Microstructural Characterisation of Metallurgical Grade Porous Silicon Nanosponge Particles

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**Abstract:** Porous silicon finds numerous applications in the areas of bio-technology, drug delivery, energetic materials and catalysis. Recent studies by Vesta Sciences have led to the development of porous silicon nanosponge particles from metallurgical grade silicon powder through their own patented chemical etching process (Irish patent no. IE20060360). This discovery paves the way for a more economical production method for porous silicon. The work presented here studies the structural morphology of the porous silicon nanosponge particles using high resolution electron microscopy techniques combined with porisometry type measurements where appropriate. The related surface pore structure is examined in detail using Scanning Electron Microscopy and Transmission Electron Microscopy techniques while the internal pore structure is explored using Focused Ion Beam milling and ultramicrotomed cross-sections. Three samples of the silicon particles were analysed for this study which include the starting metallurgical grade silicon powder and two samples that have been chemically etched. Analysis of the etched samples indicates a disordered pore structure with pore diameters ranging up to 15nm on porous silicon particles ranging up to 5µm in size. Crystallographic orientation did not appear to affect the surface pore opening diameter. Internal pore data indicated pore depths of up to 1 µm dependant on the particle size and etching conditions applied.

**Keywords:** Porous Silicon (PS); Metallurgical Grade Silicon (MGS); Nanoporous Silicon; Nanosponge; Porous Structure; Scanning Electron Microscopy (SEM); Transmission Electron Microscopy (TEM); Focused Ion Beam (FIB).
1. Introduction

Porous Silicon (PS), a unique derivative of the chemical element silicon (Si), is a sponge-like structure that is formed when bulk Si is etched either chemically or electrochemically in hydrofluoric acid (HF) based solutions [1-4]. The material was originally discovered back in the 1950’s, but it wasn’t until 1990 that Canham made the discovery of its room temperature photoluminescence resulting from quantum confinement effects [1-3]. Since then, subsequent research followed focusing on developing possible PS applications in such areas as microelectronics, optoelectronics, chemical and biological sensors [4]. Mesoporous and nanoporous Si are currently being investigated for drug delivery applications [4-5]. Nanoporous Si has also recently been investigated for applications as an energetic material [6-7]. Energetic materials are an important component of military defence systems and since metallurgical grade PS is relatively inexpensive, successful characterisation and tailoring of the material could prove critical for new applications development in this field and many others.

Successful characterisation of PS involves using a host of analytical techniques including Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) to determine critical aspects such as particle size, pore size and pore volume which have been deemed essential factors in tailoring the material for energetic and also bioactive applications [6,8]. While much research has been focused on characterising electro-chemically produced PS from Si wafers [9-12] little has been published on characterising the resulting pore structures and porosity of chemically etched Si particles. This is due to the ease at which pore structures in Si wafers can be achieved and tailored through electro-chemical etching [13] and the microscopical analysis and characterisation of the resultant material has been well documented [14]. Progress in analysing ordered pore structures within porous materials in general has proved positive over the years, yet characterising disordered pore structures or pore networks proves to be a much greater challenge [15].

A method commonly used for producing PS particles is through electrochemically etching Si substrates (N-type or P-type) and ultrasonically agitating them to produce PS particles with ordered pore structures [5]. Another comprises grinding and ball milling Si substrates into a powder and then etching the material to induce porosity [16]. Chemically etching Si particles to form PS particles with disordered pore structures is a much cheaper and easier production method. However, information concerning pore depth and pore network development as a result of the chemical etching process applied is still not fully understood and given the general disordered nature of the pores, it proves more difficult to fully characterise the material.

Vesta Sciences have developed a process for producing low cost PS from Metallurgical Grade Silicon (MGS) powders through a patented chemical etching process [17-18]. This paper is focused on characterising
this MGS powder and the PS produced from it. The particles are studied extensively using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) to examine the particle structure and related pore size and pore volume. The pore orientation is studied in reference to crystallographic orientation. The structure and depth of the pores within the PS particles is also examined using Focused Ion Beam milling (FIB) and ultramicrotomed cross-sections.
2. Experimental Details

2.1 Porous Silicon Preparation

The MGS powder is supplied from Vesta Ceramics (Sweden) which is sold under the trademark of Sicomill™. The powder initially has a particle size of about 1-3mm before being jet milled. The milled particles are then separated and the particles ranging up to about 4µm in size are isolated. PS nanosponge particles are then prepared by chemically etching the isolated MGS particles using a patented etching process carried out by Vesta Sciences [17-18]. The particles are chemically etched in a nitric-acid (NO$_3$) - (HF) based mixture as described by Farrell et al [17] which induces the porosity within the MGS particles. The composition of the chemical etchant is of HF:HNO$_3$:H$_2$O at a ratio ranging from about 4:1:20 to about 2:1:10 by weight [17]. When the etching process is complete (i.e. photoluminescence is observed), the etched powder is removed from the acid bath and dried in perfluoroalkoxy (PFA) trays at 80°C for 24 hours. The result is the creation of PS nanosponge particles where each particle comprises a plurality of nanocrystals with pores then disposed between the nanocrystals and throughout the entire nanosponge particle [17]. By varying the nitric acid concentration in the etchant mixture the surface area of these powders can also be tailored [17-18]. Three samples of MGS powders are analysed in this paper which are as follows (‘2E’ refers to the specific grade of material):

1) 2E-Bulk – The starting MGS powder used to make the PS particles

2) 2E-100 – PS powder manufactured from the 2E-Bulk powder after chemically etching for 100% of the required etching time (100% etching time is defined as the point when the sample exhibits photoluminescence with an ultraviolet light [18])

3) 2E-60 – As for (2) but only chemically etched for 60% of the required etching time

Trace levels of impurities, found to be unattainable through SEM-EDS and XPS analysis, exist within the 2E-Bulk MGS powder as determined through XRF and ICP analysis [18-19]. These impurities consist mainly of Iron (Fe), Calcium (Ca) and Aluminium (Al) with smaller amounts of Carbon (C) and Oxygen (O) and lead to preferential etching relative to the etching rate of Si [18]. These impurities are discussed further in the remaining sections.
2.2 Microscopy Analysis

A JEOL JSM-840 SEM equipped with a Princeton Gamma Tech EDX system was used to obtain secondary electron images of the sample surface and EDX spectra were obtained at 20kV, using a beam current of 0.26nA. For high resolution SEM analysis the PS samples were spread onto a silver conducting paint on a 15mm aluminium stub and loaded into the Hitachi SU-70 scanning electron microscope. The SEM was operated at 3.0kv with a sample working distance of 3.6mm.

TEM specimens were prepared by loading the PS particles onto Formvar-backed carbon-coated copper grids (Agar Scientific, Stanstead, England). TEM analysis was then performed using a JEOL JEM 2100F Field Emission Electron Microscope equipped with an EDX Genesis XM 4 system 60 Energy Dispersive Spectroscopy and operated at 200kV. TEM images were recorded with a Gatan Ultrascan 1000 digital camera for standard TEM imaging modes. The TEM is also equipped with a Secondary Electron Imaging (SEI) detector which allows SEM type images to be recorded on the TEM.

To obtain the porosity of the PS material a Micromeritics ASAP 2010 system was used to measure nitrogen gas adsorption/desorption isotherms at 77K. The samples were degassed by heating under vacuum at 393K for 12 hours. The pore size data was analysed by the thermodynamics-based Barrett-Joyner-Halenda (BJH) [20] method on the desorption branch of the N\textsubscript{2} isotherm [18].

PS particle sectioning was undertaken using a FEI FIB 200 workstation operating at an accelerating voltage of 30 keV. Cross-sections through the particles were prepared for TEM by ultramicrotomy. PS particles were first embedded in BEEM™ capsules using the low viscosity UltraBed Embedding Kit™ from Electron Microscopy Sciences (EMS), USA. The blocks were cured overnight at 60°C in an oven and sectioned using a Leica Ultra-cut UCT Ultramicrotome at the Imaging and Analysis Center, Princeton University, USA. The thin sections were floated onto lacey carbon coated copper mesh grids from EMS, USA for examination with TEM.

3. Experimental Results

3.1 Particle Characterization – Size & Composition Analysis

The particle morphology was studied from a series of SEM images, obtained using the JEOL JSM-840 and a Hitachi SU 70. Two-hundred particles were studied at several different magnifications for each of the three samples. The SEM image in Fig. 1 shows a representative image of the 2E-Bulk sample with the particle size results given in Table 1. The standard deviation per sample is relatively high at approximately 30% of the
determined particle size due to the variability in particle shape in this friable material. A particle size distribution was also established per sample as indicated in Fig. 1b.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>SEM Particle size (µm)</th>
<th>Particle size distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>2E-100</td>
<td>4.51 ± 1.29</td>
<td>4.2µm - 4.5µm</td>
</tr>
<tr>
<td>2E-60</td>
<td>4.75 ± 1.35</td>
<td>4.2µm</td>
</tr>
<tr>
<td>2E-Bulk</td>
<td>4.80 ± 1.58</td>
<td>4.5µm</td>
</tr>
</tbody>
</table>

X-ray diffraction analysis indicated that the three samples analysed are crystalline with a standard Si lattice parameter, and electron diffraction studies in TEM of the PS samples deposited onto carbon coated copper grids indicated that each individual particle is a single crystal.

Fig. 1 SEM micrograph of the MGS particles in sample 2E-Bulk and the corresponding particle size distribution

SEM-EDS analysis on the 2E-100 and 2E-60 samples indicated the presence of Si and C while the XPS analysis showed Fluorine (F), O, C and Si signals. For XPS, the respective elemental peaks indicated percentage concentrations of F at 2%, C at 29%, Si at 60%, and O at 9% for 2E-100. The presence of F occurred due to the etching process, while the large amount of C is due to the presence of organics on the surface of the powder. The O content indicates the presence of the native surface silicon oxide. XPS is more surface sensitive than EDS and hence has resulted in the much larger portion of C observed. Similar results were obtained for the remaining samples 2E-60 and 2E-Bulk as previously indicated [21], but the trace elements [18-19] that exist in the materials were not detected due to the detection limits of the XPS and EDS measurement systems used.

3.2 PS Pore Characterization - SEM analysis

The images in Fig. 2 represent samples 2E-100, 2E-60 and 2E-Bulk and were obtained using high resolution scanning electron microscopy. The dispersion of pores on the surface of the PS particles in samples 2E-100 and 2E-60 is clearly visible. Sample 2E-100 displays a high surface porosity with the surface pores coalescing in some cases. In sample 2E-60 however, the pores edges are more defined and the pores appear slightly more spaced out than in 2E-100. Measurement of the pore opening diameters from the SEM images indicated that the 60% etched sample had a pore opening diameter of ~10.1±2.1nm and the 100% sample had a diameter of 9.8±2.6nm. Comparison of these results with porisometry and theoretical calculations in undertake in the
discussion section (Section 4.3). As indicated in Fig. 2, the solid unetched surface for the sample 2E-Bulk is quite evident in comparison to the porous surfaces of samples 2E-100 and 2E-60.

Fig. 2 SEM images of selected particles in samples 2E-100, 2E-60 and 2E-Bulk

3.3 PS Pore Characterization - Porosimetry & FIB SEM analysis

The Brunauer, Emmett and Teller (BET) [22] surface area and porosimetry analysis were measured by nitrogen gas adsorption in a Micromeritics Gemini V gas adsorption analyzer (Vesta Sciences). The results were then compared to results obtained from a Micromeritics ASAP 2010 system. The pore size distribution and pore volume were estimated using the Barrett-Joyner-Halenda (BJH) [20] scheme. The results of this analysis are indicated in Table 2. The surface pore volume for 2E-100 is calculated to be over twice that of 2E-60. Sample 2E-60 which is 60% chemically etched, appears to have a larger average pore size than the fully etched sample. This is likely due to the fact that the holes in the 60% etched sample are shallower, and given that the ASAP technique calculates an average diameter, the pore size appears larger.

<table>
<thead>
<tr>
<th></th>
<th>% Etched</th>
<th>Brunauer, Emmett and Teller (BET) Surface Area (m²/g)</th>
<th>ASAP – Pore Volume (cm³/g)</th>
<th>ASAP – Pore Size (nm)</th>
<th>FIB/SEM Pore Depth (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2E-100</td>
<td>100%</td>
<td>103</td>
<td>0.28</td>
<td>8</td>
<td>~1000</td>
</tr>
<tr>
<td>2E-60</td>
<td>60%</td>
<td>34</td>
<td>0.11</td>
<td>9.6</td>
<td>~600</td>
</tr>
</tbody>
</table>

*All results were obtained by Vesta Research & UL.

The calculation of the thickness of the porous layer or average pore depth within the PS particles was much more difficult to achieve. Pore size and pore depth are very much dependant on the etching conditions and parameters applied to the solid MGS material to achieve a final porous state.

To further examine the porous layer, both external and internal pore structure and obtain pore depth information, the PS particles have been fractured and also explored using a combination of FIB and TEM analysis.

Fig. 3 SEM images of PS particles sectioned using Focussed Ion Beam milling for samples 2E-100 and 2E-60

FIB milling was performed on twenty isolated PS particles from samples 2E-100 and another twenty particles from sample 2E-60. The images in Fig. 3 show selected PS particles from both these samples. The particles
were coated with Pt prior to milling which appears as the brighter region observed around the particles. In both etched samples the porous region is evident at the outermost region of the PS particle. No pore channels or networks appear to exist in the core of the PS particles analysed. Careful analysis of each of the particles from both samples suggests that the smaller the PS particle is, the more likely it is to be porous all the way through. The 2E-60 PS particles observed show an etched region to a depth of 600nm beneath the surface and approximately 1000nm for the 2E-100 sample. In all of the particles analysed after FIB sectioning, the pores observed had a circular or slightly elliptical shape with no channelling observed indicating the random nature of the pore structure beneath the surface.

In an attempt to observe the pore network beneath the surface of the PS particles, samples were crushed with a mortar and pestle and analysed with SEM are shown in Fig. 4 for sample 2E-100. The results indicate an interconnected pore network which exists beneath the surface of the PS particles. In keeping with other observations from this study, the pores observed are numerous and randomly oriented. The size of the pore channels range from 7-12nm which also corresponds well to the average pore size results achieved in Table 2 of 8nm for 2E-100 and 9.6nm for 2E-60.

**Fig. 4 SEM images of fractured particles from sample 2E-100 prepared using a mortar and pestle**

### 3.4 PS Pore Characterization - TEM Ultramicrotomy

Further analysis of the internal PS structure was carried out using TEM analysis of ultramicrotomed sections for morphological analysis [23-24]. BF-TEM analysis was carried out on numerous particles in samples 2E-100 and 2E-60 sectioned using an ultramicrotome with representative images shown in Fig. 5. The lighter contrasted areas in the images indicate that the material is porous which mainly exists in the outer region of the particles as indicated by the white hatched lines. Sample 2E-100 shows a greater majority of porous areas throughout the sectioned particle. The pore depth was found to be larger on the 2E-100 particles which support the previous results from the FIB sectioned particles.

### 3.5 PS Pore Characterization - TEM Pore Orientation & SEI

To determine if the pores present in these PS particles are related to crystallographic orientation, TEM analysis was undertaken whereby individual particles from the as-received etched material were orientated to primary zone axes and SEI images were recorded. Fig. 6 shows SEI images of sample 2E-100 oriented to (a) [100] and (b) [111] zone axes and also shows the corresponding images for sample 2E-60. For sample 2E-100, the images
indicate that the pores when viewed along [100] are larger than those observed on [111] and have begun to coalesce. However, this observation is not found routinely and is not observed on sample 2E-60 shown in Fig. 6b, indicating that crystallographic orientation does not appear to influence pore geometry. Further analysis of the samples using BF-TEM imaging, shows that in all cases the outer region of the PS particles for samples 2E-100 and 2E-60 is both electron transparent and porous. It is evident, that the SEI images are easier to interpret than the BF-TEM images as the SEI images give surface information, while the TEM images are given for the entire thickness. Therefore, when the pores are not orientated parallel to the beam or in the case of disordered pore networks, the TEM images are confusing.

Fig. 6 SEI images recorded on TEM for PS samples 2E-100 and 2E-60 recorded on (a) [100] and (b) [111] zone axes

4. Discussion

4.1 Review of etching methods applied to Silicon

The two most commonly applied methods to achieve PS formation are electro-chemical etching and chemical etching of Si in HF based solutions [25-27]. The formation of a porous layer structure through chemical etching or stain etching is also achieved by application of impurities onto the Si surface [28-33].

The MGS powder in this study contains trace levels of impurities such as Fe, Al, Ca, C and O [18] which results from the smelting and grinding manufacturing process used [18] and can be found heavily deposited at the grain boundaries of the material [19]. During the etching process, these impurities react with the nitric and hydrofluoric acid mixture causing hole initiation and porous silicon formation at the particle surfaces [18] as also described for other chemical etching techniques used with Si [28-33].

4.2 Pore geometry

From the electron microscopy analysis (section 3.2, 3.6) it is observed that once a pore forms at the surface and pore propagation is achieved through chemical etching, then the pore branches into several different directions. The analysis presented here corresponds with previous evidence that the surface pore orientation is random in nature and that crystallographic orientation does not influence pore geometry. Electron microscopy indicates the type of pores observed at the particle surface corresponds with the ‘interconnected or branched’ pores as schematically drawn in Fig 7c after Canham [14]. From observation of numerous TEM images, it is observed that the majority of the pores become interconnected or branched after the pore forms at the surface. This pore interconnectivity occurs around the surface bound porous layer of the material as previously observed in section 3.3 (Fig 4).
Measuring the depth of etching for this material is not an exact science, as in both the FIB and ultramicrotomed sections, it is difficult to know how far the area analysed was from the surface as it is only possible to analyse cross-sections. However, combined FIB and ultramicrotomy techniques with SEM and TEM analysis show porosity at the outermost regions of PS particles with a solid core. In the case of sample 2E-100 this interconnected porous layer was found to be about 1000nm deep, thus allowing interconnected porosity to that depth. This phenomenon is also observed for sample 2E-60 but to a lesser depth of about 600nm and with less surface pore coalescence.

In a TEM tilt series undertaken for this study and further SEM analysis PS particles, it is observed that smaller PS particles of up to 1µm in size can be porous throughout yet the larger particles contain a porous outer shell and a solid core. This corresponds to the relative etching conditions applied to this material given the position and presence of the impurities necessary to cause pore formation [19].

Fig. 7 Schematic indicating the types of pores that form as outlined originally by Canham [14]. Types of pores: (a, b) blind, dead-end or 'saccate', (c) interconnected or branched, (d) totally isolated or 'closed', (e) 'through' pores

### 4.3 Pore volume and surface area

The ASAP results show smaller pore diameters than the electron microscopy studies due to the presence of an oxide around the pores which is not observed in the electron microscope. Also, in gas adsorption, the results are obtained from averaging over a large range of pore sizes, whereas in the SEM they are calculated from surface pores only, which are likely to be larger.

To compare the porosimetry and electron microscopy measurements some theoretical calculations have been undertaken. The measurements of the pore size (pore opening diameter) were taken from 450 surface pores in both samples using numerous SEM images and image analysis software, the results of which are shown below in Table 3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Particle Size(^a) (µm)</th>
<th>Core Size(^b) (µm)</th>
<th>Pore Surface(^c) Area (m(^2)/g)</th>
<th>Pore Volume(^c) (cm(^3)/g)</th>
<th>Pore Volume(^c) %</th>
<th>Pore Size(^d) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2E-100</td>
<td>4.51</td>
<td>2.5</td>
<td>152</td>
<td>0.3</td>
<td>50.0</td>
<td>9.8±2.6</td>
</tr>
<tr>
<td>2E-60</td>
<td>4.75</td>
<td>3.6</td>
<td>54</td>
<td>0.11</td>
<td>35.0</td>
<td>10.1±2.1</td>
</tr>
</tbody>
</table>

\(^a\) – From SEM analysis (Fig. 1)

\(^b\) – From SEM analysis of FIB sections and TEM analysis of ultramicrotomed sections (Fig. 3 and Fig. 5)

\(^c\) – Theoretically calculated from experimental results

\(^d\) – Pore opening diameter measured from SEM micrographs (Fig. 2)

For the fully etched sample the average particle size was found to be 4.51µm. For a simple theoretical calculation, the assumption is made that the powder consists of 4.51µm diameter spherical particles (Table 1),
containing a 2.5µm diameter core with a material density of 2.33 g/cm³ for silicon. Further making the assumption that the porous region consists of about 50% by volume ratio of porous to solid material, then a theoretical pore volume of 0.30 cm³/g is calculated. This compares well with the ASAP value of 0.28 cm³/g in Table 2.

Repeating this calculation for the 60% etched sample and assuming a 35% by volume porous surface shell to a depth of 600nm, a theoretical pore volume of 0.11 cm³/g is estimated, comparing well to ASAP of 0.11 cm³/g (Table 2).

Continuing with these calculations for an estimate of the surface area per unit weight, and assuming a pore opening diameter of 9.8nm for the fully etched sample (as determined through SEM measurements – Table 3), with a pore depth of 1µm (section 4.2) and an average pore diameter of 8nm (from ASAP), a theoretical surface area of 152 m²/g is calculated. While this is higher than the 103 m²/g calculated experimentally with ASAP, adjusting the pore opening diameter to 12.4nm by taking into account the standard deviation from the SEM pore opening diameter measurements, a surface area of 102.5 m²/g is calculated which is close match to the ASAP results.

Similar calculations for 60% etched sample (pore opening = 10.1nm; depth = 600nm; average pore diameter = 9.6nm) gives a surface area of 54 m²/g comparing well to 34 m²/g from ASAP. As for the fully etched sample, adding the standard deviation from the SEM pore size measurements to give an average pore opening diameter of 12.2nm results in a calculation of 37.4 m²/g. This theoretical calculation assumes that the pores are “blind” or “through” pores as described in Fig. 7b and 7e, while in fact they are interconnected and branched. In conclusion, it is possible to estimate that percentage porosity of the porous region is approximately 50% of the volume for the fully etched sample, while it is approximately 35% for the 2E-60 sample. Analysis of the SEM images described in section 3.2 and shown in Fig. 2, confirm these estimates.

5. Conclusions

The porous silicon (PS) analysed in this study comprises of metallurgical grade silicon particles with a disordered pore structure. The combined results of TEM, SEM, FIB and ASAP analysis on these materials indicates that:

- Individual PS particles contain a porous sponge-like boundary up to 1µm thick with a solid central core. Therefore, for the fully etched condition, particles with maximum dimensions smaller than 2µm are found to be porous throughout.
• The porous structure was found to be disordered with an interconnected or branched structure. No relationship exists between crystallographic orientation and pore growth direction.
• The porous material remains crystalline with a lattice constant that corresponds to pure Si as determined by x-ray diffraction and electron diffraction analysis.
• The 2E-100 samples consist of a porous surface region that contains approximately 50% volume ratio of pores to Si. The 2E-60 sample contains approximately 35% volume ratio of pores in this porous region.

Acknowledgements
The Authors would like to acknowledge the financial support of Enterprise Ireland, Vesta Sciences (EI IP 2007 0380 Vesta/ UL) and PRTLI cycle 4. The support of Vesta Sciences and Dr Shanti Subramanian for providing PS samples, ASAP results and ultramicrotomed sections for TEM analysis. The authors would also like to thank Margaret Carey, Paula Olsthoorn, Gaye Hanrahan, Calum Dickinson, Wynette Redington, Fathima Laffir, Colm O’ Dwyer and Shohei Nakahara for analytical results and useful discussion.

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Fig. 7 3-D model developed using solid-works software indicating the types of pores that form as outlined originally by Canham [14]. Types of pores: (a, b) blind, dead-end or 'saccate', (c) interconnected or branched, (d) totally isolated or 'closed', (e) 'through' pores.

References:

13. Pap AE (2005) Investigation of pristine and oxidised porous silicon. PhD, University of Oulu, Finland, Oulu
Table 1 Particle size and distribution determined from SEM analysis

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>2E-100</th>
<th>2E-60</th>
<th>2E-Bulk</th>
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<tr>
<td>SEM Particle size (µm)</td>
<td>4.51 ± 1.29</td>
<td>4.75 ± 1.35</td>
<td>4.80 ± 1.58</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td>4.2µm - 4.5µm</td>
<td>4.2µm</td>
<td>4.5µm</td>
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Table 2 Pore geometry analysis obtained from Accelerated Surface Area and Porosimetry (ASAP) measurements and Scanning Electron Microscopy (SEM) studies of Focussed Ion Beam (FIB) sectioned particles

<table>
<thead>
<tr>
<th>% Etched</th>
<th>Brunauer, Emmett and Teller (BET) Surface Area (m²/g)</th>
<th>ASAP – Pore Volume (cm³/g)</th>
<th>ASAP – Pore Size (nm)</th>
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Table 3 Estimated pore geometry using SEM measurements and theoretical calculations

<table>
<thead>
<tr>
<th>Samples</th>
<th>Particle Size (µm)</th>
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<th>Pore Surface Area (m²/g)</th>
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</tr>
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</table>

\[a\] – From SEM analysis (Fig. 1)
\[b\] – From SEM analysis of FIB sections and TEM analysis of ultramicrotomed sections (Fig. 3 and Fig. 5)
\[c\] – Theoretically calculated from experimental results
\[d\] – Pore opening diameter measured from SEM micrographs (Fig. 2)
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Fig. 5 BF TEM images of Ultramicrotomed a) 2E-60 and b) 2E-100 PS sample. Dashed line indicates the boundary between the etched and unetched region.
Fig. 6 SEI images recorded on TEM for PS samples 2E-100 and 2E-60 recorded on (a) [100] and (b) [111] zone axes
Fig. 7 Schematic indicating the types of pores that form as outlined originally by Canham [14]. Types of pores: (a, b) blind, dead-end or 'saccate', (c) interconnected or branched, (d) totally isolated or 'closed', (e) 'through' pores.