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DEVELOPMENT AND UNDERSTANDING OF PD-BASED NANOALLOYS AS CATHODE ELECTROCATALYSTS FOR PEMFC

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DEVELOPMENT AND UNDERSTANDING OF PD-BASED NANOALLOYS AS CATHODE ELECTROCATALYSTS FOR PEMFC

by

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Dedication

Dedicated to my parents and my husband

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Development and Understanding of Pd-based Nanoalloys as Cathode Electrocatalysts for PEMFC

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Proton exchange membrane fuel cells (PEMFC) are attractive power sources as they offer high conversion efficiencies with low or no pollution. However, several challenges, especially the sluggish oxygen reduction reaction (ORR) and the high cost of Pt catalysts, impede their commercialization. With an aim to search for more active, less expensive, and more stable ORR catalysts than Pt, this dissertation focuses on the development of non-platinum or low-platinum Pd-based nanostructured electrocatalysts and a fundamental understanding of their structure-property-performance relationships.

Carbon-supported Pd–Ni nanoalloy electrocatalysts with different Pd/Ni atomic ratios have been synthesized by a modified polyol reduction method, followed by heat treatment in a reducing atmosphere at 500–900 °C. The Pd–Ni sample with a Pd:Ni atomic ratio of 4:1 after heat treatment at 500 °C exhibits the highest electrochemical surface area and catalytic activity. The enhanced activity of Pd₈₀Ni₂₀ compared to that of Pd is attributed to Pd enrichment on the surface and the consequent lattice-strain effects.

To improve the catalytic activity and long-term durability of the Pd–Ni catalysts, Pd–Pt–Ni nanoalloys have been synthesized by the same method and evaluated in PEMFC. The Pt-based mass activity of the Pd–Pt–Ni catalysts exceeds that of commercial Pt by a factor of 2, and its long-term durability is comparable to commercial Pt within the testing duration of 180 h. Both the favorable and detrimental effects of Pd and Ni dissolution on the performance of the membrane-electrode assembly (MEA) have been investigated by compositional analysis by transmission electron microscopy (TEM) of the MEAs before and after the fuel cell test.

The MEAs of the Pd–Pt–Ni catalyst have then been characterized *in-situ* by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) to better understand the performance changes during cell operation. The surface state change from Pd-enrichment to Pt-enrichment and the consequent decrease in the charge transfer resistance during cell operation is believed to contribute to the activity enhancement.

To further improve the MEA performance and durability, the as-synthesized Pd– Pt–Ni catalysts have been pre-leached in acid and Pd–Pt alloy catalysts have been synthesized to alleviate contamination from dissolved metal ions. Compared to the pristine Pd–Pt–Ni catalyst, the preleached catalyst shows improved performance and the Pd–Pt catalyst exhibits similar performance in the entire current density range.

Finally, the catalytic activities for ORR obtained from the rotating disk electrode (RDE) and PEMFC single-cell measurements of all the catalysts are compared. The improvement in the activities of the Pd-Pt-based catalysts compared to that of Pt measured by the RDE experiments is much lower than that obtained in single cell test. In other words, RDE tests underestimate the value of the Pd-Pt-based electrocatalysts for real fuel cell applications. Also, based on the RDE data, the Pd-Pt-Cu catalyst exhibits the highest catalytic activity among all the Pd-Pt-M (M = Fe, Ni, Cu) catalysts studied.

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CHAPTER 1

Introduction

1.1 FUEL CELLS

Global demand for energy is on the rise, while tolerance for pollution and potentially hazardous forms of power generation is on the decline. To reduce our dependence on oil as the primary transportation fuel source, and to address environmental concerns associated with the use of fossil energy carriers, the development of clean, secure, and sustainable energy is becoming increasingly important. Unconventional energy technologies like solar cells, wind power, and nuclear energy are drawing enormous interest. However, most of the non-combustion power generation forms have limitations to provide the prescribed levels of power consistently, and on demand, which constraints the widespread use of these alternative technologies, especially as a primary source of electric power (*i.e.*, base load power). Solar energy, for example, depends on sunlight. Extended days of cloudy skies can severely limit the generation of electricity, and power availability is generally considered to be between 25 to 35 %. In this regard, fuel cells that employ hydrogen as a fuel are appealing as an alternative power generation technology.

1.1.1 Basics of fuel cells

In essence, fuel cells are electrochemical energy conversion devices, which consume fuel and oxidant with the help of electrocatalysts on the electrodes to produce electricity (Fig. 1.1). Like other electrochemical devices, a fuel cell consists of a positive electrode (cathode), a negative electrode (anode), and an ion-conducting electrolyte. The production of electricity by fuel cells involves the oxidation of a fuel and the reduction of

an oxidant, which are fed, respectively, into the anode and cathode compartments. This process generates ion flow through the electrolyte and electron flow through the external circuit [1-2].



Figure 1.1: Operating principle of a fuel cell, directly converting chemical energy into electrical energy.

In a fuel cell, electricity can be continuously produced as long as reactants are provided, and the device converts chemical energy directly into electrical energy without other stages in between that may cause efficiency loss. Therefore, unlike conventional heat engines, fuel cells are not limited by maximum Carnot's cycle efficiency and can have very high efficiency. Additionally, fuel cells have little or low emission compared to traditional combustion engines. When pure hydrogen and oxygen are used as fuel and oxidant, respectively, zero emission could be achieved as water is the only product in the reaction [1-2]. Even when carbon-containing fuels are used, CO₂ emission is reduced due

to the high efficiency of the fuel cell and the absence of combustion avoids the production of NO_x and particulate pollutants.

Fuel cells are different from other electrochemical cells like batteries; fuel cells consume reactants from an external source, which must be replenished – a thermodynamically open system. In contrast, batteries store electrical energy chemically and hence represent a thermodynamically closed system [1-2].

1.1.2 Electrochemical thermodynamics and source of irreversible voltage losses

Ideally, the best-attainable performance of a fuel cell is dictated only by the thermodynamics of the electrochemical reactions that occur. For example, the overall reaction in a hydrogen/oxygen (H_2/O_2) fuel cell is

$$H_2 + \frac{1}{2}O_2 \to H_2O \tag{1.1}$$

The standard theoretical potential (E^{o}_{theor}) for the H₂/O₂ cell reaction is determined from the change in Gibbs free energy (ΔG°) for the reaction at unit activity of all reactants and products as,

$$E^{o}_{theor} = -\frac{\Delta G^{\circ}}{n \cdot F}$$
[1.2]

However, the activities of the reactants and/or products are less than unity, so the Nernst equation is used to calculate the theoretical cell voltage (E_{theor}) at non-standard conditions. Accordingly, for the H₂/O₂ cell reaction above,

$$E_{theor} = E_{theor}^{o} + \left(\frac{R \cdot T}{n \cdot F}\right) \ln\left(\frac{\left(p_{H_2}\right) \cdot \left(p_{O_2}\right)^{\frac{1}{2}}}{p_{H_2O}}\right)$$
[1.3]

where n is the number of moles of electrons produced per mole of H_2 reacted, F is Faraday's constant, R is the gas constant, T is the temperature in Kelvin, and p is the partial pressure of the gases.

When an external resistance "load" is applied to the cell, non-equilibrium exists and a net current flows through the load. The cell voltage becomes smaller as the current increases because of the irreversible losses from (i) kinetic activation loss, (ii) ohmic loss, and (iii) mass transport loss [3-6].

(i) Activation polarization (η_{act}) is the irreversible voltage loss associated with overcoming the energy barrier at the electrode reaction. Activation losses are primarily a function of temperature, pressure, concentration and electrode properties. The nature of the surface, species formed during reaction, and the intrinsic characteristics of the eletrocatalyts play a critical role in the reaction kinetics and influence of the activation polarization. η_{act} is generally described by the Tafel equation as

$$\eta_{act} = \frac{RT}{\alpha \cdot n \cdot F} \ln \frac{i}{i_0}$$
[1.4]

with α is the transfer coefficient and i_0 is the exchange current density. This equation can be rewritten as

$$\eta_{act} = a + b \log i \tag{1.5}$$

with a = $(-2.3\text{RT}/\alpha nF) \cdot \log i_0$ and b = $-2.3\text{RT}/\alpha nF$. A plot of η_{act} vs. log i yields a straight line and the slope is called Tafel slope, which measures the resistance due to charge transfer. It is obvious that there is a strong desire to find and develop electrocatalysts with a Tafel slope as low as possible.

(ii) Performance loss due to resistance to ionic current in the electrolyte and electronic current in the electrode is called ohmic polarization (η_{ohm}). It is described as

$$\eta_{ohm} = i \cdot R_{ohm}$$
[1.6]

where R_{ohm} is the ohmic resistance of the cell.

Electronic resistances are associated with the cell electrodes, gas diffusion layers, current collectors, leads, as well as contact resistance at the junctions between these components. However, ohmic losses due to electronic resistance are usually much smaller than those arising from the resistance to ion transport through the electrolyte.

(iii) Concentration polarization (η_{conc}) occurs as a result of consumption of reactants at the surface of the electrode that causes a concentration gradient to develop between the bulk and the electrode surface. Under theses conditions, the reaction rate is limited by the rate at which the reactant is delivered to the reaction site. Transport mechanisms within the gas diffusion layer and electrode structure include convection, diffusion, and/or migration of the reactants and products into and out of the catalyst sites in the anode and cathode. A simple concentration polarization can be described as,

$$\eta_{conc} = 2.303 \frac{RT}{n \cdot F} \log\left(\frac{i_{\rm lim}}{i_{\rm lim} - i}\right)$$
[1.7]

where i_{lim} is the limiting current density and it is defined as the reaction rate at which the surface concentration of the reactant is zero.

The actual cell voltage (V_{cell}) at any given current density can be represented as the reversible voltage minus the activation, ohmic, and concentration losses as,

$$V_{cell} = E_{theor} - \left(\left| \eta_{act,c} \right| + \eta_{act,a} \right) - \eta_{ohm} - \left(\eta_{conc,c} + \eta_{conc,a} \right)$$

$$[1.8]$$

This is illustrated in Fig. 1.2 in the form of a current-voltage plot obtained with a H_2/O_2 fuel cell. The overall goal is to minimize the polarization losses by developing more suitable materials (*e.g.*, different electrode structures, electrolytes with enhanced conductivity, or better catalysts) and the modification of the cell operating conditions.



Figure 1.2: Representative current-voltage plot of a H₂/O₂ fuel cell. The regions controlled by different polarization processes are marked.

1.1.3 Types of fuel cells

There are five major types of fuel cells, differentiated from one another by the electrolyte used: (i) proton exchange membrane fuel cell (PEMFC), (ii) alkaline fuel cell (AFC), (iii) phosphoric acid fuel cell (PAFC), (iv) molten carbonate fuel cell (MCFC), and (v) solid-oxide fuel cell (SOFC). While all the five fuel cell types are based on the

same electrochemical principles, they operate at different temperatures, involve different materials, and often differ in their fuel tolerance and performance characteristics as shown in Table 1.1. The five types of fuel cells and the electrode reactions involved in them are given in Fig. 1.3 [2,7,8].



Figure 1.3: The five major types of fuel cells and the reactions occurring in them.

Fuel cell type	PEMFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Solid polymer	Liquid potassium	Liquid phosphoric	Liquid lithium/	Yttria-doped
	(polypernouro- sulfonic acid)	in matrix	matrix	carbonate soaked in	Zircomum oxide
	sufforme uera j	III IIIdd IX	mutix	a matrix	
Operating	50 - 120	60 - 250	150 - 200	600 - 700	600 - 1000
temperature (°C)					
Catalyst	Pt/PtRu	Pt	Pt	Ni	Perovskites
					(ceramics)
Cell components	Carbon based	Carbon based	Carbon based	Stainless based	Ceramic based
Fuel	H_2 , methanol	H ₂	H ₂	H_2, CH_4	H_2 , CH_4 , CO
CO tolerance	Poison (<50 ppm)	Poison (<50 ppm)	Poison (<1 %)	Fuel	Fuel
Internal reforming	No	No	No	Yes	Yes
Electrical	40-50	50	40	45-55	50-60
efficiency (%)					
Power density	300-1000	150-400	150-300	100-300	250-350
(mW/cm^2)					
Power range	0.001-1000	1-100	50-1000	100-100,000	10-100,000
(kW)					
Applications	Portable,	Space, military	Stationary,	Stationary	Stationary,
	stationary,		transportation		auxiliary power
	transportation				
Balance of plant	Low-moderate	Moderate	Moderate	Complex	Moderate
Advantages	• Solid electrolyte	• High	•Up to 85%	• High efficiency	• High efficiency
	reduces corrosion	performance due	efficiency in	• Range of suitable	• Range of suitable
	and management	to fast cathode	cogeneration of	fuels	fuels
	problems	kinetics under	electricity & heat	• Inexpensive	• Inexpensive
	• Low T	alkaline	• Impure H ₂ as fuel	1	1

Table 1.1:Summary of the characteristics of the five major types of fuel cells.

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	• Quick start-up	conditions		catalysts	catalysts
Disadvantages	 Low T requires expensive catalysts Sensitive to fuel impurities 	• Expensive removal of CO ₂ form fuel & air streams required	 Pt catalyst Low current & power Large size & weight 	• High T enhances corrosion and failure of cell components	• High T enhances corrosion and failure of cell components

Currently, none of the fuel cell types are ready for commercial applications. Until significant reduction in cost and improvements in power density, reliability, and durability are made, fuel cells will remain a niche technology. Of the five types of fuel cells, PEMFCs and SOFCs offer the best prospects for continued improvement and eventual application. While PAFCs and AFCs benefited from early historical development, the other fuel cell types have caught up and offer further advantages that will make them more attractive in the long run. Both the PEMFC and the SOFC can be applied to residential power and other small-scale stationary power applications. The high-temperature SOFCs offer attractive efficiency and fuel flexibility advantages, and they also generate higher quality waste heat which can be used in combined applications. While all fuel cells operate best on hydrogen, those operating at higher temperatures offer improved impurity tolerance and the possibility for internal reforming of hydrocarbon fuels to yield hydrogen. However, the high operating temperature makes the materials requirements, mechanical issues, reliability concerns, and thermal expansion matching tasks more difficult. On the other hand, due to their high energy/power density and low operating temperature, the PEMFCs appear uniquely suited for portable and transportation applications.

1.2 PEMFC

1.2.1 Components of PEMFC

Typically, a complete PEMFC consists of seven components, namely anode flow channel (bipolar/end plate) & current collector, anode gas diffusion layer (GDL), anode catalyst layer (CL), proton exchange membrane (PEM), cathode CL, cathode GDL, and cathode flow channel & current collector, as shown in Fig. 1.4. Usually, the flow field plates fulfill both the tasks of the current collectors and the distribution of the reactants

throughout the complete electrode area. Current collectors are attached to both electrodes to enable the external electron flow.



Figure 1.4: Schematic of PEMFC [9].

The proton exchange membrane is one of the main components in PEMFC. This solid polymer electrolyte of 25 to 250 μ m thick provides the transportation pathway for the hydrogen ions from the anode to the cathode side of the cell. Simultaneously, it also separates the anode from the cathode reaction zone. The membrane is made of a polymer with pendant sulfonic acid groups [10]. Currently, the commercially available polymer

electrolyte membrane is Nafion (a product of *DuPont*), where the sulfonic acid groups are attached to a fully fluorinated Teflon-based backbone [10, 11].

The catalytic active layers are attached to either side of the membrane. Carbonsupported noble metals like platinum or noble metal alloys are widely used as electrocatalysts for PEMFC [12]. The carbon support ensures electron conductivity throughout the whole electroactive layer. It also provides the highest possible catalyst dispersion and electroactive catalyst surface. The porous system enables the gas to access the electrocatalyst and provides a path for the removal of product water from the electrode.

The gas diffusion layer (electrode backing) is placed in contact with the active layer. The GDL is usually prepared by depositing a mixture of carbon powder and polytetrafluoroethylene (PTFE) onto a carbon paper or carbon cloth. The carbon materials provide electronic conductivity for the GDL, while the PTFE helps to adjust the hydrophobicity of the GDL, ensuring fast liquid and gas transfer during cell operation.

The electrocatalytic reaction takes place at the three-phase boundary, where electrocatalyst, electrolyte, and reactant gases exist simultaneously. Both an ionic and an electronic path have to be ensured during the redox reactions. Normally, additional ionomer (usually liquid Nafion) is impregnated into the active layer to ensure good access to the H^+ ions within the catalyst layer.

1.2.2 PEMFC and DMFC

In PEMFC, hydrogen is supplied as a fuel into the anode side where it is oxidized to protons and electrons on the surface of the catalyst. While the electrons flow through the external circuit, the protons are transported through the electrolyte to the cathode side. The oxygen or air is supplied as the oxidant into the cathode side where it is reduced with protons on the surface of the catalyst to produce water. Electrochemical reactions occurring in the anode and cathode sides of PEMFC can be seen in Fig. 1.3. The overall reversible cell potential for a PEMFC is 1.23 V at the standard state.

Strictly speaking, direct methanol fuel cell (DMFC) is also a PEMFC as it uses a proton exchange membrane as the electrolyte. However, since it uses methanol as a fuel instead of hydrogen, it is termed as DMFC to distinguish it from a PEMFC using hydrogen as a fuel. In a DMFC, the same electrochemical reaction as in a PEMFC takes place at the cathode side. At the anode side of a DMFC, methanol decomposes to carbon dioxide, protons, and electrons in the presence of water. The electrochemical reactions occurring in DMFC are given in Fig. 1.3, and the overall reversible cell potential for a DMFC is 1.2 V at the standard state.

Because the liquid methanol is fed directly into the fuel cell, steam reforming of the fuel is not required and methanol is much easier to store compared to hydrogen, which needs high pressure or low temperature. Also, the energy density of methanol is much higher than that of compressed hydrogen. However, despite the similar standard cell potential, the tremendous polarization losses in DMFC (~ 0.3 V vs. ~ 0.05 V for the H₂ oxidation) lead to reduction in the operating voltage by 0.2 to 0.4 V. In addition, methanol exhibits a high diffusion rate through the state-of-the-art polymer membranes (methanol crossover) [10]. The methanol loss on the anode side (up to 50 %) [13, 14] and the decrease of the cathode potential due to the build up of a mixed potential (simultaneous oxygen reduction and methanol oxidation) account for the large efficiency losses.

1.2.3 Challenges of PEMFC

As stated in the previous sections, low-temperature PEMFCs are widely considered as the most promising type of fuel cells for portable, transportation, and stationary applications due to their high energy/power density, low operating temperature, absence of liquid electrolyte, and easy maintenance. However, commercialization of this technology is hampered by high cost, durability, and operability problems, which are linked to severe materials challenges and system issues, especially catalysts and proton exchange membrane materials.

1.2.3.1 Electrolyte materials

As discussed in section 1.2.1, electrolyte materials must conduct ions, but not electrons. They must also be gas impermeable and as thin as possible to minimize the cell resistance. Most of the PEMFC electrolytes are based on thin polymeric membranes that conduct H⁺ ions. Many of these polymer materials rely on water-based vehicle mechanism for ionic transport [15,16]. Because water is often intimately involved in the ionic transport chain in these electrolyte materials, ionic conductivity tends to be extremely sensitive to the level of hydration [17,18]. Operation under dry conditions or at temperatures greater than 100 °C is, therefore, severely limited, if not impossible. Because of these hydration and temperature issues, sophisticated water and temperature management schemes are crucially required for most of the PEMFC-based systems.

Designing a polymer electrolyte material capable of operating above 100 °C is highly desirable, as this dramatically simplifies water management, while simultaneously improving electrochemical performance and impurity tolerance. In addition, candidate PEMFC electrolyte materials must also possess high ionic conductivity and good mechanical properties and must be highly stable/durable in the PEMFC environment and reasonably inexpensive. Perfluorinated polymers, sulfonated hydrocarbon polymers, phosphoric acid-doped polybenzimidazole, polymer-inorganic composites, and solid acids are some examples of polymer-based electrolyte materials under study [2].

1.2.3.2 Electrode/catalyst materials

Since PEMFC catalysts are often based on expensive noble metal material like Pt, it is desirable to reduce the cost as much as possible. For the facile hydrogen oxidation reaction, ultra-small Pt particles are typically supported on a high-surface-area carbon powder, and only extremely small amount of Pt catalyst is required. In contrast, in the case of anode catalysts for DMFC and cathode catalyst for the oxygen reduction reaction (ORR), a much higher Pt catalyst loading is required due to both poor reaction kinetics and poisoning caused by the high methanol crossover. The approaches to reduce catalyst loading and thus catalyst cost have generally followed three basic strategies: (1) optimize the current Pt/C catalysts by decreasing Pt particle size and improving Pt distribution/dispersion, (2) develop new Pt-alloy catalysts that are even more active than pure Pt, (3) develop inexpensive, Pt-free catalysts, even if they are less active than Pt catalysts.

Many different preparation techniques have been successfully used to increase Pt dispersion by reducing the Pt particle size [19-22]. In some cases, Pt particle sizes have been decreased to less than those of the best commercially available catalysts. However, 100 % dispersion is achieved at around 1.1 nm, and any further reduction in diameter will not increase Pt dispersion. Also small particles tend to agglomerate because of their large surface area and surface energy, so there is a compromise between dispersion and durability.

On the other hand, a dual-layer approach for fabricating PEMFC electrodes has been developed to optimize the electrode structure [2]. A thin (typically 10–30 μ m thick), but highly active, catalyst layer usually consisting of a mixture of porous Pt/C catalyst and electrolyte materials is deposited directly onto the electrolyte surface. A much thicker (typically 100–500 μ m thick) inexpensive, porous, and electrically conductive electrode layer is then bonded onto the top of the catalyst layer to provide protection and facilitate current collection. This dual-layer structure maximizes catalytic activity, gas access, product removal, and electrical conductivity, while minimizing costs.

The other two strategies to reduce Pt loading, namely developing novel Pt-alloy and Pt-free catalysts, will be discussed in detail in the following section with a focus on cathode electrocatalysts, which is the main topic of this dissertation. The discussion will include both mechanistic considerations and application of various novel electrocatalysts for the oxygen reduction reaction. All the "PEMFC" motioned below refer to PEMFC with hydrogen as a fuel.

1.3 ELECTROCATALYSTS FOR ORR

1.3.1 ORR kinetics

The reaction pathways in an acidic environment are described as follows [23]: *Direct reduction*

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
 $E^{o}(O_2/H_2O) = 1.23V$ [1.9]

Indirect reduction

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
 $E^{\circ}(O_2/H_2O_2) = 0.682V$ [1.10]

followed by a further reduction via

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$
 $E^{\circ}(H_2O_2/H_2O) = 1.77V$ [1.11]

or a chemical decomposition via

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{1.12}$$
During the last decades, several different models have been developed to describe the interplay between the two competing reactions. A simplified reaction scheme [24] based on the reaction schemes introduced by Wroblowa et al. [25] and Bagotskii *et al.* [26] is presented in Fig. 1.5. This scheme is valid for both acidic and basic environments and all the electrode materials.



Figure 1.5: Simplified schematic of the ORR pathway based on the scheme suggested by Wroblowa [24-26].

Based on this scheme, the preadsorbed oxygen can be electrochemically reduced either directly to water with the rate constant k_1 (4e⁻) or to H₂O_{2ad} with the rate constant k_2 (2e⁻). The adsorbed peroxide can be electrochemically reduced to water with the rate constant k_3 , catalytically (chemically) decomposed on the electrode surface (k_4) or desorbed into the bulk of the solution (k_5).

The different reaction pathways depend on different adsorption states [23]. The adsorbed states for oxygen are schematically presented in Fig. 1.6 and the resulting possible reaction pathways are shown in Fig. 1.7.



Figure 1.6: Models for the adsorbed states of oxygen on the catalyst surfaces [23, 27].



Figure 1.7: Reaction pathways for the oxygen reduction reaction in an acidic environment [27].

For side-on adsorption (Pauling model), the O–O binding remains almost unchanged. Pathway II is then preferred and thus the formation of H_2O_2 is favored. On the other hand, end-on adsorption (Griffiths model, bridge model) stretches the O–O binding and thus decomposes the O_2 molecule. Therefore, the four electron reduction to water according to pathway I or III is favored.

The reaction pathway depends strongly on the pH of the electrolyte, the presence or absence of adsorbing anions in the electrolyte, and on the catalyst material. Usually, parallel existence of both the direct and the series pathway is found on platinum, platinum alloys, palladium, Pt-like metals, and silver. In alkaline electrolytes, the series pathway is enhanced compared to the direct pathway.

In fuel cells, in order to obtain maximum efficiency and to avoid corrosion of the carbon support and other materials by peroxide, it is desired to achieve a four-electron reduction. The oxygen reduction at Pt is characterized under most conditions by a four-electron reduction. Besides, the exchange current densities on Pt are the highest among the noble metals, about 10^{-11} – 10^{-9} A/cm² in both acid and alkaline solutions [28]. Therefore, Pt is the best electrocatalyst for ORR until now.

1.3.2 Approaches for less expensive electrocatalysts

1.3.2.1 Pt bulk alloys

United Technology Corporation (UTC) originally developed high surface Ptalloys for ORR in PAFC in the 1980s. The development started with binary alloys such as PtV/C and culminated in ternary alloys such as PtCoCr/C, PtRhFe/C, and PtIrCr/C, with the reported mass activities 2–3 times higher than that of Pt/C [29]. Later, other commercial catalyst companies such as TKK (PtNiCo), NEChemCat (PtCu, PtFeCu, and PtFeCoCu), and Johnson Matthey (JM) (high loading catalysts) also worked on Pt-alloys and patented a number of binary, ternary, and quaternary alloys that claimed better catalytic activity and improved stability over Pt/C [30]. Mukerjee et al. [31] was the first to apply Pt alloys in PEMFC in the early 1990s. Various binary Pt-M (M = Ni, Cr, Co) alloys with the Pt₃M ordered structure have been found to show enhanced catalytic activity for ORR in PEMFC. Later, Shim et al. [32] prepared Pt–Fe–M (M = Cr, Mn, Co, Ni, Cu) ternary alloys and tested in PEMFC. Also, different binary Pt-M (M = Fe, Mn, Ti) and ternary Pt–Co–M (M = Cr, Ni) alloys have been investigated [33]. Although catalytic activity comparisons have proved notoriously difficult and even contentious, there is a general consensus that certain Pt-alloys like Pt₃Cr and Pt₃Co do indeed show enhanced ORR specific activity compared to pure Pt, perhaps by as much as a factor of 2–4. Pt-Co catalysts appear especially attractive, and various studies are examining different compositions in the Pt–Co alloy system.

Although Pt-alloy catalysts appear to offer a potentially feasible route to enhance activity and lower the PEMFC cathode cost, they also create several new complications:

- Compared to pure Pt catalysts, Pt-alloy catalysts have proven harder to obtain as extremely high surface area (small particle size) dispersions on carbon supports.
- Pt-alloy catalysts contain transition metals such as Co, Cr, Fe, Ni, and Ti, which can poison the PEMFC if they leach out from the catalyst.
- The mixed-composition of Pt-alloy catalysts may make them more susceptible to accelerated degradation, corrosion, and deactivation.

Of the above listed concerns, leaching out is probably the single greatest challenge. In order to obviate leaching, researchers have introduced a pre-leached process, which is designed to remove the base-metal deposited on the carbon surface or poorly alloyed to the Pt prior to MEA preparation [34]. Pre-leached Pt-alloy catalysts have been shown to yield dramatically lower poisoning rates than their unleached counterparts, while still retaining a significant activity advantage compared to pure Pt

catalysts. Impressively, Pt–Co alloys have also shown particle coarsening/sintering/degradation rates that are actually lower than pure Pt catalysts, indicating that degradation issues may also be ameliorated by moving to these alloys.

1.3.2.2 Core-shell structure

The importance of catalyst surface composition and near surface structure in catalysis [35-37] has given rise to interest in exploring a heterogeneous core-shell structure for the catalyst design, which has many perceived advantages [38-40]. First of all, a core-shell structure can leverage on the use of a low-cost metal core and a noble metal overlayer to greatly reduce the cost of the catalyst. Second, this structure with a thin Pt shell should permit the surface Pt atoms to interact electronically with the underlying metal atoms to increase the oxygen reduction reaction activity through either a contraction of the Pt–Pt bond distance or greater Pt 3d orbital vacancies. Third, this coreshell structure permits high Pt dispersion regardless of the particle size since Pt is located only as a shell on the particle surface. If the Pt shell were only one monolayer (ML) thick, then Pt dispersion would be unity regardless of the overall particle diameter. Fourth, with a structure of base metal core and a thin Pt shell, the base metal beneath should be protected from corrosion by the Pt shell. Meanwhile, high Pt dispersions existing as a shell should also exhibit greater resistance to sintering, a problem that affects very small Pt particles.

To achieve this unique structure, two primary techniques have been developed: surface metal galvanic displacement and surface metal depletion gilding.

a: Galvanic displacement



Figure 1.8: Two distinct techniques for modifying the optical surface properties of noble metal/non-noble metal bimetallics, serving as the basis of two of the most promising synthetic strategies towards more active oxygen reduction reaction (ORR) electrocatalysts: (a) galvanic displacement and (b) depletion gilding.

The galvanic displacement method was initiated by Adzic et al. [41-44] and has been utilized over the past decade, which came to be known as the *Pt Monolayer Catalyst* concept. In this strategy, Pt monolayers were deposited onto non-Pt substrates (either metal or alloy carbon-supported nanoparticles) using galvanic displacement of layers of surface Cu atoms (Fig. 1.8). The resulting catalysts have shown very high intrinsic surface electrocatalytic activity for ORR, with a double-digit Pt-mass based activity gain. The origin of their high activity has been identified by electrochemical and surfacescience techniques, X-ray absorption near edge spectroscopy (XANES), and density functional theory (DFT) calculations. They represent one of the most promising new catalyst classes for fuel cell cathodes.

The activity of Pt monolayer electrocatalysts for the ORR is strongly substrate metal-dependent. The volcano type plot is obtained from the activity of Pt monolayers on various substrates plotted as a function of calculated d-band center of Pt monolayer [43]. Pd imparts the highest activity of Pt monolayers while Au, Ir, Ru, Re, and Rh cause a decrease in activity although they are stable supports.

However, such endeavors are limited as mainly the electrocatalytic characteristics of the prepared core-shell catalysts have been investigated in liquid electrolytes or high temperature was required to prepare the core materials. Therefore, previous studies did not expand its scope to the possibility of these catalysts being used in real fuel cell applications. In this regard, other techniques including electroless deposition [45] and Pt overgrowth (encapsulation by Pt) [46–48] have been developed for volume production and practical usage.

Electroless deposition is an autocatalytic chemical deposition in which the deposited metal on the substrate acts as an activator, which is also called a catalyst when it helps further deposition of another metal [49]. It was adopted to form a copper layer on the substrate core. For Pt overgrowth, catalyst is synthesized by a two-step reduction process. Firstly, carbon-supported nanoparticles were synthesized. Secondly, the carbon-supported catalyst acts as seeds for overgrowth of the Pt shell through a reduction of the Pt precursors [47].

The other technique, "surface metal depletion gilding," was first reported by Strasser et al. [50,51]. The active phase of the Pt alloy nanoparticle catalysts was prepared by electrochemical dissolution of Cu surface atoms (voltammetric dealloying) from the surface of Pt–Cu bimetallic compounds, until a multi-layer Pt-rich shell region is formed (Fig. 1.8). The dealloyed Pt–Cu exhibited a 4–5 fold enhancement in ORR activity on Pt-mass basis compared to pure Pt nanoparticle catalysts according to the recent MEA studies [51]. It has been postulated that after dealloying, the resulting alloy electrocatalyst consists of a Pt–Cu alloy core surrounded by Pt shell. Additionally, it was postulated that the presence of a reactive core modifies the Pt shells and leads to higher activities.

1.3.2.3 Morphology control

The fact that a majority of electrocatalytic reactions are structure sensitive or site demanding [52–56] also points out the importance to achieve an effective control of the crystalline surface structure of the nanoparticles for a well founded comparison of the electrocatalytic activity of different electrocatalysts. Studies have shown that by altering the crystallographic plane of a bulk single crystal, one can manipulate the catalytic properties of a Pt-based catalyst. For example, in ORR, the most commonly used electrolytes are HClO₄ and H₂SO₄. In the non-adsorbing electrolyte HClO₄, the activity of ORR decreases in the order (110) > (111) > (100) due to the decreased interaction strength between O₂ and the different surface structures and increased adsorption of the OH species on these surfaces. In comparison, for the adsorbing H₂SO₄ electrolyte, the activity decreases in the order (111) < (100) < (110) as determined by the adsorption and inhibiting effect of bisulfate anion [57].

Therefore, great effort has been made to synthesize shape-controlled Pt particles by varying the nucleation and growth rates of Pt clusters [58]. This is because through shape-controlled synthesis, it is possible to maneuver the shape of a nanocrystal to expose only a specific set of crystallographic planes. For example, a tetrahedron is bounded by {111} facets and a cube is covered by {100} facets, whereas a cuboctahedron is enclosed by a mix of {100} and {111} facets.

For an fcc single crystal, the surface energies associated with the low-index crystallographic planes are in the order of (111) < (100) < (110) [59]. One can alter the surface energies and thus growth rates by using various capping agents in a shape-controlled synthesis. In general, Pt nanocrystals of different shapes, such as tubes [60], cubes [61], nanowires/rods [62], prisms [63], and urchin [64] have been recently synthesized in the presence of a capping agent or surfactant [65] via reduction of a Pt precursor, decomposition of an organometallic complex, or a combination of these two routes such as hydrogenated decomposition of Pt(acac)₂[66].

Xia and coworkers [67] demonstrated that Pt multi-octahedra exhibit 2.7 times higher catalytic activity per unit surface area than the commercial Pt/C (E-TEK) catalyst due to the high ratio of {111} to {100} as exposed facets and the presence of surface steps on their surfaces [67]. In addition, the durability of 20-nm Pt multi-octahedra catalyst also increases compared to that of the Pt/C catalyst. This can be attributed to the unique morphology, *i.e.* a highly branched structure consisting of interconnected octahedral arms.

Recently, Sun and coworkers [61c] found that the specific activity of the Pt nanocubes is four times higher than those of the polyhedra or truncated cubes [61c]. Similar to the bulk single crystals, this phenomenon was attributed to the different adsorption abilities of bi-sulfates on Pt(100) as compared to Pt(111) facets.

1D nanostructures of Pt also show an increase in both catalytic activity and stability for fuel cell applications. The platinum nanowires at the cathode of a membraneelectrode assembly prepared in Dodelet's laboratory [62c] could reach 50% higher mass activity and threefold better specific activity than the commercial cathode. One of the major limitations of these shape-controlled approaches is the utilization of strong capping molecules or surfactants, which in most cases hinder or even prevent catalysis by blocking some of their active sites and by inducing steric effects [68]. Efficiently removing the surface ligands while keeping the morphology of the nanoparticles remains a huge challenge. Furthermore, the catalytic efficiency is not improved much in terms of mass activity since the Pt particles have larger sizes (in most cases, > 7 nm) and/or high aspect ratios as compared with a conventional spherical particle. Thus, new approaches for synthesizing Pt nanoparticles with controlled shapes and improved catalytic activity are still needed.

1.3.2.4 Non-platinum electrocatalysts for ORR

(1) Transition metal oxides

Various metal oxides have been investigated for ORR in the literature: (i) amorphous (e.g., $Na_{0.1}MnO_{1.96}$) [69] (ii) spinel (e.g., $Ni_xCo_{3-x}O_4$) [70], (iii) perovskite (e.g. $La_{1-x}Ca_xCoO_3$) [71], and (iv) pyrochlore (e.g. $Pb_2Ru_{2-x}Pb_xO_{7-y}$) [72] oxides. Especially, those with a perovskite or pyrochlore structure have shown remarkable activity for oxygen reduction reaction in an alkaline solution. Unfortunately, most transition metal oxides have been found to be unstable in the acidic environment of PEM fuel cell operation. Reeve et al. [73] observed that in acidic solutions, the activity declined substantially and the stability of the oxide phase was also poor. The slow dissolution of metal components of the oxide and their redeposition at the anode caused severe cumulative poisoning problems.

(2) Transition metal chalcogenides

Since Alonso-Vante et al. [74] initially proposed that semiconducting chevrelphase Ru–Mo chalcogenides (sulfides, selenides) had significant oxygen reduction activity in acid conditions, some transition metal chalcogenides MX (M= transition metal atom, X = S, Se, Te) have been investigated as promising non-noble catalysts. The unique feature of chalcogenides is the high stability in an acidic environment, especially if in combination with other transition metals [75]. These materials also show much better catalytic properties towards ORR as compared with other Pt-free catalysts. Besides, these materials are of interest in view of fundamental research. It has been found that the delocalization of electrons in a metal cluster can lead to high electronic conductivity and attenuate the relaxation of the electronic states. The availability of a reservoir of charges for the multi-electron charge transfer is also very important for enhancing the catalytic activity.

(3) Transition metal carbides or nitrides

Since Boudart and Levy [76] reported the platinum-like properties of tungsten carbide (WC) for H_2 – O_2 titration, carbides and nitrides have been intensively investigated for their suitability as a promising substitution for platinum electrocatalysts in PEMFCs. Several carbides of transition metals like tungsten, titanium, and tantalum have been found active towards oxygen reduction reaction [77-79]. Besides, TiN has been investigated as the ORR electrocatalyst in alkaline solution [80], and molybdenum nitride and tungsten nitride have been studied in acid solution and PEMFCs [81]. Although these nitride catalysts are found to show comparatively good activities for ORR, the activities are still too low compared to that of Pt.

(4) Metal-containing macrocyclic compounds

It has been known that transition metal (e.g., Fe, Co) macrocyclic compounds (*e.g.*, porphyrins, phthalocyanines, tetraazannulenes) could be used as electrocatalysts for ORR since Jasinski's discovery of the catalytic properties of Co phthalocyanine [82]. Recently, Dodelet's group [83] reported a breakthrough in the development of non-noble metal catalysts. The volumetric activity of their carbon supported iron–nitrogen catalyst

is close to the 2010 DOE performance target of 130A/cm³ for ORR on non-noble metal catalysts. However, this type of materials shows low electrochemical (chemical) stability in acidic conditions. The decomposition either via hydrolysis in the electrolyte or an attack of the macrocycle rings by peroxide intermediates was found to be the main cause of the poor stability. Attempts to improve both the catalytic activity and stability has led to the discovery that heat-treatment of transition metal macrocycles (> 800 °C) can significantly improve stability and, in some circumstances, enhance overall catalytic activity [84].

(5) Pd-based electrocatalysts

Being in the same group in the periodic table, palladium (Pd) has properties similar to that of platinum. Pd has a four-electron pathway for ORR like Pt, and it possess ORR activity closest to that of Pt among various metals [85]. Moreover, Pd is more abundant and less expensive than Pt, and it has little or no electrocatalytic activity for methanol oxidation in acid medium [86]. All these properties of Pd strongly suggest that it may be a good candidate as an ORR-selective electrocatalyst.

Although the catalytic activity of Pd towards ORR is several times lower than that of Pt and its alloys, recent reports have shown that the catalytic activity of Pd-based catalysts for ORR can be improved significantly by adding elements like Co, Fe, Cr, etc. In particular, Savadogo et al. [87] were the first to report the use of Pd alloy catalysts for ORR in 2004, and they found that the ORR activity on the Pd–Co alloy was higher than that on Pt catalyst. Also, by a rapid scanning electrochemical microscopy (SECM) technique and classical rotating disk electrode (RDE) experiments, Pd–Co, Pd–Co–Au, Pd–Ti, and Pd–Co–Mo electrocatalysts after heat-treatment at evaluated temperatures have been found to have performance similar to that of Pt for ORR [88-90]. Furthermore, Shao's group synthesized a class of electrocatalysts consisting of Pd–Fe alloys prepared by thermal treatment, whose activities surpass that of the state-of-the-art carbonsupported Pt electrocatalysts [91]. Similar to Pt alloys, a thermodynamic method using DFT reported by Fernandez at al. [89] has shown that there is a correlation between the ORR activities of Pd-M alloys with their d-band centers.

Recently, Bard *et al.* [88] have proposed a broad thermodynamic guideline for the design of improved bimetallic electrocatalysts for ORR. This guide is based on a simple four-electron reduction mechanism, which involves an initial dissociative chemisorption of oxygen molecule (step 1) followed by an electrochemical reduction of the adsorbed oxygen atoms (step 2, shown below).

$$2M + O_2 \rightleftharpoons 2MO$$
 [1.13]

$$2MO + 4H^+ + 4e^- \rightleftharpoons 2M + 2H_2O \qquad [1.14]$$

From a simple analysis of these two reactions, we can infer that metals that favor bond cleavage will stabilize the intermediate MO. Fig. 1.9 shows tabulated data for the Gibbs free energy for step 1 (reaction 1.13) versus the standard potential for step 2 (reaction 1.14) for various elements. This model involves combing one metal that will easily break the O-O bond with another metal that will easily reduce the surface oxide to water. This is can be applied to develop novel Pd-alloy catalysts.



Figure 1.9: Graph of the Gibbs free energy for step 1 versus the standard potential for step 2.

1.3.3 Origin of improved kinetics of ORR

There have been several attempts made to hypothesize or at least draw strong correlation of the enhanced activity of Pt based catalysts over Pt to several factors such as structural effects, electronic effects, surface sensitive effects, and surface roughening effects [92]:

(i) Structural effects (geometric effects): Crystalline Pt has an FCC lattice with a lattice parameter of 3.93 Å as measured from XRD measurements. It has been observed that the base-metal elements smaller than Pt, when alloyed with Pt, enter the crystal

structure through substitution and cause a lattice contraction. The increasing electrocatalytic activity of the Pt-alloys (such as Pt-Cr, Pt-V, Pt-Ti, Pt-W, Pt-Al, Pt-Ag alloys) show a strong correlation with a decrease in interatomic or nearest-neighbor distance between Pt atoms [93]. This effect has been attributed to the smaller Pt–Pt bond distances, resulting in more favorable sites that enhance the dissociative adsorption of oxygen.

(ii) Electronic effects: Electronic effects associated with d-band vacancies are expected to play an important role in activity enhancement. Based on the d-band theory, an increase in the Pt 3d orbital vacancy or a decrease in the Pt d-band center will lower the adsorption strength of the adsorbed oxygenated species, resulting in a lower Pt oxide coverage (from water activation) and/or faster electro-reduction of the oxygenated intermediates, and thus leading to enhanced ORR kinetics. Several studies [94,95] have been conducted showing that alloying of Pt with transition metals increases the Pt d-band vacancy and decreases the Pt–Pt bond distance depending on the electro-negativity of the transition metal. XANES data demonstrated that the OH_{ads} onset, which is at 0.80 V for Pt/C, shifted to more positive potentials in some Pt-alloys. Stamenkovic et al. [96] analyzed the activity towards the ORR of several Pt-3d-metal alloys, and a volcano-type plot was obtained by plotting activity *vs*. d-band center for various Pt-M alloys, with Pt–Co/C situated on the top of this curve. Similar observations were previously presented by Zhang et al. [42] for a Pt-overlayer on different metal single-crystals.

(iii) Surface sensitive effects: Different low-index surfaces have markedly different activity for electrochemical reactions. As stated in Section 1.3.2.3, for the Pt low-index single-crystal surfaces, activities towards ORR in perchloric acid increase in the order $Pt(100) \ll Pt(111) \ll Pt(110)$. These differences have been attributed to the structure-sensitive adsorption of OH_{ad} on Pt(hkl) and its inhibiting (site blocking) effect

on O_2 adsorption. The structure sensitivity of the $Pt_3Ni(hkl)$ -skin surfaces has also been reported to have the similar trend in the potential region of OH adsorption, *i.e.*, $Pt_3Ni(100)$ -skin < $Pt_3Ni(110)$ -skin <<< $Pt_3Ni(111)$ -skin, with the change in activity between the least active (100) and the most active (111) surfaces being greater than an order of magnitude [39].

(iv) Surface roughening effects: Some studies [97] suggest that surface roughening of the Pt alloy takes place due to dissolution or leaching out of the more easily oxidizable base-metal in bulk alloys, leading to higher activity via surface area increase.

1.4 MATERIALS DURABILITY ISSUES

Increasing the durability of PEMFC has become a growing focal point within fuel cell research. The stability of PEMFC is still far from ideal in today's state-of-the-art PEMFC technology and is far from the 5,000-hour target for the full range of environmental conditions (-40 °C to 40 °C), which is the minimum requirement for vehicle applications [98]. An urgent need for investigation and mitigation of durability failure modes is required for PEMFCs.

PEMFC durability depends strongly on the operating conditions. Conditions that maximize durability include constant load operation at relative humidity close to 100% and at temperature around 75 °C. Under the optimized conditions, durability is primarily governed by the slow degradation of the GDL's water removal capacity. Other durability issues include membrane degradation and Pt particle growth. In real application, PEMFC systems will be exposed to less than ideal conditions including load variability, start-stop cycling, imperfect humidification, temperature fluctuations, and occasional fuel or oxidant starvation. Under these conditions, degradation is greatly accelerated [99].

Membrane degradation is one form of failure, which results from chemical, mechanical, and ion contamination mechanisms that occur with time or under extreme conditions. Chemical degradation is due to chemical attack of the electrolyte membrane by free radicals [100,101]. Hydroxy (.OH) and hydroperoxy (.OOH) radicals are most likely drivers of membrane chemical degradation since they are among the most reactive chemical species known. Radical-induced chemical degradation leads to reduced mechanical strength and reduced proton conductivity of the membrane. Hydroxy (.OH) and hydroperoxy (.OOH) radicals are believed to arise form the decomposition of H_2O_2 , which itself is created from incomplete reduction of oxygen in the PEMFC cathode. Radicals can also be generated by reactant crossover through the membrane, which leads to molecular H₂ and O₂ reacting on the surface of the Pt catalyst. Mechanical failure can arise from pinholes or foreign materials introduced during MEA manufacturing as well as from stresses developed during temperature and humidity cycling. As for ionic contamination, sources of contaminant ions include metal bipolar plates, humidifiers, and air itself. The membrane easily absorbs ionic contaminations because the sulfonate sites have a stronger affinity for almost all metal ions (except for Li⁺) than for protons. Since protons are, therefore, displaced by these metal ion contaminants, this process leads to a net loss in proton conductivity.

Degradation of catalyst layers is another issue regarding the durability of PEMFCs, including catalyst poisoning, washout, sintering, and carbon coarsening (refer to Fig. 1.10) [98]. Degradation of the catalyst layer can affect the catalyst structure by causing loss of electronic and/or ionic conduction. It will also have a negative impact on the electrochemical surface area (ECSA), which has been accepted as one of the most important parameters for characterizing the catalytic activity of PEMFCs [102,103].



Figure 1.10: Catalysts degradation factors.

The catalyst degradation processes are generally described as follows using Pt/C as an example. Pt becomes Pt ions by direct electrochemical oxidation and/or by electrochemical oxidation to PtO_x , which then experiences chemical reaction with acid to give Pt ions. Some Pt ions diffuse into the membrane and the electrochemically inaccessible parts of the MEA [104] and are dissolved away or lost. Other Pt ions are reduced and re-deposited onto larger particles [105], which is termed Ostwald-ripening. Also, small particles move, aggregate, and recrystallize to reduce the surface energy, namely "coalescence" [106]. The latter two processes will lead to particle size growth. Moreover, carbon support corrosion at the cathode accelerates aggregation by shortening the distance between Pt particles and also decreases the anchor sites for Pt. Besides, oxidation of the carbon support can also lead to changes in surface hydrophobicity that can cause gas transport to decrease.

1.5 OBJECTIVES OF THIS DISSERTATION

The objective of this dissertation is to develop Pt-free and low-Pt content Pdbased cathode electrocatalysts with better activity and greater stability than Pt for oxygen reduction reaction in PEMFC and to understand the mechanisms of improvement or degradation.

Firstly, based on the thermodynamic guideline proposed by Bard's group [88], a novel binary electrocatalyst Pd–Ni alloy is synthesized by modified polyol reduction method and systematically investigated for ORR. Pd–Ni alloy catalysts with various compositions after heating at different temperatures are characterized structurally and electrochemically using X-ray diffraction (XRD), energy dispersive spectroscopy (EDS) in scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), cyclic voltammetry (CV), rotating disk electrode (RDE) measurements, and single cell PEMFC tests.

Secondly, to improve the long-term stability of the Pd–Ni binary alloy electrocatalysts, Pd–Pt–Ni ternary alloy electrocatalysts are synthesized by the same polyol reduction method and are evaluated in single cell PEMFC for performance and durability. The MEAs before and after the single cell testing are characterized by EDS, XPS, and TEM to understand the changes in the MEA performance under the operating conditions. Moreover, Pd–Pt–Fe and Pd–Pt–Cu ternary electrocatalyst are synthesized by the same method and evaluated in PEMFC as well.

Thirdly, to better and fully understand the mechanism for performance change in PEMFC under cell operation, the MEAs of the Pd–Pt–Ni catalyst is characterized by *insitu* electrochemical methods including electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV).

Fourthly, to alleviate contamination from dissolved metal ions and to further improve the performance and durability of the MEAs in PEMFC, the Pd–Pt–Ni ternary electrocatalysts are leached out in hot acid prior to cell operation and Pd–Pt binary electrocatalysts are synthesized by the same polyol method. MEAs of both types of electrocatalysts are then evaluated in PEMFC, characterized by EDS and XPS, and compared to the properties of fresh Pd–Pt–Ni ternary electrocatalysts.

Finally, the catalytic activities of Pd–Pt–Ni for ORR obtained from RDE method and PEMFC single cell testing are compared to illustrate the effect of different dealloying method on ORR activity and the necessity of conducting single cell test for exact performance evaluation. Furthermore, the activities of Pd–Pt–M (M = Ni, Fe, and Cu) electrocatalyts for ORR are compared using the RDE method in acid electrolyte.

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CHAPTER 2

General Experimental Procedures

2.1 CHEMICAL INFORMATION

Ammonium tetrachloropalladate $((NH_4)_2PdCl_4)$, copper acetate $(Cu(CH_3COO)_2 \cdot H_2O)$, and the 20 wt. % (Johnson Mathew) platinum on Vulcan carbon were purchased from Alfa Aesar. Nickel acetate $(Ni(CH_3COO)_2 \cdot 4H_2O)$ and ferrous acetate $(Fe(CH_3COO)_2)$ were purchased from Acros Organics. Chloroplatinic acid hexahydrate $(H_2PtCl_6 \cdot 6H_2O)$ was purchased from Strem Chemicals.

Poly(vinylpyrrolidone) (PVP, MW = 40,000) was purchased from MP Biomedicals (LLC), and Vulcan XC-72R carbon black was purchased from Cabot Corp. Sodium hydroxide (NaOH), ethylene glycol (EG), 2-propanol(Certified ACS Plus), and concentrated sulfuric acid (H₂SO₄, 98%) were purchased from Fisher Scientific.

Nafion dispersion solution (5 wt. %) was purchased from DuPont, Nafion 112 and 115 membranes (sodium form) were purchased from G.C. Processing Inc., and gas diffusion layers (GDLs) were purchased from E-TEK (BASF Fuel Cell).

All the chemicals used in this dissertation were used as-received without any further purification.

2.2 MATERIALS SYNTHESIS

All Pd-based electrocatalysts investigated in this dissertation were synthesized by a modified polyol reduction method followed by heat-treatment in a reducing atmosphere unless otherwise mentioned. In a typical experiment, required amounts of metal precursors with a concentration of 0.5 M were first dissolved in 25 mL of ethylene glycol. Required amount of Vulcan XC-72R carbon black as a supporting material and 12.5 mg of poly(vinylpyrrolidone) as a surfactant were then added to the mixture under constant stirring. 5 mL of 0.1 M NaOH solution was added dropwise into the above mixture and refluxed at ~ 198 °C (boiling point of EG) for 10 h. After cooling down to room temperature, the product was filtered, washed, dried overnight, and subsequently heat-treated at various temperatures in a flowing 10% H₂–90 % Ar atmosphere for 2 h. These as-synthesized catalyst powders typically had a total weight of approximately 50 mg with a metal loading of 20 wt. %.

The various Pd-based electrocatalysts were synthesized by similar procedures using different metal precursors and heated at different temperatures as described in the respective Chapters.

2.3 MATERIALS CHARACTERIZATION

2.3.1 X-ray diffraction (XRD)

To investigate the phase structure and crystallize size of the powdered polycrystalline samples, the X-ray diffraction (XRD) studies were carried out with a Philips Model APD 3520 X-ray diffractometer and Cu K α radiation ($\lambda = 0.154$ nm). X-ray specimens were prepared by spreading the sample powder evenly onto a glass slide and fixing the powder to the glass slide with amyl acetate liquid. The patterns were recorded within the 2 θ range of 30 to 90° with a counting time of 12 s per 0.02°. Profile fitting and lattice parameter evaluation were carried out with the JADE MDI software, and the average crystallite size values were obtained from the XRD data using Scherrer equation.

2.3.2 Energy dispersive spectroscopic analysis (EDS) in scanning electron microscope (SEM)

Energy dispersive X-ray spectroscopy (EDS) was used to determine the atomic ratios of the constituent elements in the electrocatalysts synthesized. EDS analysis was

conducted with a JEOL-JSM5610 scanning electron microscope (SEM) having an Oxford instruments EDS attachment. The incident electron energies were kept constant at 20 keV for all the samples.

2.3.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was used to obtain surface compositions and chemical states of the metals in the electrocatalysts. XPS studies were performed with a Kratos Analytical spectrometer using monochromatic Al K α radiation unless otherwise mentioned. The surface compositions of the constituent elements were determined based on the ratio of the integrated peak intensities using the Casa software.

2.3.4 Transmission electron microscopy (TEM)

Morphological and particle size and distribution characterizations were carried out with a JEOL 2010F high-resolution transmission electron microscope (TEM) operated at 200 keV.

2.4 ELECTROCHEMICAL CHARACTERIZATION

2.4.1 Cyclic voltammetry (CV) and rotating disk electrode (RDE) experiments

2.4.1.1 Glassy carbon (GC) preparation

A glassy carbon (GC) disk electrode (5 mm), polished to a mirror-like finish with a 0.05 μ m alumina suspension before each experiment, was used as the substrate for the catalyst layer. Typically, 2 mg of the carbon-supported catalyst was ultrasonicated in a mixture consisting of 1 mL of water and 1 mL of 0.15 wt. % Nafion solution until a homogeneous ink was formed. 20 μ L of the ink was applied onto the glassy carbon electrode to obtain a metal loading of 20.4 μ g/cm² and dried under an infrared lamp.

2.4.1.2 Cyclic voltammetry (CV)

Cyclic voltammetry (CVs) is typically used to characterize electrocatalytic activity in more detail. In a standard CV measurement, the potential of a system is swept back and forth between two voltage limits while the current response is measured. The voltage inversion can give useful information about the species present in solution. Fig. 2.1 shows a typical CV plot of a polycrystalline bulk Pt electrode in 0.5 M H₂SO₄. The current response below 0.4 V vs NHE is due to the adsorption/desorption of hydrogen and the current response above 0.6 V vs NHE is due to hydroxide and oxide formation/reduction. The hydrogen adsorption/desorption region can be used to measure the electrochemical surface area for Pt or Pt alloys using equation 2.1 below [1]:

$$ECSA(cm^{2}/g_{P_{t}}) = \frac{Q_{H}(\mu C/cm^{2})}{210(\mu C/cm^{2}) \times L(g_{P_{t}}/cm^{2})}$$
[2.1]

where $Q_{\rm H}$ represents the charge of hydrogen adsorption/desorption and is taken as 210 μ C/cm² to oxidize/reduce a monolayer of H₂ on smooth platinum surface, and *L* is the loading of catalyst in g/cm².



Figure 2.1: Cyclic voltammogram of polycrystalline bulk Pt electrode in N₂ saturated 0.5 M H₂SO₄ at 50 mV/s.

In this dissertation, CVs were performed with an Autolab potentiostat PGSTAT302N and a standard three-electrode cell at room temperature, employing a double junction Ag/AgCl as the reference electrode, a platinum mesh as the counter electrode, and the glassy carbon disk electrode with the catalyst layer as the working electrode. All potentials are, however, reported in this dissertation against the normal hydrogen electrode (NHE). The CV experiments were conducted in N₂ purged 0.5 M H_2SO_4 between 0 and 1.1 V at a scan rate of 50 mV/s. The potential cycling to clean and activate the electrode surface was carried out until reproducible voltammograms were

obtained (ca. 50 cycles), and the CVs obtained after a steady state has been reached are presented in this study.

2.4.1.3 Rotating disk electrode (RDE) experiments

RDE measurement is a convenient method for the quantitative evaluation of the electrocatalytic activity of high-surface-area catalysts. It is a hydrodynamic technique, where the working electrode is rotated to induce forced convection and obtain diffusion limited current (i_1) [2]. The overall current density (i) on a rotating disk electrode is related to the diffusion limited current density (i_1) and the true kinetic current density (i_k), determined by the mass-transport properties of the RDE (the Koutecky–Levich equation):

$$\frac{1}{i} = \frac{1}{i_l} + \frac{1}{i_k}$$
[2.2]

where $i_1 = 0.62nFAD^{2/3}Cv^{-1/6}\omega^{1/2}$, *n* is the total number of electrons transferred, *F* is the Faraday constant (96485 C/mol), *A* is the area of the electrode, *D* is the diffusion coefficient of oxygen in cm²/s, *C* is the concentration of oxygen in mol/cm³, *v* is the kinematic viscosity in cm²/s, and ω is the rotation rate in rad/s. Besides the kinetic activity, the number of electrons transferred can also be calculated from the Koutecky–Levich equation and the measured slope of $1/\omega^{1/2} - 1/i_l$ plot.

In this dissertation, RDE experiments were conducted with the catalyst coated glassy carbon disk electrode mounted onto an interchangeable RDE holder (Pine Instruments, USA) in O_2 saturated 0.5 M H₂SO₄. The polarization curves were recorded at 1600 rpm from 0 to 1.0 V at a scan rate of 5 mV/s.

2.4.2 Single cell PEMFC experiments

2.4.2.1 MEA preparation

Catalyst inks were prepared by initially mixing required amount of the carbonsupported catalyst, isopropyl alcohol, water, and 25 wt. % Nafion via ultrasonication for half an hour. Then, the prepared catalyst ink was directly sprayed onto the top of a commercial gas diffusion layer (BASF) (2.5 cm × 2.5 cm), followed by drying in air at 60 °C for 1 h. Thereafter, 40 mg 5 wt. % Nafion was sprayed additionally for better adhesion between the membrane and the catalyst-coated gas diffusion layer. The metal loading was kept at 0.4 mg/cm² both for the anode and the cathode in the PEMFC test. For the anode layer a commercial 20 wt. % Pt/C (Alpha Aesar) was used. MEAs were fabricated by sandwiching a Nafion membrane (DuPont) between the anode and cathode using hotpressing with a Bench Top Press (Carver Inc., Model 3851-0).

2.4.2.2 Single cell evaluation

The prepared MEAs with an active area of 5 cm² were assembled with 3-channel serpentine flow fields (Poco graphite blocks) and gold-coated current collectors and then tested in a fuel cell station acquired from Scribner Inc. (either 890 or 850e model). The relative humidity of the feed streams for the anode and cathode were set at 100 % with a backpressure of, respectively, 14 psi (96.53 kPa) and 16 psi (110.32 kPa) and a constant gas flow rate of, respectively, 0.15 L/min and 0.2 L/min; the cell temperature was 60 °C. The performance of the fuel cell was monitored by a data acquisition system, and the current–voltage polarization curves were recorded only after the operation of at least for 4 h. IR correction was carried out by correcting the cell voltage with measured ohmic resistance of the fuel cell by an in-built AC impedance analyzer operating at a frequency of 1 kHz.

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CHAPTER 3

Synthesis and Characterization of Pd–Ni Nanoalloy Electrocatalysts for Oxygen Reduction Reaction in Fuel Cells

3.1 INTRODUCTION

As stated in section 1.3.2, Pd-based catalysts have drawn much attention in recent years as a possible alternative to Pt catalysts for ORR in fuel cells. However, not only the catalytic activity of Pd for the oxygen reduction reaction (ORR) is lower than that of Pt and its alloys [1,2], but also the stability of Pd is not as good as Pt in acidic, oxidative, and high-temperature environments [3-5]. The loss of Pd may involve either formation of Pd(II), Pd(IV), and Pd(VI) surface oxides or Pd electrodissolution. To overcome these problems, efforts have been made to alloy Pd with other elements such as Ti, Fe, Co, Au, Mo, and W [6-14]. Especially, Pd-Co and Pd-Fe alloy catalysts have been found to exhibit high catalytic activity for ORR and good stability [7,15]. It has been suggested that alloying Pd with other metals having smaller atomic size such as V, Cr, Fe, and Co is particularly effective in enhancing the catalytic activity [16,17]. Also, the thermodynamic guidelines have proposed [6] alloying a metal that can cleave the O-O bond effectively with another metal that can facilitate the oxide reduction (refer to Fig. 1.9). Ni is another possible choice to alloy with Pd and enhance its catalytic activity. Lee et al. [18] reported that Pd–Ni thin film alloys fabricated by an rf sputtering method exhibit higher catalytic activity than Pd, although lower than that of Pt. Ramos-Sanchez prepared the Pd-Ni alloys by a metallic reductive precipitation [19], but the catalytic activity of the sample was much lower than that of the thin film sample fabricated by the sputtering method.
However, a systematic investigation of the effect of Ni on alloying with Pd is still lacking.

We present here the synthesis of carbon-supported nanostructured Pd–Ni catalysts with various atomic ratios by a modified polyol reduction process, followed by heat-treatment at various temperatures. The synthesized Pd–Ni alloys are characterized by X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and rotating disk electrode (RDE) and single-cell PEMFC measurements for ORR.

3.2 EXPERIMENTAL

3.2.1 Synthesis

Approximately 50 mg of carbon-supported $Pd_{100-x}Ni_x$ ($0 \le x \le 50$) electrocatalysts with 20 wt. % metal loading were synthesized by a modified polyol reduction process as described in Chapter 2. (NH₄)₂PdCl₄ and Ni(CH₃COO)₂·4H₂O were used as metal precursors. The as-synthesized Pd–Ni catalysts were subsequently heat-treated at 500, 700, and 900 °C in a flowing 10% H₂–90 % Ar atmosphere for 2 h and then cooled to room temperature. For a comparison, 50 mg of carbon-supported Pt catalyst with 20 wt. % metal loading was also synthesized by refluxing a required amount of H₂PtCl₆ (Strem Chemicals) in 25 mL of ethylene glycol. The carbon-supported Pt catalyst was not, however, subjected to any post heat treatment.

3.2.2 Structural and microstructural characterizations

As discussed in Chapter 2, phase identification was performed by XRD, bulk compositional analysis was carried out by EDS, particle size and distributions were studied with a JEOL 2010F TEM, and surface compositions were assessed by XPS with Al K α radiation.

3.2.3 Electrochemical characterization

3.2.3.1 Cyclic voltammetry and linear polarization measurements

The detailed procedure of preparing the catalyst thin film on GC electrode and the experimental parameters for CV and RDE are described in Chapter 2. It is worth pointing out that although the as-synthesized sample did not reach a steady state after 50 cycles during CV tests, the same protocol was used for all the samples for the sake of comparison. Methanol tolerance of the catalyst was assessed by scanning the potential between 0 and 1.1 V in N₂ purged 0.5 M H₂SO₄ + 1 M methanol solution at 20 mV/s. Accelerated durability tests were performed at room temperature in N₂ purged 0.5 M H₂SO₄ solution by applying cyclic potential sweeps between 0.6 and 1.1 V at a sweep rate of 50 mV/s for a given number of cycles.

3.2.3.2 Single cell evaluation

The MEA fabrication process can be found in Chapter 2. The MEAs consisting of the electrocatalysts and Nafion 112 membrane were hot-pressed at 130 °C for 2 min. The performances of the MEAs were evaluated at 60 °C with an 850e fuel cell station, following the procedures described in Chapter 2.

3.3 **RESULTS AND DISCUSSION**

3.3.1 Structural and compositional characterization



Figure 3.1: X-ray diffraction patterns of Pd and Pd₈₀Ni₂₀ after heat treatment at various temperatures. The dotted line refers to the expected position of the (111) reflection of Pd.

Fig. 3.1 compares the XRD patterns of the carbon-supported Pd and $Pd_{80}Ni_{20}$ samples before and after heat treatment at various temperatures in the reducing atmosphere. All the samples exhibit reflections characteristic of a fcc structure, and the reflections shift to higher angles with increasing heat treatment temperature, indicating lattice contraction caused by a substitution of smaller Ni for a larger Pd. The degree of shifting increases with increasing temperature, suggesting an increasing degree of alloying of Pd with Ni. However, no reflections corresponding to Ni or NiO_x could be seen in the as-prepared sample or in the samples annealed at lower temperatures due to

the poor cystallinity or low concentration of Ni. The lattice parameter values, degree of alloying, and the average crystallite size values obtained from the XRD data using the Scherrer equation for the $Pd_{80}Ni_{20}$ sample before and after heat treating at various temperatures are listed in Table 3.1. The calculation of degree of alloying is described elsewhere [16]. Since no clear shift in the positions of the reflections of the as-prepared $Pd_{80}Ni_{20}$ samples compared to those of Pd is seen, the degree of alloying (atom % Ni in the Pd lattice) is considered to be negligible. However, the degree of alloying and the crystallite size increase with increasing heat-treatment temperature, and the increase in the crystallite size is rapid on going from 700 to 900 °C. Also, comparison of the degree of alloying with the Pd : Ni ratio obtained from EDS analysis in Table 3.1 suggests that not all the Ni atoms get into the Pd lattice, indicating the presence of Ni or/and NiO_x and incomplete alloying of Ni with Pd.

Pd : Ni ratio	Lattice	Degree of	Crystallite size
from EDS $(0/)$	noremotor from	alloving: stomio	from VDD^{b}
110111 EDS (70)	parameter nom	anoying. atomic	HOIII AKD
	XRD (nm)	percentage of Ni	(nm)
	· · · · · · · · · · · · · · · · · · ·	in the alloy ^{\underline{a}}	
83.7:16.3	0.3913	0	4.6(0.1)
		-	
83 1.16 6	0 38/1	133	60(02)
05.4.10.0	0.3041	15.5	0.0(0.2)
82 9.17 1	0 3835	14 9	14.9(0.5)
02.7.17.1	0.5055	17.7	14.9 (0.3)
Q1 1·1Q 0	0 3833	15 /	35(0.4)
	Pd : Ni ratio from EDS (%) 83.7:16.3 83.4:16.6 82.9:17.1	Pd : Ni ratio Lattice from EDS (%) parameter from 83.7:16.3 0.3913 83.4:16.6 0.3841 82.9:17.1 0.3835 81.1:18.0 0.3823	Pd : Ni ratio from EDS (%)Lattice parameter from XRD (nm)Degree of alloying: atomic percentage of Ni in the alloy d 83.7:16.30.3913083.4:16.60.384113.382.9:17.10.383514.981.1:18.00.382315.4

Table 3.1: Characterization data from XRD and EDS of $Pd_{80}Ni_{20}$ before and after heat-treatment at various temperatures.

^a The details are described elsewhere [16].

^b Obtained using the (111) reflection; the numbers in parenthesis give the standard deviation.



Figure 3.2: TEM images and particle size distributions in Pd₈₀Ni₂₀ and Pd₈₀Ni₂₀: (a) assynthesized and after heat treatment at (b) 500 °C and (c) 700 °C.

<u>Fig. 3.2</u> compares the TEM photographs and the corresponding particle size distributions of the $Pd_{80}Ni_{20}$ samples before and after heating at various temperatures. As seen, the nanoparticles show spherical morphology with a uniform dispersion on carbon. While the as-synthesized and 500 °C samples have a narrow particle size distribution centered around, respectively, 5.6 and 6.7 nm, the 700 °C sample shows a broader distribution with a much larger particle size of 11.8 nm. The particle size values obtained from the TEM data are consistent with the crystallite size obtained from the XRD data.

Fig. 3.3 compares the Pd 3*d* and Ni 2*p* core level XPS data of Pd₈₀Ni₂₀ before and after heating at 500 and 700 °C. The deconvoluted peaks of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ core levels in Fig. 3(a) indicate that both Pd and PdO_y exist on the surface of all the samples due to the exposure of the samples to ambient air [20,21]. Also, with increasing heat treatment temperature or degree of alloying, the ratio of Pd : PdO_v decreases gradually from 1.42 for the as-synthesized Pd₈₀Ni₂₀ sample to 1.13 for the 500 °C sample and 0.78 for the 700 °C sample. Moreover, the Pd $3d_{5/2}$ binding energy decreased by 0.2 and 0.3 eV on heating the as-prepared samples, respectively, at 500 and 700 °C. The Ni 2p spectrum of the as-synthesized $Pd_{80}Ni_{20}$ sample shown in Fig. 3(b) exhibits the main peaks and broad and strong satellite peaks corresponding to Ni $2p_{3/2}$ and Ni $2p_{1/2}$. The main peaks centered at 855.8 and 873.5 eV and the satellite peaks centered at 861.7 and 880.2 eV indicate that the Ni on the surface exists as an oxidized Ni species like Ni(OH)₂ or NiO [22,23]. The Pd : Ni ratio determined from the XPS peak areas was 58 : 42, indicating a Ni-rich surface compared to the bulk composition obtained from the EDS data (Table 1). After heat treatment at 500 °C in the reducing atmosphere, both Ni metal (peaks located at 852.5 and 870 eV) [24] and Ni oxide or hydroxide are found with an increased Pd /Ni ratio. Also, the peaks corresponding to metallic Ni and Ni oxide vanish on heat treating at 700 °C. The observations suggest that in addition to the increasing degree of alloying with increasing heat treatment temperature, the surface may become richer in Pd. As the typical mean free path for photoelectrons in alloys is in the range of 1-2 nm, XPS data are representative of several layers beneath the outermost surface.



Figure 3.3: XPS profiles and fitting results of $Pd_{80}Ni_{20}$ before and after heat treatment at various temperatures: (a) Pd 3*d* core levels showing Pd [- - -] and PdO_y ($0 \le y \le 2$) [...], and (b) Ni 2*p* core levels. Solid lines refer to the experimental curves and dotted lines refer to the fitted curves.



Figure 3.4: Cyclic voltammograms of Pd₈₀Ni₂₀ in 0.5 M H₂SO₄ solution at a sweep rate of 50 mV/s: (a) as-synthesized sample, (b) after heat treatment at 500 °C, and (c) after heat treatment at 700 °C.

Fig. 3.4 shows the CV plots of the $Pd_{80}Ni_{20}$ sample before and after heat treatment at 500°C and 700 °C. As seen, the peak current density increases initially with cycle number, which could be attributed to surface roughening and removal of contaminants from the sample surface. Although the as-synthesized sample shows a large oxide reduction peak during the early cycles, the peak current density decrease substantially after 50 cycles, indicating instability. This could be related to the sintering of small particles and formation and dissolution of oxides (or hydroxides) of both Pd and Ni [5, 25, 26]. Interestingly, after heat-treatment at 500 °C and 700 °C, the peak current density remains the same after the initial surface cleaning, indicating much improved stability due to alloying and larger particle size.

Fig. 3.5 compares the stable CV plots obtained after the initial surface cleaning and the specific charge per unit weight of metal in Pd₈₀Ni₂₀ before and after heat treatment at various temperatures. Since the electrochemical active surface area of Pd alloy samples could not be obtained from the hydrogen desorption region due to the dissolution of hydrogen into the bulk of palladium, the charge corresponding to surface oxide reduction region was used [16] here to compare the electrochemical active surface area (ECSA). The charge transferred during surface oxide reduction can be evaluated by measuring the peak area and dividing it by the scan rate. The charge thus evaluated was further normalized with respect to the mass of the metal in the sample. It is noticed that the potential where the formation of surface oxide adsorption and the reduction of surface oxides begin does not change much with increasing heat-treatment temperature. It is found that both the peak current density corresponding to the cathodic peak and the ECSA increase with increasing heat-treatment temperature, reach a maximum at 500 °C, and then decrease. The small ECSA for the as-synthesized samples is attributed to the sintering of smaller particles on potential cycling and the dissolution of surface oxides in acid as mentioned earlier. The decrease in ECSA with heat treatment temperature above 500 °C is due to the obvious increase in particle size. Also, the peak potential

corresponding to the oxide reduction peak shifts by 25 mV to the left on going from the as-synthesized to the 500 °C sample.



Figure 3.5: (a) Reproducible cyclic voltammograms (in 0.5 M H₂SO₄ at a sweep rate of 50 mV/s) (b) and the specific charge of Pd₈₀Ni₂₀ before and after heat treatment at various temperatures.



Figure 3.6: (a) Hydrodynamic polarization (RDE) curves of $Pd_{80}Ni_{20}$ before and after heat treatment at various temperatures in O_2 saturated 0.5 M H₂SO₄ with a rotation speed of 1600 rpm and (b) mass activity and (c) specific activity measured at 0.7 V for $Pd_{80}Ni_{20}$ before and after heat treatment at various temperatures. Mass and specific activities are given as kinetic current densities (j_k) normalized in reference to, respectively, the loading amount and ECSA of the metal.

The ORR measurements were performed in O_2 -saturated 0.5 M H₂SO₄ solution with a glassy carbon rotating disk electrode (RDE), and the polarization curves for ORR on the Pd₈₀Ni₂₀ samples before and after heat treating at various temperatures are shown in Fig. 3.6(a). For all of the catalysts studies here, a mixed kinetic-diffusion control occurs in the whole potential region. The kinetic current was calculated from the ORR polarization curve using mass-transport correction and normalized to the amount of metal loading in order to compare the mass activities of different catalysts (Fig. 3.6(b)). As seen, the mass activity increases as we go from the as-synthesized sample to the 500 °C heat treated sample, and then decreases on going from 500 to 900 °C. For a better understanding of the observed differences in the ORR activity, we normalized the kinetic current against the ECSA for each catalyst as shown in Fig. 3.6(c). The specific activity (*i.e.*, kinetic current per unit surface area of the catalyst in mA/mC) is found to jump on going from the as-synthesized to the 500 °C sample, indicating an accelerated ORR kinetics on the electrocatalyst surface.

Recognizing that heat treatment at 500 °C gives the maximum mass catalytic activity for all the samples, Fig. 3.7(a) compares the CV plots of the carbon-supported Pd–Ni alloy catalysts with different Ni contents after heat treatment at 500 °C with that of home-made Pt. As seen, the onset potential of Pd–Ni for the formation of surface oxide adsorption and the reduction of surface oxides does not vary much with composition. However, the onset potential is about 50 mV lower compared to that for Pt. All the Pd–Ni catalysts show large peak area for hydrogen adsorption compared to Pt due to dissolution of adsorbed hydrogen into bulk Pd, and the decreased intensity of hydrogen desorption peak with increasing Ni content may suggest the restrained dissolution of hydrogen into bulk Pd–Ni due to the alloying of Pd with Ni. Moreover, the cathodic peak current density and the ECSA (Fig. 3.7(b)) increase with Ni incorporation, reach a maximum at 20 atom% Ni, and then decrease with increasing Ni content. Additionally, the peak potential for Pd₈₀Ni₂₀ shifts by 55 mV to the left compared to that for Pd.



Figure 3.7: (a) Reproducible cyclic voltammograms (in 0.5 M H₂SO₄ at a sweep rate of 50 mV/s) of Pd–Ni alloys after heat treatment at 500 °C and their comparison with that of home-made Pt and (b) the specific charge of Pd–Ni alloys after heat treatment at 500 °C.



Figure 3.8: (a) Hydrodynamic polarization (RDE) curves (in O₂ saturated 0.5 M H₂SO₄ with a rotation speed of 1600 rpm) of Pd–Ni alloys with different Ni contents after heat treatment at 500 °C and their comparison with that of home-made Pt, (b) mass activity and (c) specific activity measured at 0.7 V for Pd–Ni alloys after heat treatment at 500 °C, and (d) Comparison of the mass activities at various potentials of Pd after heat treatment at 500 °C, Pd₈₀Ni₂₀ after heat treatment at 500 °C, and home-made Pt.

Fig. 3.8(a) compares the hydrodynamic polarization curves of Pd, $Pd_{90}Ni_{10}$, $Pd_{80}Ni_{20}$, $Pd_{70}Ni_{30}$, $Pd_{60}Ni_{40}$, and $Pd_{50}Ni_{50}$ after heat treatment at 500 °C with that of homemade Pt. All the Pd-Ni catalysts are under mixed control of kinetics and mass transfer, and the ORR onset potential of ~ 0.85 V observed for $Pd_{80}Ni_{20}$ is similar to that of Pt and 0.1 V higher than that of Pd. The mass activity and the specific activity of Pd–Ni catalysts heated at 500 °C were calculated by the method used in Fig. 3.6(b) and are shown in Figs. 3.8(b) and (c). Both of them are found to have a "volcano" relationship with the Ni content with a maximum at 20 atom% Ni. To emphasize the differences between the best Pd-Ni catalyst and Pd and to know how far behind is the best one from Pt, we compare the mass activity of the 500 °C heat treated $Pd_{80}Ni_{20}$ with those of 500 °C heat treated Pd and home-made Pt at various potentials in Fig. 3.8(d). It is evident that the ORR activity of $Pd_{80}Ni_{20}$ is significantly higher than that of Pd, and around 36% of that of the home-made Pt at 0.8 V. The difference between $Pd_{80}Ni_{20}$ and Pt may be related the significantly larger particle size of $Pd_{80}Ni_{20}$ (6.7 ± 1.1 nm) compared to that of Pt (2.6 ± 0.7 nm).

The measured PEMFC potential-current (*V-I*) polarization curves of Pd heated at 500 °C, $Pd_{80}Ni_{20}$ heated at 500 °C, and home-made Pt are compared in Fig. 3.9(a). The *V-I* curves are mainly governed by the surface reaction kinetics up to the geometric current densities of 0.2 A/cm². At larger current densities, ohmic resistance losses as well as mass transfer effects become significant. Figs. 3.9(a) and (b) compare the mass activity for oxygen reduction of the three catalysts. The logarithmic current density scale allows for an accurate relative activity ranking. At 0.7 and 0.75 V, the $Pd_{80}Ni_{20}$ exhibits two to three times higher mass activity than Pd and half of that of Pt. The results obtained in single cell are consistent with those obtained in acid electrolyte in this study, but the difference among the catalysts in single cell is lower than those found in acid electrolyte.



Figure 3.9: Comparison of (a) the current-voltage characteristics, (b) the corresponding Tafel plots, and (c) mass activities at various potentials of Pd after heat treatment at 500 °C, Pd₈₀Ni₂₀ after heat treatment at 500 °C, and home-made Pt in single-cell proton-exchange membrane fuel cell (PEMFC) at 60 °C.

Oxygen reduction reaction in acidic media may take place through either the socalled peroxide pathway (the molecular adsorption pathway) [27] or the so-called direct four-electron transfer route (the atomic adsorption pathway) [28]. It has been suggested that palladium-based alloy catalysts promote a direct four-electron route [9,10], and Koutecky–Levich plots derived from our hydrodynamic polarization curves (Fig. 3.10) at various rotation rates for the 500 °C heat treated $Pd_{80}Ni_{20}$ clearly illustrate that the oxygen reduction pathway in this bimetallic alloy system follows a four-electron transfer (n = 4). The number of electrons transferred per oxygen molecule on the catalyst is calculated from the Koutecky–Levich equation $I^{-1} = I_k^{-1} + I_l^{-1} = I_k^{-1} + (0.62nFAD^{2/3}Cv^{-1/6}\omega^{1/2})^{-1}$ and the measured slope, where *n* is the total number of electrons transferred, *F* is the Faraday constant (96485 C/mol), *A* is the area of the electrode (0.1963 cm²), *D* is the diffusion coefficient of oxygen in cm²/s, *C* is the concentration of oxygen in mol/cm³, *v* is the kinematic viscosity in cm²/s, and ω is the rotation rate in rad/s. The values of *D*, *C*, and *v* were taken to be, respectively, 18×10^{-6} cm²/s, 1.13×10^{-6} mol/cm³, and 8.93×10^{-3} cm²/s [29,30].



Figure 3.10: (a) Hydrodynamic polarization curves of Pd₈₀Ni₂₀ after heat treatment at 500 °C at various rotation rates and (b) the Koutecky-Levich plots of Pd₈₀Ni₂₀ after heat treatment at 500 °C and home-mad Pt (n refers to number of electrons transferred).

The atomic adsorption pathway involves the dissociative adsorption of O_2 (reaction 3.1) and subsequent electroreduction and removal of the adsorbed oxygen atoms (reaction 3.2):

$$2M + O_2 \rightarrow 2MO$$
 [3.1]

$$2MO + 4H^+ + 4e \rightarrow 2M + 2H_2O$$
 [3.2]

$$AE = E(M-O_{ads}) - E(M) - 1/2E(O_2)$$
[3.3]

where the adsorption energy (AE) is defined as the change in the potential energy E of the system (substrate + adsorbate) on adsorption (equation 3.1). Lu's group [16] has reported that the AE of O_{ads} is a descriptor of the specific activity of Pd-alloy catalysts towards ORR based on the atomic adsorption pathway. They found that the smaller the AE, the easier the reductive desorption and the higher the specific activity. There are two opposing factors influencing AE, the lattice-strain and surface-ligand effects. The former causes a downshift in the metal d-band center, weakens the interaction between the substrate and the adsorbate, and enhances the ORR kinetics [31]. The Pd-Ni samples synthesized by our method after heat-treatment at above 500 \mathbb{C} have a Pd-rich surface as revealed by the XPS data, suggesting the presence of possible lattice strain. At low degree of alloying, the surface concentration of Ni is negligible and the lattice strain effect dominates. With increasing heat-treatment temperature or Ni content, more Ni atoms get into the Pd lattice, resulting in higher lattice strain, weaker M-Oads bonding, and higher specific activity. At high degrees of alloying, the surface concentration of Ni could increase and the surface-ligand effect may become dominating, resulting in a decrease in specific activity. On the other hand, the ECSA decreases much with increasing temperature, thus the mass activity show the volcano relationship with temperature due to the synergetic effect of the specific activity and ECSA. Similarly, the mass activity has the maximum at 20 atom% Ni because both the specific activity and the ECSA are maximal at that composition.

It has been demonstrated that palladium-based catalysts exhibit high tolerance to methanol oxidation and are stable in the presence of methanol [11–14]. Fig. 3.11

compares the CV plots of the 500 °C heat treated $Pd_{80}Ni_{20}$ with that of home-made Pt in the presence and absence of methanol. As seen, the CV plot of $Pd_{80}Ni_{20}$ remains unchanged on going from 0.5 M H₂SO₄ solution to 0.5 M H₂SO₄ + 1 M methanol solution in contrast to that of Pt, demonstrating the high tolerance of $Pd_{80}Ni_{20}$ to methanol and its potential as a cathode catalyst in a DMFC.



Figure 3.11: Comparisons of the cyclic voltammogram of (a) Pd₈₀Ni₂₀ after heat treatment at 500 °C and (b) home-made Pt in 0.5 M H₂SO₄ and in 0.5 M H₂SO₄ + 1 M methanol solutions at a sweep rate of 20 mV/s at room temperature.

We also performed accelerated durability tests by applying cyclic potential sweeps between 0.6 and 1.1 Vat 50 mV/s in N₂-purged 0.5 M H₂SO₄ solutions at room temperature. The CV measurements showed a loss of 20 % in ECSA for the 500 °C heat treated $Pd_{80}Ni_{20}$ after 200 cycles and 60 % after 400 cycles (Fig. 3.12), suggesting the lower durability of $Pd_{80}Ni_{20}$ for long-term operation. This may be related to the incomplete alloying of Pd with Ni due to the low alloying temperature used during the formation of the alloy (see Table 3.1). Also, even well-alloyed Ni may dissolve or leach out of the surface since thermodynamically less stable base-metals are more unstable

under potential in acidic electrolytes. From a practical point of view, the improvement of durability is critical for the Pd-based electrocatalysts, and further work is needed.



Figure 3.12: Cyclic voltammograms of 500 °C heat treated Pd₈₀Ni₂₀ before and after accelerated durability test.

3.4 CONCLUSIONS

Carbon-supported Pd–Ni nanoalloy electrocatalysts with controlled particle size and distribution have been synthesized by a modified polyol reduction method, followed by heat treatment at elevated temperatures in 10% H₂–90% Ar atmosphere. The Pd₈₀Ni₂₀ sample with a Pd : Ni atomic ratio of 4 : 1 after heat treatment at 500 °C is found to exhibit the highest ECSA and mass catalytic activity among the Pd-Ni samples investigated. The enhanced activity of Pd₈₀Ni₂₀ compared to that of Pd is attributed to Pd enrichment in the surface and the consequent lattice-strain effects and the decrease in the surface oxide adsorption energy. With a lower cost and a much higher tolerance to methanol compared to those of the Pt catalyst, the Pd–Ni alloys are attractive as cathode catalysts in direct methanol fuel cells.

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CHAPTER 4

Performance and Stability of Pd–Pt–Ni Nanoalloy Electrocatalysts in PEMFC

4.1 INTRODUCTION

As discussed in section 1.3.2, the search for more active ORR electrocatalysts with reduced Pt content is progressing in two directions; one is focusing on Pt-based catalysts and the other is focusing on non-Pt catalysts. As for real applications in PEMFC, Pt-rich Pt–Co catalysts [1,2] have shown significant improvement of $2-3\times$ compared to pure Pt in terms of Pt-mass-based activity. Adzic et al. [3] have carried out preliminary MEA tests that show great promise of Pt_{ML}/Pd₃Co with a mass activity of up to $2\times$ compared to that of Pt [4]. Another novel class of dealloyed electocatalysts developed in Strasser's group by *in situ* voltammetric dealloying has shown a Pt-mass activity improvement of $4-5\times$ in single cell PEMFC [5,6]. In the case of non-noble metal catalysts such as transition metal carbides or nitrides, their chemical instability in acidic environment and low intrinsic activities for ORR due to the low density of active sites make theses catalysts far away from practical application in PEMFCs.

In Chapter 3, we explored Pd–Ni nanoalloys as ORR electrocatalysts in fuel cells. It proved that these binary catalysts are not stable enough in the acid electrolyte, and their cell performance is still far below that of state-of-the-art Pt. Here, we are trying to improve both the performance and durability by alloying Pd–Ni with small amount of Pt, and evaluate the Pd–Pt–Ni eletrocatalyst in PEMFC single cell. Accordingly, we present here the structural and compositional characterizations of the electrocatalysts before and

after the PEMFC operation and discuss the influence of the dissolution of both Pd and Ni on the ORR activity and the durability of Pd–Pt–Ni in PEMFC. Although there have been reports on the dissolution of Pd in acid [7,8] and formation of Pt skin upon dissolution of the transition metals [9-11], we show here, for the first time, that the dissolution of Pd and Ni during the operation of the membrane-electrode-assemblies (MEA) in PEMFC results in the formation of a "Pd-rich core and Pt-rich shell" structure with enhanced catalytic activity. Finally, we synthesize and evaluate Pd–Pt–Fe and Pd–Pt–Cu ternary electrocatalyst in PEMFC as well to see whether similar phenomenon occurs.

4.2 EXPERIMENTAL

4.2.1. Catalyst Synthesis

The Pd–Pt–M (M = Ni, Fe, Cu) nanoparticle electrocatalysts were synthesized by a modified polyol reduction method as described in Chapter 2. $(NH_4)_2PdCl_4$, Ni(CH₃COO)₂·4H₂O, Fe(CH₃COO)₂, Cu(CH₃COO)₂H ₂O and H₂PtCl₆ were used as metal precursors, and the resulting black powders were subsequently heat-treated at 300 °C in a flowing 10% H₂–90 % Ar atmosphere for 2 h and then cooled to room temperature.

4.2.2. MEA Fabrication

The electrodes consisting of gas-diffusion and catalyst layers were prepared as discussed in Chapter 2. The MEAs with Pd–Pt–Ni were fabricated by sandwiching a Nafion 112 membrane (DuPont) between the anode and cathode by hot-pressing at 130 °C and 1000 psi for 2 min. The MEAs of Pd–Pt–Fe and Pd–Pt–Cu were fabricated by using Nafion 115 membrane (DuPont) and hot-pressing at 125 °C and 800 psi for 2 min.

4.2.3. Fuel cell testing



Figure 4.1: The protocol applied for single cell fuel cell testing. Step 1: supplying reactant gases (hydrogen and air), step 2: operating the cell at the constant load of 5 A (1000 mA/cm²), and step 3: purging nitrogen and removing the load.

The prepared MEAs with an active area of 5 cm² were then assembled with 3channel serpentine flow fields and gold-coated current collectors and tested in a fuel cell station (Scribner Inc., Pd–Pt–Ni and Pd–Pt–Fe were tested on model 890 and Pd–Pt–Cu was tested on model 850e), following the protocol shown on Fig. 4.1. In step 1, hydrogen and oxygen as reactant gases were supplied to the anode and cathode, respectively, without applying the load and the cell was stabilized at the open circuit potential for around 15 min; in step 2, the load was increased from 0 to 5 A (1000 mA/cm²) at an increment of 0.5 A/min for 10 min, and the cell was operated at a constant load of 5 A; in step 3, the load was removed, and the cell was shut down for overnight after 15 min of purging with nitrogen to remove the residual H₂ or O₂. The load cycles are employed in this study to simulate the on/off procedures in real automotive applications. The testing conditions are same as that described in Chapter 2. The polarization curves were taken at the beginning and the end of the testing within a day to monitor the performance change. Also, the cell voltage response with time at the constant load was recorded for long-term durability. IR correction was carried out by correcting the cell voltage with measured ohmic resistance of the fuel cell by an inbuilt AC impedance analyzer operating at 1 kHz frequency.

4.2.4. Structural, morphological, and compositional characterizations of the catalyst powders and MEAs

As discussed in Chapter 2, the phase identification for catalyst powders was performed by XRD, and the morphology and size distribution of the catalyst powders were studied with a JEOL 2010F TEM. The bulk compositional analysis was determined by EDS, and surface compositions were assessed by XPS with Al K α radiation if not mentioned otherwise. The water collected from the cathode side after the durability test was analyzed by an inductively coupled plasma (ICP) analyzer to estimate the dissolution of metals from the catalyst particles. The cross-section of MEAs were observed and tested with a JEOL 2010F TEM/STEM field emission microscope equipped with an OXFORD energy dispersive spectrometer (EDS) to determine the elemental distribution across the MEAs before and after the fuel cell durability test.

4.3 **RESULTS AND DISCUSSION**

4.3.1 Physical characterization of the Pd–Pt–Ni electrocatalysts

Fig. 4.2 compares the XRD patterns of Pd, $Pd_{80}Ni_{20}$, $Pd_{50}Pt_{30}Ni_{20}$ synthesized by the modified polyol method and commercial Pt. All the samples exhibit reflections characteristic of only a single fcc structure, suggesting a well mixing of all the constitutes and the formation of a ternary Pd–Pt–Ni alloy phase. From the enlarged profiles of the (111) reflection in Fig. 4.2(b), the reflections of $Pd_{80}Ni_{20}$ shift to higher angles compared to those in Pd, indicating the substitution of smaller Ni for Pd in the lattice. In addition, the diffraction peaks of $Pd_{50}Pt_{30}Ni_{20}$ shift to the left compared to those of $Pd_{80}Ni_{20}$, and even those of Pd, suggesting the incorporation of larger Pt atoms into the Pd–Ni lattice. The absence of peaks for either Pt, or Ni, or their oxides may be due to their poor crystallinity or low concentration. The lattice parameters and average crystallite sizes of these samples obtained from the XRD data using the Scherrer equation are given in Table 4.1.



Figure 4.2: (a) XRD patterns and (b) the enlarged (111) region of Pd, Pd₈₀Ni₂₀, and Pd₅₀Pt₃₀Ni₂₀ synthesized by the modified polyol method and commercial Pt.

Catalyst	Annealing temp. (°C)	Pd:Pt:Ni atomic ratio from SEM- EDS	Lattice parameter from XRD (nm)	Mean crystallite size from XRD (nm)
Pt			0.3919	2.4
Pd	300		0.3892	7.7
$Pd_{80}Ni_{20} \\$	300	84:16	0.3888	6.2
Pd50Pt30Ni20	300	58:31:12	0.3896	5.1

Table 4.1:Atomic ratios, lattice parameters, and crystallite sizes of the samples
synthesized by the modified polyol method and commercial Pt.

Fig. 4.3 shows the TEM images and particle size distributions of $Pd_{80}Ni_{20}$ and $Pd_{50}Pt_{30}Ni_{20}$ synthesized by the modified polyol method. The high resolution TEM images indicate the well-defined crystalline nature of the samples obtained. The ternary catalyst $Pd_{50}Pt_{30}Ni_{20}$ shows smaller particle size but with broader size distribution compared to the binary catalyst $Pd_{80}Ni_{20}$. Moreover, the TEM images reveal more agglomeration of the particles on the surface of carbon in the case of the ternary alloy, suggesting poor dispersion.



Figure 4.3: TEM/HRTEM images and particle size distributions of (a) Pd₈₀Ni₂₀ and (b) Pd₅₀Pt₃₀Ni₂₀ synthesized by the modified polyol method.

4.3.2 Electrochemical characterization of Pd–Pt–Ni electrocatalysts: MEA performance and long-term durability

Fig. 4.4(a) shows the polarization curves of Pd₅₀Pt₃₀Ni₂₀ recorded at the beginning and the end of the fuel cell test each day until it became constant on the 8th day. As seen, the cell performance keeps increasing on the entire current range with time, and the increase is tremendous for the first four days and becomes smaller for the following days. The obvious increase from the 1^{st} day to 2^{nd} day is primarily due to the activation process. After the MEA assembly and the initial 4 h of operation, both the membrane and the electrode became humidified, and the contact between the flow-field plates and the diffusion media became better. Therefore, the electrolyte resistance, the contact resistance, and the resistance within the electrode became much smaller. Afterwards, the curves move upwards both within the day and between the two sequential days. The change within the day is much smaller compared to that between the two sequential days. Although the MEA structure may keep optimized for the following days, the extent of performance enhancement caused by the MEA structure optimization is small. Fig. 4.4(b) compares the constant polarization curves of Pd₅₀Pt₃₀Ni₂₀ and commercial Pt tested under the same condition and following the same procedure. The two curves overlap below 750 mA/cm², and Pd₅₀Pt₃₀Ni₂₀ even shows better performance in the higher current density region (also the ohmic resistance dominant region).



Figure 4.4: (a) Performances of the Pd₅₀Pt₃₀Ni₂₀ catalyst, recorded with time (days) at 60 °C in a PEMFC. The empty and solid symbols refer, respectively, to the performance tested at the beginning and the end of each day. (b) Comparison of the performances of Pd₅₀Pt₃₀Ni₂₀ after becoming constant and after the durability test with that of commercial Pt at 60 °C in a PEMFC.



Figure 4.5: Comparison of the Tafel plots of Pd₅₀Pt₃₀Ni₂₀ after the performance becomes constant and after the durability test with that of commercial Pt at 60 °C in a PEMFC: (a) cell voltage vs. Pt mass activity and (b) cell voltage vs. noble metal mass activity.

Fig. 4.5 and Table 4.2 show the kinetic activities after IR-correction for both $Pd_{50}Pt_{30}Ni_{20}$ and commercial Pt based on Pt mass alone (Fig. 4.5(a)) and noble metal mass (Fig. 4.5(b)). The Pt-based mass activity of commercial Pt is 0.392 A/mg_{Pt} at 0.84V, which is comparable to the values reported by other groups, considering possible

differences in the MEAs [1,6]. $Pd_{50}Pt_{30}Ni_{20}$ exhibits high Pt-based mass activity improvement by a factor of 2 compared to that of commercial Pt. Since Pd is also noble metal and much more expensive compared to Ni, it is more reasonable to compare the activity based on total noble metal mass. From Fig. 4.5(b) and Table 4.2, $Pd_{50}Pt_{30}Ni_{20}$ and commercial Pt have almost the same noble metal mass-based activity. Since the cost of Pd is just one fifth of that of Pt, the cost will be greatly reduced.

Table 4.2:	Mass activity	of Pd ₅₀ Pt ₃₀ Ni ₂₀ and	l commercial Pt catal	lysts.
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Catalyst	Annealing temp. (°C)	Mass activity at 0.84 V ^a (A/mg _{Pt})	Mass activityat 0.84 V ^a (A/mg _{noble metal})
Pt_{100}^{b}		0.392	0.392
$Pd_{50}Pt_{30}Ni_{20}$	300	0.739 ^c	0.369 ^c
		0.269 ^d	0.134 ^d

^a IR free data

^b 20 wt% Pt on Vulcan Carbon

^c Initial constant performance

^d Performance after durability test

Considering the changes in performance with operating time, we are curious whether this novel catalyst will be durable enough for real fuel cell application. Accordingly, we ran the fuel cell for another two weeks with a total testing time of 180 h. Fig. 4.6 illustrates the cell voltage response with time at a constant load of 1000 mA/cm² during this period. The time shown in Fig. 4.6 does not include the time when the MEA is under open circuit potential or the polarization curve is recorded. Consistent with the performance change described above, the cell voltage for the $Pd_{50}Pt_{30}Ni_{20}$ catalyst shows tremendous increase within the first week. For a comparison, the cell voltage for pure Pt always remains constant at 0.680 V right after the activation procedure. After stabilizing

at 0.676 V under 1000 mA/cm², the cell voltage of $Pd_{50}Pt_{30}Ni_{20}$ remains constant, and it decreases slightly from the 19th day (after 146 h). The cell voltage tested on the 21st day is 0.655 V, indicating a loss of 3 % and slightly worse durability compared to commercial Pt. We also compare the polarization-curve voltage of $Pd_{50}Pt_{30}Ni_{20}$ recorded on the last day with that in the initial constant curve in Fig. 4.4 (b). The kinetic activities of $Pd_{50}Pt_{30}Ni_{20}$ drawn in Tafel plots and listed in Table 2 show a decrease of 1/2 to 2/3, which is much larger than that in the high current density region, namely the ohmic-controlled region. It should be noticed that the degradation in the performance, especially the kinetic activity, is closely related to the decrease of open circuit potential.



Figure 4.6: The cell voltage response at the constant load of 1000 mA/cm² during the durability test. The solid line and the dashed lines refer, respectively, to Pd₅₀Pt₃₀Ni₂₀ and commercial Pt.



4.3.3 Effect of metal dissolution on MEA performance

Figure 4.7: Core level XPS profiles of (a) Pd 3d, (b) Pt 4f, and (c) Ni 2p in Pd₅₀Pt₃₀Ni₂₀ before the fuel cell test, after the performance becomes constant, and after the durability test.

To understand why the MEA performance increases continuously with operating time and eventually resembles that of commercial Pt, we tested both the surface and bulk composition of the $Pd_{50}Pt_{30}Ni_{20}$ catalyst before and after the fuel cell operation. Fig. 4.7 compare the XPS profiles of Pd 3d, Pt 4f, and Ni 2p recorded before the MEA operation
(sample 1), after the MEA performance becomes constant (sample 2), and after the durability test (sample 3). Pd and Pt exist in both metal and oxide forms for all the three samples (the peaks are not deconvoluted here). Compared to sample 1, samples 2 and 3 show lower and lower peak intensity for Pd 3d, indicating less and less Pd on the surface with fuel cell operation. In contrast, the peak intensity of Pt 4f does not change much after the initial stabilizing period, but it does decreases slightly after the long-term durability test. As for the Ni, all the peaks detected before fuel cell testing are ascribed to Ni oxide (or hydroxide). After the fuel cell testing, all the Ni signals disappear.

We should point out that XPS tests were conducted using both Al target and Mg target for samples after the fuel cell operation. As shown in Fig. 4.8(a), the signals from the samples after the single cell testing using Al target cannot be ascribed to any peak of Ni. From the survey scan, those signals originate from the F within the Nafion membrane, which works as ionomer surrounding the catalyst nanoparticles in the electrode. However, F does not have any signals within the same binding energy range as Ni using Mg target, so we tested the samples after the single cell testing again using Mg target to avoid the interference of F. The surface metal atomic ratios estimated from XPS profiles, together with the bulk metal atomic ratios determined from EDS, are summarized in Table 4.3 for all three samples.



Figure 4.8: (a) XPS profiles of Ni 2p core level region and (b) survey scans of Pd₅₀Pt₃₀Ni₂₀ after the fuel cell test using Al target and Mg target.

Catalyst	Testing condition	Near surface composition (XPS) (atom %)	Bulk composition (SEM-EDS) (atom %)
Pd50Pt30Ni20	Before the fuel cell test	$Pd_{49}Pt_{30}Ni_{21}$	Pd ₅₇ Pt ₃₁ Ni ₁₂
	After performance becomes constant	Pd46Pt54	$Pd_{54}Pt_{41}Ni_5$
	After the durability test	$Pd_{41}Pt_{59}$	$Pd_{58}Pt_{42}$

Table 4.3:Surface and bulk compositions of the 300 °C heat-treated Pd50Pt30Ni20
catalysts.

It is clear from Table 4.3 that all the Ni on the catalyst surface is removed after the MEA testing. At the same time, the bulk atomic percentage of Ni decreases from 12 before the test to 5 after the performance becomes constant, and to 0 after the durability test, indicating that the Ni atoms below the surface leach out from the particles. Although the leaching becomes more difficult for the inner Ni and the rate of leaching slows down, Ni atoms eventually leach out of the particle totally. On the other hand, Pd on the surface also dissolves with time, as indicated by the deceasing Pd peak intensity and the Pd:Pt ratio from > 1 before the MEA test to < 1 after the MEA test. Similar to Ni, Pd atoms may also leach out during the cell operation, but this point is more difficult to prove because the Ni dissolution and leaching will also change the Pd to Pt ratio in the bulk. However, it is clear that the rate of Pd dissolution decreases since the atomic percentage of Pd changes only by 10 % after another 120 h of MEA testing. Actually, Pt on the surface also dissolves to a small degree after the MEA testing for a longer time as indicated by the decreased intensity of the Pt 4f peak seen in Fig. 4.7(b).

If we take a further look at the compositions, we find that the catalyst before the MEA testing has a Ni-rich surface as indicated by a Ni atomic percentage of 21 % on the

surface and 12 % in the whole particle. On the contrary, the Pd/Pt ratio is below 1 on the surface and above 1 across the whole particle, indicating a structure with Pt-rich surface and Pd-rich core for samples after the MEA testing. Therefore, we propose a structural model in Fig. 4.9 to account for the performance enhancement of the Pd–Pt–Ni elecrocatalysts during the PEMFC single cell test.



Figure 4.9: Structure of Pd–Pt–Ni after the fuel cell test: formation of a Pd-rich core and Pt-rich shell nanoparticles by a dissolution of Pd and Ni (blue: Pd, grey: Pt, and red: Ni).

The elemental distribution within the fresh catalyst is almost homogenous, and its surface is Pd-rich, resulting in lower activity and stability compared to that of pure Pt. On operating the MEA in the fuel cell, the electrocatalysts are subjected to both chemical and electrochemical effects, and the metals have a tendency to dissolve. Particularly, base metals like Ni are not stable in contact with acid electrolyte. Under the single cell testing condition, the Ni atoms are also likely to segregate onto the particle surface due to the attraction to oxygen-containing species [12,13]. This could result in a continuous leaching out of Ni until all the Ni atoms within the particles are removed. For catalysts

having a Ni-rich surface, like what we have here, this process is much easier and more rapid. On the other hand, the standard eletroreduction potential of Pd (0.915 V) is much lower than that of Pt (1.188 V), resulting in an instability of Pd as well. In the oxygen and water environment in the fuel cell, the surface atoms can form an oxide or hydroxide overlayer, which can dissolve easily under the MEA testing conditions [14].

Besides, the less-bonded Pd atoms can dissolve directly as Pd ions. In our experiments, we test the single cell by shutting-down and starting-up cycles, simulating a situation similar to real fuel cell application. During this process, the MEA will be subjected to more potential changes (also called load cycling), more start/stop cyclings, and more changes in temperature and humidity. Even Pt can dissolve more rapidly when undergoing such transitions from low to high potentials compared to a constant low or high potentials [15]. Moreover, starting and stopping the fuel cell together with temperature and humidity changes can affect considerably the rate of metal dissolution. This explains why the performance change between two sequential days is much larger than that within the same day. Considering a slow atom movement in the bulk compared to fast surface atom dissolution, we may expect a compositional gradient established across the particles. Eventually, an active dealloyed catalyst with a Pt-rich surface and a Pd-rich core structure is formed.

Within this core-shell structure, the lattice mismatch between the surface and core components will cause strain, which could modify the electronic properties of the surface component, most notably their d band centers [16-18]. For a Pt-rich surface and Pd-rich core, the strain may downshift the d band center of the Pt-rich surface, weaken the adsorption energy of the oxygenated intermediates, and thus enhance the ORR kinetics. The improved kinetic activity of the Pt-rich surface may also be attributed to a compression of the Pt –Pt bond distance [19-22]. It is worth pointing out that the Pt–M

(M = transitional metal) electrocatalysts with a Pt skin may eventually lose all the M and the activity enhancement due to M and become eventually pure Pt-like [13]. In contrast, our Pd-Pt-Ni catalyst with Pd could still retain enhanced activity as Pd dissolution will be much less compared to that of the transition metals like Ni. We would also like to point out that the lattice parameter of the core is further decreased when Ni is present and the consequent larger mismatch between the core and shell components could lead to larger stain effect.

4.3.4 TEM analysis of the MEA before and after the long-term durability test

As discussed before, although the $Pd_{50}Pt_{30}Ni_{20}$ electrocatalyst exhibits performance in the MEA test comparable to that of commercial Pt and the performance remains stable for more than 100 h, it eventually decreases slowly, especially in the activation polarization region, when the durability test prolongs to 180 h, suggesting lower stability compared to commercial Pt. We also discussed the dissolution and leaching out of both Pd and Ni metal ions from the catalyst nanoparticles. Naturally, one may ask where the metal ions go and the relationship between their dissolution and the MEA durability. The ICP data of the discharged water collected from the cathode side after the durability test indicated the presence of Ni in the water, but no Pd. The ICP data indicated about 5 atom % of the total Ni in the water collected. Although Pd dissolution is found from the compositional changes, no Pd could be detected in the water.



Figure 4.10: (a) TEM image of the membrane from the MEA after the durability test at its center part, (b) EDS spectrum of the particle circled in the TEM image, and (c) EDS spectrum of the area within the rectangle in the TEM image. The peak in between the Cu peaks as well as the Ca peak are from impurities.

To understand where the dissolved metal ions go, we analyzed the cross-section of the MEA by TEM before and after the durability test. Fig. 4.10(a) shows a TEM image of the middle part of the membrane after the fuel cell test. Many small particles and some agglomerations are found to sit within the membrane, which were never seen in the fresh membrane. From the corresponding EDS data (Fig. 4.10(b)) of one particle circled in the TEM picture, the particle was found to consist of Pd and Pt, mostly Pd, without any Ni at all. Thus, the dissolved Pd is redeposited in the membrane. Recognizing that cations can ion-exchange with the H⁺ ions of the sulfonic groups in Nafion [1], we examined by EDS the area next to the circled region and the result is shown in Fig. 4.10(c). The peak at 7.5 keV, which can only be ascribed to Ni, is clearly seen in this area in the membrane after the fuel cell test, and in fact, it is seen thoughout the membrane afterwards. However, no signal for Ni could be seen in the fresh membrane. The data thus confirm that the dissolved base metal ions tend to attach to the hydrophilic sites at the sulfonic groups in the Nafion membrane by ion-exchange with proton. This type of ion exchange could also occur in the ionomer of the catalyst layer, but we did not explore it.

Considering that only about 5 atom % Ni was detected by ICP in the discharged water, more Ni ions should be in the membrane. As pointed out by Gasteiger [1], the ion exchange of protons by nickel ions could lead to the following: (i) lowering of the ionic conductivity of the membrane resulting in higher membrane resistance, (ii) increase in the resistance of the cathode catalyst layer due to higher ionomer resistance, and (iii) lower diffusion of oxygen in the ionomer in the catalyst layer. A combination of the above factors, which may be hard to separate, will essentially lower the overall performance and accelerate the degradation of the fuel cell. Refering back to our performance tests, the initial constant polariztion curve of Pd₅₀Pt₃₀Ni₂₀ did not show any obvious decrease in the high current density region compared to Pt; in fact, it was little

bit better compared to Pt. Even after 180 h of operation, the polarization curve has slope similar to that of the initial curve, indicaitng a constant membrane resistance and neglectaible effect of contaminaiton from Ni. However, the kinetic acitivity of cathode catalyst layer does decrease a lot, and this may be related to the poisoning by Ni cations.

To give a clear overview of the elemental distribution throughout the MEA, we ploted the compositions in each part of the MEA determined semi-quantitivly from the TEM-EDS tests of the MEA cross-sections before and after the durability test (Fig. 4.11). Compared to the fresh MEA, Ni is totally removed from the catalyst particles under the testing condition after the durability test, consistent with our previous results. Particles rich in palladium, with a small amount of platinum, are found not only at the center of the Nafion membrane, with a $2-3 \mu m$ strip, but also in the membrane along the membrane/cathode interface. Additionally, Pd has precipitated in the anode, but not as Pd rich particles. Bi [23] has reported that soluble Pt ions formed at the cathode can be transported to the membrane by diffusion, migration, and possibly convection. They are re-deposited as Pt crystals upon reduction by crossover hydrogen, in a single thin Pt band instead of being uniform over a region between the edge of the band and the cathode. At that location, the hydrogen and oxygen are completely reacted, and the deposited Pt particles can be stable. We assume that a similar phenomenon happened here to the Pd ions, together with Pt ions. The difference is that a small amount of Pd and Pt ions are also deposited on the membrane/cathode interface. Besides, Pt ions in Bi's study could not move further toward the anode due to pseudo-steady-state, but Pd ions here move continuously until they reach the anode. The Pd-rich particles in the membrane could result in lower proton conductivity, and the deposition of Pd on the anode would lead to a decrease in hydrogen oxidation activity. This may be the main reason for the lower open

circuit potential and thus the lower performance in the whole current region, especially kinetic region, after the durability test.



Figure 4.11: Overall elemental distribution in the particles across the MEA: (a) before the fuel cell test and (b) after the durability test. Each bar represents the average atomic composition of particles in that area. The dark vertical lines indicate the interface between each electrode and the membrane. The anode in Fig. 10(b) has two elemental distributions to show the variation in composition as we approach the anode/membrane interface.

4.3.5 MEA performance of Pd–Pt–Fe and Pd–Pt–Cu electrocatalysts

Fig. 4.12 and Fig. 4.13 show the PEMFC current-potential (I–V) polarization curves of, respectively, the Pd–Pt–Fe and Pd–Pt–Cu catalysts measured at the end of each day. Clearly, both catalysts exhibit the same phenomenon as Pd–Pt–Ni in the PEMFC tests. The cell performances of both the catalysts keep increasing with time in the whole current density range until becoming constant on the 6^{th} day. In this regard, it can be speculated that all the Pd–Pt–M (M = base metal) alloy catalysts have the trend of performance improvement under cell operation upon metal dissolution.



Figure 4.12: Performance of the Pd₅₀Pt₃₀Fe₂₀ catalyst, recorded with time (days) at 60 °C in a PEMFC.



Figure 4.13: Performance of the Pd₅₀Pt₃₀Cu₂₀ catalyst, recorded with time (days) at 60 °C in a PEMFC.

4.4 CONCLUSIONS

Pd–Pt–Ni electrocatalyst has been synthesized and the MEAs fabricated with Pd– Pt–Ni have been characterized before and after the PEMFC single cell test. XRD, EDS, and TEM analyses indicate the formation of Pd–Pt–Ni ternary alloy catalysts with a narrow size distribution centered at 5 nm. The PEMFC single cell test of the Pd₅₀Pt₃₀Ni₂₀ catalyst reveals a continuous increase in performance with operation time until it becomes comparable to that of commercial Pt. The catalyst is also quite stable within the 180 h of durability test, exhibiting just 3 % degradation at 1000 mA/cm². With a lower cost and performance comparable to that of Pt, the Pd–Pt–Ni nanoalloy catalysts offer great promise. Moreover, Pd–Pt–Fe and Pd–Pt–Cu alloy catalysts also show similar trend of performance improvement under cell operation.

Compositional analysis of the MEAs before and after the fuel cell tests points to a Pd-rich core and a Pt-rich shell structure for the dealloyed particles formed under the fuel cell test condition. The strain effect caused by lattice mismatch between the Pd-rich core and the Pt-rich shell may down shift the d-band center, lower the adsorption energy of surface oxygenated intermediates, and thus enhance the surface catalytic activity. TEM observation of the MEA cross-section before and after the fuel cell test also demonstrates an unfavorable effect of metal dissolution on MEA durability. Ni dissolves and leaches out of the catalyst particles completely. Except a small amount of Ni in the water formed, most of the dissolved Ni ions ion-exchange with the protons in the Nafion membrane. In contrast, Pd dissolves partially, and the dissolved Pd ions re-precipitate as Pd-rich PdPt particles in the membrane, mainly forming a 2–3 µm band in the center and some along the cathode/membrane interface. Some Pd ions even move to the anode side and precipitate. All these factors could lead to contamination and degradation in the performance of MEAs.

The approach presented here is similar to the voltammetric dealloying used by Strasser's group [5,6] for modifying the surface catalytic properties of noble metal alloys. However, while the contamination by the base metals could be minimized with their votammetric dealloying method, our future studies need to focus on alleviating or removing the poisoning effect caused by both Ni and Pd dissolution and their transportation. Additionally, TEM data indicate a poor dispersion of Pd-Pt-Ni compared to Pt, and our future studies will focus on exploiting synthesis methods to obtain good dispersion as well on the effect of annealing temperature on the composition and performance.

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CHAPTER 5

In-situ Electrochemical Characterization of Pd-Pt-Ni-based PEM Fuel Cells

5.1 INTRODUCTION

With an aim to enhance the catalytic activity and stability, we focused in Chapter 4 on the addition of Pt to Pd–Ni to obtain Pd-Pt-Ni. The Pd–Pt–Ni catalyst was found to exhibit both good performance and stability in a PEMFC comparable to commercial Pt within the 180 h of operation carried out. Although the cell performance was low initially, it increased continuously in the whole current density range with operation time and finally became similar to that of commercial Pt.

Electrochemical impedance spectroscopy (EIS) is a powerful diagnostic tool to characterize and understand the limitations of the performance of fuel cells. The main advantage of EIS is the capacity to resolve in the frequency domain the individual contributions of the various factors in determining the overall PEMFC voltage and power losses: charge transfer activation (kinetic), ion and electronic transport (ohmic), and mass transport (concentration) [1]. Such a separation provides useful information for the development of new materials and electrode structures, optimization of the fuel cell design, and selection of most appropriate operation conditions [1-3]. On the other hand, cyclic voltammetry (CV) is a common diagnostic tool for characterizing the electrocatalyst layers. The cyclic voltammograms of metals can give important information about the state of the surface as a function of potential [4]. Modern surface science studies and density functional theory (DFT) calculations have demonstrated the

increasing importance of surface composition and near surface structure in electrocatalytic properties [5-7].

In this chapter, we characterize the cell performance of the Pd–Pt–Ni ternary catalyst using EIS and CV methods, involving the acquisition of the polarization curves and delineating the reason for the performance change with operation time based on the data diagnosis and analysis. Also, by comparing the performance changes of commercial Pt catalyst under the same operating conditions, an understanding of the reason for the improvement in the catalytic activity of the Pd–Pt–Ni catalyst is developed.

5.2 EXPERIMENTAL

5.2.1 Catalyst Synthesis

The carbon-supported 20 wt. % Pd–Pt–Ni nanoparticle electrocatalysts with a Pd:Pt:Ni mole ratio of 50:30:20 were synthesized by a modified polyol reduction method as described in Chapter 2, followed by heat-treatment at 300 °C in a flowing 10% H₂–90 % Ar atmosphere for 2 h.

5.2.2 MEA Fabrication

The preparation of electrodes can be found in Chapter 2. The membraneelectrode-assemblies (MEAs) were fabricated by sandwiching a Nafion 115 membrane (DuPont) between the anode and the cathode by hot-pressing at 125 °C and 800 psi (5515.81 kPa) for 2 min. In Chapter 4, Nafion 112 was used in MEA fabrication. Nafion 115 is used as a membrane in this chapter to fabricate the MEAs to minimize H_2 crossover, which is critical for getting good CV curves.

5.2.3 Electrochemical characterization

5.2.3.1 Cell polarization studies

The prepared MEAs with an active area of 5 cm^2 were tested in an 850e fuel cell station (Scribner Inc.), following the protocol and testing conditions stated in Chapter 4. This procedure was repeated for around one week until the performance became constant. The polarization curves followed by the EIS were recorded under the above conditions at the beginning and the end of operation each day, and the voltammograms were recorded at the end of operation each day.

5.2.3.2 AC impedance measurements

The ac impedance spectra were recorded with a Model 880 Frequency Response Analyzer (Scribner Associates, Inc.) within the frequency range of 0.1 Hz - 10 kHz under constant-current mode. The dc current density was kept at 0.1 A/cm², and the ac amplitude was 5 % of the dc current density. The anode at the hydrogen side was used as the reference and the counter electrodes, and the cathode at the oxygen side acted as the working electrode, since the overpotential for the hydrogen oxidation or evolution reaction is negligible [8]. The impedance spectrum in the high frequency range shows an inductive behavior, characteristic to the experimental setup. Such inductive characteristics have been reported by others in impedance studies on batteries and fuel cells [9]. Besides, IR correction was carried out by correcting the cell voltage with the measured ohmic resistance of the fuel cell by the inbuilt 880 impedance analyzer operating at 1 kHz frequency.

5.2.3.2 Voltammetry measurements

To accurately measure the activation polarization of the catalysts, it is essential to determine the H_2 crossover current in the fuel cell by the polarization of the N₂-purged

cathode at > 0.4 V with respect to the H₂-purged anode (at > 0.4 V, the resulting hydrogen oxidation current is purely limited by the H₂ permeation rate). This was carried out by sweeping the potential at 5 mV/s from 0.05 to 0.8 V after recording the EIS (under the same temperature). CV was performed at 20 mV/s from 0 to 1.2 V (30 °C cell temperature and 30 °C dew point of H₂/ N₂) to measure the electrochemical surface area (ECSA) of the catalysts. The charge for monolayer hydrogen adsorption/desorption was assumed to be 210 μ C/cm²_{Pt}. For linear sweep voltammetry (LSV) or CV, the H₂ anode served as the counter and reference electrodes and the N₂-purged cathode served as the working electrode. The gas flow of H₂ and N₂ for LSV and CV were controlled, respectively, at 0.2 L/min and 0.05 L/min. All the voltages here are reported vs NHE.

5.3 **RESULTS AND DISCUSSION**

5.3.1 Cell performance evaluated by I–V curves

Fig. 5.1(a) displays the PEMFC current-potential (I–V) polarization curves of the Pd–Pt–Ni catalyst measured at the end of each day. As seen, the polarization curves obtained here show obvious limiting current dictated by gas-diffusion in the cathode backing. A typical I–V curve of fuel cells is divided into three regions (active, ohmic, and mass-transfer limiting regions) to describe the polarization [10-13] based on the magnitude of the current density. For a cathode operating on pure oxygen, there should be no gas-phase transport limitations, which are unique features for an air cathode. Such typical steady-state curves with no limiting current have been obtained previously for an MEA made with Nafion 112 tested under H_2/O_2 flowing. Here, Nafion 115 was employed instead for feasible CV measurements. For a thicker membrane, water flooding is likely to take place in the cathode because the electro-osmotic flux of water cannot be easily balanced with the back-diffusive flux. The mass transfer barrier caused by flooding

will be more severe if the cell configuration is not properly designed. In addition, similar to the MEAs made with Nafion 112 in Chapter 4, the whole polarization curve here is observed to move upwards continuously with the operation of the cell until the 7th day, indicating a continuous increase in the cell performance in the entire current density region with time until it becomes constant on the 7th day.



Figure 5.1: (a) I–V polarization curves of the Pd–Pt–Ni catalyst measured at the end of each day at 60 °C in PEMFC and (b) the cell voltage changes at 0.1 and 0.8 A/cm² within each day and in the whole time period (excluding the 1st day).

To illustrate the process more clearly, the cell voltage changes within each day and the whole time period (excluding the 1st day) are summarized in Fig. 5.1(b). To investigate more closely, two types of voltage changes are taken from Fig. 5.1(a). One is taken at 0.1 A/cm² (very low current density) to reveal changes related to the oxygen reduction kinetics only. Another is taken at 0.8 A/cm² (high current density) to investigate changes regarding both kinetics and mass transfer. As seen, the cell voltage increases nearly 50 mV totally at 0.1 A/cm²; the voltage increases rapidly during the first 4 days and the increase becomes small after that. The rate of increase in the cell voltage slows down consistently with time. The exact same trend in the cell voltage is observed at 0.8 A/cm^2 as well, and the ratio of the two increases almost remains the same with time. This may imply that the cell voltage increase is primarily attributed to kinetic aspect and mass transfer plays a negligible role here. We should point out that for all discussions in this paper, the change before the 2^{nd} day is not included. The cell operation at constant potential on the 1st day is just for MEA activation, and the cell performance will definitely improve for each MEA due to an optimization of its structure during this period. However, it does not exclude the possibility that the improvement in the Pd-Pt-Ni catalyst may be much larger than that in other kind of catalysts due to the dissolution of both Pd and Ni.

5.3.2 EIS analysis of the cell voltage increase

Although the I–V curves usefully illustrate estimated fuel cell performance, they provide no detailed information on the individual contribution of an MEA. In order to exactly identify the cause of the increase in cell voltage with time, the cell resistance was analyzed by ac impedance method. Fig. 5.2(a) presents the EIS curves of the Pd–Pt–Ni catalyst in the single cell PEMFC, which were recorded at a cell current density of 0.1 A/cm² in the activation polarization region. The EIS spectra of PEMFC are practically

entirely determined by the cathode when pure hydrogen is used at the anode [14]. The impedance curves here are characterized by a single distorted capacitive semicircular impedance arc over the whole frequency range, reflecting the charge transfer dominance in the cathode overpotential loss [15]. The presence of a 45 ° branch at the high frequency end reflects a contribution of protonic resistivity in the catalyst layer to charge transfer resistance [1]. The tiny arc at the low frequency end (inductive arc) corresponds to the relaxation and diffusion of adsorbed oxygenated intermediate species [16]. Typically, the difference between the *x*-intercept values at the high- and low-frequency ends of the semicircle corresponds to the charge transfer resistance (R_{ohm}), the sum of the ionic and electronic contributions throughout the cell [1,17]. Usually, R_{ohm} is attributed to the ionic resistance of the electrolyte (R_M) in view of the negligible electronic contribution [18].

To show the resistance change more clearly, the charge transfer resistance and the ohmic resistance measured at the beginning and the end of each day are plotted in Fig. 5.2(b). As seen, the ohmic resistance, namely the membrane resistance, remains nearly constant (~0.024 Ω) as a function of time. However, the charge transfer resistance decreases continuously with time (~20%) and becomes almost constant on the 7th day. This suggests that the increase in cell voltage should not be ascribed to the electrolyte membrane but to the change in the electrode. Moreover, the decrease in the charge transfer resistance between two sequential days is much larger than that within one day.



Figure 5.2: (a) Nyquist plots of the Pd–Pt–Ni catalyst at 0.1 A/cm² in PEMFC. The solid and empty symbols refer, respectively, to the impedance spectra tested at the beginning and the end of that day and (b) the corresponding charge transfer resistance and the ohmic resistance changing with operation time.

While the effective charge transfer resistance is largely determined by the rate of the interfacial oxygen reduction process, the protonic conductivity and oxygen permeability limitations within the catalyst layer also contribute. During our testing period, an increase in protonic conductivity is not expected based on Fig. 5.2(a); the 111

oxygen diffusion resistance within the catalyst layer and in the backing should not change much due to the constant testing conditions of MEA. The latter evident by the same trend and ratio of voltage increases at the low and high current densities (Fig. 5.1(b)). In this regard, the interfacial kinetics may be the only source for the reduced charge transfer resistance. The charge transfer resistance is related to the reaction kinetics as [19,20]

$$R_{ct} = RT / nFi_0$$

$$[5.1]$$

where
$$i_0 = nFAk_0C_0^{*(1-\alpha)}C_R^{*\alpha}$$
 [5.2]

R is the molar gas constant (J/mol·K), *T* is the temperature in K, *n* is the number of electrons transferred, *F* is the Faraday constant (C), i_0 is the exchange current (A), *A* is the reaction area (cm²), k_0 is the standard heterogeneous rate constant (cm/s), C_0^* and C_R^* are the respective bulk concentrations of, respectively, the oxidized and reduced species (mol/L), and α is the transfer coefficient. The smaller the charge transfer resistance, the higher the exchange current density for ORR and the faster the ORR reaction. Therefore, in our study, the decreased charge transfer resistance in the Pd–Pt–Ni cathode with testing time indicates the enhanced electrocatalytic activity towards ORR, which eventually leads to the improvement in cell performance. Moreover, from Fig. 5.2(b), the effect of cell operation on the decrease in charge transfer resistance is much obvious under start-up and shutdown cycles (accompanying dynamic load) than under constant load within the same day.

5.3.3 CV analysis of catalytic activity enhancement

To investigate what causes the catalytic activity enhancement under cell operation, the electrochemical surface area is first examined. It has been reported that metal dissolution from alloy interfaces would roughen the electrochemical interface and result in increased surface area [21]. The cyclic voltammograms of the Pd–Pt–Ni catalyst recorded at the end of each day are displayed in Fig. 5.3, and the ECSA values are

calculated by measuring the charge in the hydrogen adsorption region (between around 0.4 V and the plateau just prior to the start of the hydrogen evolution reaction) after double-layer correction and assuming a value of 210 mC/cm² for the adsorption of a hydrogen monolayer [22-24]. It is clearly observed from Fig. 5.4 that the ECSA values continue to decrease with testing time (from 94 to 82 m²/g), excluding the possibility of surface roughening as the origin of activity enhancement. During the fuel cell operation, dissolution and redeposition of noble metal particles can cause particle growth and formation of crystals within the electrolyte membrane [25,26]. In addition, electrocatalyst particle migration and coalescence can occur [27]. All these can lead to a rapid loss of active surface area. This is more problematic when the power demands are altered continuously, such as in the stop–start operation applied here [28,29].



Figure 5.3: Cyclic voltammetries of the Pd–Pt–Ni catalyst measured at 20 mV/s at the end of each day in PEMFC.



Figure 5.4: Mass activity and specific activity at 0.85 V and the ECSA value of the Pd– Pt–Ni catalyst changing with operation time.

To reveal the effect of metal dissolution on the kinetics straightforwardly, the quantitative changes of mass activity and specific activity in the kinetically controlled regime with single cell operation are shown in Fig. 5.5, and their variation at 0.85 V is plotted against time in Fig. 5.4. Obviously, the mass activity of the Pd–Pt–Ni catalyst gradually increases under cell operation (about 190 %), until it becomes nearly constant on the 7th day. The specific activity invariably increases on the entire time axis, about 235 %, which should account for the catalytic activity enhancement. We would like to point out that the current density of 0.1 A/cm² on the raw I–V curve corresponds to the cell potential of 0.85 V after IR correction. This is why we compare the kinetic activity at 0.85 V.



Figure 5.5: Mass activity and (b) specific activity of the Pd–Pt–Ni catalyst measured in different days at 60 °C in PEMFC.

Since the electrochemical catalytic reactions take place on the interface of the catalyst, the specific activity (*i.e.* the kinetic current density normalized by ECSA) reflects the intrinsic characteristics of a catalyst surface. CV can provide important information of the catalyst surface state, so hydrogen adsorption/desorption region (Fig. 5.6(a)) and surface oxide formation/reduction region (Fig. 5.6(b)) from CVs of the Pd–

Pt–Ni catalyst (Fig. 5.4) are carefully investigated here. As seen in Fig. 5.6(a), Pd-Pt-Ni initially exhibits one single broad peak located at around 0.2 V and 0.18 V in the anodic and cathodic directions, respectively, resembling most like a Pd surface. With cell operation, the intensity of both the peaks decreases. Further, with cell operation, the peak in the anodic direction changes from a positive slope to a negative slope between 0.1 and 0.2 V; the peak in the cathodic direction becomes split into two separate peaks, a broad one located at about 0.2 V and a tiny one located at 0.1 V. All these changes indicate that the catalyst surface is more characteristic of a Pt surface. On the other hand, it is noticed from Fig. 5.6(b), the onset potential of the surface oxide formation shifts negatively about 0.01 V from the 2nd day to the 3rd day, but remains nearly constant thereafter. The peak potential of the surface oxide stripping shifts consistently in the positive direction from 0.78 to 0.8 V under cell operation, suggesting the effect of reduced M–O chemisorptions energy on the catalyst surface [23]. The weaker bonding between the surface should be the origin for enhanced intrinsic ORR activity [30].

Actually, this finding is in good agreement with the previous conclusion based on the surface and bulk compositional analyses of the cathode materials before and after the single cell testing in Chapter 4. From those results, upon Pd and Ni dissolution under the operation conditions, the surface of the Pd–Pt–Ni catalyst changes from Pd-enrichment to Pt-enrichment, and the fresh catalyst with a nearly homogenous elemental distribution finally has a compositional gradient across the particles (*i.e.* a Pt-enriched surface region surrounding a Pd-rich particle core). The lattice parameter mismatch between the core and shell parts could induce strain in the outer shell layer, which might downshift the dband center of surface metal atoms and reduce the adsorption energy of the hydroxyl species on the interface (also called "electronic effect"). The combined surface morphology and electronic effect contribute to the activity enhancement and thus overall performance improvement.



Figure 5.6: The enlarged regions of the (a) hydrogen adsorption and desorption and (b) surface oxide formation and its reduction in the cyclic voltammograms of the Pd–Pt–Ni catalyst.



Figure 5.7: (a) I–V polarization curves, (b) Nyquist plots at 0.1 A/cm², and (c) cyclic voltammograms of commercial Pt measured on the 2nd day and 7th day in PEMFC

5.3.4 Cell performance change with commercial Pt

To illustrate the specialties of the distinct cell voltage increase for the Pd–Pt–Ni catalyst, the performances on the 2nd day and last day of commercial Pt including the I–V

polarization curves, impedance spectroscopy, and cyclic voltammogram are shown in Fig. 5.7. Disparate from the Pd–Pt–Ni catalyst, the cell performance of commercial Pt shows little change from the beginning to the end, with the cell voltage increase of 4 mV at 0.1 A/cm² and 0 mV at 0.8 A/cm². Correspondingly, the charge transfer resistance decreases only by 1.4 % totally. The small improvement in performance is believed to be attributed to the formation of better three-phase interface through cell operation. In addition, the characteristics of the CV of commercial Pt remain constant, only the ECSA decreasing from 99 to 89 m²/g due to the particle growth under cell operation.

5.3.5 Comparison of the Pd-Pt-Ni catalyst with commercial Pt

The cell performance and catalytic activity of the Pd–Pt–Ni catalyst are compared with those of commercial Pt in Fig. 5.8 and Table 5.1. The slightly lower cell voltage (~10 mV at 0.1 A/cm²) and metal-based mass activity of the Pd–Pt–Ni catalyst compared to those of commercial Pt correspond to the slightly higher charge transfer resistance. The Pt-based mass activity of the Pd–Pt–Ni catalyst compared to that of commercial Pt exhibits an enhancement by factor of 1.8, showing the advantage and promise of the newly designed alloy catalyst as a cathode for PEMFC. The smaller ECSA of the Pd–Pt–Ni catalyst suggests that alloying Pt with other metals may not effectively increase the active surface area. However, the specific activity of the alloy catalyst does improve by a factor of 1.9, which is attributed to the formation of a Pt-rich surface and the positive shift of the surface oxide adsorption/desorption potential upon Pd and Ni dissolution under cell operation conditions.



Figure 5.8: Comparison of the (a) I–V polarization curves, (b) Nyquist plots at 0.1 A/cm², and (c) cyclic voltammograms of the Pd–Pt–Ni catalyst and commercial Pt measured on the 7th day in PEMFC.

 Table 5.1:
 Kinetic parameters, ECSA, onset potential for surface oxide formation, and peak potential for surface oxide stripping for the Pd–Pt–Ni catalyst and commercial Pt catalysts in PEMFC.^a

Catalyst	Mass activity at 0.85 V (A/mg _{metal})	Charge transfer resistance at $0.1 \text{ A/cm}^2(\Omega)$	Mass activity at 0.85 V (A/mg _{Pt})	Specific activity at 0.85 V (µA/ cm ² _{Pt})	$\frac{\text{ECSA}}{(m^2/g_{Pt})}$	Onset potential for surface oxide formation (V)	Peak potential for surface noxide stripping (V)
Pt	0.3102	0.0968	0.3102	348.6	89	0.67	0.76
Pd ₅₀ Pt ₃₀ Ni ₂₀	0.2591	0.1022	0.5511	672.1	82	0.70	0.80

^a The activity values reported are IR-corrected

5.4 **CONCLUSION**

The performance of the Pd-Pt-Ni-based electrocatalyst in PEMFC has been investigated with operation time using I-V polarization, and the reason for the performance change has been identified using EIS and CV methods. The cell performance of the Pd-Pt-Ni catalyst is found to increase continuously in the entire current density range with testing time until it becomes constant on the 7th day, with the rate of increase slowing down gradually. From the EIS analysis, the membrane resistance remains invariable with time, while the charge transfer resistance of the cathode reaction decreases continuously until becoming nearly constant. This implies that the cell voltage increase should be attributed to the enhanced interfacial oxygen reduction reaction kinetics. The reduced ECSA measured by CV suggests that the increase in the specific activity of Pd-Pt-Ni as the reason for the enhanced catalytic activity. The surface analysis by CV on the hydrogen adsorption/desorption and surface oxide formation/reduction regions reveals that the surface changes from a Pd-rich state to a Ptrich state due to metal dissolution under cell operation and the peak potential of the surface oxide stripping shifts positively. This essentially accounts for the activity enhancement and thus for the overall performance improvement. Compared to commercial Pt, the Pd-Pt-Ni catalyst shows an improvement in Pt-mass activity and specific activity at 0.85 V, respectively, by a factor of 1.8 and 1.9. The results obtained here confirm and substantiate the previous conclusions obtained from the compositional analysis and illustrate EIS and CV as simple and powerful methods for fuel cell performance examination and analysis.

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CHAPTER 6

Preleached Pd–Pt–Ni and Binary Pd–Pt Nanoparticles as ORR Electrocatalysts in Proton Exchange Membrane Fuel Cells

6.1 INTRODUCTION

As discussed in section 1.3.2, nanostructured platinum-based Pt–M (M = 3d transition metals like Fe, Co, Ni and Cu) alloy electrocatalysts are of particular interest as they offer a significant increase in intrinsic electrocatalytic activity compared to pristine Pt for the ORR [1-6]. The promoted activity of the alloys for ORR has been attributed to decreased Pt–Pt distance [7-10] and the formation of an electronic structure with greater 5d orbital vacancies [11-16]. However, as reported in the literature [17-22], leaching out of transitional metal components under electrochemical operating conditions becomes one of the most important obstacles for their application. The dissolution not only limits the lifetime of a PEMFC, but also diminishes the catalytic activity over time due to only Pt left in the catalyst layer.

Similar conclusion has been reached in our previous study on $Pd_{50}Pt_{30}Ni_{20}$ nanoalloy electrocatalyst from PEMFC evaluation (Chapter 4). The $Pd_{50}Pt_{30}Ni_{20}$ catalyst showed an interesting increase in performance with operation time and exhibited a Ptmass activity as high as twice that of commercial Pt at 0.84 V vs. normal hydrogen electrode (NHE). However, the cell voltage of $Pd_{50}Pt_{30}Ni_{20}$ at a constant load of 1000 mA/cm² decreased about 3 % after 180 h of operation, and Pd was deemed to be not perfect for long-term durability. Both Ni and Pd were found to dissolve under the PEMFC operating conditions. The dissolved Ni ions readily ion-exchange with protonic sites at the sulfonic groups in Nafion. The dissolved Pd ions, upon reduction by crossover hydrogen, deposit at the cathode/membrane interface and at the center of the membrane forming a band and even deposit in the anode side. All these factors combined together reduce the membrane conductivity, block oxygen diffusion, and decrease hydrogen oxidation activity, leading to degradation in overall performance.

It is known that the stability and catalytic activity are closely related to surface segregation, and Pt-rich surface can be formed by either annealing at high temperatures or dissolution in acid solutions [11]. Mukerjee et al. [3] have proposed pre-leaching of Pt–M alloys to minimize the contamination of the MEA during operation. Gasteiger [23] has reported promising performance enhancements in specific and mass activities by a factor of, respectively, $3 \times$ and $2.5 \times$ with good durability compared to Pt for multiply leached Pt_xCo_{1-x} catalysts. With this perspective, we present here a preleaching of our Pd-Pt-Ni catalysts in concentrated sulfuric acid at elevated temperature to see its effect on the MEA performance. Our previous study on Pd₅₀Pt₃₀Ni₂₀ showed that the operation in PEMFC typically resulted in a final catalyst composition of ~ $Pd_{60}Pt_{40}$ under the conditions chosen in our study. Accordingly, we also synthesize Pd₆₀Pt₄₀ directly using the same method as for the ternary Pd-Pt-Ni catalyst to see whether Pd₆₀Pt₄₀ is the active catalytic phase. Furthermore, the absence of Ni in the initial catalyst composition could avoid contamination and offer better performance and durability. With these perspectives, we compare here the synthesis, characterization, and performance evaluation in PEMFC of Pd₅₀Pt₃₀Ni₂₀, preleached Pd₅₀Pt₃₀Ni₂₀, and Pd₆₀Pt₄₀.

6.2 EXPERIMENTAL

6.2.1 Catalyst Synthesis and Characterization

The Pd-Pt(-Ni) nanoparticle electrocatalysts were synthesized by a modified polyol reduction method as described in Chapter 2. (NH₄)₂PdCl₄, Ni(CH₃COO)₂·4H₂O

and H_2PtCl_6 were used as metal precursors, and the resulting black powders obtained after the reaction were subsequently heat-treated at 300 °C in a flowing 10% H_2 –90 % Ar atmosphere for 2 h and then cooled to room temperature.

For the preleaching process, the as-prepared Pd–Pt–Ni nanoparticles were treated with 1 M H₂SO₄ at 80 °C for 60 h, washed repeatedly with deionized water, and then dried overnight. The phase identification was performed by X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 0.154$ nm) with a counting time of 12 s per 0.02 °. The bulk compositional analysis was determined by energy dispersive spectroscopy (EDS) with a JEOL-JSM 5610 scanning electron microscope (SEM) having an Oxford Instruments EDS attachment. Surface compositions were assessed by X-ray photoelectron spectroscopy (XPS) with Al radiation. We should point out that XPS tests were conducted using both an Al target and Mg target for samples after the fuel cell testing.

6.2.2 MEA Fabrication

The procedure for electrode preparation can be found in Chapter 2. The membrane-electrode-assemblies (MEAs) were fabricated by sandwiching a Nafion 115 membrane (DuPont) between the anode and cathode by hot-pressing at 125 °C and 800 psi (5515.81 kPa) for 2 min. Nafion 115 was used as a membrane to fabricate the MEAs to minimize H_2 crossover, which is critical for getting good CV curves.

6.2.3 Fuel cell testing

The prepared MEAs with an active area of 5 cm^2 were tested in an 850e fuel cell station (Scribner Inc.), following the protocol and testing conditions stated in Chapter 4. The MEAs were activated and tested at a constant load of 4 A (800 mA/cm²) continuously for around one week until the performance became constant, with a shutdown at night and restart in the morning. The polarization curves were taken at the

end of each day, and IR correction was carried out by correcting the cell voltage with measured ohmic resistance of the fuel cell by an inbuilt AC impedance analyzer operating at 1 kHz frequency. The H₂ crossover-correction and the *in-situ* CV testing were performed following the procedure discussed in Chapter 5.

6.3 RESULTS AND DISCUSSION

6.3.1 MEA performance and ORR catalytic activity in PEMFC

Fig. 6.1(a) compares the measured constant polarization curves of $Pd_{50}Pt_{30}Ni_{20}$, preleached Pd₅₀Pt₃₀Ni₂₀, Pd₆₀Pt₄₀, and commercial Pt in PEMFC. The polarization curve is dominant by kinetic process below 200 mA/cm² for the H₂/O₂ PEMFC, and it is controlled by both ohmic and diffusion processes above 200 mA/cm². As seen in Fig. 6.1(a), the polarizations of $Pd_{60}Pt_{40}$ and $Pd_{50}Pt_{30}Ni_{20}$ overlap, indicating that the $Pd_{60}Pt_{40}$ and Pd₅₀Pt₃₀Ni₂₀ catalysts have nearly the same overall performance in PEMFC under the testing conditions employed here. Also, the polarization curve of the pre-leached Pd₅₀Pt₃₀Ni₂₀ sits slightly above those of Pd₅₀Pt₃₀Ni₂₀ and Pd₆₀Pt₄₀ over the entire current density region, suggesting improvement in the overall performance of the pre-leached Pd50Pt30Ni20 compared to unleached Pd50Pt30Ni20 and Pd60Pt40. All the three catalysts show performances comparable to that of commercial Pt. To illustrate the differences in the performance more clearly, the cell voltage for all the catalysts at 100 mA/cm² and 800 mA/cm² are compared in Fig. 6.1(b). As seen, at both the low current density of 100 mA/cm^2 (where kinetic process dominates) and the high current density of 800 mA/cm^2 (where diffusion process dominates), the cell voltages of Pd₆₀Pt₄₀ and Pd₅₀Pt₃₀Ni₂₀ are almost the same and lower than that of preleached Pd50Pt30Ni20 and commercial Pt. Although the difference among the cell performances is small here, they were tested under the same procedure and condition to avoid errors caused by system and operation

differences. Also, all the experiments were repeated and they were found to show the same trend in the cell performance.



Figure 6.1: (a) Polarization curves and (b) cell voltage values at a constant load of 100 mA/cm² and 800 mA/cm² of Pd–Pt(–Ni) catalysts synthesized by the modified polyol method and commercial Pt at 60 °C in PEMFC.



Figure 6.2: Catalytic oxygen reduction activities of Pd–Pt(–Ni) catalysts synthesized by the modified polyol method and commercial Pt at 60 °C in PEMFC: (a) cell voltage vs. Pt mass activity, (b) cell voltage vs. noble metal mass activity, and (c) cell voltage vs. Pt surface area activity.

Catalyst	Testing condition	$\begin{array}{c} ECSA\\ (m^2/g_{Pt}) \end{array}$	Mass activity @ 0.88V (A/mg _{Pt})	Mass activity @ 0.88V (A/mg _{noble metal})	Specific activity @ 0.88V (µA/cm ² _{Pt})
Pt		89	0.1384	0.1384	155.5
$Pd_{50}Pt_{30}Ni_{20}$	As-received	82	0.2176	0.1077	265.4
$Pd_{50}Pt_{30}Ni_{20}$	Leached	47	0.2538	0.1555	540.1
Pd ₆₀ Pt ₄₀	As-received	46	0.2086	0.1072	448.4

Table 6.1: Testing condition, ECSA, and activity of Pd–Pt(–Ni) and commercial Pt catalysts.^a

^a The activity values reported are IR-corrected

Although cell voltage at low current densities can roughly tell the difference in cell performance in the kinetic region, it does not allow precise ranking of the relative catalytic activities. Therefore, the Tafel curves of all the catalysts are plotted, and the mass activities as well as the specific activities (also called intrinsic activity) of Pd₅₀Pt₃₀Ni₂₀, preleached Pd₅₀Pt₃₀Ni₂₀, Pd₆₀Pt₄₀, and commercial Pt are compared in Fig. 6.2 and Table 6.1. The logarithmic current density scale now allows for an accurate relative activity ranking at a fixed cell voltage. Table 6.1 also reports the electrochemical surface area (ECSA) of all the tested catalysts. The ECSA and Pt-based mass activity and specific activity at 0.88 V are consistent with the reported state-of-the-art values considering the difference in specific testing conditions [23,24]. Actually, the mass activity of commercial Pt tested here with PEMFC made with Nafion 115 is higher than our previous data obtained with PEMFC made with Nafion 112. This increase in kinetic activity is due to less hydrogen crossover and thus higher open circuit potential in PEMFC with thicker Nafion 115 membrane compared to that with thinner Nafion 112

membrane. The mass activity of $Pd_{60}Pt_{40}$ is slightly lower than that of $Pd_{50}Pt_{30}Ni_{20}$, while the preleached Pd₅₀Pt₃₀Ni₂₀ has obviously higher mass activity compared to the unleached $Pd_{50}Pt_{30}Ni_{20}$. Compared to commercial Pt, all three catalysts show much higher Pt-based mass activity. Pd₅₀Pt₃₀Ni₂₀ shows performance improvement by a factor of around 1.6, which is consistent with the previous results acquired in PEMFC made with Nafion 112. The preleached Pd₅₀Pt₃₀Ni₂₀ exhibits the highest Pt-based mass activity of 0.254 A/mg_{Pt} among the catalysts investigated here, with a $2\times$ improvement compared to pure Pt. Since Pd is a noble metal as well, it is more accurate to calculate the noble metal-based mass activity for real-world application. It is seen that the preleached Pd₅₀Pt₃₀Ni₂₀ has obviously higher noble metal-based mass activity than Pt, while the noble metal-based mass activities of Pd₆₀Pt₄₀ and Pd₅₀Pt₃₀Ni₂₀ are still lower than that of Pt, around 80 % of that of pure Pt. Given the much lower cost of Pd, only 20% of that of Pt, the final activity per dollar will be increased by a factor of around $1.5\times$. As expected, the specific activity values correlate inversely with the ECSA values. The specific activity of both preleached Pd₅₀Pt₃₀Ni₂₀ and Pd₆₀Pt₄₀ are improved tremendously compared to that of Pd₅₀Pt₃₀Ni₂₀, and all these catalysts exhibit much better specific activity than pure Pt. The preleached Pd50Pt30Ni20 shows a maximum specific activity of 540 μ A/cm²_{Pt}, which is up to 3.5 times that of commercial Pt.

Fig. 6.3 depicts the cyclic voltammograms of all the catalysts and standard Pt recorded at the end of PEMFC single cell tests. The hydrogen adsorption peak area taken in the reducing sweep was measured between ~ 0.4 V and the plateau just prior to the start of the hydrogen evolution reaction to calculate the ECSA [23,25]. The binary $Pd_{60}Pt_{40}$ and ternary $Pd_{50}Pt_{30}Ni_{20}$ catalysts typically exhibit lower ECSA than pure Pt due to their initial larger particle size. This is because these alloys generally undergo a heat treatment during preparation and Pd catalyst particles are always larger than the Pt

catalyst particles [26]. However, alloying itself may contribute to more active sites for ORR and thus larger ECSA, or else the ECSA of all alloy catalysts will be even smaller due to the much larger particle size compared to Pt (Table 6.1). $Pd_{60}Pt_{40}$ has much smaller ECSA than $Pd_{50}Pt_{30}Ni_{20}$ because of larger particle size as well. Although dealloying of catalyst surface has been reported to roughen the electrochemical surface and lead to higher surface areas [27], the data in Table 6.1 show that the ECSA of the preleached $Pd_{50}Pt_{30}Ni_{20}$ is actually much lower than that of unleached $Pd_{50}Pt_{30}Ni_{20}$. It should be noted that their particle sizes are similar from the XRD data (Table 6.2).



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Figure 6.3: (a) Cyclic voltammetries of Pd–Pt(–Ni) catalysts and commercial Pt, (b) the enlarged region of the hydrogen adsorption and desorption, and (c) the enlarged regions of the surface oxide formation and its reduction. The short bars marked in (c) represent the positions of the onset potential of the surface oxide formation and the peak potential of the reduction of the surface oxide.

Moreover, in the hydrogen adsorption/desorption region, pure Pt shows two resolved peaks associated with weakly and strongly bonded hydrogen species on different crystal faces of the Pt metal. In contrast, $Pd_{50}Pt_{30}Ni_{20}$ and preleached $Pd_{50}Pt_{30}Ni_{20}$ exhibit one single broad peak in the hydrogen desorption region, one broad peak at around 0.2 V and one tiny peak at around 0.1 V in the hydrogen adsorption region. The hydrogen peaks of preleached $Pd_{50}Pt_{30}Ni_{20}$ look much more like those of Pt compared to the nonpreleached catalysts. $Pd_{60}Pt_{40}$ also exhibits a single big broad peak in both the hydrogen adsorption and desorption regions that are noticeably different from those of monometallic Pt. The difference indicates that the changes in the adsorption site geometry are attributed to the combinational effect of Pd and Pt on the catalyst surface. Fig. 6.3(b) highlights the potential range where the surface oxide formation (Pt + $H_2O \rightarrow Pt-OH + H^+ + e^-$) and the following reduction of the surface oxide occur. Both the onset potential for surface oxide formation and the peak potential for reduction of the surface oxide are seen to shift to higher values in the order pure Pt < Pd₅₀Pt₃₀Ni₂₀ < Pd₆₀Pt₄₀ < preleached Pd₅₀Pt₃₀Ni₂₀. These two positive potential shifts suggest, respectively, a delayed formation of Pt–OH and an easier removal of OH_{ad}, *i.e.*, weaker binding of the OH_{ads}-species on the catalyst surface.

6.3.2 Origin of activity enhancement and effect of surface roughening

As discussed in the first part, all the catalysts show improved Pt-based mass activities compared to pure Pt, and the preleached $Pd_{50}Pt_{30}Ni_{20}$ displays a significant advantage in the ORR activity over pristine $Pd_{50}Pt_{30}Ni_{20}$ and $Pd_{60}Pt_{40}$. Generally, surface roughening and increased ECSA are considered as one major reason for activity enhancement. However, the decrease in the ECSA values resulting from the synthesis and annealing process (especially for $Pd_{60}Pt_{40}$) and from pre-leaching rules out the possibility of surface roughening as the origin for activity improvement. On the other hand, the reduced adsorption energy of oxygenated species on the nanoparticle surface and much improved intrinsic activity of the Pd-based catalysts do mean something else play an important role here, possibly surface morphology, electronic effect, or geometric effect [7-16]. The former two can be caused by the modification of the surface atomic environment.

6.3.3 Alloy phase analysis

To know the phase structure of the catalysts formed after the synthesis and preleaching, the XRD patterns of Pd, $Pd_{80}Ni_{20}$, $Pd_{50}Pt_{30}Ni_{20}$, preleached $Pd_{50}Pt_{30}Ni_{20}$, $Pd_{60}Pt_{40}$, and commercial Pt are compared in Fig.6.4. All the catalysts display five main

peaks characteristic of single fcc phase, indicating a well mixing of Ni and Pt with Pd and formation of Pd–Pt–Ni ternary alloy. The absence of peaks for either Pt, or Ni, or its oxides may be due to their poor crystallinity or low concentration. From the enlarged profiles of the (111) reflection in Fig. 6.4(b), the positive peak shift for Pd₈₀Ni₂₀ and the negative peak shift for Pd₆₀Pt₄₀ compared to pure Pd suggest incorporation of the smaller Ni atoms and the larger Pt atoms into the Pd lattice. The Pd₅₀Pt₃₀Ni₂₀ reflection is located at the left side of Pd₈₀Ni₂₀, and even to the left of Pd, due to again an incorporation of larger Pt atoms into the Pd–Ni lattice. The preleached Pd₅₀Pt₃₀Ni₂₀ shows the reflection at a even lower angle compared to the as-prepared Pd₅₀Pt₃₀Ni₂₀, indicating the removal of smaller atoms like Ni or even Pd out of the lattice by dealloying in hot acid. All the lattice parameters obtained from the XRD data are listed in the Table 6.2. It should be noted that the change in the lattice parameters of all the alloy catalysts is not tremendous, and this means the catalysts are not perfectly alloyed due to heat treatment at temperature as low as 300 °C. The small differences in lattice constant may suggest a less prominent role of geometric effects in the enhancement of the ORR activity in these catalysts.



Figure 6.4: (a) XRD patterns and (b) the enlarged (111) regions of the catalysts synthesized by the modified polyol method and commercial Pt.

Catalyst	Anneal- ing temp. (°C)	Testing condition	Pd:Pt:Ni atomic ratio from SEM- EDS	Lattice parameter from XRD (nm)	Mean crystallite size from XRD (nm)
Pt				0.3919	2.4 (0.1)
Pd	300	As-received		0.3892	7.7 (0.2)
Pd ₈₀ Ni ₂₀	300	As-received	84:16	0.3888	6.2 (0.1)
Pd ₅₀ Pt ₃₀ Ni ₂₀	300	As-received	58:31:12	0.3896	5.1 (0.1)
Pd ₅₀ Pt ₃₀ Ni ₂₀	300	Leached	51:44:05	0.3899	5.3 (0.1)
Pd ₆₀ Pt ₄₀	300	As-received	63:37	0.3898	7.6 (0.1)

Table 6.2:Annealing temperature, testing condition, atomic ratios, lattice parameters,
and crystallite size of the catalysts synthesized by the modified polyol
method and commercial Pt.

6.3.4 Relationship between compositional stability and cell performance

To determine the origin of the activity enhancement in the Pd–Pt(–Ni) catalysts and to find the real active phase in these catalysts for ORR, their surface and bulk compositions were measured by XPS and EDS after the synthesis and after single cell operation. The detailed XPS profiles of all the three catalysts are given in Fig. 6.5–6.7, and the estimated near surface compositions and also the bulk compositions of these nanparticles before and after the single cell testing are summarized in Table 6.3.



Figure 6.5: Core level Pd 3d XPS profiles of the Pd–Pt(–Ni) catalysts synthesized by the modified polyol method before (solid line) and after the fuel cell testing (dashed line).



Figure 6.6: Core level Pt 4f XPS profiles of the Pd–Pt(–Ni) catalysts synthesized by the modified polyol method before (solid line) and after the fuel cell testing (dashed line).



Figure 6.7: Core level Ni 2p XPS profiles of the Pd–Pt(–Ni) catalysts synthesized by the modified polyol method before (solid line) and after the fuel cell testing (dashed line).

Catalyst	Testing	Near surface of (atom	comp. (XPS) n %)	Bulk comp. (SEM-EDS) (atom %)	
	condition	Before single cell running	After single cell running	Before single cell running	After single cell running
Pd ₅₀ Pt ₃₀ Ni ₂₀	As-received	$Pd_{40}Pt_{26}Ni_{34}$	$Pd_{41}Pt_{59}$	$Pd_{58}Pt_{31}Ni_{11}$	$Pd_{54}Pt_{41}Ni_5$
Pd ₅₀ Pt ₃₀ Ni ₂₀	Leached	Pd ₄₀ Pt ₆₀	Pd ₃₃ Pt ₆₇	$Pd_{51}Pt_{44}Ni_5$	Pd ₄₈ Pt ₄₈ Ni ₄
Pd ₆₀ Pt ₄₀	As-received	Pd ₅₉ Pt ₄₁	Pd43Pt57	Pd ₆₃ Pt ₃₇	Pd ₅₇ Pt ₄₃

Table 6.3: Surface and bulk compositions of the 300 °C heat-treated Pd–Pt(–Ni) catalysts.

6.3.4.1 Compositional change during single cell operation

From the Pd 3d and Pt 4f XPS spectra (not deconvoluted here) of the Pd–Pt(–Ni) catalysts in Figs. 6.5 and 6.6, Pd and Pt exist mostly in the metallic state, with possible contamination with some oxide species. In contrast, the Ni 2p XPS profiles of $Pd_{50}Pt_{30}Ni_{20}$ in Figs. 6.7 indicate the presence of primarily (hydr)oxide species with small amount of metallic Ni (852.5 eV) [28]. Moreover, it is seen from Figs. 6.5 and 6.6 that for all the catalysts, the Pd peak reduces severely after the single cell testing, while the peak intensity of Pt decreases only slightly, suggesting significant Pd dissolution and little Pt dissolution during single cell operation. In the case of Ni in $Pd_{50}Pt_{30}Ni_{20}$, no signals are detected at all after cell testing, indicating complete removal of Ni atoms from the catalyst surface. From the surface compositions in Table 6.3, the Pd/Pt ratios in $Pd_{50}Pt_{30}Ni_{20}$ and $Pd_{60}Pt_{40}$ change from > 1 before cell testing to < 1 after cell testing, clearly demonstrating the dissolution of Pd from the particle surface under the testing. Even the preleached catalyst with Pt-dominant characteristics shows certain degree of Pd

dissolution (from 40 atom % to 33 atom %). The surface composition of $Pd_{41}Pt_{59}$ for $Pd_{50}Pt_{30}Ni_{20}$ after the cell testing again indicates a complete removal of Ni from the surface. A similar trend in the Pd and Ni dissolution is observed in the EDS bulk compositions as well, although this is not noticeable for $Pd_{50}Pt_{30}Ni_{20}$ since the decrease in Ni atomic percentage will change the percentage of Pd and Pt at the same time. It is worth to point out that the 1 % decrease in the bulk Ni atom% in the preleached catalyst after cell operation implies continuous, but slower and slower leaching out of Ni from the nanoparticles. Actually, our previous durability tests of PEMFC fabricated with the same $Pd_{50}Pt_{30}Ni_{20}$ catalyst and Nafion 112 demonstrated a leaching of 100 % of Ni and the final formation of a Pd–Pt binary catalyst.

6.3.4.2 Compositional change when leaching in hot acid

It is widely accepted that base metals are unstable in contact with acid electrolyte, especially with the enrichment of base metals at the surface of the catalyst particle and/or in presence of their oxide species. It has been postulated that these surface base metal atoms are rapidly removed in hot acid [29], just as what we see in the compositional change for the nominal $Pd_{50}Pt_{30}Ni_{20}$ from $Pd_{40}Pt_{26}Ni_{34}$ to $Pd_{40}Pt_{60}$ after leaching. This would result in a continuous dissolution of the remaining Ni atoms from the inside, as proved from the decreased amount of Ni for preleached $Pd_{50}Pt_{30}Ni_{20}$ after the cell operation. However, it is problematic to tell the degree of leaching in hot acid just based on the compositional change. Noticeably, Pd also dissolves in the hot acid at the same time. It should be noted that chemical treatment of alloys in air saturated acids represents an electroless dissolution process at an open circuit (mixed) potential with the open circuit potential governed by all the redox systems (metal and surface reactions) present [24]. Chemical dissolution of Pd–Pt–Ni alloys in air saturated acid occurs at a constant potential between the Ni standard potential (- 0.25 V vs. NHE) and the open circuit

potential of a pure Pt cathode catalyst in a hydrogen/air fuel cell (typically around 0.95–1 vs. NHE). This constant potential is definitely higher than the Pd standard potential (0.915 vs. NHE), and thus Pd dissolves from the surface and even from the inside as Ni does. It was reported by Strasser's group [24] that cyclic voltammetric dealloying led to a more complete Cu dissolution than chemical acid leaching. However, the compositional data of preleached Pd₅₀Pt₃₀Ni₂₀ before the cell operation and Pd₅₀Pt₃₀Ni₂₀ after the cell operation (Table 6.3) suggests that chemical leaching in acid results in a similar degree of metal dissolution as single cell operation. This is acceptable because catalysts are not subjected to more positive potentials and surface cycling during single cell test compared to those applied during voltammetric surface dealloying.

6.3.4.3 Structural model for performance enhancement

As discussed above, dissolution of Pd and Ni from the surface results in an enrichment of Pt on the surface. The surface composition is changed via preferential Ni and Pd dissolution. The resulting Pt-rich surface may have more active sites for ORR activity and/or lower binding between metal atoms and oxygenated species. In addition, by comparing the surface composition with the bulk composition after the fuel cell operation, all the catalysts form a distinct structure with Pd-rich core and Pt-rich shell. The strain introduced in the outer shell by an inner core with smaller lattice parameter could reduce the coverage of the ORR inhibitor (OH_{ad}) and enhance the catalytic activity. In this regard, Pt-rich shell surrounding an increasingly Pd-rich core is referred as the active phase for all the Pd-based catalysts studied here, as discussed in Chapter 4.

Before the fuel cell testing, the preleached $Pd_{50}Pt_{30}Ni_{20}$ has undergone Pd and Ni dissolution and atomic rearrangement on the surface and across the particle under severe chemical environment. When it comes to single cell, the remaining Pd and Ni are again subjected to both chemical and electrochemical effects, and they will further dissolve as

the fuel cell testing progresses. This could make for more Pt-enrichment in the shell and further contraction of the Pd-rich core, and correspondingly, much higher strain between and the core and the shell components. All these factors combined together will result in a further enhancement of the intrinsic catalytic activity. However, the ECSA is much reduced during leaching in acid electrolyte, and the final mass activity is moderately improved through the preleaching procedure. Another crucial role of preleaching catalysts in acid prior to fuel cell testing is to get rid of Ni and Pd as much as possible if only the activity is not affected. In this case, the contamination caused by either dissolved Ni ions or Pd ions to the whole MEA, including both the membrane and electrodes, could be considerably alleviated, and the catalyst performance and durability will be greatly enhanced. The favorable effect of preleaching on overall cell performance has already been demonstrated in our experiments, although it is not enormous within the testing period in this study. It should be more obvious in the long-term durability test.

 $Pd_{60}Pt_{40}$ experiences the same compositional and structural change as $Pd_{50}Pt_{30}Ni_{20}$, and considering a similar beginning composition, they are expected to have similar final compositions after the fuel cell testing in both the surface and bulk aspects. This is what actually happened (see Table 6.3), and the only difference is the presence of Ni in the Pd–Pt–Ni particle but not in the Pd–Pt particle. This first illustrates that $Pd_{60}Pt_{40}$ is not the active phase for ORR. Also, based on the structural model for the origin of activity enhancement, existence of Ni in the core should further decrease the lattice constant of the core and hence increase the lattice mismatch between the core and the shell, enhancing the strain effect. The intrinsic activity towards ORR should thereby be increased. However, what is observed is the opposite, *i.e.*, $Pd_{60}Pt_{40}$ has higher intrinsic activity than $Pd_{50}Pt_{30}Ni_{20}$. Under the cell operation, the dissolved Ni ions can poison the MEA by readily ion-exchanging with the protonic sites in the ionomer of the catalyst

layer and membrane, lowering the overall MEA performance and accelerating the degradation of fuel cell. Whereas the detrimental effect of dissolved Ni ions is not obvious on the membrane conductivity (known from ohmic resistance), it does harm the catalyst based on the present results. Either the advantage of Ni contribution to activity enhancement is overwhelmed by the disadvantage of Ni ion contamination, or it is negligible due to presence of small amount of Ni. However, $Pd_{60}Pt_{40}$ has much lower ECSA possibly due to the large particle size, so its mass activity is a little lower than that of $Pd_{50}Pt_{30}Ni_{20}$. Nevertheless, its durability should still be improved compared to $Pd_{50}Pt_{30}Ni_{20}$.

6.3.4.4 Possible stable active phase in the Pd-Pt-Ni catalyst

Finally, the question of what is the most active catalyst phase for ORR needs to be answered. Is it the Pd–Pt with a surface composition of Pd₃₃Pt₆₇ and a bulk composition of Pd₄₈Pt₄₈Ni₄? The compositional change after the single cell testing suggests that chemical dissolution procedures did not result in a thermodynamically and, therefore, compositionally stable active catalyst phase. Also, compositional change after the durability test (around 200 h) in our previous study indicated a slow but continuous Pd dissolution and full removal of Ni atoms. Consequently, we cannot tell for sure the exact stable active phase until the durability test of the preleached Pd₅₀Pt₃₀Ni₂₀ is performed. It has been reported that surface Pd can be covered and somewhat protected by the Pt overlayer, even though surface base metals cannot be [29]. It would also work here for Pt-rich surface despite the comparatively less protection. Even if Pd dissolution under the MEA operation is sustained and no stable active phase is obtained, the rate of Pd dissolution decreases with testing time, consistent with the formation of more intrinsically stable particles. From a practical point of view, this bulk-diffusion-controlled dissolution process could be as long as that of the fuel cell device lifetime. Then, the major problem comes to the contamination of the MEA components by dissolved Pd ions and much decayed durability. The preferred catalyst phase would be as little Pd as possible after leaching in acid, provided that it has the comparable ORR activity. Of course, all present findings have not ruled out the existence of a stable Pd rich core-Ptrich shell structure.

6.4 CONCLUSIONS

To improve the performance and durability of Pd-based Pd-Pt-Ni alloy electrocatalysts for ORR in PEMFC, we have subjected the as-prepared Pd-Pt-Ni catalyst to acid-leaching and synthesized a binary Pd-Pt alloy catalyst with a composition close to that formed from the Pd-Pt-Ni catalyst after the fuel cell testing. The preleached catalyst shows improved performance in both the kinetic and high current density regions compared to pristine Pd-Pt-Ni, with a Pt-mass activity twice that of state-of-the-art Pt at 0.88 V vs NHE. The binary Pd-Pt exhibits performance similar to that of Pd-Pt-Ni in the entire current density range. ECSA values obtained from cyclic voltammetry exclude the possibility of surface roughening as the origin for activity enhancement. The compositional analysis before and after the fuel cell testing and leaching in acid points out that the Pd-rich core and Pt-rich shell structure are formed during processing and the consequent strain effect caused by the lattice parameter mismatch between the core and shell components are the main reason for the improvement in activity. The strain induced in the outer shell could downshift the d-band center of Pd and Pt and reduce the binding energy between the metal atom and the adsorbed oxygenated species, resulting in higher specific activity towards ORR. The surface compositional change and geometric effect due to lattice constant change may also play a role in the activity improvement. Besides, removal of unstable Pd and Ni to the largest degree prior to fuel cell testing can constrain their further dissolution during the MEA operation to a minimum, effectively alleviating

contamination of dissolved metal ions to the whole MEA and thus improving the overall performance and durability.

Overall, preleaching is proved to be an effective means to improve the performance because of both the formation of Pt-rich surface and mitigation of contamination through selective metal dissolution. However, the resulting surface is not quite stable with our compositions. The surface after leaching is similar to that found after potential cycling, having a corrugated atomic arrangement [11]. This so-called Pt-skeleton surface (here PtPd-skeleton surface) is less active and less stable than the Pt-skin having a smooth outmost atom arrangement and acting as a more effective protective layer for atoms underneath. Therefore, the best way to obtain both excellent performance and durability is to develop a stable active phase with a Pt skin surface. Nevertheless, fairly rapid dissolution of 100% base metal and partial Pd from Pt_{ML}/Pd₃X materials with cycling has been reported, due to the difficulties of reproducing uniform, pin-hole free Pt monolayer via scalable chemistries [29]. Under this situation, tuning the active catalyst phase with appropriate amount of base metal and ways to prevent diffusion of dissolved Pd ions could prove useful.

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CHAPTER 7

Comparison of the Catalytic Activities of Pd–Pt–M (M = Ni, Fe, Cu) Measured by Rotating Disk Electrode and Single Cell Tests for Oxygen Reduction Reaction

7.1 INTRODUCTION

To develop new or modified catalysts with improved activity for fuel-cell applications, well-defined measurement methodologies are required to quantitatively determine and unambiguously compare the electrocatalytic activities under fuel cell relevant conditions (i.e., continuous reactant flow, steady state, 60–80 °C). The most straightforward method for this is to produce a membrane-electrode assembly (MEA) and to measure the catalytic activity in a single cell configuration. However, testing catalysts in the form of a MEA in fuel cells is quite intricate and time-consuming. Therefore, a facile alternative was developed on the basis of the rotating disk electrode (RDE) method [1,2]. The supported catalyst thereby is deposited onto a glassy carbon disk and can be readily tested in an ordinary electrochemical glass cell. However, due to a strong diffusion resistance of oxygen gas produced by a relatively thick Nafion film (1–6 μ m), extensive mathematical modeling involving a large number of poorly defined geometric parameters and material properties were required initially for the determination of the electrode kinetics from the experimental data [3-5].

Later, by attaching the catalyst powder onto the glassy carbon electrode via a submicrometer thick Nafion film placed on top of the dried catalyst layer, Schmidt et al. [1,6] were able to minimize the film diffusion resistance. Thereby, the kinetic current densities could be determined directly from the RDE data by using the general masstransport correlations [1,7] for flat electrodes. In addition, the significantly reduced catalyst loading extends the potential region where the kinetics can be studied, making it possible to predict the performance of large-scale fuel cell electrodes on the basis of RDE measurements [8]. From the studies of Gasteiger *et al.* [9] and Strasser *et al.* [10-12], the RDE method not only produces the same activity ranking for different catalysts as is observed with H_2/O_2 MEA testing, but also results in a quantitative agreement within a factor of 2 if the measurements are taken at comparable temperatures in non-adsorbing 0.1 M HClO₄ electrolyte. Actually, in most cases, it is difficult for newly proposed catalysts to translate the high kinetic activity observed under ideal conditions in the RDE to operational MEAs [13].

In Chapter 6, we synthesized and evaluated Pd₅₀Pt₃₀Ni₂₀, preleached Pd₅₀Pt₃₀Ni₂₀, and Pd₆₀Pt₄₀ as cathodic catalysts for ORR in PEMFC single cell. Here, we analyze their catalytic activity based on RDE tests, and compare the results with those from single cell tests. Unexpectedly, what we get from the RDE method is not in good agreement with what we had from the single cell test. In essence, all the Pd–Pt(–Ni) catalysts tested are found to be inferior to commercial Pt-based on the RDE tests, although they show superior activities compared to commercial Pt in single cell test. Through compositional analysis and monitoring the activity changes according to the surface change from the Pd-rich state to the Pt-rich state, we recognize that potential cycling and single cell operation are two different delloying processes, in which different rate and degree of metal dissolution take place, resulting in the formation of different composition and structure both on the surface and across the catalyst particles and hence in differences in the catalytic activity. By pointing out the discrepancies in the activities obtained from these two methods, we point out the importance of performing single cell fuel cell tests to determine the real activities of the newly developed catalyst for real fuel cell applications. Additionally, we also compare the activities of Pd–Pt–M (M = Ni, Fe, and Cu) electrocatalyts for ORR using the RDE method in acid electrolyte to investigate the influence of various alloying elements on catalytic activities.

7.2 EXPERIMENTAL

7.2.1 Materials synthesis

The 20 wt. % Pd–Pt(–Ni) nanoparticle electrocatalysts supported on carbon were synthesized by a modified polyol reduction method as described in Chapter 2. $(NH_4)_2PdCl_4$, Ni(CH_3COO)_2·4H_2O, Fe(CH_3COO)_2, Cu(CH_3COO)_H _2O, and H_2PtCl_6 were used as metal precursors, and the resulting black powders obtained after the reaction were subsequently heat-treated at 300 °C in a flowing 10% H₂–90 % Ar atmosphere for 2 h. For the preleaching, the as-prepared Pd–Pt–Ni nanoparticles were treated with 1 M H_2SO_4 at 80 °C for 60 h, washed repeatedly with deionized water, and then dried overnight.

7.2.2 Activity evaluation by the RDE method

The preparation of the catalyst thin films on GC electrode and the testing procedures of CV and RDE methods are described in detail in Chapter 2.

7.2.3 Effect of potential and cycling on the surface texture

The $Pd_{50}Pt_{30}Ni_{20}$ catalyst was used to study the surface texture change and corresponding activity change with potential cycling. The catalyst thin film electrode was prepared following the above procedure, and was subjected to a potential cycling in the same three-electrode system in nitrogen-purged 0.5 M H₂SO₄. The potential was swept linearly with time at a scan rate of 1000 mV/s from an initial voltage (usually 0 V) to an upper voltage limit, which was varied from 0.85 to 0.95, 1.05, and 1.2 V to observe the effect of potential on the surface structure. The cyclic voltammograms (CV) were

recorded periodically at a scan rate of 20 mV/s within a certain potential range to see the effect of cycle number. The standard reduction potentials of Pd and Pt are, respectively, 0.915 and 1.118 V vs. NHE, which means Pd will be stable below 0.915 V and Pt will be stable below 1.118 V. This is why we chose 0.85, 0.95, 1.05 and 1.2 V as the upper potential limit to differentiate the effect of different metal dissolution on the surface structure and consequent activity change.

7.2.4 Effect of surface texture change on activity

Identifying the surface changing process of the Pd–Pt-based alloy catalyst by the method described in section 7.2.3, the activity change with potential cycling was focused within 0 - 0.95 V and 0 - 1.05 V (see details in section 7.3.2). The Pd₅₀Pt₃₀Ni₂₀ catalyst electrode was cycled at a scan rate of 1000 mV/s in nitrogen-purged 0.5 M H₂SO₄, and the CVs were recorded at 20 mV/s every 100 cycles. When a repeatable CV was observed, the RDE experiment was performed in oxygen-saturated 0.5 M H₂SO₄ at a scan rate of 5 mV/s to test the activity. From then on, CVs and linear sweep voltamograms (LSVs) were recorded every 100 cycles to monitor the activity change. When the whole CV began to attenuate but retaining the same shape, CVs and LSVs were recorded every 500 cycles afterwards.

7.3 RESULTS AND DISCUSSION

7.3.1 ORR activities obtained from RDE and single cell PEMFC

Fig. 7.1 shows the cyclic voltammograms of $Pd_{50}Pt_{30}Ni_{20}$, preleached $Pd_{50}Pt_{30}Ni_{20}$, $Pd_{60}Pt_{40}$, and commercial Pt in nitrogen-purged 0.5 M H₂SO₄ at room temperature. Three peaks corresponding to hydrogen adsorption and two peaks corresponding to hydrogen desorption from different Pt planes can be clearly identified with pure Pt. In contrast, there is only a single adsorption/desorption peak in the case of

Pd-Pt(-Ni). This remarkable difference indicates the changes in the adsorption site geometry caused by the coexistence of Pd and Pt on the particle surface. In the cathodic scan, the peak potential corresponding to the reduction of the surface oxide follows the order $Pt < Pd_{50}Pt_{30}Ni_2 < Pd_{60}Pt_{40} < preleached Pd_{50}Pt_{30}Ni_2$. The positive shift of the oxide stripping peak suggests weaker binding of the OH_{ads} species on the surface of the catalyst nanoparticles [9]. The electrochemically active surface area (ECSA) can be calculated by measuring the charge in the hydrogen adsorption region (0.05 to 0.40 V) after doublelayer correction and assuming a value of 210 mC/cm² for the adsorption of a hydrogen monolayer [8]. The ECSA values of all the catalysts are given in Table 7.1. Alloying Pd with Pt reduces the ECSA to a large degree, but the addition of Ni into Pd–Pt increases the ECSA again. Although dealloying of the alloy interfaces has been reported to increase the ECSA by roughening the electrochemical interface, the data in Table 7.1 clearly show that the ECSA decreases after leaching the Pd₅₀Pt₃₀Ni₂₀ catalyst in acid. The results obtained here are consistent with those obtained from the PEMFC single cell test. The only difference is that the hydrogen peaks in the CV of single cell test show large current density near 0 V due to hydrogen crossover form the anode.



Figure 7.1: Cyclic voltammograms of the Pd–Pt(–Ni) catalysts synthesized by the modified polyol method and commercial Pt in N₂-purged 0.5 M H₂SO₄ at room temperature with a scan rate of 50 mV/s.

Table 7.1:Electrochemical properties of 300 °C heated Pd–Pt(–Ni) and commercial Pt
catalysts measured by the RDE method.

Catalyst	Testing condition	$\frac{\text{ECSA}}{(m^2/g_{Pt})}$	Mass activity @ 0.88V (A/mg _{Pt})	Mass activity @ 0.88V (A/mg _{noble metal})	Specific activity @ 0.88V (µA/cm ² _{Pt})
Pt		74	0.0165	0.0165	22.2
Pd ₅₀ Pt ₃₀ Ni ₂₀	As-received	65	0.0136	0.0067	21.0
Pd ₅₀ Pt ₃₀ Ni ₂₀	Leached	35	0.0110	0.0067	31.1
Pd ₆₀ Pt ₄₀	As-received	49	0.0056	0.0029	11.4

The ORR measurements were performed in O₂-saturated 0.5 M H₂SO₄ solution with a glassy carbon rotating disk electrode (RDE), and the polarization curves for ORR on $Pd_{50}Pt_{30}Ni_{20}$, preleached $Pd_{50}Pt_{30}Ni_{20}$, $Pd_{60}Pt_{40}$, and commercial Pt are shown in Fig. 7.2. For all the catalysts synthesized by the polyol method, a mixed kinetic-diffusion control occurs in the whole potential region. Half-wave potentials of 0.738, 0.731, and 0.683 V are measured, respectively, for Pd₅₀Pt₃₀Ni₂₀, preleached Pd₅₀Pt₃₀Ni₂₀, and Pd₆₀Pt₄₀. All of them are lower compared to the 0.769 V of commercial Pt, indicating their lower catalytic activity compared to commercial Pt. Fig. 7.3 and Table 7.1 show a quantitative comparison of the Pt mass-based (A/mg_{Pt}) (Fig. 7.3(a)), noble metal massbased (A/mg_{noble metal}) (Fig. 7.3(b)), and Pt surface area-based (μ A/cm²_{Pt}) (Fig. 7.3(c)) activities of all catalysts investigated in the kinetically controlled regime. To have a clear idea how the catalytic activity is improved compared to pure Pt in RDE, the Pt mass activities of all catalysts are normalized by that of commercial Pt (the resulting value is termed as "activity factor"), and plotted in Fig. 7.4 for a comparison. As seen, all the three catalysts show lower Pt mass activity than Pt, following the order $Pd_{60}Pt_{40} <$ preleached $Pd_{50}Pt_{30}Ni_{20} < Pd_{50}Pt_{30}Ni_{20}$. The activity of $Pd_{60}Pt_{40}$ is lowest, which is only 1/3 of that of commercial Pt.



Figure 7.2: Hydrodynamic polarization curves of the Pd–Pt(–Ni) catalysts synthesized by the modified polyol method and commercial Pt in O₂ saturated 0.5 M H₂SO₄ at room temperature and 1600 rpm.

To clearly show the improvement in catalytic activity in single cell tests, the Pt mass activities obtained in single cell tests (from Table 6.1) are normalized to that of commercial Pt and plotted in Fig. 7.4 as well. Obviously, all the three catalysts ($Pd_{50}Pt_{30}Ni_{20}$, preleached $Pd_{50}Pt_{30}Ni_{20}$, and $Pd_{60}Pt_{40}$) exhibit higher activity than pure Pt, and the activity of preleached $Pd_{50}Pt_{30}Ni_{20}$ shows an improvement by a factor of 2 compared to Pt. Considering the difficulty for new catalysts to translate the high kinetic activity observed under ideal conditions in the RDE to operational MEAs, the expected performance of Pd–Pt(–Ni) catalysts in single cell test should be even lower compared to that of Pt. However, the actual activity factors for $Pd_{50}Pt_{30}Ni_{20}$, preleached $Pd_{50}Pt_{30}Ni_{20}$, and $Pd_{60}Pt_{40}$ are improved, respectively, by 94 %, 200 %, and 340% compared to those obtained in the RDE test (shown in Fig. 7.7). The disparate activity factors obtained from RDE and from single cell tests signify something is clearly different between the RDE and single cell tests.



Figure 7.3: Catalytic oxygen reduction activities of the Pd–Pt(–Ni) catalysts synthesized by the modified polyol method and commercial Pt in 0.5 M H₂SO₄ at room temperature: (a) Pt mass activities, (b) noble metal mass activities, and (c) specific activities.



Figure 7.4: Mass activity factors of the Pd–Pt(–Ni) catalysts synthesized by the modified polyol method obtained from the RDE and single cell tests.



Figure 7.5: ECSA factors of the Pd–Pt(–Ni) catalysts synthesized by the modified polyol method obtained from the RDE and single cell tests.
To determine what really causes the improvement in the mass activity factors in the single cell test, we first analyze the change in the ECSA values from RDE to single cell test. We normalize all the ECSA values to that of pure Pt and compare them in Fig. 7.5. The ECSA values measured with the MEAs (from Table 6.1) are generally larger than those measured in acid electrolyte. However, the slight increase in ECSA (5% for $Pd_{50}Pt_{30}Ni_{20}$ and 12% preleached $Pd_{50}Pt_{30}Ni_{20}$) cannot account for the remarkable mass activity increases in the single cell test since activity is expected to scale linearly with ECSA.

For a better understanding of the observed differences in the ORR activities determined from RDE and single cell experiments, we analyze the specific activities, which are calculated by normalizing the effective current against the ECSA and represent the intrinsic characteristics of the catalysts. The effective current means kinetic current in RDE or current after hydrogen crossover-correction in single cell test. Similarly, to clearly show the differences in activity compared to Pt, all the specific activities (from Table 6.1 and Table 7.1) are normalized to that of pure Pt both in the RDE and single cell tests and are compared in Fig. 7.6. As shown, Pd₅₀Pt₃₀Ni₂₀ has a slightly lower specific activity and Pd₆₀Pt₄₀ has much lower specific activity than Pt in RDE, suggesting simply alloying Pt with Pd by synthesis method employed here does not result in an enhancement of the intrinsic activity, but the addition of Ni does contribute to the activity improvement. Moreover, preleached Pd₅₀Pt₃₀Ni₂₀ has 40% higher specific activity compared to Pt due to the prior dissolution of Ni and Pd in acid and formation of a Pt-rich shell and Pd-rich core structure. In contrast, all the considered catalysts exhibit much better specific activity than pure Pt in single cell test. The preleached Pd₅₀Pt₃₀Ni₂₀ shows a maximum specific activity up to 3.5 times of that of commercial Pt. The specific activity factors of Pd₅₀Pt₃₀Ni₂₀, preleached Pd₅₀Pt₃₀Ni₂₀, and Pd₆₀Pt₄₀ obtained from single cell tests are improved, respectively, by 71%, 247% and 460% compared to those determined from the RDE experiments. This should be the main reason for the different mass activity factors between the RDE and single cell tests.



Figure 7.6: Specific activity factors of the Pd–Pt(–Ni) catalysts synthesized by the modified polyol method obtained from the RDE and single cell tests.



Figure 7.7: Mass activity factors, ECSA factors, and specific activity factors at 0.88 V of the Pd–Pt(–Ni) catalysts obtained from the RDE and single cell tests.

We should point out that all the data reported here from both the RDE and PEMFC single cell tests are repeatable and reliable. For the standard Pt, the Pt mass activity obtained from the RDE experiment is lower by an order of magnitude compared to the value reported by other groups [11–12]. Since the ECSA value is similar, indicating the dispersion of the catalyst ink is good, the problem lies in the intrinsic characteristic of the Pt catalyst. The difference in the preparation of the catalyst ink (like the ratio of Nafion to water), the thickness of the catalyst film, the type of acid electrolyte, and the testing temperature should induce different adsorption rates for the oxygenated species and different rate of charge transfer on the catalyst interface. This is why the mass activities are different. Comparing the mass activity of the standard Pt in this study to that obtained by others in the same group [14,15], they are consistent at various potentials, suggesting the validity of the operation and data collection. On the other hand, all the data collected in PEMFC single cell testing including the ECSA, Pt mass activity, and specific activity of standard commercial Pt are consistent with the reported state-of-the-art values, considering the differences in catalyst loading, MEA preparation method, and specific testing conditions [9,10]. In fact, whether the absolute activities obtained in our study are identical with the reported values, or whether the absolute activities obtained from our RDE experiment are comparable with those from single cell testing is not so important for the purpose here, as for each case, all the catalytic activities have been normalized to that of standard Pt tested under the same conditions.

7.3.2 Compositional and structural changes during cycling and PEMFC single cell testing (see Table 6.3 and Table 2 in Ref. 2)

Based on our previous study, both Pd and Ni dissolve under the chemical and electrochemical conditions during single cell operation. The fast removal of Pd and Ni

atoms from the catalyst surface and continuous but gradual leaching out of Pd and Ni from the inside result in a structure with Pt-rich shell and Pd-rich core. The strain introduced in the outer shell layer by lattice parameter mismatch between the core and shell parts could downshift the metal d-band center, reduce the adsorption energy of hydroxyl species in the interface, and thus increase the intrinsic activity (also called "electronic effect"). Besides, the surface morphology with the Pt-enrichment on the surface and the change in bond distance between the noble metal atoms (also called "geometric effect") induced by compositional and structural changes may also contribute to the improvement in specific activity.

However, potential cycling in acid electrolyte is a different process from single cell operation. Activity test by RDE after repetitive potential cycling is much more severe than single cell testing under steady-state conditions. Borup et al. [16] have illustrated this point clearly by conducting aging tests with steady-state conditions (both constant voltage and constant current) and using an accelerated testing technique. Typically, the controlled cyclic voltammetric sweeps cover a wide potential range from 0 to 1.2 V, and they entail repeated cycles of surface atomic oxidation/dissolution followed by surface oxide reduction. These processes are likely combined with a larger extent of potentialinduced surface atomic rearrangements, which expose subsurface atomic layers and lead to a faster and more complete metal atom dissolution [17-22]. As reported, a surfaceenrichment by Pt is always associated with the potential cycling technique and dissolution of non-noble metals [23], which also takes place during single cell operation. However, the particle surface formed after potential cycling consists of more Pt compared to that after the single cell operation. It is possible that the catalyst with such a Pt-richer surface has passed through the active compositional state and the catalytic activity is already below the optimum. At the same time, the formation of the Pt-rich phase could happen not only on the particle surface, but also inside the particle due to the high rate and high degree of dealloying. This suggests a more homogenous elemental distribution across the whole catalyst particle, and thus less lattice constant mismatch between the outer and inside components. Therefore, there is less strain effect in the outmost layers, resulting in lower d-band vacancy in the noble metal atoms, stronger metal-oxygen bonding, and lower specific activity.

On the contrary, the solid electrolyte in the MEA and the constant load applied in the single cell test provide a relatively mild and less corrosive condition. Accordingly, the metal dissolution will be slower, and there will be more Pd (and Ni) atoms left inside the catalyst particle. We cannot be sure that the surface composition formed during singe cell operation is the most active state, but the strain effect induced by the obvious mismatch between the outer and inner lattice parameters will contribute to the activity increase. Even though there are other chemical factors like temperature, humidity, and pressure in the single cell influencing the metal dissolution, the electrochemical potential still plays the most important role in changing the composition and structure of the catalyst.

Actually, from Table 6.3, the single cell operation results in a similar degree of metal dissolution as the chemical preleaching process in acid. On the other hand, Mani et al. [10] have reported that at a given synthesis condition, electrochemical dealloying methods are more effective in the removal of Cu from the precursor compared to chemical dealloying procedures. The above two facts substantiate that single cell operation and potential cycling are two different delloying processes, leading to different metal dissolution and thus formation of different composition and structure both on the surface and across the catalyst particle.

Additionally, particle size growth is accelerated during potential cycling compared to the steady-state condition in single cell, resulting in a larger loss of ECSA

and thus lower catalytic activity. Metal solubility is a function of potential, with the solubility increasing by two orders of magnitude from potentials of 0.7 to 1.0 V [24]. Thus, particles grow more rapidly during cycling to high potentials like 1.1 V in our study. Meanwhile, noble metal atoms like Pt will tend to dissolve when sweeping to high potentials, and then precipitate out of solution as the potential is decreased. Therefore, the number of cycles is the dominant effect in the loss of ECSA, while the time at high potential has a secondary effect.

7.3.3 Activity change during cycling and PEMFC single cell testing

It would be straightforward to recognize the differences in the compositional and structural changes taking place during cycling and PEMFC single cell testing if we know the surface and bulk compositions of the considered catalysts after the potential cycling. However, it is not facile to test the compositions of the catalysts loaded onto the glassy carbon disk due to the limitations in the analysis methods. In Chapter 6, with the Pd and Ni dissolution under the cell operation conditions, the MEA performance including the catalytic activity increased continuously and gradually with time. This could be explained by the changes in the morphology and structure on the catalyst surface and the consequent changes in the intrinsic characteristics of the catalyst such as the charge transfer resistance. If parallel compositional and structural changes occur under the potential cycling and single cell operation, the catalytic activity measured with potential cycling should exhibit similar increase as in single cell testing consistent with similar surface texture changes. In this regard, we designed an experiment to find the surface texture changes first and then tested to see how the activity changes. Here, the Pd₅₀Pt₃₀Ni₂₀ catalyst was chosen to show the changes and similar phenomenon could be observed for the other two catalysts as well.





Figure 7.8: Cyclic voltammograms of $Pd_{50}Pt_{30}Ni_{20}$ recorded in N₂-purged 0.5 M H₂SO₄ at room temperature with a scan rate of 20 mV/s in the potential range of: (a) 0 - 0.85 V, (b) 0 - 0.95 V, (c) 0 - 1.05 V, and (d) 0 - 1.2 V.

As seen in the CVs of $Pd_{50}Pt_{30}Ni_{20}$ recorded at 0 - 0.85 V (Fig. 7.8(a)), the shoulders appear at 0 V, which is characteristic of Pd alone, and increase constantly with cycling. Meanwhile, one broad peak in the anodic direction, one broad peak and one tiny peak in the cathodic direction become more and more prominent after cycling. In addition, one peak corresponding to the reduction of surface oxide appears with cycles. The CVs recorded at 0 - 0.95 V (Fig. 7.8(b)) until 1500 cycles also show changes similar to that found under 0 - 0.85 V. From 1500 to 6000 cycles, the shoulder at 0 V shrinks; other peaks in the hydrogen region decrease a little with the one broad peak splitting into two separate peaks in both the anodic and cathodic directions. At the same time, the peak potential for the reduction of the surface oxide becomes a little more positive. All these changes indicate that the surface tends to resemble more like the Pt surface. After 6000 cycles, the whole CV shrinks with more and more prominent characteristics of Pt surface. CVs recorded at 0 - 1.05 V (Fig. 7.8(c)) display exactly the same change as those recorded at 0 - 0.95 V, but every change occurs sooner with cycling due to the higher upper potential limit (step 1: from 0 to 1000 cycles; step 2: from 1000 to 1500 cycles; step 3: after 1500 cycles). For 0 - 1.2 V (Fig. 7.8(d)), although the CV first exhibits characteristics dominated by Pd, the entire curve shrinks rapidly with cycling, showing the main characteristics of Pt surface.

In summary, the CVs undergo shape change following three steps. The first step is surface cleaning. After the complete removal of the contaminants from the catalyst surface, the peaks in the whole region become more and more notable, showing clearer characteristics of both Pd and Pt, but with the majority of Pd feature. The second step is Pd dissolution. As described for the change from 1500 to 6000 cycles with 0 - 0.95 V, the CVs show characteristics more of Pt and less of Pd, suggesting the surface is dominated by Pt atoms instead of Pd atoms due to Pd dissolution from the catalyst surface. The third step is current decay. Both Pd and Pt dissolve from the catalyst surface, and the entire CV deteriorates and becomes constant with characteristics resembling that of Pt surface. When the upper potential is 0.85 V, only Ni atoms dissolve from the surface and the surface cleaning is slow. When the upper potential goes up to 1.2 V, both Pd and Pt dissolve rapidly, leading to a drastic decrease in current density in the whole potential range. When the upper potential is between 0.915 and 1.118 V, Pd atoms dissolve fast together with Ni, while Pt is nearly stable. Only under this condition, changes in the catalyst surface morphology are clear. Recall that the surface texture of the Pd–Pt–Ni catalyst changes from Pd-dominant to Pt-dominant under single cell testing condition in Chapter 5, which corresponds to the second step discussed here. Therefore, we focus on the activity change during the second step with cycling.

7.3.3.2 Activity change upon surface texture change with cycling

Obviously, the RDE and single cell tests are two different methods for activity measurement, so we cannot compare the activity change directly referring to the same time period. On the other hand, the catalytic reactions take place at the interface. Modern surface science studies and density functional theory calculations have demonstrated the importance of catalyst surface composition and near surface structure in catalysis [25-28]. Consequently, we studied the variation of activity change with the surface texture change by the basic surface technique – cyclic voltammograms.

Figs. 7.9 and 7.10 show the CVs and resultant LSVs of $Pd_{50}Pt_{30}Ni_{20}$ measured after different cycle numbers within 0 – 0.95 V. As expected, from the beginning to 500 cycles (Fig. 7.9(a)), the catalyst surface is under cleaning and the catalyst begins to show its original activity. From 600 to 1000 cycles (Fig. 7.9(b)), the catalyst surface changes from Pd-rich state to Pt-rich state due to Pd and Ni dissolution. The steep portion of the LSVs (Fig. 7.10 (b)) is slightly shifted to higher potentials, indicating a minor increase in

the ORR activity due to the formation of Pt-rich surface. After 1500 cycles, the catalyst surface keeps enriching with Pt and the ECSA reduces due to particle size growth with cycling, resulting in a gradual decrease in activity (shown in Fig. 7.10(d)). To validate the activity change relating to the surface structure change, similar experiments were also performed within 0 - 1.05 V and the same phenomenon was observed (see Fig. 7.11 and Fig. 7.12).

The quantitative activity changes in the kinetically controlled regime with cycling and with single cell testing are shown, respectively, in Figs. 7.13 and 7.14. To clearly compare the effects of potential cycling and single cell operation on the catalytic activity, the changes in activity at 0.85 and 0.8 V for $Pd_{50}Pt_{30}Ni_{20}$ are calculated using the following equation and summarized in Table 7.2:

$$\Delta i\% = (i_i - i_f) / i_i \tag{1}$$

where i_i and i_f are the activities corresponding to, respectively, the initial Pd-rich surface after cleaning during cycling (at 500 cycle for 0 - 0.95 V or 400 cycle for 0 - 1.05 V) or after activation during single cell operation (on the 2nd day) and the final Pt-rich surface before deterioration during cycling (at 700 cycle for 0 - 0.95 V or 600 cycle for 0 - 1.05V) or after the performance becomes constant during cell operation (on the 8th day). As seen, the activity increase during cycling at 0.85 V is ~ 30 %, only 1/6 of that during single cell testing; the increase during cycling at 0.8 V is ~ 20 %, just 1/10 of that during single cell testing (for MEA made with Nafion 115). In the case of MEA made with Nafion 112, the difference in activity increase between potential cycling and single cell testing is even more. This again validates the different degrees of compositional and structural changes occurring during cycling and PEMFC single cell testing and accounts for the disparate activity factors measured with RDE and single cell tests.



Figure 7.9: Cyclic voltammograms of $Pd_{50}Pt_{30}Ni_{20}$ recorded in N₂-purged 0.5 M H₂SO₄ at a scan rate of 20 mV/s within 0 – 0.95 V, showing the three steps of surface texture change with cycling: (a) surface cleaning, (b) initial Pd dissolution, and (c) surface decay.



Figure 7.10: Hydrodynamic polarization curves of Pd₅₀Pt₃₀Ni₂₀ recorded in O₂ saturated 0.5 M H₂SO₄ at room temperature and 1600 rpm with a sweep rate of 5 mV/s within 0 – 0.95 V: (a) corresponding to the surface change in step 2, (b) enlarged high-potential region in (a), (c) corresponding to the surface change in step 3, and (d) enlarged high-potential region in (c).



Figure 7.11: Cyclic voltammograms of Pd₅₀Pt₃₀Ni₂₀ recorded in N₂-purged 0.5 M H₂SO₄ at a scan rate of 20 mV/s within 0 – 1.05 V, showing the three steps of surface texture change with cycling: (a) surface cleaning, (b) initial Pd dissolution, and (c) surface decay.



Figure 7.12: Hydrodynamic polarization curves of Pd₅₀Pt₃₀Ni₂₀ recorded in O₂ saturated 0.5 M H₂SO₄ at room temperature and 1600 rpm with a sweep rate of 5 mV/s within 0 – 1.05 V: (a) corresponding to the surface change in step 2, (b) enlarged high-potential region in (a), (c) corresponding to the surface change in step 3, and (d) enlarged high-potential region in (c).



Figure 7.13: Mass activities of $Pd_{50}Pt_{30}Ni_{20}$ in 0.5 M H_2SO_4 at room temperature after various cycle numbers: (a) within 0 – 0.95 V and (b) within 0 – 1.05 V.



Figure 7.14: Mass activities of Pd₅₀Pt₃₀Ni₂₀ at 60 °C in PEMFC after various days: (a) MEA made with Nafion 115 and (b) MEA made with Nafion 112.

Potential (V vs. NHE)	Activity increase during potential cycling (%)		Activity increase during single cell testing (%)	
	0–0.95 V	0–1.05 V	Nafion 115	Nafion 112
0.85	27	49	183	
0.8	22	22	234	1054

Table 7.2: Changes in the activities of $Pd_{50}Pt_{30}Ni_{20}$ during potential cycling and single cell testing.

Back in Fig. 7.7, the specific activity factors of $Pd_{50}Pt_{30}Ni_{20}$, preleached $Pd_{50}Pt_{30}Ni_{20}$, and $Pd_{60}Pt_{40}$ obtained in single cell tests are improved by, respectively, 71, 247, and 460 % compared to those found with the RDE test. $Pd_{50}Pt_{30}Ni_{20}$ and $Pd_{60}Pt_{40}$ are supposed to undergo the same degree of improvement in activity factor due to the same degree of Pd and Ni dissolution (see Table 6.3). However, what we use in single cell test is the whole MEA, a relatively closed system compared to the pure catalyst film in acid electrolyte. The dissolved Ni ions can poison the entire MEA by ion-exchanging with H⁺ in Nafion, lowering the overall MEA performance and accelerating the degradation of the fuel cell. Therefore, the improvement in the specific activity factor of $Pd_{50}Pt_{30}Ni_{20}$ in the single cell test is much smaller than that of $Pd_{60}Pt_{40}$. Similar explanation also works for different degrees of improvement in the activity factor of $Pd_{50}Pt_{30}Ni_{20}$ and the preleached $Pd_{50}Pt_{30}Ni_{20}$. On the other hand, preleached $Pd_{50}Pt_{30}Ni_{20}$ went through smaller changes in both the surface and bulk compositions during single cell testing compared to $Pd_{60}Pt_{40}$.

7.3.4 Comparison of the ORR activities of Pd–Pt–M (M = Ni, Fe, and Cu) electrocatalyts using RDE method

Fig. 7.15 compares the cyclic voltammograms of $Pd_{50}Pt_{30}Fe_{20}$, $Pd_{50}Pt_{30}Ni_{20}$, and $Pd_{50}Pt_{30}$ Cu₂₀ in nitrogen-purged 0.5 M H₂SO₄ at room temperature. The same shape characteristics of a single broad peak and a shoulder near 0 V in the hydrogen adsorption/desorption region suggest similar surface structure for all the three catalysts, dominant by Pd. The peak potential corresponding to the reduction of surface oxide in the cathodic scan follows the order of E_p (Pd₅₀Pt₃₀Ni₂₀, 0.76 V) < E_p (Pd₅₀Pt₃₀Cu₂₀, 0.765 V) < E_p (Pd₅₀Pt₃₀Fe₂₀, 0.769 V), indicating similar M–OH_{ads} binding strength on the catalyst surface. The ECSA values calculated from the hydrogen adsorption region (0.05 to 0.40 V) are listed in Table 1, and they follow the order of Pd₅₀Pt₃₀Fe₂₀ < Pd₅₀Pt₃₀Ni₂₀ < Pd₅₀Pt₃₀Cu₂₀.



Figure 7.15: Cyclic voltammograms of the Pd–Pt– M (M = Ni, Fe, Cu) catalysts synthesized by the modified polyol method and commercial Pt in N₂-purged 0.5 M H₂SO₄ at room temperature with a scan rate of 50 mV/s.

The hydrodynamic polarization curves for ORR on $Pd_{50}Pt_{30}Fe_{20}$, $Pd_{50}Pt_{30}Ni_{20}$, and $Pd_{50}Pt_{30}$ Cu₂₀ are displayed in Fig. 7.16. All three catalysts show a mixed kineticdiffusion control in the whole potential region. Fig. 7.17 and Table 7.3 show a quantitative comparison of the Pt mass-based (A/mg_{Pt}) (Fig. 7.17 (a)), the noble metal mass-based (A/mg_{noble metal}) (Fig. 7.17(b)), and the Pt surface area-based (μ A/cm²_{Pt}) (Fig. 7.17 (c)) activities for all three catalysts in the kinetically controlled regime. As seen, the mass activities of all three catalysts follow the order $Pd_{50}Pt_{30}Fe_{20} < Pd_{50}Pt_{30}Ni_{20} <$ $Pd_{50}Pt_{30}Cu_{20}$, with the highest value of $Pd_{50}Pt_{30}Cu_{20}$ 1.5 times that of commercial Pt. Also, comparing Pd–Pt–M with Pt, it is found that alloying Pt with Pd and different M does not modify much the intrinsic activity. Additionally, the difference in mass activities of all catalysts is attributed to the different ECSA values.



Figure 7.16: Hydrodynamic polarization curves of the Pd–Pt– M (M = Ni, Fe, Cu) catalysts synthesized by the modified polyol method and commercial Pt in O_2 saturated 0.5 M H₂SO₄ at room temperature and 1600 rpm.



Figure 7.17: Catalytic oxygen reduction activities of the Pd–Pt– M (M = Ni, Fe, Cu) catalysts synthesized by the modified polyol method and commercial Pt in 0.5 M H₂SO₄ at room temperature: (a) Pt mass activities, (b) noble metal mass activities, and (c) specific activities.

Catalyst	ECSA (m ² /g _{Pt})	Mass activity @ 0.88V (A/mg _{Pt})	Mass activity @ 0.88V (A/mg _{noble} _{metal})	Specific activity @ 0.88V (µA/cm ² _{Pt})
Pt	74	0.0165	0.0165	22.2
$Pd_{50}Pt_{30}Fe_{20}$	49	0.0118	0.0058	24.0
$Pd_{50}Pt_{30}Ni_{20}$	65	0.0136	0.0067	21.0
Pd ₅₀ Pt ₃₀ Cu ₂₀	107	0.0255	0.0124	23.7

Table 7.3: Electrochemical properties of $300 \,^{\circ}$ C heated Pd–Pt–M (M = Fe, Ni, Cu) and commercial Pt catalysts measured by the RDE method.

7.4 CONCLUSIONS

The catalytic activities of three Pd-Pt(-Ni) alloy catalysts ($Pd_{50}Pt_{30}Ni_{20}$, preleached $Pd_{50}Pt_{30}Ni_{20}$, and $Pd_{60}Pt_{40}$) measured by RDE method and single cell fuel cell test have been compared. The mass activities obtained from single cell test are much more improved (compared to commercial Pt) than those obtained from the RDE experiment. The small increase in ECSA values of MEA cannot account for the remarkable improvement in mass activities. The tremendous increase in specific activities of all the three Pd-Pt(-Ni) alloy catalysts compared to Pt determined from single cell test is the origin for the activity enhancement.

Based on the compositional analysis performed in our study and in Mani's study [10], potential cycling and single cell operation are two different alloying processes. During potential cycling, eletrocatalysts are subjected to more severe electrochemical conditions, undergo more rapid and complete metal dissolution (especially for Pd and Ni), and thus have more enrichment by Pt on the surface and more homogenous structure across the whole particle. This leads to less modification in the electronic structure of the noble metal in the outer surface layers, resulting in smaller changes in intrinsic activities compared to that in pure Pt.

We have also designed experiments to understand the three steps involved in the surface structure change of the Pd–Pt-based alloy catalysts: surface cleaning, initial Pd dissolution, and severe Pd dissolution or surface decay. Corresponding to the change from the Pd-dominant surface to the Pt-dominant surface, the activity increase during single cell testing is extraordinarily higher than that during potential cycling. This explains the final distinct activities obtained from single cell test and RDE test.

The results suggest that the catalytic activity obtained from single cell test may be different from that measured in RDE test. Therefore, it is necessary to perform the single cell tests to determine the activity of the catalysts for real applications. Furthermore, based on the observations and investigations of processes occurring during single cell tests (*e.g.*, dissolution and migration of Pd atoms), better catalysts with desirable composition and surface structure could possibly be designed.

Lastly, based on the RDE method, $Pd_{50}Pt_{30}Cu_{20}$ exhibits the best mass activity among all the Pd–Pt–M (M = Fe, Ni, Cu) catalysts studied, with an improvement of $1.5 \times$ compared to that of commercial Pt. The differences in ECSA contribute to the differences in mass activities.

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CHAPTER 8

Summary

With an aim to improve both the electrocatalytic activity and stability of Pt-based electrocatalysts for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cell (PEMFC) and to reduce the cost of the electrocatalysts, various non-platinum and low-platinum nanostructured Pd-based alloys have been developed and investigated systematically and thoroughly in this dissertation to understand the structure-property-performance relationships.

Carbon-supported Pd–Ni nanoalloy electrocatalysts with controlled particle size and distribution have been synthesized by a modified polyol method, followed by heat treatment at elevated temperatures in 10% H₂–90% Ar atmosphere. The samples have been characterized by XRD, EDS, TEM, XPS, CV, RDE measurements, and single cell PEMFC tests for ORR. XRD and TEM data reveal an increase in the degree of alloying and particle size with increasing heat treatment temperature. XPS data indicate surface segregation with Pd enrichment on the surface of $Pd_{80}Ni_{20}$ after heat treatment at \geq 500 °C, suggesting possible lattice strains in the outermost layers. Electrochemical data show that $Pd_{80}Ni_{20}$ heated at 500 °C has the highest mass catalytic activity for ORR among the Pd–Ni samples investigated. In spite of significantly higher stability and catalytic activity than Pd and higher tolerance to methanol than Pt, the Pd–Ni catalysts exhibit lower stability for long-term operation based on the accelerated durability tests.

Pd–Pt–Ni ternary alloy electrocatalysts with smaller and more homogenous nanoparticles have been synthesized by the same polyol reduction method to improve both the catalytic activity and stability of the Pd–Ni binary alloy electrocatalysts. The

single cell PEMFC evaluation reveals an interesting phenomenon: the MEA performance of the Pd–Pt–Ni catalysts increases continuously in the entire current density range under cell operation until it reaches a value comparable to that of commercial Pt. The MEA is also quite stable within the 180 h of durability test, showing just 3 % degradation at 1000 mA/cm² in the end. The compositional characterizations of the MEA before and after the single cell testing suggest the formation of a Pd-rich core–Pt rich shell structure during single cell testing due to the dissolution of Pd and Ni. The strain effect (also electronic effect) caused by the lattice mismatch between the surface and core components can enhance the catalytic activity and thus the overall cell performance. TEM observation of the MEA cross-section demonstrates redeposition of the Pd ions upon reduction by crossover hydrogen within the whole MEA and ion-exchange of Ni ions with the protons at the sulfonic groups in Nafion. The contamination caused by both the Pd deposition and Ni ion-exchange may account for the MEA degradation. Moreover, Pd–Pt–Fe and Pd–Pt– Cu ternary electrocatalysts also exhibit similar performance increase during single cell tests.

To fully understand the changes in the MEA performance during cell operation for the Pd–Pt–M ternary electrocatalysts, the MEA of Pd–Pt–Ni has been characterized by *in-situ* electrochemical methods including EIS and CV. The invariable membrane resistance and continually decreasing charge transfer resistance from EIS illustrate that the enhanced interfacial kinetics at the cathode contributes to the cell voltage increase. From the CV data, the ECSA values decrease with cell operation; the catalyst surface changes from Pd-enrichment to Pt-enrichment, and the peak potential of surface oxide stripping shift positively upon metal dissolution under the operation conditions. The latter serves as the origin for the enhancement in catalytic activity and the overall cell performance. Preleached Pd–Pt–Ni nanparticles and binary Pd–Pt nanoalloy have been investigated as cathode catalysts for PEMFC. The electronic effect, together with the surface morphology and geometric effect, induced by compositional and structural changes upon metal dissolution, may result in activity improvement for all the Pd-Pt-based catalysts. From this standpoint, preleaching the catalyst in acid electrolyte prior to fuel cell test proves to be an effective method to further enhance the overall performance and durability by pre-selective dissolution of unstable Pd and Ni, resulting in larger changes in composition and structure and alleviating contamination by dissolved metal ions. The preleached catalyst shows surface catalytic activity improvement by a factor of 2 in terms of Pt-mass activity and 3.5 in terms of specific activity compared to commercial Pt. On the other hand, Pd–Pt with a similar composition to that of Pd–Pt–Ni after the fuel cell test exhibits performance similar to that of Pd–Pt–Ni, but its durability should be much improved due to the absence of Ni and the consequent poisoning effect.

The catalytic activities of Pd–Pt–Ni alloy catalysts analyzed by the RDE method are compared with those analyzed by the PEMFC single cell test. The improvement in the catalytic activities of Pd–Pt–Ni alloy catalysts compared to commercial Pt measured by the RDE test are much lower than those obtained from the single cell test. Catalysts under cycling potential are subject to more severe electrochemical conditions, and thus undergo more rapid and complete change in composition and structure upon metal dissolution, resulting in more homogenous particles with less modification of surface electronic structure. On the other hand, the significant surface change from the Pd-rich state to Pt-rich state during single cell operation leads to a much significant increase in catalytic activity. The study demonstrates the importance and necessity of single cell tests for evaluating the real activities of nanoalloy electrocatalysts in practical applications. In addition, RDE measurements of the Pd–Pt–M (M = Fe, Ni, Cu) catalysts reveal that Pd–

Pt–Cu has the best catalytic activity for ORR, demonstrating the differences in the influence of various elements on modifying the catalytic activities.

List of Publications

- J. Zhao, A. Sarkar, A. Manthiram, "Synthesis and characterization of Pd-Ni nanoalloy electrocatalysts for oxygen reduction reaction in fuel cells", Electrochim. Acta 55 (2010) 1756-1765.
- 2. J. Zhao, J. Karalee, A. Manthiram, "Performance and stability of Pd–Pt–Ni nanoalloy electrocatalysts in PEMFC", J. Phy. Chem. C. (submitted).
- J. Zhao, A. Manthiram, "In-situ electrochemical characterizations of Pd–Pt–Nibased PEM fuel cells", J. Electrochem. Soc. (submitted).
- J. Zhao, A. Manthiram, "Preleached Pd–Pt–Ni and binary Pd–Pt nanoparticles as ORR electrocatalysts in proton exchange membrane fuel cells", Appl. Catal. B. (submitted).
- J. Zhao, A. Manthiram, "Comparison of the catalytic activities measured by rotating disk electrode and single cell tests for oxygen reduction reaction", Electrochim. Acta (submitted).

Vita

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