

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Importance of electrocatalysis

An electrocatalyst is a material that participates in and increases the rate of an electrochemical reaction without being consumed in the process <sup>[142]</sup>. The catalyst basically provides an alternative reaction pathway by lowering the activation energy for the reaction as shown in Figure 2.1.

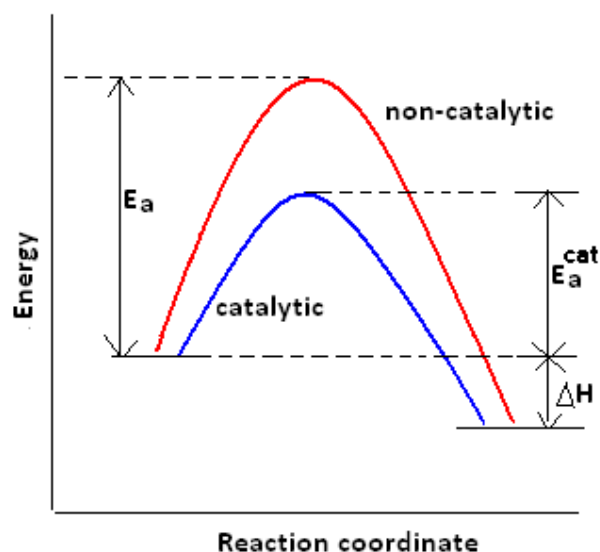


Figure 2.1 Activation energy for catalytic and non-catalytic pathways of a chemical reaction<sup>[80]</sup>

An important feature of heterogeneous catalysis is that the products of reaction must be removed rapidly from the catalyst surface in order to generate free active sites<sup>[80]</sup>. Catalysis in general accounts for around three billion dollars per annum of the US chemical industry alone and it can be estimated that each US dollar spent on catalysis creates around 155 dollars' worth of products<sup>[134]</sup>.

The aim of electrocatalysis is to design surfaces so as to obtain a high current density

(high rate of conversion) close to the equilibrium potential (at low overpotential) of the electrochemical reaction under investigation. Electrode reactions such as SO<sub>2</sub> oxidation on platinum are irreversible, therefore they have slow kinetics hence the need for a catalyst. The reaction may require a substantial overpotential to drive it at a practical current density and by designing an appropriate surface that stabilises an adsorbed species to an optimum extent may provide a new, low energy activation route from reactant to product<sup>[20, 104-105]</sup>.

## **2.2 Catalyst parameters**

Selecting the right catalyst will have an impact on the electrical chemical efficiency allowing the SDE to operate at conditions closer to the reversible cell potential and it will also have a positive influence in achieving long-term performance stability. The current catalyst of choice for oxidation of SO<sub>2</sub> within the SDE is platinum supported on carbon<sup>[1-56]</sup>. References 1 to 56 highlights the fact that a great deal of research have been conducted to optimise the use of Pt as catalyst under different operating conditions.

Electrocatalyst qualities required for an efficient SDE operation are long term stability and durability, good electrical conduction, good selectivity, large specific surface area, low cost and abundant raw materials. These properties are important for realising long term performance with low catalyst overpotential and minimal or no maintenance and replacements cost<sup>[29, 1]</sup>.

In the case of fuel cell electrocatalysts for oxygen reduction reaction, Thompsett *et al.*<sup>[134]</sup> of Johnson Matthey Technology Centre, Sonning Common, UK stated that the catalyst requirements can only be met by Pt and Pt-transition metal alloys supported on carbon over all the commercially available materials. However, the following will also affect the catalytic activity:

### **2.2.1 Catalyst supports**

The primary aim of applying a catalytically active component to a support is to obtain the catalyst in a highly dispersed form, i.e. high surface area, and hence in a highly active form when expressed as a function of the weight of the active component. This feature of supported catalysts is especially important with regard to precious metal catalysts, because it allows more effective utilization of the metal than can be achieved

in bulk metal systems. However, in the case of base metal catalysts, the use of the support is often primarily aimed at improving catalytic stability. This can be achieved by suitable interaction between the active material and support<sup>[101]</sup>.

Supported catalysts are of special interest, for they allow for higher activity and stabilisation due to the fine dispersion of small metallic particles<sup>[99, 88]</sup>. They provide access to a much larger number of catalytically active atoms than in the corresponding bulk metal, even when the latter is ground to a fine powder. Platinum usage is minimised by dispersing the catalyst over a high surface area support such as Vulcan carbon XC-72R ( $>75\text{m}^2\text{g}^{-1}$ )<sup>[88]</sup>.

It is well known that the activity of a catalyst depends significantly on the size of the Pt particles and their dispersion pattern over the support structures. It has been found that the optimal dispersion pattern and Pt particle size can be obtained by using an ideal supporting material. The ideal support should have a high surface area, good electrical properties, and high electrochemical stability under harsh conditions and the electrocatalyst should be easily accessible to the reactants<sup>[101]</sup>.

Supported catalysts have several advantages over unsupported catalysts. Supported catalysts have relatively higher stability than unsupported catalysts in terms of agglomeration under fuel cell operating conditions. The porosity of carbon black assures gas diffusion to the active sites. The electric conductivity of the carbon support allows electron transfer from the catalytic sites to the conductive carbon electrodes and then to the external circuit. The small dimensions of catalyst particles (nanoscale) are dispersed on a support to maximise the contact area between catalyst and reagents<sup>[99]</sup>.

The catalyst support used in a fuel cell operation environment should be corrosion resistant and highly electrically conductive. Among all kinds of carbon supports (activated carbon, carbon black, graphite and graphitised materials), carbon black is the most commonly used for electrocatalysts due to its high conductivity, excellent corrosion resistance appropriate pore structure and high surface area. Normally, graphitization is required in order to achieve a better level of corrosion resistance<sup>[143]</sup>.

The most commonly used carbon support is Vulcan XC-72. Carbon supports with high surface areas in Proton Exchange Membrane Fuel cell (PEMFC) electrodes are susceptible to corrosive conditions. If the support is oxidised to  $\text{CO}_2/\text{CO}$ , Pt may be lost from the support<sup>[101]</sup>. An increase in carbon support oxidation will result in increased

amounts of Pt to be lost. If the support is partially oxidised to surface oxide, it may accelerate the increase of the particle size of Pt due to agglomeration as the presence of surface oxides may weaken the platinum-support interaction, leading to a lower resistance to surface migration of Pt particles<sup>[138]</sup>.

Carmo *et al.*<sup>[132]</sup> performed methanol oxidation tests and the results showed an increase in the cell potential by PtRu/C electrocatalysts on a Vulcan carbon XC-72 system compared to the PtRu/C E-TEK formulation. This can be explained due to the better conductivity of this carbon support, enhancing the speed of the electron transference in the methanol oxidation reaction (MOR). The improved results can furthermore be attributed to good particle distribution on the carbon surface and suitable particle size distribution of the PtRu catalyst.

Metal oxides are however, usually employed as support for metal catalysts. It is well known that the adhesion and interaction between the metal particles and the support are important factors that influence the stability, activity and selectivity of a catalyst. This is the reason most recent researchers investigating electrocatalysis focus on the employment of metal oxides as support. The success of transition metals as catalysts depends on the unpaired d-electrons and unfilled d-orbitals which are available to form bonds with the adsorbate. Adsorption varies with transitional metal depending on the number of unpaired electrons per atom and hence adsorption may be modified by alloying or inclusion of the catalyst in a non-metallic lattice<sup>[103]</sup>.

### **2.2.1.1 Niobium pentoxides (Nb<sub>2</sub>O<sub>5</sub>)**

Niobium oxides are considered as a substrate due to their excellent chemical stability in acid solutions<sup>[128]</sup>. Niobium-based materials are effective catalysts for many catalytic reactions; e.g. oxidative dehydrogenation of alkanes, selective oxidation of alkanes to carboxylic acids and ammoxidation of nitriles. They are also efficient for energy, environmental and sustainable-related processes like hydrogen production, as fuel cell electrocatalysts in photocatalysis, and as three-way catalysts in the removal of NO<sub>x</sub><sup>[97, 122, 133]</sup>.

Justin *et al.*<sup>[122]</sup> conducted electrochemical experiments that showed that methanol electro-oxidation is dependent on the Pt amount loaded and peak current densities of the methanol electro-oxidation is significantly higher (80%) on Pt-Nb<sub>2</sub>O<sub>5</sub>(2:2)/C than Pt-Ru(2:1)/C. Furthermore, Pt-Nb<sub>2</sub>O<sub>5</sub> (2:2)/C electrocatalysts exhibited slower current

decay with time than Pt-Ru (2:1)/C, suggesting good tolerance behaviour towards CO-like intermediates. The enhanced electrode response is attributed to the synergistic effect between Pt and Nb<sub>2</sub>O<sub>5</sub>. The work shows that Pt-Nb<sub>2</sub>O<sub>5</sub>/C is a promising anode catalyst for direct methanol fuel cells in terms of its activity and stability towards methanol electro-oxidation.

Rotating disk electrode (RDE) tests demonstrated that the Pt/Nb<sub>2</sub>O<sub>5</sub>/C electrocatalyst (5μg.cm<sup>-2</sup> Pt) showed higher half-wave potentials than that of a commercial Pt/C (10μg.cm<sup>-2</sup> Pt) electrocatalyst. The Pt mass activity obtained from the Pt/Nb<sub>2</sub>O<sub>5</sub>/C electrocatalyst is about 3 times higher compared to that of the commercial Pt/C electrocatalysts. However, measurements also indicate that the electrocatalytic activity for the oxygen reduction reaction of the Pt/Nb<sub>2</sub>O<sub>5</sub>/C electrocatalyst is lower than that of the commercial Pt/C [128]. Guerrero *et al.* [84] stated that small amounts of Nb promotes the preferential oxidation of CO, helping to completely remove CO from H<sub>2</sub>-rich streams at lower temperatures than the unpromoted Pt catalyst.

### 2.2.1.2 Tantalum pentoxides (Ta<sub>2</sub>O<sub>5</sub>)

Tantalum is resistant to corrosion as it forms an oxide layer under all practical conditions. In a study of Pt<sub>1-x</sub>Ta<sub>x</sub> alloys, it was shown that all of the tantalum was retained across the whole of the Pt<sub>1-x</sub>Ta<sub>x</sub> binary range after exposure to 0.5M H<sub>2</sub>SO<sub>4</sub> at 80°C for a week. This means that if a PtTa catalyst composition with improved performance is developed, it is likely that the composition will give a stable performance over time [100].

A study investigating methanol electro-oxidation showed Pt nanostructurally encapsulated by a tantalum oxide matrix to exhibit much higher current density when compared to a typical Pt thin film electrode for methanol electro-oxidation. The excellent activity of the nanostructured electrode (mainly due to the Ta<sub>2</sub>O<sub>5</sub> layer and increased surface area of the Pt) was found to be responsible for transporting methanol as fuel and protons as well as supporting the Pt nanophases [78].

Park *et al.* [78] stated that the active surface area of Pt-Ta<sub>2</sub>O<sub>5</sub> for the catalytic oxidation of methanol, proved to be higher than that of a Pt-thin film which was measured using the hydrogen adsorption (Pt-H) method. The improved performance of Pt-Ta<sub>2</sub>O<sub>5</sub> is as a result of the increased number of active reaction sites. The inclusion of tantalum pentoxide was responsible for an improved activity over a Pt thin film alone. No

reaction on Ta<sub>2</sub>O<sub>5</sub> alone was exhibited however given the extremely low current densities obtained. This suggests that the Ta<sub>2</sub>O<sub>5</sub> layer could play a role as a channel for protons without preventing any reaction on the Pt.

In order to survey new CO-tolerant anodes for the Polymer Electrolyte Fuel Cell application, the addition of TaO<sub>x</sub> and NbO<sub>x</sub> to a Pt catalyst was examined in the electrochemical oxidation of CO in a sulphuric acid solution. The voltammetric peak potentials for oxidation of CO pre-adsorbed on the Pt surface, shifted to lower potentials as a result of these additives, indicating an enhancement of electrocatalysis for CO oxidation compared to Pt alone<sup>[90]</sup>.

### 2.2.1.3 Zirconium dioxide (ZrO<sub>2</sub>)

ZrO<sub>2</sub> as a material has a high melting point (2715°C), outstanding thermal and chemical stability, excellent mechanical properties, corrosive resistance and has been used as a catalyst support<sup>[92,89, 119]</sup>. Zirconium is alloyed with other materials due to its high corrosion resistive nature and has shown minimal structural change under high sulphuric acid concentration and temperature. The resistivities of platinum-zirconium alloys are a little higher than that of pure platinum<sup>[89]</sup> due to its elevated hardness, creep resistance and strength especially at high temperatures<sup>[79, 91]</sup>.

The strength of the alloy increases with an increase in the total volume fraction of zirconium. The addition of very small amounts of zirconium makes the platinum alloy structure more stable than platinum only<sup>[89]</sup>. Zirconium with unfilled d electron shells can be used to alter the electron density around noble metals such as platinum<sup>[79, 91]</sup>. Although zirconium has difficulty being reduced to the metallic state, this Group IV element has been alloyed with platinum as catalyst in the phosphoric acid fuel cell mainly due to its corrosion resistivity<sup>[76]</sup>.

**Table 2.1 Acid corrosion resistance of Zirconium compiled by D.F Taylor<sup>[91]</sup>**

| Solution                            | Temperature<br>(°C) | Days | Corrosion rate<br>(Inch/yr) |
|-------------------------------------|---------------------|------|-----------------------------|
| 50wt%H <sub>2</sub> SO <sub>4</sub> | 19-26               | 35   | 0                           |
| Conc H <sub>2</sub> SO <sub>4</sub> | 19-26               | 36   | Very soluble                |
| 20wt%H <sub>2</sub> SO <sub>4</sub> | 95-100              | 4    | 0.00018                     |
| Conc H <sub>2</sub> SO <sub>4</sub> | 145                 | 30   | Very soluble                |

Szymanski *et al.* [92] alloyed platinum with zirconium resulting in an alloy exhibiting electrophilic character as a result of the modification of its electron density. This was corroborated by poisoning experiments conducted on the platinum alone and Pt<sub>3</sub>Zr for the hydrogenation of benzene. It was found that Pt<sub>3</sub>Zr was more resistant to hydrogen sulphide poisoning than platinum alone and it was easily reactivated by heat treatment in hydrogen by weakening the Pt-S bond on the alloy catalyst due to a platinum electron deficiency.

AC impedance tests revealed that zirconium and tantalum alloys showed excellent corrosion resistance to the 5wt% sulphuric acid solution at temperatures up to 180 and 220°C respectively. Potentiodynamic polarisation tests revealed that passivation of zirconium and tantalum alloys are stable over a wide range of applied potentials. The corrosion potential of zirconium alloys was stable at all temperatures below 200°C [79]. Table 2.1 shows the acid corrosion resistance of zirconium in sulphuric acid concentration.

When compared with Pt/C (20wt% E-TEK), Pt-ZrO<sub>2</sub>/C gave higher catalytic activities for ethanol electro-oxidation. The effect of a Pt: ZrO<sub>2</sub> molar ratio on the catalytic activity was investigated using cyclic voltammetry (CV) and the lowest peak potential for ethanol electro-oxidation appeared at the molar ratio of 1:4 [87].

Liu *et al.* [121] prepared Pt<sub>4</sub>ZrO<sub>2</sub>/C and Pt/C catalysts and evaluated the sintering resistance and corrosion resistance properties using accelerated ageing tests (AAT) and a continuous cyclic voltammetry test. XRD patterns showed that the particle size of Pt<sub>4</sub>ZrO<sub>2</sub>/C decreased after AAT. The Pt<sub>4</sub>ZrO<sub>2</sub>/C catalyst maintained a higher electrochemical area and much more platinum compared to the Pt/C catalyst after AAT. The continuous cyclic voltammetry tests also gave similar results. The preliminary experiments indicate that the addition of ZrO<sub>2</sub> into the platinum catalysts can significantly improve the durability of the catalyst in terms of sintering resistance and corrosion resistance. The proposed anchor effect of ZrO<sub>2</sub> to Pt is responsible for preventing Pt<sub>4</sub>ZrO<sub>2</sub>/C catalysts from sintering during the accelerated ageing test.

## 2.2.2 Preparation of electrocatalysts

The preparation or synthesis of an electrocatalyst is a very important step when it comes to the development of electrocatalysts, as the catalyst preparation method has a great influence on catalytic activity. If a catalyst is prepared for a particular reaction, its

activity will be directly proportional to the surface area exposed to the reacting species. Moreover, size and shape of the particles in a bulk catalyst affect the activity of a catalyst<sup>[95,102]</sup>.

The principle of the catalyst preparation technique involves two stages. First, rendering a metal-salt component in a fine form onto a support and secondly, conversion of the supported metal salt to a metallic or oxide state. The first stage is known as dispersion and is achieved by impregnation, adsorption from the solution, co-precipitation, or deposition, while the second is the thermal treatment in either an inert atmosphere or an active atmosphere of either oxygen or hydrogen<sup>[95]</sup>.

When the active atmosphere is hydrogen the process is known as reduction. Although calcination/reduction can cause major problems in catalyst preparation on the large scale, it is a generalization to say that once the metal species has been bound to the support surface its degree of dispersion and location will be retained during subsequent treatment<sup>[95]</sup>.

The catalytic surface area of a supported catalyst (its dispersion) depends significantly on the preparation procedure. Parameters that influence catalyst dispersion include the nature and concentration of the precursor and support, the duration, temperature and atmosphere (in contact with the catalyst surface) of the preparation steps<sup>[102]</sup>.

### **2.2.2.1 Types of dispersion**

#### **(a) Impregnation**

Impregnation, as a means of preparing a supported catalyst, is achieved by filling the pores of a support with solution of the metal salt from which the solvent is subsequently evaporated. The catalyst is prepared either by spraying the support material with a solution of a suitable metal salt, such that the required weight of the active component is incorporated into the support without using an excess of solution. This is then followed by drying and subsequent decomposition of the salt at an elevated temperature, either by thermal decomposition or reduction<sup>[95]</sup>.

As an example of impregnation, Garsany *et al.*<sup>[124]</sup> mixed carbon nanotubes with 4.1ml of 10mM H<sub>2</sub>PtCl<sub>6</sub> (Aldrich) in an isopropyl alcohol-water (1:3 v/v) solvent at 50°C for 6h under vigorous stirring. The resulting slurry was dried at 100°C to remove the solvent,



and then heat-treated by a 2h exposure to pure H<sub>2</sub> flow at 500 °C.

### **(b) Precipitation**

The preparation of supported catalysts by the co-precipitation of metal ions with support ions usually produces an intimate mixing of catalyst and support. This precipitate, when calcined, produces a refractory support with the active component dispersed throughout the bulk as well as at the surface. However, in the preparation of multi-component catalysts, it is possible under improper conditions to obtain a heterogeneous product because of the different solubility products ( $K_{sp}$ ) of the constituents<sup>[95]</sup>.

Carbon nanotubes were vigorously mixed with 4.1ml of 10mM H<sub>2</sub>PtCl<sub>6</sub> (Aldrich) in an isopropyl alcohol-water (1:3 v/v) solvent mixture at 50 °C for 6h. Then the suspension was heated up to 80 °C and the pH of suspension was adjusted to 8.5 using 0.5Na<sub>2</sub>CO<sub>3</sub> solution. An abundant amount of KBH<sub>4</sub> was added to accomplish a chemical reduction over a period of 2h. The resultant suspension was filtered, washed and vacuum-dried at 90 °C for 4h<sup>[124]</sup>.

### **(c) Adsorption**

Adsorption is the selective removal of metal salts or metal ions from their solution by a process of either physisorption or chemical bonding with active sites on the support. Depending upon the strength of adsorption of the adsorbing species, the concentration of the active material through the catalyst particle may be varied and controlled. This technique permits a greater degree of control over the dispersion and distribution of the active species on the support<sup>[95]</sup>.

### **(d) Deposition**

Deposition, as used in preparing supported catalysts, is the laying down or placing of the active components on the exterior surface of a support. One means by which this may be achieved is the preparation of catalysts by sputtering, which involves condensing a metal vapour onto finely dispersed support and is normally performed under vacuum. Alternatively, the process may be performed in the liquid phase by the deposition of a metal solution onto a suspended support<sup>[95]</sup>.

Liu *et al.*<sup>[121]</sup> prepared Pt<sub>4</sub>ZrO<sub>2</sub>/C and Pt/C catalysts by a modified polyol process. First

the Vulcan carbon XC-72 (Cabot corp. BET: 235m<sup>2</sup>/g denoted as C) was mixed with water and acetone (volume ratio of 3:1). Zirconyl nitrate was added and then excessive NH<sub>4</sub>OH was added under constant stirring to form a precipitate. The resultant sample was filtrated and washed with deionised water and dried at 100°C in air for 10h. This material was finally calcined at 500°C in N<sub>2</sub> for 3h to obtain ZrO<sub>2</sub>/C. The Pt<sub>4</sub>ZrO<sub>2</sub>/C and Pt/C were prepared by the reduction of H<sub>2</sub>PtCl<sub>6</sub> in an ethylene glycol (EG) solution on ZrO<sub>2</sub>/C and XC72 powders. In the two catalysts, the weight ratio of Pt:C was maintained at 20:80 and in Pt<sub>4</sub>ZrO<sub>2</sub>/C the atomic ratio of Pt:Zr was 4:1. Pt<sub>4</sub>ZrO<sub>2</sub>/C and Pt/C were calcined at 500°C in N<sub>2</sub> for 3h.

### **(e) Other methods**

The surfactant-stabilized method can be used to prepare Pt/C electrocatalyst. Carbon nanotubes (CNTs or carbon black), 4.1ml of 10mM H<sub>2</sub>PtCl<sub>6</sub> and surfactant 3-(N,N-dimethyldodecylammonium) propanesulfonate (SB12) were mixed in a methanol-water (1:3v/v) solvent mixture and sonicated to form a uniform suspension. The methanol was used as the reducing agent. The pH of the suspension was adjusted to 7.0 and the suspension was pre-heated in a 50°C water bath for 15min and transferred to another water bath maintained at 90°C for 60min under constant stirring. Afterward, it was cooled in a cold water bath, filtered and finally washed by an abundant amount of ethanol and deionised water to remove the surfactant. The residue was vacuum-dried at 90°C for 4h <sup>[126]</sup>.

According to Li et al. <sup>[126]</sup> the influence of different Pt deposition methods on the dispersion of Pt onto CNTs can be explained using the illustration in Figure 2.2. The Pt size in the impregnation and precipitation methods is controlled by the structure of the support materials, whose pores facilitate the adsorption of Pt precursors and the resultant Pt particles. These methods are suitable for the catalyst preparation on a porous substrate (e.g Vulcan XC72 carbon, 252.5m<sup>2</sup>/g).

For the colloidal method, the size of Pt nanoparticles is largely controlled or stabilised by the protecting agents, such as ligands, surfactants or polymers. In the ion exchange method, the surface groups of support materials provide the anchorage sites for the Pt precursor and particles and determine the dispersion and distribution of the catalyst particles. In the case of impregnation and precipitation catalysts, a broad size distribution is obtained with average particle sizes of 9.8 and 4.8nm. A schematic

illustration of different types of catalyst dispersion is shown in Figure 2.2.

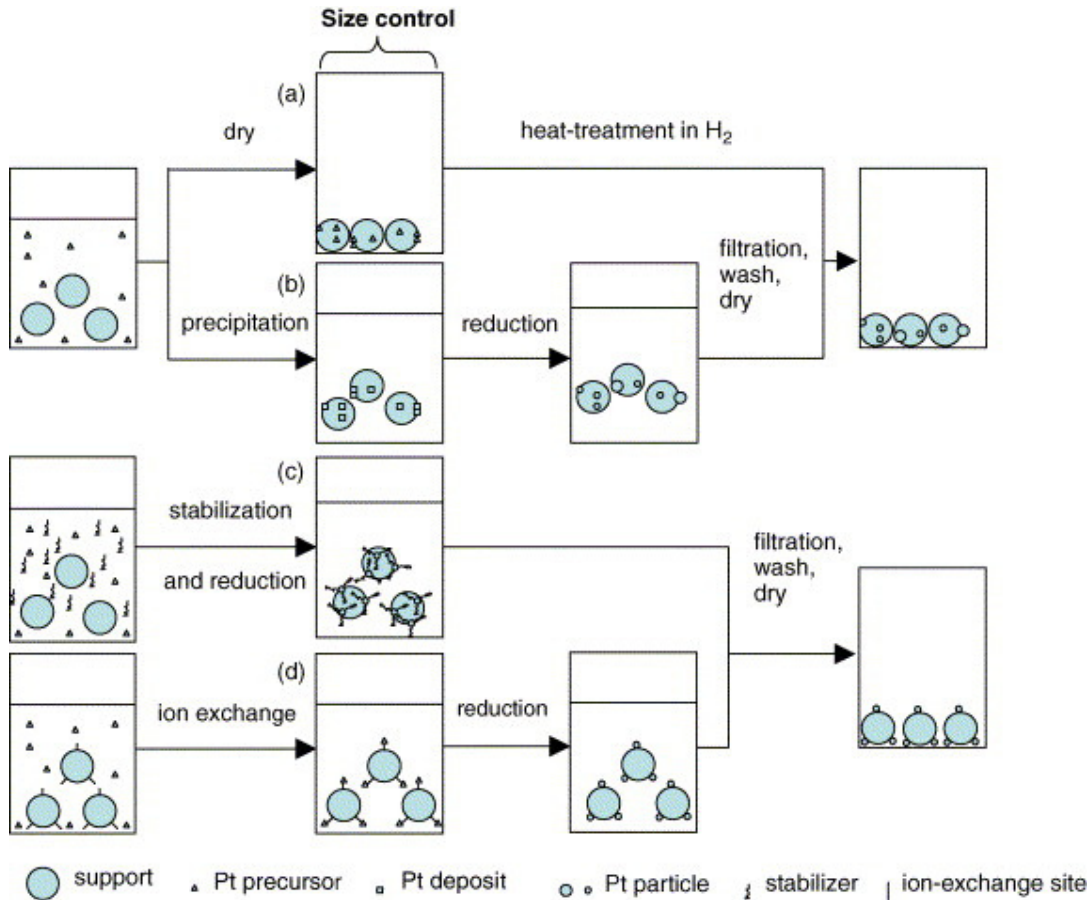


Figure 2.2 Schematic illustrations of (a) impregnation (b) precipitation (c) colloidal and (d) ion exchange methods <sup>[126]</sup>.

### 2.2.2.1 Thermal treatment

Thermal treatment of fuel cell catalysts plays an important role in the improvement of electrocatalytic activity and stability resulting in an enhancement of the oxygen reduction reaction (ORR). These catalysts primarily include unsupported and carbon supported Pt, Pt alloys, non-Pt alloys and transition metal macrocycles. With respect to Pt-based catalysts, heat treatment can induce particle size growth, an improved degree of alloying and changes in the catalyst surface morphology from amorphous to more ordered states, which affect the ORR activity and stability. In addition, heat treatment of catalyst carbon supports can also affect the ORR catalytic activity of the supported

catalyst significantly. However, if the thermal treatment temperature is too high (>1000°C), even though the stability of the catalyst is improved, catalytic activity could be diminished<sup>[143]</sup>.

Antolini *et al.*<sup>[144]</sup> used different low/medium temperature methods to prepare carbon supported Pt-M alloys (M = first row transitional metal). The study revealed that the metal particle size of the carbon supported alloy catalysts synthesised by these methods is smaller than that obtained by high temperature methods. The degree of alloying of catalysts synthesised by low/medium temperature methods is related to the preparation method and to the amount of the non-precious metal (in the case of the reduction with NaBH<sub>4</sub>). The degree of alloying is the same or slightly lower than that obtained by alloy formation at high temperatures.

### 2.2.3 Preconditioning

According to Seo *et al.*<sup>[6]</sup> the key to successful electro-oxidation of sulphur dioxide in acid media is the electrode preconditioning process. The required active electrode surface is obtained by scanning three or four times between 0.15 and 1.5V vs. SCE directly into the electrolytic cell in 0.1M sulphuric acid. The initial scan to a high anodic voltage during the preconditioning step causes an oxide film to be formed on the electrode surface. This is then stripped when the repeat scan is started at a negative voltage corresponding to that at which hydrogen evolution begins. The resulting stripped electrode has the desired surface characteristics. When the electrode is properly conditioned, successive scans are completely reproducible.

Lu and Ammon<sup>[112]</sup> obtained steady-state potentiostatic polarization curves for SO<sub>2</sub> oxidation in 50wt% sulphuric acid on smooth platinum at 25°C. The pre-treatment of the electrode is conducted by maintaining the potential at 1.0V vs. RHE for 30 min. The polarization curve exhibits maximum current density and a Tafel region. The rest potential at 25°C is about 0.49V vs. RHE.

### 2.2.4 Pt loading, dispersion and utilization

In general, slight increases of the Pt loading increases catalyst activity. However, doubling the Pt metal content does not double the activity, as particle size increases with Pt loading leading to a decrease in the electrochemically active surface area per unit mass of Pt. This suboptimal response to increased loading creates challenges for

catalyst synthesis<sup>[134]</sup>.

Lee *et al.*<sup>[34]</sup> states that from an economical point of view, Pt loading is a critical issue due to the high price of Pt. In a SO<sub>2</sub>-saturated 50wt% H<sub>2</sub>SO<sub>4</sub> solution, it was found that an increase in Pt loading led to a considerable improvement of SO<sub>2</sub> oxidation kinetics in a low potential region as compared to that in a high potential region. However, the area-specific activity for the SO<sub>2</sub> oxidation reaction decreased due to the reduction of Pt utilization as the Pt loading amount increased.

### 2.2.5 Pt dissolution and sulphur poisoning

Sulphur is known as a severe poisoning agent of many heterogeneous reactions. The change from catalytic to poisoning properties of sulphur is coverage dependent. When the amount of sulphur on the surface exceeds the optimum coverage, the SO<sub>2</sub> oxidation rate begins to drop progressively as the quantity of deposited sulphur increases. The continuous accumulation of sulphur via multilayer growth leads to the thickening of the deposit, which eventually transforms into an inhibiting sulphur layer<sup>[55]</sup>.

Garsany *et al.*<sup>[124]</sup> observed that sulphur coverage of 14% caused a 95% loss in mass activity on Pt/C electrodes. When 37% of the Pt surface was covered with sulphur, the reaction pathway of the oxygen reduction reaction on the Pt/C catalyst changed from a 4-electron process reaction to peroxide, a reagent which can aggressively attack Nafion. This sulphur coverage on Pt/C resulted from contamination by submersion in SO<sub>2</sub>-containing solutions. The initial sulphur coverage of the Pt was determined from the total charge consumed as the sulphur was oxidised from S<sup>0</sup> at 0.05V vs. RHE to water soluble sulphate (SO<sub>4</sub><sup>2-</sup>) at >1.3V. Electrodes were then evaluated for their ORR activity. A significant (33%) loss in Pt mass activity was measured when approximately 1.2% of the Pt surface had adsorbed the sulphur containing species. The authors concluded that adsorbed sulphur is not removed under typical steady-state operating conditions of a proton exchange membrane fuel cell, so it will affect operation by decreasing mass activity of the catalysts and by enhancing formation of the deleterious H<sub>2</sub>O<sub>2</sub> by-product<sup>[124]</sup>.

Kodera *et al.*<sup>[82]</sup> reported on the electrochemical corrosion of a Pt electrode in a strong sulphuric acid. The electrochemical measurements were conducted using a Pt-flag working electrode, Ag/AgSO<sub>4</sub> reference electrode and Pt counter electrode at 25°C.

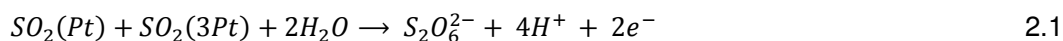
The measured cyclic voltammograms significantly changed in the H<sub>2</sub>SO<sub>4</sub> concentration range of 0.5-18mol.dm<sup>-3</sup>, especially from 14 to 18mol.dm<sup>-3</sup>. After successive potential cycling for 15h in 16 mol.dm<sup>-3</sup>H<sub>2</sub>SO<sub>4</sub>, a weight loss of the Pt-flag electrode was realised. In contrast, controlled potential electrolysis by cathodic polarisation caused a weight gain, which was attributed to sulphur deposition resulting from H<sub>2</sub>SO<sub>4</sub> reduction. The subsequent anodic polarization produced corrosion of the deposited sulphur. The alternating polarisation generated platinum corrosion and resulted in Pt dissolution in solution<sup>[82]</sup>.

Spotnitz *et al.*<sup>[4]</sup> characterised the electrochemical behaviour of sulphur dioxide in sulphuric acid solutions at a platinum rotating disc electrode. Cycling the potential in these solutions between about -0.10 and 1.2V vs SCE results in activation of the electrode so that diffusion-controlled SO<sub>2</sub> oxidation currents can be observed in the double layer region of platinum. Without activation SO<sub>2</sub> oxidation proceeds noticeably only in the potential region of surface oxide formation. Evidence indicates that activation results from the formation of a catalytic layer of sulphur species. The catalytic activity of this layer decays with time in the course of SO<sub>2</sub> oxidation. The formation of sulphur species through oxidation of adsorbed sulphur and formation of platinum oxides complicate the voltammetric behaviour of the system.

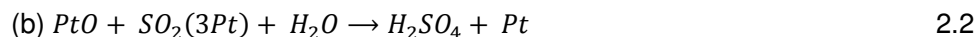
SO<sub>2</sub> oxidises at different potentials between 0.85V and 1.2V vs. SHE. Beyond 1.2V, the current density decreases as the SO<sub>2</sub> oxidation reaction is inhibited. The inhibition phenomenon is not complete and a significant residual current becomes apparent during the reverse scan, even after holding the potential at 1.5V for a short period of time<sup>[42]</sup>.

Audry and Voinov<sup>[44]</sup> proposed that the oxidation of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> on bare and oxide covered platinum proceeds in sulphuric acid solutions via different reaction paths. Inhibition oxidation process occurs by (a) reaction product adsorption, (b) replacement of SO<sub>2</sub>-Pt by PtO, and (c) replacement of SO<sub>2</sub>-3Pt by 3PtO.

(a) The electrochemical oxidation of SO<sub>2</sub> on bare platinum is written as in the article<sup>[44]</sup>.



SO<sub>2</sub> oxidation can proceed on bare below +0.9V vs. SHE is inhibited when the PtO starts forming at around 1.20V vs. SHE.



This will be accompanied by:



(c) Inhibition then occurs at higher potentials because of the replacement on the surface of SO<sub>2</sub>-3Pt by 3PtO when the electrode is completely covered by oxygen above 1.65V vs. SHE.

### 2.3 The use of Pt/C as electrocatalyst for SO<sub>2</sub> electro-oxidation

Platinum has been used as a catalyst for the oxidation of SO<sub>2</sub> in the industrial production of sulphuric acid. Oxidation of SO<sub>2</sub> by platinum based catalysts continues to attract interest due to the fact that platinum particles can be redistributed and regain high catalytic activity<sup>[53, 90]</sup>. The applications of noble metal based catalysts are limited by their scarcity and cost, hence improving their catalytic performance and cost reduction is important<sup>[5]</sup>.

In 1980 Struck *et al.*<sup>[9]</sup>, using smooth platinum as an anode at 25°C, reported that kinetics of the anodic oxidation of SO<sub>2</sub> becomes worse with increasing sulphuric acid concentrations. At H<sub>2</sub>SO<sub>4</sub> concentrations higher than 60wt% the catalysis of the anodic oxidation of SO<sub>2</sub> becomes extremely low between 400 and 600mV vs. SHE in the same solution. An increase in current with increasing temperature is observed despite the decrease in solubility of SO<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub> with rising temperature. The increase in current is due to improved kinetics with increased temperature.

Seo and Sawyer<sup>[5, 6]</sup> studied SO<sub>2</sub> electro-oxidation using cyclic voltammetry and chronopotentiometry on smooth activated platinum electrodes in 0.1M sulphuric acid. They found the shape of the voltammetric waves to be sensitive to the initial potential ranging from -0.15 to 0.3V vs SCE, as the height of the wave was greatly enhanced. With a shift of the initial potential to -0.15V, two anodic peaks were resolved. They attributed the first anodic peak at about 0.4V vs SCE to a pure electron transfer reaction (in the absence of surface oxides) and the second at about 1.0V vs SCE to a reaction between SO<sub>2</sub> and surface oxides.

In 1982 Struck *et al.*<sup>[2]</sup> reported that a current density of 200mA.cm<sup>-2</sup> was generated in the SDE when 390 and 50mV<sub>RHE</sub> overpotential was applied at the anode and cathode

respectively, during SO<sub>2</sub> electro-oxidation reaction in a 50wt% H<sub>2</sub>SO<sub>4</sub> solution<sup>[120]</sup>. It is therefore necessary to reduce the anodic overpotential in order to improve the performance of the SDE.

Colon-Mercado and Hobbs<sup>[18]</sup> studied the catalytic activity and stability of Pt/C and Pd/C in 3.5-10.4M sulphuric acid solutions with temperatures ranging from 30-70°C. Pt/C exhibited superior catalytic activity and stability compared to Pd/C for SO<sub>2</sub> electro-oxidation in concentrated H<sub>2</sub>SO<sub>4</sub> solutions. Tafel plots for Pt/C showed lower potentials (ca.100mV) and higher exchange current densities. Deterioration of Pt/C is evident when polarized in 10.4M H<sub>2</sub>SO<sub>4</sub> solutions at 50°C or higher. Operating conditions targeted for the SDE include H<sub>2</sub>SO<sub>4</sub> as high as 10.4M and temperatures of 80°C. The activation energy for the oxidation of SO<sub>2</sub> on Pt/C was found to be at least half of that on Pd/C.

Summers *et al.*<sup>[14]</sup> conducted an investigation of the electrocatalytic activity of Pt/C and Pd/C for the oxidation of SO<sub>2</sub> and reported that the improvement in the SO<sub>2</sub> oxidation kinetics upon an increase in temperature is readily observed by the change in open circuit potential. In the case of Pt, as the temperature increases the open circuit potential decreases. In the case of Pd the same is true at temperatures below 40°C. Once the system approaches 50°C, the deterioration of the Pd catalyst is so great that the activity drops drastically. In view of the kinetic results the Pt catalyst is superior to the Pd catalyst. It is also apparent that the use of acid concentrations higher than 50wt% H<sub>2</sub>SO<sub>4</sub> will decrease the SDE power efficiency by increasing SO<sub>2</sub> oxidation overvoltage.

## **2.4 Mechanism of SO<sub>2</sub> oxidation on Pt**

As mentioned in Chapter 1, a large and unexplained overpotential exists for this reaction which significantly impacts on the efficiency and economic viability of the HyS cycle. This overpotential needs to be reduced whilst the current density or the electrode kinetics needs to be increased.

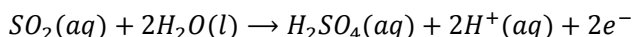
This is a direct result of the slow rate of SO<sub>2</sub> oxidation at the anode, which contributes approximately 70% towards the overpotential and the largest source of improvement in SDE performance will arise from the identification of a means to increase electrode kinetics i.e. the rate of oxidation of SO<sub>2</sub> at the anode resulting in increased current density<sup>[40]</sup>.



This can be accomplished by the development of a superior electrocatalyst. An improved understanding of the oxidation mechanism may therefore allow optimization of electrode materials and a lowering of the electrode overpotential<sup>[40]</sup>.

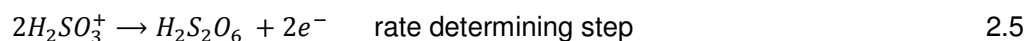
It is widely accepted, even taken for granted, that the electrochemical oxidation of aqueous SO<sub>2</sub> proceeds according to the following pathway:

From chapter1, Equation 1.2



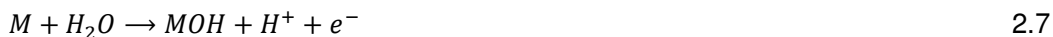
Quijada *et al.*<sup>[24]</sup> investigated the electrochemical oxidation of aqueous SO<sub>2</sub> at platinum electrodes in an acidic medium by means of cyclic voltammetry and in situ Fourier Transform IR (FTIR) spectroscopy. In the potential zone ranging from 0.55 to 1.50V vs RHE the oxidation reaction of SO<sub>2</sub> takes place at a Pt surface initially covered by a sulphur-oxygen adsorbate. At the higher potentials, oxygen adsorption begins to prevail and blocks Pt sites in such a way that SO<sub>2</sub> oxidation is inhibited due to a current efficiency decrease. Fortunately, it appears that cycling down below 0.55V would result in a substantial increase in the electrode performance, because the SO<sub>2</sub> oxidation reaction is promoted considerably.

Appleby and Pichon<sup>[111]</sup> studied SO<sub>2</sub> oxidation on both smooth and platinum black electrodes in 44wt% sulphuric acid at 50°C. No electrode pre-treatment was mentioned. On smooth electrodes, potential sweep experiments revealed two oxidation peaks, one at 0.7V (RHE) and the second at 1.2V. The first exhibited diffusion character (peak current proportional to the square root of scan rate) whereas the second appeared to be a surface reaction (peak current proportional to the scan rate) and the maximum oxidation current was dependent on the potential scan rate. A detrimental effect of acid concentration on the oxidation kinetics was observed, which was attributed to the lower water activity in concentrated H<sub>2</sub>SO<sub>4</sub>. On both smooth and platinum black electrodes the reaction order was second order in sulphur dioxide. They interpreted their results in terms of the following mechanism



The adsorbed intermediary ( $H_2SO_3^+$ ) finally produces  $H_2SO_4$ . In this scheme, while enhancing  $SO_2$  transport in the boundary layer, local stirring could increase the desorption rate of the intermediate reactant as well, at the expense of the second step. For a given potential scan rate, a significant increase in the oxidation current was always observed after the first completed potential scan, as if the first cycle awakened the electrode and activated the catalyst. The optimum  $SO_2$  oxidation current occurred at a temperature near  $20^\circ C$  and an acid concentration between 20 and 30wt%. Although thermally-activated processes are known to be enhanced by temperature, a strong negative effect of this parameter on the  $SO_2$  oxidation current is observed here. Sulphur dioxide solubility, and hence its concentration in the laboratory cell, actually decreases with temperature and could be responsible for this behaviour<sup>[111]</sup>.

A possible reaction pathway may include the following reaction steps with M representing an active site on the electrode surface, as illustrated by Lu and Ammon<sup>[110]</sup> as follows



Audry and Voinov<sup>[44]</sup> used cyclic voltammetry to study the  $SO_2$  oxidation on a smooth platinum wire electrode in 44wt% sulphuric acid at  $50^\circ C$ . Electrode pre-treatment consisted of holding the electrode at the initial potential of the potential sweeps for 10min. They found that, for initial potentials of 0.55-0.85V (RHE) and an anodic limit of 1.75V, the electrode could be somewhat activated by a single sweep. They postulate that the reaction on an activated surface takes place via a dithionate intermediate step. Potential sweeping activates the surface by removing adsorbed dithionate or some of its decomposition products.

Samec and Weber<sup>[22]</sup> state that a potential oxidation pathway of aqueous  $SO_2$  is the formation of  $HSO_4^-$



The bisulphate ion then combines with one proton to form sulphuric acid.



The net result of these two reactions is indeed the above-mentioned accepted reaction pathway:



According to Seo and Sawyer<sup>[5]</sup>, however, the oxidation pathway is probably the oxidation of  $SO_2$  to  $SO_4^{2-}$



The sulphate ion then combines with one proton to form the bisulphate ion:



Followed by the bisulphate ion then combining with one proton to form sulphuric acid:



These reactions again result in the above-mentioned pathway:



Although both the above studies found that aqueous  $SO_2$  oxidises according to the same net chemical equation, the reaction pathways proceed according to differing intermediate compounds. It is unknown what the lifetimes of these intermediates are, i.e. which reaction determines the overall rate of the net equation, which could have a negative impact due to possible side reactions.

## 2.5 Alternative electrocatalysts

In 1999 Scott and Taama<sup>[12]</sup> studied the anodic oxidation of sulphur dioxide, in concentrated aqueous solutions of sulphuric acid, on anodes of palladium, palladium coated graphite and palladium coated Ebonex®, platinised titanium, stainless steel, lead dioxide, glassy carbon and impregnated graphite and non-impregnated graphite by linear sweep voltammetry. They reported on the effects of sulphuric acid concentration and temperature on the oxidation kinetics. The palladium, platinised titanium, lead dioxide, graphite and carbon electrodes showed suitable activity towards sulphur dioxide oxidation.

Lu and Ammon <sup>[110]</sup> observed that palladium and palladium oxide showed improved catalytic performance compared to platinum for SO<sub>2</sub> oxidation. The activation energy for SO<sub>2</sub> oxidation on a palladium electrode was ~25kcal mol<sup>-1</sup>.

Colón-Mercado *et al.* <sup>[21]</sup> conducted experiments using 45wt% Pt/C, 45wt% PtRu/RuO<sub>x</sub>-C, 30wt% Pt<sub>3</sub>CoIr/C, 30wt% Pt<sub>3</sub>Co/C, 30wt% Pt<sub>3</sub>CoNi/C and 30wt% Pt<sub>3</sub>CoCr/C as anodes for SO<sub>2</sub> oxidation in 30wt%H<sub>2</sub>SO<sub>4</sub> at 25 °C. All catalysts exhibited good stability after multiple CV cycles. It was reported that 30wt% Pt<sub>3</sub>Co/C, 30wt% Pt<sub>3</sub>CoNi/C, 30wt%Pt<sub>3</sub>CoCr/C alloy catalysts exhibited 5-25mV lower oxidation potentials compared to commercial Pt/C(45wt% Pt/C), however Pt alloyed with Ir and Ru showed lower activity.

Polycrystalline gold electrodes have been found to exhibit a good intrinsic electrocatalytic response towards the oxidation of aqueous SO<sub>2</sub> in acidic media. The oxidation reaction starts at potentials slightly higher than 0.6V vs. SHE, displaying a characteristic voltammetric peak for irreversible processes whose maximum rate is diffusion limited. SO<sub>2</sub> does not strongly adsorb on this metallic substrate and this poor capability of gold as a SO<sub>2</sub> chemisorber allows the deleterious effect of this adsorbed species on the kinetics of the bulk oxidation process to be avoided. At higher sulphur coverages a gradual reduction of the electrocatalytic activity is exhibited until a complete inhibition of the SO<sub>2</sub> oxidation reaction is attained <sup>[24]</sup>.

Koutsopoulos *et al.* <sup>[53]</sup> conducted an investigation on the catalytic oxidation of SO<sub>2</sub> over platinum based catalysts. The active metal was supported on silica gel or titania (anatase) by impregnation. The activities of the silica supported catalysts were found to follow the order Pt-Rh/SiO<sub>2</sub> > Pt/SiO<sub>2</sub> > Pt-Al/SiO<sub>2</sub>. For the samples supported on titania the respective order was Pt/TiO<sub>2</sub> > Pt-Rh/TiO<sub>2</sub> > Pt-Al/TiO<sub>2</sub>. Careful selection of the pH of the impregnation solution and the reduction temperature of the precursor salts resulted in a very active catalyst with an average particle size of 1.7nm.

Koutsopoulos *et al.* <sup>[52]</sup> used several types of titania (anatase) as supports for pure platinum and Pt-Pd bimetallic alloy catalysts. These catalysts were prepared by a wet impregnation technique and a flame aerosol synthesis process obtaining metal loadings of 2wt%. The prepared catalysts were tested for SO<sub>2</sub> oxidation activity at atmospheric pressure in the temperature range 250-600 °C. The SO<sub>2</sub> to SO<sub>3</sub> conversion efficiency of Pt-Pd alloys were significantly higher than that of the individual metals. The effects of the preparation method and the type of titania used had an influence on

the catalytic activity because different titania exhibited different catalytic activity.

Lee *et al.* [131] showed that the incorporation of aluminium in carbon black supported platinum electrocatalysts significantly increased the overall electrocatalytic activity for SO<sub>2</sub> oxidation. The performance of the platinum aluminium electrocatalyst anode was significantly better than that of a pure platinum electrocatalyst. Its superior capacity for oxidising SO<sub>2</sub> was demonstrated by the fact that it generated twice the current than that of the platinum electrocatalyst at the anode potential of 500mV vs. RHE. The synergistic effect of aluminium was observed when amounts of aluminium, as small as 1% were incorporated with platinum. A maximum increase of 68% in the electrocatalytic activity was observed for 10% aluminium incorporated in highly dispersed platinum crystallites.

In the temperature range of 20-500 °C, several SO<sub>2</sub> chemisorption forms on the surface of the SnO<sub>2</sub> samples, both undoped and Sb-doped, were shown to exist. The SO<sub>2</sub> chemisorption on the surface of the SnO<sub>2</sub> samples (both undoped and Sb-doped) were characterized by the different strengths of their binding to the surface and effective charge, their ratio being dependent on the temperature and Sb contents. The SnO<sub>2</sub> samples were used as sensitive electrodes for detecting SO<sub>2</sub> in solid electrolyte-based potentiometric sensors. [58].

## **2.6. Electrochemical catalyst testing**

### **2.6.1 Electrocatalytic measurements**

The rate constants of electrochemical reactions depend on the potential difference (V) at the metal-solution interface. Potential difference (V) is the energy required by the electrode to provide a given amount of current whilst current density is described as a measure of the rate of electron transfer at equilibrium, for example if the potential is increased current density also increases [85,96,104,105].

The current-voltage relationship is important because it can be used to determine the performance of the system. Therefore the current produced in an electrochemical cell will depend on the kinetics of the electrochemical reaction at the electrode surface. The heterogeneous reaction rate at the electrode surface is described by the following equation

$$\text{Rate (mol.s}^{-1}\text{.cm}^{-2}) = \frac{i}{nFA}$$

2.15

The current-voltage relationship will vary with a change in temperature, pressure and concentration of the reaction media. Efficiency losses are due to the resistance of the electrolyte and change in the electrode potentials (due to concentration polarization [85,96,104,105]).

According to Pletcher *et al.* [104] a rotating disc electrode (RDE) gives a well-defined, steady state mass transport regime (shown in Figure 2.3). The mass transfer coefficient is a function of the square root of the rotation rate of the disc. The concept of the Nernst diffusion layer provides a basis for a good qualitative understanding of experiments and more quantitative models allow an exact prediction of voltammetric response [104,105].

This rotating disk electrode consists of a polished disc of a metal or carbon (with a radius of 0.1-1.0cm) in the centre of a larger coplanar disc of some insulating sheath that forms the end of a cylinder, of significantly larger diameter. This cylinder, with its end immersed in solution, is rotated perpendicularly to the surface of the disc at a speed low enough not to induce turbulence (typically 1000 revolutions per minute, rpm). The sheath needs to be polished so that there is no step where the disc and the sheath meet. Only the front face of the disc is exposed to the electrolyte solution [85, 96,104,105].

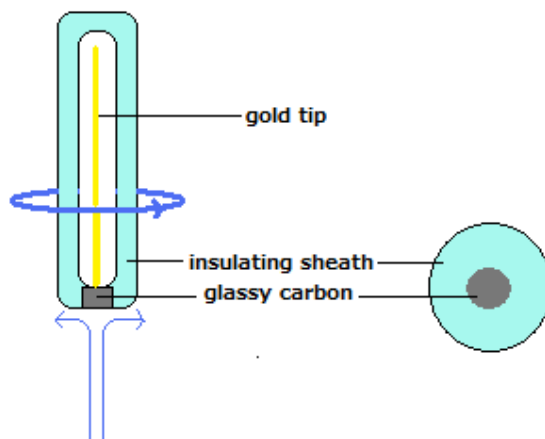


Figure 2.3 Sketch of a rotating disc electrode (RDE)

The RDE acts as a pump and solution is pulled vertically upwards towards the disc and

then thrown. The rate of pumping can also be seen to increase with the rotation rate of the disc,  $\omega$ . Solvent molecules next to the disc surface sticks to it and rotate with the same speed as the electrode. Molecular solvent layers progressively further from the electrode surface are subjected to an increasing centrifugal force and flung outwards on spiral paths. This decreases the pressure in the vicinity of the disc resulting in a pressure gradient, which causes convection upwards to the disc electrode<sup>[104,105]</sup>.

Once a stable rotation speed is reached the solution flows upwards, outwards and circulates back to the bottom of the vessel. This is a hydrodynamic steady-state. This steady-state gives rise to regions in the voltammograms where current is independent of the potential, defined as limiting current plateaus. The limiting current corresponding to this plateau obeys the Levich equation.

$$I_{\text{lim},c} = 0.620nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C_o^b \quad 2.16$$

Where  $I_{\text{lim},c}$  is the limiting current (A),  $n$  the number of electrons exchanged in the reaction,  $F$  the Faraday constant (96485C.mol<sup>-1</sup>),  $\omega$  the rotation rate of the electrode (rad.s<sup>-1</sup>),  $C_o^b$  the concentration of the reacting substance ( $b$ ) in solution (mol.m<sup>-3</sup>) and a electrode surface area (m<sup>2</sup>).  $D$  is the diffusion coefficient (m<sup>2</sup>s<sup>-1</sup>) and  $\nu$  is the kinematic viscosity (m<sup>2</sup>/s). If known, the diffusion coefficient can be used in the Levich equation to find the number of electrons involved in the overall oxidation reaction, which can indicate the expected reaction product. The Levich equation is used for fast electron transfer<sup>[85, 96, 104,105]</sup>.

The Koutecky-Levich equation (equation 2.17) is applicable to surface reactions obeying strictly first order reaction kinetics. The reactions therefore are too slow to allow convective-diffusion control to be operative.

$$\frac{1}{I_c} = \frac{1}{0.620nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C_o^b} + \frac{1}{nFAk_hC_o^b} \quad 2.17$$

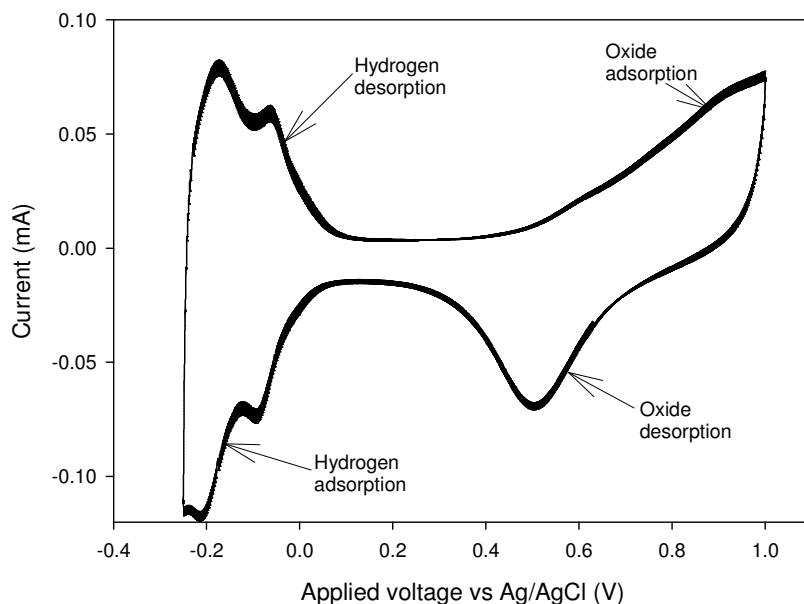
$I_c$  is the overall current density on the disk electrode and the first term of equation 2.17 is the boundary layer diffusion-limited current density while the second term represents the kinetic current density<sup>[104-106]</sup>.  $k_h$  represent the heterogeneous rate constant.

## 2.6.2 Cyclic voltammetry

The technique for determining the electrochemical surface area of fuel cell electrodes

by CV analysis has been used for several decades. The procedure involves cycling the electrode of interest over a voltage range where charge transfer reactions are adsorption-limited at the activation sites. The electrode potential is such that the number of reactive surface sites can be obtained by recording the total charge required for monolayer adsorption/desorption<sup>[137]</sup>.

CV scans are presented as a voltammogram of current density vs. the working electrode potential as shown in Figure 2.4. The voltammograms exhibit multiple peaks associated with both the oxidation and reduction reactions. Each peak is indicative of adsorption onto or desorption from a particular crystal index of platinum<sup>[137, 104, 105]</sup>.



**Figure 2.4 Cyclic voltammetry of Pt electrode in 1M H<sub>2</sub>SO<sub>4</sub>, 100mV/s scan rate**

Integration of the hydrogen desorption/adsorption peaks that result as a consequence of the forward and reverse scans, is used to estimate the electrochemically active surface area (EAS) of the electrocatalyst<sup>[137]</sup>. The values of the electrochemical active surface area are obtained by measuring the charge from the hydrogen desorption peaks after subtracting the charge from the double-layer region and with the assumption that the smooth Pt electrode gives the hydrogen adsorption charge of  $210\mu\text{C}\cdot\text{cm}^{-2}$ <sup>[137, 125]</sup>.

The EAS area of the catalysts, which is determined by the magnitude of the hydrogen



adsorption-desorption peaks, in turn depends mainly on the size of the Pt particles and the presence of different crystallites of Pt, i.e. Pt(111), Pt(110) and Pt(100) facets<sup>[125]</sup>.

The measurement of electrochemical active surface area is an important diagnostic tool for fuel cell catalyst experiments, electrode and membrane electrode assembly (MEA) developers and manufacturers. The EAS measurements are used in RDE studies to determine if the catalyst has dissolved in the electrolyte during the RDE experiments<sup>[137]</sup>.

Lee *et al.*<sup>[34]</sup> showed that the increase in Pt loading led to the increase of electrochemical active surface area, theoretical active area and Pt utilization. The theoretical active area value was calculated from the following equation

$$A_{theo} = 6 \frac{m}{\rho d} \quad 2.18$$

where  $m$  is the mass of pure Pt in the Pt/C electrode (g),  $\rho$  is the density of the bulk Pt ( $\text{g}\cdot\text{m}^{-3}$ ) and  $d$  represents the average Pt particle diameter (cm).

In Appendix A Figure A.2 shows the increase in platinum crystalline size (as measured by X-ray diffraction and the corresponding decrease in electrochemically active surface area (EAS) per unit mass of platinum with increased platinum loading in a conventionally prepared fuel cell catalyst<sup>[134]</sup>.

Summers *et al.*<sup>[14]</sup> observed that the high current density peak is due to monolayer oxide-formation of the catalyst layer in 30wt% $\text{H}_2\text{SO}_4$  at around 0.75V vs. SHE for Pd and 0.8V vs. SHE for Pt. As the acid concentration is increased, the peak intensity for the oxide formation decreases indicating that the formation of oxides is more limited. The low potential peak in the potential region between 0.24 and 0.1V vs. SHE corresponds to hydrogen adsorption-desorption on the catalyst surface. The acid strength increases the intensity of the hydrogen adsorption-desorption peaks increases. The area under the hydrogen adsorption-desorption peak gives an idea of the electrochemically active surface area available for reaction. A reduction in the surface area indicates that the metal particles are either agglomerating on the carbon surface or the metal catalyst is not stable in the solution and is dissolving.

### 2.6.3 Linear polarisation

Several important electroanalytical methods are based on current-voltage curves,

which are obtained by measuring the variation of current in a cell as a function of its potential. Equation 2.20 predicts that at constant electrode potentials, a linear relationship should exist between the cell voltage and the current. In fact, departures from linearity are often encountered, under these circumstances the cell is said to be polarised<sup>[105]</sup>.

$$E_{cell} = E_{cathode} - E_{anode} \quad 2.19$$

Polarization at a single electrode can be studied by coupling it with an electrode that is not readily polarised. Such an electrode is characterised by being large in area and being based on a half-cell reaction that is rapid and reversible<sup>[105]</sup>. The degree of polarization of an electrode is measured by the overvoltage or overpotential ( $\eta$ ), which is the difference between the actual cell voltage at equilibrium and the theoretical voltage under standard conditions

$$\eta = E_e - E^\circ \quad 2.20$$

where  $E_e < E^\circ$ . It is important to realise that polarisation always reduces the electrode potential for a system. Thus, if  $E_e$  is smaller than  $E^\circ$  then  $\eta$  is negative.

When an electrochemical cell reaction is driven by an external source of energy, the measured voltage may not be that calculated from  $E^\circ$ , even though the cell reaction is at standard conditions. Standard conditions imply  $T = 298.15\text{K}$  ( $25^\circ\text{C}$ ),  $P = 1\text{bar}$  and an activity of  $1\text{mol/L}$  for each component. Under non-standard conditions the Nernst equation (Equation 1.8) comes into play, which changes the cell potential<sup>[85, 96, 104-106]</sup>. For  $\text{SO}_2$  electro-oxidation the Nernst equation is as follows

$$E_{cell} = E^\circ - \frac{RT}{nF} \ln \frac{[\text{H}_2\text{SO}_4][\text{P}_{\text{H}_2}]}{[\text{SO}_2]} \quad 1.8$$

From the above equation it therefore follows that under standard conditions  $E_{cell} = E^\circ$  and under non-standard conditions  $E_{cell} > E^\circ$ .

The cell potential is a combination of the cathodic half-cell potential and anodic half-cell reaction according to:

$$E_{cell} = E_{cathode} - E_{anode} = 0 - 0.158 = -0.158\text{V} \quad (\text{under standard conditions})$$

The drive is therefore to develop an electrocatalyst that will lower the overpotential so

as to get the cell potential as close as possible to the standard potential,

## **2.7 Surface characterisation of the catalyst**

Surface characterisation plays a crucial role in electrocatalysis as it can relate the physical characteristics of a catalyst to its electrochemical activity. It can furthermore determine the extent of adsorption and desorption of the reactants and products, respectively. The surface of a solid in contact with a liquid or gaseous phase usually differs substantially from the interior of the solid both in chemical composition and physical properties<sup>[105]</sup>.

The elucidation of the structures, compositions and chemical properties of both the solids used in heterogeneous catalysis and the adsorbates and intermediates present on the surfaces of the catalysts during reaction is vital for a better understanding of the relationship between catalyst properties and catalytic performance. This knowledge is essential to develop more active, selective and durable catalysts and also to optimise reaction conditions<sup>[154]</sup>.

The activity will be proportional to the surface area exposed to a reacting species, which provides useful information about the physical nature of surfaces but less about their chemical nature. The most effective surface study methods are those in which the primary beam, secondary beam or both are made up of electrons, ions or molecules and not photons<sup>[105]</sup>.

### **2.7.1 Transmission electron microscopy**

Electron microscope (EM) is a straightforward technique useful for the determination of the morphology and size of solid catalysts. Electron microscopy can be performed in one of two modes by scanning of a well-focused electron beam over the surface of the sample, or in a transmission arrangement<sup>[154]</sup>.

The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light. What you can see with a light microscope is limited by the wavelength of light. TEMs use electrons as “light source” and their much lower wavelength make it possible to get a resolution a thousand times better than with a light microscope<sup>[141]</sup>.

Transmission electron microscopy is available in two modes: a bright-field mode where

the intensity of the transmitted beam provides a two dimensional image of density or thickness of the sample and a dark-field mode where the electron diffraction pattern is recorded. A combination of topographic and crystallographic information including particle size distributions can be obtained in this way <sup>[154]</sup>.

TEM has a higher resolution than SEM (down to 0.1nm) and is often used to image nanosized catalysts such as metal oxide particles, supported metals and catalysts with nanopores. SEM and TEM work best for studying solids and are not well suited to detect reaction intermediates on catalyst surfaces <sup>[154]</sup>.

Samples are viewed to the order of a few angstroms ( $10^{-10}$ ). For example, you can study small details in the cell or different materials down to near atomic levels. The possibility for high magnifications has made the TEM a valuable tool in medical, biological and materials research <sup>[141]</sup>.

### 2.7.2 X-Ray Diffraction

X-Ray diffraction (XRD) provides a convenient and practical means for the identification of crystalline compounds. The X-ray powder diffraction method is unique in that it is the only analytical method that is capable of providing qualitative and quantitative information about the compounds present in a solid sample <sup>[105]</sup>.

X-ray diffraction is currently of prime importance in elucidating crystalline compounds. X-ray powder methods are based upon the fact that an X-ray diffraction pattern is unique for each crystalline substance, thus if an exact match can be found between the pattern of an unknown and an authentic sample, chemical identity can be assumed <sup>[105]</sup>.

XRD analysis is typically limited to the identification of specific lattice planes that produce peaks at their corresponding angular positions  $2\theta$ , determined by Bragg's law

$$2d\sin\theta = n\lambda \qquad 2.21$$

where  $n$  is an integer,  $d$  is the spacing between the planes in the atomic lattice,  $\theta$  is the angle between the incident ray and the scattering planes and  $\lambda$  is the wavelength of the incident wave.

The characteristic patterns associated with individual solids make XRD quite useful for the identification of the bulk crystalline components of solid catalysts <sup>[154]</sup>. X-ray diffraction is used to determine the average crystalline or grain size of catalysts. The

XRD peaks are intense and sharp only if the sample has sufficient long-range order and become broader for crystalline sizes below about 100nm. Average particle sizes below about 60nm can be roughly estimated by applying the Debye-Scherrer equation

$$D = 0.89\lambda / (B_0^2 - B_e^2)^{1/2} \cos\theta \quad 2.22$$

where  $B_0$  is the measured width (in radians) of a diffraction line at half-maximum and  $B_e$  the corresponding width at half-maximum of a well-crystallised reference sample <sup>[154]</sup>.

This technique does present some limitations when applied to catalysis. XRD is not useful for the detection of reaction intermediates on catalytic surfaces. Due to its low sensitivity, the concentration of the crystalline phase in the sample needs to be reasonably high in order to be detected. XRD can only detect crystalline phases and fails to provide useful information on the amorphous or highly dispersed solid phases so common in catalysts. It probes bulk phases and is not able to selectively identify the surface structures where catalytic reactions takes place <sup>[154]</sup>.

## 2.8 Conclusions

It would seem that very little research has been conducted on  $\text{SO}_2$  electrolysis. Current operating performance of the SDE is in the order of  $200\text{mA}/\text{cm}^2$  (current density) at  $0.9\text{V}$  (operating potential), which has to be improved to  $500\text{mA}/\text{cm}^2$  at  $0.6\text{V}$ . Operating parameters, e.g.  $\text{H}_2\text{SO}_4$  concentration, pressure and temperature have different effects on the electrochemical oxidation of  $\text{SO}_2$ . Optimum conditions for the operation of SDE have not been pinpointed and only go to show that little work has been afforded to the SDE. This leaves a huge room for future improvement of the SDE and the HyS process as a whole.

Indications are that superior catalysts could be obtained in that (i) specific base metal additions to platinum did result in improved catalytic activity, and that (ii) gold and palladium exhibited superior catalytic activity to platinum in certain instances. However superior catalytic activity has to go hand in hand with improved catalyst lifetime. This leaves room for improvement. Preconditioning of the electrocatalyst, by cycling the electrode to either high or low potentials, has a definite effect on the catalytic activity of the catalyst. This could result in the formation of metal oxides and sulphur deposition on the electrode and it has been found that both formation of metal oxides and sulphur deposition can be either beneficial or inhibiting.

There seems to be no consensus as to the exact mechanism for the electrochemical oxidation of  $\text{SO}_2$ . According to the mechanism of  $\text{SO}_2$  oxidation, different intermediates are possible. However, failure to pinpoint the exact mechanism will result in uncertainty as to the exact nature of possible intermediates. This will have a negative effect on enhancing the kinetics of  $\text{SO}_2$  oxidation as the intermediates cause side-reactions which inhibit the process. Better understanding of the oxidation mechanism may allow optimization of electrode materials and a lowering of the electrode overpotential.