Development of novel proton exchange membranes and anode catalysts for fuel cells

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**DEVELOPMENT OF NOVEL PROTON EXCHANGE
MEMBRANES AND ANODE CATALYSTS FOR FUEL
CELLS**

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ABSTRACT

The depletion of fossil fuel and environmental pollution have led to an urgent demand for alternative energy sources and more efficient energy conversion methods. Fuel cells are a kind of electrochemical devices that can convert the chemical energy of fuels to electrical energy directly. The advantages of the fuel cell technologies are their high energy utilization efficiency and very low pollutant emissions.

Proton exchange membrane fuel cell (PEMFC) is one of the most promising clean energy technologies under development in fuel cell families. Direct methanol fuel cell (DMFC) is a special form of low temperature fuel cells based on PEMFC technology. PEMFC and DMFC are extremely attractive for use in future transportation and portable electronic devices. However, there are still several major obstacles limiting their widespread commercialization and application. E.g., the production, storage and distribution of hydrogen are still the major limitations for the development of PEMFC. CO poisoning to the catalysts remains a serious problem for PEMFC and DMFC. The sluggish anode reaction of methanol oxidation and the methanol crossover causing a mixed potential reduction significantly retard the commercialization process of DMFC.

If PEMFC and DMFC were operated at higher temperatures, many problems could be simplified and solved. Proton exchange membrane (PEM) is one of the most important components in PEMFC and DMFC. Dupont's perfluorosulfonic acid (PFSA) polymer membranes (Nafion[®]) are the most widely used PEM owing to their high proton conductivity, good thermal and chemical stabilities. However, their proton conductivity is

critically dependent on the humidity and water content in the membrane structure. So it is a challenge to develop PEMs for the operation at high temperatures and low humidity conditions.

In this thesis, a novel proton-conducting inorganic membrane based on self-assembled phosphotungstic acid/meso-silica (HPW/meso-silica) has been developed for the high temperature operation of DMFC. The principle of the self-assembly was discussed and the properties of the HPW/meso-silica inorganic membranes were investigated in detail. The results indicate that HPW can be self-assembled into the mesoporous silica without degradation. The proton conductivity of the inorganic membranes depends on the HPW content and the micro-structure formed between HPW and meso-silica. The best conductivity was 0.091 S/cm at 100 °C under 100% relative humidity (RH) and 0.034 S/cm at 200 °C under 3% RH, respectively. The cell with a 25wt% HPW/meso-silica membrane showed a power output of 235 mW/cm² at 150 °C for DMFC. The results provide a solid confidence for further design and development of high temperature PEMFC and DMFC.

The self-assembly technique was also developed to introduce highly ordered mesopores into Nafion membranes. The corresponding principle of the self-assembly was proposed. The structure and properties of the mesoporous Nafion membranes were investigated and characterized detailedly. The mesoporous Nafion membranes showed much higher water retention ability and higher proton conductivity as compared to the pristine Nafion membrane. The cells with the mesoporous Nafion membranes showed evidently higher power output and much better stability, particularly under reduced RH and elevated temperatures. The ability to retain water even under completely dry conditions indicates that it is possible to develop PEMFC without external humidity supplier.

Furthermore, a novel multilayer membrane impregnated with HPW was developed based on the mesoporous Nafion membranes. The multilayer membrane exhibited a significantly higher conductivity than the pristine Nafion membrane at both high and low humidity conditions. The cell with the multilayer membrane was much less sensitive to the change of the RH of the reactant gases. When the RH of inlet gases changed from 100% to 50%, the cell performance with the multilayer membrane showed a decrease of 0.07 mV/min, much smaller than 0.45 mV/min observed for the cell with Nafion 1135 membrane. In addition, when the cells were operated at higher temperatures, e.g., 120 °C, the maximum power density of cells with the multilayer membrane is nearly three times that with the pristine Nafion 1135 membrane. The multilayer membrane significantly widens the RH operating window of the PEMFC at elevated temperatures.

The search for efficient and inexpensive electrocatalysts for methanol oxidation is another challenge. Considering the performance and price, palladium (Pd) should be a good alternative electrocatalyst. In this study, two types of Pd-based catalysts, $\text{Pd}_x\text{Pt}_{1-x}/\text{Ti}$ and Pd-oxides/C were studied for methanol oxidation in alkaline media. The results indicated that Pd-based catalysts exhibited significantly improved catalytic activities as compared to the pure Pd and Pt catalysts. A new tungsten carbide (WC) material was also developed as catalyst supports for DMFC. The WC composite supports showed an obvious promotion effect for the electrocatalysis of Pt catalysts for the methanol oxidation reaction (MOR) in acid solutions.

Key words: Anode catalyst; DMFC; Mesoporous structure; PEMFC; Phosphotungstic acid; Proton exchange membrane

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LIST OF ABBREVIATIONS

AAEM	Alkali Anion Exchange Membrane
AEM	Anion Exchange Membrane
AFC	Alkaline Fuel Cell
AFM	Atomic Force Microscopy
AMT	Ammonium Metatungstate
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
CA	Chronoamperometry
CCM	Catalyst-Coated Membrane
CE	Counter Electrode
CMC	Critical Micellization Concentration
CMT	Critical Micellization Temperature
CNT	Carbon Nanotube
CV	Cyclic Voltammetry
DAFC	Direct Alcohol Fuel Cell
DMFC	Direct Methanol Fuel Cell
ECSA	Electrochemical Surface Area
EDS	Energy Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FE-SEM	Field Emission Scanning Electron Microscope

FRA	Frequency Response Analysis
FT-IR	Fourier Transform Infrared
FTIR-ATR	Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance
GCE	Glass Carbon Electrode
GDE	Gas Diffusion Electrode
GDL	Gas Diffusion Layer
HOR	Hydrogen Oxidation Reaction
HPA	Heteropolyacid
HPW	Phosphotungstic Acid
HRTEM	High Resolution Transmission Electronic Microscopy
IEC	Ion Exchange Capacity
ITO	Indium Tin Oxide
KU	Keggin unit
LSV	Linear Sweep Voltammetry
MCFC	Molten Carbonate Fuel Cell
MEA	Membrane Electrode Assembly
MOR	Methanol Oxidation Reaction
MWCNT	Multi-walled Carbon Nanotube
OCV	Open Circuit Voltage
ORR	Oxygen Reduction Reaction
PAFC	Phosphoric Acid Fuel Cell
PBI	Polybenzimidazole
PEEK	Polyether-etherketones
PEM	Proton Exchange Membrane

PEMFC	Proton Exchange Membrane Fuel Cell
PEO	Poly(ethylene oxide)
PFSA	Perfluorosulfonic Acid
PI	Polyimide
PPO	Poly(propylene oxide)
PTFE	Polytetrafluoroethylene
RDE	Rotating Disk Electrode
RH	Relative Humidity
RHE	Reversible Hydrogen Electrode
SAXS	Small-Angle X-ray Scattering
SBA	Santa Barbara Amorphous type material
SCCM	Standard-state Cubic Centimeter per Minute
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
SOFC	Solid Oxide Fuel Cell
SWCNT	Single-walled Carbon Nanotube
TEM	Transmission Electronic Microscopy
TEOS	Tetraethyl Orthosilicate
T _g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
WC	Tungsten Carbides
WE	Working Electrode
XRD	X-ray diffraction

CHAPTER 1 Introduction

The invention of fuel cells dates back to the middle of the 19th century. The first fuel cell was demonstrated by a Welsh scientist and barrister Sir William Robert Grove in February 1839. In 1893, Friedrich Wilhelm Ostwald experimentally determined the interconnected roles of the various components of the fuel cell: electrodes, electrolyte, oxidizing and reducing agents; provided much of the theoretical understanding of how fuel cells operate. In 1955, W. Thomas Grubb, a chemist working for the General Electric Company, further modified the original fuel cell design by using a sulphonated polystyrene ion exchange membrane as the electrolyte. In the 1960s, Pratt and Whitney licensed Bacon's U.S. patents for use in the U.S. space program to supply electricity and drinking water.

One of the major factors that have influenced the development of fuel cells is the increasing concern about the environmental consequences of fossil fuel use in production of electricity and for the propulsion of vehicles. The heavy dependence of the industrialized countries on oil became apparent during the oil crises in the 1990s. However, a more important factor is the increasing global awareness of how human activities influence the environment and how a sustainable development can be achieved with a tremendously increasing world population.

Fuel cells with much higher efficiencies as compared to internal combustion engines (ICE), may help to reduce the dependence on fossil fuels and the green house gas emissions into the atmosphere. Fuel cells offer the ability to generate electricity and heat at the point

of use. The traditional electrical infrastructure means that large amounts of electricity are generated at central locations where the resulting heat is not usually used effectively. The renewable energy from wind, water and sun are not suited to cover the electrical base load due to their irregular availability. However, the combination of the sources to produce hydrogen in cooperation with fuel cells may be a good option for future power generation.

1.1 Basic principles of fuel cells

The fuel cell reaction is a chemical process consisting of two electrochemical half-cell reactions. The simplest and common reaction encountered in fuel cells is the case of hydrogen/oxygen fuel cells, where the anode reaction is the oxidation of hydrogen, and the reaction at the cathode is the oxygen reduction reaction. The overall reaction is:

From a thermodynamic point of view, the maximum electric work obtained from the above reaction corresponds to the free energy change of the reaction. The reaction (1.1) is spontaneous because the free energy of the products is less than that of the reactants. The standard free energy change of the fuel cell reaction is represented by the equation:

$$\Delta G = -nFE_r \quad (1.2)$$

where ΔG is the free energy change, n is the number of electrons involved in the reaction, F is the Faraday constant, and E_r is the reversible potential. If the reactants and products are in their standard states i.e., at a temperature 25 °C and 1 atm pressure, the equation can be rewritten as:

$$\Delta G^0 = -nFE_r^0 \quad (1.3)$$

Thus, for the reaction (1.1), the calculated value of E_r is 1.23 V.

Water is the product of the fuel cell reaction and can be produced either as liquid water or steam. The higher heating value (HHV) corresponds to the released heat when water is produced as liquid water and the lower heating value (LHV) when water is produced as steam.

The enthalpy change (ΔH) of a fuel cell reaction represents the entire heat released by the reaction at a constant pressure, can be presented as:

$$\Delta H = -nFE_r \quad (1.4)$$

where E_r is the thermoneutral potential, having a value of 1.48 V for the reaction (1.1).

1.2 Efficiency of fuel cells

In order to compare fuel cells with other systems such as ICEs an evolution of the system efficiency is necessary. Fuel cells are not limited by the Carnot cycle and in the case of H_2/O_2 fuel cells the production of water is represented by the following two half-cell reactions:

All the available energy from the above reaction can be converted to electrical energy in an ideal process. Considering that ΔH is the total energy available in the process and ΔG is the energy that can be converted to electrical energy, the theoretical or reversible efficiency of the fuel cell reaction is then expressed as:

$$\varepsilon_r = \frac{\Delta G}{\Delta H} \quad (1.7)$$

Here, ΔG is less than the enthalpy change because of the entropy of the reaction, which generates heat rather than electricity. The efficiencies based on the LHV and HHV of the reaction in a H_2/O_2 fuel cell are 94% and 83%, respectively.

The voltage efficiency of a fuel cell is given by the expression:

$$\varepsilon_v = \frac{E(i)}{E_r} \quad (1.8)$$

where $E(i)$ is the cell potential at a given current density (i) and E_r is the reversible potential. The efficiency can be less than 100% due to the fact that the $E(i)$ of fuel cells is lower than the E_r due to the loss related to the activation, ohmic, and mass transport overpotentials. The incomplete oxidation of the reactant fuels and the fuel crossover from anode to cathode also result in a loss of efficiency.

1.3 Types of Fuel Cells

Fuel cells are classified primarily by the kind of electrolyte they employ. This classification determines the kind of chemical reactions that take place in the cell, the catalysts required, the temperature range in which the cell operates, the fuel required, and other factors. These characteristics, in turn, affect the applications for which these cells are most suitable.

There are several types of fuel cells currently under development, e.g., alkaline fuel cell (AFC), proton exchange membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and solid

oxide fuel cell (SOFC), each with its own advantages, limitations, and potential applications. An overview of these fuel cells is given in Table 1.1.

Table 1.1 Major types of fuel cells currently in use and development.

Type	AFC	PEMFC	DMFC	PAFC	MCFC	SOFC
Operating temp. (°C)	<100	60-120	60-120	160-220	600-800	800-1000 (500-600)
Anode reaction	$\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$	$\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$
Cathode reaction	$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	$\frac{3}{2}\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O}$	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	$\frac{1}{2}\text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$	$\frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$
Electrolyte	KOH	PEM	PEM	H_3PO_4	$\text{Li}_2\text{CO}_3 + \text{K}_2\text{CO}_3$	$\text{ZrO}_2 + \text{Y}_2\text{O}_3$
Charge carrier	OH^-	H^+	H^+	H^+	CO_3^{2-}	O^{2-}

1.3.1 AFC

AFCs are one of the first fuel cell technologies developed, and they are the first type widely used in the U.S. space program to produce electrical energy and water on-board spacecrafts. These fuel cells use a KOH solution as the electrolyte and can use a variety of non-precious metals as a catalyst at the anode and cathode. AFCs generally operate at temperatures of 23 °C to 70 °C. The high performance of AFCs is owing to the facile rate at which chemical reactions take place in the cell. They have also demonstrated efficiencies near 60% in space application. The disadvantage of the AFCs is the carbonate formation at the electrodes and in the alkaline electrolytes. In fact, even a small amount of CO_2 in air and H_2 can affect their operation, making it necessary to purify both the H_2 and O_2 used in

the cells. This purification process is costly. Susceptibility to poisoning also affects their lifetime, further adding to cost.

1.3.2 PAFC

PAFCs use liquid phosphoric acid as the electrolyte. The acid is contained in a Teflon-bonded silicon carbide matrix and porous carbon containing a platinum catalyst is used as electrodes. The PAFCs are considered the “first generation” of modern fuel cells. They are one of the most mature cell types and are typically used for stationary power generation. PAFCs are more tolerant toward impurities in the reformat fuels. The efficiency of PAFCs can be as high as 85% when used for the co-generation of electricity and heat but less efficient at generating electricity alone (37%-42%). The key issue of the PAFCs is the serious corrosion associated with the phosphoric acid. PAFCs are also less powerful than other fuel cells, given the same weight and volume. As a result, the fuel cells are typically large and heavy. PAFCs require expensive platinum catalysts, which raises the cost of the fuel cells.

1.3.3 MCFC

MCFCs are currently being developed for natural gas and coal-based power plants for electrical utility and industrial applications. MCFCs are high temperature fuel cells that use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert lithium aluminum oxide (LiAlO_2) matrix. MCFCs can reach efficiencies approaching 60%, considerably higher than that of PAFCs. Due to the high temperature at

which MCFCs operate, these fuels can be converted to hydrogen within the fuel cell by a process called internal reforming, which also reduces the cost of the system. MCFCs are not prone to carbon monoxide or carbon dioxide “poisoning”. They can even use carbon dioxides as fuel, making them more attractive for fueling with gases made from coal. The primary disadvantage of MCFCs is their durability. The high temperatures at which these cells operate and the corrosive electrolyte used accelerate the component breakdown and corrosion, decreasing cell life.

1.3.4 SOFC

SOFCs use a hard, non-porous ceramic compound as the electrolyte. Because the electrolyte is a solid, the cells do not have to be constructed in the plate-like configuration typical of other fuel cell types. SOFCs are expected to be around 50%-60% efficient on converting fuel to electricity. SOFCs operate at very high temperature around 1000 °C. High temperature operation removes the need for precious metal catalyst, thereby reducing cost. It also allows SOFCs to reform fuels internally, which enables the use of a variety of fuels and reduces the cost associated with adding a reformer to the system. In addition, they are not poisoned by carbon monoxide, which can even be used as fuel. This property allows SOFCs to use gases from coal gasification. High temperature operation has disadvantages. It results in a slow startup and requires significant thermal shielding to retain heat and protect personnel, which may be acceptable for utility applications but not for transportation and small portable applications. The high operating temperature also places stringent durability requirements on materials. The development of low cost materials with high durability at cell operating temperature is the key technical challenge.

1.3.5 PEMFC

PEMFCs use a solid polymer membrane as the electrolyte. In PEMFCs, hydrogen is split into protons and electrons on the anode. Protons are transported through the electrolyte to the cathode, and electrons move through an external circuit. On the cathode, protons, electrons and oxygen are combined to produce water and heat. Figure 1.1 shows the principle of PEMFCs.

Figure 1.1. Principle operation diagram for PEMFC.

PEMFCs operate at relatively low temperatures of around 80 °C. Low temperature operation allows them to start quickly (less warm-up time) and produces less wear on system components, resulting in better durability. However, it requires that a noble metal catalyst, typically Pt be used to split hydrogen to electrons and protons, adding to system cost. The Pt catalyst is also extremely sensitive to CO poisoning so that it is necessary to

employ an additional reactor to reduce CO in the fuel gas if hydrogen is derived from an alcohol or hydrocarbon fuel. Binary PtRu catalysts are much more tolerant as compared to pure Pt to CO. PEMFCs are used primarily for transportation, portable and stationary applications. Due to their fast startup time, low sensitivity to orientation, and favorable power-to-weight ratio, PEMFCs are particularly suitable for use in passenger vehicles, such as cars and buses.

An exploded view of PEMFCs components is shown in Figure 1.2. The components include: (1) proton exchange membranes; (2) electrically conductive porous backing layers; (3) catalyst layers (the electrodes) sandwiched between the backing layer and the membrane; (4) gaskets for gas tight seal and electrical insulation; (5) cell plates with gas channels on one side (end plates or plates for single cells) or on both sides (bipolar plates) that delivers the fuel and oxidant to the reactive sites; (6) other materials e.g. interconnecting, cooling, manifold and others.

Figure 1.2. An exploded view of PEMFC components.

A significant barrier to using these fuel cells in vehicles is the infrastructure for hydrogen transportation and storage. Most fuel cell vehicles powered by pure hydrogen must store the hydrogen on-board as a compressed gas in pressurized tanks. Due to the low energy density of hydrogen, it is difficult to store enough hydrogen on-board to allow vehicles to travel the same distance as gasoline-powered vehicles before refueling, typically 300-400 miles. Some liquid fuels, e.g., methanol, ethanol, natural gas, liquefied petroleum gas and gasoline, can be used as fuel, but the vehicles must have an on-board fuel processor to reform them to hydrogen. This requirement increases costs and maintenance.

The second important problem is associated with the electrocatalyst. It is well known that Pt is the most active catalyst for both hydrogen oxidation reaction (HOR) at the anode and oxygen reduction reaction (ORR) at the cathode. In PEMFCs the major loss of performance is due to the slow ORR and mass transport limitations especially when air is used. Significant efforts have been made to develop platinum alloy catalysts to increase the kinetics of ORR and to tailor the electrode structure to decrease transport limitations. When hydrogen is obtained from reformed gas, significant power losses may arise due to platinum poisoned by tracer amount of CO in reformed gas as described above. Therefore, a big challenge is to develop CO resistant catalyst for HOR.

The most important component in PEMFCs is the electrolyte membrane. Although the US General Electric Company (GE) initiated the development of PEMFCs in the 1950s, it was the introduction of Nafion by DuPont that ensured continuing interest in these systems. Initially, Nafion was manufactured for membrane cells used in the production of chlorine. By 1990, Ballard had overcome many of the engineering problems associated with PEMFC systems, which had simulated many groups in US and Japan to improve the properties of the original Nafion materials. Nowadays, Nafion is the most common membrane

electrolytes used in PEMFCs owing to their high proton conductivity and good thermal and chemical stability. But, the costs of Nafion membranes remain high so that many efforts are being applied to the development of cheaper, usually fluorine-free membrane materials. In addition their proton conductivity is critically dependent on the humidity and water content in the membrane structure. Thus an alternative proton exchange membrane which can be operated at high temperature/low humidity remains a critical challenge.

The high temperature/low humidity operation of PEMFCs presents many advantages over conventional operation, such as improved reaction kinetics in anode and cathode, improved tolerance of catalysts to contaminants and simplified water management and system design, etc. The main objective of the project is to develop novel proton exchange membranes to meet this grand challenge.

1.3.6 DMFC

DMFCs are a special form of low temperature fuel cells based on PEMFCs technology. Although the power efficiency of hydrogen PEMFCs continues to show steady improvements, problems remain with the use of hydrogen because hydrogen is not a primary fuel and must be obtained from in-situ reformation of solid or liquid hydrocarbons (petroleum, coal, methanol) or be pre-purified and stored as pressurized gas, or in the form of an admixture with a metal alloy, carbon or some other absorbent. In all cases, either a considerable weight confinement or increased engineering complexity adds to the cost.

In DMFCs, methanol is not reformed into hydrogen gas but is used directly. Methanol possesses a number of advantages as a fuel, such as it being a liquid and therefore can be easily transported, stored, dispensed within the current refueling network. Methanol is

cheap and plentiful, and the only products of the reaction are CO_2 and water. Above all, the use of methanol as a fuel highly simplifies the engineering problems at the front end of the fuel cells, driving down complexity and cost. DMFCs rely upon the oxidation of methanol on a catalyst layer to form carbon dioxide. Water is consumed at the anode and is produced at the cathode. Protons are transported across the PEM (often made from Nafion) to the cathode where they react with oxygen to produce water. Electrons are transported through an external circuit from anode to cathode, providing electrical power to connected devices.

The theoretical reactions involved in DMFCs are as follows:

During the past 10 years, there was a marked shift away from developing PEMFCs in favor of DMFCs. There are already working DMFCs prototypes used by the military for powering electronic equipment in the field. Figure 1.3 is a schematic diagram of a DMFC.

Figure 1.3. Schematic diagram of a direct methanol fuel cell.

However, methanol crossover from the anode to the cathode is a main problem, which not only depresses cathode performance, but also reduces cell efficiency. This has significantly restricted the DMFCs technology from its inception. Many efforts have been made to modify the Nafion membranes to reduce the methanol crossover, or develop alternative membranes with low methanol permeability and high proton conductivity.

Owing to the high degree of irreversibility of the oxygen reduction reaction, even under open circuit conditions, the overpotential at the oxygen electrode in a H₂/Air PEMFC is about 0.2 V. This represents a loss of about 20% from the theoretical maximum efficiency. The situation is even worse in DMFCs. In DMFCs, both the methanol oxidation and oxygen reduction reactions are highly irreversible. Therefore there is a loss of about 0.2 V at the anode under open circuit conditions, and an additional loss of about 0.1 V or more at the oxygen electrode because of the methanol crossover. So it is another challenge to seek novel catalysts with high activity and high CO tolerance for DMFCs.

Recently, an alkali anion exchange membrane (AAEM) was invented for DMFCs operating in alkaline media. This is a very interesting development because the fuel cell is utilizing a solid-state electrolyte rather than an alkaline liquid. AAEM is a semipermeable membrane generally made from ionomers and designed to conduct anions while being impermeable to gases such as oxygen or hydrogen. The advantage of the AAEM in the fuel cell is the potential to use non-noble metals such as iron, cobalt or nickel due to the low overpotentials associated with electrochemical reactions at high pH. In comparison against AFC, AAEM fuel cells also protect the electrode from carbonate formation, which can cause seriously poisoning effects and decreasing lifetime during operating AFC.

1.4 Objectives

Currently, the development of high temperature PEMs and anode catalysts for PEMFCs is the subject of a world-wide quest in fuel cell areas. There are several major challenges for operating PEMFCs at high temperature ($>100\text{ }^{\circ}\text{C}$), such as membrane dehydration, degradation of electrodes and humidification issues. Mesoporous materials possess the unique capillary effects and long-range ordered structures, which are helpful for the water retention and ion transport. So the novel organic/inorganic composite membranes with highly ordered mesoporous structures should have potential applications for PEMFCs. The main objective of this study is to develop novel mesoporous structures based PEMs, which can be operated at high temperature and/or low humidity conditions for PEMFCs. The structures and properties of the membranes developed will be characterized and investigated in detail.

On the other hand, the development of Pt-free catalysts for PEMFCs with comparable activities to Pt still remains a big challenge. Pd-based catalysts can be highly active for the oxidation of a large variety of substrates in alkaline environment. So novel Pd-based anode catalysts for DMFCs will be developed and investigated.

1.5 Scope

The scope of this study is:

- Development of novel proton exchange membranes for high temperature and/or low humidity PEMFCs.
 - Synthesis and characterization of nano-composite inorganic proton exchange

membranes based on mesoporous silica self-assembled with phosphotungstic acid (HPW).

- Synthesis and characterization of mesoporous Nafion membranes.
- Synthesis and characterization of the multilayer Nafion membrane impregnated with HPW.
- Development of novel anode catalysts and catalyst supports for DMFCs.
 - Synthesis and characterization of nano-structured $\text{Pd}_x\text{Pt}_{1-x}/\text{Ti}$ catalysts.
 - Synthesis and characterization of nanocrystalline Pd-oxides/C catalysts.
 - Synthesis and characterization of nano-structured tungsten carbide composites as catalyst supports.

1.6 Novelty and contributions

The novelty of this thesis is that a novel self-assembly method was developed to fabricate PEMs with long-range ordered mesoporous structures and a new methodology for synthesizing multilayer membranes was exploited. Moreover, a microwave heating technique was developed to synthesize anode catalysts and catalyst supporting materials. The contributions are that two new meso-structured PEMs and a kind of multilayer PEMs have been successfully explored for applications in PEMFCs. Two novel Pd-based catalysts and a new kind of catalyst supporting materials were prepared for applications in DMFCs.

1.7 Thesis layout

- ✧ Chapter 1: Introduction.

- ✧ Chapter 2: Literature Review.
- ✧ Chapter 3: A Novel Inorganic Proton Exchange Membrane Based on Self-Assembled HPW/meso-silica for DMFCs.
- ✧ Chapter 4: Highly Ordered Mesoporous Nafion Membranes for PEMFCs.
- ✧ Chapter 5: A Novel Multilayer Nafion Membrane Impregnated with HPW for PEMFCs.
- ✧ Chapter 6: Nano-Structured $\text{Pd}_x\text{Pt}_{1-x}/\text{Ti}$ Anodes by Electrodeposition for Alcohol Electrooxidation.
- ✧ Chapter 7: Electro-Oxidation of Methanol and Ethanol on Pd/C Catalyst Promoted by Transition Metal Oxides in Alkaline Media.
- ✧ Chapter 8: Nano-Structured Tungsten Carbide Composites Synthesized by Microwave Heating Method as Catalyst Supports for DMFCs.
- ✧ Chapter 9: Conclusions and Recommendations.

CHAPTER 2 Literature Review

2.1 Proton exchange membrane for high temperature and/or low humidity PEMFCs

Proton exchange membrane fuel cells (PEMFCs) are one of the most promising clean energy technologies under development. Owing to their inherently high energy efficiency, they are extremely attractive for use in future transportation when compared to that of internal combustion engines. PEMFCs potentially need low maintenance requirements due to fewer moving parts, and a more comfortable and quieter ride due to lower noise and vibrations. Moreover, the attributes, such as high power density and rapid start-up, make them a great promise for mobile applications such as portable electronics [1-5].

The electrolyte in PEMFCs is a proton exchange membrane (PEM), typically a film made from an inert polymer containing acidic groups, which is the key component of PEMFCs. As shown in Figure 2.1, the basic requirements for the membrane are as follows: Firstly, it must have high proton conductance to minimize cell resistance and maximize cell efficiency. Secondly, it has to be electrically insulating to prevent shorting. Thirdly, the membrane functions as a barrier to the reactant gases, so it must have good mechanical properties, uniformity, free of defects, and suitably low permeability to fuels and oxidants. Fourthly, to maintain these properties for the lifetime of the systems, it must also have excellent chemical stability towards hydrolysis, oxidation, and reduction [6-11].

Figure 2.1. Basic requirements for a good proton exchange membrane.

2.1.1 Perfluorinated ionic membranes

Perfluorosulfonic acid (PFSA) membranes were first discovered and developed for fuel cells by DuPont as Nafion[®] in the late 1960s [12]. Various types of PFSA polymers, such as Flemion[®] and Aciplex[®] membranes were developed subsequently. The bonding energy of C-F is 485 kJ/mol and larger compared with those of C-H (350 kJ/mol for aliphatics and 435 kJ/mol for aromatics). This basic feature gives a remarkable stability to various fluoro compounds. Nafion is the first one of synthetic polymers with ionic properties. Nafion's unique ionic properties are a result of incorporating perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) backbone. The chemical basis of Nafion's superior conductive properties remains a focus of research. Protons on the SO₃H (sulfonic acid) groups hop from one acid site to another. Pores allow movement of cations but the membranes do not conduct anions or electrons. Nafion can be manufactured with various cationic conductivities and received a considerable amount of

attention as a proton conductor for PEMFCs because of its excellent thermal and mechanical stability [12-14].

The chemical structure of Nafion is shown in Figure 2.2. The perfluorinated backbone imparts a chemical and thermal stability, while the pendant sulfonic acid group imparts strong acidic characteristics for facile proton transport. The combination of extremely high hydrophobicity of the perfluorinated backbone with the extremely high hydrophilicity of the sulfonic acid functional groups gives rise to some hydrophobic/hydrophilic nano-separation. The sulfonic acid functional groups aggregate to form a hydrophilic domain. When this hydrophilic domain is hydrated, protonic charge carriers within inner space charge layers move by dissociation of the acidic functional groups. The occurrence of water dynamics assists proton conductance (see the right graph of Figure 2.2). The proton conductivity of PFSA-based membranes is critically dependent on the humidity and water content in the membrane structure [15-18].

Figure 2.2. Schematic illustration of the microstructures of Nafion [11].

Figure 2.3 shows the dependence of the proton conductivity of PEMs including Nafion on the humidity. The proton conductivity decreases significantly with the decrease of the water content in the membrane, and the acceptable conductivity can only be obtained in well saturated environments [16, 19]. Therefore, it is very important to keep a high water content in the membranes to achieve high power density in PEMFCs operation.

Figure 2.3. Dependence of proton conductivity on the humidity of the membrane for different PEMs including Nafion [20].

Membranes in PEMFCs are generally filled with water to keep the conductivity high. Water management is one of the major issues in PEM technology and will affect the overall system power and system efficiency [21-23]. For practical operations, the fuel cells with Nafion membranes rely on external humidifiers for the hydration of gas streams prior to the entry of the cell. However, these humidifying and relative control units increase the cost, complexity and design barriers of the whole system. For PEMFC operation at temperature ≤ 100 °C under an atmospheric pressure, it often involves a dual phase water system, i.e.,

liquid water and water vapor. A lack of water in the membranes and gas diffusion electrodes decreases their proton conductivity and significantly increases the cell resistance. On the other hand, if the humidification is too high, water will condense and the electrodes will be flooded, particularly in the cathode, which is so called “flooding” [3, 21, 24].

Figure 2.4 shows the different modes of water transportation through PEMs. The effect that water is carried by protons crossing the membrane from anode to cathode is named electro-osmotic drag. The back diffusion of water from cathode to anode is caused by a gradient of water content. If a differential pressure exists due to the production of water at cathode, hydraulic pressure may also force water from cathode to anode. If the latter is absent, the net water flux across the membrane is a combination of electro-osmotic drag and diffusion, which has a profound impact on fuel cell performance. However, if PEMFCs are operated at above 100 °C under atmospheric pressure, then only water vapor would exist in PEMFCs. So the transport of water in membranes, catalysts layer and diffusion layers will be easier to balance. The transport of reactants (H_2 and O_2) in electrode layers is also expected to be enhanced, and no flooding problem will occur at the cathode side. Additionally, the reduction in the amount of liquid water will increase the exposed surface area of the electrocatalysts and improve the ability of the reactants to diffuse in the reaction layers. Moreover, the operation of PEMFCs at elevated temperatures is critical in order to accelerate the reaction kinetics and reduce catalyst poisoning effects particularly by CO [25-27].

Figure 2.4. Schematic diagram illustrating the modes of water transport in a working H_2/O_2 PEMFC [28].

2.1.2 Modified hybrid membranes based on PFSA

At high temperature and low humidity operation, conventional PFSA membranes dehydrate and their conductivity decreases dramatically. Thus considerable efforts have been made to improve the properties of PFSA membranes for high temperature and/or low humidity operation.

Nano-silica particles have been used to modify Nafion membranes. Tang et al. [29] synthesized a novel Nafion/ SiO_2 nano-composite membrane based on the self-assembled Nafion- SiO_2 nano-particles. Their results showed that the self-assembled Nafion- SiO_2 nano-particles significantly enhance the durability of the Nafion/silica nano-composite membrane as compared to that of conventional Nafion/silica composite and pristine Nafion 212 membranes under accelerated wet/dry cyclic tests at 90°C . The high durability was due to the excellent interface between the Nafion polymeric matrix and the self-assembled

Nafion-SiO₂ nano-particles. With the addition of 5wt% self-assembled Nafion-SiO₂ nano-particles, the nano-composite membrane showed a significantly improved performance stability at the cell/humidifying temperature of 100 °C/60 °C under a current density of 600 mA/cm².

Jin et al. [30] prepared Nafion composite membranes with mesoporous silica nano-spheres as inorganic fillers. The mesoporous MCM-41 silica nano-spheres displayed highly ordered and monodispersed porous structure. The silica fillers were added with 1~3wt% and the thickness of membranes were controlled to be 120~130 µm. The incorporation of mesoporous silica nano-spheres enhanced water retention properties, improved thermal stability, and reduced methanol crossover of pristine Nafion. The composite membranes showed slightly lower tensile strength but better structural durability than the Nafion membrane. The proton conductivity of the composite membranes slightly decreased with increasing the amount of fillers. But the methanol crossover of the composite was not proportionally decreased with increasing the amount of fillers. The composite membrane containing 1wt% of fillers displayed a higher OCV and a better DMFC performance than the Nafion cast membrane.

Watanabe et al. [31] designed and synthesized self-humidifying polymer electrolyte membranes for high temperature PEMFCs. SiO₂ or TiO₂ nano-particles were introduced into Nafion membranes by the SiO₂ or TiO₂ colloid prepared by the hydrolysis. Then platinum nanocrystallites were dispersed into the membranes by the cation exchange treatment with a [Pt(NH₃)₄]Cl₂ solution at 60 °C overnight, followed by reducing the exchange Pt²⁺ with hydrazine. The resistance value of Pt-TiO₂-PEM and Pt-SiO₂-PEM was 0.17 to 0.057 Ω cm² under humidification of both the anode and cathode gases at T_h=105 °C. Their results indicated that these new types of PEMs consisting of Pt catalysts

and oxide materials could adsorb and recombine water at low humidity or higher temperatures. At the same time, it could effectively suppress H_2 and O_2 crossover.

Jung et al. [32] studied the Nafion/PTFE/silicate (NPS) membrane for high temperature PEMFCs. When the test temperature was increased to 90~110 °C, the performance of the cell with Nafion 112 was very poor, but the cell with the NPS membrane showed a reasonable performance. The results revealed that the presence of nano-silicate particles in NPS membrane enhanced the water uptake at high temperatures and low gas humidity, also reduced the water loss due to electro-osmosis at high current densities.

H^+ form mordenite powders were firstly used as a precursor for the fabrication of hybrid membrane for PEMFCs operation above 100 °C by Kwak et al. [33]. The contents of the powder were 3, 5, 10 and 20wt% in the membrane. The optimum amount of mordenite was determined to be about 10wt%. The presence of mordenite increased the water retention of the membrane, which was most likely due to the hygroscopic and high ionic exchange properties of mordenite.

Tatsumisago et al. [34] reported the proton conductivity value of silica containing phosphotungstic acid (HPW) was about 10^{-2} to 10^{-1} S/cm. Shao et al. [35] prepared and characterized hybrid Nafion-silica membranes doped with HPW for high temperature PEMFCs. The hybrid Nafion-silica membranes doped with HPW exhibits proton conductivity, which was similar to that of the native Nafion membrane at 100% relative humidity, but much higher at low humidity.

Malhotra et al. [36] investigated membrane-supported nonvolatile acidic electrolytes for high temperature PEMFCs. The results indicated that the supported acid was to provide high concentration of protons in the membrane pores by undergoing proton-transfer

reactions. The technique was demonstrated by utilizing a solution of HPA in acetic acid or tetra-n-butylammonium chloride for impregnating the Nafion membrane and operating the fuel cells at low humidity levels. A dramatic improvement in fuel cell output was obtained at elevated temperatures as compared with the conventional PEMFCs. The authors believed that the approach may eventually allow directly use of low temperature re-formable fuels such as methanol and ethanol in fuel cells.

Costamagna et al. [37] studied the Nafion 115/zirconium phosphate composite membranes for operation of PEMFCs above 100 °C. Zirconium phosphate was incorporated into Nafion 115 via an ion exchange reaction involving Zr^{4+} ions followed by precipitation of zirconium phosphate by immersion of the membrane in H_3PO_4 . Their results showed that it was possible to operate a PEMFC at temperature ≥ 130 °C and the impregnation with a hygroscopic insoluble salt gave significant improvement in performance under dehydrating conditions. Si et al. [38] studied Nafion-Teflon- $\text{Zr}(\text{HPO}_4)_2$ composite membranes for high temperature PEMFCs. The test results indicated that the as-prepared membrane showed an increased resistance, but good performance at elevated temperatures.

The incorporation of hygroscopic inorganic nano-particles such as SiO_2 and TiO_2 improves the water retention properties of Nafion membranes. This approach has shown significantly improvement of PEMFC performance at high temperature or low humidity conditions. However, because of the rather low glass transition temperature (T_g) of PFSA, the modified PFSA membranes are normally operated at ~ 120 °C. Moreover, the inherently low proton conductivity of the inorganic materials decreases the composite membrane's conductivity with increasing the additive content. In addition, due to the non-homogeneous nature of the hybrid membranes, phase separation is a problem due to the difference in

swelling and thermal expansion coefficients which affects the durability of the cell performance. The local stress around the inorganic particle surface, caused by the gradient water concentration and poor compatibility with the membrane, may decrease the mechanical properties of the membrane, followed by the accelerated fuel crossover.

2.1.3 Polyaromatic polymers

Polybenzimidazole (PBI) is an aromatic heterocyclic polymer with a T_g of 425-436 °C. It is a basic polymer ($pK_a=5.5$) which can be complex of strong acids or very strong bases. PBI membrane doped with acids has received much attention mainly for use as PEM above 100 °C. Li et al. [39] studied the water uptake and acid doping of PBIs as electrolytes for fuel cells. The infrared and Raman spectra proved the presence of strong hydrogen bonds between phosphoric acid and nitrogen atoms of the imidazole rings, which indicated that PBI membranes were easily to be doped by phosphoric acid and to be used as membrane electrolytes for fuel cells. The same authors also prepared and characterized PBI-based polymer membranes for high temperature PEMFCs [40]. Poly 2,2'-m-(phenylene)-5,5'-bibenzimidazole was dissolved in a strong acid and in a small number of organic solvents. Then the membranes could be obtained by a recasting method. The operation at temperatures up to 200 °C was demonstrated using hydrogen reformed from a simple methanol reformer without further CO removal. A lifetime of over 5000 hrs of continuous operation at 150 °C had been achieved, which indicated that the as-prepared PBI membrane was a very promising candidate for high temperature PEMFCs.

Asensio et al. [41] prepared and characterized phosphoric acid-impregnated poly(2,5-benzimidazole) (ABPBI) membranes for PEMFCs operating at high temperatures. The

results demonstrated that acid-doped PBI was a promising membrane for PEMFCs. The as synthesized ABPBI membrane showed high proton conductivity and the conductivity increased with temperature and RH. A relatively good cell performance was obtained at 130 °C through the ABPBI membrane.

Polyether-etherketones (PEEK) are thermoplastic polymers with an aromatic non-fluorinated backbone, in which 1,4-disubstituted phenyl groups are separated by a number of linkages, -O- and -CO-. PEEK shows excellent thermal stability and chemical resistance under engineering applications. The T_g of nonsulfonated PEEK is 146 °C. The intermolecular interaction through hydrogen bonding increases with increasing the degree of sulfonation, resulting in higher T_g up to 210 °C at 80% sulfonation [42].

Alberti et al. [43] systematically investigated the conductivity of sulfonated polyether etherketone (S-PEEK) membranes as a function of relative humidity in a wide range of temperature (80-160 °C). Their results indicated that S-PEEK seems to be very promising for application in medium temperature fuel cells. Liu et al. [44] synthesized PEEK membranes with pendant sulfonic acid phenyl groups using a mild sulfonation method. The membrane exhibited a high proton conductivity of 0.15 S/cm at 100 °C, but no cell performance was reported. Zaidi et al. [45] prepared a series of composite membranes of sulfonated PEEK with embedded HPAs. These membranes showed a rather high conductivity of 10^{-2} S/cm at ambient temperature and up to the maximum of about 10^{-1} S/cm above 100 °C, and an increased T_g compared with the pure PEEK membrane.

Yamada and Honma [46] synthesized a polystyrene sulfonic acid (PSS) composite by self-assembly of $-SO_3H$ onto HPW surface, achieving a proton conductivity of 1×10^{-2} S/cm at 180 °C. Nevertheless, the power density of the cell based on a PSS with 10wt% HPW composite membrane was very low, ~3 mW/cm at 160 °C in H_2/O_2 .

Polyaromatic polymers have displayed many promising potentials for high temperature PEMFCs. However, the long term stability and reliability of PEMFCs still need to be proved. The chemical stability of membranes in oxidizing and reducing environments at elevated temperatures is also very important in considering the durability of high temperature PEMFCs. It is believed that the radical species attack the polymer hydrocarbon chains, leading to degradation of the membrane. The diffusion of acid groups out of the matrix is another problem. The formation of phosphoric acid methyl esters in turn causes the degradation of the membrane.

2.1.4 Proton-conducting inorganic membranes

Recently, there are some reports on proton-conducting inorganic membranes for fuel cell applications. Nogami et al. [47] synthesized P_2O_5 - SiO_2 proton-conducting inorganic membranes by the sol-gel method using $PO(OCH_3)_3$ and $Si(OC_2H_5)_4$. The highest conductivity was 2.2×10^{-2} S/cm at 50 °C. A H_2/O_2 fuel cell was constructed and demonstrated using the inorganic glass electrolyte. The output power was about 6 mW/cm². The authors claimed that although it was still smaller by one or two orders of magnitude than that for the cell using polymer membranes, considering the high conductivity, chemical and thermal stability, and low fabrication cost for the glasses, the oxide glass membranes were believed as a substitute for polymer membranes.

Uma et al. [48] synthesized and investigated P_2O_5 - TiO_2 - SiO_2 inorganic glass electrolytes. Their results indicated that P_2O_5 concentration influenced the structures and thermal stability of the glass electrolytes. A maximum proton conductivity of 3.6×10^{-2} S/cm was obtained from the sample 9 P_2O_5 -6 TiO_2 -85 SiO_2 glass.

Nagao et al. [49] studied a proton conducting In^{3+} -doped SnP_2O_7 electrolyte for intermediate temperature fuel cells. The conductivities of undoped and In^{3+} -doped SnP_2O_7 were measured in unhumidified air from 80 °C to 300 °C. In^{3+} -doped SnP_2O_7 showed the highest conductivity of 1.95×10^{-1} S/cm at 250 °C. Using the electrolyte with a thickness of 1.2 mm, the peak power density reached at 152 mW/cm².

Heo et al. [50] investigated the proton conducting $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ electrolyte in the intermediate temperature range of 150-300 °C. The cathodic polarization was significantly improved by applying an intermediate layer of $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ and 30wt% Pt/C catalyst powders at the interface between the electrolyte and cathode. A power density of 264 mW/cm² was achieved at 250 °C with the 0.35 mm thick electrolyte.

Tomita et al. [51] synthesized Al^{3+} -doped SnP_2O_7 proton conducting electrolytes for the intermediate temperature fuel cell operation. The conductivity was determined in unhumidified air from 50-350 °C. Their results indicated that the partial substitution of Al^{3+} for Sn^{4+} contributed to a big enhancement in conductivity. The substitution limitation for Al^{3+} ions was found to be 5mol%. $\text{Sn}_{0.9}\text{Al}_{0.05}\text{P}_2\text{O}_7$ displayed the highest conductivity of > 0.1 S/cm in the temperature range of 150-350 °C.

Mesoporous inorganic materials have a pore size range of 2-50 nm and have high specific surface area, open channels of large dimension, an open framework with an ordered or disordered interconnected internal structure, and a chemical and structural stability. These properties may be beneficial for their use as possible solid-state electrolyte alternatives. Recently high proton conductivities were reported on mesoporous thin films.

Yamada et al. [52] prepared a TiO_2 - P_2O_5 mesoporous nanocomposite by sol-gel method. The TiO_2 - P_2O_5 mesoporous nanocomposite displayed a high water-holding

capacity at an intermediate temperature region and showed a high proton conductivity of 2×10^{-2} S/cm at 160 °C under 100% RH.

Halla et al. [53] synthesized and characterized a mesostructured solid electrolyte composite material, meso-SiO₂-C₁₂EO₁₀OH-CF₃SO₃H. The meso-SiO₂-C₁₂EO₁₀OH-CF₃SO₃H composite material showed a proton conductivity of 1×10^{-3} S/cm at room temperature under 90% RH.

Athens et al. [54] synthesized acid-functionalized mesoporous aluminosilica films, which exhibited a conductivity of 1.7×10^{-2} S/cm at 80 °C with 50% RH and a conductivity of 1.5×10^{-2} S/cm at 160 °C. The conductivity values measured above 135 °C are higher than those measured under identical conditions for Nafion 117. This was attributed to the improved water retention properties and stable conducting channels provided by the perfluorosulfonic-acid and aluminosilica-grafted cubic mesostructured films.

Marschall et al. [55] prepared and investigated SO₃H-functionalized Si-MCM-41 materials by condensation synthesis and microwave treatment. A rather high conductivity value of ~0.2 S/cm was achieved with 40% SO₃H-MCM-41 at 140 °C under 100% RH.

Jin et al. [56, 57] synthesized a phosphonic acid functionalized silica by co-condensation of diethylphosphatoethyltriethoxysilane (DPTS) and tetraethoxysilane using surfactant cetyltrimethylammonium bromide as a template, followed by acidification of phosphonate to phosphonic acid. The prepared silica nanospheres showed the conductivity values of 3×10^{-4} S/cm with 20% RH and 0.015 S/cm with 100% RH at 130 °C. HPW has also been incorporated into the porous matrix for potential application of high temperature PEMs.

Nogami et al. [58-60] synthesized an inorganic meso-structured composite membrane consisting of a mixture of HPW and phosphomolybdic acid. The composite membrane

reached a maximum conductivity, 9.1×10^{-2} S/cm at 90 °C under 85% RH. A cell performance of 46.3 mW/cm² was obtained through the inorganic PEMs at 28 °C.

Although the inorganic proton-conducting membranes possess the chemical and structural stabilities, the cell performance is very low and far from practical application requirements. Thus substantial efforts are still needed to develop new PEMs, which can be used at high temperatures and low RH with high conductivity, good stability, durability and cell performance.

2.2 Anode catalysts for DMFCs

Direct methanol fuel cells (DMFCs) are a subcategory of PEMFCs. In DMFCs, because methanol and water is fed directly into the cell, steam reforming is not required. Storage of methanol is much easier than hydrogen as it does not need high pressure or low temperature. This is because methanol is a liquid from -97.0 °C to 64.7 °C. The waste products in this type of fuel cells are carbon dioxide and water. DMFCs are promising power sources for portable electronic devices and electric vehicles [61]. In the past decades, the significant progress has been achieved to DMFCs as a result of improved electrolyte materials, electrocatalysts, updated membrane electrode assembly (MEA) fabrication technology and advanced water management. However, there are still several major obstacles for the development of DMFCs. Compared to the HOR, even on Pt catalysts the catalytic activity for the MOR (1.9) is not very effective [62].

2.2.1 Pt-based catalysts

Very few electrode materials have been shown to be capable of adsorbing methanol in acid media, and of these only Pt-based materials display a high enough stability and activity to be attractive as catalysts. It is assumed that the MOR on Pt-based catalysts proceeds by the adsorption of molecules followed by several steps of deprotonation (see Figure 2.5). Based on the generalized chemisorption scheme neglecting structural influences of Pt surface heterogeneity, three adjacent Pt sites are initially needed for dissociative methanol adsorption to COH_{ads} , but up to two of these sites are liberated again during subsequent reaction steps yielding either linear-bonded ' CO_L ' or bridge-bonded ' CO_B ' species. This diagram shows that CO is formed during the MOR. The Pt or Pt-based catalysts are highly susceptible to CO poisoning. CO reduces the catalyst activity by blocking active sites normally available for fuel chemisorption and dissociation, and binds any further reaction.

Figure 2.5. Schematic diagram of methanol oxidation on Pt showing the consecutive stripping of hydrogen atoms [63].

CO is generally produced during the reforming or as an intermediate in the MOR. CO molecules strongly absorb on the surface of Pt, occupying hydrogen oxidation reaction sites

and severely hinder the further reaction. The performance of PEMFC is drastically depressed by trace CO in hydrogen feed gas or methanol reaction owing to the strong adsorption of CO on Pt catalyst. According to the literature, a significant loss in cell performance can be caused by a CO content of as low as 10-20 ppm at 80 °C [64-66]. As a result, in order to reduce CO concentrations to <10 ppm, purification of the reformat gas is necessary. Many efforts have been made to reduce the influence of CO, including feeding oxidant into the fuel, developing CO-tolerant catalysts and advanced purification. However, all these approaches have significant drawbacks. An alternative method is to increase the operating temperature of PEMFC to effectively alleviate CO adsorption on the catalyst. It is well known that adsorption of CO on Pt is associated with a high negative entropy, indicating that adsorption is strongly favored at low temperatures, and disfavored at higher temperatures [22, 43].

An interesting aspect of high temperature operation is the significantly reduced CO poisoning. Figure 2.6 exhibits the adsorption behavior of CO on Pt as a function of temperature at CO concentrations ranging from 1 to 100 ppm under a H₂ pressure of 0.5 bar. It clearly shows that operation at a higher temperature would significantly increase the ability of a fuel cell anode to perform in the presence of small amounts of CO by decreasing the coverage of CO on the catalyst surface. CO tolerance is dramatically increased thereby allowing fuel cells to use lower quality reformed hydrogen, which will also offer cost advantage for hydrogen production and perhaps no requirement for the CO cleanup in a fuel processing system.

Figure 2.6. CO coverage on Pt catalyst as a function of temperature at various CO concentrations. The partial pressure of H_2 is 0.5 bar [67].

It was found early on that additions of other metals to Pt could enhance its catalytic activity dramatically. Some species such as Ru, Sn, Mo, and Rh have exhibited a promotion effect on the catalytic activity for methanol oxidation [68-80]. It is virtually undisputed that PtRu is a better catalyst for methanol oxidation than Pt and that the catalytic action of PtRu proceeds mainly by the so-called ‘bifunctional mechanism’. Ru sites adsorb oxygen-containing species at 0.2-0.3 V lower potentials than the pure Pt surface. The adsorbed carbonaceous species are preferentially oxidized at these sites by surface diffusion from sites where adsorption occurs [63, 65, 66]. Pt-based catalysts, especially Pt-Ru alloys were widely studied and used as anode catalysts for DMFCs. However, it is still necessary to employ higher loadings than that for H_2 oxidation, which in turn incurs the high cost penalty.

2.2.2 Catalysts for methanol oxidation in alkaline media

At present the main factor preventing fuel cells from successful commercialization is their high price. Mass production may reduce manufacture costs, but it will not reduce the materials cost. PEMFCs operate at ambient conditions using Pt and Pt alloys for the oxidation of fuel at anode side, as well as for the oxygen reduction at cathode side. It is obvious that high cost of Pt significantly increases the price of fuel cell devices. Solving this problem in short term aspect can be reached by using less Pt at both anode and cathode sides, but for wide use of fuel cells, alternatives to Pt should be developed [81].

Notable efforts are therefore being carried out to design new catalytic structures for DMFC anodes that contain less or no Pt, and are able to oxidize methanol with fast kinetics and low degradation. Within this context, Pd is emerging as an attractive replacement for Pt in DMFCs. Pd is more abundant in nature and less expensive than Pt, but cost-associated issues are not the main driving force behind the increasing interest in Pd, as it remains a rare noble metal whose introduction for a wide use would lead to an irreversible increase in its market price. The real attraction for Pd-based electrocatalysts is originated by the fact that, unlike Pt-based electrocatalysts, they can be highly active for the oxidation of a large variety of substrates in alkaline environment, where non-noble metals are also sufficiently stable for electrochemical applications.

Besides allowing for the potential use of non-noble metal catalysts at both anode and cathode, the DMFCs operating in alkaline media are attracting increasing interests also due to successful developments in the design and production of anion-exchange membranes (AEMs) [82-84]. The drawback of traditional alkaline fuel cells (AFCs) to undergo electrolyte carbonation is strongly minimized by the use of an anion conductive polymeric

membrane. The advantages of operating under alkaline conditions are the following: 1) usability of both noble and non-noble metals to fabricate the electrocatalysts; 2) methanol crossover from the anode compartment to the cathode compartment reduced by electro-osmotic drag of hydrate hydroxyl ions; 3) improved kinetics at both cathode and anode, especially the low anodic overvoltages for methanol oxidation; 4) reduced adsorption of ions that might limit electrocatalysis; 5) reduced corrosion of the materials, including catalysts and carbons; 6) easier water management, as water is formed at the anode side where an aqueous solution already exists, while the electro-osmotic drag transports water away from the cathode, preventing its flooding.

Yu et al. [85] studied the electro-oxidation of methanol on a platinized electrode in various alkaline media to examine the role of OH_{ads} species and the influence of anions in the electrolyte. The activity of the methanol oxidation reaction in aqueous alkaline systems was observed to vary with the pH or OH species coverage on the electrode surface. The activity decreased in the order of $\text{NaOH} > \text{Na}_2\text{CO}_3 > \text{NaHCO}_3$.

Shen et al. [86] prepared Pd/C promoted with nanocrystalline oxides for alcohol oxidation in alkaline media by an intermittent microwave heating method. The as-prepared electrocatalysts were superior to Pt-based catalysts in terms of activity and poison tolerance.

Xu et al. [87] prepared Pt and Pd electrocatalysts supported on carbon microspheres (CMS) for methanol and ethanol oxidation in alkaline media. The results indicated that the catalysts on CMS exhibited better performance than those on carbon black. The Pd/CMS showed a very good catalytic activity for methanol and ethanol oxidation under alkaline conditions.

Kumar et al. [88] synthesized a wide compositional range of Pd-Ni alloy electrocatalysts by an electro-deposition route. It was found that the Pd content in the

electrodeposited alloy decreased as the plating current density increased and all of the electrodeposited alloys were nanocrystalline in nature. The alloys showed a significantly improved activity for methanol oxidation under alkaline conditions.

Qiu et al. [89] prepared a series of bimetallic Pd-Ni thin films using double-potential step electrodeposition technique. The surface morphologies, compositions and electrocatalytic activity of the as-prepared thin films strongly depended on the electrodeposition conditions. The oxidation of methanol and ethanol molecules on the bimetallic Pd-Ni catalysts was mainly ascribed to the electrocatalysis of Pd components. The role of Ni was to enhance the catalytic performance of the bimetallic catalysts through assisting Pd to oxidize the CO-like adsorbed species on the film surfaces. Their results indicated that the bimetallic Pd-Ni electrocatalysts generated the higher catalytic activity and the stronger tolerance to CO poisoning.

Pd dissolves slowly in sulfuric, nitric and hydrochloric acid. Pd catalysts are not very sensitive to oxygen and moisture, but it is necessary to apply precautions to avoid oxidation of coordinated phosphines. The major drawback of the known Pd-based electrocatalysts is their instability and relatively lower activity. The challenge is therefore to design new Pd-based catalyst architectures capable of increasing the activity and efficiency while maintaining high electrochemical stability.

2.3 Catalyst supports for DMFCs

Supports have been found to possess strong influence on the properties of the catalysts. Most common Pt-based catalysts are usually supported on porous conductive materials. The support materials are necessary to achieve fine dispersion, high utilization and stable

nanoscale metallic particles, which is the prerequisite to obtain a high catalytic performance of catalysts. The support materials can also interplay with catalytic metals, which influence the catalytic activity. The durability of the catalysts is also greatly influenced by the supports. Generally, the requirements for catalyst support materials can be summarized as: high specific surface area, high conductivity, highly electrochemical stability under fuel cell operating conditions, low combustive reactivity under both dry and humid air conditions at low temperatures (150 °C or below). In addition, the interaction between catalytic metals and the support materials should be considered in improving the catalytic activity and durability [62, 90].

Carbon blacks are frequently used as catalyst supports for DMFCs anode catalysts because of their relatively high stability in both acidic and basic media, good electric conductivity and high specific surface area [91]. There are many types of carbon blacks, such as Vulcan XC-72, Ketjen Black, Acetylene Black, etc. They are usually manufactured by pyrolyzing hydrocarbons such as natural gas or oil fractions taken from petroleum processing. These carbon blacks show different physical and chemical properties, such as specific surface area, porosity, electrical conductivity and surface functionality. Among these factors, the specific surface area has a significant effect on the performance and preparation of supported catalysts. Vulcan XC-72 with a surface area of $\sim 250 \text{ m}^2/\text{g}$ has been widely used as a catalyst support, especially in DMFC anode catalyst preparation.

The family of carbon nanotubes (CNTs) is the most well-known nanostructured carbon, which has shown very promising potentials in catalyst support for fuel cell applications owing to their unique electrical and structural properties. The reported studies have shown that CNTs were superior to carbon blacks as catalyst supports for PEMFCs [92-96].

In addition, novel nanostructured materials, such as carbon nanofibers (CNFs) [97], mesoporous carbon [98-101], fullerene-based carbon (C_{60}) [102], conductive diamonds [103] and conductive oxides [104] have been studied as catalyst supports for DMFCs [90].

Recently, the carbides of transition metals, especially tungsten carbides (WC) as catalyst support, have attracted more and more attention due to their special properties, such as their stability in acid solutions and anodic potentials, selectivity, a specially strong resistance to catalytic poisons (carbon monoxide, hydrocarbons and hydrogen sulfide), a higher activity toward the dissociation of methanol and water, and good electrical conductivity.

Chhina et al. [105, 106] investigated the thermal and electrochemical stability of WC with and without a catalyst dispersed on it, to evaluate the potential suitability of the material as an oxidation-resistant catalyst support. Electrochemical testing was performed by applying oxidation cycles between +0.6 V and +1.8 V and monitoring the activity of the supported catalyst over 100 oxidation cycles. Comparisons of activity change with cumulative oxidation cycles were made between C and WC supports with comparable loadings of catalyst by weight, solid volume and powder volume. WC was found to be more thermally and electrochemically stable than the currently used carbon support material Vulcan XC-72.

Wang et al. [107] developed a simple strategy for in-situ simultaneous synthesis of WC/graphitic carbon (WC/GC) nanocomposite as a highly efficient catalyst support for DMFCs. Their results indicated that the Pt-WC/GC catalyst exhibited a substantially higher mass activity of 205.6 mA/mg Pt and a lower onset potential of 0.24 V, compared with 62.3 mA/mg Pt and 0.3 V for the Pt/C catalyst, suggesting that WC/GC promoted Pt catalyst possessed a better catalytic activity for methanol electrooxidation than Pt/C.

Ganesan et al. [108] synthesized and characterized W_2C microspheres as catalyst supporting materials. The Pt electrocatalysts supported on W_2C microspheres showed a higher activity for methanol oxidation than a commercial Pt-Ru/C catalyst by a factor of 2.4. The better performance was ascribed to the ability of W_2C to stabilize the uniform dispersion of Pt relative to carbon supports. In addition, in the presence of Pt, W_2C was active in the MOR and water decomposition. The formation of hydroxy groups from water decomposition was helpful for the removal of metal-poisoning CO from the surface.

Joo et al. [109] prepared two types of WC supports via the impregnation method. They found that the WCl_6 precursor was more favorable for the formation of WC due to the increased contact area between the precursor and the carbon black. The presence of WC displayed a positive effect on the catalytic performance of Pt for methanol oxidation owing to the promoted CO removal. Ham et al. [110] synthesized mesoporous WC as Pt catalyst support. The Pt/WC showed not only two times higher mass activity but also much higher resistance to CO poisoning for H_2 electrooxidation than a commercial Pt/C catalyst.

Zhao et al. [111] prepared WC modified MWCNT as Pt catalyst support by an intermittent microwave method. The Pt-WC/MWCNT catalysts showed an evidently better performance than that of Pt/C for methanol electrooxidation in terms of the onset potential and peak current density. The synergistic effect between Pt nanoparticles and WC, and the structural effect of the MWCNTs could be the reasons for the high activity.

However, the conventional synthesis process normally used solid carbon precursors such as carbon black or carbon nanotubes, which often resulted in the aggregation of WC particles, leading to the damage of the original support materials and loss of activity and stability. The large crystallite size and poor dispersion of WC materials are among the key issues to prevent WC being widely applied as catalyst supports.

2.4 Summary

As reviewed above, significant efforts have been made on the development of the membranes for high temperature and/or low humidity operation. These include: modified PFSA membranes, polyaromatic polymers, and proton-conducting inorganic membranes. However the modified PFSA composite membranes are limited by the T_g (~130 °C) of the polymer matrix and the inherently low proton conductivity of the inorganic additives. The long term stability and reliability of PEMFCs with polyaromatic polymers need to be proved. The cell performance with proton-conducting inorganic membranes is still very low. Thus, the grand challenge is to develop new and novel PEMs, which can be used at high temperature and/or low humidity with good stability, durability and cell performance. In this project, the major objective is to develop new PEMs for PEMFCs operated under high temperature and/or low humidity conditions.

Another major area in DMFCs is the development of alternative and new electrocatalysts for methanol oxidation. Pd has a poor catalytic activity in acid media but displays a quite high activity in alkaline media. Pd is not only relatively cheap but also abundant in natural resources as compared with Pt. Thus, developing Pd-based catalysts as substitutes for Pt catalysts is of both theoretical and practical significance to accelerate commercialization of DMFCs. Furthermore, the catalyst supporting materials such as WC-based supports show the significant effort on the activity and durability of Pt catalysts. Thus, it is interesting to investigate the effect of WC materials synthesized by microwave heating method on the dispersion and activity of Pt catalysts.

CHAPTER 3 A Novel Inorganic Proton Exchange Membrane Based on Self-Assembled HPW/meso-silica for DMFCs

3.1 Introduction

One of the key components of PEMFCs and DMFCs is the proton exchange membrane (PEM) that functions as the proton conducting electrolyte as well as the fuel and oxidant separator. Perfluorosulfonic acid (PFSA) polymers such as Nafion are the most common used membrane in PEMFCs and DMFCs because of their good mechanical properties, excellent chemical stabilities and high proton conductivities under highly hydrated conditions [12]. The state-of-the-art PEMs based on Nafion are unstable at temperatures higher than 100 °C and the proton conductivities of the PEMs decrease significantly due to the dehydration and degradation of the membranes [112, 113]. However, the operation of fuel cells at temperatures above 100 °C can provide many advantages, such as the elimination of CO poisoning of platinum electrocatalysts, faster electrode reaction kinetics, simplified water and heat management, higher energy efficiencies, and reduced usage of precious Pt and Pt alloy catalysts [25, 26].

Several high-temperature PEMs have been developed so far including nonfluorinated hydrocarbon ionomers [114, 115], acid-doped polymers [116] and acid base ionic liquids [117]. Another strategy is to develop PFSA-based composite membranes through modification with fillers such as SiO₂, TiO₂, mordenite, ZrO₂, and zirconium phosphate [29, 31, 33, 118-120]. Some inorganic materials such as P₂O₅-SiO₂, P₂O₅-TiO₂-SiO₂, In³⁺-doped

SnP_2O_7 , and porous silica grafted by sulfonic groups were also extensively investigated as promising electrolyte membranes for high temperature operation due to the high chemical and structural stabilities [47-49, 54, 55, 59, 121-124]. On the other hand, replacing the pure silica with composite silicate of strong acidity, e.g., the $\text{CsHSO}_4\text{-SiO}_2$ [125], $\text{P}_2\text{O}_5\text{-SiO}_2$ [126, 127], $\text{P}_2\text{O}_5\text{-TiO}_2\text{-SiO}_2$ [48, 121] or $\text{P}_2\text{O}_5\text{-ZrO}_2\text{-SiO}_2$ [128] have improved the proton conductance to a value around 0.01 S/cm. Although each material has its own advantages, most of them have failed to satisfy the requirements of high temperature and low humidity operation. For example, the polymers based membranes can not deliver required stability and durability due to the degradation and decomposition of polymer chains at high operating temperatures and humidity-induced mechanical stress on the “soft” polymer structure [129, 130]. The introduction of the hydrophilic oxide particles can enhance the membrane’s water retention ability and operation temperature. However, the incorporation of oxide particles leads to the reduced mechanical properties and the decreased proton conductivity with increasing the filler contents.

Mesoporous inorganic materials with a wide pore size range of 2-50 nm, highly ordered interconnected internal structure and high structural stability, could be potentially important materials for applications as PEMs at elevated temperatures [52-54, 59, 131, 132]. The conductivity of mesoporous silica film was reported to be in the range of 10^{-6} S/cm to 10^{-4} S/cm under 40% to 90% RH [133]. However, the conductivities of these mesoporous materials were too low to be practical for fuel cell applications.

Heteropoly acids (HPAs) are a class of solid crystalline acid made up of a particular combination of hydrogen and oxygen with certain metals and non-metals. Phosphotungstic acid (HPW) possesses the highest stability and strongest acidity among the HPAs. The metal addenda atoms linked by oxygen atoms form a cluster with the hetero-atom inside

bonded via oxygen atoms. The conjugate anion of a HPA is known as a polyoxometalate. Many HPAs are possible due to the different combinations of addenda atoms and different types of hetero atoms. Two of the better known groups of these are based on the Keggin ($H_nXM_{12}O_{40}$) and Dawson ($H_nX_2M_{18}O_{62}$) structures [134, 135].

In this chapter, we describe in detail the synthesis and characterization of an inorganic PEM based on highly ordered mesoporous silica with trapped HPW molecules via a self-assembly route assisted with a structure-directing surfactant. The self-assembled HPW/meso-silica inorganic PEM displays a proton conductivity of 0.091 S/cm at 100 °C under 100% RH and 0.034 S/cm at 200 °C under 3% RH. The cell with a 25wt% HPW/meso-silica membrane can achieve a power output of 19 mW/cm² at 25 °C and 235 mW/cm² at 150 °C in methanol fuel. Initial stability of the cell in methanol fuel is also demonstrated.

3.2 Experimental

3.2.1 Preparation of the self-assembled HPW/meso-silica

Materials used in this work include tetraethyl orthosilicate (TEOS, Sigma-Aldrich), HPW ($H_3PW_{12}O_{40} \cdot nH_2O$, Sigma-Aldrich), Pluronic P123 (MW=5800, $EO_{20}PO_{70}EO_{20}$, BASF®), Hydrochloric acid (HCl, Sigma-Aldrich), Sulfuric acid (H_2SO_4 , Sigma-Aldrich), polyimide (PI, $[C_{40}H_{58}O_6N_2]_n$, $M_w = \sim 100,000$), 1-methyl-2-pyrrolidone (NMP, Sigma-Aldrich), Teflon emulsion (PTFE, Sigma-Aldrich), carbon black (Vulcan XC-72, Cabot Corp.), Methanol (99.99%, Sigma-Aldrich) and Nafion solution (5wt% in isopropanol and water, DuPont).

Mesoporous silica SBA-15 (Santa Barbara Amorphous type material) was prepared according to the procedure reported by Zhao et al [136]. The self-assembled HPW/meso-silica was prepared as follows. TEOS was initially dissolved into ethanol at a fixed ratio. Then a quantitative HPW solution was dropwise added to the above TEOS mixture with vigorously stirring. P123 surfactant solution was separately prepared by dissolving P123 in ethanol with a fixed weight ratio. The protonated TEOS precursor solution was dropwise added into the P123 surfactant solution with vigorously stirring for 5 hrs. Subsequently, the pH value of the mixture was adjusted to 1 by dropwise addition of 2.0 M HCl solution with vigorously stirring. The concentration of P123 surfactant added to the silica gel solution was controlled as 1.2 mol% of TEOS. The content of HPW in the synthesized HPW/meso-silica nanocomposites was controlled in the range of 1-35wt%. The mixed solution was transparent suspension. The as-prepared solution was then placed into indium tin oxide (ITO) Petri dishes and evaporated thoroughly at 40 °C for a few days. The surfactant was removed by the heat treatment at 400 °C for 1 h in nitrogen with a flow rate of 100 SCCM (standard-state cubic centimeter per minute), and then in air with a flow rate of 100 SCCM at the same temperature for another 24 hrs. The synthesized HPW/meso-silica powders with different HPW contents were collected and stored in sealed bottles.

3.2.2 Membrane processing

Membrane fabrication was carried out by using the self-assembled HPW/meso-silica electrolyte and PI as the binder. PI powder (10wt%) dissolved in NMP was mixed thoroughly with the self-assembled HPW/meso-silica powder in an agate mortar and the mixture was dried at 180 °C for 2 hrs. The dried powder was then hot-pressed (by Carver®

3586) in a stainless-steel die under 380 °C and 30 MPa for 30 min. Then the self-assembled HPW/meso-silica inorganic PEM was obtained. The image shown in Figure 3.1 is the optical picture of a 25wt% HPW/meso-silica nanocomposite disc before the test. The membrane was solid, homogeneous and crack-free, white in color. Its thickness is 0.2 mm and the diameter was 5 cm.

Figure 3.1. Optical picture of a 25wt% HPW/meso-silica nanocomposite membrane disc used in the present study. The diameter of the disc was 5 cm.

3.2.3 Preparation of a single cell

A carbon paper (Toray TGPH-060) was immersed into a 10wt% Teflon (PTFE) emulsion for 10 min, followed by drying in 80 °C for 2 hrs. The consequent thermal treatment was carried out under the protection of an inert gas to remove the dispersion agent contained in the PTFE emulsion and finally sintered at 340 °C for another 30 min. The final PTFE concentration in the carbon paper was controlled at ~30wt%.

The gas diffusion sublayer was coated on one surface of the above pre-prepared carbon paper. The loading was 3 mg/cm² which was composed of 30wt% PTFE and 70wt%

carbon powders. The as-prepared gas diffusion layer (GDL) was treated at 240 °C for 30 min under inert gas and finally sintered at 340 °C for another 30 min.

The electrodes were PtRu/C with 4 mg/cm² in anode and Pt/C with a loading of 0.5 mg/cm² in cathode (50wt% PtRu/C and 60wt% Pt/C, Johnson Matthey). A Nafion solution was impregnated into the catalyst layer as the binder and the dry loading of Nafion was 0.3 mg/cm². The catalysts were coated on the membrane directly at room temperature, followed by drying at 100 °C for 2 hrs. The catalyst-coated membrane (CCM) was sandwiched in between two GDLs. The active area of the cells was 4 cm². Figure 3.2 illustrates the flow of the CCM processing.

Figure 3.2. Schematic chart of the catalyst-coated membrane.

3.2.4 Physical characterization

A thermogravimetric analyzer (TGA, Perkin-Elmer TGA 7) was used to study the properties of the HPW with temperature. The TGA tests were conducted from 25 °C to 800 °C at a heating rate of 2 °C/min in air.

The SAXSess high-flux small-angle X-ray scattering (SAXS) instrument was used to investigate the meso-structure of the various electrolytes in the nanometer range. The PW 3830 X-ray generator was used as X-ray source. The program SAXSquantTM (by Anton Paar GmbH.) was used to reduce the data from SAXS experiments.

A SHIMADZU XRD-6000 Diffractometer System was used to study phase composition and phase change of the various electrolytes.

A transmission electron microscope (TEM, JEM-2010FEF) was used to study the morphology of the various self-assembled HPW/meso-silica inorganic electrolytes. Micrographs were collected at 200 KV accelerating voltage and vacuum level $<10^{-5}$ Pa. The resolution is 0.19 nm.

The composition analysis of the electrolytes was carried out by energy dispersive spectroscopy (EDS) in the JEOL 2010FEF microscope, which was operated at 200 KV accelerating voltage.

Fourier transform infrared (FT-IR) spectra were collected to examine the structural variations of the self-assembled HPW/meso-silica inorganic electrolytes by using a Perkin Elmer FT-IR Spectrometer with 2 cm^{-1} resolution in the range of $400\text{--}4000\text{ cm}^{-1}$.

The nitrogen adsorption and desorption isotherms at 77K were measured using a TriStar II 3020 Surface Area and Porosity System (by Micromeritics[®]). Brunauer–

Emmett–Teller (BET) surface areas were estimated over a relative pressure (P/P_0) range from 0.05 to 0.30. Pore size distribution was obtained from the analysis of the desorption branch of the isotherms using the Barrett–Joyner–Halenda (BJH) model.

3.2.5 Electrochemical characterization

The electrochemical impedance spectroscopy (EIS) was collected using a potentiostat-galvanostat Autolab PGSTAT30 FRA interfaced via USB to a personal computer. The EIS measurements were carried out at open circuit voltage (OCV). The alternating current (ac) modulation voltage was set to be 10 mV. The impedance spectra were collected in the range of frequencies from 1 MHz to 1 Hz.

The cell performance using methanol as fuel was tested at different temperatures controlled by an auxiliary heating system. A Greenlight fuel cell test station (FCATS-G050, Canada) was used to conduct the cell performance measurements. The methanol fuel (2M) flow rate was 5 mL/min and pure oxygen flow rate was 100 SCCM. Oxygen gas was humidified at 100% RH for the cell tested below 100 °C, but for the tests above 100 °C, oxygen gas was humidified at 80 °C under 100% RH. The back pressure in the oxygen side was 100kPa. Figure 3.3 shows the diagram of the setup for the DMFC test in our present study.

Figure 3.3. Schematic of the set-up for the test of DMFC.

The RH of the humidified gas at elevated temperatures can be calculated according to the following formula:

$$RH = 10^{\frac{7.5 \times 237.7 \times (T_{dc} - T_c)}{(237.7 + T_{dc}) \times (237.7 + T_c)}} \quad (3.1)$$

where T_{dc} is the dewpoint temperature in Celsius (80 °C in this case) and T_c is the cell temperature in Celsius. Thus, the RH of the humidified gas will be 46, 18, 10 and 3% for the different testing temperatures 100, 130, 150 and 200 °C, respectively.

3.3 Results and discussion

3.3.1 Principle of self-assembly of HPW/meso-silica

The HPAs are well known as superionic conductors in their fully hydrated states, particularly those based on the Keggin structure. It is known that HPW has the highest stability and strongest acidity among the Keggin-type HPAs. There are three types of exterior oxygen atoms: O_b , O_c , and O_d in the Keggin unit (KU), and O_a is the central

oxygen atom (see Figure 3.4). For the fully hydrated Keggin structure of HPW, it is speculated that channels around the anions can contain up to 29 water molecules, only six of which occupy ordered sites on the bridging oxygen atoms. The remainder is able to form multiple protonic species, with varying hydrogen bond strengths.

Figure 3.4. The structure of HPW.

Figure 3.5 shows TGA curves of pure HPW, testing in air atmosphere at a heating rate of 2 °C/min from ambient temperature to 800 °C. As shown in Figure 3.5, the first weight loss arises from room temperature to 100 °C, which is mainly due to the loss of physically adsorbed water, accounting for ~8wt% loss. The second weight loss from 100 °C to 240 °C is mainly due to the dissociation of the crystal water, accounting for ~3wt% loss. The last weight loss occurs at 380 °C up to 530 °C, which indicates that the HPW molecules possess good stability and water retention ability at high temperatures.

Figure 3.5. TGA curve of the pure HPW.

Figure 3.6 shows the pathway for the self-assembled HPW/meso-silica inorganic electrolytes. HPW is soluble in water, forming negatively charged $\text{PW}_{12}\text{O}_{40}^{3-}$ ions. A combined study of solid-state NMR and quantum chemical DFT indicates that the isolated acidic protons are immobile, but hydrated acidic protons are highly mobile in HPW KUs [137]. Under normal conditions, the proton adsorption on the SiOH surface groups of the meso-silica is very low. However, the presence of HPW would decrease the pH of the precursor as HPW is highly acidic in water and this in turn would significantly increase the proton adsorption of SiOH groups, forming positively charged SiOH_2^{+1} [138]. When HPW molecules, silica precursor and TEOS, are mixed in water, self-assembly will occur between the positively charged silica and the negatively charged HPW by the electrostatic force. With the addition of structure-directing agent, P123, the tube-cumulated mesoporous HPW-silica with the template of P123 surfactant is formed through the cooperative hydrogen bonding and self-assembly between the HPW-silica structure and P123 surfactant [139]. With the phase separation of P123, the colloidal complex forms ordered mesoporous

silica with the HPW self-assembled in the mesoporous structure. The surfactant template is then removed by the heat treatment at 400 °C.

Figure 3.6. Synthesis of the HPW/meso-silica inorganic electrolytes via self-assembly principle.

3.3.2 Structural and physical properties

The structures of the various self-assembled HPW/meso-silica inorganic electrolytes were investigated by SAXS. As shown in Figure 3.7, the strong and well-resolved diffraction peak at *ca.* $q=0.7 \text{ nm}^{-1}$ (q is the momentum transfer) corresponds to the (100) lattice plane, which is a characteristic peak of the hexagonal mesoporous silica structure. The peaks at higher scattering angles are (110) and (200) reflections associated with $p6mm$ hexagonal symmetry of SBA-15 [139]. The results exhibit uniform mesoporous arrays with a long-range order when the additive HPW content in the SBA-15 is $\leq 25\text{wt\%}$. The

intensities of (100), (110) and (200) peaks decrease with increasing HPW content. Nevertheless, the (100), (110) and (200) peaks can still be seen for the self-assembled HPW/meso-silica inorganic electrolytes with HPW contents equal or less than 25wt%. When the HPW content was increased to 35wt%, the ordered mesostructure of silica could not be formed. The collapse of the ordered mesoporous structure of silica is also indicated by the significant shrinkage and depress of the diffraction peak (100). The characteristic (110) and (200) peaks are no longer observable. At the same time, the diffraction peak (100) shifted to a high scattering angle, implying the degradation of the ordered mesostructure. This indicates that excess HPW introduced in the self-assembly procedure is detrimental to the ordered SBA-15 mesostructure. This is further confirmed by the TEM observations.

Figure 3.7. SAXS spectra of the as-prepared SBA-15 and the self-assembled HPW/meso-silica.

Figure 3.8 shows the TEM micrographs of the as-prepared SBA-15 and the different self-assembled HPW/meso-silica inorganic electrolytes. The pure mesoporous SBA-15 synthesized in the present study exhibits the characteristic meso-structure with highly ordered 2D nanochannels. The aspect ratio is in a big range, from few hundreds to few thousands. The diameter of the pores was obtained from statistical calculations from the TEM images. The center to center distance of the nanochannels is ~ 7.3 nm (Figure 3.8(a)). From the TEM images viewing along the pore axis, the diameter of the hexagonal mesostructure is 4.3 nm for the 5wt% HPW/meso-silica (Figure 3.8(b)), 4.2 nm for the 15wt% HPW/meso-silica (Figure 3.8(c)) and 3.8 nm for the 25wt% HPW/meso-silica (Figure 3.8(d)). The inserted image in Figure 3.8(d) was obtained via imaging along the [001] zone axis direction. The high-resolution TEM image unambiguously demonstrates that the hexagonal packing of the nanochannels is well-aligned along the zone axis [001] direction. The results show that the uniformly ordered mesoporous arrays are still maintained when the HPW content is less than 25wt%. The top-surface feature is reflective of long-range ordering of the mesochannels and their macroscopic alignment [140]. Both TEM and SAXS results indicate the successful assembly of HPW molecules into the mesoporous SBA-15 structure. However, for the 35wt% HPW/meso-silica, the mesostructure becomes discontinuous and the nanochannels are not clear (see Figure 3.8(e)). The collapse of the ordered mesoporous structure is consistent with the observed significant shrinkage and depress of the diffraction peak (100) (see Figure 3.7).

The EDS spectra of the 5wt% HPW/meso-silica was shown in Figure 3.8(f). The characteristic spectra of the element P and W can be detected, which indicates that HPW indeed exists in the nanocomposite systems. Also, from the spectra, Cu elements are derived from the copper substrate used.

Figure 3.8. TEM images for (a) the as-prepared SBA-15, (b) 5wt% self-assembled HPW/meso-silica, (c) 15wt% self-assembled HPW/meso-silica, (d) 25wt% self-assembled HPW/meso-silica and (e) 35wt% self-assembled HPW/meso-silica. The (f) is for the EDS spectrum of 5wt% self-assembled HPW/meso-silica. The inset in (c) is the TEM image viewing along the pore axis. The scale bar applies to all TEM micrographs.

The effect of HPW assembly on the structure of mesoporous silica was further studied by FT-IR spectroscopy. Figure 3.9 is for the FT-IR spectra of the as-synthesized SBA-15 and the self-assembled HPW/meso-silica nanocomposites with different HPW contents. For the pure HPW, the characteristic bands are observed at 1081 (P-O_a), 983.9 (W=O_d), 893.9 ($\text{W-O}_b\text{-W}$), and 803.9 cm^{-1} ($\text{W-O}_c\text{-W}$), which coincide with those reported in the literature for the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ KUs [141]. The corresponding bands can be also detected at the respective position for the assembled HPW/meso-silica nanocomposites with different HPW contents. The FT-IR results confirm again the successful assembly of the Keggin structure $[\text{PW}_{12}\text{O}_{40}]^{3-}$ into the mesoporous SBA-15 without degradation, and also indicate that the heat treatment of the HPW/meso-silica precursor at 400 °C has no detrimental effect on the HPW Keggin structure assembled in the meso-silica structure. The small shift in frequency in the FT-IR spectra and the reduced intensity may indicate the rigid bonding of HPW in the meso-silica structure, similar to the HPW embedded silica-gel system [142], thereby mitigating leaching problem.

Figure 3.9. FT-IR spectra of the as-synthesized SBA-15 and the self-assembled HPW/meso- silica.

Figure 3.10 exhibits the N_2 adsorption-desorption isotherms of the as-prepared SBA-15 and the different self-assembled HPW/meso-silica inorganic electrolytes. The isotherms are all of type IV and have a hysteresis loop of H1 type according to the IUPAC classification [143], typical for materials with pores of constant cross section. The initial part of the curves is attributed to monolayer-multilayer adsorption. The capillary condensation of all the samples conformably occurred at $p/p_0 = 0.4$ -0.6, where hysteresis loops appears. The isotherms indicate that a classical open cylindrical pore-shape was found for all the samples. However, the heights of the hysteresis loops decreased with increasing the HPW content, which corroborates that the HPW molecules have effectively encapsulated the silica's mesopores through the self-assembly process. The hysteresis loop for the 35wt% self-assembled HPW/meso-silica become very small, indicating the significant structural change of SBA-15 due to the excess HPW introduced, which is consistent with that of the SAXS and TEM results.

Figure 3.10. Adsorption (solid) and desorption (open) isotherms of nitrogen for the as-prepared SBA-15 and the self-assembled HPW/meso-silica.

Both the pore volumes and pore size distributions strongly depend on the HPW content as shown in Figure 3.11. All the curves have narrow peaks indicating the quite narrow pore size distribution. In the case of the as-prepared SBA-15, the primary pore diameter (D_{BJH}) and pore volume (V_{BJH}) calculated from the adsorption data using the Barrett-Joyner-Halenda (BJH) model is 4.9 nm and $0.78 \text{ cm}^3/\text{g}$, respectively. However, both D_{BJH} and V_{BJH} decrease with increasing the introduced HPW. D_{BJH} is 4.6, 4.2, 3.9 and 3.4 nm and V_{BJH} is 0.38, 0.31, 0.28 and $0.24 \text{ cm}^3/\text{g}$ for the SBA-15 self-assembled with 5, 15, 25, and 35wt% HPW, respectively. The other extracted BET parameters were listed in Table 3.1. The decrease in the pore diameter and pore volume is an indication of the successful self-assembly of HPW inside the mesoporous SBA-15 structure, being consistent with TEM and SAXS results.

Figure 3.11. Pore volume of the as-prepared SBA-15 and the self-assembled HPW/meso-silica.

Table 3.1. The BET data of the as-prepared SBA-15 and the self-assembled HPW/meso-silica.

Samples	BET Surface Area (m ² /g)	BJH Pore Volume (cm ³ /g)	BJH Pore Size (Å)
SBA-15	777	0.78	49
5wt% HPW/meso-silica	422	0.38	46
15wt% HPW/meso-silica	370	0.31	42
25wt% HPW/meso-silica	346	0.28	39
35wt% HPW/meso-silica	314	0.24	34

3.3.3 Conductivity and stability

The proton conductivities and stabilities of HPW/meso-silica nanocomposites were measured in the temperature range of 20-200 °C using the four-electrode technique. Figure 3.12 displays the EIS curves for the different HPW/meso-silica membranes measured at different temperatures.

The specific proton conductivity was calculated through the below fomula:

$$\sigma = \frac{L}{R \cdot A} \quad (3.2)$$

where σ is the proton conductivity, R is the ohmic resistance, A is the surface area of the membrane and L is the thickness of the membrane. L was measured for each sample by a micrometer.

Figure 3.12. EIS curves of (a) 5wt% HPW/meso-silica membrane (b) 15wt% HPW/meso-silica membrane, (c) 25wt% HPW/meso-silica membrane and (d) 35wt% HPW/meso-silica membrane, measured at different temperatures.

The impedance spectra of the as-obtained PEMs consist of a higher-frequency loop determined by the charge-transfer resistance of PEMs. The lower-frequency loop is completely absent because of without gas-phase transport limitations under OCV testing conditions. The software provided in the Autolab was used to fit the higher-frequency loop of the impedance spectra. The intercept of the fitting curve with the horizontal axis was the resistance of the PEMs. The errors of the conductivities measured are less than 10% and the conductivity results were taken from the average value of at least five readings for each

sample. Figure 3.13(a) shows the proton conductivities of HPW/meso-silica nanocomposites as a function of HPW contents measured at different temperatures. The conductivities strongly depend on the HPW content in the mesoporous nanocomposites. The pure mesoporous SBA-15 exhibits a low proton conductivity of 9.02×10^{-8} S/cm at 20 °C and 3.21×10^{-5} S/cm at 100 °C under 100% RH. The conductivity of HPW/meso-silica only starts to increase significantly when the assembled HPW is higher than 5wt% (see the inset in Figure 3.13(a)). This indicates that effective proton conducting path in the mesoporous silica could only be established if there are sufficient HPW molecules assembled in the mesoporous silica. The results imply that the threshold of HPW level for the proton conductivity of mesoporous silica is ~5wt% for the HPW/meso-silica nanocomposite synthesized via self-assembly assisted by a structure-directed surfactant. The proton conductivities of the HPW/meso-silica composite membranes increase with the increase of HPW content. And the best conductivity was obtained from the 25wt% HPW/meso-silica composite membrane. In the case of the 25wt% HPW/meso-silica membrane, the proton conductivity is 0.03 and 0.09 S/cm at 25 °C and 100 °C under 100% RH, respectively, which is close to the proton conductivity of the state-of-the-art of Nafion membranes [144, 145]. The proton conductivity of HPW/meso-silica membranes developed in the present study is also substantially higher than that of HPW contained inorganic composites synthesized by the conventional sol-gel derived HPW/silica [146] or HPW/epoxy composite [147]. As the HPW content is increased to 30-35wt%, the conductivity decreases again. The decrease in the conductivity is most likely related to the distortion of the mesoporous structure by the excess of HPW loading as shown by the TEM and SAXS results.

Figure 3.13. (a) Conductivity measured at different temperatures under 100% RH as a function of HPW contents in HPW/meso-silica nanocomposite; (b) Arrhenius plots for the conductivity of the HPW/meso-silica nanocomposites measured at 20~200 °C. At 20~100 °C the humidity is 100% RH, at 120-200 °C the inlet gas was humidified at 80 °C; (c) activation energies as a function of HPW content in meso-silica nanocomposite. Activation energy was measured in the temperature range 20~100 °C under 100% RH.

The proton conductivity variation trend agreed with the Arrhenius law, indicating that the proton conduction was dominated by a thermal activation process. The activation energy (E_a) of conductivity for each membrane was estimated from the gradient of the fitting line by the following equation [148].

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \quad (3.3)$$

where E_a is activation energy, σ is the proton conductivity, σ_0 is a pre-exponential parameter, R is the gas constant and T is the Kelvin temperature.

Figure 3.13(b) shows the Arrhenius plots of proton conductivity of the HPW/meso-silica membranes. At the temperature range of 20~100 °C, the conductivity was measured under 100% RH. At above 100 °C, the conductivity was measured with the inlet gas humidified at 80 °C. The proton conductivity of the 25wt% HPW/meso-silica membrane is 0.09 S/cm at 100 °C under 100% RH, 0.02 S/cm at 160 °C under 8% RH and 0.034 S/cm at 200 °C under 3% RH. The sudden drop in the conductivity value as the temperature increased from 100 °C to 120 °C indicates that the conductivity of the HPW/meso-silica membranes is also sensitive to humidity as there is a substantial change in the RH for the testing temperatures above 100 °C. The activation energy for the proton conductivity of the HPW/meso-silica membranes was calculated from the slopes of the conductivity values measured in the temperature range of 20~100 °C under 100% RH and the results are given in Figure 3.13(c). For the pristine mesoporous SBA-15, the activation energy is 60 kJ/mol. When the HPW doping level is less than 5wt%, the conductivity increment is very small. However, when the HPW content is higher than 5wt% the activation energy starts to decrease significantly. The activation energy decreases significantly with increasing the

HPW contents. The lowest activation energy was obtained with a value of 14 kJ/mol for the 25wt% HPW/meso-silica, which is significantly lower than 60 kJ/mol for the pristine mesoporous SBA-15. The activation energy of proton conduction strongly depends on the HPW content, which indicates that the establishment of effective paths for protons transport is very important in the assembled HPW/meso-silica nanocomposites. The quite lower activation energy of the 25wt% HPW/meso-silica, as compared to that of the pure SBA-15, shows that the proton conduction becomes much more facile. The results indicate that HPW molecules may be assembled along the nanochannels of the meso-silica during the self-assembly process, leading to form well-ordered and continuous proton-conducting pathways. On the other hand, when the HPW content is higher than 25wt% the values of the activation energy become bigger. The most likely reason for the increase could be related to the collapse of the mesoporous structure caused by the excess HPW. The disordered mesoporous structure would impede the pathways for proton conduction via the assembled HPW molecules. It is very interesting to find that the ordered nanochannels facilitate the protons transport. The proton conductivity of the HPW/meso-silica membranes measured at the temperature range of 120 to 200 °C increases with temperature despite the RH decreases with temperature (Figure 3.13(b)). This is because the capillary effect of the mesopores has provided more water molecules to aid the proton transportation under the high temperatures and low humidity conditions. This also implies that the ordered mesoporous structure has the capability to retain water molecules at elevated temperatures.

Figure 3.14. Conductivity stability of (a) 5wt% HPW/meso-silica and (b) 25% HPW/meso-silica nanocomposites measured at different temperatures. For the measurements at 40, 80 and 100 °C, the RH was 100%, for the measurements at 130 °C the inlet gas humidified at 80 °C with 100%RH was used.

The stabilities of the proton conductivity of HPW/meso-silica membranes were also investigated. Figure 3.14 shows an example of the stability of the proton conductivity measured at different temperatures for 50 hrs for the 5wt% and 25wt% HPW/meso-silica

nanocomposites. The conductivities of the two HPW/meso-silica membranes are quite stable over the temperature range. The conductivity measured at 130 °C is lower than that measured at 40 °C. This is because the RH for the conductivity measurement at 130 °C is only 18%, significantly lower than 100% RH in the case of the conductivity measurements at 40-100 °C. Nevertheless, the good stability of the proton conductivity indicates that there is no leaching or loss of the assembled HPW in the mesoporous silica structure, because any loss or change of HPW contents would affect the conductivity of the HPW/meso-silica membranes. The good stability also indicates that the water content retained in the mesoporous silica is very stable, probably attaching with the HPW KUs or inside walls of the meso-silica. The self-assembled HPW/meso-silica inorganic membranes offer a significant advantage over solid acid electrolytes, such as CsH_2PO_4 and CsHSO_4 [149, 150], as the structure and phase of the self-assembled HPW/meso-silica does not change with temperature and RH under the conditions studied. The mechanism and model of proton transport in nanochannels or nanopores are also being developed [151, 152].

In PFSA polymer electrolytes such as Nafion, the proton conductivity and water diffusion in the membrane are closely related to each other and H^+ movement is normally explained by Grotthuss (hopping) and vehicle mechanism [153, 154]. However, the pronounced proton donating, but poor proton accepting properties of sulfonic acid does not allow the formation of high concentrations of $-\text{SO}_3\text{H}_2^+$ and SO_3^- by self-dissociation in a water-free hydrogen bond network. This in turn determines that PFSA polymer electrolytes like Nafion have a strong dependence of conductivity on humidity [155]. The significant dependence of conductivity on the HPW content in the HPW/meso-silica nanocomposites implies that H^+ could attach to the water molecules of HPW KUs, forming H_3O^+ ion, and hopping to the water molecules of neighboring HPW KUs. This appears to be supported by

the results that the increase in the HPW content in the nanochannels of mesoporous silica could decrease the hopping distance between neighboring HPW KUs, leading to the decrease in the activation energy and the increase in the conductivity. Although the exact protons conduction mechanism for the HPW/meso-silica nanocomposites is far from clear, the high proton conductivities and good stabilities at elevated temperatures and low RH demonstrate the applicability of the HPW/meso-silica nanocomposites as the high-temperature PEMs for fuel cells.

3.3.4 Cell performance

To demonstrate the viability of the HPW/meso-silica nanocomposite as a PEM for DMFCs, a cell was fabricated using the 25wt% HPW/meso-silica membrane (the membrane thickness is 0.2 mm) and conventional Pt-based electrocatalysts. Figure 3.15(a) shows the cell performance using methanol as fuel at different temperatures. The OCV was ~0.74V at 25 °C and increased to 0.83 V at 150 °C. The maximum power density of the cell was 19 mW/cm² at 25 °C under 100% RH and increased substantially to 235 mW/cm² at 150 °C under 10% RH. The significant increase of the cell performance with the testing temperature indicates the significantly enhanced reaction rates of the methanol oxidation and oxygen reduction reactions at elevated temperatures. This is also indicated by the significant reduction of the voltage loss at the low current densities (the circled region in Figure 3.15(a)) as the test temperature increases. We further measured the stability of the cell in the methanol fuel at 150 °C under a constant cell voltage of 0.5 V (Figure 3.15(b)). The initial cell current was 440 mA/cm² and decreased to 402 mA/cm², a reduction in cell current of 38 mA/cm² over a 42 hrs testing period. The reduction of the cell performance

could be related to the deterioration of the Pt-based catalysts at high temperatures as nano-sized Pt catalysts could undergo significant agglomeration at elevated temperatures.

Figure 3.15. (a) Cell performance in methanol/O₂, measured at different temperatures. Anode: PtRu/C (Pt loading: 4 mg/cm²); Cathode: Pt/C (Pt loading: 0.5 mg/cm²); and (b) initial stability of the cell in methanol/O₂ measured at 150 °C.

The performance data shown in Figure 3.15 are very encouraging and demonstrate the promising potential of the inorganic HPW/meso-silica as a high temperature PEM for

DMFCs. Reducing the membrane thickness and optimization and development of new electrocatalysts with high activity and compatibility with the inorganic HPW/meso-silica nanocomposite membranes are expected to significantly increase the cell performance and stability, and thus to enhance the overall efficiency of DMFCs. The high proton conductivity and structural stability of the HPW/meso-silica nanocomposite membranes at elevated temperatures would lead to the high power output and significantly simplify the DMFCs system.

The HPW/meso-silica nanocomposite membranes have also exhibited the promising potential for H₂/O₂ PEMFCs in our previous studies. The cell with the 25% HPW/meso-silica nanocomposites showed a power output $\sim 165 \text{ mW/cm}^{-2}$ at 80 °C [156]. So far, the self-assembled HPW/meso-silica inorganic nanocomposites have been developed as a new type of high-temperature PEMs in our studies, which also offers the opportunities for the development of non-platinum group electrocatalysts for fuel cells.

3.4 Conclusions

In summary, a novel inorganic HPW/meso-silica nanocomposite PEM was successfully synthesized using a self-assembly process assisted by a structure-directing Pluronic P123 surfactant. The conductivities of the HPW/meso-silica nanocomposites strongly depend on the HPW content and the micro-structure. The threshold of the HPW content in the nanocomposites is 5wt% and the best conductivity was obtained on 25wt% HPW/meso-silica with a proton conductivity of 0.091 S/cm at 100 °C under 100% RH and 0.034 S/cm at 200 °C under 3% RH. The results indicate that the formation of ordered mesoporous arrays with HPW anchored in the mesoporous silica walls is helpful for

protons transport. In the case of HPW/meso-silica nanocomposites with excess HPW (>25wt%), the distortion or collapse of the mesoporous structure would result in the increase in activation energy and the decrease in proton conductivity. The applicability of the HPW/meso-silica nanocomposite as a PEM was demonstrated in DMFCs operating at elevated temperatures. The good performance and stability of the inorganic membrane for high temperatures operation would lead to significantly simplifying fuel cell systems, and also promoting the development of non-platinum group electrocatalysts.

CHAPTER 4 Highly Ordered Mesoporous Nafion Membranes for PEMFCs

4.1 Introduction

Perfluorosulfonic acid (PFSA) polymers such as Nafion are the most widely used membranes in PEMFCs owing to their high proton conductivities and good thermal and chemical stabilities [10, 11]. Recent SAXS simulation results show that the structure of hydrated Nafion can be described by randomly packed water channels surrounded by partially hydrophilic side braches, forming inverted-micelle cylinders [157]. At 20 vol% water, the diameter of the water channels is in the range of 1.8 and 3.5 nm. The proton conductivity of PFSA-based membranes is, however, critically dependent on the relative humidity (RH) and water content in the membrane structure [15-17] and it decreases significantly with the decrease in the RH and water content in the membrane. The acceptable conductivity can only be obtained in a well saturated environment [19, 158]. Therefore, a high water content of the membrane in PEMFCs is essential for achieving high power density and long-term stability. For practical operations, the fuel cells based on PFSA membranes such as Nafion rely on external humidifiers for the humidification of gas streams prior to the entry of the cell. However, these humidifying and related control units increase the cost, complexity and design barriers of the fuel cell systems.

The operation of a fuel cell at elevated temperatures ($>100\text{ }^{\circ}\text{C}$) is also very important in order to accelerate the reaction kinetics and reduce catalyst poisoning particularly by CO

[25-27]. However, increasing the operation temperature can lead to the loss of water content in the membrane, resulting in the rapid deterioration of the cell performance. So it is important to improve the water retention ability and proton conductivity of Nafion-based membranes for PEMFC operated under low humidity and high temperature conditions.

Many strategies have been developed to improve the water retention ability to enhance the proton conductivity of Nafion. One of the most commonly adopted methods is to introduce hygroscopic inorganic nanoparticles into the membrane, including silica [29, 159, 160], TiO_2 [161], and mordenite [33]. However, the inherently low proton conductivity of the inorganic particles decreases the hybrid membrane's conductivity with increasing the additive content. Due to the non-homogeneous nature of the hybrid membranes, phase separation occurs due to the differences in swelling and thermal expansion coefficients between the inorganic additives and Nafion, which affect the mechanical properties and durability of the cell performance.

Mesoporous carbon and carbon-silica have been studied as supports for Pt catalysts in PEMFCs to enhance the electrocatalytic activity and water retention ability for the operation at reduced RH and elevated temperatures [99, 162]. Capillary condensation occurs in narrow hydrophilic channels or pores, and the saturation vapor pressure decreases with decreasing the diameter of the capillaries, resulting in the water condensation at a reduced humidity [163]. The unique feature of capillary condensation is that vapor condensation occurs below the saturation vapor pressure of a pure liquid due to the increased van der Waals interactions between vapor molecules inside the confined space of a capillary. Thus, the introduction of nano- or meso-structures into the Nafion is expected to significantly enhance the water retention ability of the membrane, without a detrimental effect on the membrane's intrinsic mechanical and chemical properties. This modified

membrane is also expected to achieve a high conductivity and performance for PEMFCs operated under low humidity and/or high temperatures conditions.

The soft template method using surfactant or diblock copolymers has been well established for the synthesis of highly ordered mesoporous silica or silica-based structure [139, 164, 165]. However, introducing a highly ordered mesoporous structure into a polymer matrix is not easy. Most synthetic strategies of mesoporous polymers are related to the hard template methods and it is necessary to use toxic chemicals such as hydrofluoric acid to generate ordered mesopores by removing the template [166, 167].

In this chapter, a facile method is developed to introduce highly ordered mesopores into Nafion via a micelle templating method. In this method, a nonionic surfactant, PEO₁₂₇-PPO₄₈-PEO₁₂₇ (Pluronic F108) is used to control the micelle size in the polymer mixture. Pluronic F108 is a typical triblock copolymer with a sequence of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO). Triblock polymers of PEO-PPO-PEO are amphiphilic molecules which are both surface active and capable of micellar formation in aqueous solutions [168, 169]. When the surfactant embedded in the synthesized micelle/Nafion precursor is removed by reflux with hot water, well-ordered mesoporous structures are formed in Nafion.

4.2 Experimental

4.2.1 Synthesis of ordered mesoporous Nafion

The mesoporous Nafion (meso-Nafion) membranes were synthesized as follows. Firstly, a solution of 20 wt% non-ionic block copolymer, PluronicTM F108 ($M_w = 14600$,

BASF Corp.) was mixed with 2-propanol (99.9%, Sigma-Aldrich) and deionized (DI) water (2-propanol : H₂O = 90wt% : 10wt%) at room temperature under stirring. The as-prepared F108 solution was then transferred into a beaker and the pH value was adjusted to 1 by addition of 2 M H₂SO₄ with stirring for 2 hrs. Nafion 520 ionomers (EW=1000, 5wt% Nafion, DuPont, USA) were dropwise added into the beaker containing the F108 solution and stirred for another 2 hrs. Then, the mixtures were poured into Petri dishes and placed into a vacuum oven for heat treatment at 50 °C for 5 hrs, 90 °C for 2 hrs and finally at 120 °C for 1 h. The microscopic phase separation on a nanometer scale was developed through self-assembly due to the interaction between hydrophilic parts of Nafion ionomers and the hydrophilic PEO groups of F108, which lead to the ordered arrangement of the micelles and Nafion ionomers. After the heat treatment, the membranes were immersed in DI water, boiled and refreshed several times to remove the F108 surfactant until the transparent membranes were obtained. The thickness of the meso-Nafion membranes was in the range of 125 ± 5 μm. For simplification, the as-prepared mesoporous membranes were denoted as 5%-meso-Nafion, 10%-meso-Nafion and 15%-meso-Nafion based on the additive amount of F108 during casting the membranes. The optical photos of the as-obtained 10%-meso-Nafion and pristine Nafion 115 (Nafion[®] perfluorinated membrane with the thickness of ~0.125 mm) membranes are shown in Figure 4.1.

Figure 4.1. Optical photos of (a) Nafion 115 and (b) 10%-meso-Nafion membrane.

4.2.2 Structural and physical properties characterization

The mesoporous structures of the Nafion membranes with different F108 contents were examined using SAXS measurements according to the same operation as described in section 3.2.4.

A thermogravimetric analyzer (Perkin-Elmer TGA 7) was used to study the thermal and water retention properties of the Nafion 115 and meso-Nafion membranes. The as-prepared membranes were placed under 80% RH environments and room temperature for 48 hrs. Then the TGA tests were conducted from 25 °C to 500 °C at a heating rate of 5 °C/min in air.

Water uptake measurements of the membranes were performed by placing membrane samples in a 100% RH environment for 24 hrs, followed by measurement of sample weight (W_{wet}), vacuum drying at 80 °C for 24 hrs and measurement of dry weight (W_{dry}). The water uptake (λ_{water}) was calculated using the following equation.

$$\lambda_{water} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (4.1)$$

The mechanical strength of the membranes was measured with a mechanical tester (Instron Model 5543) at room temperature. A 100N load cell was used and the strain rate was 20mm/min.

4.2.3 Electrochemical characterization

The proton conductivities of the meso-Nafion and Nafion 115 membranes were measured using an impedance analyzer (Autolab PG30/GRA, Eco Chemie, Netherlands). Samples were sandwiched between two Pt sheets (2cm×2cm) in contact with a graphite plate under a constant pressure. The temperature and relative humidity were controlled by a fuel cell test station (Greenlight G50 with HyWARE II software, Greenlight innovation corp., Canada). One Pt sheet was used as the working electrode and the other as the reference and counter electrodes. The electrochemical impedance spectroscopy (EIS) was conducted in the frequency range of 1 MHz to 1 Hz under the signal amplitude of 10 mV.

The membrane-electrode-assembly (MEA) was made using Nafion 115 and meso-Nafion membranes. E-TEK 20wt% Pt/C catalysts and 5wt% Nafion solution were used to make the catalyst layer with Pt loading of 0.5 mg/cm² and dried Nafion loading of 1 mg/cm². PTFE-treated carbon paper (TGP-H-030) was used as the gas diffusion electrodes. The MEAs were hot-pressed at 125 °C under 10 MPa for 90 s. Single cells were assembled with the hot-pressed MEAs and graphite flow field plates. The active area of the cell was 2.5cm×2.5cm. The hydrogen flow rate was 200 SCCM and the oxygen flow rate was 300

SCCM. No back pressure was applied. The test temperature and relative humidity were controlled by the Greenlight G50 fuel cell test station.

4.3 Results and Discussion

4.3.1 Principle of the self-assembly

The self-assembly process driven by non-covalent interactions, which is now universally recognized to be crucial in the proliferation of all biological organisms, offers considerable advantages over the stepwise bond formation in the construction of large supramolecular assemblies [170]. PEO-PPO-PEO triblock copolymers are typically amphiphilic polymers and may undergo micellization in water or some solvents through the hydrophobic self-aggregation of poly(propylene oxide) (PPO) blocks. A number of PEO-PPO-PEO triblock copolymers have been reported to form micelles in water at room temperature when the polymer concentration is above a critical micellization concentration (CMC) or when the temperature is increased from room temperature (or below) to be higher than a critical micellization temperature (CMT) for a given PEO-PPO-PEO concentration [171]. The micellization of a PEO-PPO-PEO polymer in water is due to the hydrophobic association of PPO blocks. A generally accepted micellar structure of PEO-PPO-PEO is uniform or the same size spheres with dense cores consisting mainly of PPO blocks and hydrated PEO swollen coronas [172].

Figure 4.2. Schematic diagram for the synthesis of mesoporous Nafion membranes via a self-assembly process. The dotted circle refers to the ordered mesopores formed in the membrane.

The pathway for synthesizing the meso-Nafion membranes is schematically shown in Figure 4.2. Nafion is a copolymer consisting of a hydrophobic poly-tetrafluoroethylene backbone chain and regularly spaced shorter perfluorovinyl ether side-chains, each terminated by a strongly hydrophilic sulfonate ionic group [14, 18]. Owing to the existence of F108 micelles serving as soft templates, the microscopic phase separation on a nanometer scale can be developed through self-assembly due to the interaction between the hydrophilic sulfonated ionic groups of Nafion ionomer and the hydrophilic parts PEO of F108, leading to the ordered arrangement of the copolymer ionomers in short ranges. After

removing the templates, the uniform mesopores can be remained in the membranes. In this study, we have found that homogeneous F108/Nafion precursor can be synthesized with the F108 content of 5-15wt%. Below 5wt% of F108, an unbroken membrane can not be produced due to an insufficient number of surfactant molecules required to form the micelles. Above 15wt% of F108, the micelles are prone to agglomerate so that macropores and discontinuous channels were produced.

4.3.2 Structural and physical properties of the meso-Nafion membranes

Figure 4.3 is the AFM micrographs of the Pristine Nafion 115 and the meso-Nafion membranes. The AFM was conducted by a tapping mode. The surface of the pristine Nafion 115 membrane is smooth (Figure 4.3(a)), a typical characteristic of conventional Nafion membranes. With the addition of 5wt% F108 during the casting of the Nafion membrane, the surface of the 5%-meso-Nafion is no longer smooth. Instead, the surface is characterized by well-defined and highly ordered mesoporous channels (Figure 4.3(b)), which are also clearly visible on the surface of the 10%-meso-Nafion (Figure 4.3(c)) and 15%-meso-Nafion (Figure 4.3(d)). It was reported that the hydrodynamic micelle diameter of triblock copolymer with PEO-PPO-PEO sequence such as Pluronic F108 was in the range of 8-18 nm [169, 173]. The pore diameter of the mesoporous structures of meso-Nafion would be expected to be smaller. However, it should be pointed out here that the typical parallel channels formed on the surface are most likely induced by the evaporation of the solvent during the re-casting of the Nafion membranes and thus the mesoporous channels formed inside the Nafion membrane might not be necessarily the same as that formed on the surface.

Figure 4.3. 2D and 3D AFM micrographs of the surface morphology of (a) Nafion 115; (b) 5%-meso-Nafion; (c) 10%-meso-Nafion; and (d) 15%-meso-Nafion. The scale bars in (d) are also suitable for (b) and (c).

The meso-structure of the Nafion membranes with different contents of F108 was studied by the SAXS. The SAXS profiles are shown in Figure 4.4, in which (a) is before removing F108 surfactant and (b) is after removing F108 surfactant. It is worth to note that these SAXS tests were carried out at high vacuum (< 1 mbar), so the membranes were in a dry state already. Two well-resolved peaks, at $q \approx 0.3$ and $q \approx 1.6$ (nm^{-1} , q is the momentum transfer) can be observed obviously for the meso-Nafion membranes in presence of F108 (Figure 4.4(a)), which indicates the existence of ordered meso-structured micelles serving as the templates. After removing the F108, the peaks at lower scattering angles disappeared but the shoulder-like peaks at higher scattering angles are still preserved (Figure 4.4(b)), which indicates that 2D meso-structure with symmetries of $p6mm$ could be formed into the

membranes. The higher-order peaks can be attributed to the sharp peak at the cylinder diameter in radial distribution function, and they are thus a general feature for arrays of relatively closely packed cylinders [157]. The presence of SAXS peaks should be contributed by the ordered channels surrounded by polymer clusters. In other words, this would essentially be a novel channel model derived after the self-assembly process. Their interfacial area, and thus the total energy of the interfaces between the hydrophilic and hydrophobic regions, is significantly lower than irregularly shaped channels, given the significant stability of chains and side branches [174]. On the other hand, the pristine Nafion is featureless in this region, indicating that Nafion structure has no ordered mesopores. This is supported by the Gierke model that is the most popular for describing Nafion structure [175-177]. The SAXS and AFM results clearly indicate that the highly ordered 2D meso-structures have been developed into the Nafion membranes by the micelle-templating method with self-assembled Pluronic F108 surfactant.

Figure 4.4. SAXS Patterns of the meso-Nafion membranes before (a) and after (b) removing the F108 surfactant.

Figure 4.5 is the TGA curves of the as-prepared membranes, which were equilibrated at room temperature under 80% RH for 48 hrs before the measurement. The initial weight loss of ~5wt% for the membranes measured from room temperature to 100 °C can be attributed to the loss of free water or physically adsorbed water. For the Nafion 115 membrane, the additional weight loss before 280 °C is ~1%. However, for the meso-Nafion synthesized with 5, 10, and 15 wt% F108, the corresponding weight loss is 20%, 30% and 37%, respectively. Such significantly high weight losses are clearly due to the loss of the water trapped or condensed in the mesopores of the meso-Nafion membranes. On the other hand, F108 residues, if there is any, would decompose at a much lower temperature of ~200 °C. The mesoporous structure introduced by the micelle templating method with self-assembled surfactants is capable of retaining a much higher water content than the random packed water channels in the conventional Nafion [157]. Both membranes start to degrade at a temperature ~300 °C due to the decomposition of SO₃H groups followed by pyrolysis of the CF₂-backbone of the PFSA membranes at the temperature around 350 °C.

Figure 4.5. TGA curves of Nafion 115, F108 and the different meso-Nafion membranes. F108 has been removed from the meso-Nafion membranes before the measurements.

The water uptake, tensile strength and dimensional changes of the membranes were measured and tabulated in Table 4.1. It can be seen that the water uptake of meso-Nafion membranes increases with the F108 content, but the tensile strength decreases with the F108 content. In the case of 10%-Meso-Nafion, water uptake is as high as 81%, significantly higher than 27.8% of the recasting Nafion membrane, but its tensile strength is slightly lower than that of the recasting Nafion membrane.

Table 4.1. Water uptake, tensile strength and dimensional changes of the membranes.

Membrane type	Water	Tensile	strength	Dimensional changes (%)		
	uptake (%)	(MPa)		Length	Width	Thickness
Recasting Nafion membrane	27.8	28.6±0.5		13.9	15.3	9.3
Nafion 212	16.1	32.6±0.5		8.0	4.1	1.2
Nafion 115	18.6	29.4±0.5		12.1	6.8	7.4
5%-meso-Nafion	65.2	24.8±0.5		30.5	28.6	35.5
10%-meso-Nafion	81	22.4±0.5		34.3	34.2	36.6
15%-meso-Nafion	113	19.2±0.5		45.1	38.0	39.8

4.3.3 Electrochemical properties and cell performance

The effect of RH on the proton conductivity of the Nafion 115 and meso-Nafion membranes was examined at 80 °C and the results are shown in Figure 4.6.

Figure 4.6. (a) Conductivity plots of Nafion 115 and the different meso-Nafion membranes measured at 80 °C with different RH; (b) EIS curves for Nafion 115, (c) EIS curves for 5%-meso-Nafion, (d) EIS curves for 10%-meso-Nafion, (e) EIS curves for 15%-meso-Nafion membranes at different RH.

For the pristine Nafion 115, the conductivity was 0.085 S/cm under 100% RH but dramatically reduced to 0.013 S/cm at 40% RH, a reduction of 85% in conductivity. The conductivity decreases significantly with the reduction in RH, consistent with that reported in the literature [178]. In the case of 10%-meso-Nafion, the conductivity was 0.11 S/cm under 100% RH and reduced to 0.069 S/cm at 40% RH, which is more than five times that of the pristine Nafion 115 under identical test conditions. The conductivities of meso-Nafion membranes are all much higher than that of the Nafion 115 at low RH, which clearly indicates that the meso-Nafion membranes are much less sensitive to the change in RH. This is a very important property for PEMFC applications.

The performances of single cells with the meso-Nafion and Nafion 115 membranes were evaluated at 80 °C and 120 °C. The thickness of the meso-Nafion membranes was 125 ± 5 μm , similar to that of pristine Nafion 115. Figure 4.7(a) is the cell performance tested at 80 °C and 100% RH and Figure 4.7(b) is the corresponding cell stability measured under a cell voltage of 0.7 V. The OCV values of cells with meso-Nafion membranes are in the range of 0.95 to 0.97 V, close to 0.95 V of the cell with pristine Nafion 115. However, the cells with meso-Nafion membrane show a higher performance as compared to that of Nafion 115 particularly in the high currents. The best performance was observed for the cell with the 10%-meso-Nafion membrane with a maximum power density of 1.05 W/cm^2 , significantly higher than 0.7 W/cm^2 measured on the cell with the pristine Nafion 115. The significantly higher power output is clearly due to the high conductivity of the meso-Nafion. Nevertheless, despite the differences in the power performance, the stability behavior for the cells with Nafion 115 and meso-Nafion membranes is similar (Figure 4.7(b)), indicating the similar degradation behavior of both the pristine Nafion 115 and meso-Nafion under 100% RH. The difference in the cell performance between Nafion 115 and meso-Nafion

increases significantly when the cells are operated at a reduced humidity of 60 %RH (Figure 4.7(c)&(d)). The maximum power density of the cell with 10%-meso-Nafion is 0.63 W/cm^2 , more than 2 times 0.28 W/cm^2 of the cell with pristine Nafion 115. Moreover, as the RH is reduced to 60%, the decay rate of the cell performance with Nafion 115 is significant. The initial current was 0.28 A/cm^2 and decreased to 0.15 A/cm^2 after testing for 3600 sec, a reduction of 46% in cell current. On the other hand, the reduction in the cell current for the cells with meso-Nafion membranes is much smaller. For example, for the cell with 10%-meso-Nafion, the initial current was 0.32 A/cm^2 and decreased to 0.28 A/cm^2 after testing for 3600 sec, a reduction of 12.5% in cell current. As the operating temperature increased to 120°C , the difference in the cell performance with Nafion 115 and meso-Nafion becomes even more obvious (Figure 4.7(e)). In this case, H_2 and O_2 were humidified at 80°C . The maximum power outputs of the cells with 5%-meso-Nafion, 10%-meso-Nafion and 15%-meso-Nafion membranes were 0.19, 0.30, and 0.26 W/cm^2 , respectively, significantly higher than 0.13 W/cm^2 for the cell with Nafion 115. The differences in the cell stability between Nafion 115 and meso-Nafion membranes are the most striking. For the cell with pristine Nafion 115, the current output decreased to 0.04 A/cm^2 at a cell voltage of 0.7 V after tested for 5400 sec and was not stable (Figure 4.7(f)). Very different from that of the pristine Nafion 115, after the initial decay, the current for the cells with meso-Nafion became stable and reached a stable output of 0.14 A/cm^2 in the case of the 10%-meso-Nafion membrane, which is nearly 4 times that of the cell with the pristine Nafion 115. The results demonstrate that the meso-Nafion membranes as described here can bring significant advantages for PEMFCs operating under reduced RH and elevated temperatures conditions.

Figure 4.7. Performance and stability of single cells with Nafion 115 and meso-Nafion membranes measured (a,b) in H₂/O₂ at 80 °C and 100% RH, (c,d) in H₂/O₂ at 80 °C and 60%RH, and (e,f) in H₂/O₂ at 120 °C and gases were humidified at 80 °C; Nafion 115 (○, curve A); 5%-meso-Nafion (▽, curve B); 10%-meso-Nafion (□, curve C); and 15%-meso-Nafion (△, curve D). Stability curves in (b, d, f) were measured under a cell voltage of 0.7 V. Anode & cathode: Pt/C (Pt loading: 0.5 mg/cm²).

Figure 4.8 presents the corresponding performance for the cells with the pristine Nafion 115, 5%-meso-Nafion, 10%-meso-Nafion and 15%-meso-Nafion, respectively. And Table 4.2 summarizes the maximum power densities of the cells with the Nafion 115 and meso-Nafion membranes. The tests were performed at 80 °C with different RH.

Figure 4.8. Performance of single cells (a) with the Nafion 115 membrane, (b) with the 5%-meso-Nafion membrane, (c) with the 10%-meso-Nafion membrane and (d) with the 15%-meso-Nafion membrane, as a function of RH in H_2/O_2 , measured at 80 °C. RH: 20% ($\square$); 40% ($\circ$); 60% ($\triangle$); 80% (∇); 100% ($\star$).

Table 4.2. The maximum power density of cells with Nafion 115 and meso-Nafion measured at 80 °C with different RH.

Membrane	Power density, W/cm ²				
	20% RH	40% RH	60% RH	80% RH	100% RH
Nafion 115	0.03	0.12	0.28	0.50	0.72
5%-meso-Nafion	0.13	0.19	0.39	0.55	0.87
10%-meso-Nafion	0.19	0.35	0.63	0.83	1.05
15%-meso-Nafion	0.12	0.26	0.58	0.70	0.95

In all cases, the cells with meso-Nafion membranes exhibit much better power output than the cell with Nafion 115. The differences in cell performances increase with the decrease in the RH. The results demonstrate that the high power output of the cells with the meso-Nafion is due to the high water retention ability and high proton conductivity of the mesoporous membranes.

Figure 4.9(a) is the performance of single cells with the Nafion 115 and 10%-meso-Nafion measured at 25 °C under dry H₂ and O₂ gases. The H₂ and O₂ gases were dried by passing through a molecular shiver. The cell with 10%-meso-Nafion shows a higher performance than that of the pristine Nafion 115 membrane, most likely due to the enhanced conductivity of the meso-Nafion membrane. The stabilities of the cells were tested under dry gas conditions at a constant cell potential of 0.7 V and the results are shown in Figure 4.9(b). The initial current is due to the residual water in the membrane. As the test continued, the water content in the membrane reduced, which led to the decrease in

proton conductivity and thus the performance. For the cell fabricated with pristine Nafion 115, the cell current decreased very fast and reached zero after tested for about 1000 s. The zero current of the cell with Nafion 115 is due to the complete dehydration of the Nafion membrane under the conditions studied, which leads to the complete loss of proton conductivity. This indicates that the pristine Nafion 115 is no longer proton conductive under completely dry conditions, consistent with previous studies [158]. The current output of the cell with the meso-Nafion membrane also decreased but the decreasing rate is much slower. Most interesting, after tested for ~1500 s under the dry gas conditions, the current density reached a stable output of $\sim 0.02 \text{ A/cm}^2$. This result is very encouraging as it clearly indicates that the mesoporous structure introduced in the Nafion membrane is capable of retaining water and the meso-Nafion membranes can be operated under completely dry gas conditions.

Figure 4.9. (a) Performance and (b) stability of a single cell fabricated with Nafion 115 and 10%-meso-Nafion membranes, measured under dry H_2 and O_2 conditions at 25°C . Anode: Pt/C catalyst, 0.5 mg/cm^2 ; Cathode: Pt/C catalyst, 0.5 mg/cm^2 . The stability tests were measured under a constant cell potential of 0.7 V .

4.4 Conclusions

In summary, highly ordered mesoporous structures were successfully introduced into a conventional proton conducting PFSA membrane. Very different from conventional hybrid or multilayer modification, the introduced mesoporous structure via the soft micelle-templating method did not significantly alter the inherently chemical and physical properties of Nafion. The meso-Nafion membranes display much higher water retention abilities, higher proton conductivities, higher power outputs and much better stabilities, particularly under reduced RH and elevated temperatures, as compared to the pristine Nafion 115. The ability of the meso-Nafion membranes retaining water even under completely dry conditions indicates that it is possible to develop PEMFCs without an external humidity supplier. Though more works are needed to understand the mechanism for the formation of the mesoporous structures in Nafion, it is expected that the PEMFC system with novel meso-Nafion membranes would have a higher power density, lower humidification requirement, reduced water management and thus more compact systems and less cost, as compared to that with the conventional Nafion membranes.

Finally, similar to the soft-templating approach to the mesoporous silica [139], the mesoporous structure in Nafion could also be controllable by the types and concentration of surfactants to form 2D and 3D structures with better conductivities, stabilities and water retention abilities.

CHAPTER 5 A Novel Multilayer Nafion Membrane Impregnated with HPW for PEMFCs

5.1 Introduction

Current PEMFCs work at relatively low temperatures of around 80 °C. However, one of the major issues of low temperature operation is the poisoning of Pt-based anode catalysts by the trace amount of CO present in fuels. Increasing the operating temperature to over 100 °C promises important benefits with respect to alleviated problems of CO poisoning, improved reaction kinetics in anode and cathode [67, 179, 180]. On the other hand, the low humidity operation of PEMFCs presents many advantages over conventional operation, such as simplified water management, system design and reduced cost, etc [181-184]. However, the most common membrane currently used for PEMFCs, such as Dupont's Nafion or perfluorosulfonic acid (PFSA) polymers, shows a significant loss in conductivity at elevated temperatures and low humidity due to the dehydration of the membranes [9, 18, 185]. The dehydration also results in membrane shrinkage and consequent poor contact between the membrane and the electrodes [186]. Therefore, a fully hydrated membrane at elevated temperatures and low humidity is desirable for efficient proton conduction in the membranes. It still remains critical challenges to maintain proper hydration of the membranes for the operation of the PEMFCs under high temperatures and/or low humidity conditions.

Large efforts have been made to modify Nafion with inorganic particles like sulfonated SiO₂, ZrO₂ or TiO₂ [29, 32, 34, 37, 129, 187-192]. Mesoporous MCM-41 silica as a new inorganic filler was also introduced into the Nafion polymer matrix [30]. These efforts show some promising results, such as enhanced water retention properties and thermal stability. An incorporation of nanoscaled and highly dispersed Pt was reported to lead to the reaction of the diffusing H₂ and O₂ to form water which improves the humidification of the membranes [31, 193, 194].

Another approach is the impregnation with heteropolyacids (HPAs) into Nafion membranes. As one of the most attractive inorganic proton donors, HPAs have been shown to be highly proton-conductive and have a stable structure [134, 135]. Ramani et al. [195-198] prepared different Nafion/HPA composite membranes using recasting method with different HPAs, such as HPW, STA (silicotungstic acid), PMA (phosphomolybdic acid), and SMA (silicomolybdic acid). The additive particle size was on the order of 1-10 μm . No improvement in conductivity was observed as compared to Nafion at low humidity conditions. They also fabricated Nafion composite membranes with stabilized HPW, which was treated by ion exchanging with larger cations such as Cs⁺, NH₄⁺, Rb⁺ and Tl⁺. The leaching of additives was significantly lowered to ~5%. They further reduced the additive particle size to 30 nm, which enhanced the proton conductivity of the composite membrane by up to 35%.

Malhotra et al. [36] impregnated HPW dissolved in different solvents into Nafion 117 membranes and a power output of 450 mW/cm² was achieved at 120 °C humidified with 50 °C gas on the cell with Nafion/HPW membrane (using tetra-*n*-butylammonium chloride as solvent). Shao et al. [35, 186] have synthesized the hybrid Nafion-silicon oxide membrane doped with HPW for high temperature operation of PEMFCs. The HPW

molecules were firstly supported on a silica gel and the as-obtained powders were then recast with Nafion ionomer. Similarly Sacca et al. [199] prepared the Nafion-based membrane using HPW supported on a nanopowdered ZrO_2 as fillers. A peak power of $\sim 300 \text{ mW/cm}^2$ was obtained at 90°C with dry gases. However, HPW molecules are prone to agglomerate to form big particles or clusters during the recasting process. It would cause the phase separation between HPW and Nafion matrix, which in turn will lower the conductivity and performance of the composite membranes. In addition, there are rarely effective solutions to resolve the HPW leaching problem, which will lead to an instability of the hybrid membranes.

In this chapter, a new Nafion membrane impregnated with HPW was developed for the low humidity and high temperatures operation of PEMFCs. In this method, HPW was impregnated into a mesoporous Nafion membrane, the synthesis of which has been described in Chapter 4. The purpose of HPW impregnation is to further improve the proton conductivity and water retention properties of the membranes, especially under high temperatures and low humidity conditions. The preparation procedure and properties of the membranes were studied in detail. The results show that the multilayer membrane possesses very good proton conductivities under both high and low humidity, effectively alleviates and resolves the problem of HPW leaching. Moreover, very different to the pristine Nafion membrane, the fuel cells assembled with the multilayer HPW-impregnated membrane show good performance and negligible decay when the relative humidity (RH) of the inlet gases changed from 100% to 50%. This work demonstrates that the novel multilayer membrane impregnated with HPW is a promising and potential membrane for the development of high performance and high stability PEMFCs with high tolerance to RH variation at elevated temperatures.

5.2 Experimental

5.2.1 Synthesis of the multilayer membrane

The multilayer membrane consists of a central layer impregnated with HPW and two side layers. Firstly, a 10%-meso-Nafion membrane was fabricated using soft-templating method as described in section 4.2.1. The 10%-meso-Nafion membrane was then immersed into HPW solutions with different concentration, heated at 80 °C for 2 hrs, followed by heating the membrane at 130 °C for 1h, then cooled down to ambient temperature. The fabrication procedure of the side layer is as follows. Firstly, Nafion ionomers were transferred to a *N,N*-Dimethylformamide (DMF, Sigma-aldrich®) solution by distilling until the solution temperature reached 153 °C to remove water and solvent. The quantitative Nafion/DMF mixture was sputtered onto the as-prepared HPW-impregnated meso-Nafion membrane to form side layers, followed by heating at 90 °C for 2 hrs and 160 °C for 1 h. The thickness of the side layers can be controlled by the sputtering time. Finally the multilayer membrane impregnated with HPW was obtained.

Figure 5.1 describes the fabrication procedure of the multilayer membrane impregnated with HPW. Firstly, the meso-Nafion membrane was prepared using the soft template method. HPW molecules were then impregnated into the meso-Nafion membrane. The next step is to fabricate two side layers adhering to the central layer by sputtering method. Finally, the multilayer membrane was heated at high temperatures.

Figure 5.1. The fabrication procedure for the multilayer membrane impregnated with HPW, where the cross-sections of the membranes are schematically shown.

The commercial Nafion 1135 was used as the benchmark for evaluating the properties of the multilayer membranes. The membranes were treated according to the standard procedure in a 5wt% H_2O_2 solution at 80 °C for 30 min, in Milli-Q water at 80 °C for 30 min, and in an 8wt% H_2SO_4 solution at 80 °C for 30 min. After each treatment, the membranes were rinsed in Milli-Q water three times to remove traces of H_2O_2 and H_2SO_4 .

5.2.2 Physical properties and structure characterization

The surface and cross-section morphology of the membranes were examined using scanning electron microscopy (SEM, JEOL JSM-6360). The composition and elemental mapping were obtained by energy dispersive spectroscopy (EDS, Oxford UK). The cross

sectional specimens of the multilayer membrane were prepared by breaking the membrane under liquid nitrogen (77 K). The samples were Au-sputtered under vacuum before SEM examination.

The thermal properties of the membranes were determined using a thermogravimetric analyzer (Perkin-Elmer TGA 7) at a heating rate of 5 °C/min from room temperature to 1000 °C under a continuous air flow with a flow rate of 60 SCCM.

The characteristics of HPW molecules in the multilayer membranes were examined by a Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR, Perkin Elmer FT-IR Spectrum) with a resolution of 2 cm⁻¹. A diamond crystal was used as the ATR plate.

The mechanical strength and water uptake of the membranes were measured according to the same procedure as described in section 4.2.2.

EW value of the membranes was calculated from the ion exchange capacity (IEC value) of the membrane ($EW = 1000/IEC$). The IEC value was determined by titration. Membranes were soaked in 50 mL of 1 M NaCl aqueous solution for 24 hrs, and then titrated by 0.01 M NaOH solution. Phenolphthalein (C₂₀H₁₄O₄) solution 1wt% in ethanol was used as the indicator. The IEC was derived from $IEC = (V_{NaOH}N_{NaOH})/W_{dry}$, where V_{NaOH} , N_{NaOH} and W_{dry} are the volumes of NaOH consumed, the concentration of NaOH, and the weight of dried membranes, respectively.

5.2.3 Electrochemical characterization

The proton conductivities of the membranes were measured according to the same procedure as described in section 4.2.3.

To evaluate the cell performance of the PEMFCs, a membrane electrode assembly (MEA) was made by sandwiching the membrane between Pt/C (50wt%, Johnson Matthey) anode and cathode. The active area of the cells was $2.5\text{cm} \times 2.5\text{cm}$. The loading of Pt in the catalyst layer is 0.5 mg/cm^2 for anode and 1 mg/cm^2 for cathode. The carbon papers (Johnson Matthey) were used as the gas diffusion layer and waterproofed firstly by 30wt% PTFE for its outer and inner surface. The MEA was hot-pressed at $130\text{ }^\circ\text{C}$ and 5 MPa for 3 min. The serpentine-shaped flow channels of anode and cathode cut into the graphite blocks were such that the fuel and oxidant can flow over the electrodes on each side of the MEA. The electrochemical performance and stability of the single cell with the multilayer membrane or Nafion 1135 membranes were evaluated using the Greenlight fuel cell test station (FCATS-G050, Canada) with H_2 as fuel and air as oxidant. H_2 and air flow rates were 200 SCCM and 500 SCCM, respectively. The humidity of the H_2 and air was kept at the same level and the cell performance was measured as a function of RH. Prior to the measurement, cells were activated by polarization at a constant current until a stable performance was obtained.

5.3 Results and Discussion

5.3.1 Structural and physical properties of the multilayer membrane

Figure 5.2 shows the dependence of impregnated HPW content on the HPW concentration. It can be clearly observed that the impregnated HPW content is related to the HPW concentration. When the HPW concentration is 0.2 mol/L, the HPW loading in the 10%-meso-Nafion reaches a saturated level, about 19wt%. There is nearly no increase with

further increasing the HPW concentration. Thus the 10%-meso-Nafion impregnated in 0.2 mol/L HPW solution with HPW content of ~19wt% was used as the central layer to fabricate the multilayer membrane.

Figure 5.2. Impregnation content dependence of the concentration of HPW solution.

Figure 5.3 (a) shows the cross sectional SEM images of the multilayer membrane. As can be seen, the composite membrane was composed of three layers, two side layers and a central layer, which is the mesoporous Nafion membrane impregnated with HPW. The total thickness of the multilayer membrane is ~100 μm and the thickness of side layers is ~10 μm . The inserted picture on the top right part of Figure 5.3 (a) is the interface morphology between the central layer and side layer. The side layers are in good adhesion to the central layer. The F and W elements are quite uniformly dispersed in the membrane (Figure 5.3 (b) and (c)). The distribution of W elements is quite uniform, indicating the successful impregnation of HPW in the mesoporous Nafion membrane without agglomeration.

Figure 5.3. (a) Cross sectional SEM image of the multilayer membrane and SEM image of the interface shown on the top right corner, (b) Elemental F map, (c) Elemental W map, and (d) EDS spectrum of the multilayer membrane.

Figure 5.4 shows the FTIR-ATR spectra of the pristine Nafion 1135 and the multilayer membrane. The pristine Nafion 1135 presents its inherently characteristic spectrum, the C-O-C symmetric stretching at 960 cm^{-1} , the SO_3 stretching vibrations at 1055 cm^{-1} , the CF_2 asymmetric and symmetric stretching at 1200 and 1100 cm^{-1} [200-202]. The multilayer

membrane possesses not only the inherent bands of Nafion 1135, but also the characteristic bands observed at 1081 (P-O_a), 983.9 (W=O_d), 893.9 ($\text{W-O}_b\text{-W}$), and 803.9 cm^{-1} ($\text{W-O}_c\text{-W}$), which coincide with those reported in the literature for $[\text{PW}_{12}\text{O}_{40}]^{3-}$ Keggin units [203, 204]. The FTIR-ATR results confirm again the successful impregnation of the Keggin structure $[\text{PW}_{12}\text{O}_{40}]^{3-}$ into the multilayer membrane without depolymerization or degradation.

Figure 5.4. FTIR-ATR spectra of the different membranes, (A) Nafion 1135, (B) meso-Nafion impregnated with HPW and (C) multilayer membrane.

Thermal properties of the membranes were determined using TGA. The membranes were firstly placed under 80% RH environment at room temperature for 48 hrs, followed by the TGA tests. Figure 5.5 is the TGA results for the different membranes. The HPW loading in the multilayer membrane is 13wt%. After 20 hrs immersing in DI water, it still has 11wt% HPW loading at ambient temperature, which demonstrates that the HPW is very stable in the multilayer membrane. This indicates that the multilayer structure effectively

alleviate the leaching of HPW. For comparison, the commercial Nafion 1135 was directly immersed into a 0.2 mol/L HPW solution and treated by the same impregnation process, the HPW loading is only 1wt%. The HPW completely leached out after immersing the membrane in DI water for 30 min. This indicates that the HPW molecules are not stable in the Nafion 1135 membrane via the direct impregnation. As can be seen in Figure 5.5, the first weight loss of all the membranes from room temperature to 100 °C can be ascribed to the loss of free water or physically adsorbed water. Below 100 °C, the Nafion 1135 membrane shows a weight loss of ~5wt%, the Nafion 1135 impregnated with HPW has a weight loss of ~9wt%. But in this temperature range the multilayer membrane presents an approximate 32wt% weight loss, which should be attributed to more water being absorbed in the multilayer membranes. All the membranes start to degrade at a temperature ~280 °C due to the decomposition of SO₃H groups followed by pyrolysis of the CF₂-backbone of the polymer at temperature around 350 °C.

Figure 5.5. TGA results of the different membranes.

Table 5.1 summarizes the physical and chemical properties of the Nafion 1135 and the multilayer membrane. As shown, the water uptake of the multilayer membrane is 28.4%, nearly two times that of the pristine Nafion 1135 membrane, but the tensile strength is almost the same. The EW value of the multilayer membrane is slightly lower than that of the Nafion 1135 membrane.

Table 5.1. Physical and chemical properties of Nafion 1135 and the multilayer membrane.

Membrane type	Thickness (μm)	Water uptake (%)	EW (g/mol)	Tensile strength (MPa)
Nafion 1135	90 $\pm$ 2	16.5	1100	27.2 $\pm$ 0.5
Multilayer Membrane	100 $\pm$ 5	28.4	1061	26.8 $\pm$ 0.5

Proton conductivity, being a fundamental property of a PEM, was chosen as a measure of comparison. Figure 5.6 exhibits the effect of RH on the proton conductivity of the multilayer membrane and Nafion 1135. For the multilayer membrane, the proton conductivity is 0.11 S/cm under 100% RH, slightly decreases to 0.072 S/cm when RH decreased to 40% RH at 80 °C. For the Nafion 1135 membrane, the conductivity is 0.09 S/cm under 100% RH at 80 °C, but significantly decreases to 0.015 S/cm under 40% RH at 80 °C. The conductivities of the multilayer membrane are all much higher than those of Nafion 1135 under different RH at 80 °C. The improvement in proton conductivity is reasonable, because the multilayer membrane has shrunken clusters of sulfonic acid moieties and the uniformly dispersed HPW molecules, which can form a bridge between shrunken clusters and significantly shorten the distance for proton hopping under high and

low humidity according to the Grotthuss mechanism [205, 206]. Moreover, the enhancement in water uptake is helpful for the creation of a continuous pathway for protons across the medium in terms of the proposed vehicular mechanism [207, 208].

Figure 5.6. Conductivity plots of Nafion 1135 and the multilayer membrane measured at 80 °C under different RH.

5.3.2 Cell performance and durability

Figure 5.7 shows the performance and stability of a single cell assembled with Nafion 1135 membrane at 80 °C under 100% and 50% RH of inlet gases. When the humidity of the inlet gases decreased from 100% to 50%, the electrochemical performance of the cell with Nafion 1135 decreased significantly (Figure 5.7(a)). It can be attributed to the significant decrease of the Nafion membrane's proton conductivity at the low RH. The stability was measured at a constant current density of 600 mA/cm² (see Figure 5.7 (b)). The cell at 100% RH was stable at 0.52-0.54 V. However, when the RH of the inlet gases dropped to

50% the cell voltage decreased rather rapidly. During a period of 300 min, the voltage decreased from 0.42 to 0.28 V and the decreasing rate was 0.45 mV/min. The decay in the cell voltage is clearly caused by the dehydration of the MEA.

Figure 5.7. (a) Cell performance, and (b) stability of the cell with Nafion 1135 membrane measured at 80 °C under 100% RH and 50% RH humidified gas. Anode Pt loading: 0.5 mg/cm² 50wt% Pt/C, cathode Pt loading: 1 mg/cm² 50wt% Pt/C. H₂ flow rate: 200 SCCM, air flow rate: 500 SCCM. The stability was measured under a constant current density of 600 mA/cm².

Figure 5.8 represents the electrochemical performance and stability of a single cell assembled with the multilayer membrane at 80 °C under different RH. The cell stability was also tested under a constant current density 600 mA/cm². As can be seen in Figure 5.8 (b), the cell with the multilayer membrane shows a remarkably high stability as compared to the cell with the pristine Nafion 1135. This is indicated by the negligible cell voltage decay when the inlet gases were changed from 100% to 50% RH, which is clearly related to the high water retention ability of the multilayer membrane. When the RH switched to absolutely dry gas, the decreasing rate was 0.18 mV/min, which is still substantially lower than the 0.45 mV/min observed for the cell with the Nafion 1135 membrane under 50% RH. The excellent stability of the cell with the multilayer membrane is also demonstrated by the cell performance, as shown in Figure 5.8 (a). There is only a small decrease when the RH changed from 100% to 50%. This indicates that the cell with the multilayer membrane is much less sensitive to the change of RH of the reactant gases. The central layer can serve as a water reservoir and improve the membrane stability operating at higher temperature owing to the impregnation with HPW molecules [35, 36, 195-197]. With reducing the RH to absolutely dry gas, the cell performance also drops. However, the reduction in cell performance is substantially smaller than that of the cell with the Nafion membrane. The multilayer membrane can significantly widen the RH operating window of the PEMFCs at elevated temperatures.

Figure 5.8. Cell performance (a), and stability (b) of the cell with the multilayer membrane measured at 80°C under 100% RH, 50% RH and absolutely dry inlet gas. Anode Pt loading: $0.5 \text{ mg}/\text{cm}^2$ 50wt% Pt/C, cathode Pt loading: $1 \text{ mg}/\text{cm}^2$ 50wt% Pt/C. H_2 flow rate: 200 SCCM, air flow rate: 500 SCCM. The stability was measured at a constant current density of $600 \text{ mA}/\text{cm}^2$.

Figure 5.9 (a) shows the performance for the cells with Nafion 1135 and the multilayer membrane measured at 120 °C. The peak power density for the cell with the multilayer membrane is 420 mW/cm², which is much higher than the cell with Nafion 1135. This is due to the multilayer membrane possessing higher water retention ability and higher conductivity under high temperature and low humidity conditions. The cell performance stability at 120 °C was measured at a constant voltage 0.6 V and the results are exhibited in Figure 5.9 (b). The cell with the multilayer membrane shows a good durability. After the test of 20 hrs, the current reduction (from 310 mA/cm² to 240 mA/cm²) is only 3.5 mA/h. But the cell with Nafion 1135 membrane shows a 19.1 mA/h (from 260 mA/cm² to 50 mA/cm²) during the 11 hrs testing period, which is most likely caused by the dehydration of the Nafion 1135 membrane.

Figure 5.9. (a) Cell performance and (b) stability of the cells with Nafion 1135 and the multilayer membrane, measured at 120 °C humidified at 80 °C. (○) for the cell with multilayer membrane, (□) for the cell with Nafion 1135. Anode Pt loading: 0.5 mg/cm² 50wt% Pt/C, cathode Pt loading: 1 mg/cm² 50wt% Pt/C. H₂ flow rate: 200 SCCM, air flow rate: 500 SCCM. The stability was measured under a constant voltage of 0.6 V.

5.4 Conclusions

A novel multilayer Nafion-based membrane impregnated with HPW has been developed for the applications of PEMFCs operated under high temperature/low humidity conditions. The higher conductivity and higher water retention ability significantly improve the cell stability and enhance the tolerance to RH variation in comparison with the conventional Nafion membrane. At the same time, the multilayer structured membrane can effectively resolve the HPW leaching problem. The novel synthesis method for the multilayer membrane should have potential applications on membrane technologies.

CHAPTER 6 Nano-Structured Pd_xPt_{1-x}/Ti Anodes by Electrodeposition for Alcohol Electrooxidation

6.1 Introduction

Direct alcohol fuel cells (DAFCs) generate electric power by feeding liquid fuels directly to the anode, and are particularly attractive as small and lightweight power sources. Among the different possible alcohols, methanol is the most promising liquid fuel because it has several advantages, such as an abundant availability at low cost, easy handling, transportation and storage, high theoretical energy density comparable to that of gaseous hydrogen. Other alcohols, such as ethanol and isopropanol, have also been considered as alternative fuels in fuel cells [61, 209-213].

Carbon supported and unsupported PtRu alloys are commonly used as electrocatalysts for methanol oxidation in direct methanol fuel cells (DMFCs) [80, 214]. PtSn bimetallic catalysts for the electrooxidation of ethanol have been investigated by several research groups [73, 78]. It has been shown that the electrooxidation of ethanol is more sluggish than that of methanol oxidation reaction on Pt-based catalysts in acidic media. In addition, the high price and limited source of Pt constitute a major barrier to the development of DAFCs. On the other hand, if DAFCs are operated in an alkaline medium instead of an acidic one, the kinetics of the electrode reactions will be significantly enhanced and Pt-free catalysts with low cost can be used [82, 83, 215-217]. It is reported that the greater availability of OH⁻ ions and a higher OH⁻ coverage on the electrode surface will contribute to the

considerable increase in the kinetics of the alcohol oxidation reaction in alkaline media [216, 218-222].

It is well known that the electrodeposition is one of the most efficient methods for the growth of metal nanoparticles. This is a powerful technique for the deposition of many metals since it is rapid and facile, allowing easy control of the nucleation and growth of metal nanoparticles with various sizes, shapes and distributions [223]. Titanium (Ti) can be used as a substrate of catalysts due to its excellent conductivity and chemical stability. In comparison to conventional anodes, using pure metal Ti as a substrate, the low charge-transfer resistance between the catalyst particles and the substrate, and the increased hydrophilic properties of the anodes may contribute to the increase in performance. The Ti-supported catalysts have presented a significant electrocatalytic activity for methanol oxidation. There are several reports on the novel electrode structures for DMFCs based on Ti mesh [75, 221, 222, 224].

In this chapter, we report the preparation and characterization of Pd_xPt_{1-x} nanoparticles, which were electrodeposited on the Ti substrate surface with different atomic ratios. The morphology and composition of the catalysts were analyzed by scanning electron microscopy (SEM) and X-ray energy dispersion spectroscopy (EDS). Their activity and stability for alcohol electrooxidation were measured in an alkaline medium by cyclic voltammetry (CV) and chronoamperometry (CA) methods.

6.2 Experimental

6.2.1 Preparation of the Pd_xPt_{1-x}/Ti electrodes

The chemical reagents (methanol, ethanol, isopropanol, potassium hydroxide, ammonia, hydrochloric acid, hydroperoxide, PdCl₂ and H₂PtCl₆ · xH₂O, etc.) used in these experiments were all analytical grade purity and Ti foils were 99.99% purity. All the above materials were purchased from Sigma-Aldrich[®]. All the solution used was freshly prepared with deionized water of $\geq 18.2 \text{ M}\Omega \cdot \text{cm}$.

The working electrodes were prepared by the electrodeposition method with a controlled atomic ratio of Pd and Pt onto Ti substrate. Firstly, the surfaces of the Ti foils were polished with 50 nm alumina grinding powers, followed by rinsing the foils by plenty of deionized water and soaking them into a mixture solution of HCl (7.4wt%) and H₂O₂ (5.0wt%) for 10 min to remove oxidized layer and contaminations. After that, rinse the Ti foils and dip them into the precursor solution by a consentaneous criterion, ensuring the wording electrodes in an exact orientation. The pH value of the precursor solution was adjusted to be 9.5 and the metal ions concentration (the sum of Pd²⁺ and Pt⁴⁺) was controlled at 5 mM with the designated Pd²⁺ and Pt⁴⁺ stoichiometric composition. The electrodeposition was performed by CV scanning from 0 V to -0.8 V at a scan rate of 5 mV s⁻¹ and the process was repeated for five times. Finally, the as-prepared electrodes were rinsed with DI water for the subsequent tests.

6.2.2 Physical characterization

A Field Emission Scanning Electron Microscope (FE-SEM, JEOL JSM-6340F, Japan) was used to characterize the morphology and the particle size distribution of the catalyst.

EDS (Oxford, UK) was used to determine the atomic ratio of Pd and Pt in Pd_xPt_{1-x}.

6.2.3 Electrochemical characterization

The electrochemical experiments were carried out by using Autolab PGSTAT30 electrochemical workstation. A standard three-electrode cell was used and controlled at 25 °C using a water bath during the experiments. The cell consisted of a 0.5 cm² titanium foil coated by Pd and Pt catalysts as the working electrode, a 3 cm² Pt foil as the counter electrode, and a saturated calomel electrode (SCE, 0.241 V versus SHE) as the reference electrode. A salt bridge with a Luggin capillary closing to the working electrode was used between the cell and the reference electrode.

6.3 Results and discussion

6.3.1 Morphology and composition analysis

The morphology and size distribution of the catalysts were acquired by FE-SEM. A typical result is shown in Figure 6.1 (a). It can be clearly observed that the particles of the catalysts are all spherical in shape and there is no obvious agglomeration, which proves that these catalysts possess a good three-dimensional structure and highly specific surface area.

The average particle size is around 10 nm, quite uniform and narrow-dispersed, as seen in Figure 6.1 (b). We also found that the morphology and particle size distribution of the $\text{Pd}_x\text{Pt}_{1-x}$ electrocatalysts with different Pd/Pt atomic ratio are almost the same.

Figure 6.1. FE-SEM image of the $\text{Pd}_{0.8}\text{Pt}_{0.2}/\text{Ti}$ catalyst (a), and size distribution histogram (b).

The element composition analysis of the catalysts was conducted by EDS and the Pd and Pt contents in the catalysts are tabulated in Table 6.1. Pd and Pt elements can be distinctly detected in their corresponding pure catalysts and they can be also simultaneously observed in the bimetallic catalysts ($\text{Pd}_{0.8}\text{Pt}_{0.2}/\text{Ti}$, $\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{Ti}$ and $\text{Pd}_{0.2}\text{Pt}_{0.8}/\text{Ti}$). The characteristic peaks of Ti element still can be observed clearly, which means that the surface of the Ti substrate has not been completely covered by the catalyst layer. This is consistent with the FE-SEM results as shown in Figure 6.1 (a). The atomic ratio obtained from EDS is in excellent agreement with the nominal ratio, which corroborates that the electrodeposition method is an easy and feasible route to synthesize binary or ternary catalysts with controlled composition and structure on Ti substrates.

Table 6.1. The element composition of the Pd_xPt_{1-x}/Ti catalysts by EDS.

Sample	Pd/Ti	Pd _{0.8} Pt _{0.2} /Ti	Pd _{0.5} Pt _{0.5} /Ti	Pd _{0.2} Pt _{0.8} /Ti	Pt/Ti
Pd content (%)	100	80.8	48.6	21.3	0
Pt content (%)	0	19.2	51.4	78.7	100

Figure 6.2. EDS spectra of Pd/Ti (a), Pd_{0.8}Pt_{0.2}/Ti (b), and Pt/Ti (c).

6.3.2 Methanol electrooxidation on Pd_xPt_{1-x}/Ti

The effect of the pure Ti foil for methanol oxidation was investigated in a 1.0 M methanol and 1.0 M KOH solution. Figure 6.3 shows the CV curve at a sweep rate of 50 mV s⁻¹ from -0.9 V to 0.3 V. It is clearly observed that the pure Ti foil does not have a catalytic activity for methanol oxidation. The similar results were also observed for the pure Ti foil for ethanol and isopropanol oxidation in the alkaline medium.

Figure 6.3. CV test of the pure Ti foil in 1.0 M methanol and 1.0 M KOH solution at a scan rate of 50 mV s⁻¹, 298 K.

Figure 6.4 shows the CV curves of the as-prepared Pd_xPt_{1-x}/Ti catalysts for methanol oxidation in a N₂-saturated 1.0 M KOH + 1.0 M methanol solution, measured at a sweep rate of 50 mV s⁻¹ in the potential range from -0.9 to 0.3 V. The performances, such as the onset potential (E_s), the peak potential (E_p), the peak current density (j_p) and the current density j at -0.4 V are given in Table 6.2. All the activities were normalized based on the

surface area of the working electrode. The alcohol electrooxidation on the electrodes is characterized by two well-defined current peaks in the forward and reverse scans. The forward scan peak represents the electrochemical oxidation reaction of the freshly chemisorbed species coming from the alcohol solution [225]. The reverse scan peak is primarily related with removal of carbonaceous species which are not completely oxidized in the forward scan. The j_p is normally a very important parameter to evaluate the catalytic activity of a catalyst. The highest j_p acquired for the methanol oxidation is 22.3 mA cm^{-2} on Pd_{0.8}Pt_{0.2}/Ti, which is four times higher than that on the Pt/Ti electrode and three times that on the Pd/Ti electrode. The results indicate that Pt is highly susceptible to CO poisoning. CO reduces the catalyst activity by blocking active sites normally available for fuel chemisorption and dissociation and hindering any further reaction. In addition, the E_s for Pd_{0.8}Pt_{0.2}/Ti shows an evidently negative shift compared to the Pd/Ti and Pt/Ti electrodes, which represents an improvement in the electrocatalytic kinetics [64, 70, 80, 214, 226].

Figure 6.4. CV curves of the catalysts in 1.0 M methanol + 1.0 M KOH solution at a scan rate of 50 mV s^{-1} , 298 K.

Table 6.2. The electrochemical performances of as-synthesized catalysts for methanol electrooxidation in 1.0 M methanol + 1.0 M KOH solution at a sweep rate of 50 mV s⁻¹, 298 K.

Catalysts	E_s / V	E_p / V	j_p / mA cm ⁻²	j at -0.4 V / mA cm ⁻²
Pd/Ti	-0.51	-0.22	7.7	0.5
Pd _{0.8} Pt _{0.2} /Ti	-0.53	-0.23	22.3	2.1
Pd _{0.5} Pt _{0.5} /Ti	-0.53	-0.25	13.2	0.7
Pd _{0.2} Pt _{0.8} /Ti	-0.53	-0.24	7.4	0.8
Pt/Ti	-0.52	-0.27	5.4	1.0

Figure 6.5 is the CA curves showing the different stability of the Pd_xPt_{1-x}/Ti catalysts for methanol electrooxidation. The potential was constantly held at -0.4 V and the change in current with time was recorded and plotted. As can be seen, there is a continuous current drop with test time elapsing, which is very rapid at the initial stage, then followed by a much slower decay. The rapid current decay means the quick poisoning phenomena on the catalyst surface, indicating the low tolerance to carbonaceous or CO intermediates formed during the methanol oxidation reaction. Based on the CA examinations, it is obviously found that the decreasing rate of the current on Pd_{0.8}Pt_{0.2}/Ti catalyst is the lowest, indicating that the Pd_{0.8}Pt_{0.2}/Ti catalyst possesses the best stability for methanol oxidation.

Figure 6.5. CA curves of the catalysts for methanol oxidation in 1.0 M methanol + 1.0 M KOH solution, measured at a constant potential -0.4 V.

6.3.3 Ethanol electrooxidation on Pd_xPt_{1-x}/Ti

The ethanol electrooxidation reaction on the Pd_xPt_{1-x}/Ti electrodes was performed in a 1.0 M ethanol + 1.0 M KOH solution at a scan rate of 50 mV s⁻¹. The curves are shown in Figure 6.6 and the corresponding performance data of E_s , E_p , j_p and j at -0.4 V are listed in Table 6.3. The j_p on Pd_{0.8}Pt_{0.2}/Ti is 20.0 mA cm⁻², much higher than 11.1 mA cm⁻² on Pd/Ti and 1.9 mA cm⁻² on Pt/Ti. The acquired j at -0.4 V for ethanol oxidation is 8.8 mA cm⁻² on Pd_{0.5}Pt_{0.5}/Ti, which is about two times that on Pd/Ti and six times that on Pt/Ti. The E_s on the bimetallic catalysts is all negative to the pure Pd/Ti and Pt/Ti. The negative shift of the onset potential implies an improvement in the electrocatalytic kinetics benefiting from a synergistic effect between Pd and Pt. The results also indicate that the content of Pd and Pt in the Pd_xPt_{1-x}/Ti catalysts has an obvious influence on the catalytic activity for ethanol oxidation. The Pd_{0.8}Pt_{0.2}/Ti exhibits the highest electrooxidation current and Pd_{0.5}Pt_{0.5}/Ti

has the most negative onset potential. However, the pure Pt/Ti displays the worst catalytic activity for ethanol electrooxidation in alkaline medium. These bimetallic catalysts should have a potential application for the development of direct ethanol fuel cells because ethanol is a more attractive and friendly fuel [28, 210, 211, 227-232].

The overall oxidation reaction equation for the direct ethanol fuel cells in alkaline medium is:

But in fact, the ethanol electrooxidation reaction is considered to be very complex and the reaction will proceed in multiple steps because several intermediates and reaction products will be formed. Those parallel reactions will cause a considerable reduction of the fuel efficiency and produce undesirable by-products. The most possible anodic reaction of the ethanol oxidation in alkaline medium could be written as follows:

The acetic acid formed is the main intermediate during the ethanol oxidation reaction in alkaline medium and may not be further oxidized. The breaking of the C–C bond for totally oxidizing ethanol to CO₂ is a major problem in the ethanol electrooxidation reaction [233].

Figure 6.6. CV curves of the catalysts in 1.0 M ethanol + 1.0 M KOH solution at a scan rate of 50 mV s⁻¹, 298 K.

Table 6.3. The electrochemical performances of as-synthesized catalysts for ethanol electrooxidation in 1.0 M ethanol + 1.0 M KOH solution at a scan rate of 50 mV s⁻¹, 298 K.

Catalyst	E_s / V	E_p / V	j_p / mA cm ⁻²	j at -0.4 V / mA cm ⁻²
Pd/Ti	-0.68	-0.26	11.1	4.8
Pd _{0.8} Pt _{0.2} /Ti	-0.69	-0.24	20.0	6.4
Pd _{0.5} Pt _{0.5} /Ti	-0.74	-0.42	9.2	8.8
Pd _{0.2} Pt _{0.8} /Ti	-0.64	-0.29	4.7	2.5
Pt/Ti	-0.63	-0.30	1.9	1.3

The stability for the ethanol electrooxidation on Pd_xPt_{1-x}/Ti electrodes was investigated using the CA method. The results are shown in Figure 6.7. The current decays very rapidly

on Pt/Ti, but, relatively slowly on Pd/Ti. The ratio of Pd and Pt in the $\text{Pd}_x\text{Pt}_{1-x}/\text{Ti}$ catalysts significantly affects the stability. The $\text{Pd}_{0.8}\text{Pt}_{0.2}/\text{Ti}$ shows the best stability for ethanol oxidation. The good stability should be contributed by the relatively lower chemisorption ability of the bimetallic catalysts or the quick removal of the adsorbates.

Figure 6.7. CA curves of the catalysts for ethanol oxidation in a 1.0 M ethanol + 1.0 M KOH solution, measured at a constant potential -0.4 V.

6.3.4 Isopropanol electrooxidation on $\text{Pd}_x\text{Pt}_{1-x}/\text{Ti}$

Figure 6.8 illustrates the CV curves of isopropanol electrooxidation on the $\text{Pd}_x\text{Pt}_{1-x}/\text{Ti}$ electrodes. The corresponding performance data of E_s , E_p , j_p and j at -0.4 V are listed in Table 6.4. Similar to methanol and ethanol oxidation, the electrooxidation of isopropanol is also characterized by two well-defined current peaks in the forward and reverse scans. The peak current density on $\text{Pd}_{0.8}\text{Pt}_{0.2}/\text{Ti}$ is 4.7 mA cm^{-2} , nearly 15 times that on Pt/Ti electrode. The j at -0.4 V is 3.7 mA cm^{-2} on $\text{Pd}_{0.8}\text{Pt}_{0.2}/\text{Ti}$, which is much higher than the currents on the other $\text{Pd}_x\text{Pt}_{1-x}/\text{Ti}$ electrodes. The $\text{Pd}_{0.8}\text{Pt}_{0.2}/\text{Ti}$ shows a relatively better performance for

isopropanol electrooxidation. However, in fact it is very difficult to completely oxidize isopropanol in this kind of low temperature fuel cell system [234-236].

Figure 6.8. CV curves of the catalysts in 1.0 M isopropanol + 1.0 M KOH solution at a scan rate of 50 mV s⁻¹, 298 K.

Table 6.4. The electrochemical performances of as-synthesized catalysts for isopropanol electrooxidation in 1.0 M isopropanol + 1.0 M KOH solution at a scan rate of 50 mV s⁻¹, at 298 K.

Catalyst	E_s / V	E_p / V	j_p / mA cm ⁻²	j at -0.4 V / mA cm ⁻²
Pd/Ti	-0.65	-0.34	3.3	2.8
Pd _{0.8} Pt _{0.2} /Ti	-0.68	-0.32	4.7	3.7
Pd _{0.5} Pt _{0.5} /Ti	-0.70	-0.36	1.9	1.8
Pd _{0.2} Pt _{0.8} /Ti	-0.69	-0.35	0.6	0.6
Pt/Ti	-0.69	-0.31	0.3	0.2

The stability of the $\text{Pd}_x\text{Pt}_{1-x}/\text{Ti}$ electrodes for isopropanol electrooxidation was also studied by the CA method and the results were shown in Figure 6.9. Similarly, the currents decay fast initially and reach a steady state after tested for a long time. The Pt/Ti catalyst shows the worst stability for isopropanol electrooxidation in alkaline medium. The ratio of Pd to Pt in the $\text{Pd}_x\text{Pt}_{1-x}/\text{Ti}$ catalysts also has a big influence on the catalytic activity and stability. The $\text{Pd}_{0.8}\text{Pt}_{0.2}/\text{Ti}$ still performs the best stability for isopropanol oxidation.

Figure 6.9. CA curves of the catalysts for isopropanol oxidation in 1.0 M ethanol + 1.0 M KOH solution, measured at a constant potential -0.4 V.

The bimetallic catalyst, $\text{Pd}_{0.8}\text{Pt}_{0.2}/\text{Ti}$ displays the highest catalytic activity and the best stability for the electrooxidation of alcohols investigated. Meantime, through the comparison of the performance for the different bimetallic catalysts, one knows that the peak current density decreases monotonously with decreasing the Pd content. The composition of the bimetallic catalysts possesses an obvious influence on the catalytic activity, and the presence of the second component exhibits an obviously enhancing effect,

which can be interpreted by the bifunctional mechanism or ligand effect involved in the alcohol electrooxidation [70]. Considering both aspects of performance and price, palladium would be a good alternative electrocatalyst for low temperature fuel cells. The results in the present study clearly show that the Pd_{0.8}Pt_{0.2}/Ti has the best activity and stability for the electrooxidation of methanol, ethanol and isopropanol and is a promising catalyst for DAFCs in alkaline medium. Nevertheless, more detailed studies on the mechanism, the intermediate and product formation will be carried out in the future works, which can be expected to give an important insight into the factors that determine the relative rates of the multiple pathways for alcohol electrooxidation in alkaline medium.

6.4 Conclusions

Nano-structured bimetallic Pd_xPt_{1-x} catalysts supported on Ti substrate with varying Pd:Pt atomic ratio have been successfully prepared by electrodeposition. The electrodeposition method is found to be convenient for synthesizing nanocomposite catalysts on a metal substrate surface. The particle size of the as-synthesized bimetallic catalysts is around 10 nm and uniformly dispersed on the Ti substrate surface without agglomeration. The electrochemical results indicate that the atomic ratio of Pd:Pt possesses a clear influence on the catalytic activity. The Pd_{0.8}Pt_{0.2}/Ti catalyst displays the highest electrocatalytic activity and the best tolerance to carbonaceous intermediates for the investigated alcohols in alkaline medium.

CHAPTER 7 Electro-Oxidation of Methanol and Ethanol on Pd/C Catalyst Promoted by Transition Metal Oxides in Alkaline Media

7.1 Introduction

The study of the electro-oxidation of liquid fuels, such as methanol and ethanol has a direct application due to their use as an alternative fuel in fuel cells. So far the PtRu/C is recognized the best anode catalyst for DMFCs [214, 237]. However, it is obvious that Pt and Ru are costly and their supply is limited. It appears difficult to break through this bottleneck in acidic media. On the other hand, there is an increasing interest in the application of alkaline fuel cells [82-84, 215-217]. It is known that the anodic oxidation of methanol in alkaline media is more feasible than that in acidic media. If direct alcohol fuel cells (DAFCs) are operated in alkaline media, the kinetics is significantly improved and much less expensive catalysts can be used [238, 239]. The search for efficient and inexpensive electrocatalysts is challenging.

In this chapter, we reported the synthesis and characterization of a series of Pd catalysts promoted by transition metal oxides (Pd-oxides/C) using microwave heating method. The catalysis behavior of the as-prepared Pd-oxides/C catalysts for methanol and ethanol oxidation was evaluated in alkaline media. The results show that Pd-oxides/C catalysts have a much better activity than the pure Pd/C. The transition metal oxides, especially the composite oxides, CoNiO_x, have significantly promoting effects on the Pd catalyst for methanol and ethanol electro-oxidation reaction.

7.2 Experimental

7.2.1 Catalyst preparation

A certain amount of aqueous solution of $\text{Co}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2 + \text{Ni}(\text{NO}_3)_2$ was mixed with 200 mg carbon black (Vulcan XC-72R, Cabot Corp., USA). The mixture was dried in an oven at 80 °C to form a gel, followed by heating in a microwave oven. The compound with transition metal oxides dispersed on carbon black surface was then obtained. Subsequently, a quantitative $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ solution was mixed with the composite powders at ambient temperature. The nominal Pd loading was controlled at 50wt% and the molar ratio of Pd to oxides was kept at 4:1. The pH value was adjusted to 10 by a dilute ammonia water, followed by dropwise addition of 0.01 M NaBH_4 solution under ultrasonication. Finally, the products were collected by filtration and washed with distilled water, and then dried at room temperature in a vacuum oven.

7.2.2 Structure characterization

XRD examination was conducted using an X-ray diffractometer (Rigaku D/MAX 2200 V-PC) employing Cu K_α radiation ($\lambda=0.15418$ nm) at a scan rate of 1 °/min. The scan range is from 10 ° to 80 °.

The TEM images of the catalysts were acquired using a JEOL 2010 microscope operating at 160 kV.

The composition of Pd-oxides/C was determined by energy dispersive spectroscopy (EDS, Oxford UK).

7.2.3 Electrode preparation and electrochemical characterization

The Pd-oxides/C powders were dispersed in isopropanol with a 5 wt% Nafion solution and ultrasonicated for 30 min. The above catalyst ink was then deposited on the surface of a glassy carbon electrode (GCE) with a geometric area of 0.33 cm^2 . Before use, the GCE was polished with 50 nm alumina powders. The as-prepared electrode was dried at $80\text{ }^{\circ}\text{C}$ for 30 min in a vacuum oven. The Pd loading was 0.3 mg cm^{-2} .

The electrochemical measurements were carried out in a three-electrode cell at ambient temperature using an electrochemical workstation (Autolab, PGSTAT30). A platinum foil (3.0 cm^2) and a saturated calomel electrode (SCE, 0.241 V versus RHE) were used as the counter and reference electrodes, respectively. The used chemicals were all analytical reagents from Sigma-Aldrich® and the used solution was freshly prepared with deionized water ($\geq 18.2\text{ M}\Omega\cdot\text{cm}$). The electrochemical active surface area (ECSA) of the catalysts was evaluated by the cyclic voltammetry (CV) method. The linear sweep voltammetry (LSV) and chronoamperometry (CA) measurements were carried out for evaluating the electrochemical properties of the catalysts in a N_2 -saturated 1.0 M KOH solution containing 1.0 M methanol or ethanol at a sweep rate 50 mV s^{-1} .

7.3 Results and discussion

7.3.1 Structure and morphology analysis

Figure 7.1 represents the XRD patterns of Pd/C and Pd-oxides/C electrocatalysts. The diffraction peaks at *ca.* 12.7° are for the C (002) plane. The peaks at *ca.* 40.2°, 46.8° and 68.2° represent the Pd (111), Pd (200) and Pd (220) planes respectively, which are the main diffraction peaks of Pd crystallites. No peaks for Co₃O₄, NiO or CoNiO_x oxides were observed and no peak displacements were caused by the addition of oxides. However, the EDS spectra of Pd-oxides/C clearly show the presence of these oxides, which indicates that these oxides mainly exist in an amorphous state.

Figure 7.1. XRD patterns of (a) Pd/C, (b) Pd-Co₃O₄/C, (c) Pd-NiO/C and (d) Pd-CoNiO_x/C.

The mean particle size of the catalysts was calculated from the Pd (111) peak width according to the Scherrer equation [240, 241]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (7.1)$$

where D is the mean particle diameter, λ is the X-ray wavelength, β is the peak width at half height in radians and θ is the diffraction angle. The results are shown in Table 7.1. The particle sizes of Pd calculated from XRD spectra are slightly smaller than those measured by TEM. It is reasonable because the size calculated from XRD generally intends to be smaller than that from TEM images. Nevertheless, there is no obvious change in particle size between Pd/C and Pd-oxides/C.

Table 7.1. Mean particle sizes of the catalysts.

Sample	Pd/C	Pd-Co ₃ O ₄ /C	Pd-NiO/C	Pd-CoNiO _x /C
Particle size of Pd (nm) ^a	4.7	3.9	4.2	4.1
Particle size of Pd (nm) ^b	5.8	4.9	5.4	5.1

^a Determined by XRD; ^b Estimated by TEM

The morphology and size distribution of the catalysts were obtained by TEM. The TEM images of Pd/C and Pd-oxides/C electrocatalysts are given in Figure 7.2. The TEM images clearly exhibits that the Pd metal particles have been successfully anchored on the supports without aggregation. The Pd particle size is about 5.3 ± 0.4 nm, quite uniform and narrowly dispersed.

Figure 7.2. TEM images of (a) Pd/C, (b) Pd-Co₃O₄/C, (c) Pd-NiO/C and (d) Pd-CoNiO_x/C. Scale bar = 20 nm.

Figure 7.3 is the EDS spectra of the catalysts. Pd and C elements can be detected evidently in all the samples. The Cu elements are derived from the copper mesh substrate. The characteristic peaks of Co, Ni and O elements can be observed in the corresponding EDS spectrum, which corroborates the existence of the transition metal oxides.

Figure 7.3. EDS spectra of (a) Pd/C, (b) Pd-Co₃O₄/C, (c) Pd-NiO/C and (d) Pd-CoNiO_x/C.

7.3.2 Electrochemical properties of the Pd-oxides/C catalysts

The activity of an electrode is not only controlled by the catalytic properties but also by the ECSA and the microstructure. The peaks on CV curves in the potential region $-500 \text{ mV} < E < -200 \text{ mV}$ (vs. SCE) under alkaline conditions are associated with the hydrogen

adsorption process in the anodic scan [72, 88]. The ECSA is calculated by using the Equation (7.2) through the CV measurement in the N₂-saturated 1.0 M KOH solution.

$$ECSA = k \times \frac{Q_H}{[M]} \quad (7.2)$$

where Q_H represents the coulombic charge for hydrogen desorption (mC cm⁻²) and $[M]$ represents the Pd loading in the electrode. Based on Figure 7.4, the calculated ECSA values are 27.5, 26.9, 28.1, 27.2 m²/g for Pd/C, Pd-Co₃O₄/C, Pd-NiO/C and Pd-CoNiO_x/C, respectively. They are quite similar, indicating that the alcohol oxidation reaction mainly depends on the inherent catalytic activity of the catalysts [242-244].

Figure 7.4. CV results of the Pd/C and Pd-oxides/C catalysts in 1.0 M KOH solution. The scan rate is 5 mV/s.

The electrochemical activity of the electrocatalysts for methanol oxidation in alkaline media was investigated by the LSV method. The experiments were carried out in a three electrode cell with a N₂-saturated 1.0 M KOH solution containing 1.0 M methanol at a

sweep rate in 50 mV s^{-1} ranging from -0.8 V to 0.4 V , and the results are shown in Figure 7.5. Some values of the Pd/C and Pd-oxides/C for the methanol electrooxidation reaction, such as the onset potential (E_s), the anodic peak potential (E_p), the current densities (j_p) at E_p and at a potential of -0.3 V (vs. SCE) are tabulated in Table 7.2. All the activities were normalized based on the surface area of the working electrode. The current density at the peak potential (j_p) is normally a very important parameter to evaluate the catalytic activity of catalysts. It can be clearly observed that Pd-oxides/C catalysts represent rather higher catalytic activity than the pure Pd/C catalyst. The j_p of the Pd-CoNiO_x/C is 61.12 mA cm^{-2} , more than three times 18.48 mA cm^{-2} of the Pd/C. The E_s of the Pd-CoNiO_x/C shifted negatively 30 mV compared with Pd/C. It is well known that the voltage output of a fuel cell at a current density depends on the half cell potentials of both the anode and cathode, therefore, the more negative the anodic potential the higher full cell voltage will be, providing the cathodic potential is fixed [86, 223, 232, 245, 246].

Figure 7.5. LSV curves of Pd/C and Pd-oxides/C catalysts in 1.0 M methanol + 1.0 M KOH solution.

Table 7.2. The electrochemical performance of Pd/C and Pd-oxides/C catalysts in 1.0 M methanol + 1.0 M KOH solution.

Sample	E_s (V)	E_p (V)	j_p (mA cm ⁻²)	j at -0.3 V (mA cm ⁻²)
Pd/C	-0.47	-0.08	18.48	3.93
Pd-Co ₃ O ₄ /C	-0.49	-0.11	40.92	6.52
Pd-NiO/C	-0.50	-0.12	46.60	10.11
Pd-CoNiO _x /C	-0.52	-0.09	61.12	14.0

The stability of the electrocatalysts for methanol oxidation was investigated using the CA method at a constant potential -0.3 V. As can be seen in Figure 7.6, there is a continuous current drop with test time elapsing, which is rapid at the beginning, followed by a slower decay. The decreasing rate of current density of Pd/C is the fastest, indicating that the Pd/C has the worst tolerance for carbonaceous intermediates. On the contrary the Pd-CoNiO_x/C shows the best stability for methanol electro-oxidation.

Figure 7.6. CA curves of Pd/C and Pd-oxides/C catalysts in 1.0 M methanol + 1.0 M KOH solution.

The catalytic activity of the Pd/C and Pd-oxides/C for ethanol oxidation was also measured by the LSV method (see Figure 7.7). The sweep rate is 50 mV s^{-1} in the potential range from -0.8 V to 0.4 V . Some electrochemical properties of the catalysts for ethanol oxidation in alkaline media are listed in Table 7.3. As shown, the j_p and j at -0.3 V of Pd-oxides/C are all much higher than that of Pd/C, indicating that Pd-oxides/C catalysts have considerably better ethanol oxidation activity than the Pd/C. Meanwhile, the E_s of Pd-oxides/C catalysts shows an obviously negative shift compared to the -0.59 V of Pd/C. The Pd-CoNiO_x/C exhibits the highest catalytic activity.

Similar to methanol oxidation, CO is formed during the oxidation of ethanol. This CO species can block the surface of the catalyst and hinder any further reaction. For this reason a number of co-metals or oxides are usually added to the catalyst to facilitate CO removal by oxidation to CO₂ [247-254]. In this case these transition metal oxides can activate water either from solution or hydroxide ions at lower potentials than Pd, and the activated water oxidize the adsorbed CO species, therefore to liberate active sites [5].

Figure 7.7. LSV curves of Pd/C and Pd-oxides/C catalysts in 1.0 M ethanol + 1.0 M KOH solution.

Table 7.3. The electrochemical performance of Pd/C and Pd-oxides/C catalysts in 1.0 M ethanol + 1.0 M KOH solution.

Sample	E_s (V)	E_p (V)	j_p (mA cm ⁻²)	j at -0.3 V (mA cm ⁻²)
Pd/C	-0.59	-0.14	21.95	12.17
Pd-Co ₃ O ₄ /C	-0.63	0.07	81.49	21.58
Pd-NiO/C	-0.68	0.08	87.33	27.39
Pd-CoNiO _x /C	-0.67	0.06	110.72	43.67

Figure 7.8. CA curves of Pd/C and Pd-oxides/C catalysts in 1.0 M ethanol + 1.0 M KOH solution.

The stability of the catalysts for ethanol oxidation was also examined by the CA method at a constant potential -0.4 V and the results are shown in Figure 7.8. It can be obviously observed that the current decays rapidly with time in a parabolic style. The Pd-oxides/C catalysts show a higher catalytic activity and better stability. At the same time, the

Pd-CoNiO_x/C still displays the best stability for ethanol oxidation. The results corroborate that the transition metal oxides, especially the CoNiO_x composite material plays a significant role in the catalytic activity enhancement of Pd/C for ethanol oxidation. Thus the Pd-CoNiO_x/C catalyst would have a potential application for direct ethanol fuel cells in alkaline media.

7.4 Conclusions

In summary, Pd/C and Pd-oxides/C catalysts have been successfully obtained by a microwave heating technique. Their structure, composition and morphology were analyzed, and their electrochemical performances were investigated for methanol and ethanol oxidation in alkaline media. The Pd-oxides/C catalysts exhibit much higher catalytic activity than the pure Pd/C. The peak current density of the Pd-CoNiO_x/C catalyst for methanol oxidation in alkaline media is 61.12 mA cm⁻², more than three times 18.48 mA cm⁻² of the Pd/C. For ethanol oxidation, the peak current density is 43.67 mA cm⁻², nearly four times that of the Pd/C. Moreover, the Pd-oxides/C catalysts also show the rather better stability for both methanol and ethanol oxidation in alkaline media. The promotion effect is ascribed to the fact that these transition metal oxides can oxidize CO species at lower potentials, facilitating CO removal. Therefore, these new Pd-oxides/C catalysts should have potential applications for alkaline DAFCs.

CHAPTER 8 Nano-Structured Tungsten Carbide Composites Synthesized by Microwave Heating Method as Catalyst Supports for DMFCs

8.1 Introduction

In DMFCs, because methanol and water are fed directly into the cell, steam reforming is not required. Storage of methanol is much easier than hydrogen as it does not need high pressure or low temperature [62, 63, 90, 93, 255]. The anodic reaction in DMFCs is the oxidation of methanol to produce protons, electrons and CO₂. Currently, platinum is the most widely used catalyst for the methanol electro-oxidation, but its activity is easily poisoned by CO adsorbed on the Pt catalyst. As such, PtRu has gained a significant popularity over Pt. However, the activity for methanol oxidation still needs to be enhanced. Due to the limited supplies of both Pt and Ru, PtRu bimetallic catalysts are relatively costly, which in turn leads to the hindrance of commercialization of DMFCs [256-258].

In order to achieve fine dispersion, high utilization and stable nanoscaled metallic particles, catalyst-supporting strategies have been explored [90]. Carbon particles are frequently used as catalyst supports because of their relative stability in both acidic and basic media, good electric conductivity and high specific surface area. Recently, to further improving the catalytic activity and resistance to intermediates of metallic particles, many efforts have been made to develop new catalyst supporting materials. For examples, novel nano-structured carbon materials, such as carbon nanotubes (CNT) [92, 93] and carbon

nanofibers (CNF) [97] have been investigated as catalyst supports for proton exchange membrane fuel cells (PEMFCs) because of their unique structure and properties. In addition, mesoporous carbon [98], conductive diamonds [103] and conductive oxides [104] have been studied as catalyst supporting materials for PEMFCs or DMFCs.

Recently, carbides of transition metals, especially tungsten carbide (WC) materials, have attracted a considerable attention due to its special properties, such as the stability in acid solutions and anodic potentials, an exceptionally strong resistance to catalytic poisons, a higher activity toward the dissociation of methanol and water, and good electrical conductivity [105, 106, 259, 260]. The activity and stability of pure WC can be further improved by formation of WC-containing composites, such as WC-silica [261] and WC-carbon [262]. Jeon et al. [263] prepared and investigated the Pt/WC/C catalyst for methanol electrooxidation. The WC/C material was synthesized using a high temperature reduction method, followed by depositing Pt on the surface. The results indicated that Pt particles were selectively deposited on the WC surfaces and a hydrogen spillover behavior was observed on the Pt/WC/C catalyst. The Pt/WC/C demonstrated the improved CO electrooxidation activity by giving a 42% higher specific activity for MOR as compared with the Pt/C catalyst. Wang et al. [107] synthesized the WC/graphitic carbon nanocomposite using an in situ simultaneous synthetic route at 1000 °C with an ion exchange resin as a carbon resource, WO_4^{2-} as a tungsten precursor and $[\text{Fe}(\text{CN})_6]^{4-}$ as the graphitization catalyst. The WC/graphitic composite were demonstrated as a highly efficient catalyst support for methanol electrooxidation due to its specific structure and the combined functionalities of WC and graphitic carbon. The Pt/WC/graphitic catalyst exhibits a mass activity of $205.6 \text{ mA mg}_{\text{Pt}}^{-1}$, three times higher than Pt/C. Ganesan et al. [264] investigated the platinized mesoporous WC for MOR. The precursor of the

mesoporous WC was synthesized by polycondensation and then calcined at 1173 K. The mass activity of 3.5% Pt/meso-WC was $1851 \text{ mA mg}_{\text{Pt}}^{-1}$, which was higher by a factor of six than the activity of $307 \text{ mA mg}_{\text{Pt}}^{-1}$ of the commercial 20wt% Pt-Ru/C E-TEK. Based on the results, the role of WC was not only a support for Pt, but also an active phase working together with Pt for MOR. Joo et al. [109] prepared and characterized the WC supported on carbon black (Vulcan XC-72) using two different tungsten precursors. The carbonization was carried out at 1000°C for 3 hrs. The as-prepared catalysts, Pt/WC-W and Pt/WC-A, showed a much better activity for MOR than E-TEK. Zhao et al. [111] studied the origin of the high performance of Pt catalysts supported on WC/multi-walled carbon nanotubes (MWCNT) for MOR. The WC/MWCNT was synthesized using a microwave heating method, but no information was provided for particle size and distribution of the WC/MWCNT. The results indicate that the synergistic effect between Pt nanoparticles and WC and the structural effect of the MWCNTs could be the reasons for the high activity. Some differently structured WC and WC-containing materials as catalyst supports have also been investigated for hydrogen electrooxidation, ethanol electrooxidation and oxygen electroreduction [265-271]. However, the conventional synthetic routes using solid carbon precursors such as carbon black or carbon nanotubes often suffer from the aggregation of WC particles, leading to the damage of the original support materials and loss of activity and stability. The common high temperature heating method is time-costing, resulting in the relatively large particle size and low specific surface area.

In this chapter, we report a novel and simple route to in-situ synthesize nano-structured WC-carbon composites (briefed as WC/C_x) using water soluble glucose as C precursor and ammonium metatungstate as W precursor by a microwave heating method, which is a versatile technique for the synthesis of nano-materials [272]. The results show that the Pt

catalyst supported on WC/C_x composites exhibits a much better catalytic activity and stability as compared to the Pt supported on Vulcan carbon XC-72.

8.2 Experimental

8.2.1 Preparation of the WC-containing composite supports

Materials used in this work include glucose (99.9%, C₆H₁₂O₆, Sigma-Aldrich), Pluronic P123 (EO₂₀PO₇₀EO₂₀, BASF®), ammonium metatungstate (AMT, (NH₄)₆H₂W₁₂O₄₀ · xH₂O, Sigma-Aldrich), hexachloroplatinic acid (H₂PtCl₆ · xH₂O, Sigma-Aldrich), carbon black (Vulcan XC-72, Cabot Corp.), Methanol (99.99%, Sigma-Aldrich) and Nafion solution (5wt% in isopropanol and water, DuPont).

First, 5 g glucose and Pluronic P123 (P123 : glucose = 5wt%) were mixed in 60 mL de-ionized water under magnetic stirring for 30 minutes. The pH value of the above mixture was adjusted to 1 by addition of 2 M HCl solution, followed by adding a certain amount of AMT into the solution. Here, the nominal molar ratios of WC:C were 1:1, 1:10 and 1:20 (the final products were assigned as WC/C, WC/C₁₀ and WC/C₂₀, respectively). The above mixtures were dried completely at 80°C, followed by grinding in an agate mortar to form a fine powder. The powders were heated in a microwave oven (JJ-101) for 30 min at a nitrogen atmosphere, then cooled down to room temperature. The temperature of the reactants was monitored by an infrared temperature detector in the microwave oven. The heating temperature was set at 1000 °C, which can be achieved in 30 seconds. The obtained products were treated in 2 M NaOH solution and finally filtered with distilled water.

8.2.2 Preparation of the catalysts

The catalysts were prepared using the improved impregnation method [273, 274]. First, the quantitative WC/C_x composite supports were dispersed into a H₂PtCl₆ aqueous solution and the Pt loading was controlled at 20wt% to the supports. After ultrasonic mixing for 30 minutes, the suspension was stirred at 400 rpm to form a thick slurry, followed by drying the slurry in an oven at 60 °C. After that, the agglomerates were ground in an agate mortar. The obtained powders were heated in a tube furnace at 300 °C under a 5% H₂ balanced with Ar atmosphere for 2 hrs, followed by cooling down to room temperature in nitrogen atmosphere. The Pt catalyst supported on Vulcan XC-72 with a Pt loading amount of 20wt% (Pt/VC) was also prepared for comparison according to the same preparation procedure.

8.2.3 Physical and structural characterization

X-ray diffraction (XRD) patterns of the catalysts were obtained on an XRD-6000 diffractometer employing Cu K_α radiation ($\lambda=0.15418$ nm) at a scan rate of 5 °/min and the scan range from 20 ° to 80 °. The composition and state of the WC/C_x composite materials were examined by Raman spectroscopy (Renishaw[®] RM1000). The morphology of the catalysts was studied by a transmission electron microscope (TEM, JEOL 2010) operating at 200 kV. The WC content was determined by energy dispersive spectroscopy (EDS, Oxford UK). The nitrogen adsorption and desorption isotherms at 77K were measured

using a Micrometrics TriStar II 3020 system. Brunauer–Emmett–Teller (BET) surface areas were estimated over a relative pressure (P/P_0) range from 0.05 to 0.30.

8.2.4 Electrochemical characterization

The electrochemical measurements were carried out in a conventional three-electrode cell using a potentiostat/galvanostat (Autolab PGSTAT30) at ambient temperature. A glassy carbon electrode (GCE, 5 mm in diameter) was used as the working electrode, and a platinum wire as the counter electrode, a saturated calomel electrode (SCE, 0.241 V *versus* RHE) as the reference electrode. A salt bridge with a Luggin capillary was connected to the reference electrode. To load the electrocatalyst suspension onto GCE, the electrocatalyst powder was ultrasonically mixed in ethanol to form a homogeneous ink with the catalyst concentration 5 mg/mL, followed by dropping 10 μ L of the electrocatalyst ink onto the surface of GCE. Then, 10 μ L 0.5 wt% Nafion solution was coated onto the surface to fix the electrocatalysts. All potentials reported in the present study were given versus SCE reference electrode. The electrocatalytic activity for methanol oxidation was characterized by collecting CV curves in a nitrogen-purged 0.5 M H_2SO_4 + 0.5 M methanol solution at a scan rate of 50 mV/s. The stability was examined by CA test at a constant potential 0.6 V.

8.3 Results and discussion

8.3.1 Structure and morphology analysis

XRD was used to determine the presence of crystalline Pt on the supports and the average crystallite sizes of the tungsten carbides. As shown in Figure 8.1, the diffraction peaks representing a simple hexagonal phase of WC were observed at 31.4° (001), 35.6° (100) and 48.3° (101) from the different WC/C_x supports. The peaks around 40.1° (111), 46.4° (200) and 67.5° (220) indicate that Pt was successfully loaded on to the supports. There are no impurity peaks corresponding not only to tungsten trioxide or metallic tungsten, but also to W₂C (hcp-phase) and WC_{1-x} (fcc-phase). The last two tungsten carbides are common impurities observed if the preparation conditions are not carefully controlled [110, 275].

Figure 8.1. XRD patterns of the as-prepared catalysts: (A) Pt/WC/C; (B) Pt/WC/C₁₀; (C) Pt/WC/C₂₀; (D) Pt/VC. Note: (♦) for WC peaks, (●) for Pt peaks.

Figure 8.2 is the Raman spectra showing the graphitic modes of carbon in the WC/C_x composites, indicating that the carbon exists in both graphitic and nongraphitic forms [104]. The spectra illustrate two main peaks at 1594 (G band) and 1340 cm⁻¹ (D band). The G band corresponds to the E_{2g} vibration of graphitic carbon with a sp² electronic configuration. On the other hand, the D band is associated to the A_{1g} mode of diamond-like carbon with a sp³ configuration. The graphitic degree of a carbon material is evaluated by using the relative intensity ratio of the G band (I_G) to D band (I_D) [276]. It is worth to note that the I_G/I_D ratios of carbon in the various supports decreased with increasing the carbon content, which is consistent with the phenomenon observed by Nakamizo et al. [277]. The I_G/I_D ratio for WC/C has been calculated to be 1.17 (>1), which indicates that the carbon in the WC/C composite has a well defined crystalline structure.

Figure 8.2. Raman spectra for the catalyst supports: (A) WC/C; (B) WC/C₁₀; (C) WC/C₂₀.

Figure 8.3 shows the nitrogen adsorption-desorption isotherms of the as-prepared catalyst supports. The adsorption isotherms were measured at 77 K, by gradually increasing the nitrogen pressure, P , from zero up to the saturation pressure, P_0 . The initial part of the curves can be attributed to monolayer-multilayer adsorption. The capillary condensations of all the samples conformably occurred at a high pressure, around $P/P_0 = 0.8\sim 1.0$, indicating a classical accumulation of nanoparticles with high surface area. However, the heights of the hysteresis loops are different with variation of WC content. Evidently, the hysteresis loop increased with decreasing the WC content. The BET surface area is $85.8 \text{ m}^2 \text{ g}^{-1}$ for WC/C, and significantly increases to $294.6 \text{ m}^2 \text{ g}^{-1}$ for WC/C₂₀, which is higher than $267 \text{ m}^2 \text{ g}^{-1}$ of the commercial Vulcan XC-72 [61, 278].

Figure 8.3. Adsorption (solid symbols) and desorption (open symbols) isotherms of nitrogen for the catalyst supports: WC/C ($\square$), WC/C₁₀ ($\triangle$), WC/C₂₀ ($\circ$).

Table 8.1 summarizes the properties of the different WC/C_x supports. The WC contents in the supports were analyzed by EDS. The final molar ratios of WC:C are slightly

lower than the nominal values, which could be due to that the small amounts of uncarbonized metallic tungsten or tungsten oxides were removed in the alkali treatment process. As calculated by Scherrer equation choosing the WC (001) peaks [279-281], the crystallite sizes of WC slightly decreased with increasing the carbon content, which could be due to the relatively large carbon content that facilitates the dispersion of W precursors and restrains the growth of WC particles. The results indicate that the nano-structured WC/C_x composites are in-situ synthesized successfully using the microwave heating method.

Table 8.1. The properties of the as-prepared WC/C_x composite supports.

Catalyst supports	Crystallite Size ^a / nm	I _G /I _D	BET Surface Area / m ² g ⁻¹	WC:C molar ratio ^b
WC/C	12.6	1.17	85.8	1 : 1.5
WC/C ₁₀	9.2	0.85	256.8	1 : 11
WC/C ₂₀	8.4	0.83	294.6	1 : 21.6

^a calculated by XRD; ^b obtained by EDS.

TEM images and EDS spectra of the different catalysts are shown in Figure 8.4 and the size distribution of Pt is given in Figure 8.5. In the case of Pt/WC/C, the average particle size is 5.4±2 nm and the dispersion of Pt is characterized by a broad distribution with a large number of aggregates (Figure 8.4a). The low specific surface area of supporting materials is not preferable for obtaining a fine dispersion of catalysts [136, 282]. The Pt particles densely cover the WC/C surfaces but do not form bigger particles. It was confirmed by the high resolution TEM images (Figure 8.4b). For Pt/WC/C₁₀ and Pt/WC/C₂₀, the average particle size of Pt is 4.0±1 and 3.0±1 nm, respectively. The reduction in the Pt

particle size could be due to the increase of the specific surface area of the catalyst supports. The Pt particle size in the Pt/VC catalyst is around 2.8 ± 1 nm. The particle sizes of Pt on the different supports obtained by TEM agree quite well with the results calculated by XRD using the Pt (111) peaks (see Table 8.2).

Figure 8.4. TEM images of (low (a) and high (b) magnification) Pt/WC/C; (c) Pt/WC/C₁₀; (d) Pt/WC/C₂₀; (e) Pt/VC; (f) EDS spectra of the different catalysts.

Figure 8.5. The distribution histogram of the Pt particle size in (a) Pt/WC/C, (b) Pt/WC/C₁₀, (c) Pt/WC/C₂₀, (d) Pt/VC.

8.3.2 Catalytic activity and stability analysis

The electrocatalytic activity of the Pt catalysts on the different supports for DMFCs was examined at room temperature. Figures 8.6 and 8.7 show the CV curves of the catalysts in a nitrogen-saturated 0.5 M H₂SO₄ solution in the absence and presence of 1.0 M CH₃OH, respectively. In the CV curves measured in the 0.5 M H₂SO₄ solution (Figure 8.6), the hydrogen adsorption/desorption area was used to evaluate the electrochemical surface area (ECSA). The estimated ECSA values are summarized in Table 8.2. The Pt on the WC/C_x composite supports showed much higher ECSA values than that (297.4 cm²/mg) of the Pt/VC. But from the TEM and XRD measurements, the diameters of Pt particles in Pt/WC/C_x catalysts were found to be 3-6 nm. Thus, the much higher ECSA values for the Pt/WC/C_x catalysts could be accounted for by the active participation of WC in the electrochemical hydrogen oxidation together with Pt. The similar interplay between Pt and WC was also observed for electrooxidation of methanol on Pt/WC [108, 110, 263, 264, 283, 284]. WC alone without Pt showed a low activity under the same reaction condition. Thus hydrogen may adsorb first on Pt and then migrate to WC surface probably by a hydrogen spillover mechanism [285, 286]. The electrooxidation then takes place on both Pt and WC, and gives a higher mass activity than the activity obtained from Pt alone. The ECSA of the Pt/WC/C₁₀ is higher than Pt/WC/C, most likely due to the smaller size and much better dispersion of the Pt nanoparticles on WC/C₁₀. On the other hand, the ECSA of the Pt/WC/C₂₀ is smaller than Pt/WC/C₁₀. This is because the WC particles in the WC/C₂₀ support may be partially capped or surrounded by the excessive carbon so that some of them become electrochemically inaccessible.

Figure 8.6. Mass-normalized CV curves of the different catalysts in a N_2 -saturated 0.5 M H_2SO_4 solution at a scan rate of 20 mV/s.

The methanol oxidation activity is reflected by the magnitude of the anodic peak current in the forward scan while the peak in the reverse scan is due to the reactivation of Pt associated with the removal of the residual carbon species [287]. As shown in Figure 8.7, in the forward scan, the onset potential on Pt/WC/C and Pt/WC/C₁₀, is 0.34 V, showing a negative shift as compared to 0.38V of Pt/WC/C₂₀ and Pt/VC. Their peak potentials for MOR are located at 0.60 V for Pt/WC/C and Pt/WC/C₁₀, 0.62 V for Pt/WC/C₂₀ and Pt/VC catalysts. The mass catalytic activities (peak current density, which have been normalized to the Pt loading) are 198, 260, 313 and 275 mA/mg for Pt/VC, Pt/WC/C, Pt/WC/C₁₀ and Pt/WC/C₂₀, respectively. The best catalytic activity was obtained on Pt/WC/C₁₀. The results show that the content of WC has a great impact on the performance of the electrocatalysts.

The lower specific surface area of the WC/C supporting materials results in the relatively poor dispersion of Pt nanoparticles, decreasing the utilization efficiency of Pt catalysts. On the other hand, because Pt particles are selectively deposited on the WC surfaces as investigated by Jeon et al. [263], some WC particles in the WC/C₂₀ composite have been covered or shielded by the passive carbon film, resulting in less contribution of WC to MOR. The Pt/WC/C₁₀ catalyst shows the highest mass activity and relatively low onset potential, which are desired for MOR [264]. Further reducing the Pt particle size would enhance the catalytic activity. The current peak ratio of I_f (the forward peak current density)/ I_b (the backward peak current density) could be used to express the CO tolerance on Pt surface. The higher I_f/I_b ratio means a better CO tolerance. The I_f/I_b ratios are 0.68, 1.13, 1.08 and 1.02 for Pt/VC, Pt/WC/C, Pt/WC/C₁₀ and Pt/WC/C₂₀, respectively. This result further demonstrates the enhanced CO tolerance on Pt/WC/C_x catalysts. The promotion effect of WC is obvious and the such improvements can be explained by the synergistic effect between the WC and Pt nanocrystals [265]. The electrooxidation of methanol is a very complex reaction involving many poisonous intermediate species that may poison the Pt surface by blocking active sites for the further reactions. In the presence of Pt, WC is active in the electrochemical methanol oxidation and water decomposition [108, 284]. The formation of hydroxyl groups from water activation is essential for the removal of metal-poisoning CO from the surface.

Figure 8.7. Mass-normalized CV curves of the different Pt catalysts in N_2 -saturated 0.5 M H_2SO_4 + 1 M CH_3OH at a scan rate of 50 mv/s.

Table 8.2. The properties and electrochemical parameters of the different catalysts.

Catalysts	Pt particle size / nm	ECSA / $cm^2 mg^{-1}$	Onset potential / V	Peak current / $mA mg_{Pt}^{-1}$	Peak potential / V	Ratios of I_f/I_b
Pt/WC/C	4.8	368.2	0.34	260	0.60	1.13
Pt/WC/C ₁₀	4.0	423.6	0.34	313	0.60	1.08
Pt/WC/C ₂₀	3.2	405.8	0.38	275	0.62	1.02
Pt/VC	3.3	297.4	0.38	198	0.62	0.68

The stability of the catalysts was evaluated by the CA method at a constant potential 0.6 V and the results are shown in Figure 8.8. As can be seen, there is a continuous current drop with testing time, which is very rapid at the initial stage, followed by a much slower decay. The rapid current decay represents the poisoning effect on the catalyst surface. The

Pt/VC catalyst shows the fastest decrease among these catalysts, indicating the lowest tolerance to CO or carbonaceous intermediates formed during the methanol oxidation reactions. The Pt/WC/₁₀ catalyst exhibits the best stability due to the high synergistic effect between WC and Pt as discussed above.

Figure 8.8. CA curves for (A) Pt/VC, (B) Pt/WC/C, (C) Pt/WC/C₁₀ and (D) Pt/WC/C₂₀ catalysts in N₂-saturated 0.5 M H₂SO₄ + 1 M CH₃OH at a constant potential: 0.6 V.

8.4 Conclusions

In summary, the nano-structured WC/C_x composites that could act as highly efficient catalyst supports for DMFCs were successfully in-situ synthesized using water soluble carbon and tungsten sources by a microwave heating method. It was found that the WC crystallite size decreased with increasing the carbon content. The performance of the

Pt/WC/C_x catalysts for MOR was studied and evaluated in acidic media. The Pt/WC/C_x catalysts exhibited an evidently better performance and stability as compared to the Pt/VC catalyst, due to a synergistic effect of WC on the electrocatalysis of Pt catalysts for MOR. The catalytic activity of the catalysts is significantly affected by the WC content and the structure of the supports. The Pt/WC/C₁₀ shows the best activity and stability, which is considered to be due to the high synergistic effect from WC/C₁₀ and better utilization of Pt.

CHAPTER 9 Conclusions and Recommendations for Future Work

9.1 Conclusions

In this thesis, the major works are focused on the development of novel proton exchange membranes to fulfill the requirements of PEMFCs or DMFCs operating at high temperatures and low humidity environments. At the same time, some research works on the development of anode catalysts and catalyst supporting materials have been done. The following conclusions can be drawn:

1. A novel inorganic PEM based on the self-assembled HPW/meso-silica was developed for the high temperature and low humidity operation of DMFCs. The micro-structure of the HPW/meso-silica is significantly affected by the HPW content. The proton conductivity of the inorganic membranes depends on the HPW content and the micro-structure formed between HPW and meso-silica. The formation of ordered mesoporous arrays with HPW anchored in mesoporous silica walls is essential for proton transportation. This kind of inorganic membrane inherits the inherently chemical and structural stability of the inorganic matrix. The best conductivities obtained on the 25wt% HPW/meso-silica inorganic membrane were 0.091 S/cm at 100 °C under 100% RH and 0.034 S/cm at 200 °C under 3% RH, respectively. The conductivity stability was very good at each measured temperature. The maximum power density for the methanol/O₂ cell reached to 19 mW/cm² at 25 °C and increased substantially to 235 mW/cm² at

150 °C. In the stability test, the initial cell current was 440 mA/cm² and decreased to 402 mA/cm² over a testing period of 42 hrs. This reduction could be due to the degradation of the electrodes at the high temperature operation. The good performance and stability demonstrate the promising potential of the self-assembled HPW/meso-silica inorganic membrane for high temperature and low humidity applications in PEMFCs and DMFCs. The significant increase of the cell performance with the testing temperature indicates the significantly enhanced reaction rates for both the fuel oxidation and oxygen reduction reactions at elevated high temperatures, which would lead to significantly simplify the fuel cell systems.

2. The self-assembly technique was also advanced to develop a novel meso-Nafion membrane. Very different from conventional modifications, the introduced meso-structure in the Nafion membrane via the self-assembly process does not destroy the inherent properties of the Nafion ionomers. The meso-Nafion membrane showed a much higher water retention ability and higher proton conductivity. The cell with the meso-Nafion membrane showed a much higher power output and a much better stability, particularly under reduced RH and elevated temperatures as compared to the pristine Nafion 115. The ability to retain water even under completely dry conditions suggests a possibility to develop PEMFCs without an external humidity supplier.
3. The impregnation of HPW molecules into the meso-Nafion membranes may further increase the proton conductivity and dimensional stability. At the same time, in order to resolve the HPW leaching problem, an innovative synthesis methodology was developed to fabricate a multilayer membrane consisting of a central layer (meso-Nafion membrane impregnated with HPW) and two side layers. The multilayer membrane showed the significantly higher conductivity than the pristine Nafion

membrane under both high and low humidity conditions, which can be attributed to the improved water retention ability and the uniformly dispersed HPW molecules introduced. Meanwhile, this new multilayer membrane can effectively prevent the HPW leaching. The higher water retention ability significantly improved the cell stability and enhanced the tolerance to RH variations. In addition, when operated at 120 °C, the cell with the multilayer membrane represented a much better performance and stability compared to the cell with Nafion 1135. Thus the multilayer membrane can significantly widen the RH operating window of the PEMFCs at elevated temperatures.

4. The nano-structured bimetallic $\text{Pd}_x\text{Pt}_{1-x}$ catalysts supported on Ti substrate with varying Pd:Pt atomic ratio have been successfully prepared by an electrodeposition method, which was found to be convenient for synthesizing nanocomposite catalysts on metal substrate surface. The morphology and composition of the catalysts were characterized in detail. The particle size of the as-synthesized bimetallic catalysts was around 10 nm and uniformly dispersed on the Ti substrate surface without agglomeration. The electrochemical results indicated that the atomic ratio of Pd:Pt possessed an influence on the catalytic activity. The $\text{Pd}_{0.8}\text{Pt}_{0.2}/\text{Ti}$ catalyst displayed the highest electrocatalytic activity and the best tolerance to carbonaceous intermediates for the investigated alcohols in alkaline medium. Considering both aspects of performance and price, this bimetallic catalyst should be a good alternative electrocatalyst for alkaline DAFCs.
5. A series of Pd catalysts promoted by transition metal oxides (Pd-oxides/C) were synthesized using a microwave heating method. Their structure, composition and morphology were characterized by different techniques, and the results indicated that these transition metal oxides existed on the carbon black surface in a highly-dispersed amorphous state. The catalysis behavior of the as-prepared Pd-oxides/C catalysts for

methanol and ethanol oxidation was evaluated in alkaline media. The Pd-oxides/C catalysts exhibited the rather better catalytic activity and stability than the Pd/C. The transition metal oxides, especially the composite oxides, CoNiO_x , have high promotion effects on the Pd catalyst for methanol and ethanol electrooxidation reactions. The promotion effect was ascribed to that these transition metal oxides can oxidize CO species at lower potentials, facilitating CO removal. The Pd-oxides/C catalysts should have potential applications for alkaline DAFCs.

6. The nano-structured WC-carbon composites that could act as highly efficient catalyst supports for DMFCs were successfully synthesized using water soluble carbon and tungsten sources by a microwave heating method. The Pt catalysts supported on the composites were prepared using the improved impregnation method. The Pt/WC/C_x catalysts exhibited an evidently better performance and stability as compared to the Pt/VC catalyst, which indicated that the WC possessed an obviously synergistic effect on the electrocatalysis of Pt catalysts for MOR. The catalytic activity and stability of the catalysts was significantly affected by the WC content and the structure of the supports.

9.2 Recommendations for future work

Based on the works done so far, the following research directions are suggested:

1. Using the as-developed self-assembly method to synthesize HPW/meso-silica electrolytes with 3D continuous meso-structures. It is worthy pointing out that the membranes possessing 3D meso-structures maybe have some better properties than 2D meso-structures. In addition, it is viable to develop anhydrous PEMs suited for high

- temperature operation based on CsHSO_4 /meso-silica electrolytes using the as-developed self-assembly technique.
2. The mechanism for the formation of the mesoporous structure in Nafion should be investigated and understood more clearly. Different mesopore sizes and meso-structures can be introduced into Nafion membranes by controlling the type and concentration of surfactants.
 3. Using the multilayer membrane technology to fabricate membranes that can reduce methanol crossover that still remains a critical challenge limiting the commercialization of DMFCs. A methanol-barrier layer can be used as the central layer by the incorporation of some specific nanoparticles or polymers. The influence of the thickness of the different layers should be studied further.
 4. Investigating the effect of different structures and composition of Pt-based and Pd-based catalysts for direct alcohol fuel cells.
 5. The different WC-containing materials as catalyst supports could be developed by the microwave heating method, for example, WC/carbon nanotubes or WC/graphene due to their special structures and characteristics.

List of Publications and Conference Presentations

Journal Paper

- 1) **Jinlin Lu**, Haolin Tang, Shanfu Lu, Hongwei Wu San Ping Jiang*, *A novel inorganic proton exchange membrane based on self-assembled HPW-meso-silica for direct methanol fuel cells*, Journal of Materials Chemistry, 21 (2011) 6668-6676.
- 2) **Jinlin Lu**, Shanfu Lu, San Ping Jiang*, *Highly ordered mesoporous Nafion membranes for fuel cells*, Chemical Communications, 47 (2011) 3216-3218.
- 3) **Jinlin Lu**, Shanfu Lu, Deli Wang, Meng Yang, Zili Liu, Changwei Xu, San Ping Jiang*, *Nano-Structured Pd_xPt_{1-x}/Ti Anodes Prepared by Electrodeposition for Alcohol Electrooxidation*, Electrochimica Acta, 54 (2009) 5486-5491.
- 4) **Jinlin Lu**, Changwei Xu, San Ping Jiang*, *Electro-oxidation of ethanol on nanocrystalline Pd/C catalyst promoted with oxide in alkaline media*, International Journal of Nanoscience, 8 (2009) 203-207.
- 5) **Jinlin Lu**, Zihui Li, San Ping Jiang, Pei Kang Shen*, Lin Li*, *In-Situ Synthesized Nano-Structured Tungsten Carbide Composites by Microwave Heating Method as Catalyst Supports for DMFCs*, Journal of Power Sources, Accepted.
- 6) **Jinlin Lu**, San Ping Jiang*, Lin Li, *A Novel Multilayer Nafion Membrane Impregnated with Phosphotungstic Acid for PEMFCs*, Advanced Functional Materials, Under review.
- 7) Meng Yang, Shanfu Lu, **Jinlin Lu**, San Ping Jiang*, Yan Xiang*, *Layer-by-layer self-assembly of PDDA/PWA-Nafion composite membranes for direct methanol fuel cells*, Chemical Communications, 46 (2010) 1434-1436.

- 8) Shanfu Lu, Deli Wang, **Jinlin Lu**, Jie Zeng, San Ping Jiang*, *HPW/MCM-41 mesoporous silica composites as novel proton exchange membranes for elevated temperature fuel cells*, ECS Transactions, 25 (2009) 1927-1933.
- 9) Shanfu Lu, Deli Wang, San Ping Jiang*, Yan Xiang*, **Jinlin Lu**, Jie Zeng, *HPW/MCM-41 Phosphotungstic Acid/Mesoporous Silica Composites as Novel Proton-Exchange Membranes for Elevated-Temperature Fuel Cells*, Advanced Materials, 22 (2010) 971-976.
- 10) Haolin Tang, Mu Pan*, Shanfu Lu, **Jinlin Lu**, San Ping Jiang*, *One-step synthesized HPW/meso-silica inorganic proton exchange membranes for fuel cells*, Chemical Communications, 46 (2010) 4351-4353.

Conference Presentations

- 1) **Jinlin Lu**, Changwei Xu, San Ping Jiang*, *Electro-oxidation of methanol and ethanol on nanocrystalline Pd/C catalyst promoted with oxide in alkaline media*, The 2008 Asian Conference on Nanoscience and Nanotechnology (AsiaNANO2008), Singapore, 3-6 November 2008.
- 2) **Jinlin Lu**, San Ping Jiang*, Shanfu Lu, *HPW/MCM-41 mesoporous silica composites as novel proton exchange membranes for elevated temperature fuel cells*, The 216th ECS Meeting in Vienna, Austria, 4-9 October, 2009.
- 3) **Jinlin Lu**, Zihui Li, San Ping Jiang*, *Nano-Structured Tungsten Carbide Composites by Microwave Heating Method as Catalyst Supports for Direct Methanol Fuel Cells*, The 12th Asian Conference on Solid State Ionics, Wuhan, China, 2-6 May, 2010.

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