Effect of open pore and pore interconnectivity in the Ni-SDC cermet anode microstructure on the performance of solid oxide fuel cells

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Abstract. In nickel-samarium-doped ceria (Ni-SDC) cermet anode layers, the open pores and interconnected pores in the microstructure are the main factors that affect the mechanical and electrical properties. In this work, porous Ni-SDC cermet anode layers are fabricated using various quantities of potato starch (0 to 25 wt.%) as a pore forming in the anode powders. The properties of the Ni-SDC cermet anode layers were characterised by FESEM-BSE microscopy, Archimedes method for density measurement, Vickers hardness, flexural strength, and DC four-point electrical conductivity. The findings revealed that the different content of potato starch greatly affected the percentage of porosity and pore interconnectivity in the microstructure and consequently altered the mechanical and electrical properties of the Ni-SDC cermet anode. The degree of shrinkage, relative density, mechanical strength and electrical conductivity of the Ni-SDC cermet anodes decreased as their pore former content increased. Furthermore, the research shows that the large porosity (> 40%) in the Ni-SDC cermet anode microstructure affected the continuity of Ni-Ni, SDC and Ni-SDC phases and thereby affected the mechanical and electrical properties. The Ni-SDC cermet anode with 10 wt.% exhibited sufficient porosity, Vickers hardness, flexural strength and electrical conductivity of 34%, 48 MPa, 72 MPa and 2028 S/cm (at 800 °C), respectively. Therefore, optimisation of porosity in the Ni-SDC cermet anode microstructure strongly contributes to the well-connected pore channels for the rapid diffusion of hydrogen for oxidation and mechanical strength.

1. Introduction
Solid oxide fuel cells (SOFCs) are extremely efficient at converting chemical energy to electrical energy [1]. The key benefits that make SOFCs suitable for both stationary and portable applications are the high energy conversion, fuel flexibility, use of inexpensive catalysts, and recycling utilisation of exhaust heat.
A cutting-edge technology SOFCs are made up of three layers: the anode and cathode electrodes, as well as an intermediate layer that serves as an ion-conducting electrolyte [3]. The anode is a critical component of the SOFC because it offers active sites for hydrogen oxidation by interacting with oxide ions in the solid electrolyte, hence enabling fuel access and product removal [4]. Nickel-samarium-doped ceria (Ni-SDC) cermet anodes have attracted attention as a SOFC anode material due to their outstanding hydrogen-catalytic capabilities and internal reforming of hydrocarbon fuels [5]. This is because the combination of Ni and SDC significantly enhanced the anode's catalytic activity toward hydrogen fuel oxidation and also promoted efficient hydrocarbon fuel internal reforming [6].

The hydrogen adsorption/diffusion process on Ni surfaces and charge transfer process in SDC electrolyte can be significantly tailored by changing their composition, microstructure, and fabrication conditions. Many studies have sought to improve microstructure of the Ni-SDC anode to facilitate mass transport of the reactants and increase its mechanical strength and electrical conductivity. In these studies, the following processing parameters were examined: (1) Ni-SDC ratio [7], (2) combination of coarse and fine Ni and doped ceria powders [8], (3) effect of Ni powder synthesis on the performance of the Ni-SDC [9], (4) effect of different synthesis techniques on the preparation of Ni-SDC [10], (5) influence of calcination temperature [11], (6) effect of the reduction conditions of Ni on its mechanical and electrical properties [12], and (7) effect of pore former addition and sintering temperature on the microstructure [13]. These studies demonstrated that the performance of the Ni-SDC cermet anode can be tailored substantially by a change in its microstructure and porosity. In this regards, the anode structure should possess excellent permeability; better connectivity of the Ni-SDC, Ni-Ni, and SDC-SDC particles in the cermet [14]; and adequate pores in the structure (30 - 40%) [15]. Additionally, a continuous connection of pores is required for the rapid diffusion of reactants to and from the triple phase boundary (TPB) [16].

The porosity of the microstructure of the anode has an effect on the anode's performance [17]. Reducing the pore size or porosity from the anode microstructure can significantly limit gas diffusion and subsequently increase interfacial polarization resistance [18]. Conversely, high porosity will decrease the TPB area available for reaction [19]. Typically, the anode structure has a porosity of 30 - 40% [20]. This level of porosity can be achieved by optimising the microstructural properties of NiO-based composite anodes. Porous Ni-SDC cermet anodes are often fabricated by addition of organic pore formers or reduction using hydrogen gas.

Among the pore formers, starch is a commonly used pore former in the preparation of porous materials because it is cheap, renewable nature, widely available, and environmental friendliness [21]. Potato starch is a commonly used pore-forming agent in ceramic manufacture [22]. This natural biomaterial is completely consumed during the firing process, leaving no remnant in the final ceramic body. This is because of its chemical composition, which is predominantly a polysaccharide that is composed of just carbon (C), hydrogen (H), and oxygen (O). However, addition of organic pore formers to the initial powders and reduction of the nickel oxide (NiO)-SDC composite anode can cause drastic changes in its porosity, density, and physical and mechanical properties. In this study, potato starch is used as a pore former to produce porous Ni-SDC cermet anodes, and the influence of the pore former on the final product are investigated.

In the present communication, attention was mainly focused on elucidating the influence of porosity, particle distribution and particle to particle connectivity on mechanical and electrical properties of Ni-SDC cermet anode. In this work, a systematic approach was established to examine the effects of porosity on the mechanical and electrical properties of Ni-SDC cermet anodes to which different weight percentages of a pore former, in order to understand the microstructure-mechanical-electrical performance relationship.
2. Methodology

2.1. NiO-SDC powder preparation
The nickel oxide (NiO)-SDC composite anode powder (60 wt.% of NiO and 40 wt.% of SDC) were prepared by mechanical mixing using high speed ball milling technique. Both the NiO powders of average particle size of 5 nm and \((\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9})\) SDC powders with average particle size of 500 nm were used as raw materials. The true theoretical density of NiO and SDC powders were 6.67 g/cm\(^3\) and 7.1417 g/cm\(^3\), respectively. All of the raw materials were purchased from Sigma Aldrich, Malaysia. The commercial powders of NiO and SDC were mixed together with ethanol and ball-milled for 24 h. The slurry was then dried in an oven at 120 °C for 12 h. The dried powder was calcined at 700 °C for 2 h to obtain the desired NiO-SDC composite anode powder. To investigate the effects of amount of pore former on the microstructure and electrical properties of Ni-SDC cermet anode, the NiO-SDC composite anode powder was ball milled with potato starch with different wt.% from 0 to 20 wt.%. The mixed powders were designated as NS0, NS5, NS10, NS15 and NS20, respectively. Potato starch was purchased from Sigma Aldrich, Malaysia. Potato starch has a moisture content of 18 - 21% and an average diameter of 48 µm [23].

The prepared anode composite powder was pressed at 50 MPa to fabricate a disk-shaped sample. The as-prepared green pellets were subsequently sintered at 1350 °C for 5 h in air. The sintered pellet of NiO-SDC cermet anode was reduced to metallic Ni-SDC cermet anode with mixture of wet hydrogen and wet nitrogen gas (10% H\(_2\) and 90% N\(_2\)) at 800 °C for 5h.

2.2. Characterization
The phase composition of the prepared powder was conducted by X-ray Diffraction (XRD) with CuK\(\alpha\) (\(\lambda = 0.15418\) nm) using an X-ray diffractometer (Shimadzu XRD-6000, Bruker, Karlsruhe, Germany). The powder morphology of the prepared powders was observed through transmission electron microscopy (TEM, HitachiHT7700, Tokyo, Japan) at 120 kV. The density and porosity of the Ni-SDC cermet samples were performed by Archimedes method with deionised (DI) water at room temperature. The degree of thermal shrinkage was also calculated for the Ni-SDC cermet. Field emission scanning electron microscopy (FESEM), combined with back scattering electron (BSE) microscopy (Hitachi FESEM SU5000, Tokyo, Japan) was utilised to examine the morphology of the Ni-SDC cermet pellets. The Vickers hardness tester (ZHV 30-m, Zwick Roell Indentee, Stourbridge, UK) was used to measure the Ni-SDC cermet's hardness. The flexural strength of the Ni-SDC cermet was determined using the piston-on-three-ball method in accordance with the ISO 6872:2008 standard. Using the van der Pauw technique, a DC four-point electrical conductivity of the Ni-SDC cermet was measured in humidified hydrogen at 300 to 800 °C.

3. Results and Discussion

3.1. Powder analysis
From figure 1(a), it is obvious that no phase shifts or chemical reactions happened during the mixing and calcination of NiO and SDC powders. There were no secondary peaks of impurities observed in this sample, indicating that the composite anode powder was chemically compatible after mixing and calcination. Cubic NiO (JCPDS #96-432-9324) and face-centred cubic fluorite SDC (JCPDS #96-434-3152) have been identified as the two principal phase structures [24]. The NiO–SDC composite anode showed no structural change and was composed entirely of two distinct phases with steep and strong peaks. The theoretical densities of the NiO-SDC composite powder were 6.85 g/cm\(^3\). These findings corresponded to previously published values in the literature [25].

Figure 1(b) shows a TEM image at 5000x magnification of NiO-SDC composite anode powder. The TEM results showed a consistent distribution of small spherical particles and a non-spherical distribution of macro-sized particles. SDC particles are small, spherical particles and NiO particles are larger, non-spherical particles. A similar observation was made during the synthesis of NiO–SDC composite anode
at a 60% by weight NiO concentration [26]. Furthermore, homogeneously dispersed SDC particles operate as an inhibitor, limiting NiO particle grain growth. As a result, the macro-sized non-spherical sized particles in the NS-24 sample can be identified as NiO particles [27].

![Figure 1. NiO-SDC and composite anode powders (a) XRD patterns and (b) TEM images at 5000x.](image)

### 3.2. Sintered pellet properties

Prior to microstructural and electrical analysis of the sintered pellets of NiO-SDC composite anode, all the samples were reduced to metallic Ni-SDC cermet anode with mixture of wet hydrogen and wet nitrogen gas (10% H₂ and 90% N₂) at 800 °C for 5h. The impact of potato starch addition and consequently the degree of thermal shrinkage can be reflected on the sintering behaviour of the pellets. It is clearly found that the thermal shrinkage decreased with increasing the amount of potato starch (table 1). This means that the percentage of thermal shrinkage decreases corresponding to the increasing of the potato starch addition amount, indicating the percentage of the pores increases with the increasing of the potato starch addition. In addition, increasing potato starch loading hinders the degree of thermal or sintering shrinkage because it eliminates the influence of pellet densification behaviour. The relationship between the potato starch addition amount and the relative densities of Ni-SDC cermet is listed in table 1. When the amount of potato starch is increased, the relative density of the Ni-SDC cermet anode drops proportionately. For instance, the NS0 show a higher relative density of 83% than the NS5 cermet with 70% relative density. Densities were reduced as a result of the enhanced porosity created by the potato starch addition and reduction process [13]. In general, the percentage of porosity increases with increasing potato starch content.

The reduced pellets of Ni-SDC cermet anode are depicted in cross-sectional images in figure 2 (a-e). FESEM imaging revealed no significant differences in particle shape and size. Three distinct and equally distributed interfaces were identified in the microstructure. SDC, Ni, and pores are symbolised by the white, grey, and dark grey colours, respectively. Increasing potato starch wt.% resulted in higher porous morphological structure. It appears that the size of the grains of Ni-SDC pellets had no correlation with the addition of potato starch, however, the density and porosity of the pellets was dependent on the starch content. The pore distribution was uniform with lots of fine pores and fine-grained microstructure was evident. The potato starch addition and reduction process has a stronger influence on the connection between Ni-SDC, Ni-Ni and SDC-SDC particles and distribution of Ni and SDC within the anode microstructure [15]. It is notable that the grain-grain contact regarded as the greater importance to facilitate better oxidation of H₂ from Ni contact and mechanical support for Ni from SDC contact. Ni–Ni and SDC–SDC had a loose agglomeration in the NS10 sample, which produced a highly porous
structure. When starch addition exceeded 10 wt.%, there was weak connection between particles, and in the reduced sample, a more agglomerated morphology was observed (figure 2(e)). The adequate level of porosity was induced with 10 wt.% and 15 wt.% potato starch are evident in the micrographs and consistent with the porosity measurement. Therefore, the NiO-SDC composite anode with 5 wt.% and 10 wt.% of potato starch as pore former can satisfy the functional demands of anode SOFCs.

Table 1. Thermal shrinkage, relative density, porosity, flexural strength and Vickers hardness properties of Ni-SDC cermet anode with different potato starch content.

| Sample | Shrinkage (%) | Relative Density (%) | Porosity (%) | Flexural Strength (MPa) | Vickers Hardness (MPa) |
|--------|---------------|----------------------|--------------|-------------------------|-----------------------|
| NS0    | 22.7 ± 0.3    | 83 ± 0.7             | 17 ± 0.7     | 169 ± 2.5               | 165 ± 1               |
| NS5    | 20 ± 0.2      | 70 ± 0.6             | 30 ± 0.6     | 98 ± 4                  | 72 ± 1.5              |
| NS10   | 20 ± 0.4      | 65 ± 1.4             | 35 ± 1.4     | 73 ± 3                  | 48 ± 2.3              |
| NS15   | 19.5 ± 0.1    | 56 ± 1.7             | 44 ± 1.7     | 59 ± 2                  | 33 ± 1.7              |
| NS20   | 18.6 ± 0.1    | 57 ± 1.2             | 43 ± 1.2     | 35 ± 3                  | 14 ± 2.8              |

Figure 2. FESEM images of Ni-SDC cermet anode (a) NS0, (b) NS5, (c) NS10, (d) NS15, and (e) NS20.

The flexural strength and Vickers hardness of the Ni-SDC cermet composites with different potato starch addition were listed in table 1. The results show that the flexural strength and Vickers hardness value decreased with increasing potato starch content from 0 to 20 wt.% It seems that the difference in mechanical properties is mainly attributed by a difference in porosity, which is in good agreement with their relative density from Archimedes method. In general, it is essential to highlight that the degradation of the mechanical strength with increasing the potato starch addition is consequence of increase in porosity and change in microstructure. Increase in porosity not only show adverse effect on the
mechanical characteristics of Ni-SDC cermet anode but also on the catalytic activity of the Ni-SDC cermet anode materials.

3.3. Electrical properties
The electrical conductivity of Ni-SDC cermet anode is strongly dependent on the potato starch addition amount as shown in figure 3. When the potato starch addition amount increases from 5 to 20 wt.%, the DC electrical conductivity of the Ni-SDC cermet anode decreased from 2163 to 1022 S/cm, which is significantly lower than that of NS0 (3642 S/cm) at 800 °C. This decrease is mainly attributed to the porous microstructure and particle connectivity which disrupts the electronic pathways in the cermet anode, thereby can lose or have diminished electrical conductivity [28]. It is undeniable that the addition of potato starch has a significant impact on the amount of pores present. It can be observed that the volume of open pores is increasing in correlation with the quantity of pore forming used (figure 2). In contrast, the volume of closed pores decreased with the increasing potato starch amount. This is because the increase in potato starch addition helps to extend the pores. Moreover, the adequate addition of pore forming agent will facilitate presences of macro-sized pores and uniform pore size distribution in the anode microstructure, thus increasing the cell performance.

![Figure 3. Electrical conductivities of Ni-SDC cermet anode with different potato starch content measured between 300 °C and 800 °C.](image)

4. Conclusion
In this study, effects of amount of pore former on the microstructural and electrical properties of nickel-samarium doped ceria cermet anode were investigated in detailed. As electrical and mechanical studies demonstrate that a continuous network structure comprising Ni-Ni, SDC-SDC, and Ni-SDC particles in cermet, along with sufficient porosity, meets the functional requirements of a solid oxide fuel cell anode. The porosity, mechanical and electrical properties of NS5 and NS10 is sufficient enough to meet the requirement for an SOFC anode. Therefore, in order to maintain an acceptable performance of anode-supported SOFC, the amount of potato starch addition should be in the range between 5 to 10 wt.% for Ni-SDC cermet anode prepared by ball milling technique.
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