SYNTHESIS AND ELECTROPHORETIC DEPOSITION OF
TIN OXIDE (SnO₂)

A Thesis
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ABSTRACT

Submicron tin oxide (SnCh) was obtained from thermal decomposition of tin oxalate (SnC2C>4) precipitated at room temperature from a mixture of solutions of tin (II) chloride (SnC^) and oxalic acid (H2C2O4).

Aqueous precipitation of SnC204 was firstly investigated. Variation of synthesis parameters included starting material concentrations, addition methods and mixing times. This resulted in the formation of SnC204 particles with different morphologies, namely subangular equiaxed and elongated prisms. Occasional intergrowths and secondary nuclei were also seen. Upon calcination, SnC>2 powder was observed to be tacky and subsequent grinding was found to cause nanosized SnC>2 particles to agglomerate into variable sized plates. However, the particle size and morphology of the SnC>2 powders were found to have no obvious correlation with the SnC2C>4 precipitation conditions.

Aqueous-alcohol precipitation was developed, based on the previously conducted aqueous precipitation. SnC2C>4 of elongated prismatic morphology was precipitated, but, the SnC>2 obtained was different from that obtained from aqueous precipitation in that it consisted of smaller nanosized Sn02 particles (upon calcination of larger SnC2C>4) and platy agglomerate formation was avoided (avoidance of grinding procedure).

From both of the precipitation methods, it was inferred that the prismatic morphology was the preferred form of SnC204. SnC204 formation was also found to be influenced by overall concentrations in the precipitating system, which affected the ionic collision frequency and diffusion distance, resulting in variable SnC204 particle sizes and morphologies.

The tackiness of the SnC>2 powder led to further investigation of Sn02 powder constituents, which then revealed that they were contaminated with alkali impurities, which initially were present in the distilled water. Although an extended leaching procedure was not found to be successful, a processing window of 1 hour for SnC>2 was observed.
Stabilisation of SnO2 suspensions was found to be better in aqueous media rather than non-aqueous (alcohols and ketones), as determined by zeta potential analysis and sedimentation tests. A detailed concept of the effects of zeta potential and sedimentation (includes enhanced sedimentation region (ESR)) on colloidal processing, i.e., suspension stability, was introduced. Suspension stability (using electrostatic stabilisation) was categorised into three relative types on the basis of factors including surface charge density on particles and particle-particle bridging and interactions.

Two systems, Sn-Al-O and Sn-Si-O, were investigated at their invariant temperatures and the ternary phase diagrams, which have not been reported elsewhere, were then constructed (at nine isothermal temperatures for each). Also, the binary diagram for the system Sn02-Si02, which has not been reported in the literature, was constructed. The systems compatibilities were confirmed experimentally at 1000°C, with the incidental finding that micron-sized fibres of single crystal SnC with preferential [110] growth direction were obtained. It was also deduced that 1000°C can be used for the sintering of SnO2 coatings without undesired reaction or mutual solubility.

Successful electrophoretic deposition (EPD) of commercial SnO2 powder on dense sapphire (0001) was obtained by the use of pH 2 SnO2 suspension, but not with pH 9 suspensions (as expected); this led to a review of the basis for EPD requirements in terms of suspension properties. Thus, another conceptual approach to EPD processing and setup was proposed in terms of zeta potential, suspension stability and net particle charge. The obtained homogeneous deposition of commercial SnO2 powders contradicted the findings of the only published works of EPD on insulating dense substrates. Based on discussion and comparison, the critical factors in the design of EPD processing on dense insulating substrates and the associated mechanisms (based on conductivity) responsible for the deposition were developed.

However, the EPD of synthesised SnO2 powders yielded inhomogeneous coatings, even with voltage application of up to 30 V. Microcell effects, which were deduced based on localised particle leaching in the suspension, were proposed. Although the deposition was relatively unsuccessful, this condition demonstrated the possibility of aqueous EPD with the usage of high voltages without the occurrence of water electrolysis (typically at 4 V), which has not been observed in the published literature.
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CHAPTER 1 INTRODUCTION

Tin oxide (SnO₂) or cassiterite is the main ore of tin which has been used in many applications [1]. The applications mostly require SnO₂ to be incorporated in the form of either thick or thin film, with the latter more popular. Examples of thin film SnO₂ applications include gas sensors for gases such as liquefied petroleum gas (LPG), carbon monoxide (CO), hydrogen sulphide (H₂S), methane (CH₄) and nitrogen oxide (NO₂) [2-6]; transparent films to strengthen glassware; transparent coatings and conductive coatings [7]. The most attractive application of SnO₂ which is as thin film of microgas sensors is due to its sensitiveness towards even small concentrations of toxic gas and humidity in very short response time.

Fabrication of SnO₂ into thin films has been investigated by means of conventional deposition techniques such as spray pyrolysis [8], evaporation [9], chemical deposition (CVD) [10], physical vapour deposition (PVD) [11], electrodeposition [12] and dip coating [6]. Techniques such as sputtering, spraying, evaporation, CVD and PVD are known to be expensive due to sophisticated equipment and controlled environment requirements. Cost-effective coating techniques like electrodeposition and dip coating are advantageous and therefore have been applied for coating SnO₂ [6, 13]. However, electrophoretic deposition (EPD), which is a subcategory for electrodeposition is relatively new for SnO₂ and has not been investigated in detail as yet as a potential technique for SnO₂ depositions [13].

So far, even the EPD of SnO₂ on conductive substrates (i.e. metals) has not really been widely investigated. In fact there were only two studies published on EPD of SnO₂ on conductive substrate [14, 15] and no published work on the EPD of SnO₂ on non-conductive substrates yet, to date. The available literature on non-conductive EPD involved only the deposition of materials such as yttria stabilised zirconia on porous non-conductive substrate (NiO-YSZ) for solid oxide fuel cell (SOFC) applications [16-24]. Attempts and trials of EPD employing dense non-conductive substrate have not been successful [16, 18]. However, since EPD is denoted as a very fast thin film deposition technique with a simple experimental setup, it has a huge potential as a mean for SnO₂ deposition on non-conductive substrates such as sapphire and quartz.
Another main issue that is normally neglected during coating fabrication of oxides is the phase compatibility between the depositing material and the substrate. The addressed issue is particularly critical considering the sintering procedure that is usually operated at high temperatures. By conducting the phase compatibility studies, recognition of the proper temperature range that should be applied without having the consequences of degradation of coatings and substrates due to solubility and reaction between the two can be achieved. To this date, there is only one study of phase compatibility between SnO₂ and sapphire [25] and none with quartz that has been published.

In the present work, a systematic SnO₂ processing approach starting from the powder production, through to its fabrication into coatings on non-conductive substrates was investigated. The work was divided into several parts. In the first part, the synthesis of SnO₂ powder consisting two types of precipitation methods was studied, namely aqueous precipitation and non-aqueous precipitation in order to produce well-dispersed particles with small particle size distributions. The precipitation method was chosen as the SnO₂ synthesis method due to its simplicity, low cost and shorter times. Furthermore, unforeseen and unexpected outcome from the precipitation studies has required extended SnO₂ powder studies to investigation of contamination and leaching.

The second part focused on investigating the stabilisation of the SnO₂ suspension (aqueous and non-aqueous) conducted on both synthesised SnO₂ and commercial SnO₂ powder suspensions.

With regard to substrate selection, two possible candidates: sapphire and quartz were firstly examined theoretically in terms of their suitability and compatibility with SnO₂ through phase diagram studies and thermodynamic calculations. The third part involves in investigating the phase compatibility of SnO₂-sapphire and SnO₂-quartz experimentally.

The fourth part consisted of preliminary EPD experimental setup studies. A variety of substrate designs were trialled and assessed to select the design that would provide maximal conductivity and further provide the best deposition for the SnO₂ powders. The trialled tests were carried out using commercial SnO₂ suspensions.
Finally, the fifth part of the work involves conducting EPD of the commercial and synthesised Sn\(\text{O}_2\) powder on sapphire substrates. Relationships between deposition time and the voltage applied were analysed with a view to determining the optimal conditions for EPD of Sn\(\text{O}_2\) on a non-conducting substrate.

There were five main aims that were established in this research based on the literature review study on Sn\(\text{O}_2\) and other relevant processes and techniques:

1) To synthesise Sn\(\text{O}_2\) powder with well dispersed particles by chemical precipitation method in a mix of alcohol and aqueous environments.

2) To study the commercially available and synthesised Sn\(\text{O}_2\) behaviour in aqueous and non-aqueous systems with regard to electrophoretic deposition process suspension suitability.

3) To examine the phase compatibility of Sn\(\text{O}_2\) with sapphire and quartz using FACT-Sage thermodynamics software and Thermo Chemix software and validation of the results experimentally.

4) To deposit Sn\(\text{O}_2\) films by electrophoretic deposition of commercially available Sn\(\text{O}_2\) powder on sapphire by developing an operational experimental setup and parameters.

5) To utilise further the experimental setup and results from electrophoretic deposition of commercially available Sn\(\text{O}_2\) powder to deposit synthesised Sn\(\text{O}_2\) powder on sapphire.

Completion of the present work was found to contribute numerous significant findings to the field of Sn\(\text{O}_2\) processing ranging from its' synthesis, theoretical phase equilibrium analysis, phase compatibilities, suspension preparation, suspension stability and thin film coating technology. Absence of publications in the following findings of the present work indicates the upmost originality of the work;

i) Sn\(\text{O}_2\) was successfully prepared by liquid (aqueous medium) and mixed liquid phase synthesis (aqueous-alcohol medium). Throughout detailed morphological analysis of Sn\(\text{O}_2\) and tin oxalate (SnC\(_2\)O\(_4\)), it was found that two factors; ionic collision frequency and diffusion distance, were found affecting overall concentration. The detailed justifications about the affect of the two factors to
2.1 Tin Oxide

2.1.1 General properties

Tin oxide or stannic dioxide (SnO₂) is a very stable material which has tetragonal or rutile structure as its most common structure. SnO₂ exists in nature as the mineral cassiterite [1, 26]. In the SnO₂ unit cell (Figure 2.1), the Sn atom is surrounded by six oxygen atoms. Furthermore, each of the oxygen anions has four coplanar Sn⁴⁺ ions as nearest neighbours at the corners of a rectangle plus two next-nearest neighbours on the remaining two corners of the Sn-coordinating distorted octahedron.

![Figure 2.1 Unit cell of SnO₂](image)

The lattice constants for the SnO₂ unit cell are a = 0.474 nm, b = 0.474 nm and c = 0.318 nm, illustrated as Figure 2.2.
Figure 2.2 Unit cell of SnC>2 showing the lattice parameters values [27]

Table 2.1 below summarises the physical and chemical properties of Sn02.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
<th>Reference</th>
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<tr>
<td>1 Formula</td>
<td>Sn0₂</td>
<td>[26]</td>
</tr>
<tr>
<td>2 Molecular weight</td>
<td>150.709 g/mol</td>
<td>[26]</td>
</tr>
<tr>
<td>3 Atomic volume</td>
<td>16.3 cm³/mol</td>
<td>[26]</td>
</tr>
<tr>
<td>4 Density</td>
<td>6.850 kg/m³</td>
<td>[26]</td>
</tr>
<tr>
<td>5 Viscosity, at melting point</td>
<td>1.85 mPa</td>
<td>[28]</td>
</tr>
<tr>
<td>6 Melting point</td>
<td>1630°C</td>
<td>[29]</td>
</tr>
<tr>
<td>7 Boiling point</td>
<td>2527°C</td>
<td>[30]</td>
</tr>
<tr>
<td>8 Thermodynamic constants</td>
<td>• Enthalpy of formation</td>
<td>-138.0 kcal/mol</td>
</tr>
<tr>
<td></td>
<td>• Gibbs energy of formation</td>
<td>-123.3 kcal/mol</td>
</tr>
<tr>
<td></td>
<td>• Entropy of formation</td>
<td>11.7 cal/mol</td>
</tr>
<tr>
<td></td>
<td>• Specific heat at constant</td>
<td>12.6 cal/mol</td>
</tr>
<tr>
<td></td>
<td>pressure</td>
<td></td>
</tr>
</tbody>
</table>
2.1.2 Densification of SnO$_2$

Densification of powder could lead to a stronger final product and can be achieved by sintering [31, 32]. During the sintering process, thermal energy is transferred to the powder usually by firing [33]. Sintering mechanism can be generally divided into two i.e either leading to densification or non-densification of materials as shown in Table 2.2.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mechanism</th>
<th>Densification</th>
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<tbody>
<tr>
<td>Polycrystalline</td>
<td>Lattice diffusion from grain boundary</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Grain boundary diffusion</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Plastic flow</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Surface diffusion</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Evaporation-condensation</td>
<td>No</td>
</tr>
<tr>
<td>Amorphous</td>
<td>Viscous flow</td>
<td>Yes</td>
</tr>
</tbody>
</table>

In densifying mechanisms, diffusional transport of matter takes place and leads to growth of necks between the particles that consequently bond the particles together [32].

Pure SnO$_2$ is a material which can not be densified by natural sintering, since its sintering mechanism is dominated by the non-densifying mechanism (surface diffusion and evaporation-condensation) [34-41]. During sintering, densification and grain growth takes place simultaneously. When the two non-densifying mechanisms occur, the curvature of the neck surface (which is the force for sintering to occur) is reduced and this will cause decrease of the densifying mechanism rate and thus allow grain growth to occur [32].

During sintering of SnO$_2$, the surface diffusion mechanism takes place in the temperature range 500-1000°C [42] and above 1300°C, evaporation-condensation mechanism dominates due to the reaction following Equation 2.1 [41, 42]:

$$\text{SnO}_2 \leftrightarrow \text{SnO(g)} + ^{\text{O}_2}(g) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
However, the sinterability of SnO₂ can be increased by addition of additives such as CoO, MnO₂, CuO, Sb₂O₃, ZrO₂, V₂O₅ and BaCO₃ [34-41].

### 2.1.2 Applications of SnO₂ Films

SnO₂ has been used for numerous scientific, technological and industrial applications. SnO₂ is a wide band n-type semiconductor and is also chemically stable. Owing to these properties, they are commonly used in gas sensors, liquid crystal displays, anodes for lithium ion batteries and transistors and as catalysts, antistatic coatings, and anticorrosion coatings and transistors [7, 43]. Furthermore, for most of these applications SnO₂ must be in the form of thick or thin films.

**Gas Sensors.** SnO₂ has been extensively investigated for applications as gas sensors due to its sensitivity at low operating temperatures [43]. For this application, SnO₂ may be fabricated as either thick films or thin films. This is done to take advantage of high surface-to-volume ratio of the coatings which will improve the sensor performance. They are usually coated onto different substrates such as alumina, silicon wafers, or sapphire. Gases such as carbon monoxide, hydrocarbons, ethanol, ammonia, hydrogen, nitrogen oxides and hydrogen sulphide can be detected using SnO₂ gas sensors [3-5, 43, 44]. The principle of operation of these sensors is that the gas to be detected removes the oxide ion from the sensor causing the resistance of the sensor to decrease, providing a corresponding measurement [43].

**Electrodes.** High theoretical current capacity value of 1491mAh/g is one of the important reasons that SnO₂ is used as anodes in batteries [45]. This value is higher than that of carbon, which is only 373 mAh/g, implying that SnO₂ could replace the current carbon material in anodes [46]. In this application, lithium is inserted into SnO₂ where an alloy of Li-Sn is formed in a LiO₂ matrix [47]. Li-ion batteries are considered as future prospect as an alternative form of energy for automobiles [48].

**Catalysts.** SnO₂ has been investigated as catalysts for oxidative dehydrogenation reactions and carbon monoxide catalytic oxidation [49]. Apart from this, SnO₂ can also be used in the selective catalytic reduction of nitrogen oxide by hydrocarbons and in Pd supported SnO₂ catalysts for the reduction of nitrogen oxide in the presence of CO-NO-
0$_2$ mixtures at 180°C [50]. SnO$_2$ redox catalytic properties could be modified with other heteroelements in order to improve the properties in different catalytic reactions. For example, copper, chromium, palladium and antimony are added for total oxidation of carbon monoxide and hydrocarbons; antimony, bismuth, and vanadium for the partial oxidation and ammoxidation of hydrocarbons while phosphorus and bismuth are added for oxidative coupling and oxidative dehydrogenation reactions [49].

**Coatings.** Coatings of SnO$_2$ usually occur as thin films of various sizes depending on their specific applications. In glass industries, 'invisible' SnO$_2$ thin film of less than 0.1 nm is used as a surface film on glass to strengthen glassware such as bottles and jars. As a result, the strength of the glass is increased and abrasion resistance improved. Furthermore, SnO$_2$ film of thickness ranging from 0.1 to 1.0 nm behaves as electrically conductive layers. Therefore this range of SnO$_2$ films can be used for electro-luminescent devices such as display signs, fluorescent lamps, antistatic cover-glasses, and on aircraft windscreens [7].

2.2 **SnO$_2$ Powder Synthesis**

2.2.1 **Ceramic powder synthesis**

Both natural ceramic raw materials and synthetic raw materials had been used earlier for ceramic powder processing. However, recently synthetic raw materials have assumed greater importance due to [51]:

i) Inadequacy of many natural ceramic raw materials: Material synthesis with high degree of control of almost any crystalline ceramics in the form of fine particles has been developed. The synthesis process employs relatively pure chemicals (including acids, bases and solvents), which enhance the degree of purity of the produced materials.

ii) Variable purity levels of natural minerals and compounds: The purity of natural materials and compounds do not meet the standards for most applications. However, this could be overcome by using synthetic powders. Furthermore,
intentional addition of compounds could also be regulated and successfully achieved.

iii) Difficulties in obtaining powders in different sizes and shape ranges: Since the synthesis process can be controlled, these disadvantages arising from natural materials can be avoided and powders with specific sizes and shapes can be easily obtained.

Ring [51] has classified ceramic powder synthesis into four major methods — solid phase reactant synthesis, liquid phase reactant synthesis and gas phase reactant synthesis. However, only liquid phase reactant synthesis will be examined and emphasized in detail since it relates to the present work. Figure 2.3 summarises the three discrete methods of Ring summary [51].

---

**Figure 2.3** Schematic diagram showing the various ceramic powder synthesis methods [51, 52]
From Figure 2.3, it is seen that liquid phase reactant synthesis consists of four main methods; drying/precipitation, hydrothermal synthesis, sol-gel synthesis and the emulsion process, which are explained in the following section.

2.2.1.1 Precipitation

Precipitation is a process where insoluble substances are precipitated out from a solution. During precipitation, two processes take place simultaneously [53]:

i) Primary processes - mixing of the reactant, nucleation and growth of particles.

ii) Secondary processes - aggregation, ageing and ripening

The primary process starts off when overall concentration of reactants increases until a supersaturated condition is induced in the solution. Supersaturation is the driving force for the nucleation and growth process. Equation 2.2 [53, 54] defines supersaturation, \( A_{fi} \)

\[
A_{fi} = \frac{|x_s|}{|i_c|} 
\]

where;

- \( x_s \) = chemical potentials of molecules in solution
- \( i_c \) = chemical potentials of molecules in bulk of a crystal phase

A solution is supersaturated when \( A_{fi} > 0 \) and is undersaturated when \( A_{fi} < 0 \). The \( A_{fi} \) can be further described by Equation 2.3 [54, 55];

\[
A_{fi} = k_B T \ln S 
\]

where;

- \( k_B \) = Boltzmann constant
- \( T \) = temperature
- \( S \) = supersaturation ratio

The supersaturation ratio may be defined as \( a/a_e \), ratio of actual and equilibrium activities in a solution [56] or further simplified as \( C/C_s \), ratio of molecular concentrations where \( C \) is the solute concentration and \( C_s \) is the equilibrium solubility of the solute [56]. Based on Equation 2.3, the supersaturated condition may be
From Figure 2.4, when AG is at the maximum and S>1, the critical nuclei size, \( r^* \) is achieved. The \( \Delta G_{\text{max}} \) shown in the figure indicates the energy required for activating nucleation. Therefore, at this point, the clusters larger than the critical nuclei size (\( r^* \)) will form stable nuclei by lowering their energy and the clusters smaller than the critical nuclei size (\( r^* \)) will dissolve. The supersaturation condition is then relieved and eventually limited; and the stable nuclei further grow according to Ostwald ripening [56, 58].

In precipitation synthesis, specifically for nanoparticle synthesis, Ostwald ripening has been manipulated in order to produce powders of particles with narrower size distributions [59]. In achieving this, temperature is raised after nucleation and subsequent growth. Next, the solubility of the solvent is increased, thus inducing Ostwald ripening. Small particles are then dissolved in the solution as the solid concentration in the solvent is lower than the equilibrium solubility of the small particles. These nanoparticles will carry on minimising its size, with increasing solubility, dissolving until it is completely dissolved in the solution. However, larger particles continue to grow as the concentration of the solids in the solvent is higher than the equilibrium solubility of larger particles. In the end, the growth process will cease.
when the concentration of solid in the solvent equals the equilibrium value for the large nanoparticles [59, 60],

Synthesis of SnC>2 powder by precipitation is a very common practice, compared to other synthesis methods. Table 2.3 summarised parameters and materials used in the previous studies on the precipitation synthesis of Sn02.

Table 2.3 Summary of studies conducted on precipitation synthesis of SnC>2

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Brief Procedure</th>
<th>Particle size</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic tin • Nitric Acid • Ammonium hydroxide (NH4OH)</td>
<td>• Stirred until pH 8 • Re flux at 100°C for 2 hours • Centrifuged and washed with ethanol and distilled water • Dried at 100°C for 5 hours</td>
<td>5.3-26.6 nm</td>
<td>[61]</td>
</tr>
<tr>
<td>Tin tetrachloride (SnCl4) • Urea ((NH2)2CO)</td>
<td>• Both solutions mixed with 2:1 (SnCl4:urea) ratio. • Solution heated to 90°C, held for 90 minutes with stirring. • Washed with distilled water five times in centrifuge</td>
<td>7.7-35.9 nm</td>
<td>[62]</td>
</tr>
<tr>
<td>Tin tetrachloride pentahydrate (SnCl4.5H2O) • Ammonium hydroxide (NH4OH) • Hydrophylic carbon black powder</td>
<td>• SnCl4.5H2O mixed with distilled water to make up aqueous SnCl4 • NH4OH added to SnCl4 while stirring. • White precipitate mixed with carbon powder. • Dried at 70°C for 10 to 20 hours • Dried powder calcined at 600°C for 4 hours in air.</td>
<td>7.5 nm</td>
<td>[63]</td>
</tr>
<tr>
<td><strong>Tin Tetrachloride Pentahydrate (SnCl(_4),5H(_2)O)</strong></td>
<td><strong>Ammonia (NH(_4)OH)</strong></td>
<td><strong>Precipitate centrifuged and washed with deionized water</strong></td>
<td><strong>Filtered</strong></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td><strong>Tin tetrachloride pentahydrate (SnCl(_4),5H(_2)O)</strong></td>
<td><strong>Ammonium hydroxide (NH(_4)OH)</strong></td>
<td><strong>Transparent solution was then heated at 150°C for 12 hours in a Teflon vessel</strong></td>
<td><strong>Cooled to room temperature.</strong></td>
</tr>
<tr>
<td><strong>Tin tetrachloride (SnCl(_4))</strong></td>
<td><strong>Ammonium hydroxide (NH(_4)OH)</strong></td>
<td><strong>Stirred until pH 9.5</strong></td>
<td><strong>Washed thoroughly</strong></td>
</tr>
<tr>
<td><strong>Tin tetrachloride (SnCl(_4))</strong></td>
<td><strong>Ammonium hydroxide (NH(_4)OH)</strong></td>
<td><strong>pH adjusted to 7</strong></td>
<td><strong>Washed with deionized water</strong></td>
</tr>
<tr>
<td><strong>Tin tetrachloride (SnCl(_4))</strong></td>
<td><strong>Ammonium hydroxide (NH(_4)OH)</strong></td>
<td><strong>Precipitate washed with isopropyl alcohol</strong></td>
<td><strong>Dried at 110°C for 24 hours</strong></td>
</tr>
<tr>
<td><strong>Tin tetrachloride (SnCl(_4))</strong></td>
<td><strong>Distilled water</strong></td>
<td><strong>Heated in autoclave at 100-160°C for 24 hours</strong></td>
<td><strong>Washed with absolute ethanol and acetone</strong></td>
</tr>
<tr>
<td><strong>Tin tetrachloride (SnCl(_4))</strong></td>
<td><strong>Stirred for 4 hours</strong></td>
<td><strong>Aged at ambient temperature for</strong></td>
<td><strong>11.1 nm</strong></td>
</tr>
<tr>
<td>Step</td>
<td>Reagents/Conditions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>---------------------</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 1 | CTAB  
- Ammonium hydroxide (NH₄OH)  
- Tin tetrachloride (SnCl₄)  
- Ethanol  
- Tin (II) chloride (SnCl₂)  
- triblock copolymer poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethane oxide) (P(EO)-P(PO)-P(EO)) (PI23)  
- Ethanol  
- Tin (II) chloride dihydrate (SnCl₂·2H₂O)  
- Hydrochloric Acid  
- Ammonium hydroxide (NH₄OH)  | 96 hours  
- Filtered and washed with water  
- Dried at ambient temperature  
- Mixed  
- Dried at 150°C  
- Stirred at 45°C for 2 hours  
- Dried at room temperature for 24 hours  
- pH fixed at 6.0-6.5  
- Immersed in ice water for 1 hr and ultrasonic cleaner  
- Agitated at 0°C  
- Precipitate washed with water and alcohol  
- Dried and heated with gentle infrared lamp  
- Heated until all most of the solvent and other volatiles are distilled off the condenser arm and solid material is obtained.  
- Precipitate filtered and washed with distilled water.  | 15.0 nm  
[70]  
15.0 nm  
[71]  
8.0-15.0 nm  
[44]  
16.0 nm  
[72] |
<table>
<thead>
<tr>
<th>Precursors</th>
<th>Process Details</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin (II) chloride (SnCl₂) Ammonium hydroxide (NH₄OH) Distilled Water Methanol</td>
<td>Precursors heated until almost all of the solvent and other volatiles are distilled off the condenser arm and solid material obtained. Precipitate filtrated and washed with distilled water. Sintering in nitrogen and air</td>
<td>[72]</td>
</tr>
<tr>
<td>Sodium Stannate Hydrate (Na₂Sn0.3H₂O) N-cetyl-N, N, N-trimethylammonium bromide solution Hydrochloric acid (HCl)</td>
<td>Mixed precursor solution stirred Thermally treated under static condition at 96°C for 72 hours and cooled afterwards. Washed by deionized water and filtered Dried at 96°C overnight.</td>
<td>[73]</td>
</tr>
<tr>
<td>Sodium Stannate (Na₂SnO₃) Glucose Sulfuric acid (H₂SO₄)</td>
<td>Mixed solution pH is 9.0 Stirred in incubator under magnetic stirring at 25°C Precipitation completed at pH 6 Precipitate suctioned filtered</td>
<td>[74]</td>
</tr>
</tbody>
</table>

It is observed that from the summary of previous research on the precipitation process, main controlled parameters which control the production of smaller and more dispersed particles are temperature and pH. Therefore this suggests that the precipitation process can be controlled in the nucleation stage. The preferred temperatures are higher than room temperature and the environmental pH chosen is mostly in the alkaline region. However some studies have tried to control the precipitation process by alcohol washing using ethanol. The importance of alcohol washing, using ethanol is that it can prevent water bridging during drying which would develop agglomeration among the particles later [75, 76].

There are advantages and disadvantages to the precipitation process. The precipitation is cost effective due to a simple setup and minimal chemical requirements. Moreover, the
duration for precipitation is very short, making it both energy and time effective as well. Furthermore, with improved precision, precipitation can obviously produce powders with well controlled shapes, sizes and particle distributions to a certain degree.

However, the disadvantages lie in its drying and calcination processes which both contribute to agglomerate or aggregate formation. Overcoming this problem using alternative means of freeze drying or heating and calcining in controlled atmospheres would be costly.

2.2.1.2 Hydrothermal synthesis

Hydrothermal synthesis is a precipitation synthesis method with application of high temperatures and pressures [52]. The solvents may be water, or other polar or non-polar compounds. The synthesis takes place in sealed vessels that may be equipped with polymer linings which function as a protective layer to prevent corrosion of the vessel. Autoclaves are the vessels usually used for hydrothermal synthesis. Table 2.4 summarises previous studies involving hydrothermal precipitation of SnO₂.

<table>
<thead>
<tr>
<th>Method</th>
<th>Starting Materials</th>
<th>Brief Procedure</th>
<th>Particle Size</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Hydrothermal synthesis | • Metallic tin  
• Nitric Acid (HN0₃) | . Heated for at 150°C for 24 hours  
• Centrifuged and washed with distilled water  
. Dried at 150°C for 24 hours | 4.4-90.0 nm | [77]      |
|                   | • Metallic tin  
• Nitric acid (HN0₃) | . Heated at 150°C for 6 hours during treatment | 5.0 nm        | [78]      |
<table>
<thead>
<tr>
<th>Process</th>
<th>Reagents</th>
<th>Description</th>
<th>Size (nm)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol-Gel and Hydrothermal</td>
<td>Tin tetrachloride (SnCl₄)</td>
<td>Heated hydrothermally at 150°C for 12 hours</td>
<td>4.0-80.0 nm</td>
<td>[80]</td>
</tr>
<tr>
<td>Sol-Gel and Hydrothermal</td>
<td>Tin tetrachloride (SnCl₄)</td>
<td>Washed with water repeatedly and acetone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sol-Gel and Hydrothermal</td>
<td>Tin tetrachloride (SnCl₄)</td>
<td>Dried and kept in vacuum desiccator</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emulsion and Hydrothermal</td>
<td>Tin tetrachloride pentahydrate (SnCl₄·5H₂O)</td>
<td>Magnetically stirred for 30 minutes</td>
<td>2.6-2.9 nm</td>
<td>[82]</td>
</tr>
<tr>
<td>Emulsion and Hydrothermal</td>
<td>n-pentanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emulsion and Hydrothermal</td>
<td>n-hexane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emulsion and Hydrothermal</td>
<td>Ci₈H₁₇BrN (CTAB)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emulsion and Hydrothermal</td>
<td>Urea</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emulsion and Hydrothermal</td>
<td>Ammonium hydrogen carbonate (NH₄CO₃)</td>
<td>Suspended in ammonia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emulsion and Hydrothermal</td>
<td>Ammonium hydroxide (NH₄OH)</td>
<td>Hydrothermal treatment in autoclave at 200°C for 3 hours. Dried at 120°C for 24 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emulsion and Hydrothermal</td>
<td>Ammonium hydroxide (NH₄OH)</td>
<td>Magnetically stirred for 15 minutes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emulsion and Hydrothermal</td>
<td>Ammonium hydroxide (NH₄OH)</td>
<td>Ultrasonicated for 15 minutes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emulsion and Hydrothermal</td>
<td>Ammonium hydroxide (NH₄OH)</td>
<td>Transparent microemulsion placed in Teflon-lined d-steel in oven at 130°C and 150°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emulsion and Hydrothermal</td>
<td>Ammonium hydroxide (NH₄OH)</td>
<td>Treated under reduced pressure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emulsion and Hydrothermal</td>
<td>Tin powder</td>
<td>Solution heated in hydrothermal autoclave at 150°C for 6 hours</td>
<td>3.0 nm</td>
<td>[79]</td>
</tr>
<tr>
<td>Emulsion and Hydrothermal</td>
<td>Sulfuric acid (H₂SO₄)</td>
<td>Cooled to room temperature naturally</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emulsion and Hydrothermal</td>
<td>Hydrogen peroxide (H₂O₂)</td>
<td>Product filtered and washed with distilled water and alcohol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| **Ethanol** | pressure in rotary evaporator  
| • Washed repeatedly with ethanol  
| • Dried at 100°C for 2 hours  |

The advantages of hydrothermal synthesis include formation of powders directly from solution, the ability to form anhydrous, crystalline or amorphous powders, the ease of manipulation of reaction temperature to control particle size, and to the ease of chemical, compositional and stoichiometric control of obtained powders and produced powders which are highly reactive during sintering.

The disadvantage of this technique is that it is expensive involving considerable time and energy. Additional costs may also be incurred from the requirement of expensive autoclaves for the synthesis.

2.2.1.3 Sol-gel synthesis

The sol-gel process basically involves the steps of sol preparation, gel formation and calcination of gels. Precursors in the process could be inorganic salts or metal alkoxides [52], However, the latter is more often used and is formed by a reaction of metal with alcohol.

Preparation of sols may be done by [51, 52]:

i) dispersion of particles in a liquid medium

ii) hydrolysis and polycondensation reaction of precursors which produce polymeric sols

iii) peptisation process where flocculated precipitates are produced from electrolyte and base solutions are reacted with acids causing the breakdown of the precipitates into smaller particles

Gelation of the sols is achieved by disrupting the stability of the sol through water removal or adjustment of pH towards the isoelectric point pH of the sols. The gel
produced may be a monolithic body which takes the shape of the original form of the sols [52]. In order to successfully obtain a powder, the gels are either:

i) dried under high vacuum, ground to obtain precursor gel powder, and later calcined.

ii) dried, calcined and milled

With regard to SnO₂ powder preparation, the sol-gel technique is the second most commonly used technique used after precipitation. The summary of previous research involving sol-gel techniques for SnO₂ powder preparation is given in the Table 2.5.

Table 2.5 Summary of previous studies involving sol-gel synthesis of SnO₂

<table>
<thead>
<tr>
<th>Starting Materials</th>
<th>Brief Procedure</th>
<th>Particle Size</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Metallic tin .Nitric Acid (HNO₃) • Citric Acid • Ammonium hydroxide (NH₄OH)</td>
<td>• Stirred until pH 8 • Reflux at 100°C for two hours • Centrifuged and washed with ethanol and distilled water • Dried at 100°C for 5 hours</td>
<td>2.8-5.1 nm</td>
<td>[83]</td>
</tr>
<tr>
<td>• Tin granulate .Nitric acid (HNO₃) • Citric acid • Ammonium hydroxide (NH₄OH)</td>
<td>• pH solution adjusted to pH 8 • Refluxed at 100°C for two hours • Centrifuged and washed with water and ethanol • Dried at 100°C for 5 hours in air</td>
<td>2.9-6.1 nm</td>
<td>[84]</td>
</tr>
<tr>
<td>• n-butanol solution of tin(II)-ethylexanoate • Deionized water .Nitric acid (HNO₃)</td>
<td>• Molar ratio of water to Sn is 4 • pH solution adjusted with nitric acid to be pH 1 • Gel dried at 95°C</td>
<td>10.0-40.0 nm</td>
<td>[85]</td>
</tr>
<tr>
<td>• Tin Tetrachloride (SnCl₄)</td>
<td>• Reflux for 2 hours • Cooled to room temperature • Prolonged dialysis for 7 days • Washed with ethanol</td>
<td>4.0-40.0 nm</td>
<td>[86]</td>
</tr>
<tr>
<td>Process</td>
<td>Reaction Details</td>
<td>Wavelength (nm)</td>
<td>Reference</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------</td>
<td>----------------</td>
<td>------------</td>
</tr>
<tr>
<td>Tin Tetrachloride Pentahydrate (SnCl₄.5H₂O) • Hydrazine monohydrate (N₂H₄.H₂O)</td>
<td>Stirred at reflux for 10 days • Washed by water and ethanol • Drying 110°C under air for 12 hours</td>
<td>2.7-4.1</td>
<td>[50]</td>
</tr>
<tr>
<td>Tin tetrachloride pentahydrate (SnCl₄.5H₂O) • Ammonium hydroxide (NH₄OH)</td>
<td>pH reaction of mixture is 4 • Resultant sol washed with distilled water • Dried at 80°C for several hours</td>
<td>2.9-9.0</td>
<td>[87]</td>
</tr>
<tr>
<td>Tin tetrachloride pentahydrate (SnCl₄.5H₂O) • Ammonium hydroxide (NH₄OH) • Methanol</td>
<td>Stirred • Precipitate dried at 110°C for 12 hours</td>
<td>2.9-9.0</td>
<td>[88]</td>
</tr>
<tr>
<td>Tin tetrachloride pentahydrate (SnCl₄.5H₂O) • Alcoholic tin tetrachloride (SnCl₄)</td>
<td>Aged in a constant-temperature water bath • Suspension obtained • Top portion of solution discarded • Suspension dried</td>
<td>2.0-6.0</td>
<td>[89]</td>
</tr>
<tr>
<td>Tin tetrachloride pentahydrate (SnCl₄.5H₂O) • Ammonium hydroxide (NH₄OH)</td>
<td>pH is adjusted to pH 6 • Heated to 80°C • Washed with distilled water</td>
<td>2.0-6.0</td>
<td>[90]</td>
</tr>
<tr>
<td>Tin tetrachloride (SnCl₄) • Ethylene glycol</td>
<td>Stirred at 80°C until transparent solution is obtained • Aged for 20 minutes • Dried at 150°C for 24 hours</td>
<td>2.6-10.2</td>
<td>[91]</td>
</tr>
</tbody>
</table>
The advantage of sol-gel processing is the precise control achieved over all stages of processing during synthesis since the processing steps are regulated from the molecular level of precursors.

However the major drawback is that the precursors are expensive and the process requires very careful atmospheric control.

2.2.1.5 Emulsion synthesis

An emulsion is basically composed of two immiscible liquid phases one of which is dispersed under agitation in the form of small droplets into the other. The two common types are water in oil emulsions (W/O) and the oil in water (O/W) emulsions. The dispersed droplets may be of macroscopic or colloidal size and depending on the nature of the dispersed phase, emulsion can be grouped as macroemulsion (> 400 nm), miniemulsion (100^-100 nm) or microemulsion (100 nm) [52, 58].

The two distinct immiscible liquid layers appear to be homogenously dispersed due to re-coalescing of the unstable dispersed droplets. In order to stabilise the system, suitable emulsifiers (which are surface reactive agents) are added to prevent the re-coalescing of the droplets, producing a stable dispersion [52].

The end mixture of two liquids with a dispersed phase and a support phase by the emulsifier would be utilized for producing solid particles. After removal of water or by increasing the system pH, precipitation will be forced to occur, thus producing solid salts or hydroxides. Further washing, drying and calcination of the particles yield a powdery end product.
REFERENCE


[19] M. Matsuda, T. Hosomi, K. Murata, T. Fukui, M. Miyake, "Fabrication of bilayered YSZ/SDC electrolyte film by electrophoretic deposition for reduced-