New catalyst materials for hydrogen fed fuel-cells and hydrogen storage on double walled carbon nanotubes

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New Catalyst Materials for Hydrogen Fed Fuel-Cells and hydrogen storage on Double walled carbon nanotubes

A thesis submitted in fulfilment of the requirements for the award of the degree

Doctor of Philosophy

From
University of Wollongong

By
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July 2011
I, Huimin Wu, declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting & Electronic Materials, Faculty of Engineering, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

July 2011
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Abstract

Hydrogen, as a clean and efficient energy carrier, has been proposed as an alternative energy source. Usage and storage are the two main interrelated issues for hydrogen. Fuel cells are considered to be the green power sources for the 21st century and may make the “hydrogen economy” a reality. Among all the noble metals, Pt exhibits the highest catalytic activity towards the oxygen reduction reaction, and carbon-supported Pt is still the state of-the-art electrocatalyst for fuel cells. However, in order to further reduce the voltage losses associated with the cathode performance and reduce costs, it is necessary to develop oxygen reduction reaction (ORR) electrocatalysts that are more catalytically active but cheaper than platinum. At the same time, the ability to store hydrogen onboard vehicles is a key technological issue for the development of fuel cells. This thesis consists of two parts devoted respectively to new catalyst materials for oxygen reduction of PEM fuel cells and hydrogen storage on Carbon-Based Adsorbents.

I. New catalyst materials for oxygen reduction of PEM fuel cells

Proton exchange membrane fuel cells (PEMFCs) are a class of devices used for the conversion of chemical energy into electrical energy. Noble metals, such as Pt supported on high surface area carbons, are typically used as electrocatalysts for PEM fuel cells [5-7]. The resultant high cost is one of the obstacles preventing the popular usage of PEM fuel cells. In order to reduce costs, one method is to synthesize platinum-based binary or ternary electrocatalysts. Another approach is to prepare Pt nanoparticles supported on carbon materials. I have focused on new catalyst materials for oxygen reduction of PEM fuel cells and achieved the following:
Abstract

1. Synthesis of two kinds of Pt-M alloy (Pt-Ni and Pt-Co) through the chemical reduction method - Electrochemical testing and physical characterization of as-prepared catalysts have also been conducted. Although these Pt$_x$Ni and Pt$_{1-x}$Co$_x$ alloy catalysts contain a reduced content of Pt, they exhibit significantly enhanced catalytic activity towards oxygen reduction compared to pure platinum catalyst.

2. Synthesis of two kinds of special core-shell structure catalyst materials - Structural characterization to confirm the special structure was carried out. And electrochemical tests show that although the Co$_{core}$-Pt$_{shell}$ particles have a much reduced content of Pt, they exhibit significantly enhanced catalytic activity toward oxygen reduction as compared to pure Pt catalyst,

3. Acid treatments to improve the surface properties of carbon – The results show that the Pt nanocatalysts exhibited enhanced activity in the oxygen reduction reaction (ORR) on the activated carbon compared to the pristine carbon black.

4. CNTs and graphite as catalyst supports - 20wt% Pt/C catalysts with Vulcan XC-72 (BASF), pristine double-walled carbon nanotubes (DWCNTs), and activated double-walled carbon nanotubes as the carbon sources, are investigated. The results show that the Pt nanocatalysts exhibited enhanced electrochemically active surface areas and improved activity in the oxygen reduction reaction (orr) on the activated DWCNTs compared to the pristine DWCNTs or the Vulcan XC-72. Also, I have found that the use of graphene can be promising in effectively reducing the carbon corrosion problem.

II. Hydrogen storage on Carbon-Based Adsorbents

Hydrogen has emerged as one of the most promising candidates for the replacement of current carbon-based energy services because of its zero CO$_2$ emission. Storage is one of
the key issues for the realization of fuel-cell powered vehicles using hydrogen as the energy carrier. However, how to store hydrogen easily and cheaply is still a big problem. As research on hydrogen storage is an important subject, and carbon nanotubes are new materials for hydrogen storage, I have carried out the hydrogen storage properties of CNTs. The achievements are as follows:

1. Hydrogen storage properties of double-walled carbon nanotubes (DWCNTs) at ambient temperature - Using Pd catalyst for dissociation of H₂ into atomic hydrogen and KOH activation for formation of defects on DWCNT surface, the defect sites on DWCNTs as adsorption sites of atomic hydrogen were created by chemical activation using KOH. Pd nanoparticles loaded on DWCNT surfaces for dissociation of H₂ into atomic hydrogen, which spills over to the defect sites on the DWCNTs. Both led directly to enhanced hydrogen storage compared to that on pristine carbon nanotubes. So I found that the hydrogen storage capacity can be enhanced by chemical activation and loading with Pd nanoparticles.

2. Effects of different reductants for palladium loading on the hydrogen sorption characteristics of double-walled carbon nanotubes (DWCNTs) - Pd nanoparticles were loaded on DWCNT surfaces for dissociation of H₂ into atomic hydrogen, which spills over to the defect sites on the DWCNTs. When using different reductants, the reduction capabilities and other effects of the different reductants are different, which affect the hydrogen storage capacity of the DWCNTs. I have found that the hydrogen storage capacity can be enhanced by loading with 2% Pd nanoparticles and selecting a suitable reductant. Furthermore, the sorption can be attributed to the chemical reaction between atomic hydrogen and the dangling bonds of the DWCNTs.
Key words: cathode catalyst; oxygen reduction reaction; Platinum-Nickel; chemical reduction; PEM Fuel cells; Pt-Co alloy; Core-shell nanostructure; Ni@Pt nanoparticles; Hydrogen storage material; Carbon nanotube; Chemical activation; Adsorption; Dissociation; Spillover; Different reductant.
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### NOMENCLATURE

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<tr>
<td>PEMFC</td>
<td>Proton exchange membrane fuel cell</td>
</tr>
<tr>
<td>DFAFC</td>
<td>Direct formic acid fuel cell</td>
</tr>
<tr>
<td>DEFC</td>
<td>Direct ethanol fuel cell</td>
</tr>
<tr>
<td>AFC</td>
<td>Alkaline fuel cell</td>
</tr>
<tr>
<td>PCFC</td>
<td>Proton ceramic fuel cell</td>
</tr>
<tr>
<td>DBFC</td>
<td>Direct borohydride fuel cell</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric acid fuel cell</td>
</tr>
<tr>
<td>MCFC</td>
<td>Molten carbonate fuel cell</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid oxide fuel cell</td>
</tr>
<tr>
<td>DMFC</td>
<td>Direct methanol fuel cell</td>
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<tr>
<td>ORR</td>
<td>oxygen reduction reaction</td>
</tr>
<tr>
<td>MEA</td>
<td>membrane electrode assembly</td>
</tr>
<tr>
<td>GDL</td>
<td>gas diffusion layers</td>
</tr>
<tr>
<td>PTFE</td>
<td>poly-tetrafluoroethylene</td>
</tr>
<tr>
<td>$\eta_a$</td>
<td>activation polarization</td>
</tr>
<tr>
<td>$\eta_o$</td>
<td>ohmic polarization</td>
</tr>
<tr>
<td>$\eta_c$</td>
<td>concentration polarization</td>
</tr>
<tr>
<td>FCV</td>
<td>Fuel-cell vehicles</td>
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### Nomenclature

<table>
<thead>
<tr>
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<tr>
<td>DOE</td>
<td>Department of Energy</td>
</tr>
<tr>
<td>PEM</td>
<td>proton exchange membrane</td>
</tr>
<tr>
<td>fcc</td>
<td>face-centered cubic</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>MO</td>
<td>molecular orbital</td>
</tr>
<tr>
<td>ToFSIMS</td>
<td>time-of-flight secondary ion mass spectrometry</td>
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<tr>
<td>PTCDA</td>
<td>perylene tetracarboxylic dianhydride</td>
</tr>
<tr>
<td>E\text{onset}</td>
<td>onset electrode potentials</td>
</tr>
<tr>
<td>RHE</td>
<td>reversible hydrogen electrode</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>HSAG</td>
<td>High surface area graphite</td>
</tr>
<tr>
<td>CB</td>
<td>carbon black</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>MCs</td>
<td>mesoporous carbons</td>
</tr>
<tr>
<td>OMCs</td>
<td>ordered mesoporous carbons</td>
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<tr>
<td>CNTs</td>
<td>carbon nanotubes</td>
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<td>carbon nanocoils</td>
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<tr>
<td>SWCNT</td>
<td>single-wall carbon nanotubes</td>
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<td>MWCNT</td>
<td>multiwall carbon nanotubes</td>
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<tr>
<td>Abbreviation</td>
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<td>--------------</td>
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<tr>
<td>DWCNH</td>
<td>Double-wall carbon nanohorn</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>ACFs</td>
<td>Activated carbon fibers</td>
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<tr>
<td>CNFs</td>
<td>Carbon nanofibers</td>
</tr>
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<td>GNFs</td>
<td>graphite nanofibers</td>
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<td>BDDs</td>
<td>Boron-doped diamonds</td>
</tr>
<tr>
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<td>templated carbons</td>
</tr>
<tr>
<td>MOFs</td>
<td>metalorganic frameworks</td>
</tr>
<tr>
<td>DWCNTs</td>
<td>double walled carbon nanotubes</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FEG-SEM</td>
<td>field emission gun scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>HRTEM</td>
<td>high resolution TEM</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauere-Emmette-Teller</td>
</tr>
<tr>
<td>TPD</td>
<td>temperature- programmed-desorption</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammograms</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
</tr>
<tr>
<td>ECSA</td>
<td>electrochemically active surface area</td>
</tr>
<tr>
<td>HOR</td>
<td>hydrogen oxidation reaction</td>
</tr>
<tr>
<td>2D</td>
<td>two-dimensional</td>
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<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<td>--------------</td>
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</tr>
<tr>
<td>DI</td>
<td>de-ionised</td>
</tr>
<tr>
<td>SAED</td>
<td>selected area electron diffraction</td>
</tr>
<tr>
<td>$H_{\text{upd}}$</td>
<td>underpotentially deposited hydrogen</td>
</tr>
<tr>
<td>$i_{\text{kin}}$</td>
<td>kinetic current</td>
</tr>
<tr>
<td>$i_{\text{lim}}$</td>
<td>limiting current</td>
</tr>
<tr>
<td>$i_{\text{obs}}$</td>
<td>observed current</td>
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</table>
Chapter 1 Introduction

1.1 General background

Ever increasing energy consumption, rising public awareness of the need for environmental protection, and the existing nature of fossil fuels have resulted in a great research effort focused on alternative/renewable energy sources. Small-scale generation systems, such as wind turbines, photovoltaic cells, micro-turbines, fuel cells, etc., could play an important role in meeting the consumer demand by using the concepts of distributed generation. The term “distributed generation” means any small-scale generation that is located near the customers rather than at central or remote locations. The major benefits of distributed generation systems (DGs) are savings in losses over long transmission and distribution lines, installation costs, local voltage regulations, and the ability to add a small unit instead of a larger one during peak load conditions [1]. Among the different distributed generation systems, the greatest interest is being focused on fuel cells, because they have the potential capability of providing both heat and power.

Fuel cells are static energy conversion devices that convert the chemical reaction of fuels directly into electrical energy and produce water as its byproduct [2,3]. Conventional heat engines, on the other hand, produce electricity from chemical energy with the use of intermediate mechanical energy conversion, which results in reduced efficiency compared with fuel cells. The fuel cells combine the best features of engines and batteries; like an engine, they can operate for as long as fuel is available without any intermediate mechanical energy conversion, while the characteristics of fuel cells are similar to those of a battery under load conditions [4]. Some of the special issues in distributed power generation, which involve interfacing the fuel cells with grid connections and taking
advantage of their relevant aspects to control the grid voltage and frequency to improve the quality of supply, are also discussed in the literature [5].

Cells are classified according to the choice of electrolyte and fuel. Presently six major different types of fuel cells are available.

1) Proton exchange membrane fuel cell (PEMFC):
   (a) Direct formic acid fuel cell (DFAFC); (b) Direct ethanol fuel cell (DEFC).

2) Alkaline fuel cell (AFC):
   (a) Proton ceramic fuel cell (PCFC); (b) Direct borohydride fuel cell (DBFC).

3) Phosphoric acid fuel cell (PAFC)

4) Molten carbonate fuel cell (MCFC)

5) Solid oxide fuel cell (SOFC)

6) Direct methanol fuel cell (DMFC)

They are further classified on the basis of operating temperature. Low operating temperature is in the range of (50–250) °C and is used for PEMFC, AFC, and PAFC fuel cells, while high operating temperature in the range of (650–1000) °C and used for MCFCs and SOFCs.

At the same time, with increasing demands for environmental protection from pollution from the current use of fossil fuels, hydrogen, as a clean and efficient energy carrier, has been proposed as an alternative energy source. Usage and storage are the two main interrelated issues for hydrogen. The ability to store hydrogen onboard vehicles is a key technological issue for the development of fuel cells. However, how to store hydrogen easily and cheaply is still a big problem [6]. Up to now, none of the materials and methods for hydrogen storage has been found to meet all the demands required for commercial electric-vehicle applications.
1.2 Statement of problems

1.2.1 Fuel cells

A comparison of the major six fuel cells types based on their inlet fuels, electrolyte material, cost, advantages, disadvantages, and their suitability for application is presented in this chapter. From the comparison, it is clear that the PEM fuel cell is more suitable for residential and commercial applications due to its low working temperature (50–100 °C) and fast start up, but for the medium and large-scale power applications the best choices are MCFCs and SOFCs. The SOFCs operate at the highest temperature among the all fuel cells, providing very high efficiency, internal reforming, fuel flexibility, and high quality by-product heat for cogeneration operation. This means that the efficiency of the system can reach as high as 80% with combined cogeneration operations and low emission of greenhouse gases. However, its high initial cost is the major drawback.

Therefore, further research is going on with these fuel cells to reduce the operating temperature and to reduce their higher installation cost.

1.2.2 Hydrogen storage

For hydrogen energy, researchers in the hydrogen-storage field must face the challenge: how to combine high hydrogen storage capacity and fast kinetics at ambient temperatures. Meeting this target requires major advances in new materials, such as novel nanotubes that can physisorb hydrogen inside the tubes and in the open interstitial pore spaces between the tubes.

1.3 Importance of study
Among all the noble metals, Pt exhibits the highest catalytic activity towards the oxygen reduction reaction, and carbon-supported Pt is still the state-of-the-art electrocatalyst for PEM fuel cells. However, in order to further reduce the voltage losses associated with the cathode performance, it is necessary to develop oxygen reduction reaction (ORR) electrocatalysts that are more catalytically active than platinum. On the other hand, Pt is expensive, and the world’s supply is limited. In order to reduce costs, one method is to prepare Pt nanoparticles supported on carbon, which helps to lower the platinum loading in the PEM fuel cells. Another approach is to synthesize platinum-based binary or ternary electrocatalysts. It is an urgent and challenging issue to find a cheaper catalyst for fuel cells.

The use of hydrogen requires an effective, safe, and stable storage medium. The US Department of Energy has set target system gravimetric and volumetric energy densities at 6.5 wt% and 62 kg H₂ per m³, respectively [7]. There are a number of potential ways in which this could be achieved, including compressed hydrogen at pressures of up to 700 bar (10 000 psi), liquid hydrogen, and metal hydride storage. All of these methods have both advantages and drawbacks. So, it is very important to find a suitable method of hydrogen storage for application.

1.4 Objectives and scopes of research

In order to reduce the cost of fuel cells and increase the new materials’ capability for hydrogen storage, the research work reported in this thesis has been focused on the following areas:

(1) Chapter 1 Introduction
(2) Chapter 2 Literature review

(3) Chapter 3 Experimental details

(4) Chapter 4 Pt-M alloy nanoparticles as cathode catalyst for PEM fuel cells

(5) Chapter 5 $M_{\text{Core}}$-$Pt_{\text{Shell}}$ structure nanoparticles as cathode catalyst for PEM fuel cells

(6) Chapter 6 The effects of carbon support on cathode catalysts performance for PEM fuel cells

(7) Chapter 7 The effect of chemical processing on hydrogen storage capacity of double-walled carbon nanotubes

(8) Chapter 8 General conclusions and outlook

References


Chapter 2 Literature review

2.1 Catalyst materials for oxygen reduction of Proton Exchange Membrane fuel cells

Fuel cells are considered to be the green power sources for the 21st century and may make the “hydrogen economy” a reality. The main driving force for fuel cell research, development, and commercialization is the increasing concern about global pollution caused by energy emission, especially from transportation and stationary applications [1]. Fuel cell vehicle technologies are those that enable mass production of affordable hydrogen-powered fuel cell vehicles and the hydrogen-supply infrastructure to support them. Among the vehicle technology options, proton exchange membrane(PEM) fuel cells, also referred to as solid polymer fuel cells, are favored for use in automobiles ([2], and many others). This preference is due to the high power density, relatively quick start-up, rapid response to varying loads, and low operation temperature provided by PEM fuel cells.

2.1.1 The principles and applications of PEM fuel cells

2.1.1.1 The principles of PEM fuel cells

Fig. 2-1 depicts the key components of PEM fuel cells. As shown, a single PEM fuel cell comprises three types of components: a membrane electrode assembly(MEA), two bipolar plates, and two seals. The MEA is the key component of the PEM fuel cell. The MEA is sandwiched between two graphite plate current collectors, with machined
microchannels, as in microchannel reactors [3], for gas distribution. In its simplest form, the MEA consists of a membrane, two dispersed catalyst layers, and two gas diffusion layers (GDL). The membrane separates the half reactions, allowing protons to pass through to complete the overall reaction. The electrons created on the anode side are forced to flow through an external circuit, thereby creating current. The GDL serves as the electron collector and allows direct and uniform access of the fuel and oxidant to the catalyst layer, which stimulates each half reaction. The PEM requires water for effective proton transport, which limits the practical operating temperature of atmospheric fuel cells to about 80 °C (when water vapor pressure is roughly half an atmosphere). However, if the pores of the gas-diffusion layers are filled with liquid water, transport of oxygen and hydrogen to the catalyst layers is impeded, severely limiting the fuel cell performance. This is avoided by imparting hydrophobicity to the gas-diffusion layer to allow gas and liquid phases to co-exist within pores. The gas-diffusion backing typically involves a carbon cloth, about 350μm in thickness and woven from carbonfibers, on one side of which the catalyst layer is deposited. The carbon cloth is treated with 40–70 wt.% poly-tetrafluoroethylene (PTFE, e.g., Teflon®) mixed with 10–20 nm carbon particles, followed by sintering to melt the PTFE and coat the carbonfibers[4], rendering it quite hydrophobic. The initial porosity of the carbon cloth is 70–80%, but its final porosity is 55–65%. The catalyst layer is 5–50 μm in thickness and contains catalyst materials supported on the surface of largely non-porous carbon black particles. The interstitial spaces among the carbon particles are filled with an ionomer solution (e.g.,Nafion®) to allow proton transport [5], and occasionally with some
poly-tetrafluoroethylene, although the latter may not be necessary for thin catalyst layers [6]. The deposition of the catalyst layer on the gas-diffusion electrode is accomplished by painting, spraying, or filtration of the catalyst/ionomer dispersion. A polymer electrolyte membrane (e.g. Nafion® 115 or 117), 50–175 μm thick, is hot-pressed at a temperature slightly above its glass transition temperature between the two electrodes, so that the catalyst layers are on either side of the membrane. Procedures such as alternate fabrication were also employed by Lee et al [8]. The bipolar plates typically have four functions: (1) to distribute the fuel and oxidant within the cell; (2) to facilitate the water management within the cell; (3) to separate the individual cells in the stack; (4) to carry current away from the cell. In the absence of dedicated cooling plates, the bipolar plates also facilitate heat management.

![Fig.2-1 Schematic diagram of PEMFC Structure [8]](image)

For PEM fuel cells, the oxidant is oxygen or air, and the fuel is H₂. The catalyzed cathode reaction within the catalyst layer is:

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \text{V} = 0\text{V vs. SHE} \quad [2-1]
\]

And the corresponding anode reaction is:

\[
2H_2 \rightarrow 4H^+ + 4e^- \quad \text{V} = 1.229\text{V vs. SHE} \quad [2-2]
\]
The whole reaction is:

\[ O_2 + 2H_2 \rightarrow 2H_2O \quad E = 1.229V \text{ vs. SHE} \quad [2-3] \]

where SHE is standard hydrogen electrode.

The \( H_2 \) is split into protons and electrons at the anode electrocatalyst. Protons find their way to the cathode through the PEM, while the electrons arrive at the cathode via the external circuit after performing useful work. Here, aided by the electrode potential, the protons and electrons recombine with \( O_2 \) at the catalyst surface to form water. As shown in Fig.2-2:

![Fig.2-2 Schematic diagram of the operating principles of a PEMFC][8]

A PEM fuel cell is a part of a galvanic cell, and will change the energy of the chemical reaction to electrical energy. The Gibbs energy of the chemical reaction (\( \Delta G \)) and the ideal potential (\( \Delta U_0 \)) follow the equation:

\[ \Delta G = -nF\Delta U_0 \quad [2-4] \]

Where \( n \) is the electron transfer number and \( F \) is the Faraday constant.

The ideal efficiency of PEM fuel cells is 92.5%, and the actual efficiency can be up
to 60-80%. This is obviously higher than that of the Carnot cycle (<40%).

In practice, owing to different loss of the electrode, electrical power from the PEM fuel cells can effectively only be obtained when the actual potential is obviously lower than the ideal potential. Typical I-V curves are shown in Fig. 2-3. We can see that the polarizations are of three types: (1) activation polarization ($\eta_a$); (2) ohmic polarization ($\eta_o$); (3) concentration polarization ($\eta_c$). It is these polarizations that cause the actual potential to deviate from the ideal polarization ($\eta$).

\[ V_{cell} = V_{cathode} - V_{anode} - iR \quad \text{[2-5]} \]

\[ V_{cell} = \Delta E_e - |\eta_{cathode}| - |\eta_{anode}| - iR \quad \text{[2-6]} \]

Where $\Delta E_e = E_{cathode} - E_{anode}$, indicating ideal balanced potential;

$V_{cathode}$: potential on cathode electrode;

$V_{anode}$: potential on anode electrode;

Fig.2-3 Ideal and actual PEM fuel cell Voltage/Current characteristics [8]
Chapter 2

$V_{cell}$: actual working potential of PEM fuel cell;

$\eta_{\text{cathode}} / \eta_{\text{anode}}$: the polarization potential on cathode or anode electrode;

$i$: the working current of PEM fuel cell;

$R$: the ohmic resistance of the PEM fuel cell.

So, the developing of high activity cathode and anode catalysts is an effective way to reduce the activation polarization of the electrode, increase the working potential, and raise the energy density of PEM fuel cells.

2.1.1.2 The applications and challenges of PEM fuel cells

The very first fuel cell was invented in 1839 by Sir William Robert Grove, although no practical use was found for another century. General Electric Company (GE) began developing fuel cells in the 1950s and was awarded the contract for the Gemini space mission in 1962. The 1 kW Gemini fuel cell system had a platinum loading of 35 mg Pt/cm$^2$ and performance of 37 mA/cm$^2$ at 0.78 V [7]. In the 1960s improvements were made by incorporating Teflon in the catalyst layer directly adjacent to the electrolyte, as was done with the GE fuel cell at the time. Considerable improvements were made from the early 1970s onward with the adoption of the fully fluorinated Nafion membrane. However, research and development of PEM fuel cells did not receive much attention or funding from the federal government, in particular the US Department of Energy (DOE), or industry until a couple of decades ago or so, when breakthrough methods for reducing the amount of platinum required for PEM fuel cells were developed and subsequently improved by Los Alamos National Laboratory (LANL) and others.
Notably, Raistrick of LANL came up with a catalyst-ink technique for fabricating the electrodes [8]. This breakthrough method made it possible to increase the utilization of active catalyst and at the same time to reduce the amount of precious platinum metal needed.

The major application of PEM fuel cells is in transportation primarily because of their potential impact on the environment, e.g. the control of emissions of greenhouse gases (GHG). Other applications include distributed/stationary and portable power generation. Most major motor companies work solely on PEM fuel cells due to their high power density and excellent dynamic characteristics as compared with other types of fuel cells. Fuel-cell vehicles (FCV) have been developed and demonstrated, e.g. the GM Hydrogen 1, Ford Demo IIa (Focus), Daimler Chrysler NeCar4a, Honda FCX-V3, Toyota FCHV, Nissan XTERRA FCV, VW Bora HyMotion, and Hyundai Santa Fe FCV. Auto makers such as Toyota, Honda, Hyundai, Daimler, and General Motors (GM) have announced plans for commercializing their fuel-cell vehicles by 2015 [9]. Distributed PEM fuel cell power systems are primarily focused on small-scale applications (50–250 kW for decentralized use or <10 kW for households) [10]. Early designers considered fuel cells for residential power supply, in which the waste heat of fuel cells can be utilized for household usage – this significantly increases the overall efficiency [11]. Backup power for banks and telecommunication companies has been receiving growing interest recently because of the extremely high cost associated with power breakdowns. Several units, such as Plug Power GenSys and Ballard FCgen™ 1020 ACS fuel cell systems, have been developed and deployed in many locations. Another promising area
is portable power supply, considering that the limited energy capacity of batteries is unlike to meet the fast-growing energy demands of modern portable electric devices such as lap tops, cell phones and military radio/communication devices. PEM fuel cells provide continuous power as long as hydrogen fuel is available, and they can be fabricated in small sizes without efficiency loss. Major electronics companies, such as Toshiba, Sony, Motorola, LG, and Samsung, have in-house R&D units for portable fuel cells. Through the research and development efforts during the past decade, Pt loading of $\sim 0.3 \text{ mg/cm}^2$ has been achieved in many demonstration units. The target set by the US Department of Energy (DOE) is 0.2 mg/cm$^2$ by 2015, with a corresponding volumetric performance goal of 650 W/L. A cost of $61/	ext{kW}$ for a cell was achieved in 2009, whereas a lifetime of around 2500 h was reported for transportation PEM fuel cells. For stationary power generation, a lifetime of 20,000 h was achieved in 2005. Currently, over 200 fuel-cell vehicles, more than 20 fuel-cell buses, and about 60 fuelling stations are operating in the United States. Approximately 75,000 fuel cells for stationary power, auxiliary power, and specialty vehicles have been shipped worldwide, and among them, about 24,000 systems were manufactured in 2009, approximately a 40% increase over 2008 [9].

Although many technical and associated fundamental breakthroughs have been achieved during the last two decades, the worldwide commercialization of PEM fuel cells has not yet eventuated [12–13]. The two greatest barriers are durability and cost [9]. Fuel cell components, such as the MEA [14], suffer degradation during long-term operation. The lifetime required of a commercial fuel cell is over 5000 operating hours.
for lightweight vehicles and over 40,000 h for stationary power generation with less than a 10% performance decay [15,16]. Currently, most fuel cells exhibit major performance decay after around a thousand hours of operation [15,17,18]. The DOE targets are to achieve a lifetime of 40,000 h by 2011 with 40% efficiency for distributed power and 5000 h durability by 2015 with 60% efficiency for transportation. Note that the 3 M Company recently achieved over 7500 h of durability for the membrane electrode assembly (MEA) in their single-cell testing at the laboratory level, making it feasible to meet the DOE 2010 target [19]. In the past several years, the fuel cell cost has been reduced from $275/kW in 2002 ($108/kW in 2006 and $94/kW in 2007) to $73/kW in 2008, which equates to almost $6000 for an 80 kW system, which is still more than twice as expensive as internal-combustion engine systems. In 2009, the cost was further bought down to $61/kW ($34/kW for balance of plant, including assembly and testing, and $27/kW for the stack), a greater than 35% reduction in the last two years. One important component of the fuel cell cost is due to the MEA, which consists of a Nafion membrane and catalyst (usually Pt-based) layers. The Pt loading has been reduced by two orders of magnitude in the past decade, and there is still room for further loading reduction. The 2010 and 2015 DOE targets for the fuel cell cost is $45/kW and $30/kW, respectively, for transportation applications [19]. Fig. 4 shows the breakdown of fuel cell cost.

2.1.2 Cathode reaction and kinetics

A cathode reaction of PEM fuel cells is oxygen reduction reaction (ORR), but the
research on the reaction mechanism is sparse and inferior to that on the hydrogen reaction. Oxygen reduction is an irreversible reaction, and the ideal potential is 1.23 V. Even if we use a noble metal, such as Pt, etc., the polarization potential is about 0.2 V.

The kinetics of oxygen reduction is also a complicated 4-electron process, involving many intermediate particles (such as hydrogen peroxide, metal oxide). So, it is very necessary to do some research on cathode catalysts for PEM fuel cells.

Normally, the oxygen reduction reaction is through 4-electron or 2-electron steps. The following is the reduction process in acid or alkaline solution [20]:

1. direct 4-electron reaction

   (1) Acid system:
   \[ \text{O}_2 + 4\text{H}^+ + 4e \rightarrow 2\text{H}_2\text{O} \quad E^\circ = 1.229 \text{ V vs. SHE} \]  
   [2-7]

   (2) Alkaline system:
   \[ \text{O}_2 + 2\text{H}_2\text{O} + 4e \rightarrow 4\text{OH}^- \quad E^\circ = 0.401 \text{ V vs. SHE} \]  
   [2-8]

2. electron reaction:

   (1) Acid system

   The first step
   \[ \text{O}_2 + 2\text{H}^+ + 2e \rightarrow \text{H}_2\text{O}_2 \quad E^\circ=0.67\text{V vs. SHE} \]  
   [2-9]
The second step

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e} \rightarrow 2\text{H}_2\text{O} \quad E^\circ = 1.77 \text{ V vs. SHE} \quad [2-10] \]

or \[ 2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \quad [2-11] \]

(2) alkaline system

First step

\[ \text{O}_2 + \text{H}_2\text{O} + 2\text{e} \rightarrow \text{HO}_2^- + \text{OH}^- \quad E^\circ = -0.065 \text{ V vs. SHE} \quad [2-12] \]

Second step

\[ \text{HO}_2^- + \text{H}_2\text{O} + 2\text{e} \rightarrow 3\text{OH}^- \quad E^\circ = 0.867 \text{ V vs. SHE} \quad [2-13] \]

or \[ 2\text{HO}_2^- \rightarrow 2\text{OH}^- + \text{O}_2 \quad [2-14] \]

The reaction mechanism and the effects of the electrocatalyst on the oxygen reduction reaction (ORR) have been extensively studied and discussed. Many reaction mechanisms have been proposed to describe the ORR in aqueous electrolytes. Among these models, the Damjanovic model (Fig. 5) is one of the most extensively employed: this is due to its applicability over a wide potential region [21–22]. The Damjanovic model describes the ORR as a multi-electron reaction, \( \text{O}_2 \) molecules in the vicinity of the electrode are irreversibly reduced directly to \( \text{H}_2\text{O} \) through 4-electron transfer (at a constant rate, \( k_3 \)) or to \( \text{H}_2\text{O}_2 \) through 2-electron transfer (constant rate, \( k_1 \)). The \( \text{H}_2\text{O}_2 \) formed can be reduced to \( \text{H}_2\text{O} \) through 2-electrons transfer (constant rate, \( k_2 \)) or diffuse into the bulk solution. The low value of the limiting current obtained from ORR in aqueous solutions is due to the low solubility of oxygen.

\[ \begin{align*}
\text{O}_2 & \xrightarrow{k_1} \text{O}_{2,\text{ad}} \\
\text{O}_{2,\text{ad}} & \xrightarrow{k_2} \text{H}_2\text{O}_{2,\text{ad}} \xrightarrow{k_3} \text{H}_2\text{O}
\end{align*} \]

Fig. 2-5 Damjanovic model for oxygen reduction reaction.

PN Ross Jr. et al. [9,10] thought that although the above model has some questions to
resolve, it actually works through 2-electron transfer in the oxygen reduction reaction when Pt or Pt alloy is used as the cathode catalyst. Anyway, the step where oxygen absorbs one electron and is transformed to an intermediate material is the key step and controls the whole reaction. The reaction can be described by the following equation:

\[
i = nFKC_{O_2}(1-\Theta_{ad})^x \exp(-\beta F Z/RT) \exp(-\gamma r \Theta_{ad})/RT\]  

[2-15]

\(n\): electron transfer number;

\(K\): constant of the chemical reaction;

\(C_{O_2}\): concentration of \(O_2\) in the solution;

\(\Theta\): surface coverage of adsorption;

\(X\): 1 (single adsorption) or 2 (double adsorption);

\(I\): current density;

\(E\): potential;

\(\beta/\gamma\): symmetrical factor, 1/2;

\(r\Theta_{ads}\): apparent activation energies of adsorptions.

Obviously, electrode surfaces can influence the catalytic behavior towards oxygen reduction. The catalytic behavior also has some relationship to the adsorptions of oxygen and intermediate materials.

E. Yeager [23] described how the oxygen undergoes three kinds of adsorptions on the surface of the electrode according to the three models below:

(A) Griffiths model (Fig. 2-6A):

Oxygen molecules have a reaction with metal in a landscape orientation, and the \(\pi\)-orbital of the oxygen molecule has an interaction with the empty \(d_{z^2}\)-orbital of the
central atom. At the same time, the partly occupied $d_{xz}$ or $d_{yz}$-orbital of the central atom feeds back to the $\pi^*$-orbital of the oxygen molecule. This interaction is very strong, can weaken the O-O bond, and can even cause dissociation of the oxygen molecule, which will favor direct 4-electron reduction. When the reaction takes place on a clean Pt or iron phthalocyanine surface, the activation of oxygen normally follows this model;

(B) Pauling model (Fig.2-6B):

Only one side of the oxygen molecule gets close to the transition metal, and the $\pi^*$-orbitals have an interaction with the $d_{z^2}$-orbital of the central metal. Following this adsorption model, only one atom of oxygen experiences strong activation, and this will lead to the 2-electron reaction. Oxygen behavior will agree with model on most electrode materials.

(C) Bridge model (Fig.2-6C):

If the characteristics of the central atoms and the position are suitable, the oxygen molecule can have an interaction with two central atoms, and the two oxygen atoms can be activated at the same time. This model will lead to the 4-electron reaction.

![Fig.2-6 Different adsorption models for O₂ on electrode.](image)
However, there is currently no spectroscopic proof for this oxygen adsorption model on different electrode surfaces.

In principle, the models of Giggiths and Pauling will belong to single-position adsorption, but the bridge model describes the double-position adsorption. From the results of research, if we deposit some Ag atoms on the surface of Pt, this will prevent oxygen reduction and lead to bridge adsorption model on the Pt surface.

From the applications point of view, Pt and Pt alloy are ideal cathode catalysts in acid or alkaline solution. From research to optimize the catalyst and the technology of preparing gas diffusion in the electrode, the loading of Pt can be reduced to under 0.5 mg·cm⁻² [24]. In alkaline solution, Au [25], Ag [26], and carbon electrode have some practicability, but the lifetime and capability of the output current make them inferior to Pt electrode.

A large variety of transition metal (e.g., Fe and Co) macrocyclic complexes, such as the N₄-, N₂O₂-, N₂S₂-, O₄-, and S₄-systems have all shown a certain level of catalytic activity towards oxygen reduction [27]. It is well known that N₄-chelates of transition metals such as iron- and cobalt-porphyrins, phthalocyanines, and tetraazannulenes are the most popular active catalysts for oxygen reduction. This could be partially attributed to the inductive and mesomeric effects of the ligands on the central ion. Two major transition metal chalcogenides have been explored as electrocatalysts for fuel cell oxygen reduction: Chevrel phase-type compounds (e.g., Mo₄Ru₂Se₈) and amorphous phase compounds (e.g., RuₓMoₓ-Seₓ, RuₓSₓ). Some transition metal oxides, such as NiO [28], perovskite [29], spinel [30], and CrO₂[31], were researched as cathode catalysts.
for fuel cells, but the activation and stability are not good in acid or alkaline solution. Some details of these cathode catalysts are given below.

2.1.3 Cathode catalysts

2.1.3.1 Pt catalyst

The high cost of proton exchange membrane (PEM) fuel cell technology is one of the major challenges hindering its commercialization. Unfortunately, Pt-based catalysts are currently the only choice of electrocatalysts in practical PEM fuel cells. Because the dominant polarization in a PEM fuel cell comes from the slow cathodic oxygen reduction reaction (ORR) rather than the anodic hydrogen oxidation reaction, reducing the Pt loading (particularly in the cathode catalyst layer) without compromising fuel cell performance is an effective strategy to meet the cost requirements for fuel cell commercialization [32-34]. In other words, the design of novel catalysts requires not only reducing the amount of Pt used, but also enhancing catalytic activity and stability.

Platinum has a face-centered cubic (fcc) crystal structure with a lattice parameter of 3.93 Å. The surface energies ($\gamma$) of the low-index crystallographic planes are in the order of $\gamma(111) < \gamma(100) < \gamma(110)$ [35,36]. The commonly observed Pt nanoparticles are in the thermodynamically favored spherical shape, enclosed by low-index facets, such as Pt\{100\} and Pt\{111\}. In terms of catalytic activity, the nanosized Pt catalyst offers several advantages, including larger surface to volume ratio [37], increased Pt utilization, and a greater number of available catalytic sites as compared with Pt bulk single crystals. These advantages make it the most active catalyst for many electrochemical reactions, including both oxygen reduction and hydrogen oxidation in
fuel cells. In general, the intrinsic reactivity and selectivity of Pt catalysts are controlled by the crystalline structures and morphologies of the particles. Therefore, different facets on Pt nanoparticles have different catalytic activities towards fuel cell reactions. This is probably due to the distinct adsorption properties of the different chemical species on these facets.

Feliu and co-workers [38, 39] intensively studied the effects of surface orientation of single Pt crystals on ORR electron transfer, and they concluded that the ORR is actually a structure sensitive reaction in both sulfuric and perchloric media. The orientation of the steps and terraces on the surface plays a significant role in determining the electrocatalytic activity of an electrode. Experimental results confirmed that in ORR electrocatalyzed by Pt catalyst, if H₂SO₄ is being used as an electrolyte, Pt{100} presents a higher ORR activity than Pt{111}. This was found to be due mainly to the adsorptive and inhibiting effects of the bisulfate anion [40]. Regarding the effect of electrolyte ions on the catalytic activity of Pt facets, systematic investigations of the adsorption of bisulfate anions have been carried out by Zelenay et al. [41], Varga et al. [42], and Gamboa-Aldeco et al. [43]. Their studies showed that bisulfate coverage on a Pt(100) electrode was less than one-third of the coverage on a Pt(111) electrode in the same concentration of sulfuric acid solution. Pt(111) can adsorb bisulfate anions much more strongly and in a wider potential range than Pt(100), due to the different properties of their respective facets. However, this seems less clear when HClO₄ is used as an electrolyte; in this case, the catalytic activity increases thus: Pt{110} > Pt{111} > Pt{100}. This finding was determined to be the result of selective interaction between
O₂ and different exposed facets, as well as increased adsorption of the OH species on these Pt surfaces. Armand and Clavilier [44,45] investigated the influence of specific anion adsorption on the electrochemical behavior of Pt(100), (110), and (111) surfaces in an acidic medium, carrying out voltammetric cycling in both sulfuric and perchloric acid solutions and using hydrogen as a structure-sensitive probe. They showed that the atomic surface structure of Pt(100) and (110) facets underwent reconstruction during electrode cycling, resulting in a more stable and densely packed surface structure. However, this did not occur for Pt(111). They concluded that the surface modification experienced by the (100) and (110) orientations after electrode cycling in the potential range where specific adsorption occurred resulted from the specific adsorption of anions. There was no evidence to indicate any structural transition between Pt(100) and (110) after electrochemical treatment.

Controlling the synthesis process to produce favored catalyst morphologies, including surface structures with designed crystal facets, thus seems quite important in creating highly active, Pt-based catalysts. It is worth emphasizing that some crystal facets with special features (high-index facets, facets with terraces) on the catalyst surface play a major role in catalytic activity enhancement because they offer a greater number of active sites located at edges or corners of the rough surface of the Pt particles [46,47]. Wang et al. [48] demonstrated that a Pt nanocube catalyst was four times more active in 0.5 M H₂SO₄ than a Pt nanoparticle, in terms of ORR specific activity. This might be due to the high exposure of the Pt{100} facets, which may provide optimal binding energy between platinum atoms and the adsorbed species for ORR [49]. Furthermore,
some nanostructures enclosed within high-index facets could contain more unsaturated atomic steps, edges, and kinks, which are believed to be more catalytically active than the commonly formed nanostructures within low-index facets [50]. Tian et al. [51] reported that Pt tetrahexahedra with exposed high-index planes (e.g. \{730\}, \{210\}, and \{520\} facets) exhibited 2–4 times more efficiency per unit surface area towards ethanol oxidation compared to a commercially available Pt/C catalyst, is the particles of which are usually enclosed with low-index planes such as \{111\} and \{100\}.

2.1.3.2 Pt-based catalyst

Alloying Pt with some relatively small base metals has the advantages of reducing the amount of Pt used, while at the same time improving activity and stability as compared to pure Pt catalysts [52, 53]. It has been demonstrated that when Pt is alloyed with Cr, Mn, Fe, Co, or Ni, a two- to four-fold improvement in ORR specific activity (\(\mu\text{A cm}^2\text{Pt}\)), compared with a pure Pt catalyst, could be achieved. The mechanisms for such enhanced activity have been investigated intensively and reviewed in the literature, with the result that changes in surface electronic structure and adsorption properties after Pt alloying have been identified as reasons for the enhancement [54-56]. Norskov et al. [57] studied nanoscale effects on electrocatalytic activity using density functional theory (DFT) calculations and showed that alloys of Pt and, for example, Ni, Co, Fe, and Cr (where Pt is segregated on the surface) have smaller oxygen binding energies than pure Pt. Their results provided good explanations for experimental observations that the Pt skins on these alloys have higher catalytic activity than pure Pt.
Unfortunately, leaching or dissolution of the base metal from the alloy surface to the acidic solution has been identified as the major cause of catalyst deactivation. As well analyzed by Gasteiger et al. [58], there are at least three possible causes for the leaching of base-metal from a Pt alloy/ C catalyst in PEMFCs: (i) excess base-metal may be deposited onto the carbon support during preparation; (ii) there may be incomplete alloying of the base element with Pt due to a low alloying temperature applied during formation of the alloy; and (iii) even a well-alloyed base-metal may leach out of the surface under PEMFC operating conditions and leave a Pt-enriched surface or skin, since thermodynamically, base-metals are unstable under PEMFC potentials in acidic electrolytes (as even Pt-alloys do not have high enough heats of mixing to confer stability). Therefore, some treatment of the Pt-alloy catalyst is necessary to improve its stability.

2.1.3.3 Transition metal chalcogenides

Two major transition metal chalcogenides have been explored as electrocatalysts for fuel cell oxygen reduction: Chevrel phase-type compounds [59,60] (e.g. Mo$_4$Ru$_2$Se$_8$) and amorphous phase compounds (e.g. Ru$_x$Mo$_y$Se$_z$, Ru$_x$S$_y$).

2.1.3.3.1. Chevrel phase-type compounds

These compounds have a cluster structure, with a repeating crystal lattice containing a metal ion cluster in the centre, surrounded by several non-metal ions. For example, in a binary compound of $M^1_eX_8$ type ($M^1 = \text{high valence transition metal}$, e.g., Mo; $X =$
chalcogen, e.g., S, Se, Te), each lattice contains a central octahedral metal cluster with six metal ions surrounded nearly cubically by eight chalcogen ions. There are also ternary compounds, such as Mo₆M²⁺X₈ (M²⁺ = intercalated metal guest ion), and pseudobinary compounds, such as Mo₆M³⁺X₈ (M³⁺ = foreign metal ions which replace the Mo in octahedral M₁ clusters). Cluster compounds of this type have been tested as electrocatalysts for oxygen reduction. All of them appeared to have some level of activity. The Mo₆M²⁺X₈ compound was found to be electrochemically unstable due to de-intercalation at positive electrode potentials. Extensive studies were focused on the mixed transition metal cluster compounds (Mo₆M³⁺X₈, called pseudobinaries). When M³⁺ = Ruthenium (Ru), this compound displayed the best activity among other metals tested. Alonso-Vante et al. [60] observed that Mo₆₋ₓRuₓX₈ could catalyze the electroreduction through a four-electron pathway from O₂ directly to H₂O. This remarkable activity was attributed to the presence of octahedral mixed metal clusters. These clusters might act as reservoirs for electron transfer from the electrode to coordinated O₂ on the clusters. It was also observed that the clusters could change volume during the reduction process. When the cluster lost four electrons, metal metal bonds became weaker, which increased cluster volume by approximately 15%. At this stage, Mo₄Ru₂Se₈ was found to be one of the best non-platinum oxygen reduction catalysts for PEM fuel cell reactions. Compared to the metal macrocyclic complexes, such as iron and/or cobalt porphrins and phthalocyanines, Mo₆₋ₓRuₓX₈ catalysts seemed to be more promising. For example, at a normal voltage range for fuel cell operation, Mo₄Ru₂Se₈ was inferior to Pt catalyst by only 30–40%. It was expected that further
optimizing the catalyst layer structure might lead to an improvement in catalyst performance.

Mo$_4$Ru$_2$Se$_8$ was synthesized via a high-temperature solid-state reaction by heating stoichiometric amounts of high purity elements in sealed quartz ampoules for 24 h at 1470 K. The solid powder formed was melted at 1970 K for another 48 h in a high-pressure (0.7 GPa) argon filled furnace. After cooling, the loose powder was agitated in an ampoule. In order to obtain a homogeneous product, the powder was again thermally treated at 1970 K for 120 h. The final product was analyzed, and 4% impurity was found in the powder. As discussed above, Chevrel phase-type compounds seem to display some remarkable electrocatalytic activities toward oxygen reduction, and their activities could be affected by the content and nature of the foreign metal ions in the cluster. However, now Alonso-Vante rarely cites his pioneering paper published in Nature, in which he initially proposed that semiconducting Chevrel-phase Ru–Mo chalcogenides (sulfides, selenides) had significant oxygen reduction activity in acid conditions [61]. The main reason could be that the Chevrel phases may not be the dominating active sites for oxygen electroreduction, although the nominal compositions were the same as for the Chevrel phases. This will be further discussed in the following part of this section. Nevertheless, this pioneering work is important, and it opened up a new area of catalysis.

2.1.3.3.2 Amorphous transition metal chalcogenides

The process for catalyst synthesis by means of high-temperature solid-state reaction
was complicated and costly. It required an environment of extremely high temperatures in a vacuum, where undesired by-products were formed. New synthesis routes that are operated under moderate conditions are definitely needed in order to simplify the process, reduce costs, and allow the production of transition metal chalcogenides at lower temperatures in the form of nanoparticles whose size and shape can be controlled. Again, it was Alonso-Vante et al. [60] who proposed and validated a new low temperature chemical precipitation method through mixing metal carbonyls and the corresponding chalcogen in an organic solvent such as xylene or 1,2-dichlorobenzene. Careful examination of the Mo$_x$Ru$_y$SO$_z$/Mo$_x$Ru$_y$SeO$_z$ and Ru$_{x}$S$_y$/Ru$_x$Se$_y$ systems [62–64] revealed that the compounds formed had a polycrystalline and amorphous structure rather than a Chevrel structure. The reaction products consisted of nanoscale Ru metals and octahedral clusters of Ru, which contained carbon in the centre, surrounded by carbonyl groups. Ruthenium/ carbide/carbonyl compounds are expected to be the active centers. These complexes do not form a crystalline compound, but they are present as a film on the ruthenium colloids. Catalyst synthesized by this low temperature chemical precipitation method (e.g., Mo$_x$Ru$_y$SeO$_z$) showed efficient electrocatalytic activity towards oxygen reduction in acid medium [60,63]. The precipitation process was performed in an argon atmosphere at 140 °C for 20 h. Chemicals such as molybdenum hexacarbonyl, trisruthenium dodecacarbonyl and selenium were mixed in a dried-xylene solution, which was constantly stirred and refluxed. The obtained precipitate was filtered and washed with dried-diethylether and then dried in the air. The synthesis temperature depended on the boiling point of the solvent used, e.g., 140 °C for xylene.
and 180 °C for 1, 2-dichlorobenzene [65–68]. It was found that if the synthesis was conducted in an aprotic solvent, the precipitate particle sizes were on the nanoscale. However, because this method involved some complex chemical reactions, a mixture containing several polynuclear compounds with amorphous structures could be produced, depending on the synthesis temperature. It was very difficult to separate and characterize this mixture by traditional chemical methods, due to their low solubility, which is probably one of the drawbacks of this synthesis method. Another disadvantage of this method could be that the yield of the final product is always below 100% (normally 40–60%) [69]. Several groups such as those of Hammnet [63], Sebastian [70–72], and Tributsch [73,74] carried out the same synthesis process using Ru-based electrocatalysts for oxygen reduction. Hammnet et al. [75] found that carbon-supported MRu$_5$S$_5$ (M = Rh or Re) could give the best electrocatalytic activity. It was even better than that of Mo$_4$Ru$_2$Se$_8$ synthesized by a high-temperature solid-state reaction. A study by Schmidt et al. [76] showed that carbon-supported Ru$_x$Mo$_y$Se$_z$ had similar catalytic activity to carbon supported Ru catalyst, suggesting that only the pure ruthenium formed the catalytic site and that both Mo and Se probably did not participate in the electrocatalysis process. However, Bron et al. [77] demonstrated that the presence of selenium may have acted as a bridge to facilitate efficient electron transfer between the Ru-complexes and the colloids, while protecting the catalysts from electrochemical oxidation through surface modification of the catalyst by carbonyl and carbide–carbonyl complexes, or carbon compounds, which led to an enhanced stability. Solorza-Feria et al. [78,79] proposed a new low temperature pyrolysis route at a synthesis temperature of
The catalysts that were produced showed good stability and electrocatalytic activity towards oxygen reduction in acidic medium. The synthesis was performed by pyrolyzing a mixture of Ru$_{12}$(CO)$_{12}$ and elemental sulfur in a sealed glass ampoule at 300 °C for 24 h. The resulting powder was rinsed twice with a 1:1:1 mixture of hexane, chloroform and ethyl acetate to remove unreacted reactants. The powder was then dried overnight at 120 °C. The final amorphous product, Ru$_x$S$_y$(CO)$_n$, was tested for O$_2$ electroreduction, and some considerable catalytic activity was found. It seemed that the heat-treatment temperature played an important role in the synthesis process to produce a better catalyst. Tributsch et al. [80] found a reduction in catalytic activity of heated, unsupported Mo$_x$Ru$_y$SeO$_z$ after release of carbon monoxide and carbon dioxide (between 250 and 350, and above 600 °C). Based on this, Tributsch et al. assumed that the high catalytic activity of their catalysts was due to the interaction of ruthenium and carbon ligands. One possible reason for this is that the carbon species may stabilize the Ru metal interface by preventing Ru particles from rapidly transforming into RuO$_2$ in an exothermic reaction. The other effect of carbon species may be an alteration of the distribution of interfacial electronic states, which is caused by the formation of Ru complexes. Trapp et al. [62] also found improved activity of heated carbon-supported Ru-based catalysts at a temperature of 350 °C. More recent work by Campbell showed that heating carbon-supported Ru$_x$Se catalyst at 600 °C completes the reaction between the ruthenium and selenium and causes decarbonylation. Even when the heating temperature was as high as 600 °C, catalyst activity was not compromised if the carbon species was present. More recently, Campbell revealed an environmentally friendly
aqueous method for preparing active catalysts such as Ru₅Se. As suggested in the patent publication [81], it was not necessary to use the expensive starting material Ru₃(CO)₁₂ and the toxic solvent xylene for the synthesis. He proposed a mixture of active carbon, ruthenium (III) chloride, and selenium dioxide in a water/propanol solvent with constant stirring at 80 °C for 1 h. The resulting mixed solution was then allowed to cool at room temperature. An aqueous solution of NaOH containing NaBH₄ was then added to the solution to carry out the chemical reduction reactions. The excess NaBH₄ was removed by heating the mixture to 80 °C for 5 min. The formed powder was filtered, washed in water, and dried overnight at 80 °C. The dried powder was then placed in a quartz lined tube furnace under nitrogen and heated to 600 °C for 2 h. In this way, a carbon-supported catalyst, which has the chemical formula Ru₅Se, was produced, and it was tested for oxygen reduction in an electrochemical environment. It was claimed that the electrocatalytic activity of this carbon-supported Ru₅Se catalyst was very close to that of carbon-supported platinum catalysts. Traditional impregnation is another method for catalyst preparation. One possible drawback of this method is that the temperature used to sinter the catalyst particles is relatively high, which could reduce the catalyst active area. In this impregnation process for Ru₅Seₙ synthesis [82], a solution of ruthenium oxalate or carbonyl was mixed with a carbon support to form a slurry, which was then dried to remove the solvent. The formed solid was then heated to decompose the salt, in order to produce the desired form of solid carbon-Ru salt. For selenium incorporation, the solid was dispensed in a solution containing H₂SeO₃. After the chemical reaction between the carbon-Ru salt and the H₂SeO₃, Ru₅Seₙ catalyst was
produced. The low temperature chemical precipitation method [63] described above has the advantage of allowing the reaction to be performed in a solution to form bimetallic catalysts at low temperature. The prepared catalysts normally have a higher active area. However, this method was limited to those reactants with similar precipitation chemistry or properties, which are easily reduced chemically to metals. In order to minimize this limitation, a colloid method was developed, although the reproducibility was relatively low [80,83]. The first step for the catalyst synthesis was to make colloidal Ru nanoparticles through RuCl₃ reduction in a solution of tetrahydrofuran (THF) containing N(C₈H₁₇)₄Bet₃H, followed by an addition of absolute ethanol liquid. After that, the mixture was centrifuged to obtain the solid powder. After the incorporation of selenium, RuₓSeᵧO₂ nanoparticles were prepared. The produced catalyst was tested for O₂ reduction, and fairly high electrocatalytic activity was observed. The high catalytic activity was attributed to its large surface area, narrow particle size distribution, and ability to prevent particle aggregation.

2.1.3.4 Macrocyclic complexes

A large variety of transition metal (e.g., Fe and Co) macrocyclic complexes, such as the N₄-, N₂O₂-, N₂S₂-, O₄- and S₄- systems all showed a certain level of catalytic activity towards oxygen reduction [84]. It is well known that N₄-chelates of transition metals, such as iron- and cobalt-porphyrins, phthalocyanines, and tetraazannulenes are the most popular active catalysts for oxygen reduction. This could be partially attributed to the inductive and mesomeric effects of the ligands on the central ion. Materials in this
class of non-noble catalysts were also considered as the most promising materials to replace the expensive noble metal Pt catalysts in PEM fuel cells [84]. Beck et al. [85] proposed that the mechanism of the electroreduction of oxygen catalyzed by N4-chelates of transition metal mainly involved a modified ‘redox catalysis’. The first step in the oxygen reduction was the adsorption of oxygen on the catalyst metal center to form an oxygen-catalyst adduct, followed by electron transfer from the metal center to bound O2 and the regeneration of the reduced N4-chelates as in the following steps [85]:

\[ XMe^{II} + O_2 \leftrightarrow (XMe^{\delta^+} + \ldots O_2^{\delta^-}) \]  \[ [2-15] \]

\[ (XMe^{\delta^+} + \ldots O_2^{\delta^-}) + H^+ \rightarrow (XMe^{III} \ldots O_2H)^+ \]  \[ [2-16] \]

\[ (XMe^{III} \ldots O_2H)^+ + H^+ + 2e \rightarrow XMe + H_2O_2 \]  \[ [2-17] \]

Depending on the nature of the central metal, the oxygen reduction could take place via four-electron reduction to water (iron complexes), two-electron reduction to H2O2 (cobalt complexes), or other pathways somewhere within this range. The central metal ion of the macrocycle seemed to play a decisive role in the oxygen reduction mechanism. For N4-chelates (phthalocyanines) the influence of the metal ion was displayed in the following order of activities [84]:

Fe > Co > Ni > Cu ≈ Mn

Alt et al. [86] explained this sequence of activity by molecular orbital (MO) theory based on oxygen adsorption. According to this model, the back bonding of filled d_{xz} and d_{yz} orbitals and empty d^2_z orbitals favors partial electron transition from the metal to the empty, or partially filled, \Pi^* orbitals of oxygen. Although iron complexes of phthalocyanine/porphyrin can promote a four-electron reduction pathway, they are not
stable. In general, cobalt complexes have higher electrochemical stability than iron ones, but they can only catalyze a two-electron reduction of oxygen. The following stability sequence of metal macrocyclic complexes was summarized [87]:

\[
\text{Co > Fe > Mn}
\]

In order to combine the advantage of the Fe complex four electron \( \text{O}_2 \) reduction with the higher electrochemical stability of Co complexes, Chu et al. [88] studied the effects of a heat-treated mixture of two transition metalloporphyrins (V/Fe, Co/Fe, Ni/Fe, or Cu/Fe) on oxygen reduction and compared it with that of heat-treated single transition metalloporphyrin. They found that the heat-treated mixture of Fe and Co tetraphenylporphyrins could give a much higher catalyzed oxygen reduction current than single Fe tetraphenylporphyrin or Co tetraphenylporphyrin. This could be attributed to the formation of a face-to-face structure with two kinds of metal active sites, as suggested by Anson et al. [89,90]. The interactions between two different transition metals and oxygen molecules could promote O-O bond breakage and cause an easier reaction to \( \text{H}_2\text{O} \). The \( \text{N}_4 \)-chelate ligand could also play an important role in oxygen reduction. In addition to serving as part of the active site, it keeps the metal in a stable form on the electrode surface. Tetraphenylporphyrin, tetramethoxyphenylporphyrin, dibenzotetraazaannulene, and phthalocyanine, all of which can form complexes with iron and cobalt, seemed to be favorable for forming catalysts. Even so, when these complexes were used in PEM fuel cells, they could not show enough chemical/electrochemical stability when compared with Pt based catalysts. For example, the Fe phthalocyanine stability was weakened due to disintegration at
temperatures above 50 °C in an acid electrolyte [91]. In order to improve the stability of these complexes, an attempt to enlarge the organic part of the molecule and to bring about stronger attachment to the support base was undertaken, but the results were not promising [92]. In 1976, Jahnke et al. [93] reported that the heat-treatment of metal N₄-chelates at high temperature could remarkably increase the catalyst activity and the stability toward oxygen electroreduction. Since then, this pioneering work has led to worldwide research interest. According to Jahnke et al., thermally pretreated 1:2 (w/w) mixtures of CoTAA and activated carbon BRX showed the maximum activity at a temperature of 600 °C for oxygen reduction [93]. Some recent research [94–96] revealed that the highest level of activity for N₄-chelates could be obtained within a pyrolysis temperature range of 500–700 °C. However, it was also discovered that a higher pyrolysis temperature (>800 °C) was necessary in order to obtain stable performance in PEM fuel cells. However, a deleterious effect on the electrode performance was observed at temperatures higher than 1100 °C [97]. An almost 50 times greater enhancement in the electrocatalytic activity was achieved at an electrode potential of 700 mV (versus SHE) when carbon-supported Co phthalocyanine was heat-treated in an environment of N₂ or Ar at 700–800 °C [98]. Even for carbon-supported Fe phthalocyanine, the stability was also improved considerably. In experiments with carbon-supported Ru phthalocyanine, heat treatment at 650 °C could increase catalytic activity by 20 times at 800 mV (versus SHE), but stability was not improved. The heat treatment does not always result in good performance for carbon-supported metal phthalocyanines. For example, the activity and stability of Zn- and Mn-phthalocyanines
were not affected by heat-treatment [98]. The duration of heat-treatment for these complexes was usually around 0.3–5 h. When heat treatment was performed at a lower temperature range (500–700 °C), the N₄-M moiety was recognized as the active catalytic site. However, at a higher temperature range (i.e., > 800 °C), the nature of the catalytic site for the high temperature pyrolysis products is still controversial. According to some research [99-101], the N₄-metal super-site disappears when the temperature is too high, suggesting that the nature of such active sites was changed due to the higher temperature hydrolysis process. In researching catalytic sites produced at high temperature, Dodelet et al. [102] investigated the activity and active sites of Fe precursors. Dodelet used time-of-flight secondary ion mass spectrometry (ToFSIMS), through pyrolysis of perylene tetracarboxylic dianhydride (PTCDA) together with Fe and N precursors. The only species detected in the results was FeN₂C₄⁺. Therefore, it was proposed that FeN₂C₄⁺ might be a catalytic site that is produced in the high temperature range. Since the structure of these N₄-chelate catalysts would be largely destroyed at high pyrolysis temperatures, it might not be necessary to use expensive metal macrocyclic complexes as precursors for active catalyst preparation [103]. It was expected that if a mixture of basic components from macrocyclic complexes, i.e., transition metal sources, such as Fe or Co, nitrogen donors and carbon supports could be treated at a high temperature, active catalytic sites such as N₄-metal or FeN₂C⁴⁺ might be obtained [104]. Several research groups have reported their work on this alternative preparation route with various transition metal, nitrogen, and carbon containing species as precursors. This approach created a very attractive means of
electrocatalyst preparation using more common starting materials that were much cheaper. In general, the most popular transition metal precursors that have been employed are Fe or Co inorganic salts, such as sulfates, acetates, hydroxides, chlorides, cyanides, [105–107] and Fe complexes such as ferrocene [108]. Inorganic precursors would be more economical for commercialization. Complex of Fe-, Co- or Cu-1,10-phenanthroline have been widely employed as precursors for catalyst preparation [109] due to coordinated bonds between the metal ion and the nitrogen ligand which appears to be critical to the formation of active catalyst sites such as MeN₄ or FeN₂C₄⁺ after heat treatment. Nitrogen sources were critical for catalytic activity. Nitrogen-containing chemicals such as polyacrylonitrile, tetracyanoquinodimethane, ethylenediamine, 1, 2-phenylenediamine, hydrogen phthalocyanine, pyrrole and their derivatives have been found to be effective precursors for catalyst preparation [106,110]. N-containing gases such as NH₃ [111] or acetonitrile [112], and N groups on a modified carbon support (e.g., HNO₃/NH₃ treated carbon support [113]) were also employed as the nitrogen sources for the preparation process. It was clear that the most important factor was the nitrogen content of the materials. Higher nitrogen content yielded higher catalytic surface site density and better electrocatalysts [114]. Carbon support was another factor affecting catalytic activity. Jaouen et al. [114] studied the effects of carbon support on catalytic activity and found that the activity of the catalyst varied with the specific surface area, pore size distribution, and the N or O content of the carbon support. Metal loading on the carbon support may also affect catalytic activity. Lalande et al. [115] studied the influence of transition metal Co loading (0–8 wt.%) on
the activity and stability of heat-treated carbon-supported Co phthalocyanine at a temperature range of 500–1100 °C. They found an optimum value for Co loading on the carbon support (3.5 wt.%). This optimum Co loading did not appear to depend on the heat-treatment temperature. They also found that this optimum Co loading value corresponded to full monolayer coverage of the Co phthalocyanine on the carbon support. Faubert et al. [116] also studied the effects of Fe loading on catalytic activity by heating PTCDA that was adsorbed by Fe acetate in an environment of Ar + H2 + NH3. It was found that the catalytic activity at first increased with an increase in Fe content, but leveled off when the Fe content was greater than 0.5 wt.%. This result suggested that excess Fe would favor the formation of aggregates, which contained catalytic inert metallic and/or carbidic iron. Lalande et al. [108] proposed a multi-step pyrolysis method for O2 reduction catalyst preparation. Wei et al. [112] did some comparisons between the carbon, nitrogen and cobalt contained catalysts prepared by one-step pyrolysis and those prepared by multi-step pyrolysis methods. In the multi-step pyrolysis method, the first pyrolysis step was to pyrolyze the carbon support (Vulcan XC-72R) with a nitrogen precursor (acetonitrile) in a flowing argon atmosphere, and then to introduce the cobalt precursor (cobalt sulphate) into the reactor for the second step. The second step was to pyrolyze the mixture of the product from the first step and the introduced cobalt precursor in a flowing argon atmosphere. The pyrolysis sequence was found to have a strong impact on the catalyst activity. However, the onset electrode potentials for electrocatalyzed oxygen reduction (E_onset) for catalysts that were produced in different pyrolyzation sequences all occurred at about 790–800 mV (versus reversible
hydrogen electrode (RHE)), similar to that obtained with cobalt-centered macrocycle compounds pyrolyzed at 1000 °C [117,118]. More recently, Ye et al. [119] proposed a new sol–gel method combined with a supercritical drying technique for the preparation of nanocomposite electrocatalysts for oxygen reduction. They claimed that a sol–gel method using a highly controllable solution, plus a supercritical drying technique with structure-preserving ability, could favor a nanoscale mixing of the constituents to produce a remarkably homogeneous solution. Chemical, physical and morphological properties of the products of this sol–gel method could have a pronounced isotropy. Compared to other preparation methods, this new sol–gel method had some unique and competitive features. The first step for this synthesis method was the mixing of an inorganic salt (e.g. Fe(NO3)3 or CoCl2) or an organometallic compound (e.g., Co(III) acetylacetonate) with polyacrylonitrile (PAN) in N,N-dimethylformamide (DMF)/water to form a well-mixed solution. The mixed solution was degassed when heated to approximately 120 °C. When the solution cooled, a polymer gel containing the metallic compound was obtained by thermally induced phase separation. The polymer gel was then pretreated at 220 °C, followed by a pyrolysis step at 900 °C under an argon atmosphere. In this way, a non-noble catalyst was produced which showed strong catalytic activity towards oxygen reduction in acid conditions and a relatively high stability.

2.1.3.5 Transition metal oxide

Because of the special structure of perovskite and pyrochlore-type ruthenium oxide
[29], it is very easy to exchange with oxygen. The pyrochlore-type ruthenium oxides in particular have very high activation in alkaline solution. Some other transition metal oxides, such as NiO [28], perovskite [29], spinel [30], and CrO$_2$ [31], were investigated as cathode catalysts for fuel cells, but the activation and stability are not good in acid or alkaline solution. The details of these cathode catalysts are given below.

2.1.4 Catalyst support

The stability of the catalyst support in the fuel cell environment is of great importance in the development of new substrates. In addition to high surface area, porosity, and electrical conductivity, corrosion resistance is also an important factor in the choice of a good catalyst support. If the catalyst particles cannot maintain their structure over the lifetime of the fuel cell, change in the morphology of the catalyst layer from the initial state will result in a loss of electrochemical activity.

Up to the 1990s, carbon blacks were almost exclusively used as catalysts support in low-temperature fuel cells. To improve the electrochemical activity and stability of the catalysts, in the last few years, new carbon materials have been tested as support for fuel cell catalysts. With respect to carbon blacks, these new carbon materials are different both at the nanoscopic level in terms of their structural conformation (for example, nanotubes) and pore texture (for example, mesopore carbons), and/or at the macroscopic level in terms of their form (for example, microspheres). Auer et al. [120] reviewed the use of activated carbons, carbon blacks, and graphites, as well as graphitized materials, as support materials for metal powder catalysts. Rodriguez-Reinoso [121] dealt with the
surface chemistry of carbon supports and the influence of the oxygen groups on the carbon surface upon the properties of the supported catalysts. The following is to provide a better insight into the catalyst supports, in the light of the latest advances on this field.

2.1.4.1 Carbon blacks and graphite materials

Carbon blacks are widely used as catalyst support in low temperature fuel cells. They are manufactured by the pyrolysis of hydrocarbons such as natural gas or oil fractions from petroleum processing [122]. Due to the nature of the starting materials, the ash content of carbon black is very low frequently well below 1 wt%. The carbon blacks are produced by the oil-furnace processes and acetylene processes. The most important production method is the furnace black process in which the starting material is fed to a furnace and burned with a limited supply of air at about 1400 °C. Due to its low cost and high availability, oil-furnace carbon black (e.g. Vulcan XC-72) has been used widely as the support for platinum catalyst in low-temperature fuel cells. It has to be remarked that Vulcan is not a well-defined oil-furnace black material. Its particles are not monodisperse.

High surface area graphite (HSAG) can be made from graphitized material by a special grinding process. Surface areas of 100–300 m² g⁻¹ make this graphite an interesting support material for precious metal catalysts [123,124]. Graphitized carbon black is another support material of interest to catalyst manufacturers. This high surface area material is obtained by recrystallization of the spherical carbon black particles at 2500–3000 °C. The partially crystallized material possesses well-ordered domains. The
degree of graphitization is determined by the process temperature.

2.1.4.2 New carbon materials

According to the International Union of Pure and Applied Chemistry (IUPAC), pores will be classified, depending on their width, as micropores (< 2 nm), mesopores (2–50 nm), and macropores (> 50 nm). Generally, carbon blacks have high specific surface area, but this is contributed mostly by micropores that are less than 1 nm in size and are therefore more difficult to access. The presence of micropores has disadvantages when the carbon is used as catalyst support. Indeed, when the average diameter of the pores is less than 2 nm, the supply of fuel may not occur smoothly, and the activity of the catalyst may be limited. Moreover, it is well known that micropores of these types of amorphous carbon particles are poorly connected. Compared with carbon blacks, mesoporous carbons (MCs) generally present higher surface areas and lower amounts, or the total absence, of micropores. In a mesoporous carbon supported catalyst, the metal catalyst particles are distributed and supported on the surface or in pores of the mesoporous carbon. A large mesopore surface area, particularly with pore size > 20 nm, gives rise to a high dispersion of Pt particles, which results in a large effective surface area of Pt with a high catalytic activity. The mesoporous structure facilitates smooth mass transportation to give rise to high limiting currents.

Recent studies have revealed that the physical properties of the carbon support can greatly affect the electrochemical properties of the fuel cell catalyst [125]. It has been reported that carbon materials with both high surface area and good crystallinity can not only provide a high dispersion of Pt nanoparticles, but also facilitate electron transfer,
resulting in better device performance [126]. On this basis, novel non-conventional carbon materials have attracted much interest as electrocatalyst support because of their good electrical and mechanical properties and their versatility in pore size and pore distribution tailoring. These materials present a different morphology from carbon blacks both at the nanoscopic level in terms of their pore texture (for example, mesoporous carbon) and at the macroscopic level in terms of their form (for example, microspheres). Some examples are supports produced from ordered mesoporous carbons (OMCs), carbon aerogels, carbon nanotubes (CNTs), carbon nanohorns (CNHs), carbon nanocoils (CNCs), and carbon nanofibers (CNFs).

The characteristics of some of these new carbon materials, the metal dispersions, and the electrochemical activity of catalysts supported on these materials, compared with those of catalysts supported on carbon blacks, are described in the following paragraphs.

2.1.4.2.1 Mesoporous carbons

The ordered mesoporous carbons have recently received great attention because of their potential use as catalytic supports in fuel cell electrodes. They have controllable pore sizes, high surface areas, and large pore volumes [127,128]. Nanoporous carbons with 3D ordered pore structures have been shown to improve the mass transport of reactants and products during fuel cell operation [128,129]. Ordered mesoporous carbons have recently been synthesized using ordered mesoporous silica templates [130].
Ordered mesoporous carbons have been tested as supports for fuel cell catalysts, and their metal dispersion and catalytic activity have been compared with those of catalysts supported on carbon blacks. Generally, all OMC supported metals presented higher metal dispersion and higher catalytic activity, both for oxygen reduction and methanol oxidation, than carbon black (CB) supported metals.

2.1.4.2.2 Carbon nanotubes

The tubular structure of carbon nanotubes makes them unique among different forms of carbon, and they can thus be exploited as an alternative material for catalyst support in heterogeneous catalysis [131] and in fuel cells due to their high surface area, excellent electronic conductivity, and high chemical stability [132]. Conventional carbon nanotubes are made of seamless cylinders of hexagonal carbon networks and are synthesized as single-wall (SWCNT) or multiwall carbon nanotubes (MWCNT). A SWCNT is a single graphene sheet rolled into a cylinder. A MWCNT consists of several coaxially arranged graphene sheets rolled into a cylinder. The graphene sheets are stacked parallel to the growth axis of the carbon nanotubes, and their spacing is typically 0.34 nm. Stacked-cup carbon nanotubes (SCCNTs) consisting of truncated conical graphene layers represent a new type of nanotubes. Multiwalled nanotubes may exhibit a high degree of uniformity of the internal diameter of single tubes, but with broad pore-size distribution in the micropore and mesopore ranges [133]. Typical characteristics of CNTs for use as catalyst support are an outer diameter of 10–50 nm, inside diameter of 3–15 nm, and lengths from 10 to 50 mm. As reported by Serp et al.
[134], pores in MWCNT can be mainly divided into inner hollow cavities of small diameter (narrowly distributed, mainly 3–6 nm) and aggregated pores (widely distributed, 20–40 nm) formed by the interaction of isolated MWCNTs. On as-prepared and acid-treated SWCNTs, instead, adsorption of N₂ has clearly evidenced the microporous nature of SWCNT samples [135]. Typically, the total surface area of as-grown SWCNTs range between 400 and 900 m² g⁻¹, whereas, for as-produced MWCNTs, values ranging between 200 and 400 m² g⁻¹ are often reported.

Prudence is required regarding the electrochemical activity of CNT-supported catalysts. Most papers are indeed very optimistic regarding the potential interest of CNTs, due to the presumed high activity of CNT-supported metals. In some cases, the authors overvalue their results, for example, comparing CNT-supported catalysts with bad CB supported catalysts. As reported in a number of papers [136-138], when used as anode and/or cathode materials in low-temperature fuel cells, Pt and Pt-M catalysts supported on carbon nanotubes presented higher catalytic activity than the same catalysts supported on carbon blacks.

2.1.4.2.3 Carbon nanohorns and nanocoils

Carbon nanohorns and carbon nanocoils, as well as carbon nanotubes, constitute a new class of carbon nanomaterials with properties that differ significantly from those of other forms of carbon. These materials have been tested as supports for fuel cell metal catalysts. The high catalytic activity of carbon nanohorn/ carbon nanocoil supported catalysts demonstrates the suitability of their application in fuel cell technology.
Single-wall carbon nanohorn (SWCNH) aggregates can be produced by CO₂ laser vaporization of carbon, and a single aggregate can take either a ‘dahlia-like’ or a ‘bud-like’ form. Kasuya et al. [139] found that ‘dahlia-like’ SWCNH aggregates were produced with a yield of 95% when Ar was used as the buffer gas, while ‘bud-like’ SWCNH aggregates were formed with a yield of 70 or 80% when either He or N₂ was used. Yudakasa et al. [139] obtained single-wall carbon nanohorns, 30–50 nm long and 2–3 nm thick, which formed aggregates that resemble dahlia flowers (diameter: 80 nm). CO₂ laser vaporization of graphite at room temperature produced a high yield (about 75%) of SWCNHs.

The structure of a nanocoil is similar to that of MWCNTs, except for its helical shape. It can be therefore said that a carbon nanocoil is a helical MWCNT [140]. Choi et al. grew carbon nanocoils on quartz substrates on which an indium tin oxide (ITO) thin film had been formed. The elemental ratio of Sn/(In + Sn) in the sputtering target was 50%. Then, an Fe-containing solution was spread on the ITO film by spin coating with two different spinning rates of 500 rpm and 1000 rpm. Carbon nanocoils were grown at 700 °C for 30 min using C₂H₄ gas.

2.1.4.2.4 Activated carbon fibers (ACFs) and carbon/graphite nanofibers

It is well known that fibers offer flexibility which is not found with the usual powdery or granular materials. Fibrous catalytic packs offer the advantages of an immobile catalyst and a short diffusion distance. Another advantage of fibrous catalysts is their low resistance to flow of liquid and gases through a bundle of fibers. Thus, they can be
used as an attractive alternative in fuel cells. For use as catalyst support, carbon fibers can be activated by carbonizing them at high temperature or treated to form carbon (graphite) nanofibers.

Activated carbon fibers represent a novel kind of porous material, with high surface area (> 1000 m²·g⁻¹), and the presence of many functional groups on the surface [141]. ACF has a reduction property such that it can reduce Pt(IV) and Pd(II) into metallic elements [142], which leads to a promising application in the preparation of catalysts without necessarily requiring special surface oxidation, as is usually the case with CB and CNTs.

Carbon nanofibers (CNFs) are also termed graphite nanofibers (GNFs). Catalytically grown carbon nanofibers are novel materials that are the product of the decomposition of carbon-containing gases over certain metal surfaces [143]. GNFs have generated intense interest in terms of their application as a catalyst support material because of their unique structure [144]. There are various types of GNFs: platelets, ribbons, herringbones, and spiral structures.

The main difference between nanotubes and nanofibers consists in the lack of a hollow cavity in the latter. Due to their peculiar structure, CNFs are mainly used as catalytic supports without any pre-treatment: indeed platelets and herringbone structures present potentially reactive groups for metal anchoring. CNF-supported catalysts were prepared for use in fuel cells and their metal dispersion and catalytic activity was compared with those of other carbon supports [145].
2.1.4.2.5 Boron-doped diamonds (BDDs)

Polycrystalline boron-doped diamond possesses properties ideally suited for an
electrocatalyst support for fuel cells. The material possesses superior morphological
stability and corrosion resistance compared to conventional sp² carbon support materials,
being able to withstand current densities on the order of 1 A cm⁻² for days, in both acidic
and alkaline conditions, without any evidence of structural degradation [146]. The
material is chemically inert, allowing for its use at elevated temperatures in oxidizing or
reducing media without loss of properties. The electrical conductivity of diamond
increases remarkably after boron doping.

Regarding the formation of diamond supported catalysts, firstly, Awada et al. [147]
demonstrated that some metals, such as Pt, Pb, and Hg, can be electrochemically
deposited on the surface of conductive diamond thin films. Bennett et al. [148] reported
the pulsed galvanostatic deposition of nanometer-sized Pt particles on electrically
conducting microcrystalline and nanocrystalline diamond thin-film electrodes. However,
the anchoring of metal atoms on a BDD surface in a stable way has to be improved.

2.1.5 The working ideas and content of this thesis

Pt-based catalysts are currently the main choice of electrocatalysts in practical PEM
fuel cells. So, the aim of this doctoral work is to reduce the content of Pt and improve
the properties of supporting materials by the following investigations:

1) Synthesis of two kinds of Pt-M alloy (Pt-Ni and Pt-Co) through the chemical
reduction method. Electrochemical testing and physical characterization of as-prepared
catalysts have also been conducted.

2) Synthesis of two kinds of special core-shell structure catalyst materials. Structural characterization to confirm the special structure was carried out.

3) Catalyst characterization after modification of a traditional carbon catalyst support (Vulcan XC-72).

4) CNTs and graphite as catalyst supports.

2.2 General Introduction of Hydrogen storage on Carbon-Based Adsorbents

2.2.1 Background on the hydrogen storage

With increasing demands for environmental protection arising from the current use of fossil fuels, hydrogen has been proposed as an alternative energy carrier, because its use creates neither air pollution nor greenhouse-gas emissions. The use of hydrogen requires an effective, safe, and stable storage medium. Storage is one of the key issues for the realization of fuel-cell powered vehicles using hydrogen as the energy carrier [149]. However, how to store hydrogen easily and cheaply is still a big problem [150]. Up to now, none of the materials and methods for hydrogen storage has been found to meet all the requirements for commercial electric-vehicle applications. Apparently, researchers in the hydrogen-storage field must face the challenge: how to combine high hydrogen storage capacity and fast kinetics at ambient temperatures. Meeting this target requires major advances in new materials and hydrogen storage technologies.

The discovery of C60 (buckminsterfullerene) by Kroto et al. in 1985 [151] has
revealed a great mystery of nanoscience and nanotechnology. An important example is a related structure, that of carbon nanotubes, discovered by Iijima in 1991, which have stimulated great interest in the research community. The carbon nanotubes possess a wide range of interesting physical and chemical properties [152]. A large number of experiments and calculations have been conducted on the hydrogen storage of carbon nanotubes [153–157], and using carbon nanotubes as a hydrogen-storage medium has been critically reviewed [158–162].

Several candidate hydrogen storage technologies including liquid or high-pressure H₂ gas, chemical hydrides, metal hydrides, and porous adsorbents, are currently being investigated. For transportation applications, the U. S. Department of Energy (DOE) has set 6.0 wt % and 45 g/L as the system capacity targets for on-board hydrogen storage for fuel-cell vehicular applications, at ambient temperature [163]. As a reference, a compact passenger vehicle powered by fuel cells would require 4 kg H₂ for a driving range of 400 km. To store hydrogen in gas tanks at the normal ambient temperature, 70 MPa is needed for compressed storage in a tank with a size of 70 L. Such a high pressure would raise safety concerns. To store hydrogen in the liquid form requires large energy consumption for liquefaction at 20 K and it also suffers from the “boil off” problem and inconvenience in maintaining such a low temperature in an on-board storage system. Among the storage technologies, the sorbent approach including metal hydrides and adsorbents, is the most promising, but also the most challenging [164–181]. Metal hydrides have been studied intensively for over four decades [64, 65]. Studies on adsorbents have been more recent and mostly focused on carbon-based materials, due to
their light weight, high surface area, and tailorable structure. Hydrogen storage on carbon-based adsorbents, including carbon nanotubes (CNTs), graphite nanofibers (GNFs), activated carbons (ACs), templated carbons (TCs), graphite, metalorganic frameworks (MOFs), etc., has now been studied intensively and extensively [66–81]. In this section, the recent developments in hydrogen storage in carbon-based materials are summarized, and the fundamentals of the different factors that affect hydrogen storage capacity are discussed, as well as the strategies needed to improve the storage performance from the viewpoints of both hydrogen storage and material synthesis chemistry. In particular, the recent studies on using the hydrogen spillover mechanism to obtain significantly enhanced storage capacities are discussed in detail. Normally, the spillover mechanism exists between metal particles and carbon materials. In this thesis, hydrogen storage in carbon materials is discussed in detail.

2.2.2 The state of hydrogen storage

Normally there are three states of hydrogen storage: gas, liquid and solid. Here, an introductions is given below:

2.2.2.1 High pressure gas storage

Hydrogen gas can be stored in huge jars sealed by water, just like natural gas at low pressure, and this method is suitable for large-scale usage of hydrogen. However, the density of hydrogen is too low for most applications, so this method is not very useful.

High pressure gas storage is the most common and direct method of hydrogen storage.
At present, most countries use bottles (40 L) to store hydrogen gas at 15 MPa. However, this type of bottle can only store about 0.5 kg of hydrogen gas, only 10% of the content of a high pressure bottle. The drawbacks of this method are the high cost of transport and low hydrogen storage.

If we use new high pressure bottles made of complex materials (35 MPa), the hydrogen storage density can reach 2%. The lining of the new complex material bottle is aluminum alloy, and the surface is composed of high strength carbon fibers, so the weight of the bottle is lighter than for the older type. Now, that an even higher pressure bottle (75 MPa) is on sale, the hydrogen storage density can reach to above 3%. Research on a 100 MPa of high pressure bottle is going on.

High pressure hydrogen storage has some advantages:

(1) It can work normally at freezing temperatures.

(2) Charging with gas is very fast, it will take only 9 min for one car.

However, this method also has some drawbacks: the hydrogen storage density could not match the criterion of the US Department of Energy, while the high pressure may lead to potential trouble.

2.2.2.2 Liquid hydrogen

Hydrogen can be stored in the liquid state, and hydrogen gas can be liquefied by adiabatic expansion. The boiling point of hydrogen is only 20.38K, and the heat of vaporization is also very low (0.91 kJ·mol/L). So, there is a very large temperature difference between the liquid hydrogen and the environment. If there is some heat transfer from the environment to the bottle, the liquid hydrogen will boil.
theoretical density of liquid hydrogen is only 70 kg/m³, so the liquid hydrogen storage can be no higher than 40 kg/m³.

When liquid hydrogen is stored in a huge bottle, there will be a problem of heat delamination. Namely, the liquid in the bottom will experience pressure from the liquid at the top, which causes the boiling point of the bottom liquid to be higher than that of the top liquid. Because of volatilization, the top liquid always has a lower temperature. After some time, there will be two layers: the top layer (cold) and the bottom layer (warmer). The top layer has a lower vapor pressure because of its lower temperature. On the other hand, the bottom layer has a higher vapor pressure because of its higher temperature. Obviously, the system is an unstable state. So, in order to avoid an accident, normally the bottle has a stirrer to prevent heat delamination.

The advantage of liquid hydrogen storage is high storage density (5%), but it also has the problems of cost and evaporation loss.

2.2.2.3 Solid state hydrogen storage

Researchers have found that some metals have a very strong affinity for capturing hydrogen. They can absorb abundant hydrogen at certain temperatures and pressures, and be transformed to metal hydrides. After that, the metal hydride can decompose to release hydrogen when it is heated. Such metals have been named hydrogen storage alloys. The common alloys are of four types: rare earths (AB₅), titanium (AB), zirconium (AB₂), and magnesium (A₂B). Hydrogen storage alloys have attracted attention from the 1970s. In order to improve the hydrogen storage properties, and
reduce the cost, researchers did some extensive exploration of the alloy compositions and preparation technologies.

The main advantage of hydrogen storage alloys is their higher capacity (40-50 kg·H\textsubscript{2}/m\textsuperscript{3}). Also, they have higher security. However, they also have some drawbacks. The mass density of hydrogen storage is low (1.5-3%).

The above three methods are the main methods suitable for practical application. High pressure hydrogen storage had the widest range of usage, but it did not match the storage criterion of the US Department of Energy. So, researchers are finding new methods of hydrogen storage.

2.2.3 Hydrogen storage on carbon materials

2.2.3.1 Hydrogen Storage on Carbon Nanotubes (CNTs)

Since the initial work on hydrogen storage on carbon nanotubes reported by Dillon et al. [182], the storage capacity of CNTs has attracted the most attention. Over 100 papers have been published in the last decade on hydrogen storage in carbon nanotubes. Storage capacities of CNTs ranging from negligible amounts to 20 wt % have been reported [182-189]. The early reported storage capacities of CNTs at room temperature were very high, but now it is confirmed that the storage capacities of pure CNTs are well below 1 wt % [187–189]. This discrepancy in the storage capacities of CNTs is due to the difficulties in accurate measurement, impurities in the carbon samples and in the hydrogen gas, and a poor understanding of the hydrogen sorption mechanism. When all errors were minimized or eliminated from the measurements, the hydrogen storage
capacities of all purified carbon nanotubes were below 0.3 wt % at 298 K and 10 MPa. The hydrogen storage capacities of carbon sorbents without metal doping and significant amounts of remaining impurities are approximately proportional to the Brunauer-Emmett-Teller (BET) surface area and pore volume. This correlation has been well established [190–192].

Although the hydrogen storage capacity of CNTs is low at ambient temperatures, it could be improved with various dopants. Doping CNTs with titanium or titanium alloys was predicted to increase the hydrogen storage capacity. Transition metals (Pd, Pt, Ni, etc.) can also be doped into CNTs to enhance their storage capacity via the hydrogen spillover mechanism [193–196]. Hydrogen spillover is a well documented phenomenon in the catalysis literature, and has been known in the catalysis community for over four decades, although it is still not well understood.

Hydrogenation is another possible route to enhance hydrogen storage in CNTs (52). Nilsson et al. reported that close to 100% hydrogenation on SWCNTs could be reached by exposing the sample to an atomic hydrogen beam.

2.2.3.2 Hydrogen Storage on Graphite Nanofibers (GNFs)

Graphite nanofiber is a type of fibrous carbon consisting of minuscule graphite platelets stacked in an ordered conformation. Hydrogen storage on GNFs was first reported by Chambers and co-workers [197]. They investigated hydrogen adsorption on nanofibers with tubular, platelet, and herringbone structures at 298 K and 12 MPa, and obtained extraordinary storage capacities of 11.26, 53.68, and 67.55 wt %, respectively.
High storage capacities in GNFs were later reported by other authors [198,199]. Like CNTs, the early reported storage capacities of GNFs were overestimated. Recent results indicate, however, that hydrogen uptakes in GNFs at ambient temperature and 10MPa are below 1 wt % [200-202].

Expanding the graphite lattice in GNFs and creating defect sites on GNFs were considered to improve the storage capacity. Poirier et al. observed enhanced hydrogen uptake on exfoliated and intercalated carbon nanofibers at 295 K [201]. Lueking et al. expanded the lattice by exfoliating GNFs at 1000°C and obtained a 1.2 wt % hydrogen uptake at 77 K and 2 MPa, a three-fold increase in hydrogen uptake compared to the starting material [203]. The intercalation and exfoliation techniques have now been mostly applied to graphite for hydrogen storage.

2.2.3.3 Hydrogen Storage on Porous Carbons

Increasing attention has been focused on the storage capacities of porous carbons. Surface area and pore volume are both considered as key factors for hydrogen storage. Beside surface area, micropore size also plays an important role in the adsorption of hydrogen. Both molecular simulations and experiments on porous carbons indicated that narrow pores have stronger interactions with hydrogen molecules due to the overlap of the potential fields from the opposing surfaces of the pore walls, thus leading to higher hydrogen uptake. On the other hand, micropores with diameters larger than 1 nm were also suggested to contribute to the storage capacity. Gadiou et al. investigated hydrogen adsorption on mesoporous carbon and activated carbon with a variety of pore sizes and
found that super-micropores with diameters between 1 and 2 nm also contributed to significant storage capacity [204]. As pore size is a crucial parameter in hydrogen adsorption on carbons, how to tune the pore size of carbon is an issue.

2.2.3.4 Hydrogen Storage on Activated Carbons (ACs)

Activated carbons (ACs) have generally higher surface areas and pore volumes than CNTs, GNFs, and graphite. ACs can be prepared from a variety of abundant raw materials at a low cost. These features make activated carbon a potentially ideal hydrogen storage candidate.

Hydrogen adsorption on ACs with different surface areas (900–2800 m²/g) and pore volumes (0.43–2.17 cm³/g) has been studied by Jin et al. [205]. Two linear relationships were observed between the hydrogen uptake and the surface area, and between the hydrogen uptake and the pore volume. Among the reported ACs, two commercially available ACs with large surface areas have attracted much attention. One is the superactivated carbon AX-21 with a BET surface area of 2800 m²/g, which has a storage capacity of 0.6 wt% at room temperature and 10 MPa and 4.8 wt% at 77 K and 4 MPa [206–208]. The other is Maxsorb activated carbon. Xu et al. studied the hydrogen storage capacity of various carbon materials, including ACs, SWCNTs, MWCNTs, and GNFs. Among these carbons, Maxsorb has the highest surface area of 3300 m²/g and hence the highest storage capacity of 0.67 wt% at 303 K and 10 MPa, and 5.7 wt% at 77 K and 3 MPa [200]. The storage capacities of the carbons were found to be proportional to their specific surface area and micropore volume.
2.2.4 The working ideas and content of this thesis

Research on hydrogen storage is a popular subject, and carbon nanotubes are new materials for hydrogen storage. So, double walled carbon nanotubes (DWCNTs) are one of the topics of this doctoral works and are investigated from two aspects (Chapter 7):
(1) Chemical processing to treat DWCNTs, and comparisons with pristine DWCNTs;
(2) Different reductants for palladium loading on DWCNTs, and comparison of the hydrogen storage capacity to allow the relationship between the palladium and the characterization results to be deduced.

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Chapter 3

Chapter 3 Experimental details

3.1 Chemicals and Materials

The chemicals and materials used for the synthesis, characterization, electrochemical testing are summarized in Table 3-1. The details of the suppliers are also provided.

Table 3-1 Chemicals and materials used in this work

<table>
<thead>
<tr>
<th>Name</th>
<th>Suppliers</th>
<th>Purity or noted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon support</td>
<td>Vulcan XC-72</td>
<td>be dried at 110 °C for 1 h before use</td>
</tr>
<tr>
<td>NiCl₂·6H₂O</td>
<td>Aldrich</td>
<td>99.9%</td>
</tr>
<tr>
<td>H₂PtCl₆·6H₂O</td>
<td>Aldrich</td>
<td>99.9%</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>Aldrich</td>
<td>99.9%</td>
</tr>
<tr>
<td>CoCl₂·6H₂O</td>
<td>Aldrich</td>
<td>99.9%</td>
</tr>
<tr>
<td>KOH</td>
<td>Aldrich</td>
<td>99.9%</td>
</tr>
<tr>
<td>Nickel acetate tetrahydrate</td>
<td>Sigma–Aldrich</td>
<td>ACS</td>
</tr>
<tr>
<td>1,2-propanediol</td>
<td>Sigma–Aldrich</td>
<td>ACS</td>
</tr>
<tr>
<td>DWCNT</td>
<td>Carbon USA (grade DW0923)</td>
<td></td>
</tr>
<tr>
<td>BASF Pt/C</td>
<td>BASF Chemical</td>
<td>20% Pt supported on Vulcan XC-72 carbon</td>
</tr>
<tr>
<td>HCl</td>
<td>Sigma–Aldrich</td>
<td>ACS</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Sigma–Aldrich</td>
<td>ACS</td>
</tr>
<tr>
<td>Pd(C₃H₆O₂)₂</td>
<td>Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>L-ascorbic acid</td>
<td>Sigma–Aldrich</td>
<td>ACS</td>
</tr>
<tr>
<td>Poly(vinylpyrrolidone)</td>
<td>Aldrich</td>
<td>Mₘ = 55,000</td>
</tr>
<tr>
<td>Hydrazine hydrate</td>
<td>Aldrich</td>
<td></td>
</tr>
<tr>
<td>Oleylamine</td>
<td>Sigma–Aldrich</td>
<td></td>
</tr>
<tr>
<td>NH₂OH HC1</td>
<td>Sigma–Aldrich</td>
<td></td>
</tr>
</tbody>
</table>
3.2 Synthesis of Nanostructured Electrocatalysts

3.2.1 Pt-M alloy nanostructured electrocatalysts

To prepare nanosized PtₙNi alloys, a mixture of NiCl₂·6H₂O and H₂PtCl₆·6H₂O was dissolved in de-ionized water with the Pt:Ni (atomic ratio) = 1:1, 2:1, and 3:1, respectively. Then an appropriate amount of carbon (Vulcan XC-72; PtₙNi:C (weight ratio) = 20:80) [1] was added to the solution and dispersed by ultrasonic probe for about 0.5 h (Brandson Ultrasonifier, 35% amplitude). After that, each solution was heated in an oil bath to 138 °C, and then 10 mL aqueous solution of superfluous NaBH₄ was added dropwise into the mixture for reduction under Ar atmosphere. The reacting dispersion was stirred and refluxed continuously for at least 30 min and then cooled down to room temperature. Finally, the black dispersion was isolated by centrifugation and washed 3–4 times with ethanol. The black powder was then dried at 60 °C in a vacuum oven overnight.

To prepare nanosized Pt₁₋ₓCoₓ (x = 0.2, 0.3, and 0.45) alloy catalysts, a mixture of CoCl₂·6H₂O and H₂PtCl₆·6H₂O was dissolved in de-ionized water in an appropriate Pt:Co ratio. Then, certain amount of carbon (Vulcan XC-72) with a weight ratio of Pt₁₋ₓCoₓ:C = 20:80 [1], was added to the solution and dispersed by an ultrasonic probe for about 1.5 h (Brandson Ultrasonifier, 35% amplitude). After that, the solution was heated in an oil bath to 142 °C, in which 15mL aqueous solution of superfluous NaBH₄ was added dropwise into the mixture for reduction under Ar atmosphere. The dispersion was stirred and refluxed continuously for at least 30 min and then cooled down to room temperature. Finally, the black dispersion was isolated by centrifugation and washed...
3–4 times with ethanol. The black powder was then dried at 50 °C in a vacuum oven overnight.

### 3.2.2 M\textsubscript{core}-Pt\textsubscript{shell} structure nanostructured electrocatalysts

To prepare Ni\textsubscript{core}-Pt\textsubscript{shell} nanostructured electrocatalysts, in a typical synthesis process, 0.357 mol/L potassium hydroxide, 0.0242 mol/L oleylamine, and 0.007 mol/L nickel acetate tetrahydrate in 130 ml 1,2-propanediol solution were heated to 120 °C in a three-neck round-bottomed flask under flowing argon gas. After stirring for 30 min, the green mixture was further heated to 135 °C, to which a solution of 1.125 mol/L sodium borohydride in 8 ml hydrazine hydride was gradually added under an argon atmosphere. The solution turned black, indicating the reduction of Ni\textsuperscript{2+} to Ni nanoparticles. Then, a fixed amount of chloroplatinic acid hexahydrate was added to the mixture to obtain Ni@Pt core–shell nanoparticles with a nominal atomic ratio of Pt:Ni = 1:5. Finally, the resulting dispersion was left to cool down to room temperature and then separated by centrifugation. The final product was then dried at 60 °C under vacuum conditions overnight.

To prepare Co\textsubscript{core}-Pt\textsubscript{shell} nanostructured electrocatalysts, the Co seed was prepared first. Briefly, poly(vinylpyrrolidone) (PVP, 78.8 mg) and CoCl\textsubscript{2}-6H\textsubscript{2}O (103.8 mg) were dissolved in 30 mL of deionized water in a three-necked flask (equipped with a reflux condenser and electric stirrer), stirred, and purged in Ar for 30 min. Keeping the saturation Ar atmosphere, a freshly prepared strong reduction solution of NaBH\textsubscript{4} (6 mg in 30 mL 0.1 mol·L\textsuperscript{-1} NaOH solution) was then added dropwise into the above solution
under stirring at room temperature for 30 min to quickly form the Co microcrystal cores. The solution was then heated to reflux, and 28 mL of a weak reduction agent, hydrazine hydrate solution, was added dropwise with stirring. The mixture was reacted for 2 h, and the redundant hydrazine hydrate was completely washed away with water.

Pt was then deposited onto the Co using the following method. H$_2$PtCl$_6$·6H$_2$O (75.3 mg), oleylamine (2.0 mL), and NH$_2$OH·HCl (50.49 mg) were mixed with 60 mL water under vigorous stirring and heated at 60 ºC for 3 h. This solution was then added to the Co seed solution, and the temperature was held constant at 60 ºC for 2 h. After 2 h, the solution was cooled to room temperature, and then filtered and washed with copious water. The final product was then dried at 60 ºC under vacuum conditions overnight.

Ni@Pt/C or Co@Pt/C electrocatalysts were prepared by dispersing Ni@Pt/Co@Pt nanoparticles on Vulcan XC-72 carbon according to the weight ratio of Ni@Pt/Co@Pt:C = 20:80, and the mixture was stirred overnight.

3.2.3 Pt/C nanostructured electrocatalysts

To prepare nanosized Pt/C catalysts, firstly, H$_2$PtCl$_6$·6H$_2$O was dissolved in de-ionized water. Then an appropriate amount of different types of carbon (Vulcan XC-72, activated carbon, graphene, DWCNTs and activated DWCNTs) was respectively added to the solution, so as to achieve a Pt:C weight ratio of 20:80, and the mixture was dispersed by ultrasonic probe for about 0.5 h. After that, 10 mL aqueous solution of superfluous NaBH$_4$ was added dropwise into the mixture to achieve reduction under Ar atmosphere. The reacting dispersion was stirred and refluxed
continuously for at least 30 minutes. Finally, the black dispersion was isolated by centrifugation and washed 3–4 times with ethanol. The black powder was then dried at 60 °C in a vacuum oven overnight.

3.2.4 Acid treatment carbon support

To prepare the activated carbon, firstly, carbon (Vulcan XC-72) was put into HCl (2 mol/L) and refluxed continuously for 8 h at 120 ºC. Then, it was refluxed for at least 8 h at 120 ºC in HNO₃ (5 mol/L). After the treatment, the sample was washed with distilled water and dried at 70 ºC in a vacuum oven overnight.

3.2.5 Activated DWCNTs

To prepare activated DWCNTs, a mixture of DWCNTs and KOH, with DWCNT:KOH (weight ratio) = 1:4 [2,3], was added into ethanol solution and stirred by a magnetic bar for several hours. Then, the mixture was put into a tube furnace and heated to 800 ºC under flowing N₂ (170 mL/min). After activation, the product was thoroughly washed with diluted HCl and water.

3.2.6 2%Pd DWCNTs

In order to load Pd nanoparticles onto DWCNTs, pristine or activated DWCNTs were mixed in ethanol with Pd(C₅H₇O₂)₂, to achieve a nominal Pd content of 2 wt% in the final material, by stirring at room temperature for 12 h. After that, the mixture was dried at 60 ºC in a vacuum oven overnight and then was reduced at 400 ºC for 3 h under H₂ gas flow (150 mL/min).
To prepare 2%Pd/DWCNTs-L-ascorbic acid and 2%Pd/DWCNTs-NaBH₄, firstly, DWCNTs were dissolved in de-ionized water. Then, an appropriate amount of Pd(C₂H₇O₂)₂ was added to the solution, which was stirred at room temperature for 1 h, to achieve a nominal Pd content of 2 wt% in the final material. After that, the different reductants (L-ascorbic acid and NaBH₄) were added dropwise into the mixture in each case to achieve reduction under Ar atmosphere. The reacting dispersion was stirred and refluxed continuously for at least 1 h. Finally, the resultant black dispersion was isolated by centrifugation and washed 3- 4 times with ethanol. The black powder was then dried at 60 °C in a vacuum oven overnight.

3.3 Physical Characterization

3.3.1 X-ray diffraction (XRD)

X-ray diffraction patterns were obtained with a GBC MMA X-ray diffractometer with Cu Kα radiation.

The average crystallite sizes of powder samples can be measured from the peak shape data in the X-ray diffraction patterns. When the average crystallite size is lower than 200 nm, the diffraction peaks will became broader. The smaller the crystallites are, the broader the peaks will be. The relationship between crystallite size and width of peaks can be described with the Scherrer equation:

\[ d = \frac{0.9\lambda}{B \cos \theta} \]  

[3-1]

\( d \): average crystallite size;

\( \lambda \): the wavelength of x-rays (Cu-Kα, \( \lambda = 1.54056 \text{Å} \)).
\( \theta \): the angular position of the diffraction peaks;

\( B \): the width of the half peak (radian)

In order to obtain precise values of \( \theta \) and \( B \), the peaks that are not effected by carbon support so far as curve fitting is concerned (removing background, Lorentz) will normally be chosen. As shown in Fig. 3-1, the values of \( \theta \) and \( B \) can be used for calculating the average crystallite sizes, \( a \), as well as the lattice parameters of the alloy according to the Scherrer equation [3-2].

![Fig. 3-1 Fitting of X-ray diffraction peak](image)

\[ a = \frac{\sqrt{2}}{\sin \theta} \lambda \]

[3-2]

Normally, an alloy lattice parameter is smaller than that of the pure metal. This change occurs because one metal have entered into the lattice of another metal, which will lead to lattice contraction. According to the law of Vegard [4], if a smaller particle enters into the lattice and forms a solid solution, the lattice parameter of the alloy will experience contraction.

Also the ratio of the alloying metal in the alloy can be calculated using eq. [3-3]:

\[ x \left(1 - \frac{r_M}{r_{M'}}\right) = 1 - \frac{a}{a_0} \]

[3-3]

\( a \): the lattice parameter of the alloy;
3.3.2 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

The morphologies and distributions of nanoparticles supported on Vulcan XC-72 carbon or other support were investigated by field emission gun scanning electron microscopy (FEG-SEM) using a JEOL 7001F instrument, with additional semi-quantitative information obtained using large area standardless energy dispersive X-ray spectroscopy (EDX) analysis.

3.3.3 Transmission electron microscopy (TEM) and high resolution TEM (HRTEM)

Transmission electron microscopy (TEM) was performed using a JEOL JEM 2011 TEM instrument. TEM specimens were prepared by making a suspension in ethanol and depositing a drop of the suspension on a standard carbon-covered copper grid.

3.3.4 The Brunauere-Emmette-Teller (BET) Method

The Brunauere-Emmette-Teller (BET) surface areas were measured with a Quanta Chrome Nova 1000 Gas Sorption Analyzer using N₂ as the adsorbate at 77 K.
3.3.5 Raman Spectroscopy

Raman measurements were obtained using a HORIBA Jobin Yvon system with a 632.81 nm wavelength Ar laser.

3.3.6 Hydrogen storage measurements

The hydrogen adsorption behavior of the samples was evaluated at room temperature by the Sieverts method using an AMC Gas Reactor Controller (Advanced Materials Corporation, USA). All samples were dried for almost 4h at 50 °C and vacuum degassed at 147 °C overnight before the sorption. The temperature-programmed-desorption (TPD) curves were measured after the adsorption of H2 for 180 min by heating the samples up to about 1000 K at the heating rate of 10 °C /min.

3.4 Electrochemical Methods

3.4.1 Electrode preparation

Electrochemical measurements were performed with a three-electrode configuration. The glass carbon (GC) electrode was polished with an Al2O3 slurry, then washed in ethanol, diluted HCl, and de-ionized water, respectively. Then, the electrode was preheated in an oven. Electrode ink was prepared by adding the catalyst powders to a 5 wt% Nafion® (DuPontTM) solution according to the ratio of 5 mg to 1 mL. The ink was subsequently treated ultrasonically for at least 1 h until the ink became attached to the bottle wall without macroscopic granules.

The working electrodes were made by casting the ink as a thin film onto a glass
carbon rotating disk electrode (geometrical area = 0.196 cm$^2$), with the Nafion acting as the binding agent. The counter electrode was a Pt wire, and the reference electrode was an Ag/AgCl/KNO$_3$(10%) electrode. So, all potentials are measured with respect to the Ag/AgCl/KNO$_3$(10%).

3.4.2 Equipment for electrochemical testing

All the electrochemical experiments were carried out on a bipotentiostat (Pine Research Instrumentation) at room temperature (25 ºC). The electrolyte solution was 0.1 mol/L HClO$_4$.

3.4.3 Tests on the activation of the oxygen reduction reaction

3.4.3.1 Principle of the rotating disk electrode [5]

Usually a rotating disk electrode is employed to test the catalyzed activity. The rotating disk electrode works by a kind of constrained convection. The thickness of the diffusion layer can be controlled by changing the rotation rate of the electrode using the following equation:

\[
I = 0.62nFD^{2/3} \omega^{1/2}v^{-1/6}(C^o-C^s) \quad [3-4]
\]

Where, I: the reaction current;

n: the reaction electron;

F: Faraday constant;

\( \omega \): angular velocity;

D: the coefficient of diffusion;
\( \nu \): the coefficient of dynamic viscosity;

\( C^0 \): the bulk concentration of the reactant

\( C^S \): the surface concentration of the reactant

When the surface concentration equals zero, the diffusion reaches saturation, so that the current will be a constant value \( (I_d) \):

\[
I_d = 0.62 n F D^{2/3} \omega^{1/2} \nu^{-1/6} C^0
\]  

[3 - 5]

From the above equation, when other conditions are not changed, the limiting diffusion current only depends on the reaction electrons and the rotation speed of the electrode. So if the rate of rotation is changed, the corresponding current can be determined from the reaction electrons\( (n) \).

3.4.3.2 Cyclic voltammograms (CV)

The electrochemical behavior of materials is very sensitive to their surface composition and structures [6]. Normally CV testing can confirm the surface conditions of electrocatalysts (reduction or oxidation peaks). CV tests were carried out with a three-electrode configuration at room temperature using an electrolyte solution which was argon-saturated 0.1 mol/L HClO4. Before the CV testing, the open potential (up to a constant value) is normally first determined, and then the CV from open potential to lower potential (negative direction) is carried out.

3.4.3.3 Linear sweep voltammetry (LSV)

In order to investigate the electrocatalytic characteristics of the catalysts with regard
to the ORR, cathodic reduction from 0.8 V vs. Ag/AgCl at a scanning rate of 10 mV/s was conducted. As the net kinetic current ($i_{\text{kin}}$) is directly proportional to the activity, the $i_{\text{kin}}$ values per unit area at 0.6 V allow a comparison of the oxygen reduction activity of the electrocatalysts. Accordingly, the $i_{\text{kin}}$ at 0.6 V was obtained according to the formula [7]:

$$i_{\text{kin}} = \frac{i_{\text{lim}} \cdot i_{\text{obs}}}{(i_{\text{lim}} - i_{\text{obs}})}$$  \[3-6\]

where $i_{\text{lim}}$ is the limiting current and $i_{\text{obs}}$ is the observed current at 0.6 V. $i_{\text{lim}}$ and $i_{\text{obs}}$ are elucidated by the example of the cathodic sweep curves shown in Fig.3.2. The $i_{\text{kin}}$ values also allow a comparison of the oxygen reduction activity of the electrocatalyst.

![Graph showing cathodic sweep curves for $i_{\text{lim}}$ and $i_{\text{obs}}$](image)

**Fig.3-2 Example for $i_{\text{lim}}$ and $i_{\text{obs}}$**

### 3.4.4 Testing catalyst stability

Since the cathode in a fuel cell is exposed to the corrosive environment of the acidic
electrolyte and oxygen, the stability of the catalyst must be studied. Normally cyclic voltammograms (CV) or chronoamperometry (i-t) are used for testing the stability of the catalyst.

Using CV to test the stability, the CV curve can be obtained at a sweep rate of 50 mV/s after 5000 or some other number of cycles. After that the electrochemically active surface area (ECSA, found by measuring the charges collected in the H\textsuperscript{upd} adsorption/desorption region after double-layer correction) can be calculated [8], and then compared with the first cycle CV curve.

On the other hand, chronoamperometry also can be used to test the stability of catalysts. Chronoamperometry tests were conducted in 0.1 mol L\textsuperscript{-1} HClO\textsubscript{4} with saturated oxygen at a constant potential (0.6 V) over a long time (normally 20-30 h). According to the data, the current-time dependence (i-t) can be obtained.

References:

Chapter 4  Pt-M alloy nanoparticles as cathode catalyst for PEM fuel cells

4.1 Introduction

Hydrogen fed fuel cells are attractive power sources for both stationary and electric vehicle applications. In particular, proton exchange membrane fuel cells (PEMFCs) are a class of devices used for the conversion of chemical energy into electrical energy [1]. The PEMFCs are the most promising candidates for transportation applications due to their high conversion efficiencies and ability to operate without greenhouse gas emissions [2,3]. Furthermore, PEM fuel cells can be operated at relatively low temperatures (under 120 °C) [4]. Recently, they have aroused great interest in both academic and industrial research.

However, the commercial viability of PEMFCs requires the development of better electrocatalysts to improve the fuel-cell performance. The major challenge for widespread applications of PEMFCs relates to the performance, durability, and cost of anode and cathode catalysts [5,6]. One of the key factors affecting the PEMFCs’ performance is a significant overpotential loss on the cathode side due to the slow oxygen reduction reaction (ORR) kinetics under typical conditions of operation [7]. Noble metals, such as Pt supported on high surface area carbons, have been mainly used as catalysts both for the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR). However, in order to further reduce the voltage losses associated with the cathode performance, it is necessary to develop ORR electrocatalysts that are more
catalytically active than platinum. On the other hand, Pt is expensive, and the world’s supply is limited. One method is to prepare Pt nanoparticles supported on carbon, which helps to lower the platinum loading in the PEM fuel cells [8, 9]. Another approach is to synthesize platinum-based binary or ternary electrocatalysts.

Several Pt-based binary systems, such as Pt–Fe [10–13], Pt-Ni [14-16], and Pt–Co [17–20], with different Pt: M (M is a transition metal) atomic compositions have been investigated and have shown enhanced electrocatalytic activity towards ORR compared to Pt catalyst alone. Moreover, the presence of an alloy element reduces the costs associated with Pt. Jalan and Taylor [21] claimed that the increased Pt catalytic activity observed for Pt alloys is related to the shortening of the Pt–Pt interatomic distance. Mukerjee et al. [22] and Min et al. [23] attributed the improvement of Pt catalytic activity to combined electronic (Pt d-band vacancy) and geometric (Pt–Pt distance) effects. Recently, Stamenkovic et al. [24, 25] found that the enhancement of the catalytic activity towards ORR on Pt3Ni and Pt3Co alloy surfaces is due to the inhibition of Pt–OHad formation on Pt sites surrounded by “oxide” covered Ni and Co atoms above 0.8 V.

This chapter reports the synthesis and characterization of a series of Pt_xNi (x = 1–3) and Pt_{1-x}Co_x (x = 0.2, 0.3, and 0.45) alloy nanoparticles on carbon matrix. The synthesized materials were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). The electrochemical performances of the as-prepared catalysts towards ORR were fully investigated and compared to that of pure Pt/C electrocatalyst. They exhibit
significantly enhanced catalytic activity towards oxygen reduction compared to pure platinum catalyst. The results show great promise for a solution to the problem of high demand for platinum in the cathode catalysts in current PEM fuel cells.

4.2 Experimental

4.2.1 Synthesis of PtₓNi/C (x = 1–3) electrocatalysts

To prepare nanosized PtₓNi alloys, a mixture of NiCl₂·6H₂O (Aldrich, 99.9%) and H₂PtCl₆·6H₂O (Aldrich, 99.9%) was dissolved in de-ionized water with the Pt:Ni (atomic ratio) = 1:1, 2:1, and 3:1, respectively. Then, an appropriate amount of carbon (Vulcan XC-72, specific surface area is 237 m²/g; PtₓNi:C (weight ratio) = 20:80) was added to the solution and dispersed by ultrasonic probe for about 0.5 h (Brandson Ultrasonifier, 35% amplitude). After that, each solution was heated in an oil bath to 138 °C, at which point 10 mL aqueous solution of superfluous NaBH₄ was added dropwise into the mixture for reduction under Ar atmosphere. The reacting dispersion was stirred and refluxed continuously for at least 30 min and then cooled down to room temperature. Finally, the black dispersion was isolated by centrifugation and washed 3–4 times with ethanol. The black powder was then dried at 60 °C in a vacuum oven overnight. A sample of pure Pt (20 wt%) on Vulcan XC-72 was also prepared by a similar procedure for comparison.

4.2.2 Synthesis of Pt₁₋ₓCoₓ (x = 0.2, 0.3, and 0.45) electrocatalysts

Similarly, to prepare nanosized Pt₁₋ₓCoₓ (x = 0.2, 0.3, and 0.45) alloy catalysts, a mixture of CoCl₂·6H₂O (Aldrich, 99.9%) and H₂PtCl₆·6H₂O (Aldrich, 99.9%) was
dissolved in de-ionized water in an appropriate Pt:Co ratio. Then, certain amount of carbon (Vulcan XC-72) with a weight ratio of Pt$_{1-x}$Co$_x$:C = 20:80, was added to the solution and dispersed by an ultrasonic probe for about 1.5 h (Brandson Ultrasonifier, 35% amplitude). After that, the solution was heated in an oil bath to 142 °C, at which point 15 mL aqueous solution of superfluous NaBH$_4$ was added dropwise into the mixture for reduction under Ar atmosphere. The dispersion was stirred and refluxed continuously for at least 30 min and then cooled down to room temperature. Finally, the black dispersion was isolated by centrifugation and washed 3–4 times with ethanol. The black powder was then dried at 50 °C in a vacuum oven overnight. A sample of pure Pt (20 wt%) on Vulcan XC-72 was also prepared by a similar procedure for comparison.

4.3 Pt$_x$Ni/C (x = 1–3) electrocatalysts

4.3.1 Physical and Structural Characterization

Fig. 4-1 shows the X-ray diffraction patterns of Pt$_x$Ni alloys and Pt catalyst deposited on Vulcan XC-72 carbon. The XRD pattern of pure nickel is characterized by three diffraction peaks at 2θ = 44.5° (1 1 1), 51.8° (2 0 0), and 76.4° (2 2 2), while that of fcc Pt is characterized by peaks at 2θ = 39.9° (1 1 1), 46.2° (2 0 0), and 67.9° (2 2 0). Therefore, the diffraction peaks at 40°, 46°, and 68° in Fig.4-1 display primarily the characteristics of fcc Pt without any trace of fcc Ni [26]. Apart from the three strong diffraction peaks of platinum, another broad diffraction peak at about 24° represents amorphous carbon. It should be noted that the major diffraction peaks of Pt$_x$Ni catalysts are gradually shifted to higher 2θ angles with increasing Ni content. This indicated a contraction of the lattice
and confirms the formation of Pt–Ni alloys due to the incorporation of Ni into the fcc structure of Pt. No characteristic diffraction peaks of metallic or Ni oxides were detected, indicating that the oxidation of Ni can be effectively prevented by the use of flowing argon gas in the reduction process. The diffraction peaks of the as-prepared Pt\textsubscript{x}Ni alloy catalysts were broader than those of Pt, which can be attributed to the smaller crystallite sizes of those alloy catalysts.

![X-ray diffraction patterns of Pt\textsubscript{x}Ni catalyst nanoparticles deposited on activated carbon matrix.]

Table 4-1 shows the values of the lattice parameters and the mean crystallite sizes of all the catalysts determined quantitatively from XRD analysis. It can be seen that the crystallite sizes and lattice parameters of the alloy catalysts decrease with increasing Ni
content, which is in good agreement with the above analyses. This can be attributed to the greater amount of Ni that can enter into the lattice of Pt with increasing Ni content, which has also been reported in the previous research [10].

Table 4-1 Average crystallite sizes and lattice parameters determined by XRD.

<table>
<thead>
<tr>
<th>Sample</th>
<th>crystallite size / nm</th>
<th>lattice parameter / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>5.90</td>
<td>3.90</td>
</tr>
<tr>
<td>Pt$_3$Ni</td>
<td>2.68</td>
<td>3.89</td>
</tr>
<tr>
<td>Pt$_2$Ni</td>
<td>2.36</td>
<td>3.86</td>
</tr>
<tr>
<td>PtNi</td>
<td>2.32</td>
<td>3.87</td>
</tr>
</tbody>
</table>

The morphologies of the as-prepared Pt$_x$Ni alloy catalysts deposited on Vulcan XC-72 carbon matrix were observed by field emission gun scanning electron microscopy (FEG-SEM). Fig. 4-2(a) shows a SEM image of a typical Pt$_2$Ni alloy catalyst. In general, the carbon matrix exhibits a fluffy cotton-like microstructure, in which Pt$_2$Ni alloy catalyst nanoparticles are embedded. We performed quantitative energy dispersive X-ray spectroscopy (EDX) analysis. For each sample, the Pt:Ni atomic ratio was equal to the nominal ratio. The distribution of Pt$_2$Ni in the carbon matrix was examined by backscattering elemental mapping (as shown in Fig.4-2(b)), from which we can see that Pt and Ni are distributed homogeneously on the micrometer domain.
Fig. 4-2 (a) FEG-SEM image of Pt-Ni catalyst nanoparticles deposited on an activated carbon matrix. (b) Backscattering element mapping of Pt and Ni, showing homogeneous distribution of the alloy elements.

Fig. 4-3(a) and (b) shows bright-field TEM images of PtNi/carbon and Pt/carbon catalysts, respectively. The dark nanoparticles are the PtNi or Pt catalysts. The bright field optical microscopy and selected area electron diffraction (SAED) were performed on the PtNi/carbon catalysts. The insets in the Fig. 4.3(a) and (b) are the selected area electron diffraction patterns with associated spotty rings patterns that correspond to the
PtNi/carbon and Pt/carbon, respectively. The bright spots on the SAEDs correspond to the (1 1 1) and (2 0 0) Pt reflections, and the additional diffuse rings correspond to amorphous carbon. It also can be seen that the catalyst particles have a particle size in the range of a few nanometers, which is consistent with the results deduced from XRD.

Fig. 4-3 Bright-field TEM images of PtNi/carbon and Pt/carbon catalysts. The insets are the corresponding selected area electron diffraction patterns. (a) PtNi/carbon. (b) Pt/carbon.
4.3.2 Electrochemical Characterization

4.3.2.1 Cyclic voltammetry (CV)

The electrochemical performance of catalyst materials is very sensitive to their surface composition and structures. Cyclic voltammograms (CV curves) of the as-prepared electrocatalysts in 0.1 mol/L HClO₄ electrolyte are presented in Fig. 4. The current values were normalized per milligram of platinum. It can be seen that all the CV curves have an obvious hydrogen adsorption-desorption region of -0.25 - 0.1 V vs. SCE, and the current peak associated with the reduction of platinum oxide is in the region of 0.4 V – 0.55 V vs. SCE, indicating the electrochemically active nature of the as-prepared nanosize PtₓNi catalysts. The cathodic current peaks associated with the reduction of platinum oxide are positively shifted by more than 5 mV for the PtₓNi and Pt₂Ni catalysts, and by about 15 mV for the PtNi catalyst, as compared to the pure Pt catalyst. This implies that the desorption of the oxygenated species (e.g., OH) from the surfaces of the alloy particles is easier than from the surface of Pt, i.e., the oxygenated species have a lower adsorption energy on the PtₓNi. This phenomenon has also been observed by Markovic and his co-workers [27-29]. Since the adsorption of OH (or other oxygenated species) on the Pt surface can inhibit its catalytic activity toward ORR, the weak adsorption of the oxygenated species would increase the surface active sites for ORR.

Furthermore, all the CV curves have the same shape, implying that Pt atoms represent the main active sites for the oxidation reaction. The reaction mechanism of oxygen reduction on platinum can be interpreted as follow [30]:
\[ \text{O}_2 + \text{Pt} \rightarrow \text{Pt-O}_2 \] [1]

\[ \text{Pt-O}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{Pt-HO}_2 \text{ (ads)} \] [2]

\[ \text{Pt-HO}_2 + \text{Pt} \rightarrow \text{Pt-HO} + \text{Pt-O} \] [3]

\[ \text{Pt-HO} + \text{Pt-O} + 3\text{H}^+ + 3\text{e}^- \rightarrow 2\text{Pt} + 2\text{H}_2\text{O} \] [4]

Fig. 4-4 Cyclic voltammograms of Pt\(_x\)Ni/carbon catalysts in argon-saturated 0.1 mol/L HClO\(_4\) electrolyte. Scanning rate: 50 mV/s

Therefore, the enhanced electrocatalytic activity of the Pt\(_x\)Ni electrode may be attributed to two factors: One is the increase of the electroactive platinum species, caused by the introduction of nickel [31]. In other words, Ni can facilitate the
desorption of the oxygenate species (e.g., OH\(^-\)) from the surfaces of alloy particles. This is because Ni has a lower electronegativity than Pt, which is responsible for a change in the electronic properties of the Pt in the alloy. The other factor is that the incorporation of Ni into the fcc structure of Pt induces contraction of the lattice. The contraction can sensitively lead to a change in the electronic properties of platinum which weakens the strength of the M-O bond. Both of these two factors can increase the speed of the above reactions, so Pt\(_x\)Ni alloy catalysts demonstrate better electrocatalytic activity. Furthermore, as the Ni content increases, the effects will be enhanced. Among all the prepared catalyst samples, PtNi catalyst exhibits the highest electrochemical reactivity.

4.3.2.2 Linear sweep voltammetry (LSV)

Fig. 4-5 shows catalytic activity towards the ORR on different particles. Obviously, the activities towards the ORR on Pt\(_x\)Ni are higher than on pure Pt particles. PtNi shows the highest activity, followed by Pt\(_2\)Ni, Pt\(_3\)Ni and Pt, agreeing with the positive shift of the oxide reduction peak in the CV.

Since the oxygen reduction reaction (ORR) on Pt surfaces has slow kinetics, it is responsible for the overpotential losses of ~0.3 - 0.4 V under typical conditions of operation [32]. However, alloying platinum with other first-row transition metals such as Ni can effectively reduce the overpotential and therefore, enhance the current density.
4.3.2.3 Chronoamperometry (i-t measurements)

Since the cathode in a fuel cell is exposed to the corrosive environment of the acidic electrolyte and oxygen, the stability of the alloy catalysts must be studied. For this purpose, chronoamperometry tests in 0.1 mol/L HClO₄ with saturated oxygen were conducted.

Fig. 4-6 shows the chronoamperometry curves of PtₓNi/carbon catalysts in oxygen-saturated 0.1 mol/L HClO₄ at the constant potential of 0.60 V. In spite of the initial high current density, there is a rapid decay in the initial period of time. It is believed that this is associated with the adsorption of impurities on the catalyst.
materials. Also, dissolution of nickel from the catalyst could lead to different surface areas for various catalysts resulting in different values of current obtained. After 4 hours operation, the ORR reduction currents were gradually stabilized for all of the catalysts.

The PtNi and Pt$_2$Ni catalysts showed much higher conversion currents than the Pt$_3$Ni and Pt catalysts, which can be attributed to the nickel hydroxide passivated surface.

Therefore, the results of all the electrochemical testing indicated that PtNi and Pt$_2$Ni alloy catalysts had better electrochemical performances towards ORR than the pure Pt catalyst.

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![Fig. 4-6 Chronoamperometric curves of Pt$_x$Ni/carbon catalysts in oxygen-saturated 0.1 mol /L HClO$_4$, measured at 0.6 V vs. SCE.](image-url)
4.4 Pt$_{1-x}$Co$_x$ (x = 0.2, 0.3, and 0.45) Electro catalysts

4.4.1 Physical and Structural Characterization

Fig. 4-7 shows the X-ray diffraction patterns of Pt$_{1-x}$Co$_x$ alloy and Pt catalyst deposited on Vulcan XC-72 carbon. The diffraction peaks at 40°, 47°, and 68° were indexed to Pt (1 1 1), (2 0 0) and (2 2 0), respectively. All diffraction lines can be indexed to the face centered cubic (fcc) phase of platinum (PC-PDF card No. 01-1194). Apart from the three strong diffraction peaks of Pt or Pt$_{1-x}$Co$_x$ phase, another broad diffraction peak at about 24° represents amorphous carbon. It should be noticed that the major diffraction peaks of Pt$_x$Co$_y$ catalysts are gradually shifted to higher 2θ angles with increasing Co content. This indicates a contraction of the lattice and confirms the formation of Pt–Co alloys due to the incorporation of Co into the fcc crystal structure of Pt.

Table 4-2 shows the values of the lattice parameters and the mean crystallite size of all the catalysts, as determined quantitatively from XRD analysis. It can be seen that the crystallite sizes and lattice parameters of the alloy catalysts decrease with increasing Co content, which is in good agreement with the above analyses. No characteristic diffraction peaks of metallic Co or cobalt oxides were detected, indicating that the oxidation of Co can be effectively prevented by the use of flowing argon gas during the reduction process.
Fig. 4-7 X-ray diffraction patterns of Pt$_{1-x}$Co$_x$ catalyst nanoparticles deposited on activated carbon matrix.

Table 4-2 Average crystallite sizes and lattice parameters determined by XRD.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm)</th>
<th>Lattice parameter ($\text{Å}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>5.90</td>
<td>3.904</td>
</tr>
<tr>
<td>Pt$<em>{0.8}$Co$</em>{0.2}$</td>
<td>6.70</td>
<td>3.882</td>
</tr>
<tr>
<td>Pt$<em>{0.7}$Co$</em>{0.3}$</td>
<td>4.60</td>
<td>3.878</td>
</tr>
<tr>
<td>Pt$<em>{0.55}$Co$</em>{0.45}$</td>
<td>4.51</td>
<td>3.864</td>
</tr>
</tbody>
</table>

Fig. 4-8 (a)–(c) shows bright-field TEM images of Pt$_{0.8}$Co$_{0.2}$/C, Pt$_{0.55}$Co$_{0.45}$/C, and Pt/C catalysts, respectively. The dark nanoparticles are Pt$_{1-x}$Co$_x$ or Pt catalysts. The selected area electron diffraction (SAED) patterns give the spotty ring patterns shown in
(a), (b), and (c) for Pt$_{0.8}$Co$_{0.2}$/Carbon, Pt$_{0.55}$Co$_{0.45}$/Carbon and Pt/Carbon, respectively, in which the major diffraction rings can be indexed to (1 1 1), (2 0 0), (2 2 0), and (3 1 1) Pt reflections and additional diffuse rings correspond to amorphous carbon. It also can be seen that the catalyst particles have a particle size in the range of a few nanometers, which is consistent with the results deduced from XRD.

Fig. 4-8. Bright-field TEM images of Pt$_{1-x}$Co$_x$/Carbon catalysts: (a) Pt$_{0.8}$Co$_{0.2}$/Carbon; (b)Pt$_{0.55}$Co$_{0.45}$/Carbon; (c)Pt /Carbon. Insets contain the corresponding SAED patterns.
4.4.2 Electrochemical Characterization

4.4.2.1 Cyclic voltammograms (CV)

The electrochemical performance of catalyst materials is very sensitive to their surface compositions and structures. Cyclic voltammograms (CV curves) curves of as-prepared electrocatalysts in 0.1 mol/L HClO₄ electrolyte are presented in Fig.4-9. It can be seen that these particles exhibit well-defined current peaks associated with hydrogen adsorption-desorption on Pt surfaces in the potential region of -0.20 - 0.1 V vs. SCE. Such hydrogen adsorption-desorption peaks only appear on the PtₓMᵧ alloy catalysts where the Pt percentage is not less than 50% in atomic ratio [33-35]. A current peak associated with the reduction of platinum oxide in the region of 0.4 V - 0.6 V vs. SCE is also well defined. The cathodic current peaks in the CV curves obtained from the Pt₁₋ₓCoₓ particles are positively shifted by more than 30 mV for the Pt₀.₅₅Co₀.₄₅ and Pt₀.₇Co₀.₃ catalysts, and by more than 20 mV for the Pt₀.₈Co₀.₂ catalyst, compared to the pure Pt catalyst. This indicates that desorption of the oxygenated species (e.g., OH⁻) from the surfaces of the alloy particles is easier than from the surfaces of the pure Pt particles, i.e., the oxygenated species have a lower adsorption energy on the alloy surfaces. Since the adsorption of OH⁻ (or other oxygenated species) on a Pt surface can inhibit its catalytic activity towards the oxygen reduction reaction (ORR), the weak adsorption of the oxygenated species would increase the surface active sites for ORR [24,25,27,28,36].

Furthermore, all the CV curves have the same shape, indicating that Pt atoms represent the main active sites for the oxidation reaction. The reaction mechanism of
oxygen reduction on platinum can be interpreted as follows [37] and in last Chapter.

Fig. 4-9 Cyclic voltammograms of Pt$_{1-x}$Co$_x$/carbon catalysts in argon-saturated 0.5 mol·L$^{-1}$ H$_2$SO$_4$ electrolyte. Scanning rate: 50 mV/s.

Therefore, the enhanced electrocatalytic activity of the Pt$_{1-x}$Co$_x$ alloy catalysts may be attributed to two factors: (i) One is the increase in electroactive platinum species, caused by the introduction of Co. In other words, Co can facilitate desorption of the oxygenate species (e.g., OH$^-$) from the surfaces of the alloy particles, because Co has a lower electronegativity than Pt, which is responsible for a change in the electronic properties of Pt in the alloy. (ii) The other reason is that the incorporation of Co into the fcc structure of Pt induces contraction of the lattice. The contraction can sensitively lead to a change in the electronic properties of platinum, which weakens the strength of the M-O bond [27].
Both of these two factors could increase the speed of the above reactions. Therefore, Pt$_x$Co$_y$ alloy catalysts demonstrated a better electrocatalytic activity than pure Pt. Furthermore, as the Co content increases, the effects will be more enhanced. Among all the prepared catalyst samples, Pt$_{0.55}$Co$_{0.45}$ catalyst exhibits the highest electrochemical reactivity.

4.4.2.2 Linear sweep voltammetry (LSV)

Fig. 4-10 shows the linear sweep voltammetry (LSV) curves of Pt$_{1-x}$Co$_x$ catalysts, further demonstrating the catalytic activity towards ORR. Obviously, the activities towards the ORR on Pt$_{1-x}$Co$_x$ are higher than for the pure Pt particles. Pt$_{0.55}$Co$_{0.45}$ shows the highest activity, followed by Pt$_{0.7}$Co$_{0.3}$, Pt$_{0.8}$Co$_{0.2}$, and Pt, agreeing with the positive shift of the oxide reduction peak in the CV. Furthermore, from the figure, during their measurement, all of the LSV curves were under mixed diffusion-kinetic control. Since the oxygen reduction reaction (ORR) on Pt surfaces has slow kinetics, it is responsible for the overpotential losses of ~0.3 - 0.4 V under typical conditions of operation [7]. However, alloying platinum with other first-row transition metals such as Co can effectively reduce the overpotential and therefore, enhance the current density.
4.4.2.3 Chronoamperometry (i-t measurement)

In order to compare the long-time performance of Pt/C and Pt$_{1-x}$Co$_x$/C catalysts towards ORR, chronoamperometry tests in 0.1 mol/L HClO$_4$ with saturated oxygen were conducted. Fig. 4-11 shows the chronoamperometry curves at the constant potential of 0.6 V. In spite of the initial high current density, there is a rapid decay in the initial period of time. After 0.5 h operation, the ORR reduction currents were gradually stabilized for all of the catalysts (except Pt$_{0.55}$Co$_{0.45}$, which shows a slight decay). The Pt$_{0.8}$Co$_{0.2}$ catalysts showed much higher conversion currents than Pt catalysts, which can be ascribed to the enhanced stability of Co in the Pt lattice. However, if the content of
Co reaches a certain value, cobalt will be enriched on the surface, and it becomes very easy for it to be dissolved in electrolyte. So, the stability of Pt_{0.55}Co_{0.45} and Pt_{0.7}Co_{0.3} is lower than that of Pt_{0.8}Co_{0.2}.

![Graph showing chronoamperometric curves](image)

**Fig. 4-11 Chronoamperometric curves of Pt\_\text{1-x}Co\_x/carbon catalysts in 0.1 mol/L HClO\_4 at 0.6 V vs. SCE**

### 4.5 Summary

Nanosize Pt\(_x\)Ni (x = 1–3) and Pt\(_{1-x}\)Co\(_x\) (x = 0.2, 0.3, and 0.45) catalysts on carbon matrix were prepared by a chemical reduction method. The as-prepared catalysts have a uniform distribution on the carbon matrix, with a particle size less than 10 nm. Electrochemical testing results indicate that the presence of Ni and Co enhances the electrocatalytic activity and long-term stability of the catalysts. The prepared Pt\(_x\)Ni or
Pt$_{1-x}$Co$_x$ alloy nanoparticles could have promising applications in PEM fuel cells as effective catalysts for oxygen reduction, with the added feature of reduced cost due to lower Pt loading.

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Chapter 4


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Chapter 5 M_{Core}-Pt_{Shell} structure nanoparticles as cathode catalyst for PEM fuel cells

5.1 Introduction

Hydrogen fed polymer electrolyte membrane fuel cells (PEMFCs) provide zero-emission power sources for automobiles and distributed power generation [1,2]. Platinum is the most effective catalyst to facilitate both hydrogen oxidation and oxygen reduction in a proton exchange membrane (PEM) fuel cell [3-5], but several critical issues still need to be addressed before such cells can be commercialized for automotive application. For example, the oxygen reduction reaction (ORR) is kinetically limited at the cathode [6-9], while Pt-based catalysts lead to high costs.

During the last decade, there has been a surge in research on nanocrystals with core-shell architectures, owing to their superior catalytic [10-14], optical [15-17], magnetic [18-20], and electrical [21] properties. Among the core-shell nanoparticles in various combinations, those made of an inexpensive metal core and a noble metal shell have received particular interest because of the functional and economic advantages that they can provide [10-15,22-24]. Arranging noble metals as thin shells on non-noble metal cores not only greatly reduces noble metal use, but could also significantly enhance their catalytic properties via the underlying interface between the core and shell metals due to the bimetallic mechanism [25].

A variety of core–shell nanoparticles have also been reported as catalysts in PEMFCs. De-alloyed Pt–Cu core–shell nanoparticles were prepared by selective dissolution of Cu atoms from nanoparticle surfaces and have demonstrated surface
catalytic improvement towards oxygen reduction [26,27]. It was proposed that a reduced Pt–Pt distance near the particle surface stabilized by the lattice contracted alloy core, might be responsible for the surface catalytic reactivity. Ru–Pt core–shell nanoparticles showed preferential oxidation of carbon monoxide in hydrogen and remarkable improvement of catalytic reactivity. Density functional theory studies suggested that the enhanced catalytic activity for the core–shell nanoparticle originates from a combination of an increased availability of CO-free Pt surface sites on the Ru@Pt nanoparticles and a hydrogen-mediated low-temperature CO oxidation process that is clearly distinct from the traditional bifunctional CO oxidation mechanism [28]. Polymer protected Pd@Pt core–shell nanostructures were synthesized by a hydrogen sacrifice strategy. The better catalytic performance of the core–shell nanoparticles could be related to near surface alloy (NSA) effects, in which subsurface metal and alloy layers affect the binding of adsorbates to the particle surface. The changes in binding enthalpies can enhance rates and selectivity in the catalytic process [29,30]. Therefore, the core–shell structure is an ideal nano-architecture for reducing the cost of catalyst material and improving catalytic reactivity.

A number of synthesis strategies have already been used for the production of core–shell structure catalysts, such as redox transmetallation [31], the ethylene glycol-assisted polyol method [32], co-reduction [33], the seed growth method [34], etc. In this chapter the synthesis, characterization, and electrochemical performance of novel Ni@Pt and Co@Pt core–shell nanoparticles as catalyst for the oxygen reduction reaction are reported. The results show that although the Ni_{core-Pt_{shell}} or Co_{core-Pt_{shell}}
particles have a much reduced content of Pt, they exhibit significantly enhanced catalytic activity toward oxygen reduction as compared to pure Pt catalyst, showing their great promise in solving the problem of the high demand for precious platinum metal in the cathodes of state-of-the-art PEM fuel cells [35].

5.2 Experimental

5.2.1 Synthesis of Ni$_{\text{core}}$-Pt$_{\text{shell}}$ electrocatalysts

In a typical synthesis process, 0.357 mol/L potassium hydroxide, 0.0242 mol/L oleylamine, 0.007 mol/L nickel acetate tetrahydrate in 130 ml 1,2-propanediol solution were heated to 120 °C in a three-neck round-bottomed flask under flowing argon gas. After stirring for 30 min, the green mixture was further heated to 135 °C, to and a solution of 1.125 mol/L sodium borohydride in 8 ml hydrazine hydrate was gradually added under argon atmosphere. The solution turned black, indicating the reduction of Ni$^{2+}$ to Ni nanoparticles. Then, a fixed amount of chloroplantinic acid hexahydrate was added to the mixture to obtain Ni@Pt core–shell nanoparticles with a nominal atomic ratio of Pt:Ni = 1:5. Finally, the resulting dispersion was left to cool down to room temperature and then separated by centrifugation.

Ni@Pt/C electrocatalysts were prepared by dispersing Ni@Pt nanoparticles on Vulcan XC-72 carbon according to the weight ratio of Ni@Pt:C = 20:80, and the mixture was stirred overnight. Then, the electrode ink was prepared by adding 5 mg Ni@Pt/C catalyst powders to a 5 wt% Nafion$^{\text{TM}}$ solution (Dupont, 1 ml). The ink was then ultrasonicated for 1 h. The catalyst ink was then painted onto a glassy carbon (GC)
electrode with a microsyringe and heat-treated at 60 °C for 1 h. As a comparison, the electrochemical performance of the commercial Pt/C catalyst BASF (20% Pt supported on Vulcan XC-72 carbon, BASF Chemical) was also examined.

5.2.2 Synthesis of Co\textsubscript{core}-Pt\textsubscript{shell} electrocatalysts

The Co seed was prepared first. Briefly, poly(vinylpyrrolidone) (PVP, 78.8 mg) and CoCl\textsubscript{2}·6H\textsubscript{2}O (103.8 mg) were dissolved in 30 mL of de-ionized water in a three-necked flask (equipped with a reflux condenser and electric stirrer), stirred, and purged in Ar for 30 min. Keeping the saturation Ar atmosphere, a freshly prepared strong reduction solution of NaBH\textsubscript{4} (6 mg in 30 mL 0.1 molL\textsuperscript{-1} NaOH solution) was then added dropwise into the above solution under stirring at room temperature for 30 min to quickly form the Co microcrystal cores. The solution was then heated to refluence, and 28 mL of a weak reduction agent, hydrazine hydrate solution, was added dropwise with stirring. The mixture was reacted for 2 h, and the redundant hydrazine hydrate was completely washed away with water.

Pt was then deposited onto the Co using the following method. H\textsubscript{2}PtCl\textsubscript{6}·6H\textsubscript{2}O (75.3 mg), oleylamine (2.0 mL), and NH\textsubscript{2}OH·HCl (50.49 mg) were mixed with 60 mL water under vigorous stirring and heated at 60 °C for 3 h. This solution was then added to the Co seed solution, and the temperature was held constant at 60 °C for 2 h. After 2 h, the solution was cooled to room temperature, and then filtered and washed with copious water. The final product was then dried at 60 °C under vacuum conditions overnight.

In order to obtain pure Co nanoparticles with a narrow size distribution, a “two-step”
reduction method was employed with NaBH₄-NaOH as the nucleating agent and hydrazine hydrate as the reduction agent, respectively. In the first step, NaBH₄-NaOH, a strong reduction agent, was used to quickly reduce part of the Co²⁺ to form the Co microcrystal cores. PVP was used as a stabilizer to control particle size. In the second step, hydrazine hydrate, a weak reduction agent, was used to control the reduction speed of Co²⁺ to achieve reduction of most of the cobalt ions and cause them to grow onto the Co microcrystal seed cores formed in the first step. With this “two-step” reduction method, it is easy to prepare pure Co nanoparticles [36].

To deposit platinum on the surface of the Co, NH₂OHHCl was carefully chosen as the reducing agent because it is well known that in a slightly acid environment, NH₂OHHCl only acts as a growth agent without forming new nuclei [37,38]. Oleylamine was chosen as the capping agent. During the heating pretreatment, where the H₂PtCl₆·6H₂O solution, the oleylamine, and the NH₂OHHCl solution were mixed, neither color change nor precipitation was observed until the addition of the Co seeds. This strongly suggests that NH₂OHHCl only acts as a growth agent in the presence of preformed nuclei.

To prepare Coₙₐₙₐₚₐₐₚₐₘₐ-C particles, an appropriate amount of XC-72 carbon (purified and oxidized by following a procedure reported in [39]) was added to the Coₙₐₚₐₚₐₚₐ-C particle solution according to the weight ratio of Co-Pt : C = 20 : 80, and the mixture was stirred overnight. As a comparison, the electrochemical performance of the commercial Pt/C catalyst BASF was also examined.
5.3 \text{Ni}_{\text{core}}-\text{Pt}_{\text{shell}}$ electrocatalysts

5.3.1 Physical and Structural Characterization

Fig. 5-1 shows the X-ray diffraction pattern of the Ni@Pt core-shell nanoparticles and the Ni nanoparticles. It should be noted that only diffraction peaks of Ni phase appeared in the XRD pattern. This could be because the outer Pt layer is too thin to be visible to X-ray diffraction. All diffraction lines can be indexed to the fcc cubic Ni phase with the space group: Fm-3m, 225. No characteristic diffraction peaks of nickel oxides were detected, indicating that the oxidation of Ni can be effectively prevented by flowing argon gas during the reduction process.

![X-ray diffraction pattern and EDX spectrum](image)

**Fig. 5-1** (a) X-ray diffraction pattern of Ni@Pt core–shell nanoparticles and Ni nanoparticles. (b) EDX spectrum of Ni@Pt core–shell nanoparticles.
The morphologies of the as-prepared Ni@Pt catalyst nanoparticles were analyzed by field emission scanning electron microscope (FESEM) and TEM observation. We also performed quantitative energy dispersive X-ray analysis (EDX) on the FESEM sample.

![Fig. 5-2. (a) Low magnification TEM image of Ni@Pt nanoparticles. The inset is the corresponding SAED pattern. (b) Lattice spacing of Ni obtained from High Resolution TEM image of Ni@Pt nanoparticles.](image)

The atomic ratio of Pt:Ni was determined to be 19.8:100.4, which is very close to...
the nominal ratio of 1 : 5. The EDX spectrum of Ni@Pt core–shell nanoparticles is shown in Fig. 5-1(b). Fig. 5-2(a) shows a low magnification TEM image of the Ni@Pt nanoparticles, from which we can see that the nanoparticles tend to stick together to form loose agglomerates. The associated selected area electron diffraction (SAED) pattern is shown as the inset in Fig. 5-2(a). The major diffraction rings can be indexed to be the cubic nickel phase. As labeled on the SAED pattern, one weak diffraction ring can be identified as Pt(111), which confirms the co-existence of Ni and Pt phase. Fig.5-2(b) shows a lattice resolved high resolution TEM (HRTEM) image of the Ni@Pt core-shell nanoparticles. The lattice planes with an interlayer distance of 0.2 nm in the core can be indexed to (111) crystal planes of Ni. The outer layer of the nanoparticles shows different contrast, which is attributed to the thin Pt layer deposited on the Ni core to form the core-shell nanostructure.

5.3.2 Electrochemical Characterization

5.3.2.1 Cyclic voltammograms (CV)

The electrocatalytic activities towards ORR of the as-prepared Ni@Pt nanoparticles and commercial Pt catalyst were evaluated by cyclic voltammetry (CV). The measurements were performed in 0.1 M HClO₄ aqueous electrolyte. Fig.5-3 exhibits two distinctive potential regions associated with H\textsubscript{upd} adsorption/desorption processed (\( \text{H}^+ + \text{e} = \text{H}_{\text{upd}} \)) within the range of 0 V < E < 0.35 V and the formation of an OH\textsubscript{ad} layer (\( 2\text{H}_2\text{O} = \text{OH}_{\text{ad}} + \text{H}_3\text{O}^+ + \text{e} \)) beyond 0.60 V, where H\textsubscript{upd} and OH\textsubscript{ad} refer to the underpotentially deposited hydrogen and the adsorbed hydroxyl species, respectively.
Furthermore, the particles exhibited well defined current peaks associated with hydrogen adsorption-desorption processes on a Pt surface, implying a Pt nature of the particle surface. The current peak associated with the reduction of hydroxyl species in the CV obtained from the Ni@Pt particles shifts more than 75 mV toward positive potential as compared to that of a pure Pt particle. This indicates that the oxygenate species on the surface of the Ni@Pt nanoparticles have weaker adsorption energy than on the pure Pt catalysts, indicating facilitated desorption of oxygenated Pt species [40–43]. A major decline in the fuel cell’s efficiency was partly attributed to the inhibition of O₂ reduction caused by OH adsorption on Pt in the potential region of 0.75 - 1 V [44,45]. Therefore, the weak adsorption of the hydroxyl species would increase the surface active sites for ORR [46-51] and thus the fuel cell’s efficiency. By measuring the charges collected in the H\textsubscript{upd} adsorption/desorption region after double-layer correction and assuming a value of 210 μC/cm² for the adsorption of a hydrogen monolayer [51], the specific electrochemically active surface areas (ECSA) of the catalysts were calculated to be 70.2 m²/g for the Ni@Pt core-shell nanoparticles and 80.1 m²/g for the BASF Pt catalyst, respectively. The lower ECSA value of the Ni@Pt nanoparticles can rule out surface roughening as the origin of the enhanced ORR catalytic activity. Therefore, both surface structure effects and electronic effects could be responsible for the enhanced ORR catalytic activity for Ni@Pt core-shell nanoparticles. As previously reported, the d-band density of states (DOS) of Pt is downshifted to lower energy for the Ni@Pt-skin structure, inducing a correlated change of chemisorption energies [52-55]. On the other hand, the Ni-induced
modification of the Pt-skin electronic structure can increase the number of active sites for O₂ adsorption [30].

Fig. 5-3. Cyclic voltammograms of Ni@Pt nanoparticles and E-TEK 20 wt% Pt catalyst in 0.1 M HClO₄ electrolyte. Scanning rate: 50 mV/s.

5.3.2.2 Linear sweep voltammetry (LSV)

The LSV curves were measured in O₂ saturated solution to investigate the ORR activity of the Ni@Pt catalyst in 0.1 M HClO₄. The activity of commercial Pt/C (BASF) under O₂ atmosphere was also investigated as the comparison. The total quantity of catalyst used on the electrodes can be calculated, so using current density (mA/g) can be
more effective for interpreting the catalytic activity than using current (mA). As shown in Fig. 5-4, the current density of the Ni@Pt is higher than that of BASF Pt/C in the potential range. This is because the Ni@Pt core-shell catalyst exhibited much higher catalytic activity towards the ORR than the BASF 20% Pt catalyst, which is in accordance with the positive shift of the ORR peak in the CV curves. Therefore, both cyclic voltammetry and polarization measurements confirmed the enhanced ORR catalytic activity for Ni@Pt core-shell nanoparticles.

Fig. 5-4. Linear scan voltammograms for Ni@Pt nanoparticles and E-TEK 20 wt% Pt catalyst in 0.1 M HClO₄ solution saturated with oxygen. Electrode rotation rate: 1600 rpm, scan rate: 5 mV/s

5.4 Coₙcore-Ptₙshell electrocatalysts
5.4.1 Physical and Structural Characterization

Fig. 5-6 shows the X-ray diffraction patterns of the Co nanoparticles (synthesized in step 1) and the Co$_{\text{core}}$-Pt$_{\text{shell}}$ nanoparticles (synthesized in step 2). Only diffraction peaks of Co phase appeared in the XRD pattern. This could be because the outer Pt layer is too thin to be visible to X-ray diffraction. All diffraction lines can be indexed to the hexagonal close-packed (hcp) Co phase with the space group: P63-mmc, 194. No characteristic diffraction peaks of cobalt oxides were detected, indicating that the oxidation of Co can be effectively prevented by flowing argon gas during the reduction process. The shift of XRD peaks toward lower 2\(\theta\) values means a lattice expansion of the Co core in the presence of the Pt shell. This is likely to be a result of the interaction between the Pt shell atoms and the Co atoms underneath [35].

![X-ray diffraction patterns](image)

Fig.5-5 X-ray diffraction patterns of (1) Co nanoparticles (synthesized in step 1), and (2) Co$_{\text{core}}$–Pt$_{\text{shell}}$ nanoparticles (synthesized in step 2).
Fig. 5-6 shows a HRTEM image of a large cluster of $\text{Co}_{\text{core}}$-$\text{Pt}_{\text{shell}}$ catalyst particles (a), an enlarged area showing the lattice spacing (b), and a TEM image of the $\text{Co}_{\text{core}}$-$\text{Pt}_{\text{shell}}$ catalyst, with the inset showing the corresponding SAED pattern (c). A Quantitative energy dispersive X-ray analysis on the sample indicates that the atomic ratio of Pt : Co is 25.2 : 74.8, which is consistent with the theoretical stoichiometric proportion of 1: 3.

Fig. 5-6. (a) HRTEM image of $\text{Co}_{\text{core}}$-$\text{Pt}_{\text{shell}}$ catalyst; (b) enlargement of indicated area showing lattice spacing; (c) TEM image of $\text{Co}_{\text{core}}$-$\text{Pt}_{\text{shell}}$ catalyst, with the inset showing the corresponding SAED pattern.

The HRTEM image in Fig. 5-6 shows that the $\text{Co}_{\text{core}}$-$\text{Pt}_{\text{shell}}$ catalyst has a particle size
in the range of 3-4 nanometers. Since the Pt shell is very thin, it is impossible to resolve the core-shell structure in this image. As shown in Fig. 5-6(b), the lattice planes with a interlayer distance of 0.22 nm in the core can be indexed to the (002) crystal planes of Co. The outer layer of the nanoparticles shows different contrast, which is attributed to the thin Pt layer deposited on the Co core to form the core-shell nanostructure. In Fig. 5-6(c), the major diffraction rings can be indexed to be the hcp cobalt phase. As labeled on the SAED pattern, one weak diffraction ring can be identified as Pt(111), which confirms the coexistence of Co and Pt phase.

5.4.2 Electrochemical Characterization

5.4.2.1 Cyclic voltammograms (CV)

The electrochemical behavior of materials is very sensitive to their surface composition and structures [35]. Therefore, very thin shells over nanometer-sized particles, which are difficult to observe by most physical methods, could be characterized by the electrochemical responses of the core-shell particles. Solid evidence for the homogeneity of the Pt coating comes from cyclic voltammetry (CV), as it can be regarded as a surface sensitive technique that only detects the electrochemical properties of surface atoms rather than bulk atoms. Fig. 5-7 shows cyclic voltammograms for the particles prepared in this work and for the BASF Pt/C particles in argon-saturated 0.1 mol/L HClO$_4$ solution at a sweep rate of 50 mV/s.

The CV curves in Fig. 5-7 exhibit two distinctive potential regions associated with H$_{upd}$ adsorption/desorption ($\text{H}^{+} + \text{e} = \text{H}_{\text{upd}}$) processed in the range of $-0.25 \text{ V} < E < 0 \text{ V}$
and the formation of a OH\textsubscript{ad} layer ( 2H\textsubscript{2}O = OH\textsubscript{ad} + H\textsubscript{3}O\textsuperscript{+} + e) beyond 0.3 V, where H\textsubscript{upd} and OH\textsubscript{ad} refer to the underpotentially deposited hydrogen and the adsorbed hydroxyl species, respectively. Furthermore, the particles exhibited well defined current peaks associated with hydrogen adsorption-desorption processes on a Pt surface, implying a Pt nature of the particle surface. The formation and reduction of hydroxyl species is in the region of 0.35-0.65 V, and the current peak associated with the reduction of hydroxyl species in the CV curve obtained from the Co\textsubscript{core}-Pt\textsubscript{shell} particles is shifted by more than 50 mV toward positive potential as compared to that of the pure Pt particles. This implies that desorption of the hydroxyl species (e.g., OH) from the surface of a Co\textsubscript{core}-Pt\textsubscript{shell} particle is easier than from the surface of a pure Pt particle. The major decline that generally occurs in a fuel cell’s efficiency has been partly attributed to the inhibition of O\textsubscript{2} reduction caused by OH adsorption on Pt in the potential region of 0.75 - 1 V [7, 56]. Therefore, the weak adsorption of the hydroxyl species would increase the surface active sites for ORR [30,49,50] and thus the fuel cell’s efficiency. By measuring the charges collected in the H\textsubscript{upd} adsorption/desorption region after double-layer correction and assuming a value of 210 \( \mu \)C/cm\textsuperscript{2} for the adsorption of a hydrogen monolayer [57], the specific electrochemically active surface areas (ECSA) of the catalysts were calculated to be 68.1 m\textsuperscript{2}/g for Co\textsubscript{core}-Pt\textsubscript{shell} /C nanoparticles and 80.1 m\textsuperscript{2}/g for the BASF Pt catalyst, respectively (Table 5-1). The lower ECSA value of the Co\textsubscript{core}-Pt\textsubscript{shell} /C nanoparticles can rule out surface roughening as the origin of the enhanced ORR catalytic activity [58]. Actually, the difference in adsorption properties between the supported metal shell and its bulk counterpart has
been shown to be a general phenomenon due to the modification of the electronic properties of surface atoms by the underlying metal via geometric strain and ligand interactions. For Pt on a Co surface, compressive strain of the Pt-Pt distance occurs, resulting in weak interactions between the Pt surface atoms and some simple adsorbates such as H, CO, and OH [59,60]. Furthermore, Cocore-Ptshell catalyst has the added feature of reduced cost, due to the lower Pt loading.

![Graph](image)

**Fig. 5-7.** Cyclic voltammograms of Co_{core}-Pt_{shell}/C and Pt/C catalysts in argon-saturated 0.1 mol/L HClO₄ electrolyte. Scanning rate: 50 mV/s.

5.4.2.2 Linear sweep voltammetry (LSV)

In order to investigate the electrocatalytic characteristics of the catalysts with regard to the ORR, cathodic reduction from 0.8 V vs. Ag/AgCl at a scanning rate of 10 mV/s was conducted. As the net kinetic current ($i_{kin}$) is directly proportional to the reduction
activity, the $i_{\text{kin}}$ values per unit area at 0.6 V allow a comparison of the oxygen reduction activity of the electrocatalysts. Accordingly, the $i_{\text{kin}}$ at 0.6 V was obtained according to the formula [61] below:

$$i_{\text{kin}} = \frac{i_{\text{lim}} \cdot i_{\text{obs}}}{(i_{\text{lim}} - i_{\text{obs}})}$$

where $i_{\text{lim}}$ is the limiting current and $i_{\text{obs}}$ is the observed current at 0.6 V. $i_{\text{lim}}$ and $i_{\text{obs}}$ are elucidated by the example of the cathodic sweep curves shown in Fig. 5-8. The $i_{\text{kin}}$ values listed in Table 1 also allow a comparison of the oxygen reduction activity of the Co$_{\text{core}}$-Pt$_{\text{shell}}$/C as compared to the BASF Pt electrocatalyst. The $i_{\text{kin}}$ value is obviously higher in the Co$_{\text{core}}$-Pt$_{\text{shell}}$/C electrocatalysts, as shown in Table 5-1. This result is consistent with the CV results above.

![Cathodic potential sweep curves for (a) Pt/C, (b) Co$_{\text{core}}$-Pt$_{\text{shell}}$/C. Scanning rate: 10 mV/s.](image-url)
Table 5-1 Comparison of the Pt/C and Co_{core}\text{-}Pt_{shell}/C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ECSA (m²g⁻¹)</th>
<th>(i_{\text{kin}}) (mAcm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>80.1</td>
<td>0.199</td>
</tr>
<tr>
<td>Co_{core}\text{-}Pt_{shell}/C</td>
<td>68.1</td>
<td>0.386</td>
</tr>
</tbody>
</table>

5.4.2.3 Testing the catalyst stability

Since the cathode in a fuel cell is exposed to the corrosive environment of the acidic electrolyte and oxygen, the stability of the Co_{core}\text{-}Pt_{shell}/C catalyst must also be studied. So, cyclic voltammetry in O₂-saturated 0.1 mol/L HClO₄ solutions at a sweep rate of 50 mV/s was performed.

![CV curves](image)

Fig. 5-9 CV curves for the Co_{core}\text{-}Pt_{shell}/C before and after accelerated durability testing. The durability test was carried out on the same sample at room temperature in an O₂-saturated 0.1 mol/L HClO₄ solution at a sweep rate of 50 mV/s
After 5000 cycles, the CV measurements showed a loss of 46% in electrochemically active surface area (ECSA) for the Co\text{core-Pt\text{shell}}/C catalyst (Fig.5-9), as compared to 42% for the pure Pt/C catalyst, suggesting that the Co\text{core-Pt\text{shell}} particles had durability similar to that of the pure Pt/C catalyst. All of the electrochemistry tests suggest that activated carbon is well suited for use as carbon support in high-performance electrocatalysts.

5.5 Summary

Nanosize Ni\text{core-Pt\text{shell}} or Co\text{core-Pt\text{shell}} catalysts can be readily fabricated by a successive reduction strategy under the assistance of surfactants. The formation of a core-shell structure has been elucidated by various techniques, including XRD, TEM, and electrochemical techniques. The as-prepared catalysts have a uniform distribution, with a particle size in the range of 3-5 nm. Electrochemical testing results indicate that Ni\text{core-Pt\text{shell}} and Co\text{core-Pt\text{shell}}/C show enhanced catalytic activity compared to that of pure Pt/C. The results show that the core-shell structure nanoparticles could have a promising application in PEM fuel cells as effective catalysts for oxygen reduction, with the added feature of reduced cost.

References:


[53] B Lim, M Jiang, PHC Camargo, EC Cho, J Tao, XM Lu, YM Zhu, YN Xia,
Science, 2009, 324, 1302.


Chapter 6 The effects of carbon support on cathode catalyst performance in PEM fuel cells

6.1 Introduction

The proton exchange membrane fuel cells (PEMFCs) are the most promising candidates for transportation applications due to their low operating temperature (< 100 ºC) and fast start-up [1-3]. Although great progress has been made in the last several years, the commercialization of this technology has several technical and economic barriers that must be addressed in terms of cost, durability, and performance.

Up to the 1990s, carbon black (Vulcan XC-72R) was widely used for platinum support in low-temperature fuel cells. The use of carbon black in catalysis has been continuously growing since the beginning of the last decade [4,5]. Its application as catalyst support offers several advantages, mostly because it is a relatively inexpensive and inert material [6-8]. Despite its widespread use, carbon can be electrochemically oxidized to surface oxides, and eventually to CO$_2$ at the cathode under PEM fuel cell conditions, which leads to Pt nanoparticles becoming sintered on or detached from the support materials, degrading fuel cell performance [9]. Therefore, much effort has been devoted to developing durable catalyst support materials [10].

One method is to activate the carbon support. It has been observed that the properties of the carbon supports, such as surface functional groups [11], have a large effect on the activity of the catalysts. These characteristics can be modified by physical or chemical treatment of the activated carbon support material. The carbon oxygen functionalities
are by far the most important chemical groups on the surface of activated carbons. The type of chemical group that can be introduced on activated carbons depends on the treatment conditions. For instance, acidic groups are produced when activated carbons are treated in solution with different oxidizing agents [12]. Usually additional acid treatments of the support material are essential to remove, at least partially, any surface contaminants and to reduce the ash content. It has been reported that acid treatment can improve the catalytic activity of activated carbon supported catalysts [13,14].

Another method is to use novel carbon supports, such as carbon aero- and xero-gels [15-17], carbon nanofibers [18-21], ordered mesoporous carbon [22-24], and carbon nanotubes (CNTs) [25,26]. Carbon nanotubes (CNTs) have attracted much interest from both a fundamental and an applied perspective since their discovery [27] and large-scale synthesis [28,29], owing to their unique properties, e.g., high electrochemical stability, high electrical conductivity, and high surface area. These CNT materials are also considered to be potentially useful supports in catalysis [30-32]. Pt nanoparticles generally display superior electrocatalytic performance when supported on carbon nanotubes compared to carbon black [33].

Recently, graphene, a single layer of carbon (carbon atoms in a two-dimensional (2D) honeycomb lattice), has attracted strong scientific and technological interest [34] with great application potentials in various fields, such as electronic devices [35], nanocomposites [36-38], sustainable energy storage and conversion devices [39,40], batteries [41], and fuel cells [42-45]. It has been proposed that carbon material with a higher graphite component can be more stable [43].
In this section, we have investigated 20 wt% Pt/C catalysts, with Vulcan XC-72 (BASF), activated carbon, pristine double-walled carbon nanotubes (DWCNTs), activated DWCNTs, and graphene, respectively, used as the carbon support source. We found that all the Pt nanocatalysts exhibited enhanced electrochemically active surface areas and improved activity in the oxygen reduction reaction (ORR) compared to the Pt on Vulcan XC-72.

6.2 Experimental

6.2.1 Synthesis of Pt/XC-72 and Pt/activated carbon electrocatalysts

To prepare nanosized Pt/C catalysts, firstly, H₂PtCl₆·6H₂O was dissolved in de-ionized water. Then, an appropriate amount from the different types of carbon (pristine carbon and activated carbon) was added respectively to the solution, so as to achieve a Pt:C weight ratio of 20:80, and dispersed by ultrasonic probe for about 0.5 h. After that, 10 mL aqueous solution of superfluous NaBH₄ was added dropwise into the mixture to achieve reduction under Ar atmosphere. The reacting dispersion was stirred and refluxed continuously for at least 30 minutes. Finally, the black dispersion was isolated by centrifugation and washed 3–4 times with ethanol. The black powder was then dried at 60 °C in a vacuum oven overnight. To prepare the activated carbon, firstly, carbon was put in HCl (2 mol/L) and refluxed continuously for 8 h at 120 °C. Then, it was refluxed for at least 8 h at 120 °C in HNO₃ (5 mol/L). After the treatment, the sample was washed with distilled water and dried at 70 °C in a vacuum oven overnight.
6.2.2 Synthesis of Pt/DWCNT and Pt/activated DWCNTs electrocatalysts

To prepare nanosized Pt/C catalysts, firstly, $\text{H}_2\text{PtCl}_6\cdot6\text{H}_2\text{O}$ was dissolved in de-ionized water. Then, an appropriate amount of the different types of carbon (DWCNTs and activated DWCNTs) was added respectively to the solution, so as to achieve a Pt:C weight ratio of 20:80, and dispersed by ultrasonic probe for about 0.5 h. After that, 10 mL aqueous solution of superfluous $\text{NaBH}_4$ was added dropwise into the mixture to achieve reduction under Ar atmosphere. The reacting dispersion was stirred and refluxed continuously for at least 30 minutes. Finally, the black dispersion was isolated by centrifugation and washed 3–4 times with ethanol. The black powder was then dried at 60 ºC in a vacuum oven overnight.

To prepare activated DWCNTs, a mixture of DWCNTs and KOH, with DWCNT:KOH (weight ratio) = 1:4 [46], was added into an ethanol solution and stirred by a magnetic bar for several hours. Then, the mixture was put into a tube furnace and heated to 800 ºC under flowing $\text{N}_2$ (170 mL/min). After activation, the product was thoroughly washed with diluted 5% HCl and water.

6.2.3 Synthesis of Pt/graphene electrocatalysts

Graphene nanosheets were synthesized by the method reported in [47]. In a typical synthesis process, natural graphite powders (SP-1, Bay Carbon, MI, USA) were oxidized to graphite oxide. One gram graphite powder and 0.5 g sodium nitrate were poured into 70 ml concentrated $\text{H}_2\text{SO}_4$ (in an ice bath). Then 3 g $\text{KMnO}_4$ was gradually
added. The mixture was stirred for 2 h and then diluted with de-ionised (DI) water. After that, 5% \( \text{H}_2\text{O}_2 \) was added into the solution until the color of the mixture changed to brilliant yellow. The as-obtained graphite oxide was re-dispersed in DI water and then exfoliated to generate graphene oxide nanosheets by ultrasonication using a Brandson Digital Sonifier (S450D, 40% amplitude). The brown graphene oxide nanosheet dispersion was poured into a round-bottomed flask, to which hydrazine monohydrate (as reducing agent) was added. The mixed solution was then refluxed at 100 °C for 2 h, over which time the color of the solution gradually changed to dark black as the graphene nanosheet dispersion was formed. The dispersion was further centrifuged for 15 min at 3000 rpm to remove a small amount of precipitate. The supernatant of the graphene nanosheet dispersion was directly dried in a vacuum oven to obtain bulk graphene nanosheet powders. The deposition of Pt on graphene was realized by a similar method to that described in Chapter 6.2.1.

6.3 Acid treatment of carbon supports for PEM fuel cell electrocatalysts

6.3.1 Physical and Structural Characterization

The XRD patterns reveal the bulk structure of the catalyst and its support. Fig. 6-1 shows the X-ray diffraction patterns of pristine carbon, activated carbon, Pt/carbon, and Pt/activated carbon. It can be seen from Fig. 6-1 that both carbon black and activated carbon have a similar amorphous structure. The amorphous peaks at 24.6° (002) and 47.1° (101) are very broad, but can still be observed. The XRD pattern also confirmed
that the acid treatment on pristine carbon did not lead to any structural change in the carbon. For the Pt/carbon and Pt/ activated carbon, the first peak in the low $2\theta$ range is attributed to the carbon support. The Pt pattern displays $39.9^\circ$ (111), and $46.5^\circ$ (200) reflections, showing a face centered cubic (fcc) crystal structure.

![X-ray diffraction patterns](image)

**Fig.6-1** X-ray diffraction patterns of (a) pristine carbon, (b) activated carbon, (c) Pt/carbon, and (d) Pt/ activated carbon

Table 6-1 shows the values of the mean crystallite size of the catalysts determined quantitatively from XRD analysis. It shows that the mean crystallite sizes of Pt/carbon and Pt/activated carbon are similar. This means that the activation did not lead to much change in the particle size.
Table 6-1 Comparison of the Pt/carbon and Pt/activated carbon

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm)</th>
<th>ECSA (m²/g)</th>
<th>$i_{\text{kin}}$ (mA cm⁻²)</th>
<th>Specific surface area of the supports (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/carbon</td>
<td>5.90</td>
<td>80.1</td>
<td>0.199</td>
<td>237</td>
</tr>
<tr>
<td>Pt/activated carbon</td>
<td>5.78</td>
<td>96</td>
<td>0.286</td>
<td>251.4</td>
</tr>
</tbody>
</table>

Fig. 6-2 shows TEM bright field micrographs of the Pt/carbon and Pt/activated carbon, respectively. The dark nanoparticles are the Pt catalyst. The TEM images of the prepared catalysts (Fig. 6-2(a) and (b)) show that the Pt particles are well dispersed on the carbon surface. Comparison of Fig. 6-2(a) and (b) indicates the slight effects of activation on the general morphology of the carbon.

![TEM micrographs](image)

Fig. 6-2 TEM bright field micrographs of (a) Pt/activated carbon; (b) Pt/carbon. The insets are the corresponding selected area electron diffraction patterns.

The selected area electron diffraction (SAED) patterns of the catalysts give spotty ring patterns, as are shown in the insets in Fig. 6-2(a) and (b), respectively. The bright spots in those SAED patterns correspond to the (111) and (200) Pt reflections, and the additional diffuse rings correspond to an amorphous carbon plane (002). It also can be
seen that the catalyst particles have particle sizes in the range of a few nanometers, which is consistent with the results deduced from XRD.

From the energy dispersive X-ray spectroscopy (EDX) of the pristine carbon and activated carbon, it can be seen that the composition has changed after the acid treatment. Before the acid treatment, the sulfur content is about 0.9%, and there are also some inorganic impurities (e.g., Cu), but after treatment, the sulfur content is 0.4%, only half as much as before. The inorganic impurities have also disappeared. At the same time, the oxygen content has increased significantly, which could be attributed to increased amounts of some functional groups containing oxygen [48].

The specific surface areas of the pristine carbon and the activated carbon were measured to be 237 m²/g, and 251.4 m²/g, respectively. It was found that acid treatment can effectively increase the BET surface areas of the carbon, which is attributed to the elimination of inorganic impurities and increased amounts of some oxygenated species functional groups, such as carboxyl. This result is consistent with the results of TEM analysis.

6.3.2 Electrochemical Characterization

6.3.2.1 Cyclic voltammograms (CV curves)

The electrochemical performance of catalyst materials is very sensitive to their surface composition and structures. Cyclic voltammograms (CV curves) of the as-prepared electrocatalysts in 0.1 mol/L HClO₄ electrolyte are presented in Fig. 6-3. The current values were normalized per unit area of the electrode. It can be seen that all CV curves have an obvious hydrogen adsorption–desorption region of −0.25–0.1 V
versus Ag/AgCl, and the current peak associated with the reduction of platinum oxide is in the region of 0.3–0.5 V versus Ag/AgCl, indicating the electrochemically active nature of the as-prepared nanosize Pt catalysts. The cathodic current peaks associated with the reduction of platinum oxide are positively shifted by more than 40 mV for the Pt/activated carbon, as compared to the Pt/carbon catalyst. This implies that the desorption of the oxygenated species (e.g., OH) from the surfaces of the Pt/activated carbon particles is easier than from the surface of the Pt/carbon, i.e., the oxygenated species have a lower adsorption energy on the Pt/activated carbon. Since the adsorption of OH (or other oxygenated species) on the Pt surface can inhibit its catalytic activity toward ORR, the weak adsorption of the oxygenated species would increase the surface active sites for ORR [49].

Furthermore, the oxidation peak of hydrogen occurs around 0 V, and this peak area could be used to determine the active Pt surface area by the electrochemical method. The specific electrochemically active surface areas (ECSA) can be used to measure the utilized efficiency of the Pt nanoparticles, and this is more important to the fuel cell reactions than surface area. By measuring the charges collected in the underpotentially deposited hydrogen ($H_{\text{upd}}$) adsorption/desorption region after double-layer correction and assuming a value of 210$\mu$C/cm$^2$ for the adsorption of a hydrogen monolayer [50], the ECSA values of the catalysts were calculated to be 80.1 m$^2$/g (Pt/carbon), and 96 m$^2$/g (Pt/activated carbon), respectively (Table 6-1). The higher performance of the Pt/activated carbon compared to that of the Pt/carbon electrode could be attributed to increased amounts of some functional groups containing oxygen, which could have
some effects on the Pt$^4+$ ions and become nucleation positions. So, the interaction between Pt and carbon would be stronger, which can change the electronic properties of Pt, causing the Pt particles to be more stable and have higher electrocatalytic performance.

Fig. 6-3 Cyclic voltammograms of Pt/carbon and Pt/activated carbon catalysts in argon-saturated 0.1 mol/L HClO$_4$ electrolyte. Scanning rate: 10 mV/s.

6.3.2.2 Linear sweep voltammetry (LSV)

In order to investigate the electrocatalytic characteristics of the catalysts for the ORR, cathodic reduction from 0.8 V versus Ag/AgCl at a scanning rate of 10 mV/s was used. As the net kinetic current ($i_{\text{kin}}$) is directly proportional to the activity, the $i_{\text{kin}}$ values per
unit area at 0.6 V allow a comparison of the oxygen reduction activity of the electrocatalysts. Accordingly, the $i_{\text{kin}}$ at 0.6 V was obtained according to the formula [51]:

$$i_{\text{kin}} = i_{\text{lim}} \cdot \frac{i_{\text{obs}}}{i_{\text{lim}} - i_{\text{obs}}}$$ [6-1]

where $i_{\text{lim}}$ is the limiting current and $i_{\text{obs}}$ is the observed current at 0.6 V. $i_{\text{lim}}$ and $i_{\text{obs}}$ are elucidated by the example of the cathodic sweep curves shown in Fig.6-4.

Fig. 6-4 Cathodic potential sweep curves for (a) Pt/carbon, (b) Pt/activated carbon. Scanning rate: 10 mV/s.

The $i_{\text{kin}}$ values listed in Table 6-1 also allow a comparison of the oxygen reduction activity of the electrocatalysts prepared using the different types of carbon. The $i_{\text{kin}}$
value was higher in the electrocatalysts prepared using activated carbon than in those prepared using pristine carbon support, as shown in Table 6-1. This result is consistent with the CV results above. All of the electrochemistry tests suggest that activated carbon is well suited for use as carbon support in high-performance electrocatalysts.

6.4 Pt/C catalysts using DWCNT support for cathode of PEM fuel cells

6.4.1 Physical and Structural Characterization

The XRD patterns of XC-72 carbon, DWCNTs, and activated DWCNTs (referred to as A-DWCNTs) are shown in Fig. 6-5(a). The diffraction peaks at 26.7⁰ and 43.7⁰ observed in the diffraction patterns of DWCNTs and activated DWCNTs can be attributed to (002) and (100) hexagonal graphite structures. For XC-72 carbon, a rather wide and shallow (002) peak is observed in its XRD pattern, implying that XC-72 is an amorphous carbon material with small regions of crystallinity, while DWCNTs and activated DWCNTs are in graphite form. Fig. 6-5(b) shows the X-ray diffraction patterns of Pt supported on XC-72, DWCNTs, and activated DWCNTs, respectively. It is found that they form a face centered cubic (fcc) structure and have major peaks at around 2θ = 39.7⁰ (111) and 46.2⁰ (200). The widths of peaks in Fig. 6-5(b) show that under the experimental conditions, the different catalysts using different supports (DWCNT and A-DWCNT) show different Pt particle sizes from the commercial Pt catalyst used for comparison (Table 6-2).
Fig. 6-5 X-ray diffraction patterns of (a) different types of carbon: (1) XC-72, (2) activated DWCNTs, (3) DWCNTs; and (b) Pt/C composites: (1) Pt/XC-72, (2) Pt/DWCNTs, (3) Pt/A-DWCNTs.

Raman spectroscopy is an efficient and non-destructive tool to characterize carbon materials, and in particular, for distinguishing defects in the carbon structure. Fig. 6-6
shows the Raman spectra of pristine and chemically activated DWCNTs [52]. Two peaks at 1580 cm\(^{-1}\) and 1350 cm\(^{-1}\) are identified as the G and D bands, respectively. The G band represents the E\(_{2g}\) phonon of C\(_{sp2}\) atoms in the graphite structure, while the D band is usually assigned to the breathing mode of \(\kappa\)-point phonons of A\(_{1g}\) symmetry in the disordered graphite structure [53].

![Raman spectra of pristine and chemically activated DWCNTs](image)

Fig. 6-6 Raman spectra of (a) pristine DWCNTs and (b) chemically activated DWCNTs.

It is well known that the intensity ratio of the D and G peaks (I\(_{1350}\) / I\(_{1580}\)) gives information on the degree of disorder of the CNTs [54]. In the present work, it was found that the intensity ratio of I\(_{1350}\) / I\(_{1580}\) was increased by activation, indicating the creation of defects at the DWCNT surface through the chemical activation process. This is attributed to the metallic potassium produced during the redox reaction between KOH and DWCNTs, which can be intercalated into the nanotubes walls and is thus
responsible for separation and degradation of graphitic layers and for the development of microporosity [55].

Fig. 6-7 shows TEM bright field micrographs of the pristine DWCNTs (Fig. 6-7(a)), the activated DWCNTs (Fig. 6-7(b)), Pt/DWCNTs (Fig. 6-7(c)), Pt/A-DWCNTs (Fig. 6-7(d)), and Pt/XC-72 (Fig. 6-7(e)). The dark nanoparticles are the Pt catalyst. Comparison of Fig. 6-7(a) and 6-7(b) indicates the effects of activation on the general morphology of the DWCNTs, with reduced homogeneity of parallel CNT walls, consistent with increased defect density in the activated sample. The TEM images of the prepared catalysts (Fig. 6-7(c), (d), and (e)) show that the Pt particles are well dispersed on the carbon surface. The SAED patterns of the catalysts gives associated spotty ring patterns, as shown in the insets in Fig. 6-7(c), (d), and (e), respectively. The bright spots in those SAED patterns correspond to the (111) and (200) Pt reflections, and the additional diffuse rings correspond to carbon. Furthermore, the particles in (c) and (d) are smaller than in (e), which is consistent with the results deduced from XRD (Table 6-2).

Table 6-2 Average crystallite sizes determined by XRD and TEM, and the as-prepared ECSA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>crystallite size / nm</th>
<th>average particle size / nm</th>
<th>ECSA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/XC-72</td>
<td>5.90</td>
<td>8.90</td>
<td>80.1</td>
</tr>
<tr>
<td>Pt/DWCNT</td>
<td>5.68</td>
<td>7.2</td>
<td>92</td>
</tr>
<tr>
<td>Pt/A-DWCNT</td>
<td>4.65</td>
<td>6.8</td>
<td>98</td>
</tr>
</tbody>
</table>
Fig. 6-7 TEM bright field micrographs of (a) pristine DWCNTs; (b) activated DWCNTs; (c) Pt/DWCNTs; (d) Pt/A-DWCNTs; and (e) Pt/XC-72, with insets in (c), (d), and (e) showing the corresponding selected area electron diffraction patterns.
The specific surface areas of XC-72 carbon, the pristine DWCNTs, and the chemically activated DWCNTs were measured to be 237 m$^2$/g, 197.8 m$^2$/g, and 320.42 m$^2$/g, respectively. It is found that chemical processing can effectively increase the BET surface areas of DWCNTs, which is attributed to the defects. This result is consistent with the results of Raman spectroscopy and TEM analysis.

6.4.2 Electrochemical Characterization

6.4.2.1 Cyclic voltammograms (CV curves)

Fig. 6-8 shows cyclic voltammograms (CVs) for the nanoparticles prepared in this work in argon-saturated 0.1 mol/L HClO$_4$ solution at a sweep rate of 20 mV/s. The CVs in Fig. 6-8 exhibit two distinctive potential regions associated with H$_{\text{upd}}$ adsorption/desorption (H$^+$ + e = H$_{\text{upd}}$) between -0.25 V < E < 0 V and with the formation of a OH$_{\text{ad}}$ layer (2H$_2$O = OH$_{\text{ad}}$ + H$_3$O$^+$ + e) above 0.3 V, where H$_{\text{upd}}$ and OH$_{\text{ad}}$ refer to the underpotentially deposited hydrogen and the adsorbed hydroxyl species, respectively. Furthermore, the particles exhibited well defined current peaks associated with hydrogen adsorption-desorption processes on a Pt surface, implying a Pt nature of the particle surface. The oxidation peak of hydrogen occurs around 0 V and this peak area could be used to determine the active Pt surface area by the electrochemical method. The specific electrochemically active surface areas (ECSA) can be used to measure the utilized efficiency of the Pt nanoparticles, and this is more important to the fuel cell reactions than surface area. By measuring the charges collected in the H$_{\text{upd}}$ adsorption/desorption region after double-layer correction and
assuming a value of 210 $\mu$C/cm$^2$ for the adsorption of a hydrogen monolayer [50], the specific electrochemically active surface areas (ECSA) of the catalysts were calculated to be 80.1 m$^2$/g (Pt/ XC-72), 92 m$^2$/g (Pt/DWCNTs) and 98 m$^2$/g (Pt/A-DWCNTs), respectively. The order of active surface area was Pt/XC-72 $<$ Pt/DWCNTs $<$ Pt/A-DWCNTs. The higher performance of the Pt/DWCNT and Pt/A-DWCNT electrodes compared to that of the Pt/XC-72 electrode could be attributed to the good accessibility and dispersion of the DWCNT supports to facilitate sufficient active Pt surface area by helping the dispersion of small Pt particles [56]. Furthermore, the pretreatment of DWCNTs with KOH results in defects on the DWCNT surface, which would act as additional anchoring sites for better adherence of Pt nanoparticles [57], thereby giving a higher electrochemically active surface area.

Fig. 6-8 Cyclic voltammograms of Pt/XC-72, Pt/DWCNT, and Pt/A-DWCNT catalysts in argon-saturated 0.1 mol/L HClO$_4$ electrolyte. Scanning rate: 20 mV/s.
6.4.2.2 Linear sweep voltammetry (LSV)

In order to investigate the electrocatalytic characteristics of the catalysts for the ORR, the specific activities (the activity per unit area of catalyst surface that is usually represented by the kinetic current density, $j_k$) of these particles toward the oxygen reduction reaction (ORR) were obtained in O$_2$-saturated 0.1 mol/L HClO$_4$.

![Linear scan voltammograms for Pt/XC-72, Pt/DWCNTs, and Pt/A-DWCNTs in 0.1 M HClO$_4$ solution saturated with oxygen, collected with a rotating disk electrode at 1600 rpm and a scan rate of 10 mV/s.](image)

Fig. 6-9 Linear scan voltammograms for Pt/XC-72, Pt/DWCNTs, and Pt/A-DWCNTs in 0.1 M HClO$_4$ solution saturated with oxygen, collected with a rotating disk electrode at 1600 rpm and a scan rate of 10 mV/s.

The values of $j_k$ were obtained from the steady-state polarization curves according to the Koutecky–Levich equation, that is (6-2) [58]
In Eq. (6-2), $j$ is the measured current density at various potentials on the steady-state polarization curve, and $j_L$ is the limiting diffusion current density. As shown in Fig. 6-9, specific activities towards the ORR of the Pt/A-DWCNTS and Pt/DWCNTs are higher than that of the Pt/XC-72 in the given potential range.

6.4.2.3 Testing the catalyst stability

Working electrodes were immersed in N$_2$ purged 0.1 M HClO$_4$, and a constant potential (0.9 V) was added. The current response as a function of time was then recorded. To quantify the extent of loss of platinum from the electrochemically active surface area, cyclic voltammetry was performed on the Pt/XC-72, Pt/DWCNTs, and Pt/A-DWCNTs in N$_2$ purged 0.1 M HClO$_4$ electrolyte at different time intervals (0, 20, 65, and 120 h). The loss of Pt surface area with time is plotted in Fig. 6-10. It can be seen that almost 70% of Pt surface area was lost for Vulcan XC-72 after 120 h, while only 48% and 35% loss is observed for DWCNTs and activated DWCNTs, respectively. Furthermore, most of the surface area loss in the case of DWCNTs and activated DWCNTs occurs within 80 h, while after 80 h, the rate of Pt area loss is very small, indicating that activated DWCNTs and DWCNTs could potentially provide much higher durability than Vulcan XC-72. It is most likely that the Pt surface area difference is caused by the different morphologies of the three different supports. The loss of Pt surface area supported on XC-72, DWCNTs, or A-DWCNTs could be due to the dissolution of Pt(0) particles, reprecipitation of Pt ions, and diffusion of Pt ions into the
membrane [59], while the interactions between Pt(0) and the carbon support material influence the drop in the active surface area of the catalyst. A in the electronic structure in the platinum catalytic layer from interaction between the platinum active phase and the carbon support phase leads to changes in catalyst durability [60]. Improving the interaction of the Pt precursor with DWCNTs during platinization can be achieved by increasing the defects in the support material [57].

Fig. 6-10 Comparison of Pt active area loss vs. time for XC-72, DWCNTs, and A-DWCNTs.

Obviously, the order of the activity towards the ORR was Pt/XC-72 < Pt/DWCNTs < Pt/A-DWCNTs. It is proposed that the Pt particles on A-DWCNTs have the highest utilized efficiency, agreeing with the results deduced from Figs. 6-8 and 6-9.
6.5 Durability investigation of graphene supported Pt nanocatalysts for PEM fuel cell

6.5.1 Physical and Structural Characterization

The XRD patterns of XC-72 carbon and graphene are shown in Fig. 6-11.

![X-ray diffraction patterns of XC-72 and graphene](image)

Fig. 6-11 X-ray diffraction patterns of (1) XC-72 and (2) graphene

For XC-72 carbon, a rather wide and shallow (002) peak is observed in its XRD pattern, implying that XC-72 is an amorphous carbon material with small regions of crystallinity. A sharper and narrower carbon (002) diffraction peak appears for graphene, which indicates its highly graphitic ordered structure. The presence of the C(004) diffraction peak in graphene is also indicative of the high crystallinity of its carbon structure [61,62]. The graphitic structure of carbon can be quantitatively characterized by the graphitization index, which indicates the degree of similarity between a carbon material and a perfect single crystal of graphite [63]. A higher
graphitization index indicates a more ordered graphitic structure [64].

Fig. 6-12 shows TEM bright field micrographs of the Pt/C before oxidation (Fig. 6-12(a)) and after oxidation (Fig. 6-12(b)), and of the Pt/graphene before oxidation (Fig. 6-12(c)) and after oxidation (Fig. 6-12(d)). The selected area electron diffraction (SAED) patterns of the catalysts give associated spotty ring patterns, as are shown in the insets in Fig. 6-12. The bright spots in the insets correspond to the (111) and (200) Pt reflections, and the additional diffuse rings correspond to amorphous carbon and graphene. The dark nanoparticles are the Pt catalyst. Although the Pt loading levels are the same, the population of Pt nanoparticles is too small for Pt/graphene as compared to Pt/XC-72, which possibly can be attributed to the structure of the support.

Fig. 6-12 TEM bright field micrographs of (a) Pt/XC-72; (b) Pt/XC-72 after oxidation treatment; (c) Pt/graphene; and (d) Pt/graphene after oxidation treatment; with insets in (a), (b), (c), and (d) showing the corresponding SAED patterns.
Comparison of Fig. 6-12(a) and (b) indicates the effects of oxidation on the general morphology of the Pt/XC-72. In general, the carbon matrix exhibits a fluffy cotton-like microstructure, in which Pt nanoparticles are embedded. Specifically, for the Pt/XC-72 before oxidation, the particles have a particle size in the range of 5-8 nanometers, and they are also distributed homogeneously on the micrometer domain. After oxidation treatment, the particle size becomes bigger. Furthermore, the Pt particles are aggregated, which will reduce the catalytic activity.

In contrast, for graphene, after oxidation treatment, the Pt particle size shows some increase in some regions. However, after oxidation treatment, some aggregation of Pt nanoparticles is indeed observed in some isolated areas on the graphene surface, as opposed to the uniform aggregation in the case of XC-72, and this is attributed to the higher corrosion resistance of graphene. Comparing Fig. 6-12(a) and (c), the Pt is better dispersed on the graphene than on the XC-72 carbon, which is attributed to the fact that catalyst nanoparticles could be easily deposited on the surface of graphene, based on its 2D flat planes [65].

6.5.2 Electrochemical Characterization

6.5.2.1 Cyclic voltammograms (CV curves)

Fig. 6-13 shows the forward scans of cyclic voltammograms for XC-72 and graphene after oxidation treatment for different durations. The current density was calculated based on the geometric electrode area. The peak current comes from the surface oxide formation due to hydroquinone-quinone redox couple on surface [66].
Fig. 6-13 Forward scans of cyclic voltammograms of (a) XC-72, (b) graphene peak current density at different intervals during oxidation treatment in N$_2$-saturated 0.1 M HClO$_4$; scan rate: 10 mVs$^{-1}$. 
Similar results have been reported by Jarvi and co-workers [67], who identified different oxidized groups, including carboxyl, hydroxyl, and carbonyl, generated on the carbon surface through X-ray photoelectron spectroscopy and thermogravimetric analysis coupled to mass spectrometry.

In Fig. 6-13(a), note that the peak in the hydroquinone-quinone region becomes stronger with treatment time, and the increased peak current suggests a higher degree of surface carbon oxidation with time.

In contrast, the peak current is barely visible in the case of graphene and shows negligible change with time (Fig. 6-13(b)), which suggests that the surface of graphene is more difficult to oxidize than XC-72 under the tested conditions, which is consistent with the results deduced from Fig. 6-12. This can be attributed to the graphitic structure of graphene; similar results have been reported in [68]. This means that graphene could potentially be more corrosion resistant and durable when used in a fuel cell.

6.5.2.2 Linear sweep voltammetry (LSV)

The catalytic activities in terms of the oxygen reduction reaction (ORR) were also examined at different time intervals by linear sweep voltammetry (LSV) measurements in oxygen-saturated 0.1 mol/L HClO₄, as shown in Fig.6-14. There were no changes in the limiting currents. It is believed that at the high voltage bias used, the reaction kinetics is so fast that the process is still diffusion limited, even after some significant reduction of Pt surface area. On the other hand, the half wave potential shows a
continuous decrease as the treatment time increases and is thus used to quantify the difference in activity. The half wave potential, defined as the potential at which the measured current reaches half of the limiting current, was extracted from the potentiodynamic curve. As listed in Table 6-3, Pt supported on XC-72 has a similar initial half wave potential to Pt supported on graphene, but as time goes on, both of them show a decrease in activity, as evidenced by the lowering of the half wave potential. However, graphene exhibits a slower decrease rate than XC-72. At the same time, the half wave potential of Pt/graphene is higher than that of Pt/XC-72. The higher performance of the Pt/graphene electrode compared to the Pt/XC-72 electrode could be attributed to the good accessibility and dispersion of the graphene supports, so as to yield sufficient active Pt surface area by helping the dispersion of small Pt particles [69].

![Graph](image)

**Fig. 6-14** Linear scan voltammograms on Pt/graphene as a function of oxidation treatment time in 0.1 M HClO₄ solution saturated with oxygen. A rotating disk electrode at 1600 rpm and a scan rate of 10 mV/s were used.
Table 6-3 Comparison of half potential for ORR of Pt supported on XC-72 and on graphene as a function of oxidation treatment time, collected with a rotation rate of 1600 rpm.

<table>
<thead>
<tr>
<th>Time(h)</th>
<th>XC-72 (V)</th>
<th>Graphene (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.58</td>
<td>0.58</td>
</tr>
<tr>
<td>20</td>
<td>0.53</td>
<td>0.55</td>
</tr>
<tr>
<td>120</td>
<td>0.45</td>
<td>0.48</td>
</tr>
</tbody>
</table>

6.5.2.3 Testing the catalyst stability

The working electrode was immersed in N₂-saturated 0.1 M HClO₄, and a constant potential (0.7 V) was added. The current response as a function of time was then recorded. To quantify the effects of oxidation treatment on the Pt electrochemically active surface area (ECSA), cyclic voltammetry was performed on Pt/XC-72 and Pt/graphene in N₂-saturated 0.1 M HClO₄ electrolyte at different time intervals (0 h, 20 h, 70 h, 120 h). The Pt ECSA was determined by measuring the charges collected in the underpotential hydrogen (H\text{upd}) adsorption/desorption region after double-layer correction and assuming a value of 210 μC/cm² for the adsorption of a hydrogen monolayer [70]. The ECSA values of the catalysts were calculated to be 80.1 m²/g (Pt/XC-72) and 98m²/g (Pt/graphene), respectively. The ECSA accounts not only for the catalyst surface available for charge transfer, but also includes the access to a conductive path to transfer the electrons to and from the electrode surface. The ECSA difference between the two catalysts may be due to the different matrix and the smaller particle size of the Pt loaded on the graphene. High ECSAs are favorable for the electrochemical oxygen reduction reaction.

The loss of Pt surface area with time during the surface oxidation experiments is
plotted in Fig. 6-15. It can be seen that almost 70% of the Pt surface area was lost for XC-72 after 120 h, while only 30% loss is observed for graphene. Furthermore, most of the surface area loss in the case of graphene occurs within 70 h, while after 70 h, the rate of Pt area loss is very small, indicating that graphene could potentially provide much higher durability than XC-72. The loss of Pt surface area supported on XC-72 and graphene could be due to the dissolution of Pt(0) particles, reprecipitation of Pt ions, and diffusion of Pt ions into the membrane [60], while the interactions between Pt(0) and the carbon support material influence the drop in the active surface area of the catalyst. A change in the electronic structure of the platinum catalytic layer from interaction between the platinum active phase and the carbon support phase leads to changes in catalyst durability [61]. Graphene with its unique graphitized basal plane can improve the interaction of Pt precursor with graphene during platinization.

![Fig. 6-15 Comparison of Pt active surface area loss vs. time for XC-72 and graphene.](image-url)
6.6 Summary

In summary, activated carbon, DWCNTs, activated DWCNTs, and graphene nanosheets were employed as an alternative support material for Pt nanoparticles for oxygen reduction, using a simple chemical reduction method and compared to BASF 20wt% Pt/XC-72. The results are summarized below:

(1) The electrochemical performance of Pt/activated carbon exhibited greatly enhanced catalytic activity towards ORR compared to Pt/carbon, because of the acid treatment, which can reduce sulfur content, eliminate inorganic impurities, and add some functional groups containing oxygen;

(2) The electrochemical performance of Pt/DWCNTs and Pt/A-DWCNTs exhibited much enhanced catalytic activity towards ORR compared to Pt/XC-72, because of their unique electrical properties. Furthermore, the performance of Pt/A-DWCNTs is higher than that of Pt/DWCNTs, which is attributed to the defects on the surface of the activated DWCNTs.

(3) The electrochemical characterizations show that graphene has improved corrosion resistance over XC-72. This is attributed to the intrinsic high graphite component and the enhanced Pt-carbon interaction. It is suggested that graphene nanosheet is a promising, low-cost, and durable electrocatalyst support for oxygen reduction in PEM fuel cells.

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Chapter 7 Effects of surface treatment on the hydrogen storage capacity of double-walled carbon nanotubes

7.1 Introduction

Hydrogen fuel is considered as an attractive alternative to fossil fuels because of zero CO₂ emissions. For the utilization of hydrogen, hydrogen storage technology is necessary, in which light and environmentally friendly materials are required to store the hydrogen [1]. However, the current challenge in the development of the hydrogen economy is the lack of suitable H₂ storage materials that may be applicable for moving vehicles [2,3]. According to the US Department of Energy [4], a carbon material needs to store 6.5% of its own weight in hydrogen to make fuel cells practical in cars.

In 1991, Iijima described for the first time the new form of carbon called carbon nanotubes (CNTs) [5]. Because of its sustainable and environmentally friendly character, hydrogen storage on CNTs has been investigated both experimentally and theoretically by many researchers [6-12]. Theoretical studies have proposed that the interaction of hydrogen with carbon nanotubes (CNTs) is through physisorption of hydrogen on the exterior and possibly the interior surfaces [13-15]. Thus, CNTs seem to be an important candidate for H₂ storage, owing to their chemical stability, large surface area, and low density [16]. In the past decade, a large number of experimental and theoretical studies of hydrogen storage in CNT-based materials have been reported [17-19]. However, the hydrogen adsorption sites and their interactions are still not well understood.
Recent investigations show that chemical activation is a very efficient method to obtain carbons with high surface area [20]. Among all the chemical activation agents, an alkaline hydroxide such as KOH is the best choice from the performance point of view, allowing activated carbon to be prepared from many kinds of carbonaceous precursors [21-31].

An alternative way of increasing the hydrogen adsorption capacities of CNTs is loading them with a transition metal. It is well known that a minor amount (~2wt%) of a transition metal or noble metal, such as Pd, Pt, or Ni, dispersed in a carbon material can dissociate hydrogen molecules to hydrogen atoms [32]. The hydrogen storage capacities for palladium loaded CNTs were found to be 30% greater than those of the original samples [33]. Anson et al. [34] prepared palladium loaded CNTs for hydrogen sorption and found more than one order of magnitude improvement of physical adsorption over the raw carbon materials. Hydrogen uptake by carbon nanofibers catalyzed by palladium during synthesis has also been studied by Lupu et al. [35], and 1.5% hydrogen uptake was attained by nanofibers with 425-455 m²/g Brunauer-Emmett-Teller (BET) surface area. Also, Rather et al. [36] investigated the hydrogen adsorption of palladium-embedded CNTs at ambient temperature and at hydrogen partial pressures of 0.66-2.2 MPa, and evaluated the enhanced storage capacity due to cumulative hydrogen adsorption by CNTs and Pd nanoparticles.

In this chapter, firstly, the hydrogen adsorption properties of pristine double walled carbon nanotubes (DWCNTs), 2wt%Pd DWCNTs, chemically activated DWCNTs and 2wt%Pd activated DWCNTs are investigated. Then the hydrogen adsorption properties
of 2%Pd/double walled CNTs (DWCNTs), using H₂, L-ascorbic acid, and NaBH₄, respectively, as reductants are studied. The results show that there is a significant enhancement of hydrogen storage capacity through chemical processing and that the choice of reductant has a significant effect on the hydrogen adsorption, with NaBH₄ performing the best among the reductants investigated.

7.2 Experimental

7.2.1 Activated DWCNTs

To prepare activated DWCNTs, a mixture of DWCNTs and KOH (Sigma-Aldrich, ≥ 90%), with DWCNT : KOH (weight ratio) = 1: 4 [37,38], was added into ethanol solution and stirred with a magnetic bar for several hours. Then, the mixture was put into a tube furnace and heated to 800 ºC under flowing N₂ (170 mL/min). After activation, the product was thoroughly washed with diluted HCl and water.

7.2.2 Synthesis of 2%Pd DWCNTs

For the 2%Pd/DWCNTs and 2%Pd/activated DWCNTs-H₂: in order to load Pd nanoparticles on DWCNTs or activated DWCNTs, pristine DWCNTs or activated DWCNTs were mixed in ethanol with Pd(C₅H₇O₂)₂, to achieve a nominal Pd content of 2wt% in the final material. The mixing was followed by stirring at room temperature for 12 hours. After that, the mixture was dried at 60 ºC in a vacuum oven overnight and then was reduced at 400 ºC for 3 h under H₂ gas flow (150 mL/min) [39].

To prepare 2%Pd/DWCNTs-L-ascorbic acid and 2%Pd/DWCNTs-NaBH₄, firstly,
DWCNTs were dissolved in de-ionized water. Then, an appropriate amount of Pd(C₂H₇O₂)₂ was added to the solution, which was stirred at room temperature for 1 h, to achieve a nominal Pd content of 2wt% in the final material. After that, the different reductants (L-ascorbic acid and NaBH₄) were added dropwise into the mixture in each case to achieve reduction under Ar atmosphere. The reacting dispersion was stirred and refluxed continuously for at least 1 hour. Finally, the resultant black dispersion was isolated by centrifugation and washed 3- 4 times with ethanol. The black powder was then dried at 60 ºC in a vacuum oven overnight.

7.3 Chemical processing of double-walled carbon nanotubes for enhanced hydrogen storage

7.3.1 Physical and Structural Characterization

Fig. 7-1 shows X-ray diffraction patterns of the pristine, activated, 2wt%Pd and 2wt%Pd activated DWCNTs, respectively. As expected, the DWCNTs correspond to a carbon with a low structural organization, as indicated by the two broad peaks at 2θ = 26.7° and 43.7°. For the 2wt%Pd DWCNTs and the 2wt%Pd activated DWCNTs, two additional peaks are observed, which can be indexed to the cubic phase of Pd as Pd(111) and Pd(200). The XRD pattern also confirmed that the loading of Pd on DWCNTs did not lead to any structural change in the carbon nanotubes.
Fig. 7-1 X-ray diffraction patterns of (a) pristine DWCNTs, (b) activated DWCNTs (c) 2 wt% Pd DWCNTs and (d) 2 wt% Pd activated DWCNTs.

Raman spectroscopy is an efficient and non-destructive tool to characterize carbon materials, in particular for distinguishing defects in the carbon structure. Fig. 7-2 shows the Raman spectra of pristine and chemically activated DWCNTs. Two peaks at 1580 cm\(^{-1}\) and 1350 cm\(^{-1}\) are identified as the G and D bands, respectively. The G band represents the E\(_{2g}\) phonon of C\(_{sp^2}\) atoms in the graphite structure, while the D band is usually assigned to the breathing mode of \(\kappa\)-point phonons of A\(_{1g}\) symmetry in the disordered graphite structure [40]. It is well known that the intensity ratio of the D and G peaks (I\(_{1350}\) / I\(_{1580}\)) gives information on the degree of disorder of the CNTs [41]. It is found that the intensity ratio of I\(_{1350}\) / I\(_{1580}\) was increased by activation, indicating the creation of defects at the DWCNT surface through the chemical activation process.
Fig. 7-2 Raman spectra of (a) pristine DWCNTs; (b) chemically activated DWCNTs

Fig. 7-3 shows TEM bright field micrographs of the pristine DWCNTs (Fig. 7-3(a)), the activated DWCNTs (Fig. 7-3(b)), and the sample with 2%Pd loaded on DWCNTs (Fig. 7-3(c) and (d)). Comparison of Fig. 7-3 (a) and (b) indicates the effects of activation on the general morphology of the DWCNTs, with reduced homogeneity of parallel CNT walls, consistent with increased defect density in the activated sample. Both the low magnification (Fig. 7-3(c)) and the higher magnification (Fig. 7-3(d)) bright field images of the Pd loaded sample exhibit a wide range of Pd nanocrystalline particle sizes, from 50 nm to less than 5 nm, and they are distributed randomly throughout the DWCNTs. The selected area electron diffraction patterns (inset, Fig. 7-3(d)) contain reflections that confirm the presence of nanocrystalline Pd.
Fig. 7-3 TEM bright field micrographs of loaded and unloaded DWCNTs: (a) pristine DWCNTs; (b) activated DWCNTs; (c) and (d) sample with 2\%Pd on DWCNTs, with inset in (d) showing the corresponding selected area electron diffraction pattern.

The specific surface areas of the pristine, chemically activated, 2wt\%Pd, and 2wt\%Pd activated DWCNTs were measured to be 197.8, 320.42, 209.1, and 248.5 m\(^2\)/g, respectively. It is thus found that chemical processing (either through activation or metal nanoparticle loading) can effectively increase the BET surface areas of DWCNTs. Among all the samples, the surface area of the activated DWCNTs was the highest. The results demonstrate that chemical activation is a very efficient method of producing carbons with high surface areas. For the 2wt\%Pd DWCNTs, defect sites could be created in the vicinity of the metal particles by the H\(_2\) reduction procedure at high temperature, due to the possible gasification of carbon catalyzed by the metal [40]. However, the surface area of the 2 wt\%Pd activated DWCNTs was higher than for the
2wt%Pd DWCNTs, but lower than for the activated DWCNTs. It is suggested that some of the defects created by KOH are recrystallized during the annealing process at high temperature [36]. Therefore, the BET surface areas of the DWCNT samples are in the order: activated DWCNTs > 2 wt% Pd activated DWCNTs > 2 wt% Pd DWCNTs > pristine DWCNTs. This result is consistent with the results of Raman spectroscopy and TEM analysis.

### 7.3.2 Hydrogen adsorption and desorption

In order to explore the mechanisms of H\(_2\) storage in DWCNTs, TPD H\(_2\) desorption measurements were conducted on pristine DWCNTs, activated DWCNTs, 2wt%Pd DWCNTs, and 2wt%Pd activated DWCNTs (as shown in Fig. 7-4). For the pristine DWCNTs and the activated DWCNTs, there are two peaks: one starts at about 300 K, while the other is at about 750 K. They may be attributed to a combination of physical absorption (starting from about 300 K) and chemical reaction (starting from about 750 K). However, for the 2wt%Pd DWCNTs and the 2wt%Pd activated DWCNTs, the desorption temperature starts at about 750 K, which is so high that atomic hydrogen must be chemisorbed on the dangling bonds of the defect sites [1].

For the 2wt%Pd DWCNTs and 2wt%Pd activated DWCNTs, hydrogen is transferred to the DWCNTs by a cooperative effect between the palladium and the carbon network. High dispersion of Pd nanoparticles leads to a high storage capacity, because it enables the maximum amount of contact between the carbon structures and the hydrogen molecules. Therefore, it can be proposed that H\(_2\) is dissociated by the Pd catalyst, and the hydrogen atoms are adsorbed on the defect sites on the CNTs [42, 43]. In the case
of the pristine and activated DWCNTs, the adsorption of hydrogen molecules on the
defect sites plays a major role through van der Waals forces [44].

![Graph showing hydrogen uptake over time for different samples](image)

Fig. 7-4 Hydrogen soak curves of the pristine DWCNTs, activated DWCNTs, 2wt% Pd
DWCNTs, and 2wt% Pd activated DWCNTs at 298 K, 30 atm.

However, when 2wt% Pd activated DWCNTs are created by first activating the
DWCNTs to create defects and then loading 2wt%Pd on the activated DWCNTs, it is
found that the hydrogen storage capacity is lower than that of activated DWCNTs, but
higher than that of 2wt%Pd DWCNTs. Based on the results from BET measurements,
it is suggested that the defects created by KOH were re-crystallized during the
annealing process at high temperature, inducing a decrease in the density of defect sites
[43]. So, even though H₂ should be dissociated by the Pd catalyst, the lower density of
defect sites could not provide enough positions for H₂ adsorption. The H₂ storage
capacities are in the order: activated DWCNTs > 2 wt% Pd activated DWCNTs > 2
wt% Pd DWCNTs > pristine DWCNTs, which is in the same order as the BET surface areas.

Fig. 7-5 Temperature-programmed-desorption of hydrogen: (a) DWCNTs, (b) activated DWCNTs, (c) 2wt%Pd DWCNTs, (d) 2wt%Pd activated DWCNTs.

7.4 Effects of different reductants for palladium loading on hydrogen storage capacity of double-walled carbon nanotubes

7.4.1 Physical and Structural Characterization

Fig. 7-6 shows the X-ray diffraction patterns (1), (2), (3), and (4) for the pristine DWCNTs, 2%Pd/DWCNTs-H₂, 2%Pd/DWCNTs-NaBH₄, and 2%Pd/DWCNTs-L-ascorbic acid, respectively. As expected, three broad peaks at 2θ = 26.7°, 43.7°, and
53° correspond to graphite (002), (100), and (004), respectively. For the 2%Pd/DWCNTs-H₂, 2%Pd/DWCNTs-L-ascorbic acid, and 2%Pd/DWCNTs-NaBH₄, two additional peaks are observed, which can be indexed to the cubic phase of Pd as Pd(111) and Pd(200). The widths of the two additional peaks in Fig. 1 indicate that under the experimental conditions, the different reductants lead to different Pd particle sizes, with the Pd particle sizes in the order: 2%Pd/DWCNTs-H₂ > 2%Pd/DWCNTs-L-ascorbic acid > 2%Pd/DWCNTs-NaBH₄. Furthermore, one can see the peaks of PdO, and the XRD patterns also confirm that the loading of Pd on DWCNTs did not lead to any structural changes in the carbon nanotubes.

Fig. 7-6 X-ray diffraction patterns of (1) pristine DWCNTs; (2) 2wt%Pd DWCNTs-H₂; (3) 2wt%Pd/DWCNTs-NaBH₄; and (4) 2wt%Pd/DWCNTs-L-ascorbic acid.

Fig. 7-7 shows TEM bright field micrographs of the pristine DWCNTs (Fig. 7-7(a)),
the 2%Pd/DWCNTs-H₂ (Fig. 7-7(b)), the 2%Pd/DWCNTs-L-ascorbic acid (Fig. 7-7(c)), and the 2%Pd/DWCNTs-NaBH₄ (Fig. 7-7(d)). The dark nanoparticles are the Pd catalyst. The selected area electron diffraction (SAED) patterns of the samples appear as the associated spotty ring patterns in the insets in Fig. 7-7(b), (c), and (d) for 2%Pd/DWCNTs-H₂, 2%Pd/DWCNTs-L-ascorbic acid, and 2%Pd/DWCNTs-NaBH₄, respectively. The bright spots in the insets correspond to the Pd(111) and (002) CNT reflections, which confirm the presence of nanocrystalline Pd. Comparison of Fig. 7-7(b), (c), and (d) indicates the effects of the different reductants on the general morphology and particle size of the Pd loaded on the DWCNTs. In Fig. 7-7(b), the bright field images of the Pd loaded sample exhibit a wide range of Pd nanocrystalline particle sizes, from 50 nm to less than 5 nm, and they are distributed randomly throughout the DWCNTs, but in the 2%Pd/DWCNTs-L-ascorbic acid (Fig. 7-7(c)), the Pd particles have particle sizes in the range of 5-10 nm, and they are distributed homogeneously on the micrometer domain. For the 2%Pd/DWCNTs-NaBH₄ (Fig. 7-7(d)), the Pd particle size is the smallest, and the particle size distribution exhibits a wide range from 3 to 8 nm. Furthermore, the dispersion of Pd particles in the 2%Pd/DWCNTs-NaBH₄ (Fig. 7-7(d)) is better than in the 2%Pd/DWCNTs-H₂ (Fig. 7-7(b)) and 2%Pd/DWCNTs-L-ascorbic acid (Fig. 7-7(c)). This result is consistent with the results of XRD analysis. From these results, it can be seen that using H₂ as a reductant at high temperature can lead to the aggregation of Pd particles. Comparing L-ascorbic acid and NaBH₄, L-ascorbic acid is a weaker reductant, which can cause slight aggregation in aqueous solution.
Fig. 7-7 TEM bright field micrographs of loaded and unloaded DWCNTs: (a) pristine DWCNTs; (b) 2wt% Pd DWCNTs-H₂; (c) 2wt% Pd/DWCNTs-L-ascorbic acid; and (d) 2wt% Pd/DWCNTs-NaBH₄, with insets in (b), (c), and (d) showing the corresponding selected area electron diffraction patterns.

The specific surface areas of the pristine DWCNTs, 2wt%Pd/DWCNTs-H₂, 2wt%Pd/DWCNTs-L-ascorbic acid, and 2wt%Pd/DWCNTs-NaBH₄ were measured to be in the order: 2wt%Pd/DWCNTs-NaBH₄ (238.5 m²/g) > 2wt%Pd/DWCNTs-L-ascorbic acid (215.1 m²/g) > 2wt%Pd/DWCNTs-H₂ (209.1 m²/g) > pristine DWCNTs (197.8 m²/g). It is found that metal nanoparticle loading can effectively increase the BET surface areas of samples. For the 2wt%Pd DWCNTs, defect sites could be created
in the vicinity of the metal particles by the reduction procedure at high temperature, due to the possible gasification of carbon, which is catalyzed by the metal [45]. Among all the samples, the surface area of the 2wt%Pd/DWCNTs-NaBH$_4$ was the highest, which can be attributed to the smallest particle size loading on the matrix. This result is consistent with the results of TEM analysis. Furthermore, the quantitative EDX analysis indicates that for each sample, the content of Pd was equal to the nominal ratio (1.98%).

7.4.2 Hydrogen adsorption and desorption

The effects of Pd nanoparticles and different reductants on the hydrogen storage properties of DWCNTs were examined by hydrogen adsorption measurements, where hydrogen was adsorbed at 30 atm and 25 ºC for 180 min. Fig. 7-8 shows the results on the H$_2$ adsorption capacities of the four samples. The amount of hydrogen storage was determined to be 1.7, 2.0, 2.55, and 3.0 wt% for the pristine DWCNTs, 2wt%Pd/DWCNTs-H$_2$, 2wt%Pd/DWCNTs-L-ascorbic acid, and 2wt%Pd/DWCNTs-NaBH$_4$, respectively. In comparison with the pristine DWCNTs, it is remarkable that the hydrogen adsorption capacity of the 2wt%Pd/DWCNTs has been significantly enhanced. The hydrogen adsorption capacities of all the samples are higher than those in References [12,45], but lower than that in Reference [46]. Furthermore, it should be noted that the larger the specific surface area, the higher the hydrogen storage capacity. This could be attributed to the greater number of adsorption sites for hydrogen in a receptor with a high surface area and full contact between the Pd and the hydrogen molecules.
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Fig. 7-8 Hydrogen uptake curves of the pristine DWCNTs, 2wt% Pd/DWCNTs-H₂, 2wt% Pd/DWCNTs-L-ascorbic acid, and 2wt% Pd/DWCNTs-NaBH₄ at 298 K, 30 atm.

In order to explore the mechanisms of H₂ storage in DWCNTs, the H₂ desorption measurements using temperature-program-desorption (TPD) on the 2wt% Pd/DWCNTs-H₂, 2wt% Pd/DWCNTs-L-ascorbic acid, and 2wt% Pd/DWCNTs-NaBH₄ (as shown in Fig. 7-9). For all samples, there is only one peak in Fig. 7-9. However, the starting temperature of the peak is very high, at about 750 K. This means that the desorption temperature starts at about 750 K, which is so high that atomic hydrogen must be chemisorbed on the dangling bonds of the defect sites [1].
Fig. 7-9 Temperature-programmed-desorption of hydrogen: (a) 2wt%Pd/DWCNTs-H₂, (b) 2wt%Pd/DWCNTs-L-ascorbic acid, (c) 2wt%Pd/DWCNTs-NaBH₄.

For the 2wt%Pd DWCNTs, hydrogen is transferred to the DWCNTs by a cooperative effect between the palladium and the carbon network. Such hydrogen transfer, the so-called spillover effect, has been already reported in other systems, such as Pt and Pd catalysts supported on activated carbon (CA) or graphite nanofibers (GNF) [47]. Such spillover effects are very likely to occur in the present material, in which dihydrogen is dissociated by the Pd particles and transferred to the carbon network, where it is chemically bound. The binding energy is stronger than for physisorption, and such hydrogen cannot be released at room temperature. A high dispersion of Pd nanoparticles leads to a high storage capacity, because it enables the maximum amount
of contact between the carbon structures and the hydrogen atoms.

7.5 Summary

(1) The combined results of Raman spectroscopy, TEM observation, and BET analysis demonstrated that the formation of defects in DWCNTs can be effectively achieved by KOH activation.

(2) These defect sites in DWCNTs induce adsorption of H$_2$ molecules, while the loading of the DWCNTs with nanocrystalline Pd is believed to promote the dissociation of H$_2$ molecules into hydrogen atoms. This mechanism has been indirectly confirmed by the TPD measurements.

(3) Furthermore, chemical activation of DWCNTs by KOH resulted in better improvement of hydrogen storage capacity than that from loading with Pd nanoparticles.

(4) This doctoral work found that the different reductants had particular effects on the Pd particle size and dispersion, which can change the hydrogen sorption characteristics.

(5) The loading of nanocrystalline Pd on the DWCNTs is believed to promote the dissociation of H$_2$ molecules into hydrogen atoms, and higher dispersion and smaller particle size of the Pd lead to the maximum amount of contact between the carbon structures and the hydrogen atoms, which can result in higher hydrogen sorption.

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Chapter 8 General Conclusions and Outlook

8.1 General conclusions

8.1.1 Cathode catalyst for PEM fuel cells

Under the strong driving force of fuel cell commercialization, great progress in PEM fuel cell catalysis has been made in the last two decades. At the present time, the most practical catalysts for fuel cell applications are still Pt-based catalysts, such as carbon-supported Pt and Pt–Ru alloy catalysts. Carbon black (Vulcan XC-72R) has been widely used for platinum support in low-temperature fuel cells.

In this thesis, achievements and major challenges, related to these catalysts, including high cost, insufficient catalytic activity, and low stability, have been reviewed, and technological developments for addressing these challenges are discussed, with a particular focus on the developments of functional and nanostructured Pt-alloy, core-shell structure catalysts and of carbon support.

It has been demonstrated that advanced alloy nanostructures and core–shell structures have showed great potential in solving issues of insufficient activity, low stability, and high cost. Based on the author’s research, the extent to which such nanostructured Pt-alloys and core-shell structure catalysts enhance catalyst activity and stability is strongly dependent on geometric and electronic effects, as well as on the type of transition metal in the Pt-alloy or special structure catalysts. Composition appears to be very important in modifying the surface structure of catalysts. Other factors, such as size, shape, and morphology, are also instrumental in varying the number of active sites and stabilizing the surface structure, as well as preventing metal dissolution.
At the same time, other types of carbon support (activated carbon, double-walled carbon nanotubes (DWCNTs), activated DWCNTs, and graphene nanosheets) were employed as alternative support materials for Pt nanoparticles for oxygen reduction using a simple chemical reduction method and compared to BASF 20wt% Pt/XC-72. The results can be summarized here:

1. Acid treatment can reduce sulfur content, eliminate inorganic impurities, and add some functional groups containing oxygen. So, the electrochemical performance of Pt/activated carbon exhibited greatly enhanced catalytic activity towards the oxygen reduction reaction (ORR) compared to Pt/carbon.

2. Because DWCNTs have unique electrical properties, the electrochemical performance of Pt/DWCNTs and activated Pt/A-DWCNTs exhibited much enhanced catalytic activity towards ORR compared to Pt/XC-72, and the performance of Pt/A-DWCNTs is higher than that of Pt/DWCNTs, which is attributed to the defects on the surface of the DWCNTs.

3. Because of its intrinsic high graphite component and enhanced Pt-carbon interaction, the results show that graphene has improved corrosion resistance over XC-72. It is suggested that graphene nanosheet is a promising, low-cost, and durable electrocatalyst support for oxygen reduction in PEM fuel cells.

8.1.2 Hydrogen storage

Some promising storage capacities have been achieved with carbon-based materials, particularly via chemical processing: activation of DWCNTs or loading of the DWCNTs with nanocrystalline Pd. Both of these approaches can lead to high storage capacity, but have different adsorption mechanisms: the defect sites in DWCNTs induce adsorption of H₂ molecules, while the loading of the DWCNTs with nanocrystalline Pd is believed to
promote the dissociation of H\textsubscript{2} molecules into hydrogen atoms.

The adsorption of hydrogen molecules on the defect sites plays a major role through van der Waals forces. When the carbon nanotubes are loaded with Pd particles, hydrogen is transferred to the DWCNTs by a cooperative effect between the palladium and the carbon network. Such spillover effects are very likely to occur in the present material, in which dihydrogen is dissociated by the Pd particles and transferred to the carbon network, where it is chemically bound. A high dispersion of Pd nanoparticles leads to a high storage capacity, because it enables the maximum amount of contact between the carbon structures and the hydrogen molecules. So, different reductants had particular effects on the Pd particle size and dispersion, which can change the hydrogen sorption characteristics.

8.2 Outlook

8.2.1 Cathode catalyst for PEM fuel cells

Although some Pt alloy catalysts with advanced nanostructures have shown remarkable activity, the dissolution of metals, including Pt and Pt alloyed with base metals, in fuel cell operation environments could cause catalyst degradation, which still remains an issue. Another issue may be the low retention of active catalyst nanostructures during fuel cell operation. For example, the crystal facets that contain more catalytically active sites could be converted to low activity facets due to thermodynamic environmental changes in the fuel cell processing. The nanosized Pt alloy catalysts still face the instability arising from Ostwald ripening. All these issues will result in the degradation of catalytic activity and stability. Furthermore, for Pt-alloys with core–shell and elongated nanostructures, the scaling up of synthesis and fuel cell testing beyond rotating disk electrode (RDE)
experiments are challenging.

Additional approaches to reducing the cost of catalysts for the ORR include other replacements for Pt-based catalysts. For example, a new class of low-cost, non-precious metal catalysts has been synthesized and is reported to be promising for use as high-activity ORR catalysts.

Future work should focus on the following aspects: (i) optimizing the geometry, composition, and structure of Pt-based catalysts to further improve their catalytic activity and stability; (ii) validating the activity and stability of these remarkable catalysts using real fuel cell operating conditions — these nanostructured catalysts have shown excellent activity and stability in electrochemical cell measurements; (iii) further exploring new catalyst morphologies to resolve the issue of low retention in highly active nanostructures; this low retention is caused by fuel cell operation; (iv) developing self-supported nanostructured catalysts to avoid the problems of carbon supports and particle growth by Ostwald ripening; and (v) developing cost-effective catalyst synthesis processes to meet the requirements for fuel cell commercialization.

Regarding the replacement of carbon black with graphene, DWCNTs, or other carbon materials as catalyst supports, further tests in fuel cells have to be performed to evaluate the electrochemical activity and the long term stability of the catalysts supported on these new promising materials.

### 8.2.2 Hydrogen storage

Some promising storage capacities have been achieved on carbon-based materials, particularly via creation of defects and spillover. However, to meet the US Department of
Energy (DOE) targets, substantially more enhancements in hydrogen capacity and understanding of the storage processes are needed.

A number of scientific and technological aspects need to be considered in further studies and sorbent development. The DOE has set 6.0 wt% and 45 g/L as the targets by 2010, and 9.0 wt% and 81 g/L as the targets by 2015 for on-board hydrogen storage systems [1]. These targets are desired for the entire system (adsorbent, storage container, and other apparatus), and therefore, the adsorbents themselves should have even higher capacities than the targets. The DOE has set the operating temperature for hydrogen storage systems to cover the range from -30 to +50 °C. Temperature dependence of the spillover storage needs to be studied. Most of the reported significant storage occurred at cryogenic temperature, which is not desirable for practical application. Storage via spillover at room temperature is a promising approach. So, developing other techniques and adsorbents for storage at room temperature is needed.

Hydrogen physical adsorption is based on weak interactions (dominated by van der Waals forces) between the hydrogen molecules and the adsorbent, and thus the adsorption and desorption processes are reversible with fast kinetics. However, the weak interactions result in low hydrogen uptake at ambient temperature. As for chemical adsorption, it is based on stronger interactions and the formation of chemical bonds between the hydrogen atom and the adsorbent. The binding energy between the hydrogen and the metal is much higher in metal hydrides (> 50 kJ/mol) and chemical hydrides (>100 kJ/mol) than with physical adsorption (<10 kJ/mol), which generally leads to irreversibility and requires elevated temperature for desorption [2]. A moderate binding energy or heat of adsorption around 15.1 kJ/mol was recently suggested as ideal for storage by Bhatia and Myers [3]. In their case, this value was strong enough to store a large amount of hydrogen gas at the charging
pressure (about 3 MPa), while weak enough to release most of that hydrogen at the discharge pressure (about 0.15 MPa). A higher value of 22–25 kJ/mol was later suggested [3]. The heats of adsorption of hydrogen storage via spillover fall in this range, and the process is reversible. The desorption step is faster than the adsorption step, and the desorption rates exceed the DOE discharge rate target. However, the charge rates are slow, and they need to be increased.

References:

