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Catalyst Synthesis Techniques

Christina Bock, Helga Halvorsen and Barry MacDougall

9.1 Introduction

This chapter deals with aspects of the synthesis of fuel cell catalysts. Practical catalysts for low-temperature fuel cells are typically in the nano-size range and are frequently formed or deposited on high-surface-area supports. Pt is the most commonly used catalyst for both cathode and anode in proton exchange membrane fuel cells (PEMFCs). In the case of the cathode, combined catalyst systems such as Pt nanoparticles supported on Au or Pt alloy catalysts, as well as Pt-skin catalysts formed in combination with the iron group metals have also attracted attention. Much work has been carried out on the development of "non-noble" metal (Pt-free) catalysts, the synthesis of which will be discussed in Section 9.5. In the case of the anode, bi-metallic catalysts are typically employed unless the fuel is neat H_2 . Pt-Ru is the state-of-the-art catalyst for both methanol and reformat fuel cells. For the latter, other anode catalysts such as Pt/MoO₃ and Pt/Sn are also considered promising.

In this chapter we present an overview of methods used to synthesize fuel cell catalysts, with a focus on catalysts for PEMFCs and direct methanol fuel cells (DMFCs). Examples for the synthesis of catalysts for other low-temperature fuel cells, such as formic acid, are not included in this chapter. The synthesis of both Pt-based and Pt-free catalysts is discussed, and dedicated sections describe methods that allow control of catalyst size and composition. First, general catalyst synthesis methods are introduced. Subsequently, the reader is introduced to particle size and "structure" control of fuel cell catalysts.

9.2 Catalysis Synthesis Methods

The purpose of this sub-section is to present to the reader with a general overview of the most common synthetic methods for fabricating Pt-based catalysts. Although no single method is superior to the others, depending on the end application of the catalyst and the instrumentation available, one method may be advantageous over

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another. Therefore, the reader is advised to consider the intrinsic advantages and disadvantages of each method when selecting which to use.

9.2.1 Low-temperature Chemical Precipitation

Platinum and platinum-based nanocatalysts can be made by chemical precipitation at low temperatures. The use of this synthesis method dates back several decades [1]. Its advantage is preparation under "mild" conditions, i.e., at low temperatures. Supported and unsupported catalysts can be made, and the process is in principle simple, involving the addition of a reducing agent to a platinum-salt solution. Bi-metallic catalysts can be made by the co-precipitation of a solution of two metal precursor salts, e.g., Pt- and Ru-salts. Ideally, the precursor salt is reduced to the metallic state and precipitates out of solution, forming unsupported catalysts that can be filtered and washed. Single and bi-metallic Pt and Ru catalysts of 3 to 12 m²g⁻¹ surface area were made by reducing and co-reducing aqueous solutions of H₂PtCl₆ and RuCl₃ using sodium borohydride and hydrazine hydrate [1]. Sodium borohydride seems to be the preferable reducing agent. The final products are PtRu alloy powders, which are frequently reduced at 300 °C in H₂. However, it has been shown more recently that H₂ treatment at such high temperatures is not essential for PtRu alloy formation and complete reduction [2].

An attractive low-temperature route is to use carbonyl precursors that decompose at low temperatures and avoid chloride contamination [3, 4]. Many studies use the synthesis methods reported by Chini and Adams for monometallic carbonyls and heterometallic carbonyls [5, 6]. The metal-carbonyl can be formed by bubbling CO through a solution of, e.g., platinum acid (H₂PtCl₆), which has been reported to result in the formation of a Pt(CO)₂ precipitate that can be washed, filtered, and dried [4]. To form supported catalysts, carbon black is added prior to the reduction of the metal-carbonyls. Unsupported particles grow more rapidly than supported particles; typically they are at least twice the size of supported particles [7]. Despite this limitation, platinum electrocatalysts as small as 3 nm have been fabricated with [Pt₃(CO)₆]₁₀⁻² as the platinum source and hydrogen as the reducing agent. Platinum alloys can be made by first fabricating the bimetallic carbonyl via:

where M = Sn, Ni, Cr, Co, and X = Cl followed by hydrogen reduction. As an example, Pt-Sn particles (of atomic ratio 3:1) with an average size of 2.4 ± 1 nm have been made by this method [7]. Supported, bi-metallic Pt-Ru catalysts have also been made by dissolving Pt and Ru-carbonyl precursors in o-Xylene [4]. Vulcan XC72 was added and the mixture was refluxed at 143 °C for 24 h to form the carbon-supported, nanosized Pt-Ru catalysts.

9.2.2 Colloidal

The colloidal method of generating nanocatalysts is similar to the chemical catalyst precipitation method. However, it involves the added benefit of a capping agent

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that allows for size control of the catalysts and prevents agglomeration of the catalyst particles. Any molecule that adsorbs onto the catalyst has the potential to act as a capping agent. The experimental procedure is as simple as combining the metal source, a reducing agent, and a capping agent together and mixing. Bi-metallic and other colloidal catalysts can be prepared by co-reduction. If dihydrogen gas is the reducing agent, it is typically bubbled through the solution. To synthesize supported catalysts a carbon support is added to the mixture before or after the formation of the catalyst particles. If a fast reducing agent is used the reactions can be completed within less than 30 minutes [8]. Conversely, slow reducing agents, like dihydrogen gas at room temperature, require longer reaction times and are generally allowed to react overnight or for at least 12 h.

Initial reports for the synthesis of bi-metallic, nanosized PtRu catalysts involved a number of steps. A well-known synthesis of bi-metallic carbon-supported Pt/Ru catalysts of high surface area (ca. 80 m²g⁻¹ Pt + Ru) is the Watanabe method [9]. They first formed colloidal "PtO₂" from platinic acid (H₂PtCl₆) with the reduction of NaHSO₃ and oxidative decomposition with H₂O₂ at a fixed pH of 5, according to the following, possible reaction scheme [10]:

Subsequently, RuCl₃ was added and the formation of a brown-colored colloid "RuO₂" was suggested to have taken place as follows:

Carbon black was added to the solution and H₂ was bubbled through it for complete reduction and formation of the carbon-supported PtRu alloys. PtRu alloy formation was proposed to have taken place, as TEM images of the formed nanosized particles indicated a face centered cubic structure (fcc) rather than hexagonally closed packed (hcp) structure typical for metallic Ru.

The colloidal synthesis method has also been successfully tailored to allow for particle size and composition control, as well as shape control for Pt-based nanoparticles. Control of these factors will be discussed in Section 9.3.

9.2.3 Sol-gel

The sol-gel technique begins with the formation of a liquid solution of suspended particles (a sol) that is aged and dried to form a semi-solid suspension of particles in a liquid (a gel), which is finally calcified, resulting in a mesoporous solid or powder. There are four distinct steps to the sol-gel technique [8]: (1) formation of the gel; (2) aging to allow fine-tuning of the gel properties; (3) drying to remove the solvent from the gel; and (4) calcination to permanently change the physical and chemical properties of the solid. The aging and calcination steps allow for fine

control of the pore size distribution and volume by controlling experimental parameters like time, temperature, heating rate, and pore liquid composition.

Metallic nanocatalysts can be incorporated into the mesoporous structure by a variety of methods. Prefabricated nanoparticles can be incorporated into mesoporous solids by adding the particles into the sol-gel mixture or, if the particles are formed by microemulsions (see Section 9.2.5), the microemulsion can be incorporated into the preformed mesoporous structure. Alternatively, metal salts can be added during gel formation or after the mesoporous structure has formed [12]. An example of the former is the synthesis of WO_3 and WO_3/Pt films that were made by synthesizing $\text{W}(\text{OC}_2\text{H}_5)_6$ and H_2PtCl_6 sol-gel solutions, followed by aging and calcination [13]. A significant drawback associated with this method is that the catalytic nanoparticles may be buried within the structure rather than near the pores. If the particles are not located near the pores they will not be accessible to reactants and therefore will not be efficient catalysts.

Adding nanocatalysts after the mesoporous structure has formed, i.e., after calcination, ensures that the particles form in the pores, provided that the particle size/pore ratio is suitable. Particle formation and deposition can be accomplished by impregnating the structure with the metal ions, followed by a reduction step (see Section 9.2.4) [13]. The impregnation technique allows for controlled particle growth, as the pore size limits particle growth. Impregnation can be facilitated by functionalizing the mesoporous structure with organic groups that anchor metal compounds and/or interact with the surface of the growing nanoparticles. For example, a gel containing acidic functionality on its backbone was required to facilitate the doping of an organic gel with $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ [14]. Functionalizing pores with cationic surfactants allows for ion exchange – i.e., the metal cations can replace the cationic surfactants [13]. Since monovalent surfactant cations are replaced with multivalent metal cations, entropy drives this efficient ion exchange. Once the ion exchange is completed the metal cations are reduced to form nanocatalysts. Chemical vapor deposition (see Section 9.2.8) is another method for adding nanocatalysts to prefabricated mesoporous structures [13]. This method should be restricted to thin films or particles (i.e., not to monolithic samples) to prevent uneven distribution of the metal compounds within the material.

9.2.4 Impregnation

Due to the ease of preparation, impregnation is one of the most commonly used techniques to fabricate catalysts. High-surface-area carbon black can be impregnated with catalyst precursors by mixing the two in an aqueous solution [15]. Other methods of impregnating a substrate involve depositing an aliquot of solution containing the catalyst precursor onto a substrate and allowing it to air dry [16]. Following the impregnation step, a reduction step is required to reduce the catalyst precursor to its metallic state. As reduction occurs after the impregnation step, the nature of the support plays a crucial role in controlling particle size [17]. Common liquid phase reducing agents are $\text{Na}_2\text{S}_2\text{O}_3$, NaBH_4 , $\text{Na}_4\text{S}_2\text{O}_5$, N_2H_4 , and formic acid. H_2 is the predominant gas phase reducing agent.

The most common platinum precursors used for impregnation are chloride salts; however, it has been argued that the metal chloride salts might lead to

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chloride poisoning, which could affect the catalytic activity of the particles [18]. To avoid chlorine poisoning, metal sulfite salts, metal carbonyl complexes, and metal nitrate salts have been used instead [17]. Metal carbonyl complexes are particularly attractive as precursors since they can easily be made by direct oxidation of the metal chloride salt with carbon monoxide. Additionally, an external reducing agent is not required, as nanoparticles can then be formed by thermal decomposition of the metal carbonyl complexes impregnated onto carbon supports [4, 19]. When forming PtRu alloys, care must be taken during the decomposition process since Ru carbonyl decomposition is more favorable than Pt carbonyl decomposition, resulting in Ru-rich products [17]. Using a single-source precursor, a single compound that contains both metals, can overcome this problem.

Experimental factors, such as reduction temperature, can significantly influence the morphology of the catalyst. For example, $(\eta\text{-C}_5\text{H}_9)(\text{Cl})\text{Pt}(\mu\text{Cl})_2\text{Ru}(\text{Cl})(\eta^3\text{-C}_6\text{H}_7)_2$ reduced under hydrogen or argon at 400 °C gave 2.5 ± 1 nm particles, while reduction temperatures of 650 °C gave 5 ± 3 nm particles [20]. The impregnation technique is a comparatively green method to synthesize catalysts; reduction reactions occur either at low or room temperatures, minimizing energy consumption, and organic solvents are avoided by using aqueous media. Drawbacks of the impregnation technique are related to using liquid solutions as the processing medium. In solution, particles can easily agglomerate. Furthermore, the high surface tension of liquid solutions can cause fragile supports, such as aerogels, to collapse [21].

9.2.5 Microemulsions

The use of microemulsions or reversed micelles to synthesize nanosized particles has been explored for almost twenty years [22, 23]. Microemulsion techniques have been used for the synthesis of semiconductor, metal, and alloy nanocrystals. Much work has been done on producing Cu and Ag nanocrystals [22, 24–26]. More recent work has also been devoted to the synthesis of Pt and PtRu nanoparticles for the use of potential fuel cell catalysts and their electrochemical characterization [27, 28]. At high water concentrations an emulsion consists of small oil droplets surrounded by surfactants in a continuous water phase, and vice versa, at high oil concentrations an emulsion consists of small water droplets surrounded by surfactants in a continuous oil phase. Since most metal precursors are inorganic salts they are soluble in water, not in oil. Therefore, emulsions with high oil concentrations and low water concentrations are used almost exclusively. Reverse micelles are water-in-oil droplets stabilized by a surfactant. A very commonly used surfactant is sodium 2-bis(2-ethylhexyl)sulfosuccinate ($\text{Na}(\text{AOT})$). A schematic of a reversed micelle using a Na^+ -ion (AOT) surfactant is shown in Figure 9.1. Alkylthiols (C_nSH), -amines (C_nNH_2), and -isocyanides are examples of other stabilizers that have also been used to make microemulsions. The droplets are displaced randomly in solution and are subject to Brownian motion. They exchange their water content and re-form into distinct micelles. The size of the water-in-oil droplets likely increases with increasing water content. The

droplet size, i.e., resulting particle size, can also be influenced by the chain length of the stabilizer.

Figure 9.1. Schematic of a reversed micelle formed using Na^+ -AOT as surfactant ion. (Reprinted with permission from O.A. El Seoud, Acidities and basicity in reversed micellar systems, in *Reverse Micelles. Biological and Technological Relevance of Amphiphilic Structures in Apolar Media*, edited by P.L. Luisi and B.E. Straub, Plenum Press, New York and London, 1984, figure on p.86.)

In order to obtain the catalyst nanoparticles, the metal salt is reduced by adding a reducing agent into the microemulsion system. Another approach is to mix the microemulsion system that contains a reducing agent with a microemulsion system that contains the metal salt [17, 29]. Once the nanocatalysts are formed they can be deposited onto a support, which is done by adding a solvent like tetrahydrofuran (THF) in conjunction with the support powder to the microemulsion [29]. The solvent destabilizes the microemulsion by competing with the surfactant to adsorb onto the particles, and in the destabilized system the particles will adsorb onto the support. However, Pt and PtRu catalysts formed using the microemulsion technique have also been directly deposited onto carbon blacks such as Vulcan XC72 by simply mixing and stirring the emulsion with the support, i.e., without the need of an emulsion-breaking solvent [27, 28]. After deposition, residual surfactant molecules are typically removed by heat treatment [17]. Emulsion systems are very sensitive to temperature and therefore the oil and surfactant must be carefully

duced by the chain length

selected [29]. Unfortunately, catalyst fabrication by microemulsion is costly since expensive surfactants and oils are needed. Furthermore, both the surfactants and the oils can have a negative environmental impact.

Size control with microemulsions appears more complicated than preliminary research indicated. Originally, the water droplets containing dissolved metal salts stabilized by a surfactant were often described as a "micro-reactor" or "nano-cage" [30]. Since the reduction is confined within the nanoscaled microemulsion it was originally believed that catalyst size is exclusively controlled by the size of the water droplets in the microemulsion [17]. However, it has been found that particle size is a more complicated phenomenon involving the nature of the reducing agent as well as the size of the water droplets in the microemulsion [29]. Small particles are formed by fast nucleation caused by a fast or efficient reducing agent [29]. Hydrazine is an example of a fast reducing agent, while dihydrogen gas is a relatively slow reducing agent.

The size of the water droplet is influenced by the ratio of water to surfactant and the surfactant concentration (at fixed water/oil ratios). As the ratio of water to surfactant increases, the size of the water droplet increases and consequently, the catalyst size also increases. However, a maximum particle size is reached and further increasing the water-to-surfactant ratio has no effect on catalyst size [27, 28, 31]. For example, in a microemulsion system of water/*n*-heptane with the surfactant sodium dioctyl sulfosuccinate the Pt-Ru particle size increases from 2.4 ± 0.1 to 3.2 ± 0.1 nm when the ratio of water to sodium dioctyl sulfosuccinate increases from 4 to 8 [28]. However, increasing the water-to-dioctyl-sulfosuccinate ratio to 10 does not result in any further increase in catalyst size [28]. Droplet size can also be controlled by varying the surfactant concentration while keeping the concentrations of water and oil constant. For example, increasing the surfactant concentration, with constant water and oil concentrations, increases the number of droplets. As a result, droplet size decreases, resulting in fewer metal ions per droplet and a consequently decreased particle size.

Droplet size, however, does not directly or absolutely control particle size. For example, it was estimated that there are five PtCl_6^{2-} ions in each water droplet in the microemulsion system of water in hexane, stabilized by the surfactant pentaethyleneglycol dodecylether [29, 32]. However, TEM analysis indicated that the platinum catalyst formed had an average diameter of 3.5 nm, which corresponds to 100–1500 metal atoms (depending on the shape of the particle). This example illustrates that the final particle is not formed inside the droplet. It is likely that the formation of catalysts via the microemulsion process proceeds by two steps: (1) nucleation of the metal catalyst inside the droplet, followed by (2) aggregation of multiple nuclei via collision and coalescence of droplets to form the final nanocatalysts [29].

9.2.6 Electrochemical

Electrochemical deposition has been used to deposit Pt and Pt-based nanoparticles on a wide variety of substrates, including glassy carbon [33], highly ordered pyrolytic graphite (HOPG) [34, 35], carbon black inside Nafion [36], carbon nanotubes [37], and PAN-based carbon fibers [38]. A number of papers also

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discuss the preparation of Ru nanoparticles onto Pt single crystals, mainly Pt(111). These were made as model catalyst systems for methanol and CO oxidation [39, 40]. Electrochemical deposition occurs at the interface of an electronically conductive substrate and an electrolyte solution containing the salt of the metal to be deposited. There are five stages to electrochemical deposition of metals [41, 42]: (1) transport of metal ions in solution to the electrode surface, (2) electron transfer, (3) formation of metal ad-atoms via adsorption, (4) nucleation and growth, two- or three-dimensional, of metal particles, and (5) growth of the three-dimensional bulk metal phase. If the growth process is stopped after the fourth step, then nanosized catalysts are produced. If, however, the particles are allowed to grow, then the end result is the formation of metal films.

Deposition occurs by supplying the substrate, called the working electrode, with a sufficient potential to reduce the metal salt to its zero valent state:

The substrate is therefore immersed in a metal salt solution, usually containing a supporting electrolyte to decrease the resistivity of the solution. The cathode, where the oxidation reaction occurs, and a reference electrode, used for potential control, are also immersed in the solution. If the binding energy of the metal ad-atom to the substrate is lower than the binding energy of the metal ad-atom to itself then 3D growth of the nuclei occurs. Conversely, if the binding energy of the metal ad-atom to the substrate is higher than the binding energy of the metal ad-atom to itself then 2D growth of the nuclei occurs. 2D and 3D growth can also be controlled by utilizing underpotential deposition (UPD) and overpotential deposition (OPD), respectively; UPD refers to deposition initiated at a potential more positive than the reversible potential of the M/M^{n+} metal ion electrode, while OPD occurs at a potential more negative than the reversible potential [33]. Electrodeposition also has the potential to deposit nanosized catalysts without the use of stabilizers, as discussed in Section 9.3.3.

9.2.7 Spray Pyrolysis

The experimental procedure of spray pyrolysis is simple. First, an aqueous solution containing the metal precursor is atomized into a carrier gas that is passed through a furnace. Second, the atomized precursor solution deposits onto a substrate, where it reacts and forms the final product [43]. The process has many advantages compared to other metal-forming techniques [44]: (1) it is very easy to dope films or form alloys in any proportion by manipulating the spray solution; (2) neither high-purity targets and substrates nor vacuum set-ups are required; (3) deposition rates and therefore film thickness can easily be controlled by controlling the spray parameters; (4) moderate operation temperatures (100–500 °C) allow for deposition on temperature-sensitive substrates and ensure that the overall process is less energy intensive; (5) the technique has relatively limited environmental impact since aqueous precursor solutions can be used; and (6) the process is scalable, with production rates as high as 1.1 kg/h [45].

this single source precursor is 1:1. This structure has been specifically synthesized, as it has sufficient volatility and good stability at low temperatures.

Figure 9.2. Drawing of a single source precursor for CVD [47]. (Reprinted with permission from Huang SF, Chi Y, Bock C, MacDougall B, Carty A. Preparation of the Ru-Pt alloyed thin-films by chemical vapor deposition using single source precursor. *Chem Vap Dep* 2003;3:9; Figure 1.)

CVD is typically used to form thin films but it can also be used to make nanoparticles. Pt-Ru particles 2 nm in diameter have been formed by vapor deposition using commercially available single metal precursors, namely platinum(II)-acetylacetonate and ruthenium(III)-acetylacetonate [48]. The precursors were adsorbed onto carbon black by sublimation and subsequently decomposed at 320 °C in H₂ or N₂. While particle size was virtually independent of sublimation temperature, the Pt:Ru ratio decreased as sublimation temperature increased from 170 to 240 °C. A maximal Pt:Ru ratio, equaling the Pt:Ru ratio of the precursor salts, was reached at 220 °C. The composition is affected by the sublimation temperature, as the vapor pressures of the two precursors are influenced by the sublimation temperature. This example illustrates how the vapor pressure of the precursors can act as a limitation upon CVD alloy formation [21]. CVD is also limited by processing temperature and mass-transfer kinetics [21]. One final disadvantage of CVD to note is that precursors can be highly toxic and therefore difficult to work with [49].

9.2.8.2 Physical Vapor Deposition (PVD)

Mechanical methods, such as cathodic sputtering, and thermal methods, like evaporation, are grouped together under the term physical vapor deposition [50]. All PVD experiments have four essential components: (1) they occur in vacuum, they have (2) a source to supply the material, called a target, (3) a substrate on which the film is deposited, and (4) an energy supply to transport the material from the source to the substrate. The types of PVD vary in how energy is imparted to the particles and how the energized particles are transported to the substrate.

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(Reprinted with permission of the Ru-Pt alloyed precursor. Chem. Vap. Dep.)

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Evaporation PVD occurs by heating the material to be deposited. Under vacuum a molecular beam of the catalyst material is formed thermally. In a molecular beam, atoms and molecules move in a well-defined direction without colliding [51]. When the system is oil-free and the substrate is atomically clean before deposition, molecular beam epitaxial (MBE) deposition is possible. Depositing alloys is difficult with evaporation PVD, since the vapor pressures of the various elements may be different and therefore the deposited film becomes richer in the less volatile species [51].

Cathodic sputtering occurs by generating a plasma between the substrate and a target, the target being made of the material to be deposited. The target acts as the cathode, emitting atoms to the substrate, which acts as the anode. Nickel coatings were developed as the anode for protonic ceramic fuel cells (PCFCs) based on $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$ as the electrolyte [51]. By utilizing a pulsed cathodic sputtering technique, the microstructure and adhesion of the thin film anode to the ceramic electrolyte were optimized, leading to higher-quality anodes and therefore longer stack life of the fuel cell. The main disadvantage associated with cathodic sputtering is low deposition rates.⁵² Sputter deposition has been frequently applied to make Pt based catalysts. Systems with multiple targets consisting of different metals have been used to prepare and screen a large range of binary, ternary and quaternary catalysts of broad composition range.

9.2.9 High-energy Ball Milling

High-energy ball-milling is a mechanical alloying process and a method of grinding and mixing materials in the absence or presence of a liquid. The milling is done in a rotating cylinder or conical mill using balls or pebbles; typically, a powdered catalyst is prepared. Ball-milling is an interesting technique that has the potential to extend the solubility limit of one element into the other, alloy difficult elements, make alloys of defined grain size down to the nanometer range, and synthesize new crystalline and quasi-crystalline phases. Ball-milling has been used to prepare CO-tolerant fuel cell catalysts [53–55]. Catalyst precursors can be prepared by milling together, e.g., Pt and Ru metal powders, a dispersing agent, and often a process control agent. It is also possible to at least partially reduce metal-oxide precursors when milling in a reducing (H_2 -containing) atmosphere. Typical fuel cell catalysts that have been prepared by ball-milling are unsupported Pt and PtRu alloy powders. BET catalyst surface areas in the range of 10 to 40 m^2g^{-1} of catalyst have been made using ball-milling [55]. After ball-milling, the powdered samples contain "impurities", namely the dispersing and process controlling agent, and typically also parts of the mill equipment (i.e., from the vials, balls, and pebbles). Tungsten carbide (WC) balls and vials are often used in ball-mill equipment to make fuel cell catalysts. Aluminum is a typical dispersing agent. Attempts have been made to leach the Al after milling in 1 M NaOH solutions. However, PtAl alloys may be formed that potentially have a beneficial catalytic effect. Typical process control agents (PCAs) used in ball-milling are organic compounds such as stearic acid, hexane, oxalic acid, and polyvinyl pyridine. The PCAs act as surface active agents, interfering with the solid by lowering the surface tension. Organic PCAs typically decompose during ball-

milling and are incorporated into the catalyst as carbides and oxides. Hence, inorganic PCAs have been tested [55]. Denis et al. [56] found the most promising PCAs to be NaF and MgH_2 ; the last has the dual function of acting as a PCA as well as a dispersing agent [55]. MgH_2 partially decomposes during milling, releasing H_2 , and perhaps forms metallic Mg that may be incorporated into the catalyst lattice.

9.3 Particle Size and Shape Control

A major breakthrough in PEMFC technology was achieved decades ago when the concept of supported catalysts was introduced. This allowed for the better distribution and hence better utilization of expensive noble metal catalysts. Pt was supported on carbon black, as shown in the example of a commercially available catalyst in Figure 9.3 [56]. A substantial gain in supporting the noble metal catalysts is, of course, the increase in the ratio of surface atoms to bulk atoms. However, as early work showed, a smaller catalyst size does not yield a higher activity [57–59]. In fact, the activity for many reactions shows a maximum at a particular particle size. A number of possible explanations have been put forward to explain the particle size effect [57–59]. One of them discusses the importance of crystal phases for catalytic reactions, as shown in Figure 9.4 [59]. Hence, the synthesis of catalysts of particular sizes and shapes has attracted a significant amount of interest for fundamental studies as well as practical applications. Achievements in these areas are discussed in this section.

Figure 9.3. TEM images of 40 wt% Pt catalyst supported on carbon (Pt/C) [56]. (Reproduced by permission of ECS—The Electrochemical Society, from He C, Desai S, Brown G, Bollepalli S.)

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Figure 9.4. Calculated mass averaged distribution (MAD, Figure 9.4(a)) and calculated surface-averaged distribution (SAD, Figure 9.4(b)) for edge (e) and corner (c) sites, and 100 and 111 crystal planes for cubo-octahedral Pt as a function of the particle size [59]. (Reproduced by permission of ECS—The Electrochemical Society, from Kinoshita K, Particle size effects for oxygen reduction on highly dispersed platinum in acid electrolytes.)

9.3.1 Mechanism for Size Control Using Colloidal Synthesis Methods

Chemical methods, specifically colloidal synthesis methods, are discussed in this section because of their simplicity for preparing catalysts on a large scale. Furthermore, colloidal synthesis methods offer the benefit of forming nanosized catalysts of controlled size and composition in a simple manner. Stabilizers can be selected so as to provide minimal blockage of the catalyst surface, as discussed below. It should be noted that the substrate, used for subsequent deposition of the prepared colloids, may affect the final catalyst particle size. However, this seems to be dependent on the synthesis method used, as well as the catalyst composition and catalyst loading on the substrate. For example, it has been found that Pt/Ru colloids could be deposited onto carbon blacks without loss of catalyst surface area per weight of catalyst, up to high weight percentages [60]. However, using the same synthesis method, the final particle size of mono-metallic Pt particles showed a dependence on the weight percentage of catalyst per weight of carbon [61].

9.3.1.1 Pt-sols Made Using Organic Stabilizers

Being able to synthesize fuel cell catalysts in the 1 to 5 nm range, i.e., the size range of interest in practical fuel cell catalysis, in a controlled manner is very important. In the case of the reduction of O_2 (ORR), Pt particles in the 3.5 to 4 nm size range are believed to be the most active catalysts, while for bi-metallic Pt/Ru catalysts the optimal size range appears to be in the range of 2.5 nm. Colloidal methods provide an excellent method to control particle size via multiple factors, such as the concentration of the metal precursor salts, the stabilizing agent, and the synthesis temperature. In many cases, the prepared colloids can be deposited onto a suitable substrate. Preferably, the stabilizer molecule is removed after deposition, as otherwise fuel access to the catalyst surface is hindered. This is of particular concern when large stabilizer molecules are used. The synthesis of Pt and other noble metal colloids has been explored for many years. A wide range of methods to prepare Au-sols was published in 1951 by Turkevich et al. [62] (where references to earlier metal sol preparation can also be found). Pt-sols have, for example, been prepared in aqueous solutions using citrate as a reducing agent and stabilizer [63]. The stabilizer adsorbs on the surface of the Pt nuclei and prevents them from agglomerating. Many factors influence the resulting particle size and size distribution, such as the rate of Pt reduction and the rate at which the stabilizer interacts with the Pt atoms. The Pt reduction rate depends on the temperature and the Pt-precursor as well as the concentration and strength of the reducing agent. The resulting particle size depends on the relative concentrations of nuclei and citrate, adsorption strength, and steric hindrance to avoid further growth. Stable, mono-metallic Pt particles in the size range of 1.6 to 3 nm have been prepared in a reproducible manner by reducing H_2PtCl_6 using citrate. Other sizes of Pt-sol have been prepared by changing the reaction temperature, and the concentrations of the Pt precursor salt and sodium citrate. An important factor in stabilizing the metal colloids is the pH of the solution. For example, the pK_a for step 3 of citric acid is 6.4 [64]. The anionic form, citrate, is the effective stabilizer; hence, the pH of the synthesis solution needs to be kept sufficiently high to ensure that the anionic form is present.

Figure 9.5. Control of Pt-Ru/C particle size via the synthesis solution pH using a modified polyol method [67]. (Reprinted with permission from J. Am. Chem. Soc., 2004, 126 (25), 8028, Figure 2. Copyright 2004 American Chemical Society.)

9.3.1.3 The Boennemann Synthesis Method

Much work has been carried out using the Boennemann synthesis method for the preparation of fuel cell catalysts [68]. In this synthesis, mono- and bi-metallic colloidal catalysts are formed by starting with the corresponding metal precursor salts that are then dissolved in tetrahydrofuran (THF), according to Equation 9.8. Tetraoctylammoniumtriethylhydroborate, $N(\text{Oct})_4[\text{BEt}_3\text{H}]$, is utilized as reducing agent and stabilizer at the same time [67]:

A number of fuel cell catalysts have been synthesized in this manner, such as Pt colloids, Pt/Sn colloids, and Pt/Ru colloids of different Pt to Ru ratios. A drawback of the Boennemann synthesis method is that oxidative removal of the stabilizer molecule requires temperatures higher than 300 °C [69]. High-temperature treatment of Pt-based catalysts should be avoided as changes in the structure, namely preferential surface segregation of Pt or RuO_2 , typically take place (this is further discussed in Section 9.4.1). To the best of our knowledge the Boennemann method has not been used to make catalysts of the same composition but different sizes.

9.3.1.4 Other Methods

More recently, a method utilizing different amounts of a large stabilizer has been reported to make Pt and Pt/Ru catalysts of controlled size [70]. The catalysts were

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formed from metal-acetylacetonate precursors reduced by polyalcohols. Oleylamine was used as the stabilizer and the resulting particle size was controlled in the size range of 3.5 to 6.5 nm Pt/Ru, utilizing different amounts of the stabilizer. The work discussed the removal of the stabilizer by a repeated washing and dispersing of the colloids in tetramethylammoniumhydroxide (TMAOH). The colloids were reported to be electrostatically stabilized in the TMAOH solution.

9.3.2 Size Control Using Electrochemical Methods

Formation of fuel cell catalysts using electrochemical methods may not be as attractive for the preparation of large-scale catalysts as, for example, chemical methods. However, electrochemical methods provide advantages over other synthesis methods that make them interesting methods for the preparation of "model" catalysts. Electrochemical deposition offers the advantages that (1) stabilizers and/or capping agents, which should be avoided since residues of stabilizers likely influence the catalytic activity of the nanoparticles, are not required and (2) the particle size can be controlled by varying the length and the amplitude of the potential pulse. The nuclei density can be increased by electrodeposition at a large overpotential [35]. However, increasing the overpotential may result in other reactions occurring in addition to the metal reduction, i.e., hydrogen adsorption and evolution [52]. If metal reduction is not the only process occurring then it is not possible to extract valuable information, such as the type of nucleation or the amount of platinum deposited, from current-time transients.

Platinum nanocatalysts have been electrochemically deposited onto highly ordered pyrolytic graphite (HOPG) from an aqueous H_2PtCl_6 solution containing HCl as the supporting electrolyte. The catalyst size was varied by varying the time the deposition potential was applied: 10 ms deposition time generated particles 2.5 ± 0.9 nm in height and 100 ms deposition time generated particles 7.2 ± 3.2 nm in height [34]. The large increase in size distribution indicates that the nucleation is progressive, i.e., the number of nuclei increases with deposition time. Ideally the deposition process occurs in an instantaneous fashion, that is, the number of nuclei is constant and equal to that at time $t = 0$ of the deposition process. Assuming that all the nuclei grow at the same rate, instantaneous nucleation results in mono-sized particles and is therefore preferable in fabricating nanocatalysts of a specific size. It has been shown that increasing the deposition overpotential or increasing the electrolyte conductivity (using chloride, sulfate, and perchlorate anions) causes a shift from progressive to instantaneous nucleation [35].

9.3.3 Assistance of Templates and Template Preparation

9.3.3.1 Preparation of Mesoporous Catalyst Films

Preparation and control of the size and structure of fuel cell catalysts in the nano-size range using templates synthesis methods has attracted some attention. The best known synthesis method is probably the deposition of metal films from lyotropic liquid crystalline mixtures developed to by Phil Bartlett's group [71–73]. They have used the method to deposit films of Pt, Pt/Ru alloys, and other metals,

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consisting of regular arrays of cylindrical pores at the nanometre scale. The Pt films prepared showed a similar area as Pt blacks, i.e., in the $20 \text{ m}^2 \text{ g}^{-1}$ range [71]. In this method, the metal is electrodeposited from a solution that contains a non-ionic surfactant such as octaethyleneglycol monohexadecyl ether or octaethyleneglycol monododecyl ether and a metal deposition salt, e.g., H_2PtCl_6 . The resulting film structure is influenced by the chain length of the surfactant as well as the deposition conditions such as the potential and electrode size [72]. In the case of Pt, the electrodeposition is complicated. Two reduction reactions can take place, as follows:

Furthermore, the Pt^{2+} in the PtCl_4^{2-} compound is not stable and dissociates into Pt and Pt^{4+} ; i.e., a competitive reaction with Equation 9.10 may take place. Depending on the electrode size, Pt films of different roughness factors (surface areas) are formed. It has been suggested this is due to different diffusion rates of Pt^{2+} away from the electrode surface. The roughness and order of the resulting films is also influenced by the deposition potential, particularly when other processes such as H_2 evolution also take place. Rougher and less ordered films are obtained in the latter case.

Figure 9.6. Schematic description of the preparation procedure of the model electrodes by deposition and postprocessing of Pt-salt micelles. (a) Preparation of the inverse micelles. (b) Pt salt loading. (c) deposition on the glassy carbon substrate by dip coating, and (d) removal of the polymer stabilizer shell and reduction of the Pt-salt core in an oxygen plasma and subsequent reduction in a H_2 atmosphere [74]. (Reprinted with permission from Langmuir, 2007, 23, 5795, Figure 1. Copyright 2007 American Chemical Society.)

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Reverse micelles or water-in-oil emulsions have also been used to make quasi 2-D films of Pt on glassy carbon substrates [74]. Homogeneously distributed Pt nanoparticles of defined size ($25 \pm 5 \text{ nm}$) and a defined average particle separation of $40 \pm 10 \text{ nm}$ were made. The steps involved in the process are illustrated in Figure 9.6. First, the micelles were formed by dispersing polystyrene (PS)-poly(2-vinylpyridine) (P2VP) in dry toluene for one week; subsequently the Pt-precursor salt was added. The emulsion was stirred for another week, prior to dip coating a glassy carbon substrate. The polymeric shell was decomposed in oxygen plasma, while reduction to Pt-metal was carried out by annealing in H_2 . It was essential to anneal the self-assembled Pt-particles in H_2 . Pt films studied after the oxygen-plasma treatment were not stable during electrochemical studies, namely the electrochemical oxidation of adsorbed CO. They appeared to have dissolved.

9.3.3.2 Preparation of Macroporous Catalyst Films

Other approaches for the electrodeposition of structured Pt based films involved polystyrene spheres that were pre-self-assembled on the substrate prior to deposition. The film thickness and pore volume can be varied by using different diameters of polystyrene spheres. 3D nano-network structures were made in this manner. Both the lyotropic liquid template and the self-assembled polystyrene template method have been employed to form Pt and "PtRu alloy" films [75, 76]. An example of a macroporous Pt-based film made using polystyrene spheres is shown in Figure 9.7.

Figure 9.7. Scanning electron micrographs of macroporous platinum and cobalt films that were electrochemically deposited through polystyrene latex spheres preassembled on gold electrode surfaces. Figures 9.7 (a) and (b) show formed cobalt films, while Figures 9.7 (c) and (d) show formed Pt films [75]. (Bartlett PN, Birkin PR, Ghanem MA, Electrochemical deposition of macroporous platinum, palladium and cobalt films using polystyrene latex sphere templates. Chem Commun 2000;17:1671; Figure 1. Reproduced by permission of The Royal Society of Chemistry.)

the model electrodes by the inverse micelles. (b) coating, and (d) removal an oxygen plasma and nission from Langmuir, y.)

9.3.3.3 Nano-structuring Substrates for Nanoparticle Deposition

Substrates themselves can also be nanostructured prior to the deposition of Pt-based nanocatalysts. Ordered nano-pits were introduced onto HOPG surfaces by oxidation with ozone at 300 °C [77, 78]. The nanostructured HOPG surfaces were subsequently used as substrates for the deposition of Pt nanoparticles by either electrochemical or thermal decomposition. Pt nanoparticles in the 2–3 nm size range were formed in this manner. For both deposition methods, electrochemical and thermal, the pits acted as nucleation sites for Pt deposition. The nucleation process was shown to be more reproducible as well as shifting to instantaneous rather than progressive nucleation in the case of Pt electrodeposition onto the nanostructured vs. the smooth, freshly cleaved HOPG substrates.

Figure 9.8. Reduced variable plots of electrochemical reduction of Pt metal onto (a) freshly cleaved, and (b) O_3 oxidized (0.15 ppm O_3 , 300 °C) HOPG. The solid lines represent experimental data. The long and short dashed lines represent theoretical curves for instantaneous and progressive nucleation, respectively [78]. (Reproduced by permission of ECS—The Electrochemical Society, from Halvorsen H, Bock C, MacDougall B, Wang D. Potentiostatic deposition of platinum clusters onto freshly cleaved and ozone oxidized highly ordered pyrolytic graphite.)

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Shape control is achieved if the capping agent encourages the growth of one crystal face over another to generate specific particle shapes. High capping agent to metal source ratios retain the shape of the nuclei with growth, while low capping agent to platinum source ratios selectively grow the {111} plane over the {100} plane. This is thought to be because at low ratios of capping agent to metal source the capping agent preferentially binds to the {100} plane, allowing preferential growth of the {111} plane, while at high capping agent to metal source ratios the capping agent binds to the {111} and {100} planes equally, therefore retaining the shape of the nuclei.

A recent publication describes combining seed-mediated synthesis, capping agent, and diffusion-controlled growth by slow reduction as the parameters for simultaneously controlling the shape and size of platinum nanoparticles [83]. The seed was prepared by reducing H_2PtCl_6 in the presence of REWOTERIC B14 (REWO), which acted as a stabilizer to prevent agglomeration. The resulting nanoparticles were 1 ± 0.2 nm. Tetrahedral Pt nanoparticles of different sizes were

prepared in a 10:1 polyvinylpyrrolidene (PVP): K_2PtCl_4 solution by adding 0, 2, 5, and 10 % seed the seed percentage being with respect to the initial Pt^{4+} concentration. Particles of 8 ± 1 , 5 ± 1 , 2.5 ± 0.5 , and 1.8 ± 0.3 nm size, respectively, were obtained after reduction overnight. Reduction of platinum salt occurs on the surfaces of the seeds, which act as nucleation centers. The high capping agent to platinum source ratio ensures the preservation of the particle's tetrahedral shape. The slow reducing agent, H_2 , has a dual function in this experiment: it assists in the formation of tetrahedral nuclei and inhibits additional nucleation by promoting narrow size distribution.

The question remains whether these catalysts retain their shape and or what shape they will adopt during exposure to electrocatalytic reactions.

9.4 Bi-metallic Catalysts

For efficient FC reactions bi-metallic catalysts are essential. Only in the case of PEMFC anodes that operate on neat H_2 is mono-metallic low-loading Pt used. In the case of neat H_2 the reaction is so fast that the amount of Pt catalyst, and hence the cost, are not of concern. However, in the case of FCs run on methanol or reformat gas (H_2 and CO), bi-metallic catalysts need to be used, the most common choices being bi-metallic catalysts consisting of Pt/Ru. Other combinations as well as ternary and quaternary catalyst formulations have also been tested. In the case of the cathode, where O_2 is reduced (ORR), Pt is the most commonly used catalyst. However, the ORR reduction kinetics are sluggish, so the amounts of Pt and hence the cathode catalyst costs are high. Other formulations, typically Pt catalysts in combination with metals from the iron group, are being considered with the goal of improving catalytic activities and replacing at least some of the Pt. The environment for both the anode and cathode reactions of PEMFCs is acidic, thus limiting the number of catalysts that can be used. Catalyst stability is of greater concern for the cathode than the anode, as in a FC the cathode operates at very positive potentials, enhancing corrosion of the catalyst and support. Catalyst sintering during operation is also a concern. To enhance the catalytic activity of the ORR catalysts, Pt has been alloyed with Fe, Cu, Ni, etc., and core-shell and skin-layer type catalysts consisting of Pt and iron group metal elements are being made and tested [85-90]. In the case of the core-shell catalyst, the core exists of one metal component that is surrounded by a skin of the active catalyst. A skin-layer catalyst typically starts with an alloy, from the surface of which the unstable component is leached.

In this section we will focus on the preparation of Pt/Ru catalysts and Pt catalysts made with the iron group. Ternary and quaternary catalysts are not discussed specifically. However, similar principles apply to their synthesis.

9.4.1 Synthesis of Alloy versus Two-phase Catalysts

A challenge for the preparation of FC catalysts is the formation of catalysts that consist of surfaces made, at the atomic level, of homogeneously distributed catalyst components. Pt forms bulk alloys of a wide range of concentrations with a number

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of metals, thus ensuring distribution on the atomic level in bulk. However, the make-up of the surface and the bulk can be substantially different. Experiments as well as theoretical studies have shown that, particularly in the case of Pt, surface segregation takes place [92, 93]. Experimental work dating back to 1977 has shown that in H_2 atmospheres Pt preferably surface segregates while the surface is enriched with RuO_2 in an air/ O_2 atmosphere of Pt/Ru catalysts, heat treated at 300 °C [91]. According to the theoretical work [92], when Pt is the host lattice it undergoes anti-segregation, meaning Pt prefers to be on the surface. Anti-segregation of Pt is the case with the majority of other metals. The exception is the combination of Pt and Pd, for which very little segregation is expected. Bulk alloys are traditionally formed by arc-melting the metals at high temperatures; hence, preferential segregation of one metal on the surface takes place. In order to limit surface segregation, catalyst synthesis needs to be carried out at low temperatures. The selection of the appropriate conditions allows for the synthesis of Pt-based catalysts at low temperatures. Alloy formation at low temperatures has also been shown to be possible [2]. For example, PtRu alloy powders of close to 45 at% Ru dissolved in the fcc Pt lattice were prepared. The key to the preparation of alloys in this manner is the very rapid and simultaneous reduction of the two noble metal precursor salts. This can be done using a large excess of strong reducing agent (e.g., NaBH_4). Synthesis of two-phase catalysts is in a sense simpler than the preparation of alloy catalysts, although the choice of the metal in the core vs. the shell will be dictated by the redox potentials of the two metal/metal-precursor salts and the respective reduction rates (discussed in Section 9.4.1.2).

9.4.1.1 Alloy Formation Energies, Phase Diagrams, and Quasi Vegard's Law

An important consideration for the preparation of multi-component catalysts is their nobility, i.e., the redox potentials, rate of reaction of the precursors, and miscibility of the metals (thermodynamic stability). One metal must be miscible in the lattice of the other in order to form an alloy. Phase diagrams are readily available and describe the existence of bulk alloys. The formation of an alloy is described by the alloy formation energy. Recently the alloy formation energy, ϵ , has been calculated for three cubic solution alloys (Pt,Ir), (Pt,Re), and (Pt,Ru) [93]. High-resolution plots of the lattice parameter vs. the atomic percentage of the metal dissolved in the host lattice, and cell energies as a function of the metal dissolved were calculated. Examples of such plots for (Pt,Ru) alloys are shown in Figure 9.9(a) and (b). ϵ was then calculated from the slope of the latter graph. Experimental data and theoretical calculations have shown that (Pt,Ru) and (Pt,Ir) alloys follow a quasi "Vegard's law" relationship over a wide range of concentrations. Fundamental differences in the bulk alloy formation of (Pt,Ru) and (Pt,Ir) alloys were suggested according to the calculated ϵ values. In the case of (Pt,Ru), the calculated bulk alloy formation energy is exothermic while the bulk alloy formation energy is calculated to be endothermic for (Pt,Ir) alloys. This suggests that (Pt,Ru) alloy formation is thermodynamically favored and achievable at low temperatures, while the endothermic formation energy calculated for (Pt,Ir) alloys suggests that (Pt,Ir) alloy formation requires external energy, i.e., higher temperatures.

Figure 9.9. Figure 9.9(a) shows the calculated cell data vs. Ru content x for (Pt_{1-x}Ru_x) system. The calculated data actually displays a very slight concavity. Figure 9.9(b) shows the total energy per simulation cell for Pt_{1-x}Ru_x alloys. The data displays a slight concavity due to the fact that the energy of a Pt-Ru bond is very slightly lower than the average of a Pt-Pt and a Ru-Ru bond [93]. (Reprinted from Journal of Alloys and Compounds, 422, LePage Y, Bock C, Rodgers JR. Small step graphs of cell data versus composition for ccp solid-solution binary alloys: application to the (Pt,Ir), (Pt,Re) and (Pt,Ru) systems, 164, Figures 2a and b, respectively, ©2006 with permission from Elsevier.)

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9.4.1.2 One-step and Two-step Synthesis: Alloy, Skeleton, and Skin-layer Catalysts

A one-step synthesis, i.e., the simultaneous reduction of the precursor salts, is more likely to result in alloy formation particularly at low temperatures. However, alloy formation in the bulk can be achieved by heat treating two-phase catalysts in a reducing environment. An example of the latter is the formation of PtCu alloys [90]. This reaction was carried out starting with commercially available Pt nanocatalysts supported on carbon black (Pt/C). The Pt/C catalysts were impregnated with $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and subsequently reduced in H_2 at temperatures between 600 and 900 °C. Nanosized PtCu alloy catalysts were reportedly made in this manner. Copper was subsequently leached from the alloyed particles (either electrochemically or chemically in acidic solutions), thus resulting in a proposed skeletal-type catalyst. Some other catalysts that have been formed similarly, by leaching, consist of Pt and Fe [88]. Skin-type Pt/Ni and Pt/Fe bulk metal catalysts have also been formed by annealing, as will be discussed in Section 9.4.2.3. In some cases such catalysts are reported to have very high catalytic activity. Another possible advantage of these catalysts could be increased stability, namely increased resistance to sintering under FC operation. For example, it has been suggested that an increased resistance to sintering for e.g., $\text{Pt}_3\text{Ni}_1/\text{C}$ over Pt/C catalysts is due to an anchoring effect of Ni upon Pt [94]. It should be noted that great care needs to be taken to eliminate even traces of O_2 in the synthesis of these catalysts at high temperatures and in the presence of transition metals such as Fe, to avoid severe corrosion of carbon.

The two-step synthesis (subsequent reduction of the precursor salts) is more likely to result in phase-separated catalysts, possibly core-shell catalysts. Typically a colloid of a particular metal is first formed then subsequently reacted with the salt of the second metal. Numerous examples of such reactions exist in the literature [95, 96]. The deposition of the second metal onto the preformed colloid can be driven by a redox reaction if the second metal is more noble than the metal of the preformed colloid, i.e., depending on the difference in the free energy (ΔG), which is determined by the difference in the equilibrium potentials, E_1 and E_2 of the redox reactions of the two metal/salts, as follows [97]:

$$\Delta G = -Z_1 Z_2 F (E_1 - E_2) \quad (9.11)$$

In Equation 9.13, Z_1 and Z_2 are the number of electrons involved for redox Reaction 9.1 and 9.2, respectively, and F is Faraday's constant. If ΔG is negative then the oxidized form, Ox_1 , will be reduced by the reductant, Red_2 . As an example, Pt can be readily deposited onto Cu surfaces and onto Au [97]. Deposition of Pt onto pre-reduced Ru surfaces has also been carried out using the same principles. Similarly, Ru has been deposited onto Cu surfaces, but to a smaller extent than Pt and Au. This is in fact seen experimentally, by preferential Ru deposition onto the rims of copper particles [97]. The equilibrium potentials, E_1 and E_2 , are given by the metal and metal-salt involved, as defined by Nernst's law. It follows that the anion of the metal salt influences the E value and hence, ΔG . Through the selection of proper complexing ions it is possible to reverse the host and depositing metals. This has been shown for Pd deposition onto Rh surfaces

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from Pd-nitrate solutions vs. Rh deposition onto Pd surfaces in chloride solutions [97].

It should be noted that deposition driven by differences in redox potentials results in the partial dissolution of the metal from the pre-formed colloid particle. The re-dissolved metal salt can be rapidly reduced and re-deposited onto the existing colloid if the reaction is carried out in a reducing environment (as is the case in, e.g., colloidal 2-step synthesis). In such a case, the shell is likely to consist of a mixture of the two metals rather than a pure metal phase.

9.4.2 Sub-monolayer Deposition of Ad-metals

9.4.2.1 Copper Underpotential Deposition (UPD)

An interesting formation of bi-metallic catalysts involves the use of underpotential deposition (UPD) of Cu onto, e.g., Au [98]. Subsequently, the copper can be displaced by metals such as Pt, Pd, or Ag that are driven through favorable ΔG values. The replacement of Cu with metal, M, is an irreversible, spontaneous redox process, expressed through the respective equilibrium potentials (E), as follows:

$$\Delta G = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{M}^{n+}/\text{M}}^{\text{red}} > 0 \quad (9.12)$$

Sub-monolayers of Pt, Pd, and a bilayer of Ag have been formed in this manner onto Au(111) surfaces.

9.4.2.2 Spontaneous Deposition

The formation of a sub-monolayer driven by a redox reaction, e.g., Pt deposition onto pre-reduced Ru surfaces, is discussed in Section 9.4.1.2. A large number of publications have also been devoted to the preparation of model catalyst systems consisting of Ru nanoparticles deposited onto single Pt crystals [39–41]. Figure 9.10 shows scanning tunnelling microscopy (STM) images of such catalysts. The most commonly used single crystal is Pt(111). The proposed reaction scheme can be summarized by the following steps: the Pt substrate is immersed in a two- to three-week-old solution of RuCl_3 in dilute HClO_4 ; aging of the solution is proposed to result in the formation of hydrated Ru(+IV)-species, e.g., $[\text{RuO}(\text{H}_2\text{O})_4]^{2+}$; spontaneous deposition of the hydrated Ru(+IV)-species in contact with the Pt is proposed to take place according to Equation 9.13, the possible complementary reaction being the partial oxidation of the Pt surface, Equation 9.14.

The adsorbed RuO_2 can then be electro-reduced according to Equations 9.17 and 9.18:

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in 9.14.

(9.13)

(9.14)

to Equations 9.17 and

Figure 9.10. Scanning tunneling microscopy images of Ru nano-particles formed onto a Pt(111) single crystal. (A) Substrate without CO and prior to deposition. (B) deposited Ru particles for 5 min., (C) higher resolution image of (B). (D) deposited Ru particles for 30 min [40]. (Reprinted with permission from Maillard F, Lu C-Q, Wieckowski A, Stimming U. J. Phys. Chem. B. 2005, 109, 16230, Figure 1. Copyright 2005 American Chemical Society.)

9.4.2.3 Annealing/Heat Treatment of Catalysts

As discussed in Section 9.4.1.1, preferential layers of Pt can be formed by annealing alloy catalysts. Promising examples of carefully annealed Pt catalysts have been reported recently [99, 100]. The annealed samples show a high activity towards the ORR, which is attributed to a lower tendency to form surface oxides.

Bulk Pt_3Ni alloys were annealed in ultra-high vacuum to form a single atom Pt skin layer. The challenge remains to synthesize nanosized structures of these catalysts.

Another example of the influence of heat treatment on the make of the catalyst and catalyst surface has been shown by Nashner et al. [101]. They supported and subsequently decomposed a $\text{PtRu}_3\text{C}(\text{CO})_{16}$ molecular cluster precursor at different temperatures in a H_2 atmosphere. Carbon supported Pt Ru nanoparticles of 1.5 nm average diameter were prepared in this manner. At 100 °C the particles consisted of a disordered structure, with a Pt enriched core and Ru on the surface, while at 300 °C an inverted structure was formed, Pt being on the surface of the equilibrated nanoparticle. The schematic of the synthesis is shown in Figure 9.11.

Figure 9.11. Schematic demonstrating the decomposition of a $\text{PtRu}_3\text{C}(\text{CO})_{16}$ molecular precursor at 673 °C in H_2 . The Pt (dark grey) is preferably deposited onto the Ru (light grey) [101]. (Reprinted with permission from J. Am. Chem. Soc. 1997;119:7760. Scheme 1. Copyright 1997 American Chemical Society.)

9.5 Non-noble Metal Catalyst Synthesis

9.5.1 Macrocyclic Complexes

There is considerable interest in the use of non-noble metals for fuel-cell catalysis, which is not surprising when one considers the cost of the noble metal Pt (at well over \$900 US per troy ounce) and its noble metal alloying additions. In a PEM fuel cell using pure hydrogen at the anode, Pt loading requirements down to 0.05 mg Pt cm^{-2} are manageable. On the other hand, the cathode component of the MEA still requires a loading of $\sim 1 \text{ mg Pt cm}^{-2}$ in the best case scenario, due to the slow kinetics of the ORR.

This is a major reason why the majority of non-noble metal catalysis research has focused on the cathode part of the fuel cell system; this work began about 1964 with a paper in *Nature* by Jasinski indicating that N_4 -metal chelates had electrochemical oxygen reduction capacity, and specifically with the discovery that CoN_4 phthalocyanine is an oxygen reduction catalyst in alkaline solution [102,

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Fe₅C(CO)₁₆ molecular
 d onto the Ru (light grey)
 97:119:7760, Scheme 1.

[103]. Subsequently, it was shown that metallic N₄ phthalocyanine components were also active for the ORR in sulfuric acid solutions, with measured catalytic activity decreasing in the order Cu>Ni>Co>Fe [103].

Another important feature of the N₄-macrocycles as oxygen cathode catalysts is the fact that they are quite tolerant to methanol oxidation, a definite advantage in a DMFC system where methanol cross-over through the membrane can occur. As well, the structure of the macrocyclic ligand can be changed (see [103], for example), with a potential modification of the complexes' catalytic ability towards oxygen. The nature of the "metal center" [Fe, Mn, Co, Ni, Cu, etc.], in conjunction with the chemical structure of the macrocycle, is found to dictate the degree of 4-electron vs. 2-electron oxygen reduction that occurs. Obviously, in operating fuel cell systems, 4-electron reduction to water is much preferred over 2-electron reduction to peroxide. It is believed that the redox potential for the metal couple in its two main oxidation states helps to dictate the catalytic activity of the macrocycles, with more positive redox potentials enhancing ORR activity [104]. Supporting the N₄-chelates on carbon or graphite is necessary for catalyst dispersion, and possible interactions with the conducting support need careful consideration. Subsequent heat treatment in inert atmospheres is necessary for both stability and catalytic activity, but the influence of "heat" is not simple, and compromises in conditioning are usually necessary (see below and, for example, [103]).

The interaction of the oxygen molecule with the metal or metal chelate surface has been studied in some detail (e.g., [105]), and linear single metal interactions (i), single metal oxygen interactions (ii), and bridged interactions (iii) have been suggested and investigated [105]:

(i)

(ii)

(iii)

Obviously, the different types of interaction will lead to different kinetics and mechanisms, and different proportions of water to peroxide in the reaction product. Much has been written and speculated about these different interactions and the influence of metal d-orbital characteristics on the overall ORR. Reviews covering this aspect of the subject can be found in references such as [103] and [105]. On the whole, these conclusion can be drawn from the significant body of research on this topic: (a) Fe and Co macrocyclic complexes appear to constitute the best catalysts for oxygen reduction; (b) Ir complexes also appear to be quite active; (c) the redox potential for the metal ion couple plays a major role in dictating the activity of the ORR, with optimal redox potentials existing for maximum activity; (d) many of the non-noble metal catalysts lack the long-term stability needed for practical fuel cell applications; and (e) heat treatment of supported non-noble metal catalysts tends to increase both their activity towards oxygen reduction and their stability, but optimum heat treatments achieve the best "balance" of the two.

From the point-of-view of synthesizing these macrocyclic complexes, considerable research has been conducted and published over the past 40+ years. Going back to the early days of research on the phthalocyanine (Pc) complexes for

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oxygen reduction, it was noted that the Pc components were insoluble in conventional solvents and water, so the catalysts were prepared by dissolving the chelates in concentrated H_2SO_4 then precipitating them onto a carbon substrate by the addition of water. Similar metal-organic chelates such as metal dibenzo-tetra-aza-annulene (MeTAA), metal tetraphenyl porphyrin (MeTPP), and its tetramethoxy derivative (MeTMPP), were discovered to have electrochemical activity [105], and were prepared on carbon supports by the impregnation method. Problems arose with the Me- N_4 chelates due to chemical attack by hydrogen peroxide generated during the ORR. The stability and activity could be improved by heating the chelates to 500–600 °C, and a number of theories have been advanced to explain these observations [103].

In 1989, the group of E. Yeager reported that the adsorption onto carbon of polyacrylonitrile (referred to as "pan") mixed with Co^{2+} or Fe^{2+} salts dissolved in dimethylformamide gave a catalyst for the ORR [106]. The material was pyrolyzed in argon at 800 °C and then used on a cathode catalyst in 85% phosphoric acid at 100 °C. A few years earlier, Yeager had published on the heat treatment of pyrrole-black polymer mixed with Co^{2+} or Fe^{2+} salts [107], and the catalytic activity for the ORR was believed to be due to the retention during pyrolysis of nitrogens of the pyrrole groups to bind the transition metal ions. Yeager and his group believed that the catalytic activity for the ORR in acid media was associated with the nitrogen precursor, the transition metal precursor, and the nature of the carbon support. The high-temperature heat treatment helps to generate nitrogen functionalities on the carbon support and reduce the metal ions to the metallic state. Upon contact with acid electrolyte, some of the metal atoms dissolve and catalytic sites develop. So, this approach was in contrast to the Me- N_4 chelate method discussed above whereby the metal and nitrogen components are part of the same precursor; instead, the metal and nitrogen belong to two different precursors. The Yeager method gave flexibility in catalyst preparation enabling the use of less expensive synthesis precursors.

In the ensuing 20+ years, much work has been done by many groups worldwide on these macrocycles as potential ORR electrocatalysts (see [103, 104]), and it has been confirmed and documented that the natures of the central metal atom (or ion) and the surrounding ligaments play crucial roles [108]. Much of that research has involved development of new synthesis methods and treatment procedures for these catalysts, which are prone to loss of catalytic activity with time and the generation of peroxide, given its associated chemical aggressiveness. While some of these novel catalysts have shown initial activities comparable to Pt, long-term performance is still the issue and until this is resolved (with, for example, optimum heat-treatment procedures), use of these novel materials in real operating fuel cell systems will not likely occur.

9.5.2 Methanol Tolerance and the Economics of these Catalysts

As stated at the beginning of this Section 9.5, a major driving force for the development of non-noble metal catalysts is the "lower-cost" factor (along with potential methanol tolerance in the case of the DMFC system). But even if the cost of large-scale synthesis of these non-Pt catalyst formulations in a fuel cell stable

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form were extremely low (and this is certainly not guaranteed), there is still some question about just how "useful" they would be in an operating system. Gasteiger et al. raise this interesting question, namely that if the cathode catalyst were free, how much of it could one afford to use [109]? For example, if the catalytic activity was $1/100^{\text{th}}$ that of Pt, one would need to use 100 times as much, which would be impractical from the point-of-view of fuel cell system volume, necessitating significant extra costs associated with additional membrane material, bipolar plates, and diffusion media (assuming that we cannot simply increase the catalyst layer thickness indefinitely because of diffusion limitations). Indeed, Gasteiger et al. suggest that the activity of a "cost-less" (i.e., free) cathode catalyst for automotive and light-duty applications would need to be no less than $1/10^{\text{th}}$ of what could be achieved with current Pt catalyst technology. And of course, the non-noble metal chelate catalysts are not "free-of-charge" and have life-time expectancies "still-to-be-determined". Gasteiger et al. point out the vital need to obtain fuel cell performance data on "innovative catalyst systems" under conditions in which the data can be truly compared to an operating Pt catalyst system without the need for too many extrapolations and assumptions. They also stress that the performance of the Pt catalyst fuel cell system must be cited under true "state-of-the-art" catalytic activities, as opposed to those where detrimental conditions (such as Pt poisoning) influence results (and where such conditions can be handled by, e.g., electrode conditioning). By comparing the best results for non-noble metal ORR catalysts from the Dodelet [110–112] and Bron [113, 114] groups, to those for "standard" Pt catalysts, the conclusion is that the latter would still be superior to the former, even if the former catalysts were "free-of-charge". The non-noble metal ORR catalysts face serious durability issues, especially given that they are more prone to peroxide generation than their Pt counterparts (i.e., the 2-electron as opposed to the 4-electron reduction) [see 113, 114]. Indeed, the non-Pt ORR catalysts containing Fe are known to be catalytically attractive but the Fe can generate ferrous ions which are well known to convert hydrogen peroxide to peroxy radicals [115]; these are highly aggressive to many materials, including Nafion. In light of the major activity and durability issues discussed above, further significant progress is needed before synthesized non-Pt-ORR catalysts can be usefully employed in real operating fuel cell systems, and this is not likely to occur for quite some time.

9.5.3 Transition Metal Chalcogenides

Another interesting class of ORR electrocatalysts that is attracting considerable attention are the non-Pt catalysts such as Ru-Mo chalcogenides (containing S, Te, or Se) or the simple Ru-Se compounds. While some noble metal is present, Pt itself is absent. Alonso-Vante was the first to show that Ru-based chalcogenides and chevreel-type phases (like Mo_4RuSe_8) show catalytic activity for the ORR in acid solutions and catalyze the 4-electron reduction to H_2O over the H_2O_2 route [116]. Indeed, the MoRuSe electrocatalysts generated only 3 to 4% H_2O_2 over the entire potential range for the ORR in acid electrolytes [117], thus demonstrating very high selectivity for the 4-electron ORR as opposed to the high degree of 2-electron reduction at pure Se electrodes. As well, these catalysts show high tolerance to

methanol oxidation, an important consideration for DMFC systems (see, e.g., [118]).

The RuMoSe compounds have chevrel phases [119] in which an octahedral cluster with six metal atoms is encased in a cube of chalcogens (see, e.g., [120]). The molecular structures of these compounds, and their subsequent electronic properties, give the mixed metals (such as Ru/Mo) a high density of electronic d-states. This in turn gives rise to an abundant electron reservoir whereby the absorbed O_2 molecules can exchange electrons and be cathodically reduced to H_2O . These Ru-based chalcogenides are usually synthesized by solid-state reactions of the pure elements at temperatures ranging from 1200 to 1700 °C, and under high pressure [117, 121]. But this means that the synthesis procedures are complicated and therefore the compounds themselves are very expensive and probably not attractive for large-scale use. Low-temperature synthesis methods have been developed, the most prominent being either the thermolysis method or the colloidal method (see [122] and references therein for a related methodology, and also [123, 124]). In the thermolysis method, $Ru(CO)_2$ and elemental selenium, in either xylene or 1,2-dichlorobenzene as solvent, are refluxed at the boiling point in an inert atmosphere. Ru/Se catalysts can also be prepared through a thermochemical treatment, by the refluxing of colloidal Ru particles in Se-saturated xylene solvent. In this method, $RuCl_3$ dissolved in tetrahydrofuran is reduced via a reducing agent in ethanol and nanosized Ru particles are formed. These particles are further treated with aqueous selenious acid to give the Ru/Se catalyst. By modifying the colloidal synthesis procedure somewhat (impregnation/reduction method), the Ru/Se catalyst can be deposited on a porous carbon support for dispersion [125]. For the Ru/Se catalysts of the "carbonyl-tailored" types studied by Bron [126], the ORR activity increased with Se content, reaching a maximum at 15 mole%. As well, the amount of H_2O_2 generated at different reduction potentials decreased with addition of Se, this being especially true in the 0.6 to 0.7 V (NHE) potential range. Thus, the results are promising for such compounds, at least on the level of small-scale laboratory production and evaluation.

Based on the extensive research performed over the past 20 years, of which only a small fraction has been presented here, there is no doubt that real advances have been made in understanding the concept of electron reservoirs created in the chevrel-type cluster units for electrocatalysis of reactions like the ORR. The investigated catalytic materials are indeed novel, and seem to have the ability to provide coordination (through their catalytic centers) for oxygen reactivity and selectivity. They have certainly thrown light on the nature of the "complicated" ORR, and have provided researchers with a controlled system for the systematic investigation of this best known cathodic reaction.

9.5.4 Conclusions

Will such compounds (or even the macrocyclics discussed earlier) soon replace Pt as the FC catalytic material of choice? The answer is most probably "no", at least in the near future. Industry will go with what is tried and true, especially when long-term performance and reproducibility are paramount in such systems for "real-

C systems (see, e.g.,

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world" applications. But this certainly does not mean that further research into these "novel" cathode formulations and their all-important synthesis procedures is not warranted. It may indeed be that some years down the road, such novel and specifically tailored electrocatalysts will replace Pt and its alloys. But until then, they will essentially remain very interesting materials for the fundamental investigations of students and researchers.

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