance spectra (EIS) of 4-channel micro-monolithic cell under open circuit voltage (OCV) using pure H_2 as a fuel.

can be effectively reduced through optimizing the electrode micro-structure of the 4-channel micro-monolithic design adopted in this study. Compared with previous studies on single-channel [31] and 4-channel [15] cells using similar material systems, the concentration polarization of the cells demonstrated in this study is reduced by 50% and 87.5%, respectively, which presents that the gas transfer in the fuel electrode is greatly enhanced. Importantly, as described in the morphology part, the distinctive advantage of the 4-channels used in this study is tear-drop shaped channel, which can greatly increase the proportion of thin diffusion areas. The first x-axis intersection represents ohmic impedance. The ohmic impedance at different temperatures is small, indicating that the electrolyte is thin enough to provide a shorter pathway for ion transfer.

In contrast, the fuel cell performance with CO_2/H_2 (80–20 vol%) mixture was tested, the results are shown in Fig. 7, and the corresponding EIS spectrograms are shown in Fig. 8. Linear trends can be observed in all three temperatures from the j-U polarization curve, which indicates that ohmic losses of the cell is dominant. This can also be clearly obtained from EIS. Compared with the pure H_2 feed, the ohmic impedance of the mixed feed is obviously larger. From the j-U curve at 800 °C, mass transfer losses at high current densities can also be observed in addition to the ohmic losses. On the whole, the total

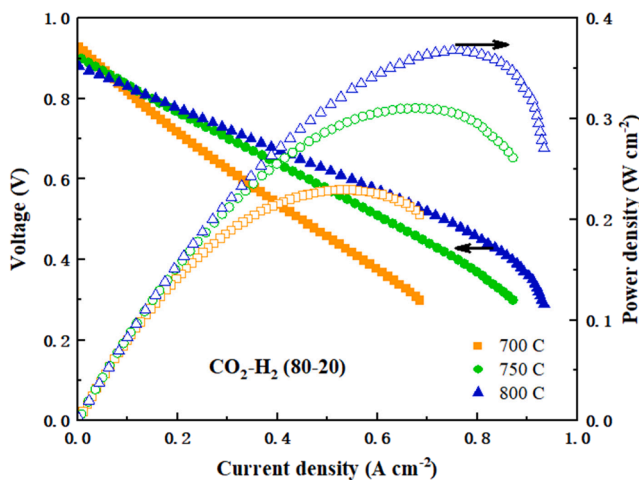


Fig. 7. j-U and j-P curves with CO_2-H_2 (80–20 vol%) as fuel and air as oxidant at different operating temperatures.

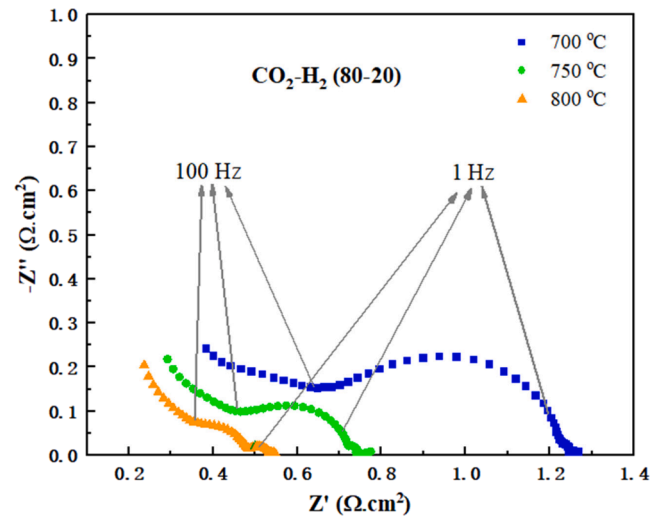


Fig. 8. Electrochemical impedance spectra (EIS) of 4-channel micro-monolithic cell under open circuit voltage (OCV) using CO_2-H_2 (80–20 vol%) as a fuel.

impedance (also known as the area specific resistance (ASR)) of mixed feed is similar to that of H_2 feed because the measurements were conducted under OCV, which mainly reflects the properties of the cell itself [10].

From the j-P, the peak power densities at 700 °C, 750 °C, 800 °C were 0.23, 0.31 and 0.37 $W \cdot cm^{-2}$, respectively. This performance is much lower than that of pure H_2 fuel, especially at high temperatures, mainly because of the insufficient fuel supply. As shown in Table 2, the performance shown here is also competitive compared with other cells using similar materials and fuel supply.

3.4. Reversible-operation analysis

The solid oxide electrochemical reactor can operate in two reversible modes of energy storage and power generation, so the operational reversibility of the 4-channel micro-monolithic cell developed here was studied. As shown in Fig. 9, the tests were performed under the conditions: CO_2-H_2 (80–20 vol%) was introduced to the fuel electrode, the oxygen electrode was exposed to air, the voltage range was 1.5 V–0.3 V, and the temperature range was 700 °C–800 °C. Among them, 1.5 V is the thermal neutral voltage of CO_2 electrolysis at 750 °C. If the applied voltage is higher than this value, part of the current will be converted into heat energy and wasted. In addition, the YSZ electrolyte will be irreversibly damaged when the voltage reaches a certain level (usually higher than 2.3 V [32]). The OCVs were found to range between 0.88 and 0.93 V, which different slightly from the theoretical level (Nernst Equation). Importantly, the consistency of OCVs during reversed

Table 2

The power density of mixed feed fuel cell with similar cell materials.

Configuration	Materials	Feed composition	Temperature (°C)	P_{max} ($W \cdot cm^{-2}$)	Ref.
Micro-tubular	Ni-YSZ/YSZ (5 μm)/YSZ-LSM	CO_2-H_2 (80 %–20 %)	700	0.23	This work
			800	0.37	
Micro-tubular	Ni-YSZ/YSZ (5 μm)/YSZ-LSM	CO_2-CO (90 %–10 %)	700	0.18	[10]
			800	0.33	
Micro-tubular	Ni-YSZ/YSZ (50 μm)/YSZ-LSM	CO_2-CO (90 %–10 %)	700	0.08	[4]
			800	0.12	

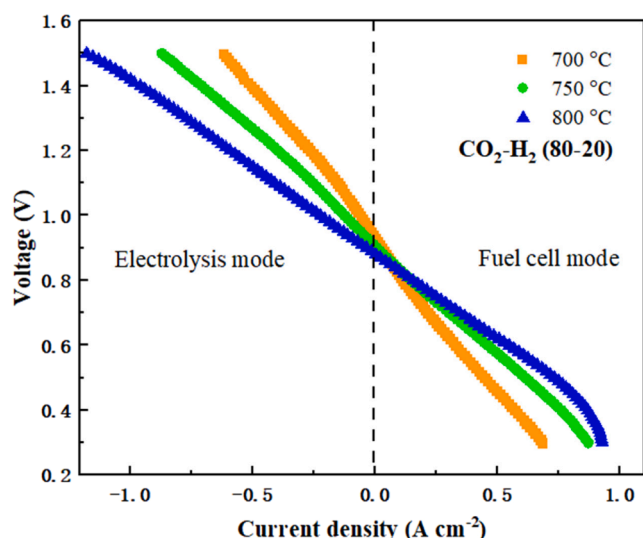


Fig. 9. *j*-*U* curves for R-SOC dual-mode operation with a feed mixture of CO₂-H₂ (80–20 vol%) at various operating temperatures.

operation indicates the continuity of fuel cell and electrolysis modes at these conditions, further highlighting the feasibility of reversible operation.

For a same R-SOC reactor, if it has better power generation capacity, it also corresponds to better electrolysis performance because of the relative linearity of the *j*-*U* curve near OCV. The performance of SOEC is often evaluated from the current density procured at OCV to 1.8 V. Per Fig. 9, the range of current densities at 1.5 V is 0.64 to 1.20 A·cm⁻² (700–800 °C). As expected in theory, the electrolyzer performance will be improved as the temperature increases, which can be attributed to the reduced activation polarization and greater kinetic energy.

The comparisons with conventional single-channel and planar design SOEC were conducted to evaluate the effect of multi-channel and tear-drop design. As shown in Table 3, the current densities of this study are within or above the results recorded in past surveys. For example, the values exceed 0.60 to 1.00 A·cm⁻² of a similar study in relation to a single-channel design [4], whilst planar SOECs also have reported the density range of 0.50 to 1.05 A·cm⁻² at 1.3 V [8]. The performance improvement could be due to the micro-structure regulation of the cell which minimized the overall polarization, especially the concentration polarization. The existence of micro-channels reduces the mass transfer resistance within the electrode, while a sufficiently thin electrolyte layer (5 μm) provides a low ohmic impedance. In addition, studies have shown that lower ohmic and polarization resistance can be obtained from higher H₂ content [33], so the overall performance is also affected by the gas feeds. It has been found that a gas feed with 80 % CO₂ and 20

% H₂ yields improved performance compared to the tests implemented at CO and CO₂ feeds [4,8,33], which may also be a factor for the competitive results obtained in this study.

4. Conclusions

In summary, a 4-channel micro-monolithic R-SOC with geometry control was fabricated through phase inversion and sintering processes. The tear-drop shaped channels are the essential structural improvement developed by this study. By evaluating the morphology and N₂ permeance test results, it can be concluded that the tear-drop 4-channel monolith has shorter gas transfer pathway and higher proportion of the electrochemically active region compared with other micro-tubular cells, which results in better gas transfer effects. This is reflected by the outstanding electrochemical performance of the novel cell design used in this study. For H₂-SOFC mode, the peak power density reached 1.20 W·cm⁻² at 800 °C. Comparing the data obtained with the values achieved from other single and multiple-channel cells of past investigations, the conclusion is that the unique micro monolithic design reduces the gas transfer resistance at the fuel electrode. Cell for CO₂ electrolysis also showed a competitive performance compared with conventional designs (including single-channel and standard planar configurations), achieving a current density ranging from -0.64 to -1.20 A·cm⁻² at 1.5 V. On the whole, the study also shows the high feasibility of reversible operation. In addition, it can be inferred that the 4-channel micro-monolithic design exhibits higher mechanical robustness, because the middle region and the spongy regions between the channels provide additional structural reinforcement. Such findings indicate the potential of using the 4-channel tear-drop structure to replace the conventional tubular counterpart.

CRediT authorship contribution statement

Bin Wang: Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Tao Li:** Methodology, Supervision, Writing – review & editing, Project administration, Funding acquisition. **Rui Xiao:** Resources, Supervision, Project administration. **U.W. Hartley:** Resources, Supervision, Project administration, Funding acquisition. **Maiki Ueda:** Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Seok Ju Han:** Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **K Li:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Table 3
Studies on CO₂ electrolysis using similar cell materials.

Configuration	Materials	Feed composition	Voltage (V)	Temperature (°C)	Current density (A·cm ⁻²)	Total resistance/ Ω·cm ²	Ref.
Micro-tubular	Ni-YSZ/YSZ (5 μm)/YSZ-LSM	CO ₂ -H ₂ (80 %-20 %)	1.5	700	0.64	1.26	This work
				800	1.20	0.54	
Micro-tubular	Ni-YSZ/YSZ (15 μm)/YSZ-LSM	CO ₂ -CO (90 %-10 %)	1.8	700	0.60	2.16	[4]
				800	1.00	1.80	
Micro-tubular	Ni-YSZ/YSZ (5 μm)/YSZ-LSM	CO ₂ -CO (90 %-10 %)	1.5	700	1.03	0.44	[10]
				800	3.10	0.21	
Planar	Ni-YSZ/YSZ (15 μm)/LSCF-GDC	CO ₂ -H ₂ (75 %-25 %)	1.3	700	0.50	0.60	[8]
				800	1.05	0.27	
Planar	LSCFN-GDC/YSZ/GDC-LSCFN	CO ₂ -H ₂ (90 %-10 %)	~1.4	800	~0.40	~1.80	[33]
Planar	Ni-YSZ/YSZ (15 μm)/YSZ-LSM	CO ₂ -H ₂ (50 %-50 %)	~1.25	850	~1.00	0.22	[6]
Planar	Ni-YSZ/YSZ (23 μm)/YSZ-LSM	CO ₂ -CO (90 %-10 %)	1.5	809	0.78	0.90	[34]
Planar	Ni-YSZ/YSZ/YSZ-LSM	CO ₂ -CO (50 %-50 %)	1.26	850	0.87	~0.25	[35]
Planar	Ni-YSZ/YSZ (10 μm)/YSZ-LSM	CO ₂ -CO (70 %-30 %)	1.29	950	1.50	/	[36]

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

- [1] Y. Zheng, J. Wang, B. Yu, W. Zhang, J. Chen, J. Qiao, J. Zhang, A review of high temperature co-electrolysis of H_2O and CO_2 to produce sustainable fuels using solid oxide electrolysis cells (SOECs): advanced materials and technology, *Chem. Soc. Rev.* 46 (2017) 1427–1463.
- [2] X. Zhang, T. Arbour, D. Zhang, S. Wei, K. Rabaey, Microbial electrosynthesis of acetate from CO_2 under hypersaline conditions, *Environ. Sci. Ecotechnol.* 13 (2023) 100211.
- [3] Y. Song, X. Zhang, K. Xie, G. Wang, X. Bao, High-Temperature CO_2 Electrolysis in Solid Oxide Electrolysis Cells: Developments, Challenges, and Prospects, *Adv. Mater.* 31 (2019) e1902033.
- [4] L. Kleiminger, T. Li, K. Li, G.H. Kelsall, CO_2 splitting into CO and O_2 in micro-tubular solid oxide electrolyzers, *RSC Adv.* 4 (2014) 50003–50016.
- [5] J. Liu, C. Su, C. Wang, L. Zhu, J. He, Influence of solid oxide fuel cell on power system transient stability, *J. Eng.* 2018 (2019) 1081–1086.
- [6] S.D. Ebbesen, M. Mogensen, Electrolysis of carbon dioxide in Solid Oxide Electrolysis Cells, *J. Power Sources* 193 (2009) 349–358.
- [7] W. Li, H. Wang, Y. Shi, N. Cai, Performance and methane production characteristics of H_2O - CO_2 co-electrolysis in solid oxide electrolysis cells, *Int. J. Hydrogen Energy* 38 (2013) 11104–11109.
- [8] Z. Zhan, L. Zhao, Electrochemical reduction of CO_2 in solid oxide electrolysis cells, *J. Power Sources* 195 (2010) 7250–7254.
- [9] L. Zhang, S. Hu, X. Zhu, W. Yang, Electrochemical reduction of CO_2 in solid oxide electrolysis cells, *J. Energy Chem.* 26 (2017) 593–601.
- [10] M.F. Rabuni, N. Vatcharasuwan, T. Li, K. Li, High performance micro-monolithic reversible solid oxide electrochemical reactor, *J. Power Sources* 458 (2020) 228026.
- [11] K. Kendall, Progress in Microtubular Solid Oxide Fuel Cells, *Int. J. Appl. Ceram. Technol.* 7 (2010) 1–9.
- [12] M. Singh, D. Zappa, E. Comini, Solid oxide fuel cell: Decade of progress, future perspectives and challenges, *Int. J. Hydrogen Energy* 46 (2021) 27643–27674.
- [13] X. Zhang, Y. Jin, D. Li, Y. Xiong, A review on recent advances in micro-tubular solid oxide fuel cells, *J. Power Sources* 506 (2021) 230135.
- [14] O. Hodjati-Pugh, A. Dhir, R. Steinberger-Wilckens, The Development of Current Collection in Micro-Tubular Solid Oxide Fuel Cells-A Review, *Appl. Sci.* 11 (2021) 1077.
- [15] T. Li, T.M.M. Heenan, M.F. Rabuni, B. Wang, N.M. Farandos, G.H. Kelsall, D. Matras, C. Tan, X. Lu, S.D.M. Jacques, D.J.L. Brett, P.R. Shearing, M. Di Michiel, A.M. Beale, A. Vamvakeros, K. Li, Design of next-generation ceramic fuel cells and real-time characterization with synchrotron X-ray diffraction computed tomography, *Nat. Commun.* 10 (2019) 1497.
- [16] T. Li, X. Lu, M.F. Rabuni, B. Wang, N.M. Farandos, G.H. Kelsall, D.J.L. Brett, P. R. Shearing, M. Ouyang, N.P. Brandon, K. Li, High-performance fuel cell designed for coking-resistance and efficient conversion of waste methane to electrical energy, *Energy Environ. Sci.* 13 (2020) 1879–1887.
- [17] T. Li, T. Kamhangdatepon, B. Wang, U.W. Hartley, K. Li, New bio-inspired design for high-performance and highly robust $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ membranes for oxygen permeation, *Journal of Membrane Science* 578 (2019) 203–208.
- [18] Y. Chi, T. Li, B. Wang, Z. Wu, K. Li, Morphology, performance and stability of multi-bore capillary $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ oxygen transport membranes, *J. Membr. Sci.* 529 (2017) 224–233.
- [19] B.F.K. Kingsbury, K. Li, A morphological study of ceramic hollow fibre membranes, *Journal of Membrane Science* 328 (2009) 134–140.
- [20] Z. Wu, R. Faiz, T. Li, B.F.K. Kingsbury, K. Li, A controlled sintering process for more permeable ceramic hollow fibre membranes, *J. Membr. Sci.* 446 (2013) 286–293.
- [21] M. Brown, S. Primdahl, M. Mogensen, Structure/Performance Relations for Ni/Yttria-Stabilized Zirconia Anodes for Solid Oxide Fuel Cells, *J. Electrochem. Soc.* 147 (2000) 475–485.
- [22] Y. Santoso, T. Chung, K. Wang, M. Weber, The investigation of irregular inner skin morphology of hollow fiber membranes at high-speed spinning and the solutions to overcome it, *Journal of Membrane Science* 282 (2006) 383–392.
- [23] T. Wang, Y. Tian, T. Li, L. Yu, Z. Ye, T. Wei, Z. Wang, J. Yao, C.E. Buckley, D. Dong, Essential microstructure of cathode functional layers of solid oxide electrolysis cells for CO_2 electrolysis, *J. CO₂ Utiliz.* 32 (2019) 214–218.
- [24] S.-Y. Park, J.H. Ahn, C.-W. Jeong, C.W. Na, R.-H. Song, J.-H. Lee, Ni-YSZ-supported tubular solid oxide fuel cells with GDC interlayer between YSZ electrolyte and LSCF cathode, *International Journal of Hydrogen Energy* 39 (2014) 12894–12903.
- [25] N.Q. Duan, D. Yan, B. Chi, J. Pu, L. Jian, High performance anode-supported tubular solid oxide fuel cells fabricated by a novel slurry-casting method, *Sci. Rep.* 5 (2015) 8174.
- [26] R. Campana, R.I. Merino, A. Larrea, I. Villarreal, V.M. Orera, Fabrication, electrochemical characterization and thermal cycling of anode supported microtubular solid oxide fuel cells, *J. Power Sources* 192 (2009) 120–125.
- [27] X. Lu, T. Li, A. Bertei, J.L.S. Cho, T.M.M. Heenan, M.F. Rabuni, K. Li, D.J.L. Brett, P. R. Shearing, The application of hierarchical structures in energy devices: new insights into the design of solid oxide fuel cells with enhanced mass transport, *Energy Environ. Sci.* 11 (2018) 2390–2403.
- [28] C. Yang, C. Jin, F. Chen, Performances of micro-tubular solid oxide cell with novel asymmetric porous hydrogen electrode, *Electrochimica Acta* 56 (2010) 80–84.
- [29] N.M. Farandos, T. Li, G.H. Kelsall, 3-D inkjet-printed solid oxide electrochemical reactors. II. LSM - YSZ electrodes, *Electrochimica Acta*, 270 (2018) 264–273.
- [30] J.S. Cronin, Y.-c.K. Chen-Wiegart, J. Wang, S.A. Barnett, Three-dimensional reconstruction and analysis of an entire solid oxide fuel cell by full-field transmission X-ray microscopy, *J. Power Sources* 233 (2013) 174–179.
- [31] X. Zhang, B. Lin, Y. Ling, Y. Dong, G. Meng, X. Liu, An anode-supported micro-tubular solid oxide fuel cell with redox stable composite cathode, *Int. J. Hydrogen Energy* 35 (2010) 8654–8662.
- [32] W. Weppner, Formation of intermetallic Pt-Zr compounds between Pt electrodes and ZrO_2 -based electrolytes, and the decomposition voltage of yttria-doped ZrO_2 , *J. Electroanal. Chem. Interfacial Electrochem.* 84 (1977) 339–350.
- [33] Z. Yang, C. Ma, N. Wang, X. Jin, C. Jin, S. Peng, Electrochemical reduction of CO_2 in a symmetrical solid oxide electrolysis cell with $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.7}\text{Nb}_{0.1}\text{O}_{3-\delta}$ electrode, *J. CO₂ Utiliz.* 33 (2019) 445–451.
- [34] N.M. Farandos, L. Kleiminger, T. Li, A. Hankin, G.H. Kelsall, Three-dimensional Inkjet Printed Solid Oxide Electrochemical Reactors. I. Yttria-stabilized Zirconia Electrolyte, *Electrochimica Acta* 213 (2016) 324–331.
- [35] C. Graves, S.D. Ebbesen, M. Mogensen, Co-electrolysis of CO_2 and H_2O in solid oxide cells: Performance and durability, *Solid State Ionics* 192 (2011) 398–403.
- [36] S.H. Jensen, P.H. Larsen, M. Mogensen, Hydrogen and synthetic fuel production from renewable energy sources, *Int. J. Hydrogen Energy* 32 (2007) 3253–3257.