

Review

Chemical and electrochemical depositions of platinum group metals and their applications

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Abstract

This paper reviews the chemical and electrochemical depositions of platinum group metals (PGMs) from aqueous solutions. With a brief introduction on the fundamental aspects of chemical/electrochemical depositions, the review describes recent advances in chemical and

Abbreviations: CD, cathode current density expressed as amperes per cm²; CE, cathode current efficiency; dc, direct current; DMFC, direct methanol fuel cell; DNS, dinitrosulfatoplatinate; Electroforming, deposition of thick metallic coating which is later removed from cathode substrate, used for preparing thick metallic foils, halograms, duplicating complicated structures etc.; NHE, normal hydrogen electrode; PCB, printed circuit board; PGM, platinum group metal; PEMFC, polymer electrolyte membrane fuel cell; PET, polyethylene terephthalate; Pt-P-salt, *cis*-diammineplatinum(II)nitrite; PWB, printed wiring board; Strike, very thin metallic coating that is given prior to the main PGM coating for changing the character of base metal; SCE, saturated calomel electrode

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electrochemical deposition technologies. It discusses the properties and applications of the deposits. The review also discusses the applications and recent progress of PGMs as fuel cell catalysts.

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Keywords: Platinum group metals; Electroless deposition; Electrodeposition; Fuel cell; Electro catalysts; Corrosion resistance; Stability constant

1. Introduction

The deposition of precious metals either chemically or electrochemically plays an important role in the development of technologies where these metals are used. Particularly this is true in the area of electrodeposition as each method with different operating parameters such as temperature, pH and current density is likely to produce different kinds of deposit structures. As the platinum group metals (PGMs) are known to be good catalysts for various chemical and electrochemical reactions, the production of such catalytic surfaces with a range of particle sizes and surface are of prime importance. The reduction of precious metal salts to the metallic state has become a focus in material science dealing with nanoparticles. Metal nano- or micro-particles serve as useful electrocatalysts in certain chemical reactions. For example nanoparticles of $\text{Pt}_{0.5}\text{Ru}_{0.5}$ are effective catalysts for the oxidation of methanol in direct methanol fuel cell (DMFC); platinum nanoparticles are useful as catalysts for oxidizing a variety of molecules such as oxygen, photo catalysts for splitting water on semi conducting TiO_2 surfaces etc.

The cathodic electroreduction of oxygen has been a major concern in the electrochemical kinetics due to its importance in energy conversion systems such as batteries and fuel cells [1,2]. The requirement for oxygen reduction is that the process proceed at low overpotential. Platinum group metals satisfies this condition and there have been many reports dealing with the construction of the platinum electrodes in dispersed form on conductive supports. Nanoscaled metal particles have usually been synthesized by impregnation-reduction method; the electrodeposition method is seldom employed. However, recently the electrodeposition technique has gained momentum and there has been a significant num-

ber of reports on the syntheses of such nanosized electro catalysts.

There is no review available in the literature on the recent developments in electrodeposition of all six platinum group metals following the first review by Reid on the electrodeposition of PGMs in 1963 [3]. Moreover this review discussed only the electrochemical method of deposition and did not address chemical depositions. The present review describes the developments in the deposition of all PGMs both by chemical and electrochemical methods. The review also focuses on the various uses of the deposited coatings with special emphasis on the functional uses in electrochemical technology of fuel cells.

2. Basic aspects of chemical and electrochemical depositions

Electrochemical deposition is a versatile technique by which a thin desired metallic coating can be obtained on to the surface of another metal by simple electrolysis of an aqueous solution containing the desired metal ion or its complex (Fig. 1). The basic concepts of electrodeposition and the electrode reactions involved are best described in the recent tutorial papers by Walsh et al. [4–6]. Electroless deposition is a method of obtaining a desired coating by chemically reducing the metal ion or its complex on to the substrate in a controlled fashion. Table 1 compares the nature of reactions occurring in these two processes.

The two processes distinctly differ in their reduction approaches. In the electrochemical method, reduction takes place by supplying current externally and the sites for the anodic and cathodic reactions are separate. For the chemical deposition method, electrons required for the reduction are supplied by a reducing agent and the anodic/cathodic reactions are on the inseparable work piece. More over these reactions proceed only on catalytically active surfaces, i.e., the newly coated metallic surface should be catalytically active enough to promote the redox reactions. All PGMs are catalytically active and can be deposited. Deposits obtained from both chemical and electrochemical processes have many applications. The first and foremost application is resistance against corrosion for the underlying layers. The other applications include wear resistance for the surfaces, decorative coating to enhance the aesthetic appeal for the objects and functional applications such as to offer low resistance for the electrical contacts, catalytic surfaces for the electrodes for chemical reactions. Electrodeposition is the only technique by which metals with high melting points (e.g.,

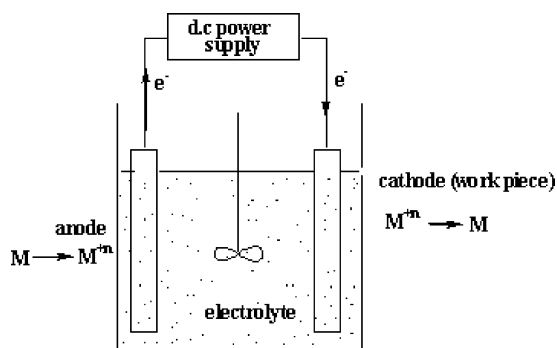


Fig. 1. Cell used for electrodeposition.

Table 1
Nature of reactions and their sites occurring in chemical and electrochemical depositions

Property	Electrochemical deposition	Chemical deposition
1. Driving force	External power supply	Reducing agent [RA] and auto-catalytic property of the deposited metal
2. Cathode reaction	$M^{n+} + ne^- \rightarrow M$	$M^{n+} + RA \rightarrow M$
3. Anodic reaction	$M - ne^- \rightarrow M^{n+}$	$RA - ne^- \rightarrow [RA]_{\text{Oxidized form}}$
4. Overall reaction	$M_{\text{anode}} \rightarrow M_{\text{cathode}}$	$M^{n+} + RA \rightarrow M + [RA]_{\text{Oxidized form}}$
5. Anodic site	Anode itself	Work piece
6. Cathodic site	Work piece	Work piece

platinum, rhodium) can be deposited. Electrodeposits have fine structure and have valuable physical properties such as high hardness, high reflectivity etc. A great advantage of the electrochemical deposition is that the thickness of the layer can be controlled to a fraction of a micron.

Metallic coatings can be classified as anodic or cathodic according to the nature of the protection they offer. Only zinc and cadmium are anodically protecting on iron or iron alloys; on the other hand the platinum group metals cathodically protect such base metals.

The reduction mechanism for an electrochemical deposition of a simple solvated metal salt is shown in Scheme 1 [7] and this mechanism can be extended to other ligand coordinated metal systems. Moreover the metal need not necessarily be four-coordinated but can be six coordinated also. The solvated metal ion present in the electrolyte arrives at the cathode under the influence of the imposed electrical field as well as by diffusion and convection (a). At the cathode it enters the diffusion layer. The field strength in the diffusion layer is not sufficiently strong to liberate the free metal ion from the solvated state but the solvated water molecules are aligned by the field (b). The metal ion then passes through the diffuse part of the double layer. As the field strength of the double layer is high (of the order of 10^7 V/cm), the solvated water molecules are removed leaving the free ion (c). Then the metal ion is reduced and deposited at the cathode via an ad-atom mechanism [7].

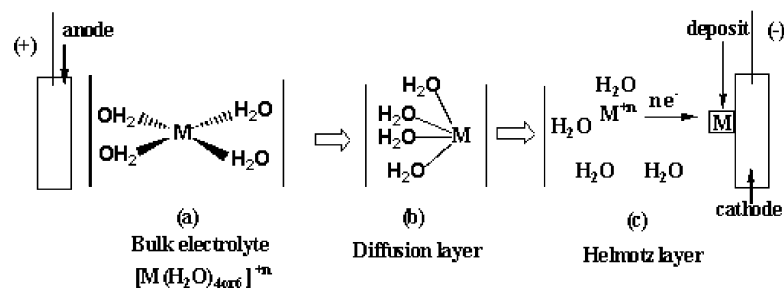
In electrodeposition baths, supporting electrolytes are added to increase the conductivity of the solutions. When a ligand is used as a complexing agent, it is always added in many fold excess relative to the stoichiometric reaction involved in the metal complex formation. Hence for simplicity, the concentrations are expressed in grams per liter (g/l). This is primarily because, after formation of the required

electroactive complex species, it should be available continuously throughout the deposition process. The presence of excess of ligand enables the continuous supply of the electro active species and also ensures the rapid formation of the electro active complex from the M^{n+} ions that are brought into the solution by the anodic reaction [$M \rightarrow M^{n+}$]. With few exceptions, many of these PGM plating baths give bright deposits and hence no additive is needed. However, in some cases, additives to relieve stresses are needed when higher thickness are plated.

2.1. The role of coordination chemistry

The platinum group metals, namely, Ru, Rh, Pd, Os, Ir and Pt are noble in their character and placed at the bottom of the emf series. The emf values (Table 2) show that it is extremely easy to reduce their ions and as a consequence, they try to remain in the metallic state. Hence these elements are often found in the earth's crust as metals or alloys such as osmoiridium, siserskite.

Finely divided metals are obtained when acidic solutions of salts or complexes are reduced by Mg, Zn, H_2 or even by citrates, oxalic or formic acids [8]. Palladium and Platinum are more reactive than other members of the group. The corrosion resistance of these PGMs stems from their noble character and when given as coating on other metals, they offer cathodic protection to the basis metal. PGMs are relatively inert with respect to chemical attack by oxygen or by many acids. The chemical reactivity is greatly affected by the size of the particles. Thus while palladium in the form of a sponge is dissolved by all mineral acids, the compact form is attacked only by acids in hot conditions. Rhodium is attacked by boiling sulfuric acid or hydrobromic acid and not dissolved by aqua regia. Iridium, ruthenium and osmium



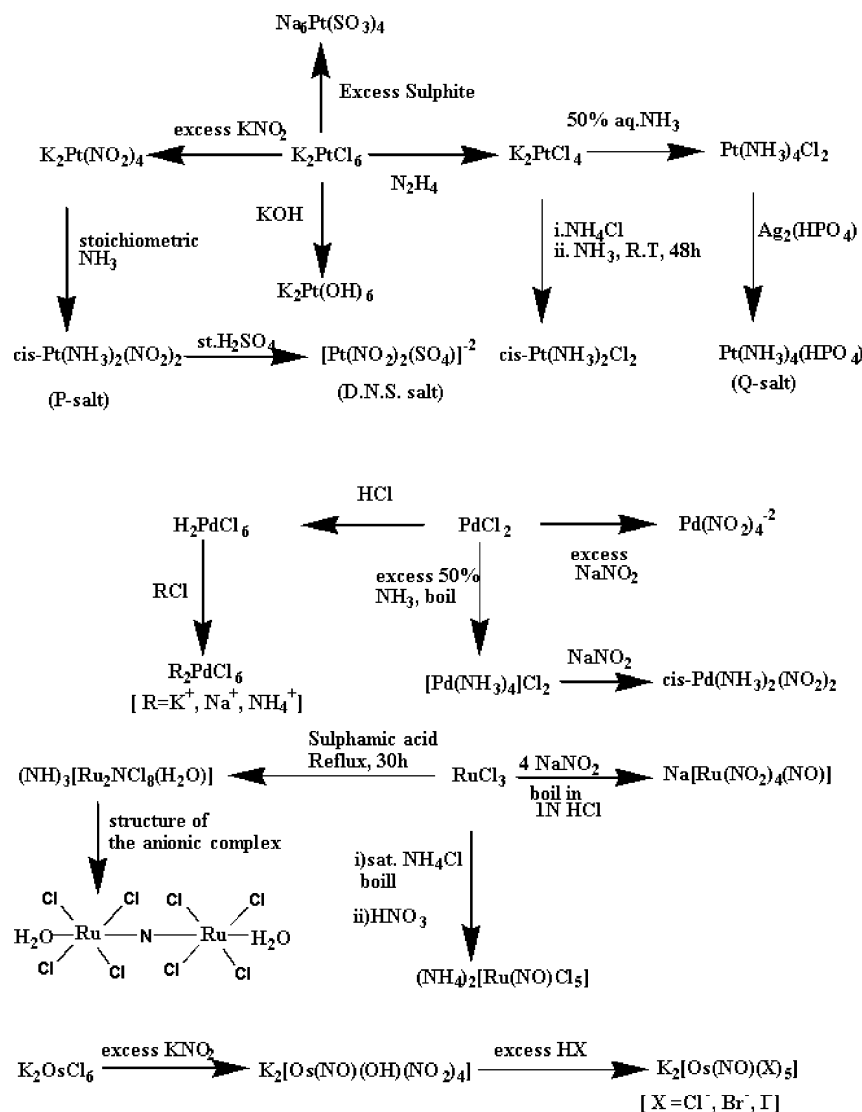
Scheme 1. Electroreduction mechanism for solvated metal ion.

Table 2
Physical data for the PGMs

Property/metal	Ru	Rh	Pd	Os	Ir	Pt
At. no.	44	45	46	76	77	78
At. wt.	101.07	102.9	106.4	190.2	192.2	195.09
Ionic radii (Å)/(ox. state)	0.82 (+3)	0.81 (+3)	0.78 (+2)	0.78 (+4)	0.82 (+3)	0.74 (+2)
Density at 20 °C (g/cm ³)	12.45	12.41	12.02	22.61	21.65	21.45
Hardness (kg/mm ²)						
(i) Metal (annealed)	200–350	120–140	37–40	300–500	200–240	37–42
(ii) Electrodeposited (kg/mm ²)	900–1000	800–900	200–400	Unknown	900	200–400
Crystal structure	hcp	fcc	fcc	hcp	fcc	fcc
Electrical resistivity ($\times 10^{-6}$ ohm cm, 0 °C)	6.8	4.33	9.9	8.12	4.7	9.85
emf (M/M ²⁺) (vs. NHE)	+0.680 ^a	+0.758 ^b	+0.951	+0.85	+1.156 ^a	+1.188

^a Calculated from thermodynamic data for M/M³⁺ reaction $\text{RuCl}_3 + 3\text{e}^- \rightarrow \text{Ru} + 3\text{Cl}^-$.

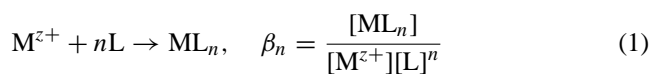
^b For the couple M/M³⁺.



Scheme 2. Synthetic routes to some of PGM metal complexes used in electrodeposition.

in compact form are practically unattacked by hot mineral acids or aqua regia. Platinum is attacked only by aqua regia. The important property of the platinum group metal complexes is the formation of intermediate hydride complexes with M–H bond by insertion reactions. Among PGMs, palladium is known to absorb large volumes of molecular hydrogen [9] followed by platinum, the property which greatly depends on the physical condition of the metal. Hence these two metals are known to be the best hydrogenation catalysts. However, this property proves to be a disadvantage (known as hydrogen embrittlement) in electrodeposition processes leading to high internal stress in the deposits. The complexes of these metals are predominantly halide ions, [e.g., PtCl_6^{2-}] ammine or nitrite ligands [e.g. $\text{Pt}(\text{NH}_3)_4^{2+}$, $\text{Pt}(\text{NO}_2)_4^{2-}$] and these simple coordination complexes, owing to their stability, are good sources of metals for the large number of electroplating baths. Scheme 2 shows syntheses of some of the PGM complexes used in plating baths.

The electrodeposition of platinum group metals is not simply an electrochemical process but it is also associated with the coordination chemistry of the depositing metal ion. Because of their nobility, the stability of simple salt solutions is poor and hence they are suitably coordinated by variety of ligands. The suitability is determined by the formation constant β_n of the complex, expressed by the Eq. (1).



For example cyanide ion forms a strong complex with some of the PGMs. If Pd^{2+} reacts with cyanide, square planar $\text{Pd}(\text{CN})_4^{2-}$ is formed where β_4 for the reaction $\text{Pd}^{2+} + 4\text{CN}^- \rightarrow \text{Pd}(\text{CN})_4^{2-}$ is about 10^{51} . This value indicates the high stability of the complex and the reduction potential of this complex species is more negative than the onset of hydrogen evolution. Thus on electrolysis only hydrogen is liberated at the cathode. This seems to be true with all the PGM cyano complexes. For this reason, high temperature electrolysis (molten state) is used if electrodeposition is desired from $\text{Pd}(\text{CN})_4^{2-}$ eliminating complications arising from water as solvent. On the other hand ligands like ammonia form moderately stable tetra-ammine complexes $\text{M}(\text{NH}_3)_4^{2+}$ with palladium or platinum ions with β_4 10^{30} and 10^{35} , respectively and electroreduction is feasible in water. Therefore the selection of the ligand should be such that the metal–ligand interaction is not too strong, but just enough to allow the discharge of metal ion at the cathode. But still hydrogen liberation and the resulting embrittlement is a topic of major concern when such complex baths are operated at low pH conditions in PGM electrodeposition.

Another important benefit arising from complexation is as follows. Because of positive values of E.M.F., the solutions of PGMs show tendency for displacement plating (immersion plating) when metals like copper are immersed for plating, resulting in loose, non-adherent deposits even before the current is applied to the electroplating cell. This leads to contamination of the electroplating bath by copper ions. This

is avoided by shifting the reduction potential of the PGM ion to more negative by complexation. On the other hand, attack on (copper like) cathode materials by the acidic PGM plating solutions is prevented by applying a very thin coating (called strike) of gold or nickel from non-corrosive baths such as gold cyanide or nickel strike bath prior to PGM plating.

3. Chemical (electroless) depositions

3.1. Choice of reducing agents and the mechanism of chemical deposition

‘Electroless metal deposition’ is the term first coined by Brenner and Riddell [10,11] as early as 1946 and is defined as an autocatalytic process of depositing a metal in the absence of an external source of electric current. The deposition is achieved by the incorporation of a reducing agent in the bath. The process is autocatalytic and proceeds on the newly formed catalytically active surface. Electroless deposition of metals has significant practical importance in modern technologies, especially in the production of new materials for applications in electronics, wear and corrosion resistant materials, medical applications, battery technologies. As will be noted in the present review, with the exception of platinum and palladium, little progress has been made in the development of electroless processes for other platinum group metals.

Table 3 gives the properties of various reducing agents used in electroless plating [12]. The solutions for electroless deposition essentially contain hypophosphite, borohydride, alkylamine boranes or hydrazine as reducing agents and the source of the metal to be deposited. The amine-boranes are addition compounds of amine and boron hydride of general formula $\text{R}_3\text{N}-\text{BH}_3$. While the use of borohydride is limited to highly alkaline medium, the amine-boranes are used for mildly alkaline, neutral or mildly acidic solutions. Metals such as silver and copper that are non-catalytic in hypophosphite are efficiently catalytic to initiate deposition spontaneously from DMAB baths.

Ohno et al. [13] have studied the catalytic activity of some metals including palladium and platinum for the anodic oxidation of reductants such as formaldehyde, borohydride,

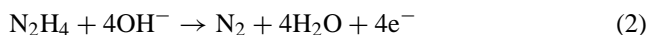
Table 3
Properties of the reducing agents

Reducing agent (no. of electrons available)	Representative chemical equation in the text	Redox potential (vs. NHE) (V)
Sodium hypophosphite (2)	5	–1.40
Hydrazine (4)	2 (or 3)	–1.16
Dimethyl amine borane (DMAB) (6)	10	–1.20
Diethyl amine borane (DEAB) (6)	10	–1.10
Sodium borohydride (8)	8	–1.20

hypophosphite, DMAB and hydrazine in electroless baths. Their results can serve as a basis for choosing reducing agents for metal deposition.

The use of boron and phosphorus based reducing agents leads to amorphous deposits along with incorporation of elemental phosphorus or boron. These incorporations in metal deposits are strictly prohibited in some applications of implantable medical devices used in defibrillation, pacing and cardiomyoplasty where a pure metal such as platinum is needed. In such cases the best option is to use hydrazine as reducing agent wherein deposits are 97–99% pure with the balance consisting of nitrogen and oxygen with other trace elements [14].

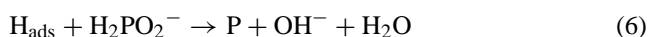
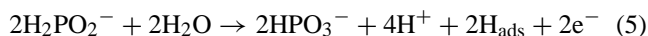
Hydrazine is a powerful reducing agent that works both in acid and alkaline media. It can reduce the higher valent metal ions to lower valent one or to the zero valent state depending on the conditions of the reaction [15,16].



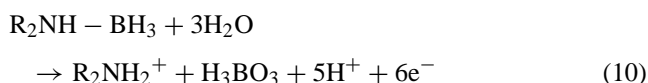
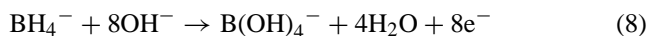
Comparing Gibbs free energy ΔG^0 of the reactions 2 and 3, [−447.7 and −88.7 kJ/mol, respectively] hydrazine is a stronger reducing agent in alkaline medium compared to acidic medium. Some hydrazine will also be oxidized to ammonia as shown by the Eq. (4).



When hypophosphite is used as reducing agent the following chemical reaction takes place with a limited utilization efficiency of 35% (Eq. (5)). Side reactions to give elemental P and molecular hydrogen will also take place (Eqs. (6) and (7))



When borohydride and dimethyl (or diethyl)amine borane are used, the following reactions take place (Eqs. (8)–(10)) with formation of elemental boron as a side product in the former case.

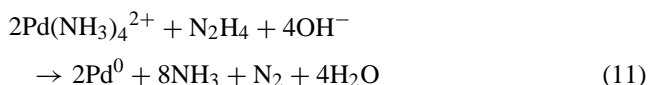


The final step in the electroless deposition mechanism is the reduction of free metal cation species or complex species by electrons facilitated by the reducing agent, to pure metal M or alloy of phosphorus or boron $\text{M}_x(\text{P or B})_y$.

3.2. Electroless palladium depositions

Electroless palladium deposition is the most extensively studied subject followed by platinum among the PGMs. Electrolessly deposited palladium has many applications in electronics as a barrier layer, conductive film, corrosion resistance non-porous deposits and for increasing the surface hardness of the components. Inorganic membranes covered with a thin electroless Pd film are used for hydrogenation/dehydrogenation reactions. Pure palladium films are useful for hydrogen separations. Palladium is largely consumed in electronics as components, in multilayered ceramic capacitors and smaller amounts in integrated circuits and plating. The next largest application is in the area of catalysis.

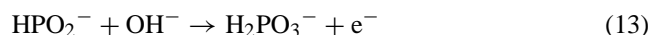
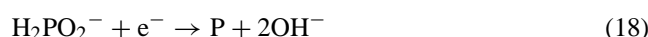
The general equation for the reduction of palladium is, $\text{Pd}^{2+} + \text{reducer} \rightarrow \text{Pd}^0$. The reaction does not have any significance as Palladium is obtained as a black powder. But if the same reaction is carried under controlled fashion in presence of a complexing agent (e.g. ammonia) and a catalytic surface (Eq. (11)), useful bright and adherent palladium layers are obtained on the surface; such reactions are basis for the palladium electroless plating processes.



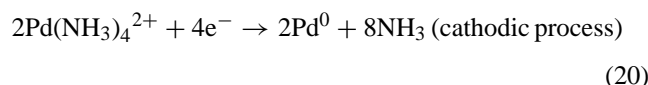
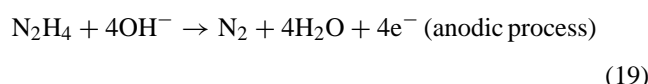
Various solutions for electroless deposition of palladium have been used in which reduction with hydrazine and hypophosphite in alkaline medium is generally practiced. Pearlstein and Weightman reported the first attempt to electrolessly deposit palladium with hypophosphite in 1969 [17a]. Rhoda reported the development of several electroless palladium solutions with hydrazine as a reducing agent [17b–d]. The main source of the palladium metal is $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$. The rate of metal deposition was found to increase with rise in temperature, Pd concentration and hydrazine concentration in the bath.

Deposition rates fall appreciably after several hours of use of plating bath in hydrazine based baths. This leaves much of the starting material unused. The main reason for this is the catalytic decomposition of hydrazine aided by freshly deposited palladium as shown in Eq. (4). In such situations fresh hydrazine can be added. There are reports [18,19] where this problem is rectified by proper modification of the bath. The latter reference [19] not only deals with chemical deposition of Pd on Zr metal, but also highlights the importance of complexing the metal ion in the deposition process. Only immersion plating took place when a Zr electrode was dipped in $\text{PdCl}_2\text{--HCl}$ solution. The coating is discontinuous and poorly adherent to the substrate. To avoid this, Pd^{2+} is complexed by ammonia to form the tetraammine complex. When this complex is reduced with hypophosphite at 50 °C, an adherent Pd coating of 5 μm thick was obtained in 3 h.

The mechanism of palladium reduction by hypophosphite can be described in the following separate anodic and cathodic reactions.

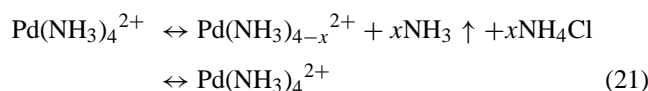
Anodic processes:*Cathodic processes:*

For hydrazine, the reducing mechanism is given by

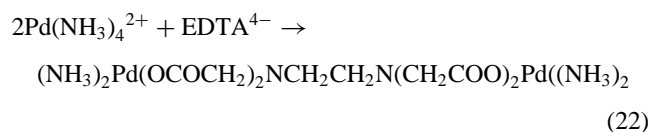


The overall reaction is given by Eq. (11)

A stable electroless palladium plating bath containing EDTA and sodium hypophosphite as reducing agent has been patented by Sergienko [20]. Pearlstein and Weightman reported the use of hypophosphite [17a] based bath consisting of palladium-ammine complex and ammonium chloride as stabilizer. Studies on hydrazine and hypophosphite baths showed that baths based on hypophosphite as reducing agent performed better in terms of bath stability and deposit quality. Thus a practical palladium electroless bath contains hypophosphite as reducing agent and in general palladium tetraammine as metal source. Ammonium chloride is most often used as stabilizer [21,22]. The stabilization is achieved for the bath by keeping the concentration of $\text{Pd}(\text{NH}_3)_4^{2+}$ species at maximum during high working temperature by the presence of excess ammonium chloride in the bath.



EDTA also serves as stabilizer for many electroless palladium solutions where it is believed to form simple square planar (N_2O_2) based chelate with $\text{Pd}(\text{NH}_3)_4^{2+}$ by ligand substitution as shown. This needs slightly higher temperature for reduction compared to ammonia based baths, owing to its higher stability.



A brief review on electroless deposition of palladium and platinum is informative [23]. Recently there has been much

progress made in electroless deposition of palladium reported in a series of patents [21,24,25]. These literature includes patents by Abys [21] and Hough et al. [24,25]. The patent by Abys et al. described electrolyte systems that are based on palladium salt with organic acids. Only a narrow class of reducing agents is used. The process yielded plating rates of about 6 $\mu\text{in./min}$. Patents by Hough et al. [21,22] described electrolyte systems based on divalent palladium complexed by ammonia or amine with other thio-organic compounds, iminonitriles as stabilizers. Essentially an alloy containing 1–3% amorphous boron is obtained. A strong laminate can be formed when plated on electroless nickel. Table 4 gives several bath formulations and their operating conditions for electroless deposition of palladium.

Another important area where an electroless palladium process used is for metallising non-metallic substrates for plating. This process makes the non-conducting substrate conducting and further electroless deposition of the desired metal is continued. Essentially, metallisation using palladium chloride involves two steps. The substrate is suitably etched for anchoring the tiny deposits. Then the substrate is dipped in SnCl_2 solution of particular concentration followed by PdCl_2 –HCl solutions. This leads to chemical reduction of Pd^{2+} ions to Pd^0 [$\text{Pd}^{2+} + \text{Sn}^{2+} \rightarrow \text{Pd}^0 + \text{Sn}^{4+}$] which anchors on to the etched surface making it conducting. Literature shows that the palladium particle size ranges from micro to a nanometer.

3.3. Electroless platinum depositions

Table 4 gives electroless bath formulations used for platinum deposition. The first noted patent was given by Oster in early 1969 [30] based on platinum sulfate and borohydride system. A process employing hydrazine (1 g/l) as reducing agent and sodium hexahydroxy platinate (10 g/l) was given by Rhoda and Vines in late 1969 [31]. The process involves addition of hydrazine to the bath either continuously or in portions as the hydrate solution or as hydrazine salts dissolved in water to initiate platinum deposition. The process works at room temperature with a deposition rate of 12 $\mu\text{m/h}$. Application of this process was suggested to be on nickel powder and graphite powder compacts and protective coatings for copper, nickel, iron, titanium and molybdenum.

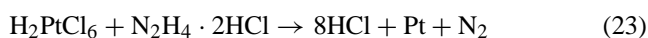
A more efficient electroless plating bath was described by Leeman et al. in 1972 [32] based on hydrazine as a reducing agent and hexachloroplatinic salts as two different processes working one in alkaline and another in acidic pH range. The acidic process is limited to plate on gold, precious metal alloys, ABS plastics while the alkaline process can be used for depositions on metals like copper and also polypropylene. We have recently shown that platinum can be deposited from the acidic process on titanium panels. A thickness of 3 μm can be achieved in 3 h using solutions containing 1 g/l of platinum metal [33]. It was also shown that titanium powder and PET can be homogeneously platinised using this process. The acidic process uses hexachloroplatinic

Table 4
Data on electroless plating systems for palladium and platinum metals

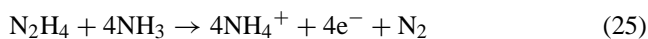
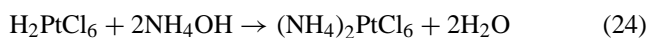
Metal source	Concentration of metal salt or complex (g/l)	Other main electrolytes in (g/l)	Medium	Reducing agent (g/l)	Temperature (°C)	Reference
PdCl ₂	2.7	(i) Ammonium hydroxide, 390 ml, (ii) Na ₂ EDTA, 20	B	Formaldehyde, 1.5 ml	64	[26]
	2.0	(i) NH ₄ OH, 150 ml	B	Sodium hypophosphite	60	[27]
	1.7	(i) Ethylenediamine, 4.8	A	Sodium phosphite	60	[28]
Pd(NH ₃) ₄ (NO ₃) ₂	2.5	Ammonium hydroxide, 200 ml Na ₂ EDTA, 20	B	Hydrazine, 0.8 mol	64	[26]
Pt(NH ₃) ₂ (NO ₂) ₂	2.0	Acetic acid, pH 3	A	Hydrazine hydrate, 3	50–80	[29]

A = acidic, B = basic, N = neutral.

acid and hydrochloric acid at 60–70 °C and the reduction to platinum metal by hadrazine is given by Eq. (19).



In alkaline process (NH₄)₂PtCl₆ and hydrazine are used. The following chemical reactions take place using a bath consisting of chloroplatinic acid, ammonium hydroxide and hydrazine at 70–75 °C.



Koslov et al. [29] have patented an autocatalytic plating process from Pt-DNP and the hydrazine system which is able to deposit platinum on alloys such as Co-super alloy, Inconel, pure Al, Al–Ti alloy, graphite; several other applications suggested are in batteries, fuel cells and capacitors.

The electroless deposition of platinum metal on to polymers is finding applications in the medical field. Platinum being biologically inert, is one of the metals used for coating implantable electrodes. As the metal deposition takes place only on a conducting surface, it is necessary to metallize or seed the non-conducting polymer for electroless deposition. In commercial electroless platinum deposition, a tin sensitizer and PdCl₂ activator are used to provide catalytic centers. But tin is toxic and therefore is not suitable for use in medical implants. Recently there is a new process avoiding usage of tin for electroless deposition of platinum on PET [34]. This involves dipping the etched PET film in a PdCl₂–DMSO complex solution followed by a dip in hydrazine solution. Hydrazine reduces Pd–DMSO complex to metallic particles on which further deposition of platinum continues

3.4. Electroless deposition of other PGMs

Very few reports are available on the electroless deposition of other platinum group metals. Noted systems for iridium are based on hydrazine complexes [35,36]. The main species involved in the process is H[Ir(N₂H₅Cl)Cl₄]. The bath works at a temperature of 60–90 °C and pH of about 2. The bath is self reducing in this temperature range and is used for the pro-

duction of iridium coatings on cation exchange membranes used for water electrolysis. It can be used to coat Ir on metals such as Cu, Fe, Ni and valve metals such as Ti, Ta and Nb. Rhodium can be deposited using sodium borohydride (0.11 M) as reducing agent from the electrolyte containing RhCl₃·4H₂O (0.01 M), ethylenediamine (0.8 M), dimethylglyoxime (0.025 M) and sodium hydroxide (1.5 M) at 90 °C [37]. Recently a rhodium electroless bath based on pyridine-2,6-dicarboxylic acid (pda) was reported by Lothar Weber et al. [38]. The bath contains Rh(III)[pda]₂[–], hydrazine and operates at 80–90 °C. The process is suitable for coating metals, ceramics and their powders. Okuno et al. [39] have demonstrated the chemical deposition of ruthenium using hydrazine hydrate in basic pH range 12.6–13.6 at 55–65 °C. The process is useful for coating ruthenium on electronic materials.

The only report available on the electroless deposition of osmium is on silicon using osmium tetroxide and a sodium hypophosphite bath around pH 10 at a temperature of 85 °C [40]. The coating is amorphous. While there are no further investigations to understand the species formed in the bath, it is believed that an anionic complex of Os is formed with sulfamic acid.

4. Electrochemical deposition

Because PGMs are costly, electrodeposition of a PGM metal is undertaken under special circumstances; when protection is needed against high temperature corrosion or for particular functional applications like catalysts in chemical transformations, low resistance contacts etc.

Platinum is extensively plated on titanium for use as anodes in the plating of precious metals. Thick platinum layers are required to protect the refractory metals from oxidation at high temperatures when used as anodes. The elements Ru, Rh and Pd are lighter elements with density approximately 12 g/cm³ and the other three elements are heavier with density approximately 22 g/cm³. The difference in the densities of these two group metals can be exploited by choosing a light metal (e.g. ruthenium, which is also cheap) as coating material so that it covers nearly the double the area for a given thickness. The hardness values provide indication of

strength and ductility of the metals (Table 2). Ru and Os are hard and strong with some brittleness. Pd and Pt are soft, low strength but ductile. In general electrodeposits are harder than the bulk materials because of fine grain structure formed in the low temperature electrodeposition processes compared to high temperature processed cast or wrought metals. Internal stress which leads to cracking of the deposit is a major problem in PGM plating and this is considerably reduced by using addition agents.

4.1. Platinum electrodeposition

Electrochemical deposition of platinum is practiced from chloride, ammine, sulfate-nitrite and hydroxy complexes [41]. The pioneering work on electrochemical deposition was done by Elkington more than 100 years ago in 1837 [42]. In general high current density during plating cannot be used as it leads to evolution of hydrogen due good catalytic activity of freshly deposited platinum

The chloride based electrolytes contain platinum complexed in the +4 state (usually H_2PtCl_6). These electrolytes suffer from a disadvantage that the substrates made up from copper like metals are sometimes corroded. In these electrolyte systems higher cathode current densities in the range $2.5\text{--}3.5\text{ A/dm}^2$ can be employed. However, in these systems the cathode current efficiencies are found to be poor in the range 15–20%. When $(\text{NH}_4)_2\text{PtCl}_6$ is used as source for Pt with sodium citrate-ammonium chloride as supporting electrolyte the current efficiency was found to be high (70%) with low applied cathode current density. Crack free, crystalline layers of Pt can be deposited from these baths up to a thickness of $20\text{ }\mu\text{m}$. However, these electrolytes are corrosive and hence most base metals require a protective layer of gold, silver or palladium. The electroplating bath works at a temperature range $45\text{--}90\text{ }^\circ\text{C}$. The platinum is self-replenished by dissolution of platinum anode as a high concentration of HCl is used.

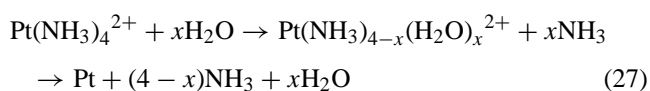
Another widely studied system is an electrolyte system based on the complex, $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$ by Keitel and Zscheher [41]. These electrolyte system allows a maximum current density of 5 A/dm^2 , highest known in platinum electrodeposition systems. The preparation of this complex is straight forward. Addition of excess of sodium or potassium nitrite to chloro platinic acid (IV) leads to reduction of Pt (IV) to Pt (II) state to form the square planar complex $\text{K}_2\text{Pt}(\text{NO}_2)_4$ with evolution of nitric oxides; and addition of stoichiometric amounts of ammonia leads to the precipitation of crystalline *cis*- $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ (or Pt-P-salt). The other supporting electrolyte includes ammonium nitrate, sodium nitrate and ammonia. The electrolyte systems suffer from a disadvantage that there will be changes in nitrite concentration which leads to irregularity in plating. The replenishment of platinum is achieved by constant addition of Pt-P-salt. Reports showed these systems give good deposits up to $7.5\text{ }\mu\text{m}$. The current efficiency varies from 10 to 40% depending on supporting electrolytes, the maximum being

achieved with sulfuric acid. A high working temperature in the range $70\text{--}90\text{ }^\circ\text{C}$ is needed.

A similar electroplating bath is based on $[\text{Pt}(\text{NO}_2)_2(\text{SO}_4)]^{2-}$ (DiNitro Sulfato, DNS) by Hopkin and Wilson [41]. This can be used for plating on many metals such as Ti, Cu even at room temperature. This platinum complex is obtained from $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$ by reacting with H_2SO_4 stoichiometrically (Scheme 2). The supporting electrolyte is 1N sulfuric acid for maintaining pH 2.

Apart from chloride electrolytes, electroplating baths based on Pt(IV) species are alkali salts of platinum hydroxides and platinum tetrachloride-phosphate electrolytes [41]. In the former system, a hydroxide complex of platinum $\text{Pt}(\text{OH})_6^{2-}$ is the main electrolyte with sodium or potassium ions as counter ions. The efficiency reported is in the range 80–100% with working temperature in the range $65\text{--}90\text{ }^\circ\text{C}$. Insoluble anodes of Ni or stainless steel (SS) are used. Despite the easy preparation of the electrolyte, the disadvantage of low stability also comes into the picture; decomposition of $\text{Na}_2\text{Pt}(\text{OH})_6$ to $\text{N}_2\text{O}\cdot\text{PtO}_2$ takes place. Another problem is that it absorbs CO_2 from air to form carbonates. Improvements in stability were also reported by addition of oxalates, sulfates or acetates. A recent report showed that stainless steel can also be crack-free plated up to $5\text{ }\mu\text{m}$ from these electrolytes [43].

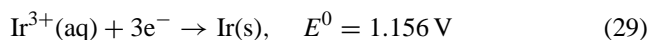
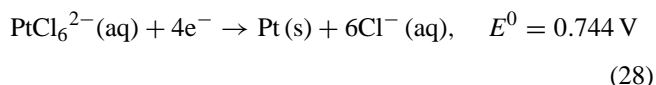
Recently, significant developments in platinum electrodeposition have been made by Johnson Matthey Ltd. and others [44–47]. Johnson Matthey Ltd. described a new bath formulation based on platinum-tetraammine complex in phosphate buffer with higher cathode current efficiency [44–46] and useful as commercial electroplating bath where high rates and thickness are required. Pletcher et al. [48–52] studied the fundamental and applied aspects of this new bath. The authors proposed a mechanism for reduction of this complex. High temperatures are needed for the reduction. The mechanism was shown to be stepwise replacement of ammonia ligands by water molecules. The high temperature is essential to drive the slow ligand displacement reaction to a reasonable rate. The following reaction is believed to occur during the electrolysis.



A report on a plating system based on $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ has appeared [49,52]. Basic electrochemical studies were performed on this complex by synthesizing the complex from PtCl_4^{2-} and $\text{Pt}(\text{NO}_2)_4^{2-}$ complexes. It was shown that it is difficult to remove the fourth NO_2^- ligand from $\text{Pt}(\text{NO}_2)_4^{2-}$ and a reasonable deposition can be achieved from the tri aqua complex species $\text{Pt}(\text{H}_2\text{O})_3(\text{NO}_2)^+$ with current density range $1\text{--}15\text{ mA/cm}^2$. However, the current efficiency was only 10–15%. A study of the hydrolysis of PtCl_4 showed that $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ is stable at very low pH in 1 M perchloric acid and this formed a basis for a room temperature plating bath [44].

Recently a fundamental study on platinum deposition from $\text{H}_3\text{Pt}(\text{SO}_3)_2\text{OH}$ solutions obtained from $\text{Na}_6\text{Pt}(\text{SO}_3)_4$ onto a glassy carbon electrode has appeared [47]. The deposits were characterized by cyclic voltammetry and SEM. A few new patents dealt with the process of platinum electroplating working on Pt-P-salt [53], $[\text{Pt}(\text{OH})_6]^{2-}$ [54] and in combination with sulfamic acids [55]. Strangman et al. [53] have patented the bath formulations based on P-salt and alkali metal carbonates. The operating temperature is in the range 15–98 °C with current density 0.05–7 A/dm². It contained the platinum salt up to 320 g/l. Kitida et al. [54] have shown that brass can be platinum plated up to as thick as 150 µm using formulations based on $\text{H}_2\text{Pt}(\text{OH})_6$. Kuhn et al. [55] obtained a patent on an electroplating bath that contains a Pt-ammine-sulfamate complex that gives crack-free, bright platinum layers up to 100 µm. Some of these systems [54,55] can be used for electroforming applications. For example work by Kuhn et al. showed that 120 µm thick platinum foil can be obtained by electroforming.

Platinum–iridium alloy coatings from amidosulfuric acid solutions have been electrodeposited on nickel-base single crystal superalloy TMS-75 [third generation super alloy containing Al (6 wt.%), Co (12 wt.%), Cr (3 wt.%), Ta (6 wt.%), Mo (2 wt.%), W (6 wt.%) and Re (5 wt.%) and rest Nickel] by electrodeposition [56]. The effects of electrolyte temperature, current density and mole concentration ratios of $[\text{Ir}^{3+}]/[\text{Ir}^{3+}] + [\text{PtCl}_6^{2-}]$ on the deposition rate, composition and crystallographic structures of Pt–Ir alloy coatings were investigated. With increasing electrolyte temperature, the deposition rate and Ir content increases, whereas the grain size of Pt–Ir alloy coatings decreases. Smooth and dense Pt–Ir alloy coatings can be obtained at 1 A/dm² and 353 K. Pt–Ir alloy coatings with expected compositions can be readily fabricated by controlling the mole concentration ratios of $[\text{Ir}^{3+}]/[\text{Ir}^{3+}] + [\text{PtCl}_6^{2-}]$ in the electrolyte. A detailed investigation of the structure and morphology of electrodeposited Pt–Ir alloy coatings is also presented in this report. XRD analysis revealed that all the coated Pt–Ir alloys have a single phase with fcc structure, and the lattice parameters of the coatings decrease linearly with increasing Ir content. The coatings are useful in increasing the performance of Pt-modified aluminate coatings. The electrochemical reductions while depositing the alloy are as follows:



Comparing the above reduction potentials, iridium can be preferentially reduced to platinum and is indeed observed in this investigation. The process is categorized as normal codeposition.

Farndon et al. have studied the electrodeposition of platinum onto a conducting ceramic, Ebonex[®] from Pt 5Q electroplating solution at 368 K [57]. Ebonex[®] is a ceramic

consisting of a mixture of Magneli phase titanium oxides, largely Ti_5O_9 but with some Ti_4O_7 and Ti_6O_{11} , with a typical conductivity of $10^3 \Omega^{-1} \text{ cm}^{-1}$. It is very stable in a wide range of environments including acidic fluoride solutions and it does not react with hydrogen.

A fundamental electrochemical study on platinum deposition on HOPG (highly oriented pyrolytic graphite) and tungsten was under taken by Glaoguen et al. [58] and Ke-laidopoulou et al. [59]. Dimiter Stoychev et al. [60] studied fundamental aspects for platinum electrodeposition on several materials including tungsten, titanium, rhenium, zirconium, stainless steel, glassy carbon (GC), polyaniline, and poly(2-hydroxy-3-aminophenazine). Efforts were made to establish experimental conditions under which the very initial, nucleation stage of the platinum electrodeposition could be studied. It was found that tungsten, titanium, and GC were suitable substrates for nucleation and growth studies in aqueous 0.1 M HClO_4 solution containing K_2PtCl_6 .

The other very useful area is platinizing the semiconductor silicon surfaces which are useful as solar cells. Photovoltaic conversion using solar cells is a most promising method for the utilization of solar energy. Photoelectrochemical (PEC) solar cells use n-type silicon electrode materials modified with ultra fine platinum particles. Garrido et al. [61] and Yae et al. [62] have shown that it is possible to deposit dispersed platinum coatings on silicon wafers of varying particle sizes from hexachloroplatinic acid electrolyte.

Platinum is the best choice among the PGMs to be used in many biosensors for its biocompatibility. De Haro et al. [63] studied electrochemical platinum coatings for improving performance of implantable microelectrode arrays. The formation and properties of electrodeposited platinum coatings grown on contacts contained in implantable flexible microelectrodes were investigated. The platinum deposits were obtained by the cyclic voltammetry method from baths containing chloroplatinic acid. The benefits of this process are ascribed to higher corrosion resistance, lower impedance and improved adhesion to the deposited platinum. These improvements can make the application of this electrochemical technique highly useful for increasing the lifetime of implantable microelectrode arrays, such as cuff structures. These medical devices, obtained by semiconductor technology could be used for selective stimulation of nerve fascicles. Table 5 lists electroplating systems for platinum metal.

4.2. Palladium electrodeposition

There is a vast amount of literature available on the subject (Table 6). The electrodeposition and material properties of palladium are greatly affected by deposition conditions like temperature and pH as these two parameters decide the amount of co-deposited hydrogen.

Palladium coatings have technological importance. Palladium exhibits many desirable characteristics like excellent tarnishing, wear and corrosion resistance with low electrical contact resistance and hence has found applications in

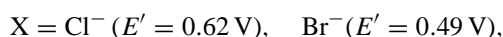
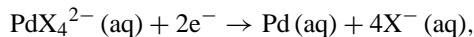
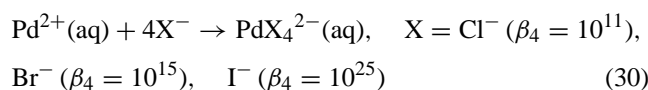
Table 5
Data on electroplating systems for platinum metal

Platinum source	Concentration as Pt metal (g/l)	Other main electrolyte in (g/l)	Medium	Current density (A/dm ²)	Temperature (°C)	Reference
H ₂ PtCl ₆	5–25	HCl, 180–300 ml	A	2.5–3.5	45–90	[41]
(NH ₄) ₂ PtCl ₆	6	Sodium citrate, 100	N	0.5–1.0	80–90	[41]
PtCl ₄	3	Na ₂ HPO ₄ , 100	B	0.3–1.0	70–90	[41]
K ₂ Pt(OH) ₆	10	K ₂ SO ₄ , 40	B	0.3–1.0	70–90	[43]
Pt(NH ₃) ₂ (NO ₂)	5–10	Ammonia, 50	B	0.3–2.0	90–95	[41]
H ₂ Pt(NO ₂) ₂ (SO ₄)	5.7	H ₂ SO ₄ , to pH 2	A	2.5	30–70	[41]

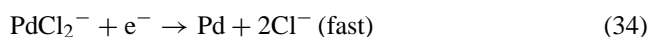
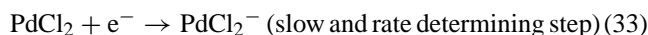
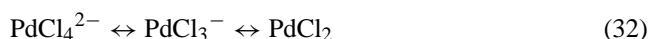
A = acidic, B = basic, N = neutral.

P.W.B fingers. Palladium coatings with thin gold flash are used as contact materials. Pd can be readily soldered using conventional soft solders and hence is good candidate in the electrical industry and PCBs. It is also used in semiconductor packaging due to their wire bonding and solderability properties.

Basic electrochemical studies on palladium dissolution and deposition were conducted by Harrison et al. [64,65]. Palladium is deposited from many bath compositions based on simple salt PdCl₂ and also from complexes such as Pd(NH₃)₂(NO₂)₂, Pd(NH₃)₂Br₂, H₂PdCl₄, Pd(NO₃)₂, Na₂Pd(NO₃)₄, Pd(NH₃)₄(NO₃)₂, Pd(NH₃)₂(NO₃)₂, Pd(NH₃)₄Cl₂. Ammonia is the most suitable complexing ligand for palladium electrodeposition and most of the available literature is on ammonia complexed to palladium solely or in combination with other ligands (Table 6). Palladium readily forms square planar complexes with ammonia or amines which show intermediate degree of stability as evident from β₄ (Section 2.1). Pd²⁺ forms an anionic complex in the presence of HCl with moderate stability (β₄ = 10¹¹) and is susceptible to easy electrochemical reduction. This is the basis for palladium deposition based on PdCl₂-HCl baths. The stability constants and half-cell potentials for anionic halo complexes are given below [66].



In the reduction mechanism of PdCl₄²⁻, it is believed that the complex dissociates sequentially to form normal PdCl₂ and then reduction occurs by step wise one electron transfers.



In Pd-ammonia baths, the high concentrations of ammonia pose problems while in operation such as evaporation and pH changes. For these reasons other non-volatile amine based systems are preferred. The most practical and thoroughly studied system is propylenediamine based [67,68] Pd(pn)Cl₂ by Abys et al. A good reference book for palladium deposition is given by him [68]. The deposits from this bath are smooth and brightness can be controlled by operating conditions like temperature, pH and current density and are found suitable for connector applications. Lai et al. [69] have studied the basic aspects of palladium deposition from Pd(en)Cl₂ baths by pulse electrodeposition method. It is believed that hydrogen adsorption is lowered in this technique and better quality deposits are obtained compared to normal dc electrodeposition. Pd-tetraammine based electroplating systems

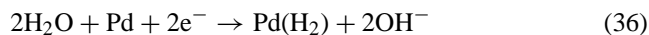
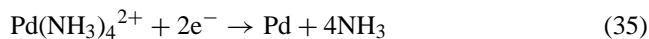
Table 6
Data on electroplating systems for palladium metal

Palladium source	Concentration as Pd metal (g/l)	Other main electrolyte in (g/l)	Medium	Current density (A/dm ²)	Temperature (°C)	Reference
PdCl ₂	1–40	Potassium phosphate, 50–100	B	0.1–50	40–70	[67,70]
	1–3	Sodium chloride, 10–60	A	0.5–5.0	25–45	[75]
H ₂ PdCl ₄	5	Sodium chloride, 40	A	0.4–1.0	50	[76]
Pd(NH ₃) ₄ Cl ₂	20	Ammonium sulfate, 20	N–B	0.5–1.5	20–40	[77,78]
	5–25	Ammonium chloride, 90	N–B	>2.5	30–50	[79]
Pd(NH ₃) ₂ (NO ₃) ₂	4	Sodium nitrate, 10–11	N–B	0.1–4.0	40–55	[76]
Pd(NH ₃) ₄ (NO ₃) ₂	10	Ammonium nitrate, 90–100	B	0.5–2.0	60–80	[76]
Pd(NO ₃) ₂	2–15	Sulfuric acid, 98	A	0.5–8.0	20–35	[76]

A = acidic, B = basic and N = neutral.

were studied [70]. These baths work at near neutral pH conditions. The electroreduction of these tetraammine complexes is easier compared to $\text{PdCl}_2\text{--HCl}$ due to complexation by ammonia. Electrodeposits from $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ are dull and gray and a brightener additive is necessary. Class I or class II brightener can be used in the above baths. Class I brighteners are generally unsaturated sulfonic compounds where the unsaturation is α or β with respect to the sulfonic group with general formula $\text{A--SO}_3\text{--B}$. A is an aryl or alkene group and B may be OH, OR, OM, NH_2 , --NH , H, R (where R is alkali metal and R is an alkyl group with less than six carbons) [68]. The class II organic brighteners are unsaturated or carbonyl compounds. Examples are --C=O , --C=C-- , $\text{--C}\equiv\text{N}$, --C=N-- , $\text{--C}\equiv\text{C--}$, --N=N-- . These additives are added in small quantities. The additives are deposited along with the metal to give specular reflections to the surface and are seen as bright deposits.

Pletcher et al. have studied the electrodeposition behavior of $\text{Pd}(\text{NH}_3)\text{X}_2$ type systems [71,72]. While depositing palladium from these baths, competitive reductions take place between palladium ions and other electroactive species.



Hence experimental parameters must be carefully selected to minimize these undesired reactions. It was also shown that a complexing agent is necessary to stabilize Pd^{2+} . At the same time the presence of strong complexing ligand would shift the Pd^{2+}/Pd couple to negative regions where Pd--H is formed. Further, the study indicated Pd^{2+} existed as $\text{Pd}(\text{NH}_3)_4^{2+}$ but not as $\text{Pd}(\text{NH}_3)_2^{2+}$.

The first and simplest Pd plating bath that operates in the acidic pH range is $\text{PdCl}_2\text{--HCl}$ system where H_2PdCl_4 complex is readily formed. The stability constant β_4 is only 10^{12} hence some immersion plating may take place. High concentrations of palladium chloride are used; the rate of deposition is high with low internal stress. It is suitable for plating high thickness coatings and also for electroforming. The system was thoroughly investigated by Raub in 1977 [73]. Another plating system that works in the acidic pH range is a $\text{Pd}(\text{NO}_3)_2$ -sulfuric acid bath [74]. This report [74] shows that addition of sulfite is necessary to bring down the concentration of free palladium to get satisfactory deposits. Sulfide incorporation is also found in the deposits due to reduction of sulfites.

4.3. Rhodium electrodeposition

The most stable oxidation state of Rh is +3 which has a great tendency to form complex ions in aqueous solutions. Rh is used as coating material on scientific, surgical instruments, contact materials in rf circuits. The high reflectivity makes Rh for use in instrument mirrors.

Rhodium is usually electroplated from sulfate, phosphate or sulfate-phosphate baths. Reports are also available on sulfamate, perchlorate, fluoborate and nitrate electrolyte systems [80]. Rhodium metal complex baths were reported based on citric, tartaric, lactic, boric acids, alkaline phosphate and aminonitrates [80]. In rhodium sulfate solutions the species present are mostly $\text{Rh}(\text{H}_2\text{O})_6^{3+}$ and some times species like $\text{Rh}(\text{SO}_4)_3^{3-}$ are also observed. The difficulty in preparation of water soluble salts of rhodium resulted in preparation of concentrated rhodium sulfate solutions containing even 100 g/l of rhodium metal. These concentrates upon addition of required amounts of water and sulfuric acid give platable solutions. Briefly the preparation of this concentrate involves dissolving rhodium black (obtained by reducing rhodium chloride) in sulfuric acid. Rhodium is precipitated as rhodium hydroxide with ammonium hydroxide. After thorough washing, it is again re-dissolved in sulfuric acid and stored as concentrate. Rhodium is plated using insoluble platinum anodes.

For decorative plating of rhodium, sulfate or sulfate-phosphate [80] containing Rh as sulfate 2 g/l, 20–30 ml/l of sulfuric acid with current density of 1–4 A/dm² at low temperatures of 30–40 °C are used. For heavy deposits Rh concentration is increased to 10 g/l with 50 ml/l of sulfuric acid. The deposits are usually cracked and current efficiency is about 75%. In sulfate-phosphate baths the current efficiency is low at room temperatures and increases to 70% at 70 °C where a marked decrease in cracking is observed. It was shown that cracking can be controlled by the addition of selenic acid [81]. The deposits are softer than with the sulfate bath. For a thick plating of Rh, the sulfate bath has advantages that derive from higher current efficiency, low internal stress and high hardness. Replenishment is done by manual addition of rhodium sulfate to the bath.

Recent work [82,83] by Pletcher et al. on Rh deposition from chlorides and sulfates in acidic media threw light on the fundamental chemistry and electrochemistry of electrolysis. The studies showed that strong acid medium, as commercially practiced now, which leads to decrease in current efficiency, is not necessary. It is possible to achieve 100% current efficiency keeping the pH in the range 2–4 during electrodeposition.

4.4. Electrodeposition of ruthenium, iridium and osmium

Ruthenium is the least expensive PGM metal and is an economical alternative to both rhodium and gold in contact finish applications. Electrical cathodes may be protected by using Ru coating as they offer excellent arc resistance. The applications of iridium coatings include for inert electrodes, sliding contacts, reflectors, mirrors, vacuum tube elements, lab wares. Electrodeposits from osmium are hard and wear resistant and its high melting point suggests usage in reed switch contacts as an arc-resistant coating alternative to lower melting rhodium coatings. The work function of osmium is

high and hence it is used in few thermoionic devices. It is used as an Os–Ir alloy known as osmiridium for the hard wearing tip of gold fountain pen nibs. Osmiridium occurs in small amounts as native metal with a composition of Os 27%, Ir 55%, Pt 10% (and rest) Ru and Rh.

The most useful starting material for iridium deposition is IrBr_3 . Good deposits can be obtained from these electrolytes [84] at a current density 0.1–0.2 A/dm^2 , pH around 1.8 with current efficiency of 30–65%. This bath enables deposition on copper, titanium, brass, nickel and mild steel up to thickness of 10 μm at the rate of nearly 1 $\mu\text{m}/\text{h}$.

The IrCl_3 /sulfamic acid system [85] works at low and higher temperatures with current efficiency range 6–63% at current density of 0.1 A/dm^2 . Recent literature on the electrodeposition of iridium includes fundamental and applied areas [85]. This study [85] focused on the electrochemistry of iridium deposited from $(\text{NH}_3)_4\text{IrCl}_6$ on titanium. The efficiency of electrodeposition process was enhanced at elevated temperatures and a good coating was achieved at 343 K.

An early ruthenium plating bath used ruthenium as ruthenium–nitrosylsulfamate in sulfamic acid at 70 °C with current density of 4 A/dm^2 . A poor current efficiency of 10–20% was observed and the formation of ruthenium tetroxide at the anode was a major problem. The introduction and use of electrolytes based on bridged dinuclear complexes $[\text{K or NH}_4]_3[\text{Ru}_2\text{NCl}_8(\text{H}_2\text{O})_2]$ by Reddy et al. in 1969 [86] was a major achievement. An aqueous solution of RuCl_3 which was previously activated in concentrated hydrochloric acid reacted with sulfamic acid for long periods at reflux and resulted in a red crystalline product. The structure was shown to be two Ru(IV)Cl_4 units bridged by nitrogen atoms as shown in Scheme 2. This bath produced smooth and bright deposits with a fairly good current efficiency of above 90% for a cathode current density of approximately 1 A/dm^2 . These coatings are crack free below 2 μm .

The literature on the electrodeposition of osmium is scant. An article by Jones [87] gives information on some electrodeposition processes. A bath based on hexachloroosmate was proposed by Notley [87]. This contains chloroosmate, works at a temperature of 70 °C, low pH and has a rather low current efficiency of about 30%. The deposits are crack-free up to only 1.5 μm . The plating rate was found to be 4 $\mu\text{m}/\text{h}$. Other processes cited in the literature are by Greenspan in 1972 from OsO_4 [88] and Crossby in 1976 from a nitrosyl complex derived from K_2OsCl_6 [89]. A study by Greenspan showed that coherent deposits of

1–4 μm are formed from electrolytes obtained from reaction of sulfamic acid with osmium tetroxide. The reaction is believed to form an anionic complex. The operating temperature is 65–75 °C with a current density range 0.2–1 A/dm^2 and a cathode efficiency of 40–80%. Crossby studied the deposition of osmium from osmium(II)–nitrosyl complex $\text{K}_2[\text{Os}(\text{NO})(\text{OH})(\text{NO}_2)_4]$ [89]. The electrolyte gave bright and adherent deposits. However, the current efficiency was poor, in the range 8–12% with a plating rate of 2–3 $\mu\text{m}/\text{h}$. Optimum plating performance was obtained from an alkaline solution from which metal can be plated directly onto the base metal without an undercoat. It was noticed that though the starting material is a nitrosyl complex, its identity was lost during plating. Table 7 lists electroplating systems for these metals.

4.5. Analysis of electroplating baths: NMR and other spectroscopic techniques

Nuclear magnetic resonance (NMR) is a most versatile and promising spectroscopic method for the elucidation of structure and concentrations of coordination species present in the electroplating solutions. It also allows us to study the course of complex forming reactions in such baths. NMR spectroscopy is reasonably sensitive in that a number of isotopes are measurable in concentrations of about 1% or less. The sensitivity varies with the magnetic properties of the isotope and under some conditions it is limited by isotope environments. The technique is not suitable for trace analysis of ppm ranged species. Precision and accuracy of NMR measurements are governed by environment factors. NMR utility is limited by the natural abundance and resonance characteristics of the observable isotope. In general only those isotopes which contain an odd number of protons in their nuclei are NMR active (with an exception of Be). Isotopes with even number of protons and neutrons do not have a magnetic moment and are NMR inactive. Table 8 lists magnetically active PGM nuclei with their relative abundances.

An article by Pletcher et al. [91] discussed the application of ^{195}Pt NMR in the analysis of the platinum plating bath. In some of his papers [48,50,52,83] ^{195}Pt and ^{103}Rh NMR are used as a probe for the characterization of the different species present in the electrolyte. When $\text{K}_2\text{Pt}(\text{NO}_2)_4$ is dissolved in methane sulfonic acid, it was shown by this technique that nitrite ligands are sequentially displaced by water molecules to form $\text{Pt}[(\text{NO}_2)(\text{H}_2\text{O})_3]^+$ while the final water molecule is

Table 7
Data on Electroplating systems for Ru, Ir, Os and Rh metals

Salt/complex	Conc. as metal (g/l)	Other electrolytes (g/l)	Medium	Current density (A/dm^2)	Temperature (°C)	Reference
$\text{K}_2[\text{Ru}_2\text{O}(\text{H}_2\text{PO}_4)]$	6–10	Phosphoric acid, 2 mol	A	–	–	[90]
$(\text{NH}_4)_2 \text{IrCl}_6$	6–8	Sulfuric acid, 0.8 mol	A	0.1	18–25	[85]
IrCl_3	5–15	Sulfamic acid, 25–50	A	0.1–0.2	50–80	[85]
K_2OsCl_6	10	Potassium bisulfate, 60	A	1–4	70	[89]
Rh as sulfate concentrate	2	Sulfuric acid, 20 ml	A	4	40–45	[82,83]

A = acidic.

Table 8
Data on magnetically active nuclei of PGMs

Isotope	Natural abundance (%)	Magnetic moment (μ_N) (nuclear magnetrons)	Spin (I) ($h/2\pi$ units)
^{99}Ru	12.81	−0.630	5/2
^{101}Ru	16.98	−0.690	5/2
^{103}Rh	100.0	−0.087	1/2
^{105}Pd	22.23	−0.570	5/2
^{189}Os	16.1	0.650	3/2
^{191}Ir	38.5	0.160	3/2
^{193}Ir	61.5	0.170	3/2
^{195}Pt	33.7	0.600	1/2

Table 9
Approximate electronic absorption bands of some PGM complexes

Complex	Absorption maximum (cm^{-1})
RuF_6^{3-}	10,000; 20,000
RuCl_6^{3-}	16,500
$\text{Ru}(\text{H}_2\text{O})_6^{3+}$	16,670; 25,510; 30,000
$\text{Ru}(\text{NH}_3)_6^{3+}$	23,000; 30,000
RhF_6^{2-}	11,600; 16,000; 19,200; 21,200
RhCl_6^{3-}	14,700; 19,300; 24,300
RhBr_6^{3-}	18,100; 22,200
$\text{Rh}(\text{en})^{3+}$	33,200; 39,600
$\text{Rh}(\text{NH}_3)_6^{3+}$	32,800; 39,200
$\text{Pd}(\text{NH}_3)_4^{2+}$	1188
PdCl_4^{4-}	18,800
PdCl_4^{6-}	20,800
$\text{Pd}(\text{NH}_3)_2\text{Cl}_2$	14,640; 15,440
IrCl_6^{2-}	17,400
IrCl_6^{3-}	16,300; 17,900; 24,100; 28,100
IrBr_6^{3-}	16,800; 22,400; 25,800
$\text{Ir}(\text{NH}_3)_6^{3+}$	31,800; 39,800; 46,800
$t\text{-Ir}(\text{en})\text{Cl}_2^+$	24,000; 29,200; 36,000

difficult to displace. While there are no other reports available on the use of ^{103}Rh NMR for the analysis of electroplating baths, basic work by Mann [92,93] significantly contributes to the understanding of solution speciation in electroplating baths.

Another useful tool for the analysis is UV–vis spectroscopy as many of the PGM complexes have measurable d–d absorptions. The d–d bands are specific to each complex species. This technique is also useful to estimate the amount of organic additive in the bath. Table 9 give absorption maxima (λ_{max}) of some of the metal complexes that are encountered in the electrodeposition of the PGMs. The λ_{max} values listed [94] are measured in different solvents and have different ϵ values. These values will be found red or blue shifted for the complexes in the plating solutions because of interference with other ionic species. Thus standard solutions are to be prepared first and recorded in terms of λ_{max} and ϵ values. The freshly prepared, unused plating bath can serve as standard solution. After several turn overs, the solutions are recorded for their particular λ_{max} values and are accordingly rectified.

5. Platinum group metals in fuel cell technologies

The possibility of producing electrical energy by continuously feeding electrochemically active materials to a suitable cell has attracted the scientific community from an early date leading to the fuel cell based on Grove's pioneering work on the gas battery [95]. The fuel cell concept did not develop until the 1950s when a high energy/density system was needed for the space programme. Now the focus is on the design of platinum or platinum alloy catalysts for fuel cell applications.

Fuel cells are considered to be alternatives to our present power sources because of their high operational efficiencies and environment-friendly working characteristics. Construction and operating costs are crucial for the successful commercialization of fuel cell technologies and hence recent developments are focussed on these two factors. Construction costs can be lowered by using much lower noble metal catalyst loading without loss of performance. The operating costs can be lowered by using hydrogen from other sources avoiding costly electrolytic hydrogen and the use of air in place of pure oxygen.

5.1. Developments in direct methanol fuel cell electrodes

Two of the most advanced low temperature fuel cells are the proton exchange membrane fuel cell (PEMFC) and the direct methanol fuel cell (DMFC). Both contain similar membrane electrode assemblies (MEA), but show a different degree of performance. The DMFC has a maximum thermodynamic voltage of 1.18 V at 25 °C and the PEMFC a maximum voltage of 1.23 V at 25 °C. In practice, the cell voltages are much less than these values. Therefore, the power density and efficiency are considerably higher in the PEMFC than in DMFC. Both types of cells are limited by the poor electrochemical activity of their cathodes. In the case of the DMFC anode, there is kinetic loss arising from poisoning by CO molecules [96]. The anode and cathode reactions for both the DMFC and PEMFC are given in Table 10. The overall cell reaction in DMFC is oxidation of methanol molecules to produce CO_2 and H_2O and for PEMFC the reaction of H_2 and O_2 to give water with tapping of energy in both cases. Instead of pure hydrogen in the PEMFC, methanol, gasoline or natural gas is converted into reformat which is a hydrogen-rich gas stream with small percentages of carbon dioxide and carbon monoxide. The drawback for the usage of reformat is poisoning of electrodes with carbon monoxide.

The platinum metal is usually dispersed on carbon supports by chemical or electrochemical reduction of platinum salts (Table 11). Platinum complexes like Na_2PtCl_6 , $\text{Pt}(\text{NH}_3)_4^{2+}$, $\text{Na}_6\text{Pt}(\text{SO}_3)_4$ are used for this purpose. Chemical reduction of platinum on to the carbon support for example, Vulcan XC-72 is brought about by dispersing chloroplatinic acid or its sodium salt in water with appropriate organic solvent by the use of ultrasonics or any other efficient stirring method, neutralizing the resulting suspension to pH

Table 10

Anodic and cathodic reactions of direct methanol and proton exchange membrane fuel cells

DMFC	PEMFC
At anode: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$ ($E_a^0 = 0.046\text{ V}$)	$2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^-$ ($E_a^0 = 0.00\text{ V}$)
At cathode: $3/2\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O}$ ($E_c^0 = 1.230\text{ V}$)	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ ($E_c^0 = 1.230\text{ V}$)
Overall: $\text{CH}_3\text{OH} + \text{H}_2\text{O} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + 3\text{H}_2\text{O}$ ($E_{\text{cell}}^0 = 1.180\text{ V}$)	$2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ ($E_{\text{cell}}^0 = 1.230\text{ V}$)

Table 11

Data on preparation of platinum or platinum alloy fuel cell catalysts

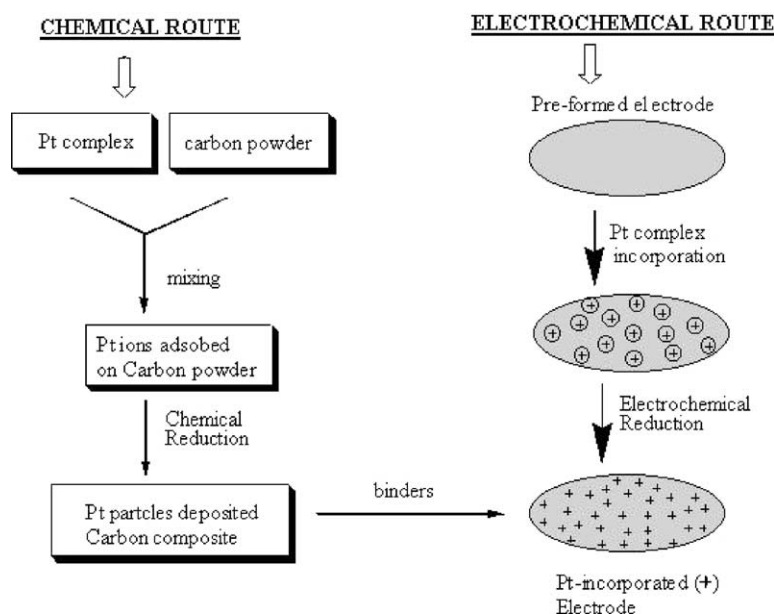
Complex	Reducing method/agent	Support	Average Size of the particles (nm)	Reference
H_2PtCl_6	Borohydride	—	—	[117,118]
$\text{Na}_6\text{Pt}(\text{SO}_3)_4$	H_2	Carbon	1.5–1.8	[119]
PtCl_6^{2-}	Electrochemical	PEM	1.5–20	[98,103,104,120–123]
$\text{Pt}(\text{NH}_3)_4^{2+}$	Electrochemical	PEM–carbon	2.0–3.0	[100–102,125]
$\text{H}_2\text{PtCl}_6 + \text{RuCl}_3$	Sodium dithionite	Mesocarbon microbeads	—	[111]
Stabilized $\text{PtCl}_2 + \text{RuCl}_3$	Alkali hydrotriorganoborates	Carbon	<2.0	[136–142]

7 if platonic acid is used. This is followed by reducing with excess reducing agents such as formaldehyde, hydrazine, borohydride. The carbon support, so obtained, is made into an electrode by sintering with proper binders [97–99] [Scheme 3]. In the electrochemical reduction method, the platinum source is purged on/in the pre-formed electrode and then reduced under potentiostatic conditions [99].

The electrochemical reduction of cationic platinum complex salts such as $\text{Pt}(\text{NH}_3)_4^{2+}$ within a porous electrode consisting primarily of carbon powder and recast Nafion membrane selectively provides Pt catalytic sites that are very effectively used [100–102]. In the case of PtCl_6^{2-} , the species is able to diffuse through the thin film of Nafion although Nafion is a cation exchange polymer and the kinetics are found to be faster [103,104]. Thus electrochemical reduction of PtCl_6^{2-} within such a type of film is likely to provide active layers with well dispersed Pt catalytic sites. The aver-

age platinum particle size is estimated to be 10–20 nm. More recently model electrodes containing platinum nanoparticles (15 nm) have been prepared by pulsed electrodeposition and tested for their electrocatalytic behavior for methanol oxidation reaction [105,106].

Now the research is focussed on the construction of more active anode electrocatalyst materials which would provide higher efficiencies in methanol dehydrogenation and to electrooxidise adsorbed CO to CO_2 . The addition of Ru significantly increases the CO tolerance of Pt. Though the origin of the enhancement is not completely understood, there are two accepted theories widely known, bifunctional mechanism and ligand model. According to the former theory, the added Ruthenium atoms activate water molecules to give Ru–OH, [$\text{Ru}^0 + \text{H}_2\text{O} \rightarrow \text{Ru–OH} + \text{e}^- + \text{H}^+$], which in turn reacts with a poisoned Pt–CO surface to yield carbon dioxide [$\text{Pt–CO} + \text{Ru–OH} \rightarrow \text{CO}_2 + \text{Pt}^0 + \text{Ru}^0 + \text{e}^- + \text{H}^+$].



Scheme 3. Generalized synthetic approaches for fuel cell electrodes.

According to the second theory, the role of ruthenium is to modify the electronic structure of the platinum surface by interacting with the platinum conduction band so that weakening of the Pt–CO bond leads to easy oxidation of CO [107]. Basic electrochemical studies for oxidation of methanol on platinum binary catalysts with Sn, Pd, Re, Au, Pd and Rh have been studied by various groups [107–112]. Catalysts Pt + Sn, Pt + Pb, Pt + Re, Pt + Ru have been prepared by Beden et al. [108] by electrodeposition. Results in this study showed that only the Pt–Ru system exhibited enhanced activity whereas other systems showed enhancement only under limited experimental conditions. Studies by Watanabe et al. [109] have shown that Au–Pt and Au–Pd electrocatalysts showed high catalytic activity in the oxidation of methanol and the reasons were explained in terms of a ‘bifunctional theory’ put forward by them. Liu et al. [111] have studied mesocarbon microbead supported Pt–Ru catalysts as anode materials for methanol oxidation. Their results showed that these electrocatalysts exhibited lower polarization characteristics than that with carbon black support.

5.2. Developments in PEM fuel cell electrodes

Platinum is deposited into/onto the polymer electrolyte membrane (PEM) to produce Pt/PEM electrodes using the impregnation-reduction method [113–116] where reduction is effected chemically or electrochemically. The common and efficient chemical reducer for this purpose is borohydride [117,118]. Another procedure for preparing a high surface area Pt dispersion carbon chemically is by the colloidal method known as the ‘sulfite’ route [119]. In this method chloroplatinic acid is converted into $\text{Na}_6\text{Pt}(\text{SO}_3)_4$ by reacting with excess sulfite salt thereby removing chlorides which would otherwise poison the catalyst; platinum oxide colloids are formed from this procedure on to the carbon supports. The final step is chemical reduction of the colloid/carbon by molecular hydrogen [119]. The average Pt particle size is 1.5–1.8 nm.

The electrodeposition method of preparing Pt/C is advantageous in achieving greater selectivities in the placement of the platinum particles into the preformed electrode, but it also has a drawback. After initial formation of a platinum particle, further deposition continues on the same particle resulting in increase of the size of the particle.

Platinum particles of size 20–1.5 nm have been electrochemically deposited from PtCl_6^{2-} solutions for use in PEMFC electrodes [98,99,104,120–123]. At present electrodeposition seems to be the only technique through which loadings in microgram range [typically 10–750 $\mu\text{g Pt}/\text{cm}^2$] are achievable [101,120–122,124]. Taylor et al. have produced 2–3 nm sized platinum particles on Nafion bound carbon black by using $\text{Pt}(\text{NH}_3)_4^{2+}$ complex by electrodeposition [100–102]. This complex species can be cation exchanged and reduced [125]. The authors of this report [125] discussed the importance of the availability of active platinum sites to the fuel in the PEM electrode. Though all the platinum parti-

cles in PEM electrode are capable of oxidizing hydrogen or reducing oxygen, only those particles which are located at the interfacial region between the polymer electrolyte and carbon, function as real electro catalysts. The electrode should be suitably designed to increase the availability of this active ‘three-phase reaction zone’ to the fuel.

The main disadvantage to PEMFC anodes is the poisoning of Pt. Even ppm levels of CO bind strongly and cover 98% of Pt [126]. This prevents the dissociative electrosorption of hydrogen $\text{H}_2 + 2\text{Pt} \rightarrow 2\text{Pt-H}_{\text{ad}}$ which lowers the cell potential produced by the MEA as much higher anode potential is needed for the electrooxidation [127]. Studies [128–131] showed that Pt–Ru alloy electrocatalysts exhibited much more tolerance towards CO poisoning than pure Pt. A recent study by Johnson and Matthey [132,133] showed a significant increase of the cell potential by facilitating dissociative electrosorption of H_2 . The advantage seems to arise from the lower particle sizes of the alloy compared to the pure Pt metal particles.

Studies on alloys of the type PtRu, PtRh, PtIr as electrocatalysts for the anode were undertaken by General Electric Co. in 1960 as unsupported metal blocks with high loadings of 30 mg/cm^2 of Platinum. Recently these have been reexamined [134] on carbon supports with loadings of 0.5 mg/cm^2 Pt at temperatures below 100 °C. However, the results showed inferior performances except for PtRu. Replacement of Ru by a 3d metal in this system (viz. PtV, PtCr, PtCo, PtNi, PtFe, PtMn) were also investigated on carbon supports [130] and all systems exhibited inferior CO tolerances compared with the PtRu alloy system. Binary and ternary carbon supported catalysts of Pt alloyed with Ru, W, Mo, Sn synthesized by impregnation–reduction and the colloid method were tested for their activity for the oxidation of H_2 containing 150 ppm of CO and methanol. The Pt–Ru–W ternary system was found to be superior [110]. Ramesh et al. have studied the hydrogen oxidation reaction on Pt–Ru, Pt–Pd, Pd–Ru deposits on carbon and demonstrated that these bimetallic systems can perform better than the corresponding single metal electrocatalysts [135].

5.3. Precursor concept

Another approach for preparing nanosized catalyst particles is given by ‘Precursor’ concept. In the case of metal particles with diameter approximately 2.5 nm, approximately 60% atoms exist on the surface. Optimum functioning of the catalyst takes place at the ratio 60% surface atoms and 40% volumetric atoms contained in the nanoparticle. When carbon-containing feeds are used, CO poisoning of the anode becomes the problem, especially in low-temperature PEM and direct methanol fuel cells. One possible way to improve low-temperature CO tolerances is by adding a second or third metal. The ‘precursor’ concept by Bonnemant et al. facilitates the synthesis of such multimetallic–nanoparticle systems via nanostructured metal colloids [136–142]. This method is useful to prepare colloids of metals of group 4–11

of the periodic table. Metal salts, usually halides, are used with alkali hydrotriorganoborates as reducing agents to obtain boron free powdered metals. The main advantages are that (i) the process yields stable metal colloids which are easy to isolate as dry powder hence easy handling (ii) the particle distribution is nearly monodisperse and (iii) bimetallic colloids are easily accessible by co-reduction.

Using this concept, a Pt₅₀Ru₅₀ bimetallic colloid catalyst was prepared using the reducing agent N(Oct)₄[BEt₃H] and the performance was found to be equal to the commercially available Pt/Ru electrocatalysts. The advantage of the ‘precursor concept’ compared with the salt-impregnation technique lies in the fact that both the size and composition of the colloid metal precursors may be tailored independently of the support. Thus the precursor concept provides an excellent tool for the preparation of bimetallic electrocatalysts of a wide range of Pt–M combinations.

6. Concluding remarks

This review has shown that there are new significant contributions in the chemical and electrochemical deposition technology of PGMs, particularly with regard to platinum and palladium. Among these, the development of very efficient plating systems for platinum based on Pt(NH₃)₄(HPO₄) with ever higher plating efficiency is noteworthy. Similarly there considerable improvements in palladium deposition. Hydrogen evolution and the resulting hydrogen embrittlement is still a major problem in PGM electroplating.

A major impediment for commercialization of PEM based fuel cell technologies is high costs associated with the platinum metal. There are attempts to counter this problem by finding new electrode materials in the form of alloys (e.g. Pt–Ru). The new ‘precursor’ route to such nanosized alloy systems is a promising method for the design of effective catalysts. Apart from being cost-effective, these alloy systems significantly modified the slow kinetics of pure platinum catalyst by oxidizing the adsorbed CO molecules. The electrochemical deposition method has an advantage over the chemical deposition method in achieving lower size particles for constructing a fuel cell catalyst. Though Pt–Ru alloy particles on carbon supports are currently the state-of-the-art catalyst for reformate and direct methanol fuel cells, there is a great need for further investigation for improvements in their performance. For PEM fuel cells, the other main challenge is to improve the utilization of all platinum particles that are loaded into the polymer electrolyte. Though all the platinum contained in the electrode is active for the oxidation of hydrogen and reduction of oxygen reactions, the final performance of the electrode depends on the availability of the ‘three phase reaction zones’ containing platinum particle to the fuel. Progress in the design of such electrodes which can improve the availability of reaction zones to the fuel is also needed.

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