Research Paper

Pore Former Addition in the Preparation of Highly Porous Anode Using Phase-Inversion Technique for Solid Oxide Fuel Cell

Siti Halimah Ahmad [1], Siti Munira Jamil [1,2], Mohd Hafiz Dzarfan Othman [1,*], Mukhlis A Rahman [1], Juhana Jaafar [1], Ahmad Fauzi Ismail [1]

[1] Advanced Membrane Technology Research Centre (AMTEC), Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM JB, Johor, Malaysia
[2] Centre for Degree Programme, School of Professional and Continuing Education (UTMSPACE), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

Highlights

• Feasibility of PEEK and corn starch as pore former in phase-inversion technique
• Addition of 2 wt.% PEEK generates more connected open pores
• Addition of 2 wt.% PEEK produced 67 % mechanically stronger

Graphical abstract

Abstract

A detailed study on the anode structure of solid oxide fuel cell (SOFC) is very crucial in developing high performance power generating devices, given how porous electrodes are known to provide a number of active sites for reaction, consequently accelerate fuel conversion. This present study investigates the feasibility of pore former addition to nickel oxide-yttria stabilized zirconia (NiO-YSZ) anode, fabricated via phase inversion-based casting and sintering technique. The loading of two types of pore former (i.e. polyetheretherketone [PEEK] and corn starch) was varied from 0 to 10 wt % of total suspension. The effects of pore former loading and its types were examined based on anode morphology using scanning electron microscopy (SEM), crystal phase by X-ray diffraction (XRD), apparent porosity based on standard ASTM C373-88, and bending strength using three-point bending test. Results had shown that higher loading of pore former increased the porosity, yet significantly reduced the bending strength. SEM images of anode displayed that by generating more connected open pores through the addition of 2 wt.% PEEK, it produced an effective porous structure. In fact, the sample recorded to be 67 % mechanically stronger compared to the best loading which is corn starch (4 wt.%). Based on these findings, PEEK can be used as pore former in anode fabrication that creates appropriate porosity, which benefits gas diffusion and also provides good mechanical strength as an anode support.
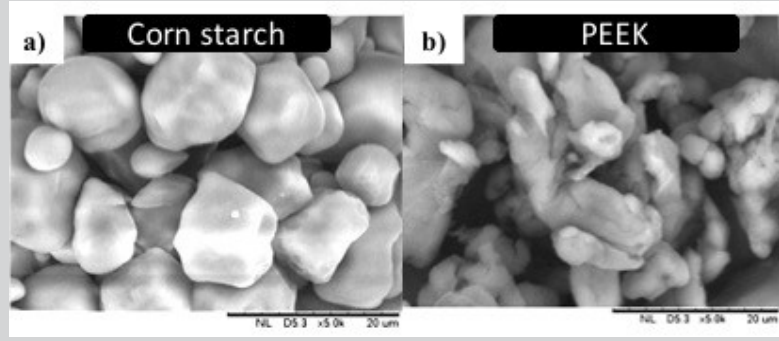
1. Introduction

In anode-supported micro-tubular solid oxide fuel cells (SOFC), the anode substrate particularly serves as a "backbone" to support the whole cell, giving a mechanical support for both thin electrolyte and cathode layer [1]. Besides that, anode tube primarily provides active sites reaction or known as triple-phase boundaries (TPB) regions for electrochemical oxidation of fuels. Without TPB regions, any electrochemical activity of anodic reaction will not happen. This is due to the breakdown in connectivity in any one of the phases such as oxygen ion conductor, electronic conductor and the gas phase [2].

As a matter of fact, TPB regions in anode are responsible in producing numbers of ionic and electronic conduction paths, besides creating path for fuels and byproducts (i.e. water and carbon dioxide) to reach and leave site reactions simultaneously [2], as illustrated in Figure 1. Consequently, the anode substrates should be permeable to gasses, possess a highly porous structure and able to retain its porosity after sintering.

For anode symmetric structure, it is established that the addition of degradable pore-forming agent to anode suspension is a promising technique

to induce pore formation in anode substrate. Pore former such as graphite [3, 4], starch [5, 6], polyether ether-ketone (PEEK) [7] and polymethyl methacrylate beads (PMMA) [8, 9] had successfully induced the macro-size pore in anode substrate for better gas transfer. The resultant pores were uniformly distributed among the networks built with cermet particles. Addition of different pore formers also affects the microstructure of porous anode in terms of porosity, pore shape and tortuosity (interconnectivity). The aforementioned features significantly determine the act of permeation through a fiber. In particular, excessive porosity may degrade its mechanical strength [8] and availability to provide active TPB areas [6]. For these reasons, achieving the most appropriate amount of anode porosity is vital to successfully fabricate an anode supported SOFC with good cell performance.

Although there are several studies on the effects of pore former addition on the anode properties, very limited literatures have reported on its particular effects when using specific techniques such as phase-inversion based-casting and sintering. By utilizing the two techniques, the artificial pore-forming agents should be chemically stable towards solvent, hence the pore former will remain its original shape even after the casting process. Following that, the particles will be burnt off at thermolysis stage of the sintering process and subsequently leaving pores in the sintered tubes. Poon and Kaiser [7] had investigated the effects of four types of pore former in producing the plasma sprayed SOFC anode coatings. Under the studied spray conditions, the flour and mesocarbon-microbead (MCMB) pore former powders were effective as plasma sprayed pore formers. However, the high-density polyethylene (HDPE) powder was unable to survive the plasma spray process and did not contribute to the final coating porosity. The PEEK pore former, promise as a pore former for plasma sprayed coatings. While Meepho et al. [5] discussed the effect of corn starch on the porosity and sintering shrinkage on NiO-YSZ substrate using electrophoretic deposition (EPD) technique. They found that 15 wt% of corn starch sample resulted in suitable porosity, thus allowing it to be used as a substrate.

In this study, a comparison between corn starch and PEEK as pore former was drawn. PEEK was chosen due to the limited number of studies conducted on its use as pore former, then compared to corn starch. From the findings, with appropriate amount of pore former in the anode that provides adequate porosity, sufficient strength intended for the fiber can be achieved.

2. Experimental

2.1. Materials

Commercial nickel oxide (NiO) (NexTech Materials, USA, particle size of 12-22 μm and specific surface area (SSA) = >1 m^2/g) and 8 mol% yttria-stabilised zirconia (YSZ) (NexTech Materials, USA, particle size of 0.3-0.5 μm and SSA = 10-15 m^2/g) were used as starting materials. A homogeneous distribution of NiO and YSZ is significant in enhancing the density of active sites reaction. Polyethersulfone (PES, Radel A300, Ameco Performance, USA), Arlacel P135 (Polyethyleneglycol 30 Dipolyhydroxystrearate, CRODA) and N-methyl-2-pyrrolidinone (NMP, QRёС™) were used as polymer binder, dispersant and solvent respectively. Pore former used in this study was corn starch and polyether ether-ketone (PEEK), both obtained from Sigma Aldrich. As can be seen in Figure 2, corn starch and PEEK were presented in different particles size and shape. Throughout phase inversion-based casting process, water was used as a coagulant bath.

2.2. Preparation of anode suspensions

0.12 wt% of dispersant arlacel was dissolved in solvent (i.e. NMP), followed by adding powders of NiO and YSZ (total powder of 60% and 40% respectively) into the mixture and was milled for 24 hours. NiO-YSZ powder is the major constituent of anode suspension, which contains a range within 50-70 wt% of total suspension, as listed in Table 1. The mixing was further carried out for an extra 24 hours after adding 1:10 PES pallets to NiO-YSZ powder, ensuring that all ceramic powder was well-dispersed in the polymer solution. Next, pore former was added into the anode suspension and ball milled for another day. Different pore former loadings (i.e. 0, 2, 4, 6, 8, and 10 wt%) in anode suspension were also studied. Anode samples were named according to the pore former and loading composition. The compositions of the suspensions were weighed accordingly, based on the desired value.

2.3. Casting and sintering process

Prior to casting, the electrolyte suspension was stirred at room temperature to degas for 1 h. The suspension was then casted on a glass plate

with a glass rod in order to form a thin film as depicted in Figure 3. It was transformed into flat sheet via casting procedure on a glass plate. Then, the flat sheet was dried in an ambient drying for 4 h and left immersed in tap water overnight. Lastly, the membrane was detached from the glass plate.
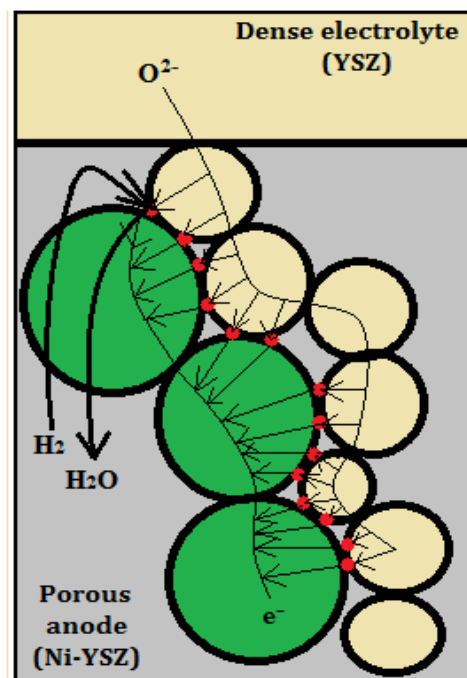

Fig. 1. The diagram of active site reaction or known as TPB in porous anode SOFC.

Table 1
Compositions of anode suspensions.

Anode Sample	Pore Former	Pore former loading (wt%)	Ceramic loading (wt%)
A-00	None	0	70
AC-02	Corn Starch	2	68
AC-04	Corn Starch	4	66
AC-06	Corn Starch	6	64
AC-08	Corn Starch	8	62
AC-10	Corn Starch	10	60
AP-02	PEEK	2	66
AP-04	PEEK	4	62
AP-06	PEEK	6	58
AP-08	PEEK	8	54
AP-10	PEEK	10	50

2.4. Characterizations

Viscosity of suspensions (after degassed) was measured by Rheology Brookfield Viscometer (DV-lll) using concentric cylinder geometry at room temperature. After that, the morphology of the flat sheet precursors and sintered anodes were examined with scanning electron microscope (SEM) (Hitachi, TM3000). The SEM micrographs on cross-section of the anode were taken at various magnifications. X-ray diffraction (XRD) was also used to identify crystal phases present in the crushed powder of NiO–YSZ anode. Aside from that, the apparent porosity of the anode samples was tested on its

ability to contain water, in accordance to the standard of STM C373-88. Last but not least, a test on mechanical strength was done on the rectangular flat sheet (60mm x 15mm x 0.2mm) using Instron 3342 through three-point

bending test. During the test, a span length of 30 mm and crosshead speed of 0.1 mm/min were applied.
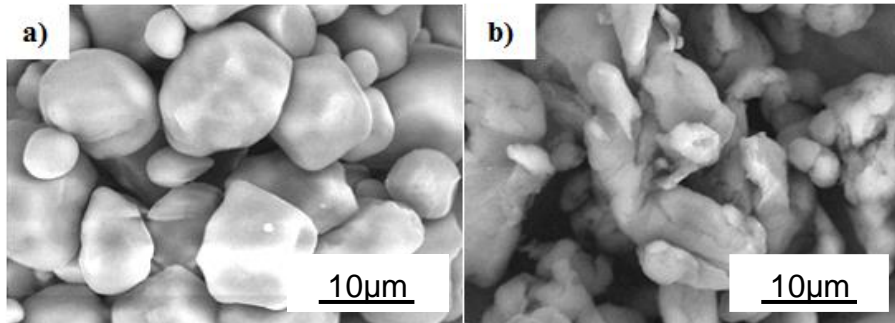

Fig. 2. Micrographs of (a) corn starch and (b) PEEK particles as pore formers.
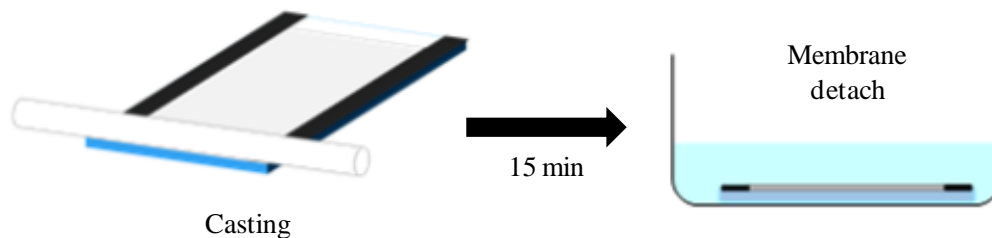

Fig. 3. Schematic diagram of phase inversion-based casting process.

3. Results and discussion

3.1. Dope suspension viscosity

Three batches of formulations were prepared in order to obtain viscosity at range 3000-5000 cP where it gives a flow able ceramic dope suspension with good rheology, suitable to be applied for casting, extrusion and co-extrusion process [10]. For the first batch, increment of pore former with constant ceramic loading shows that the addition of pore former to anode suspension had caused a huge increase in viscosity and produced very viscous suspension, futher hindering the subsequent casting process. In the second batch, pore former was added into suspension, whereas the same amount of ceramic was reduced (e.g. 2 wt% of ceramic was reduced with the addition of 2 wt% corn starch or PEEK). Figure 4 shows that the viscosity increased from 355 cP to 8368 cP for corn starch content of 2 wt.% to 10 wt.%, which is mainly due to the decreased amount of NMP as solvent in the suspension. However, as for suspension containing PEEK, the viscosity was very high. For instance, the addition of only 2 wt% and 4 wt% PEEK had produced suspensions with viscosity of 6399.6 and 5618 cP respectively.

It was believed that the primary particles of corn starch (as shown in Figure 2) are large and have less surface area, thus it requires less amount of organics to be dispersed and form a proper organic network. Meanwhile, PEEK has the nature of aggregates (see Figure 2) whereby these aggregates need to be broken down during the ball milling process, therefore requiring a lower amount of ceramic content but high in organic loading than that of the corn starch [11]. Hence, another batch formulation was applied for PEEK by further reducing the amount of ceramic particles, only then it was able to reach acceptable values for casting. Figure 4 depicts that the viscosity kept decreasing with the increase of PEEK loading due to bigger reduction of ceramic particles. The content of PEEK was increased from 2 wt.% to 4 wt%, which caused the viscosity to start reducing from 4098 cP to 3152 cP and this value was further lessened to 576.5 cP at 10 wt.% PEEK.

3.2. Pore former removal during Sintering

The anode suspension then underwent a casting process, in which the anode flat sheet (NiO-YSZ precursor) was produced. The NiO-YSZ precursor initially comprised of ceramic materials, polymer binder and pore former. Both PEEK and corn starch, which were used as the pore former, have high chemical stability and do not dissolve in organic solvents [7] such as NMP. Therefore, corn starch and PEEK remained its original shape after the membrane casting/extrusion process as it is crucial to be removed during sintering (at thermolysis stages), which then created pores in the anode structure.
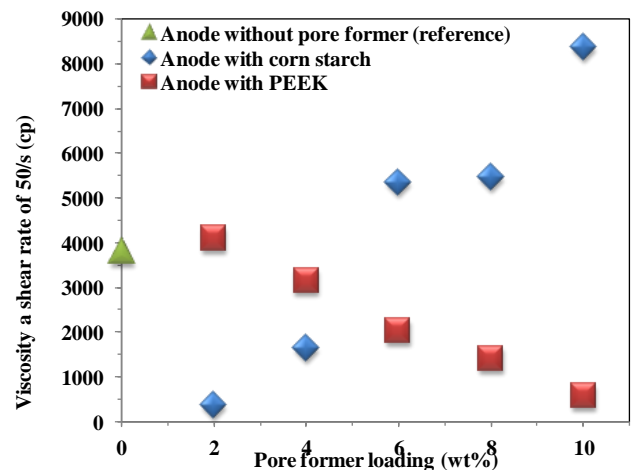

Fig. 4. Viscosity of anode suspensions with different type and loading of pore former at shear rate of 50 per second.

Prior to sintering, thermo-gravimetric analysis (TGA) was performed on both types of pore former to determine the ideal temperature for thermolysis stages. According to the TGA results (see Figure 5), the most significant reduction on the mass was the decomposition of pore formers and polymer binder [12]. Anode with corn starch and PEEK as the pore former indicated that the pore former decomposition behavior took place at a temperature range of 250 °C to 350 °C and 450 °C to 850 °C. Thus, it is believed that heating at 300 °C and 500 °C in air for 1 hour should be sufficient to completely remove the pore former from the anode structure.

In addition to that, Figure 6 shows phase identification using X-ray diffraction (XRD) analysis. Said analysis can ensure completeness of pore former removal by comparing the XRD patterns of sintered AC-04 and AP-04 samples with the original patterns of NiO and YSZ powder. As can be seen, polymer and pore formers were completely decomposed, given that no trace of corn starch and PEEK was found in the anode sample after undergoing the sintering process at 1450 °C. No other characteristic peaks other than those of NiO–YSZ were also observed.
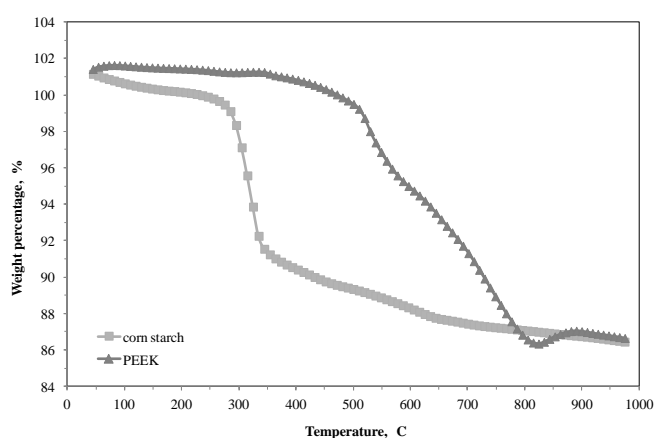
observed when evaporation time of 15 minutes was allowed prior immersion of flat sheet into coagulant bath. It is believed that within this duration, the surface of nascent flat-sheet anode had experienced high solvent evaporation and absorption of moisture from air. As a result, the solidification of the anode surface ensued before the immersion, inhibiting viscous fingering phenomenon [13].

When pore former such as corn starch and PEEK were added into anode suspension, it resulted in the formation of macropores, instead of micropores, therefore changing the structure of anode altogether. Figure 8 shows SEM images of porous anode comprising of NiO phase, YSZ phase and pore phase after undergoing sintering process at 1450 °C. In general, macropores were seen and they were distributed among the networks that are built with NiO and YSZ particles. Bigger and more connective pores were observed at higher loading of pore former (AC-10 and AP-10) to which permit higher connective and less resistive paths for the gas diffusion. Nevertheless, too many pores in anode may detriment the mechanical stability and percolation paths for electrons, oxide ions and gaseous species [12].

Besides that, it is obvious that the porosity generated within anode structure is greatly affected by the types of pore former used. This may be attributed to the differences in size and shape [14] of corn starch and PEEK powder particles as depicted in Figure 2. As can be seen, corn starch particles are present in various diameters of well-defined shape (i.e. spherical shape particles) while PEEK showcase aggregates of thin and longitudinal-shaped particles. At low corn starch loading such as AC-02 and AC-04, the spherical-shaped particles led to formation of closed pores to the anode structure. Considering that such closed pores are ineffective for gas diffusion, they should be reduced.

Fig. 5. Thermo gravimetric analysis of sintered anode with corn starch and PEEK as pore former.
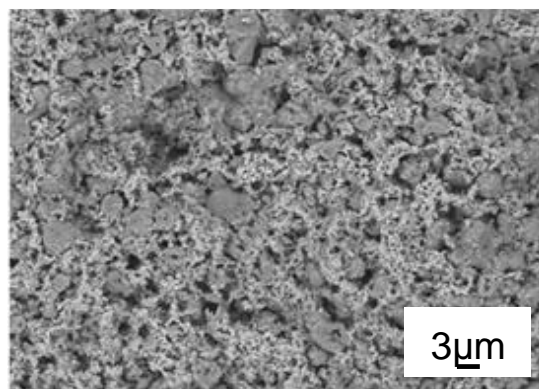
Fig. 7. SEM images of the cross-sectional plain anode structure without pore former. The anode was sintered at 1450 °C for 6 hours.

3.4. Effects of pore former on apparent porosity and mechanical strength

For anode-supported cell, anode is said to be much thicker than electrolyte and cathode. That being said, anode is required in providing sufficient mechanical strength for the deposition of remaining layers. It should also contain enough porosity that benefits gas diffusion that guarantees sufficient fuel supply and efficient reaction products removal. Since the addition of pore former could increase the porosity, likewise reduce the mechanical strength of the anode support, it is crucial to find the best loading that could produce anode with sufficient mechanical strength of ideal porosity.

Figure 9 show similar trends for anode with corn starch and PEEK, in terms of apparent porosity and bending strength respectively. With higher loading of the pore former, the porosity of the anode structure did in fact increase, though its bending strength unfortunately was reduced. Such increase in apparent porosity was due to the formations of empty spaces called pores. Hence, the number of pores increased, that is resulted from higher content of pore former burnt out from the anode during thermolysis phase in the sintering process. This is also in line with SEM images shown in Figure 8.

The highest value of the apparent porosity was recorded at 25 % and 33 % for 10 wt% corn starch and PEEK respectively, emphasizing on the total loading. Despite so, these anodes possess very low bending strength (14 and 8 MPa, respectively), which will result to the difficulty in anode handling, as has been observed experimentally. This proves that the presence of excessive
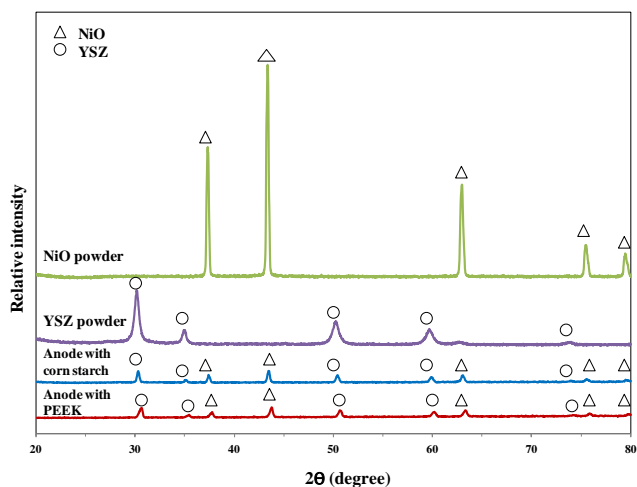

Fig. 6. XRD patterns of sintered flat sheet AC-04 and AP-04 at 1450 °C and the pattern was compared with raw powder of NiO and YSZ.

3.3. Effect of pore former on the flat sheet anode microstructure

Figure 7 illustrates the anode microstructure without pore former, showing that micropores were formed in between NiO and YSZ phases only. As expected, no finger-like formation (except for sponge-like structures) was

pores has left huge number of empty spaces, allowing bonds to be created between each ceramic particles. This however, does come off as a disadvantage in terms of the mechanical strength of the anode. The apparent

porosity and flexural strength of the original flat sheet of NiO-YSZ (without pore former) sample was at 5.8% and 127 MPa.
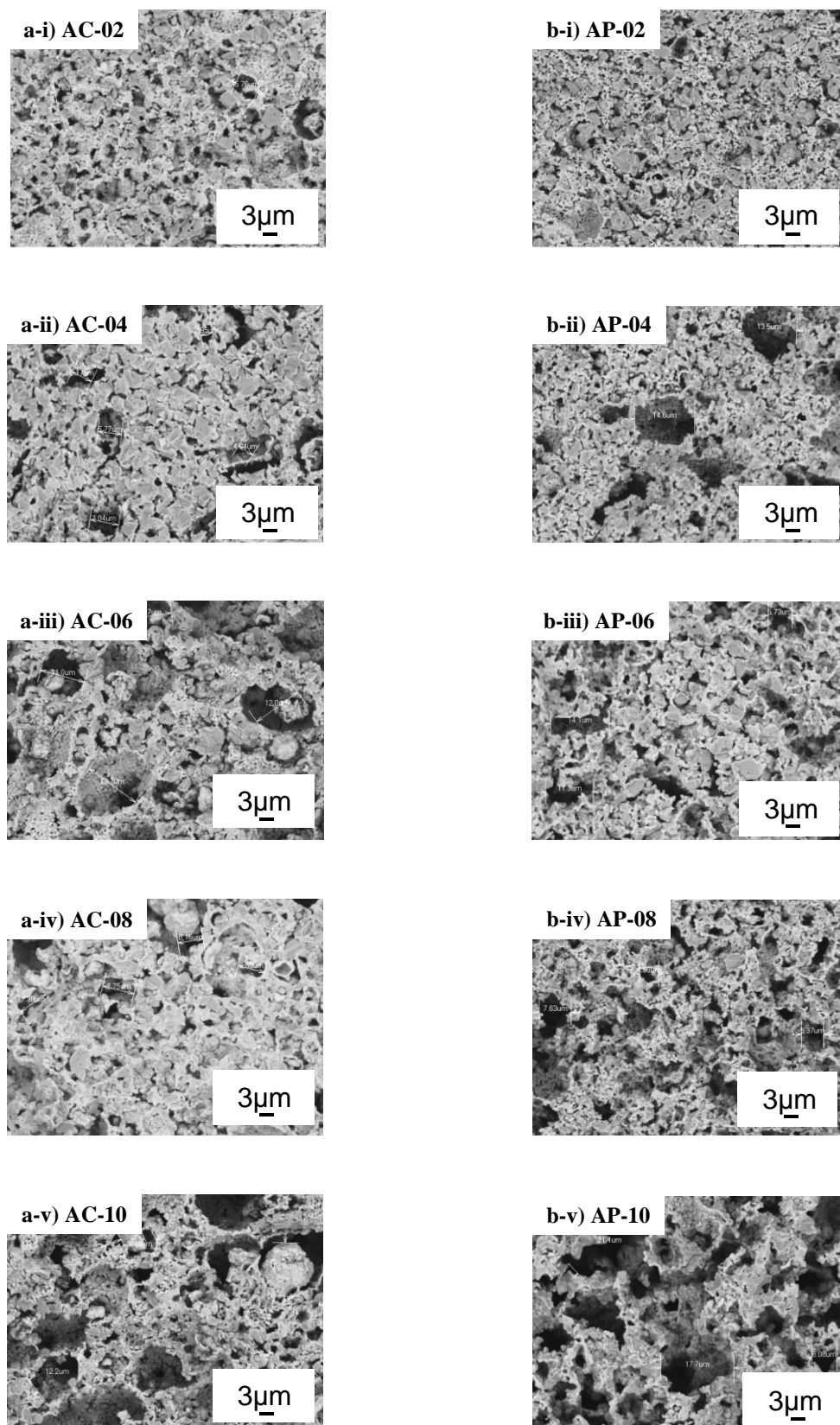
Fig. 8. SEM micrographs of cross-sectional anode (sintered at 1450 °C for 6 hours) showing the microstructures of anode substrate fabricated with various pore former (a) corn starch and (b) PEEK, at different loadings: (i) 2wt%, (ii) 4wt%, (iii) 6wt%, (iv) 8wt% and (v) 10wt% of total content.

Based on this understanding, the best amount of porosity and mechanical strength can be determined for both pore formers. For anode with corn starch, 4 wt% loading yielded the highest amount for both physical properties with 12.5 % of apparent porosity and 46 MPa of the flexural strength. However, these values were much lower than the anode with PEEK. Anode with PEEK gave a higher porosity and stronger structure of 15 % porous and 77 MPa, respectively, which was retained by 2 wt% PEEK added into anode suspension.

4. Conclusions

Thick anodes with porous structure have been successfully prepared using PEEK and corn starch as the pore former. It was found that 2 wt% PEEK of total anode content can produce a porous structure that is 67% stronger compared to the best loading of corn starch. PEEK also can be a new type of pore former besides starch, carbon and polymer beads because it is chemically stable towards solvent, whereby it does not leave residue, also generates more open pores connected to anode after being burnt at high temperature. The apparent porosity (15%) will further increase when finger-like formation is induced during phase-inversion.
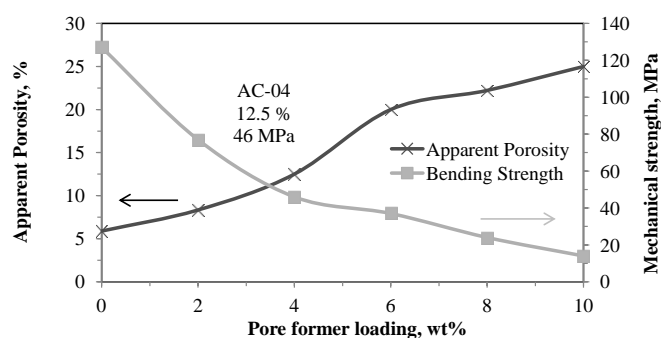

Fig. 9. The apparent porosity and mechanical strength of sintered anode as a function of corn starch loading from 0 wt% to 10 wt% of total composition.

References

[1] S. Primdahl, B.F. Sørensen, M. Mogensen, Effect of Nickel Oxide / Yttria-Stabilized Zirconia Anode Precursor Sintering Temperature on the Properties of Solid Oxide Fuel Cells, 94 (2000).

[2] J. Lee, The impact of anode microstructure on the power generating characteristics of SOFC, Solid State Ionics. 158 (2003) 225–232. doi:10.1016/S0167-2738(02)00915-3.

[3] X. Meng, X. Gong, N. Yang, X. Tan, Y. Yin, Z.-F. Ma, Fabrication of Y2O3-stabilized-ZrO2(YSZ)/La0.8Sr0.2MnO3−α–YSZ dual-layer hollow fibers for the cathode-supported micro-tubular solid oxide fuel cells by a co-spinning/co-sintering technique, J. Power Sources 237 (2013) 277–284. doi:10.1016/j.jpowsour.2013.03.026.

[4] C.C. Wei, O.Y. Chen, Y. Liu, K. Li, Ceramic asymmetric hollow fibre membranes—One step fabrication process, J. Membr. Sci. 320 (2008) 191–197. doi:10.1016/j.memsci.2008.04.003.

[5] M. Meepho, D. Wattanasiriwech, S. Wattanasiriwech, P. Aungkavattana, Preparation of NiO-YSZ substrate for electrophoretic deposition of thin YSZ film, Energy Procedia. 34 (2013) 714–720. doi:10.1016/j.egypro.2013.06.804.

[6] J.J. Haslam, A.-Q. Pham, B.W. Chung, J.F. DiCarlo, R.S. Glass, Effects of the Use of Pore Formers on Performance of an Anode Supported Solid Oxide Fuel Cell, J. Am. Ceram. Soc. 88 (2005) 513–518. doi:10.1111/j.1551-2916.2005.00097.x.

[7] M. Poon, O. Kesler, The influence of pore formers on the microstructure of plasma-sprayed NiO-YSZ anodes, J. Power Sources. 210 (2012) 204–217. doi:10.1016/j.jpowsour.2012.02.046.

[8] A. Sarikaya, V. Petrovsky, F. Dogan, Effect of the anode microstructure on the enhanced performance of solid oxide fuel cells, Int. J. Hydrogen Energy 37 (2012) 11370–11377. doi:10.1016/j.ijhydene.2012.05.007.

[9] T. Suzuki, Y. Funahashi, T. Yamaguchi, Y. Fujishiro, M. Awano, Effect of anode microstructure on the performance of micro tubular SOFCs, Solid State Ionics. 180 (2009) 546–549. doi:10.1016/j.ssi.2008.09.023.

[10] S.H. Ahmad, S.M. Jamil, M.H.D. Othman, M.A. Rahman, J. Jaafar, A.F. Ismail, Co-extruded dual-layer hollow fiber with different electrolyte structure for a high temperature micro-tubular solid oxide fuel cell, Int. J. Hydrogen Energy (2016) 1–9. doi:10.1016/j.ijhydene.2016.06.044.

[11] A. Sanson, P. Pinasco, E. Roncari, Influence of pore formers on slurry composition and microstructure of tape cast supporting anodes for SOFCs, J. Eur. Ceram. Soc. 28 (2008) 1221–1226. doi:10.1016/j.jeurceramsoc.2007.10.001.

[12] C. Jin, J. Liu, L. Li, Y. Bai, Electrochemical properties analysis of tubular NiO–YSZ anode-supported SOFCs fabricated by the phase-inversion method, J. Membr. Sci. 341 (2009) 233–237. doi:10.1016/j.memsci.2009.06.012.

[13] K. Li, Ceramic Membranes for Separation and Reaction, John Wiley & Sons Ltd, England, 2007.

[14] M. Poon, O. Kesler, The influence of pore formers on the microstructure of plasma-sprayed NiO – YSZ anodes, J. Power Sources 210 (2012) 204–217. doi:10.1016/j.jpowsour.2012.02.046.