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Cellulose as a Pore Former in Electroless Co-Deposited Anodes for Solid Oxide Fuel Cells

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Abstract

A study was conducted to investigate the feasibility of cellulose as a pore former in the manufacture of Solid Oxide Fuel Cell (SOFC) anodes using Electroless Co-Deposition (ECD). Previous work into the use of ECD to produce SOFC anodes has found that the lack of porosity restricted the maximum power density of the cell. Studies have also shown that an anode produced by ECD using rice starch as a pore former has nearly doubled the power density of a cell. Therefore by increasing the anode porosity, the cell's power density should also increase and lead to greater performance of SOFCs for the power generation market.

As the choice of pore former is closely related to the size and shape of pores produced, a whisker pore former will produce a more cylindrical pore once removed. These cylindrical pores will increase the chances of producing an interconnected pore network compared with more spherical pores, and will improve the gas diffusion through the anode. Therefore cellulose whiskers were used to not only improve the porosity of the anode but improve the gas diffusion capabilities throughout the electrode.

Coatings were produced using ECD with different types of cellulose added to act as a pore former using a constant bath loading. A range of 4 cellulose pore formers were selected to reflect different morphologies and sizes available. A fifth coating was also produced using the same methods but, without pore formers, to act as a comparison and determine any improvement produced by the addition of cellulose as a pore former.

The coatings were characterized using and a Scanning Electron Microscope with Electron Dispersive Spectroscopy capabilities. This was used to determine the pore structure which had been produced via a cross sectional analysis. A mercury porosimeter was used to determine the pore content and size in the ECD coatings.

Introduction

Solid oxide fuel cells (SOFC) are an electrochemical energy-conversion device, which offer tremendous promise for delivering high electrical efficiency [1]. They produce an electical current through an electrochemical reation between hydrogen and oxygen at a porous electrode interface, by completing a electrical circuit with the emission of the harmless byproduct, water [2]. SOFC's are composed of a dense electrolyte layer that is sandwhich between two porous electrodes (anode and cathode). The electrons generated through the oxidation of fuel at the anode are accpeted for oxygen reduction at the cathode [1], as shown in Figure 1.
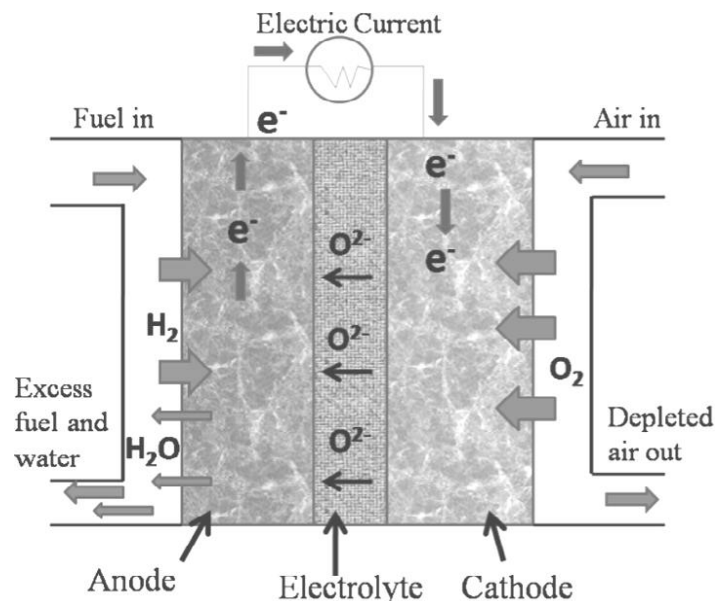

Figure 1: Schematic diagram of a SOFC [1]

However, the practical implication (domestic and industrial) of SOFC's have not yet been realized as they have high material costs, complex cell and stack fabrication, high operational temperature, issues of safety and concerns with regard to handling of gases and routine maintenance [1].

The Electroless Co-disposition (ECD) process of producing electrodes was developed to overcome many of these issues with advantages such as lower capital costs and a simplified, more cost effective process [3]. ECD is the process of depositing particles within and electroless deposited matrix to create a composite coating on a pre sensitized surface. This process can be used to create a nickel/Yttria Stabilized Zirconia (YSZ) anode for a SOFC application [3][4][5]. The anode of a SOFC must meet several stringent requirements, such as adequate electrical conductivity, thermal expansion compatibility and porosity [2]. The porosity in the anode plays an important role in the electrochemical performance of the SOFC, as it must possess suitable pore structure to allow gas permeation and transport. This porosity is commonly controlled by the use of pore formers, which provide an interconnected porosity, this is usually achieved at around 30-40% [1].

An inclusion of rice starch in the ECD process has shown to increse the power density of the cell by a factor of 2 [6]. As the the shape and size of the pore former used will closely resemble the pores it produces, a whisker shaped pore former should produce a more porous network and therotically increase the power density of the cell. Cellulose therefore provides an opertunaty to produce a highly porous structure economically, due to its ease of removal and low cost [7].

1. Scientific Approach

To evaluate the suitability of cellulose as a pore former in the Electroless Co-Deposition (ECD) process, a range of 4 different cellulose samples will be selected upon their size and morphology and included in an ECD coating. These will then be removed via pyrolysis and the change in porosity and surface/cross-sectional structure then analyzed.

To determine the heating profile for the removal of the cellulose pore former, a thermogravimetric analysis will be conducted on each sample of cellulose before the coatings are produced. This information will be used to create a generic heating profile which will used across all coatings to nullify any effect a change in heat treatment would have on the final porosity of the coating.

10 sample will be produced, 2 with each pore former and a final 2 without any pore former using the ECD process with a constant bath loading of both ceramic (YSZ) and pore former. A medium phosphorus nickel plating bath will be used at constant temperature and pH to negate any additional porosity created by the plating process. Once the coatings are produced, the predetermined heating profile will be used to remove the cellulose pore former from 1 of each type of the ECD coatings before being tested.

The resultant surface/cross-sectional structures will then be investigated using a Scanning Electron Microscope (SEM) with Electron Dispersive Spectroscopy (EDS) capabilities. This will ascertain what structures are being produced by the removal of the cellulose pore former. The change in porosity of the coatings will also be measured using mercury porosimetry before and after the pyrolysis of the cellulose pore former. This will help to determine what effect the removal of the cellulose is having on the porosity of the coating.

2. Experiments

The 4 selected cellulose samples are shown in Table 1.

Table 1: Cellulose Size and Morphology

Cellulose Name	Size	Morphology
Sigmacell	≈20µm	Crystalline particles
Avicel	≈50µm	Crystalline particles
Tencel	≈100µm	Fibrous Particles
Knife Milled Cellulose	≈200µm	Fibrous Particles

These were examined under the SEM to confirm there morphologies and size, images from the SEM can been seen in Figures 2-5.
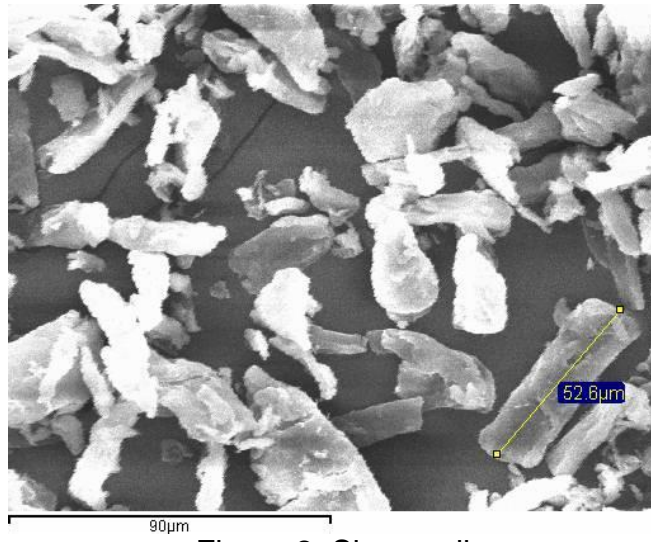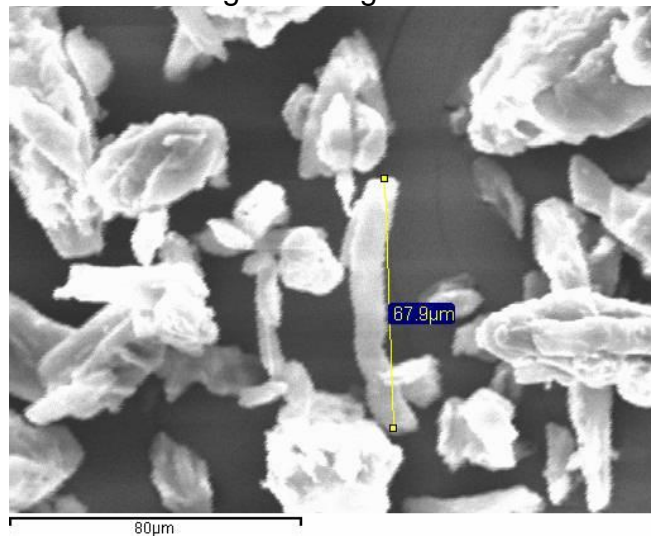
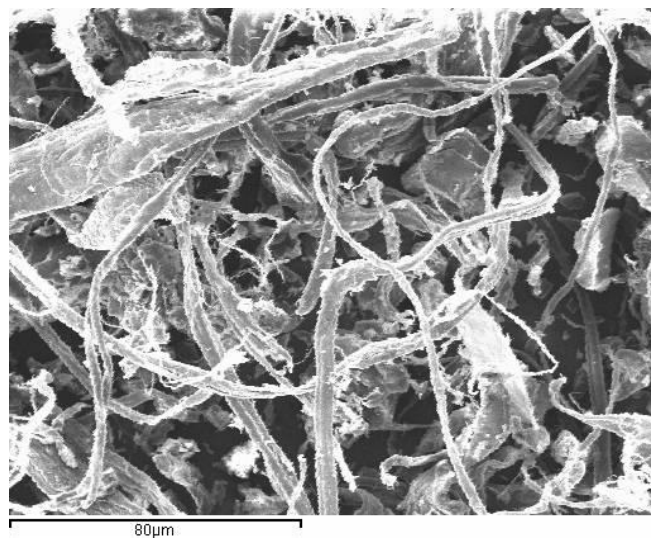Figure 2: Sigmacell

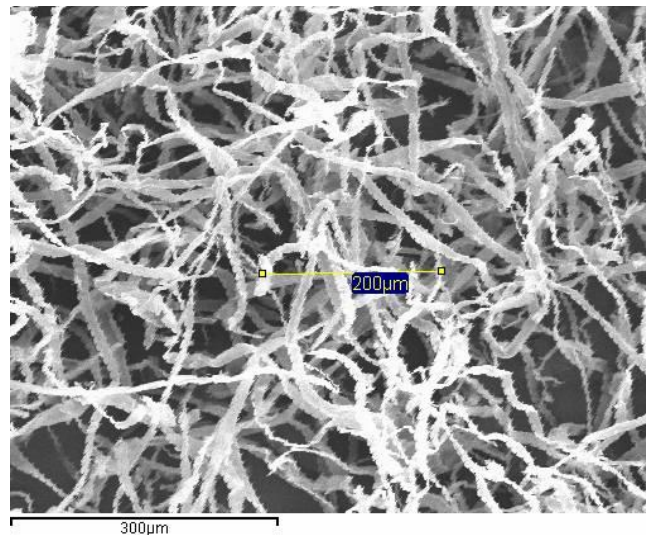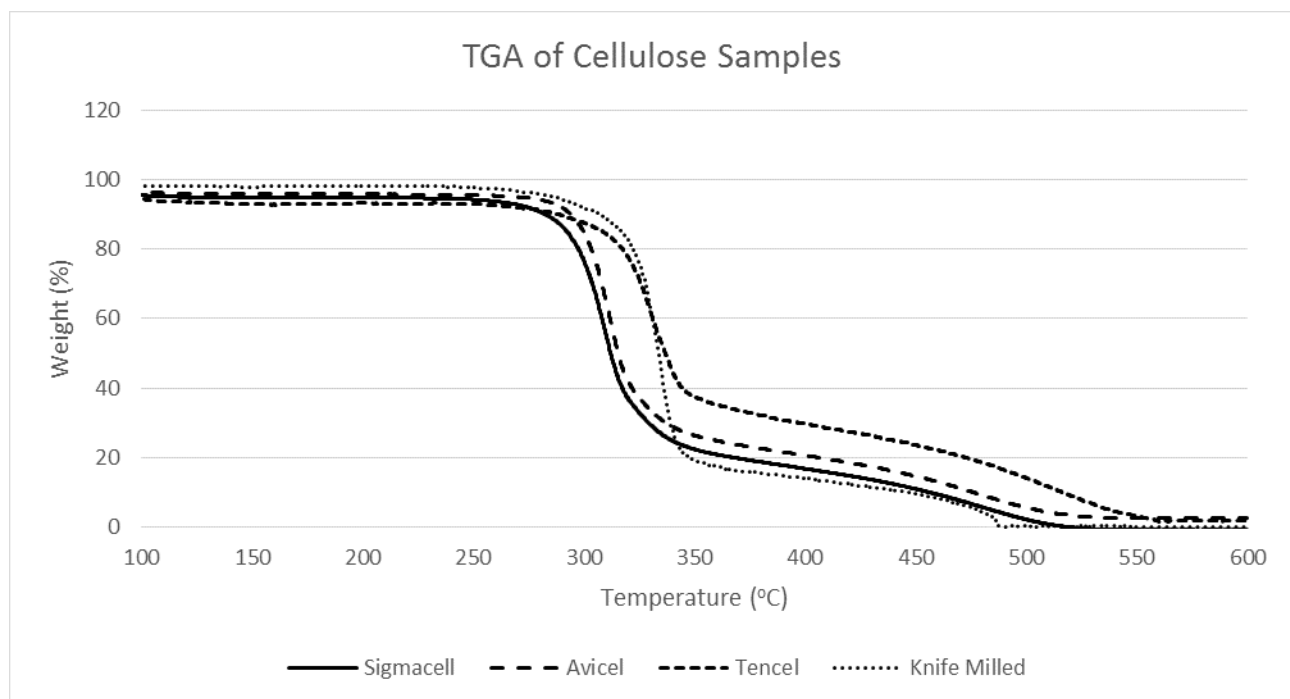Figure 3: Avicel

Figure 4: Tencel

Figure 5: Knife Milled

Figures 2-5 show that although each cellulose is stated at having uniform sizes, within each sample a large variation of sizes can be seen. Each of these celluloses was subjected to a Thermogravimetric test in air from room temperature to 600°C at 5°C/min, the results can be seen in Graph 1.

Graph 1: TGA Results of Cellulose Samples

Using these results from the TGA, a heating profile was determined and will be used for removing the pore formers from the coatings produced.

Coatings were produced on 10 substrates of 25mm by 25mm Alumina tile. The substrates were cleaned using Cuprolite (15 min, 60°C) and sensitized using a tin chloride (15 min, room temperature) and then palladium chloride (15 min, 35°C). A medium phosphorus nickel plating bath (1 hour, 89°C, pH 4.9) with a bath loading of 10g/l of pore former and 50g/l of YSZ was used to produce the co-deposition coatings.

1 of each of the coating sample was then placed into a furnace programed to ramp at 5°C/min to 450°C, dwell for 3 hours then return to room temperature at a speed of 10°C/min. All samples were then cut into 3 sections labeled A, B and C. Section A was set in resin and used to examine the cross section of the coatings before and after the removal of the pore formers. Section B was used to look at the surface structures of the coating produced and section C was used to determine the porosity of the coating using mercury porosimetry.

3. Results

Samples A/B were used to determine the structure of the coating by looking at the cross sections and surface under a SEM. The SEM images showed that after the heat treatment, the surface had more structures such as pore openings and cracks than before heat treatment, an example pore opening can be seen in figure 7.
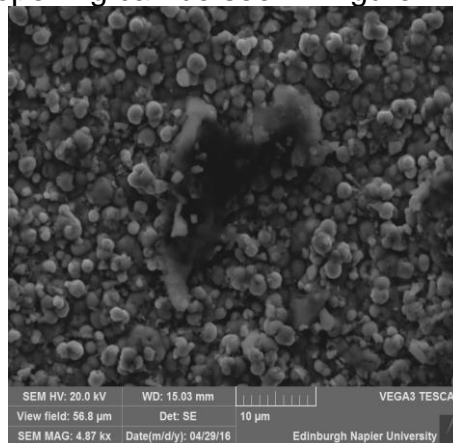

Figure 6: Sample 2B Pore

By using the EDS mapping capabilities of the SEM an carbon map was created of the site shown in Figure 7, this can be seen in Figure 8.
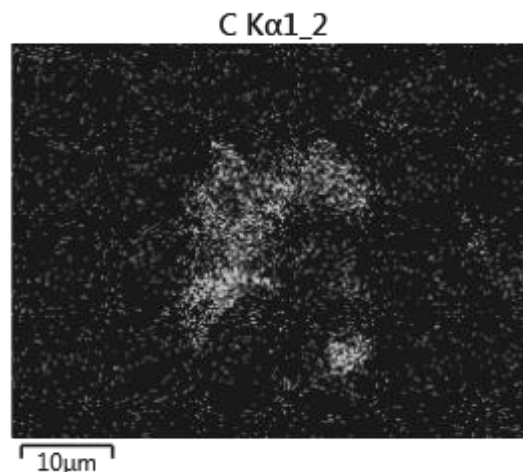

Figure 7: EDS mapping of carbon on Sample 2B Pore

Figure 8 shows there to be a localized peak in carbon around the site of the pore, created by the removal of an incorporated pore former. This meant that peaks in carbon on a mapping of the surface would indicate a pore entrance. Figure 9-12 show the coatings surface after heat treatment under 250x magnification along with an EDS mapping of carbon.
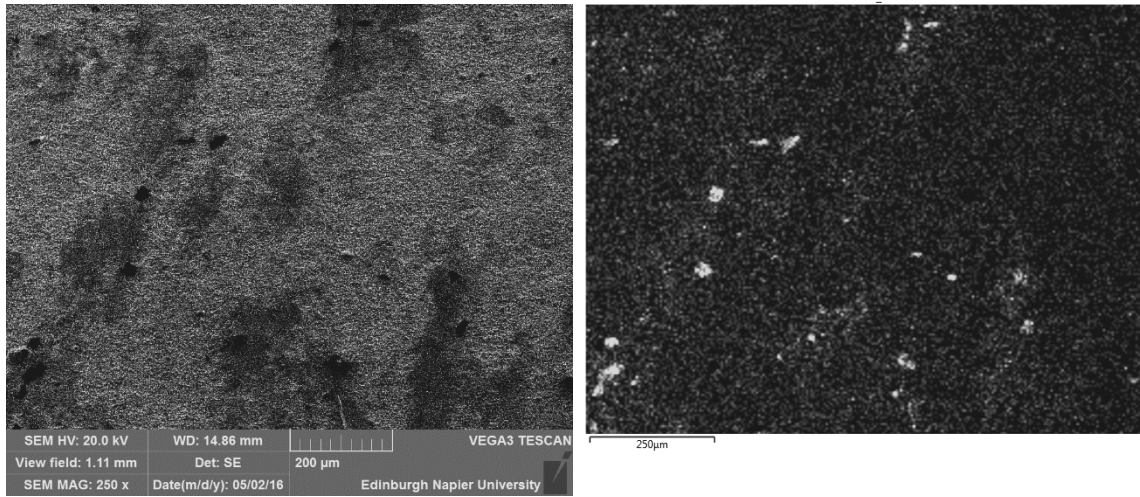
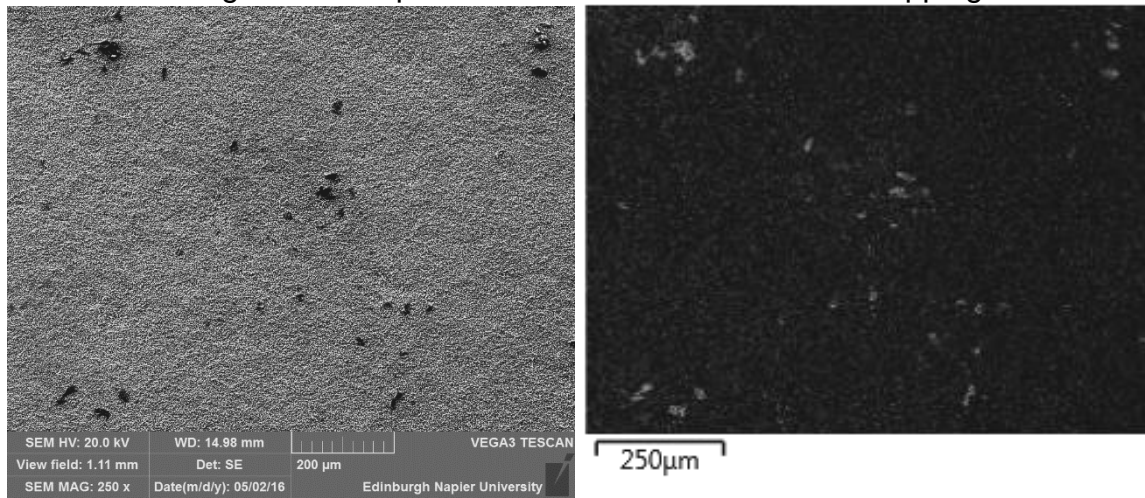Figure 8: Sample 2B surface and EDS Carbon mapping
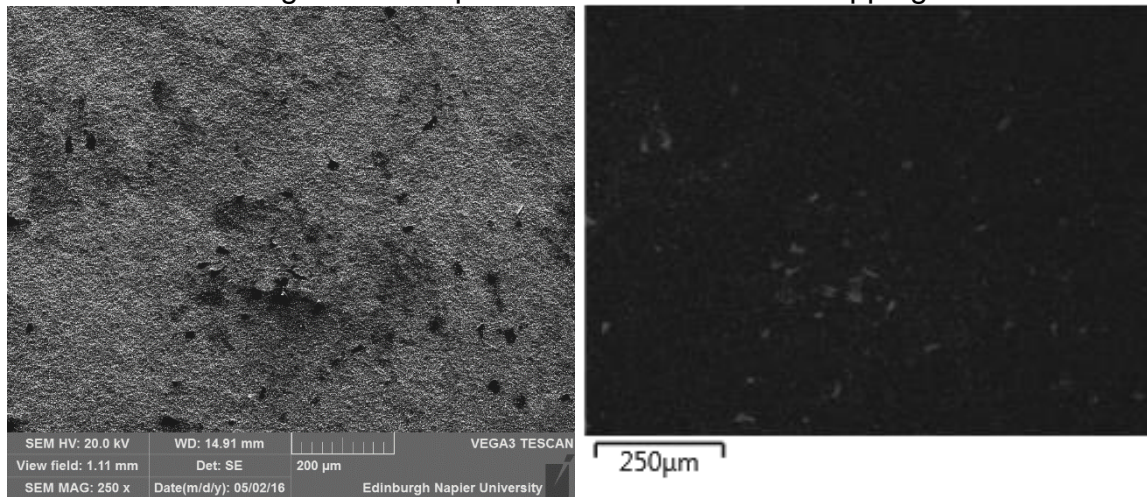

Figure 9: Sample 4B surface and EDS mapping

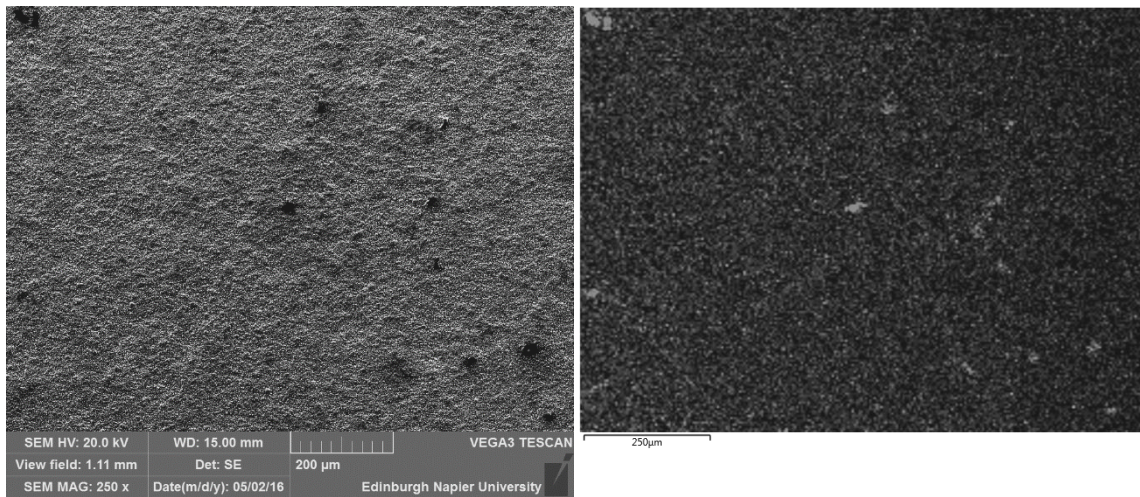Figure 10: Sample 6B surface and EDS mapping

Figure 11: Sample 8B surface and EDS mapping

As can be seen from the figures 9-12, the incorporated pore formers are producing suitable surface structures for the coating. When these are compared with the cross sections of the coatings, it is clear that the smaller particles are producing more porous structures within the coating, this can be seen in figures 13 – 16.
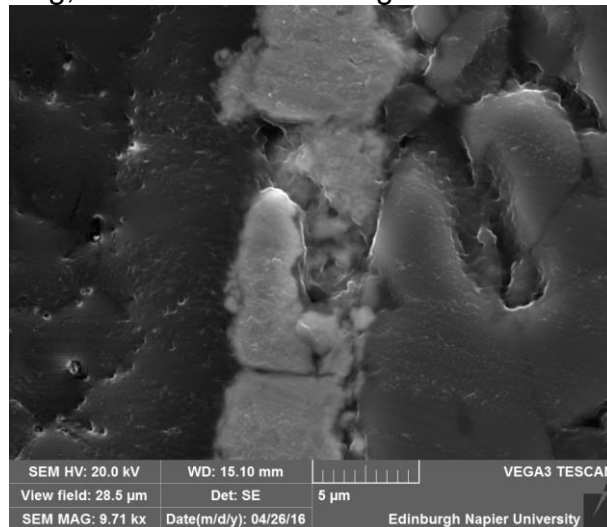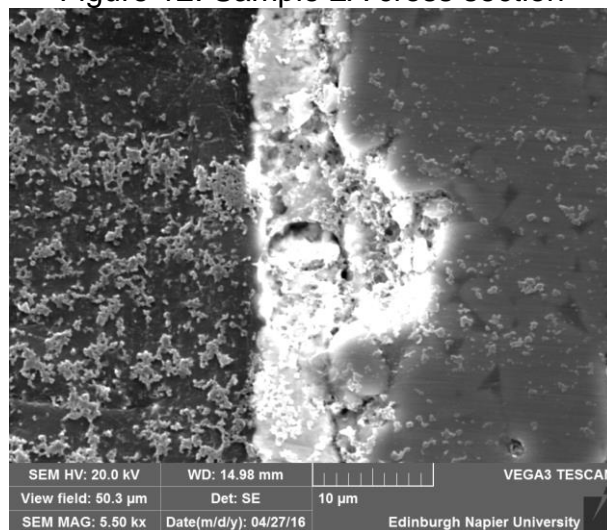

Figure 12: Sample 2A cross section
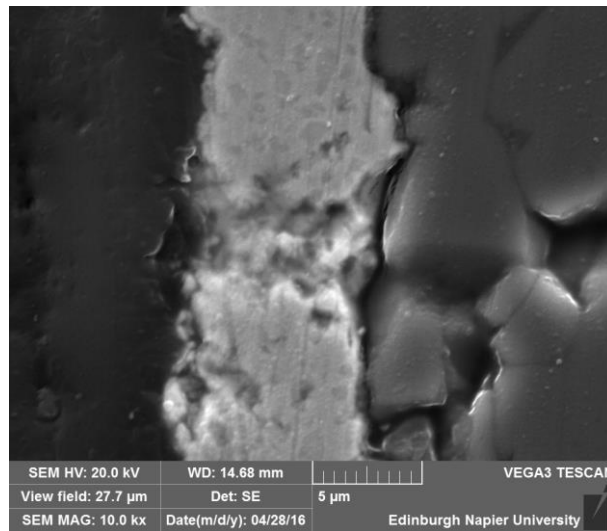

Figure 13: Sample 4A cross section
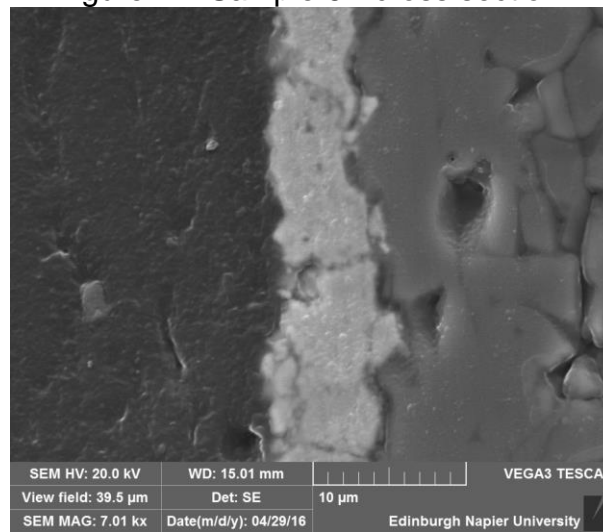
Figure 14: Sample 6A cross section

Figure 15: Sample 8A cross section

Next section C of the samples were tested using a Pascal 240 Series mercury porosimeter, these results are shown in Table 4.

Table 2: Porosimeter Results

Sample ID	Total Pore Volume (mm³/g)	Total Pore Surface Area (mm²/g)	Average Pore Diameter (µm)
Blank Tile	0	0	0
1C	0.99	0.02	0.1967
2C	3.11	0.602	0.0207
3C	0.70	0.015	0.1833
4C	3.72	0.011	1.2962
5C	0.69	0.024	0.1170
6C	0.41	0.006	0.2531
7C	1.24	0.029	0.1686
8C	1.75	0.144	0.0487
9C	0.97	0.055	0.0712
10C	1.07	0.016	0.2650

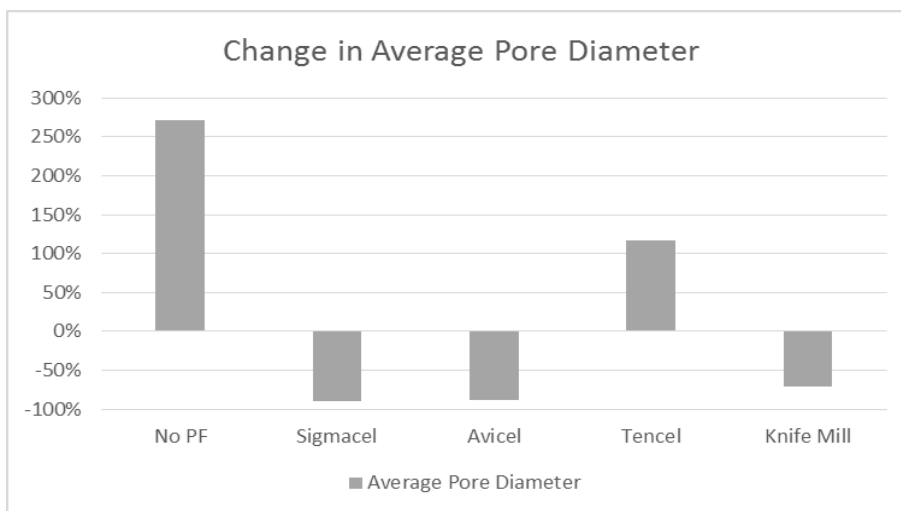The change in porosity due to pyrolysis of the cellulose pore formers are summarized in the graphs 2 – 4.
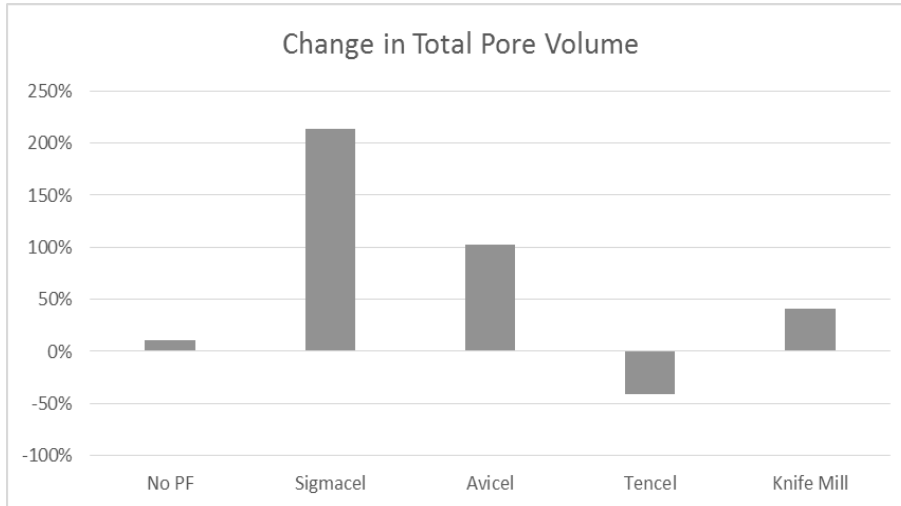
Graph 2: Change in Total Pore Volume
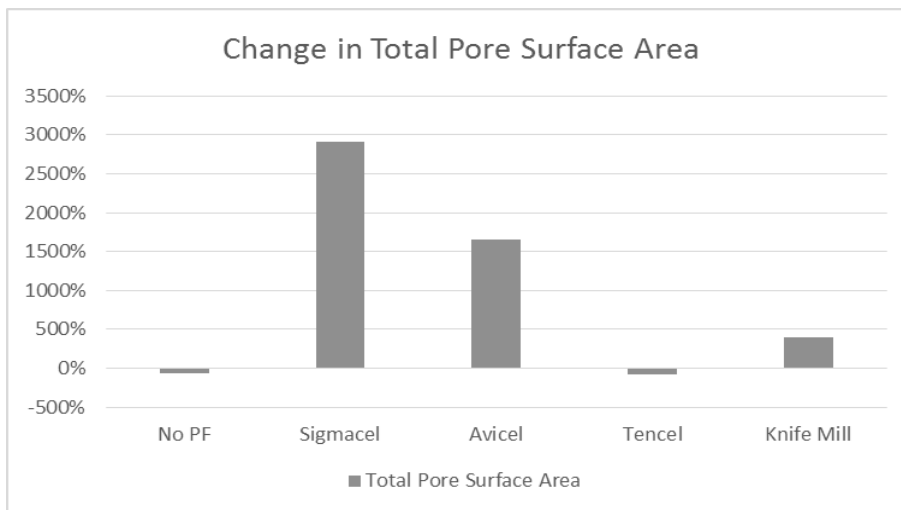
Graph 3: Change in Total Pore Surface Area

Graph 4: Change in Average Pore Diameter

4. Conclusions

The SEM results show that all the pore formers are producing surface structures which should improve the porosity of the coating, with an increase in pore openings on the surface and interconnected porous networks within the coating. However, although all samples had evidence of surface pores openings, these were significantly less in the knife milled (≈200μm) coatings than the smaller, Sigmacell (≈20μm) coatings. This shows that the smaller pore former is more easily incorporated within the coating than the larger one and is therefore producing a more porous coating once removed.

These observations are confirmed by the results of the mercury porosimetry, as the smaller particles having had the most significant impact on the porosity of the coating. Sigmacell (≈20μm) has increased the total pore volume by 214% and the total pore surface area by 2910%. However it has also reduced the average pore diameter by 89% from 0.1967μm to 0.0207μm, this might have a negative impact on a SOFC anode due to the possible reduction in gas permeability. This reduction in pore diameter could be due to densification of the coating once the pore former has been removed by pyrolysis.

These results show there is a strong link between the size of the pore former and the impact on the porosity. As the pore former size has increased, the impact on the total pore volume, total surface area and average pore diameter has decreased. However Tencel (≈100μm) has shown to have had the opposite affect from the rest of the pore formers, decreasing the Total pore volume and pore surface area but increasing the average pore diameter. This could be due to the slower burn out rate allowing less time for densification after it's for removal.

Therefore the smaller cellulose Sigmacell and Avicel are a suitable pore former for use within the ECD production of solid oxide fuel cell anodes. Although effort should be made to reduce their size to encourage greater inclusion within the coating and therefore improve the resultant porosity of the coatings. As Tencel only improved the average pore diameter, if the size could be reduce whilst keeping it morphology then it could show great promise as a pore former for the ECD process.

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