Carbon monoxide poisoning mitigation approaches for the anode of polymer electrolyte membrane fuel cells

Seyyed Mohsen Mousavi Ehteshami

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Abstract

Carbon monoxide (CO) poisoning mitigation is an important technological and fundamental challenge in the field of polymer electrolyte membrane fuel cells (PEMFC's). The presence of CO even in very low concentrations (a few tens of ppm level) is the main source of overpotential loss in the anode of PEMFC's. Therefore, the fundamental understanding of CO poisoning and providing mitigation approaches for this issue is of great interest. The possible approaches to solve the CO poisoning of PEM fuel cells can be categorized into two main technologies: on-fuel cell and off-fuel cell approaches. In this dissertation, a combination of electrochemical studies and numerical simulations are carried out to understand the mechanism of CO poisoning, and two different approaches are investigated to mitigate this issue.

Through electrochemical tests, the catalytic performance and reformat tolerance of some binary and ternary catalysts including Pt-M (M= Ru, Mo, Fe, Co, Ni), PtRuMo/C, PtCoMo/C and PtRuPb/C electrocatalysts are studied focusing on the effective factors on reformat tolerance. The anode side is fed by H₂: CO (x ppm CO balanced with hydrogen) and H₂:CO₂ (50:50 molar ratio) under identical stoichiometry and operational conditions. Reformate as the PEM fuel cells anode side feedstock, typically contains a mole fraction of hydrogen in the range of 0.4- 0.75, with CO in the range of 50-100 ppm and CO₂ making up the balance. Addition of the transition metals to Pt modifies the electronic properties and thus changes the binding energy and impurities coverage with the consequence of enhanced reformat tolerance.

Another approach to mitigate the CO issue is introduced which is an electrolytic-based selective CO oxidation system for on-board pure hydrogen production. An on-board CO removal unit is essential in any fuel processor system to be developed for production of hydrogen with low CO

concentration (<10ppm). Low process temperature (<80°C) and pressure are critical for such a gas clean-up unit. The existing technologies operate at high temperatures and pressures and need on-board oxygen or air supply for CO oxidation. In this research, a reactor with the same structure as a PEM fuel cell with Pt catalyst layer here called adsorber is used to produce hydrogen with low CO concentration at room temperature and pressure. Such a system electrochemically removes the CO molecules adsorbed on a catalyst surface from a hydrogen stream in the anode side of an electrolyzer while extra hydrogen is produced in the cathode side. The effect of different geometrical and operational parameters of PEM reactor such as the gas flow field geometry, gas diffusion layer porosity and thickness, catalysts and catalyst supports type and loading on the adsorption capacity of the adsorber is studied. Having obtained these correlations, one can design an adsorber with the best performance while using optimum amount of catalyst loading. To achieve this purpose, four different flow fields (straight, multi-serpentine, pin-type and interdigitated flow fields), gas diffusion fields with porosities of 0.78 and 0.74 and single metal catalyst (Pt) and alloyed (PtRu) supported onto two different supports including carbon black and activated carbon with metal loadings of 0.5, 1 and 2 mg.cm⁻² are studied. Results show that interdigitated geometry, Toray carbon paper and activated carbon as catalyst support yield the highest adsorption capacities.

Furthermore, the electrolytic process (regeneration) parameters are optimized with the effort of completely removing the adsorbed CO molecules. Furthermore, a thermodynamic-electrochemical model is developed to simulate the energy balance of the electrolyzer indicating that this process offsets the actual energy consumption because it produces extra hydrogen. Thermodynamically, removing CO by electricity is more efficient than by heat which leads to high energy efficiencies (>80%).

As the fundamental understanding of CO poisoning is of great interest, a numerical simulation of the PEMFC performance incorporating the CO kinetics in the anode is carried out. In this study, linear and bridged- bonded adsorbed CO are considered to occur in parallel on Pt/C and PtRu/C catalysts for the first time. This model provides a good insight of CO poisoning characteristics. A two-dimensional, isothermal, and single phase CO poisoning numerical model taking into account the transport phenomena, electrochemical reactions and multi-component gas mixture transport is developed.

Such a study on CO poisoning fundamentals and mitigation approaches are expected to provide a complete understanding of the issue, electrocatalysts requirements, and finally design of novel approaches to solve this issue.

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Nomenclature

b	Tafel slope
D_{ij}	diffusivity of the gas pair
E	Energy (J. mol ⁻¹)
F	Faraday constant (96 487 C mol ⁻¹)
G	Gibb's free energy(J.mol ⁻¹)
H	Enthalpy(J.mol ⁻¹)
I	local current density vector (Am ⁻²)
j	electro-oxidation current density (Acm ⁻³)
k_{1L}/k_{1B}	linear/ bridged bonded hydrogen adsorption rate constant
k_{-1L}/k_{-1B}	linear/ bridged bonded hydrogen desorption rate constant
k_{2L}/k_{2B}	linear/ bridged bonded hydrogen electro-oxidation rate constant
k_{3L}/k_{3B}	linear/ bridged bonded carbon monoxide adsorption rate constant
k_{4L}/k_{4B}	linear/ bridged bonded carbon monoxide electro-oxidation rate constant
k_p	permeability (m ²)
L	Membrane thickness (m)
LHV	Low heating value(J.mol ⁻¹)
MW	equivalent molecular weight

N	molar flux vector ($\text{mol m}^{-2} \text{ s}^{-1}$)
p	pressure (Pa)
Q	Power (W)
R	universal gas constant ($8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$)
S	catalyst site
T	Temperature (K)
u	velocity vector (ms^{-1})
x	gas phase mole fraction of species

Greek Characters

σ	conductivity (Sm^{-1})
φ	potential (V)
ε	porosity
η	overpotential (V)
λ	Water content
θ	fraction of catalyst sites occupied
μ	viscosity ($\text{kg m}^{-1} \text{ s}^{-1}$)
ρ	density (kg m^{-3})
ω	weight fraction

Subscripts and superscripts

<i>a</i>	anode
<i>act</i>	activation
<i>B</i>	bridged bonded catalyst site
<i>c</i>	cathode
<i>eff</i>	effective
<i>H</i>	hydrogen
<i>i</i>	components, H ₂ , CO and H ₂ O for the anode, O ₂ , H ₂ O, and N ₂ for the cathode
<i>L</i>	linear bonded catalyst site
<i>m</i>	membrane
<i>ref</i>	reference
<i>s</i>	gas distribution electrode
<i>S</i>	vacant catalyst site
<i>T</i>	total

CHAPTER 1 Introduction

1. Introduction

1.1 Hydrogen Energy

Providing a safe, environmentally friendly, and reliable energy supply is essential for having a sustainable and high quality life in terms of economical, environmental and public health aspects. An energy system must mitigate the climate change effects, reduce the toxic pollutants and plan for diminishing oil reserves; on this way, more efficient use of energy and increasing the contribution of carbon-free fuels in energy supply will be effective approaches.

Hydrogen can be produced either from primary energy sources like coal and gas or from other renewable energy sources such as concentrated solar thermal energy which in large scale is an affordable and secure choice for large-scale hydrogen production specially in areas with significant solar radiation. There is a wide range of options for sources, converters and applications illustrating the flexibility of hydrogen and fuel cell energy systems.

Fuel cells have a wide range of applications, ranging from very small fuel cells in portable devices such as mobile phones and laptops, through mobile applications such as vehicles and ships, to combined heat and power generators in domestic and industrial applications.

Hydrogen and fuel cells have many benefits over other types of power generators such as production of very low to zero carbon emissions and no emissions of harmful substances like nitrogen dioxide, sulfur dioxide, volatile organic compounds or carbon monoxide. Because of

their low noise and high power quality, they can be used in hospitals and military applications. Fuel cells can also be used as Auxiliary Power Units (APU) in combination with internal combustion engines, or in stationary back-up systems when operated with reformers for on-board conversion of other fuels. Hydrogen and electricity together represent one of the most promising ways to realize sustainable energy, while fuel cells provide the most efficient conversion device for converting hydrogen, and possibly other fuels, into electricity. Hydrogen and fuel cells simultaneously address all of the major energy and environmental challenges.

1.2 A Brief Introduction to PEM Fuel Cells

PEM fuel cells consist of cathode/anode gas channels, gas diffusion layers, catalyst layers and membrane. The membrane electrode assembly (MEA) consists of an ion exchange membrane with a thickness of 100–250 μm sandwiched between two Pt based catalyst layers with a thickness of 10–20 μm and backed by porous gas distribution electrodes (GDE), which is usually carbon paper treated by polytetrafluoroethylene (PTFE) with a thickness of 200–300 μm . The MEA is then sandwiched between two bipolar plates. These plates serve as a manifold for the transfer of feed-gas and products in and out of the fuel cell and as the current collector. The heart of a fuel cell is the active catalyst layers, since at these regions the four ingredients: membrane, catalyst, electronic conductor, and chemical reactants, required for the fuel cell operation, exist together. The schematic of PEM fuel cell is depicted in Figure 1.1. Hydrogen, which is usually humidified, enters the anode gas chamber, transports through the porous electrode by convection and diffusion, and dissolves into the membrane phase of the anode catalyst layer. In the vicinity of the anode catalyst layer, hydrogen is subsequently

oxidized, protons migrate through the membrane into the cathode side, and the carbon conductor receives electrons; the anode reaction can be written as:

Similarly, oxidant, O_2 in air, which is usually humidified, enters the cathode gas chamber, transports through the porous electrode by convection and diffusion and dissolves into the membrane phase of the active catalyst layer. Protons in the membrane pores, coming from the anode side, react with dissolved O_2 at catalyst sites in the active layer to produce water in the electrochemical reaction:

Therefore, PEM fuel cells are electrochemical devices capable of converting chemical energy of a fuel directly into electricity in the presence of an electrocatalyst. In addition to the primary benefits of fuel cells generally, PEM fuel cells have other advantages.

Fig. 1.1 Schematic representation of PEM Fuel Cell [1]. Reproduced from Ref.[1] with permission of Elsevier.

A polymer electrolyte membrane is used as the electrolyte which leads to the strong characteristics of this type of fuel cell such as operating at low temperatures around 80°C with fast load response, and fast start up.

On the way to commercialize the PEM fuel cells, the high cost of hydrogen purification and CO clean up should be overcome. It is known that presence of CO even in low ppm level (more than 10 ppm) can degrade the PEM fuel cell performance significantly. A brief introduction to PEMFC contaminations and particularly CO poisoning is presented in the following section.

1.3 PEM fuel cell contaminants

PEM fuel cell contaminants mainly include the gases produced during the hydrocarbon fuels reforming namely fuel impurities such as CO, CO₂, H₂S and NH₃; besides, oxidizer contaminants including air pollutants such as NO_x, SO_x, CO and CO₂ in fuel cells where air is used as the oxidizer and cationic ions from the corrosion of fuel cell components including Fe³⁺ and Cu²⁺ may cause significant performance drop due to poisoning of anode, cathode and the membrane, respectively.

Impurities in the fuel and oxidizer can affect the mass transfer and kinetics of electrodes. Dissolved ions can poison the membrane of the PEM fuel cell and decrease the proton conductivity of the membrane. In addition, the corrosion layer produced on the bipolar plate surface decreases the electrical conductivity of the plate.

1.3.1 Hydrogen impurities

The hydrogen used in today's fuel cell research comes mainly from commercially available sources. The main hydrogen production method is the reforming of hydrocarbons and/or oxygenated hydrocarbons such as methane and methanol [2]. Other production methods such as partial oxidation, autothermal reforming [3], electrolysis, and hydrolysis of sodium borohydride [4] are also available. Some impurities such as carbon oxides and sulfur compounds are produced inevitably during the reforming process. Reformate which is the hydrogen-rich feed stock is produced through steam reforming, partial oxidation or autothermal reforming processes. It typically contains 40 to 70% H_2 , 15 to 25% CO_2 , 1 to 2% CO , small quantities of inert gases (water vapor and nitrogen), and sulfur compounds. In addition, few ppm of SO_2 used as a tracer in natural gas distribution systems, if available in hydrogen feed, can diminish the cell performance remarkably.

In order to have a high performance and long lifetime fuel cell, pure hydrogen is needed for the fuel cell feedstock and the purification processes to remove the contaminants in the reformate gas are costly; this inspires research on development of PEMFC integrated systems able to eliminate small amount of impurities available in the reformate in particular CO ; production of such a reformate containing small amounts of impurities will be cost effective. In the following section, the focus is on CO poisoning effects on PEM fuel cells performance.

1.3.1.1 CO Impacts on PEMFC Performance

CO available in the reformate can enter through the flow field, pass through GDL and reach the reaction sites on anode catalyst layer. This will result in the decrease of the anode catalyst

layer activity thus causing fuel cell performance degradation. CO impact is the contaminant effect that has been investigated extensively in the literature. Herewith a brief introduction on the CO effects on PEM fuel cell performance, the approaches available to mitigate the CO poisoning and a comparison among them is presented.

Carbon monoxide has become a major concern in PEM fuel cells using reformat as fuel, especially at typical operating temperatures ($<80^{\circ}\text{C}$). CO binds strongly to Pt sites, reducing the active catalyst sites available for hydrogen adsorption and oxidation. It seems that the CO poisoning effect is strongly related to the concentration of CO, the exposure time to CO, the cell operation temperature, and anode catalyst types [5]. The more the concentration of CO and the longer the exposure time of the anode side catalyst layer of PEM fuel cell to CO the more degradation of fuel cell performance will be.

The fuel cell degradation is very sensitive to increases of CO ppm level. Voltage losses were less than 3% and 85% at CO levels of 50 and 70 ppm respectively [6]. Benesch *et al.* [7] reported that the time it took for cell voltages to decay to a threshold value of 0.3V were 1 and 9 h, respectively, when the cells were exposed to 50 and 10 ppm of CO. The cell voltages did not appear to drop below 0.3V when the CO concentrations were lower than 5 ppm.

Figure 1.2 shows the effect of CO concentration on the PEM fuel cell with catalysts of Pt and Pt/C. The figure shows that the CO in fuel can cause a huge voltage loss even at a level of a few ppm especially at high current densities.

The performance degradation becomes more significant when the catalyst exposure time to CO is longer [8].

Fig. 1.2 Effect of CO concentration on cell performance [9]. Reproduced from Ref.[9] with permission of Elsevier.

1.3.1.2 CO₂ Impacts on PEMFC Performance

Reformate as the PEM fuel cells anode side feedstock, typically contains a mole fraction of hydrogen in the range of 0.4- 0.75, with CO in the range of 50-100 ppm and CO₂ making up the balance. CO is well-known as a poison for hydrogen oxidation on platinum in the anode of a PEM fuel cell and a medium temperature phosphoric acid system. Besides, CO₂ has the potential of CO production through either a) a reverse water gas shift reaction [10-14] ($\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$) which is the reduction of CO₂ at the operating temperature of PEM fuel cells of 80°C or b) the electro-reduction of CO₂ through $\text{CO}_2 + \text{H}^+ \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ [15-17]; The poisoning level caused by CO₂ is beyond those accounted for by simple dilution [11-14].

Hence, on the way to develop new durable catalysts for impure hydrogen feedstock, the enhancement of the reformat oxidation should be considered over the whole range of industrial CO and CO₂ concentrations. PtRu alloy catalyst has been widely acknowledged as one of the most promising candidates for the anode side exposed to reformat feedstock [18, 19]. Although other bimetallic alloys, such as PtMo [20-22] and PtSn [23, 24], have also shown good CO tolerance, even better than that shown by the PtRu alloys. However, on the contrary, it is observed that the CO₂ tolerance of PtRu/C is greater than that of PtMo/C [10, 14, 17]. A.E. Russell et al. [10] have shown that the decreased CO₂ tolerance of PtMo compared to PtRu is owing to the difference in the mechanisms of improved CO tolerance, compared to a Pt/C reference catalyst. At PtRu the mechanism is because of the water activation which occurs at Ru sites, while at PtMo the mechanism relies on the turn-over of the Mo (IV/VI) redox couple.

1.4 CO Poisoning Mitigation Approaches: Challenges and Motivations

The possible approaches to solve the CO poisoning of PEM fuel cells can be categorized into two main technologies: on-fuel cell and off-fuel cell applications [25]. In the former, CO is removed from the hydrogen stream prior to flowing into the fuel cell stack while in the latter the impure hydrogen directly enters the PEM fuel cell. Eliminating the CO content on-board needs a process temperature as low as 80°C and a fast reaction to downsize the dimensions of the reactor. Off-fuel cell technologies produce CO free feed gas using multistage catalytic processes such as water gas shift (WGS) reaction, catalytic methanation and catalytic preferential CO oxidation which are not economic and are done at high temperatures.

CO removal has been tried on-board with no pre-processing needed beforehand. PEM fuel cell application at high temperature (temperatures more than 200°C) is the first on-board approach to mitigate the CO poisoning which needs to have heating devices to heat up the introduced gases at desired temperatures [26].

The second approach is air or oxygen bleeding including introducing hydrogen with O₂ to the fuel cell. Oxygen reduces the CO poisoning by oxidizing the CO molecules adsorbed on the anode catalyst. This only can be done when the CO content of the low volume rate hydrogen stream is less than 50 ppm; obviously it cannot suitably remove the CO in hydrogen stream needed for a typical vehicle [156]. Especially at high current densities, there is a performance loss which may not be recovered. This is due to the CO mitigation through oxidation of CO molecules adsorbed onto the electrocatalyst sites required for hydrogen electro-oxidation. Moreover, a malfunction in oxygen flow meters and controllers can lead to explosion.

Alloying Pt with another metal such as Ru, Fe or Mo has been investigated extensively to prepare CO tolerant catalysts [10, 18, 19, 21-24]. Among them, Pt-Ru alloys have been reported to be the most effective ones [19]. Other unsupported or supported Pt-based alloy catalysts have also been demonstrated to exhibit high tolerance to CO poisoning. More information on the development of high-performance and cost-effective CO-tolerant anode electro-catalysts for PEM fuel cells can be found in Chapter 2. However, these electrocatalysts cannot eliminate the effect of CO completely. In brief, the current approaches of CO poisoning mitigation are not able to completely resolve the issue due to the mentioned

barriers. Therefore, establishing novel methods and materials to address the above mentioned problems are of great desire.

1.5 Research Novelty

In this dissertation, the issue of CO poisoning mitigation is addressed by two approaches. First, development of novel electrocatalysts with enhanced tolerance towards the electrooxidation of hydrogen in the presence of both CO and CO₂. So far, very few of the investigations have considered both CO and CO₂ issues and a comprehensive and consistent theory to correlate the enhanced tolerance to the effective features is missing. In this dissertation, the author suggests that a target anode catalyst which efficiently tolerates both CO and CO₂ in the hydrogen stream could be a Pt-based multi-component material in which: 1) there are sufficient oxophilic catalyst sites on the surface in the vicinity of Pt nanoparticles, 2) the electronic structure of Pt is altered in a way that impurities are adsorbed less and weaker on Pt sites, and 3) yet the availability extent of Pt sites is enough for hydrogen oxidation, among the fuel molecules and between the fuel molecules and the catalyst surface. Second, development of an electrolytic selective CO oxidation system for production of pure hydrogen. The working principle of this system is adsorbing CO onto a catalyst layer in a PEM reactor called adsorber, then regenerating the adsorber by passing DC current or pulsed voltage to electro-oxidize the adsorbed CO to CO₂ in an electrolyzer mode. Experimental and theoretical investigations show that this method is cost effective, fast and energy efficient. The advantages of such an approach can be summarized below:

- Operational at low temperature and pressure
- Low energy consumption

- Potentially low capital investment cost
- Fast CO removal process
- H₂ produced during regeneration would partially offset the total energy needed
- Multiple impurity removal possible
- Scalable for practical application

Furthermore, as the fundamental understanding of CO poisoning is of great interest, a numerical simulation of the PEMFC performance incorporating the CO kinetics in the anode is carried out. In this study, linear and bridged- bonded adsorbed CO are considered to occur in parallel on Pt/C and PtRu/C catalysts for the first time. This model provides a good insight of CO poisoning characteristics. A two-dimensional, isothermal, and single phase CO poisoning numerical model taking into account the transport phenomena, electrochemical reactions and multi-component gas mixture transport is developed.

1.6 Introduction to PEMFC-Electrolyzer/ Adsorber System

An ideal set up applicable for on-site/board application CO removal operates at low temperature and pressure and applies polymer electrolyte membrane (PEM) reactors for the electrolytic process. These reactors are commonly used in organic synthesis, environmental remediation and power generation. The schematic of the set up is depicted in Figure 1.3. The system includes two identical PEM reactors integrated in parallel with a PEM fuel cell. This configuration ensures that at any time, the supply of feedstock passes through one of the reactors (adsorber) while the other is being regenerated. The role of the adsorber is to remove the CO present in the hydrogen stream. This is accomplished through the physico-chemical adsorption of impurities present in the hydrogen stream, such as CO, on metallic electro-

catalysts deposited on a carbon structure at a temperature less than 80°C and atmospheric pressure. The CO is accumulated on the surface of the electro-catalyst and eventually reaches the saturation point. The level of saturation is detected by an infrared based gas analyzer able to detect ppm level of CO. Once the saturation point is reached, the feedstock is switched over from the saturated adsorber to the fresh adsorber. The time interval of switching feedstock from one adsorber to the other is determined by amount of impurities in the feedstock as well as the flow rate. The time during which the adsorber can produce hydrogen with less than 10ppm CO content is termed as breakthrough time here in this study. The regeneration step needs applying a form of energy to the system. In conventional technologies, it is carried out by applying thermal energy to the system introducing more complexities to the system.

In an electrolytic system, the saturated adsorber is regenerated through an electrochemical approach which is achieved by applying a potential from a source between the anode and cathode of the electrolyzer. The saturated adsorber now acts as an electrolyzer and removes the adsorbed impurities by electro-oxidizing the adsorbed molecules and, thereby, regenerates the saturated absorber. The details of this regeneration process are described as follows: A small portion of electricity generated from the fuel cell is used to convert water into hydroxide group (OH^-) and proton (H^+). The CO adsorbed on the surface of the electro-catalyst is oxidized by OH^- into CO_2 and proton (H^+). The two H^+ are reduced at the cathode of the electrolyzer to produce H_2 , which is then combined with the purified H_2 stream and fed to the fuel cell. The reactions at the electrolyzer are as follows:

Fig. 1.3 Schematic of the adsorber/ electrolyzer system including two PEM reactors and a PEM fuel cell

The overall reaction of the adsorber/electrolyzer system is therefore:

Applying the electrochemical approach brings about favorable operating conditions (low pressure and temperature) which are unique features of this approach and are in contrast with those of existing multistage catalytic technologies, where a high temperature is a prerequisite

factor to achieve high CO conversion rates. The low temperature requirement facilitates and favors the adsorption of impurities on the electro-catalysts; the faster is the reaction rate, the smaller is the size of the reactor. The proposed system is highly suitable for on-board applications because it can operate at ambient temperature and atmospheric pressure. The system can also potentially be used as an off-board application to replace the traditional low temperature water-gas-shift reaction for CO removal.

1.7 Research Objectives

The objectives of this research are:

- To understand the mechanism of CO poisoning of Pt and PtRu through considering a realistic CO electro-oxidation kinetics.
- To understand the CO tolerance underlying mechanisms and the activity-structure correlations of CO tolerant electrocatalysts.
- To demonstrate the concept of the electrolytic CO oxidation system and investigate the scientific and technical functionality of the system i.e., to show the process can reduce the CO concentration to such a lower level that it would not pose any poisoning effect on Pt electrode.
- To evaluate the performance of PEMFC-electrolyzer/adsorber system under different structural and operational conditions and system optimization.

1.8 Research Scope

This dissertation deals with the CO poisoning issue from three areas: 1) Understanding the mechanism of CO poisoning and CO oxidation kinetics in a PEMFC via numerical simulation

of a fuel cell performance incorporating the linear and bridged- bonded adsorbed CO occurring in parallel on Pt/C and PtRu/C catalysts. 2) Electrochemical experiments are performed to investigate the CO tolerance of the binary and ternary Pt-based electrocatalysts. 3) Experiments are carried out to investigate the merit of the electrolytic CO oxidation system. Furthermore a parametric study is performed to determine guidelines for the optimized performance and efficiency of the system.

1.9 Layout of the Thesis

Chapter 1 provides a broad view over the position of hydrogen energy and PEMFC's in the power generation. A short summary of PEMFC's contaminants, CO impact on the performance and is provided. It continues with an introduction to on-fuel cell and off-fuel cell approaches for CO poisoning mitigation. Finally, the approaches investigated in this dissertation are explained.

A comprehensive review of the investigations performed in search of electrocatalysts with enhanced reformates tolerance for low temperature polymer electrolyte membrane (PEM) fuel cells are presented in Chapter 2. In addition, the fabrication processes and materials effects on PEMFCs' performance are reviewed. Furthermore, an overview on researches on the numerical simulation of the cell performance in the presence of CO is presented.

Chapter 3 presents the details of the experiments carried out and the corresponding results. These experiments are elaborated in two main sections. First, the electrochemical experiments performed to investigate the CO tolerance of the binary and ternary Pt-based electrocatalysts.

Second, experiments carried out to investigate the merit of the electrolytic CO oxidation system are presented. Furthermore a parametric study is performed to determine guidelines for the optimized performance and efficiency of the system.

Chapter 4 includes the theoretical investigations carried out including the numerical simulation of the PEMFC performance incorporating the CO kinetics in the anode. Linear and bridged- bonded adsorbed CO are considered to occur in parallel on Pt/C and PtRu/C catalysts. Furthermore, a thermodynamic-electrochemical model is developed to simulate the energy balance of the electrolyzer indicating that this process offsets the actual energy consumption because it produces extra hydrogen.

In Chapter 5 concluding remarks are presented and some future work ideas are suggested for further investigating electrocatalysts with enhanced activity and stability for PEMFC's operating on reformat gas.

Chapter 2 Literature Review

2.1 Fabrication Processes and Materials Effects on PEM Fuel Cells Performance

2.1.1 Membrane Electrode Assembly (MEA)

Design and fabrication processes for PEM fuel cells and the effects of consumed materials on the performance are briefly analyzed in this section. Yan *et al.* [27] experimentally investigated the effects of GDL fabrication process on the performance of PEM fuel cells. According to the measurements carried out, they found that the GDL fabrication process employing the two-stage method i.e., coating GDL with a micro porous layer, can improve cell performance effectively and delay the occurrence of limiting current density, because adding micro porous layer onto GDL improves gas transport and reduces ohmic resistance inside GDL effectively, and also provides proper water management capability. In addition, they concluded that in air breathing fuel cells, the cell achieves much better performance with the carbon loading of 1mg.cm^{-2} in the micro porous layer due to the presence of the thin micro porous layer and large pores in GDL.

Giorgi *et al.* [28] reported the influence of the Polytetrafluoroethylene (PTFE) content in the diffusion layer of low Pt loading electrodes for PEM fuel cells. Their results indicated that at high current densities, the performance of the electrodes decrease as the PTFE content in the catalyst layer is increased. The electrical resistance of the electrode increases as the PTFE content increases and the porosity decreases implying that the electrode porosity influences the electrode performance.

Yang *et al.* [29] investigated different electrodes fabricated with different procedures. They found that the electrode that was prepared by directly coating the catalyst layer on Nafion membrane using 3-methyl butanol as a solvent gives better performance of 800 mA/cm² at 0.6V.

Nakrumpai *et al.* [30] studied the effect of different operating parameters such as pressure, temperature and time of compression, on the preparation of MEA for a PEM fuel cell. To determine the optimum conditions for MEA fabrication, 2^k factorial of designs through response surface method were used. The obtained results showed that the main effects alone were not playing an important role on MEA performance. Instead, interactions between pressure and temperature and that between temperature and time of compression have significant effects on the performance of the prepared MEA. With low pressure, but high temperature and long time of compression, current density was improved. The optimum condition for MEA fabrication was reported to be 65 kg/cm², 137°C and 5.5 min of compression time. It was also found that to mount the MEA into the single cell of the test unit, a torque of 69 kg-cm gave the best performance. However, the obtained performance was still lower than commercial MEA. The reason might be due to the internal current loss or hydrogen crossover.

2.1.2 Flow fields

Effect of flow field geometry on the performance of PEM fuel cells has been investigated enormously in the literature. Bipolar plates play a vital role in PEM fuel cells by supplying fuel and oxidant to catalyst sites, removing reaction products, collecting the generated current and providing the mechanical strength of the cells. Production of lightweight PEM fuel cell

stacks is one of the main required factors for many power applications. It may be possible by selecting appropriate materials for bipolar plates. Design and configuration of bipolar plates and flow channels are potential areas which can make PEM fuels good competitors for other power generation alternatives [31, 32].

The flow field design and configurations facilitate the functionalities of bipolar plates. Flow field configurations include straight, serpentine, and interdigitated channels. Fuel cell manufacturers have developed other flow field designs, such as pin-type flow field, series-parallel flow field, integrated flow fields, and flow-field designs made from metal sheets. Each type of channel might be engraved in single or multiple channels. Bipolar plates should be designed in a way by which reactant gases are uniformly distributed over the active area of the anode and cathode electrodes leading to minimizing the concentration over-potentials. They should offer high electronic conductivity and mechanical strength for current collection and stack integrity, respectively. The material should be cheap, easily machined and highly resistant to corrosion.

The flow field width and depth should be in the range of 1 mm in order to assure a reasonable gas pressure loss due to friction losses. It has been reported that the power density has increased up to 50% by appropriate gas distribution through flow fields [33].

(i) Pin-type flow field

Reiser and Sawyer [34] have developed samples of the pin-type flow field. One sample is shown in Fig. 2.1. The gas streams at anode and cathode sides pass through a network of

series and parallel flow paths leading to low pressure drops. However, gas flows tend to pass through paths with the least flow resistance which may cause dead volume and stagnant areas. This can disturb the uniformity of the reactant distribution, water removal and generally fuel cell performance. Further, depleted fuel concentration may happen due to recirculation zones created behind each pin decreasing the cell and stack performance.

Fig.2.1 Pin-type flow field

(ii) Straight flow field

This flow field suffers from a similar problem of pin-type flow field which is the formation of stagnant areas. In addition, because of the short length of the parallel channels, the pressure drop is so small in each flow field while the pressure drop in the stack distribution manifold is large comparatively. This non-uniformity in pressure loss distribution leads to un-even reactant flow distributions among the cells in the stack. Some modifications have been done

to increase the pressure drop along and between two adjacent channels such as decreasing the channel width from inlet to outlet. Another problem associated with this flow field is the non-uniform stack pressure caused by variation in the ribs contact areas which are a consequence of tolerances of manufacturing.

(iii) Serpentine Flow Field

This flow field is claimed to improve the issues mentioned in straight and pin-type flow fields. However, this flow field produces a longer channel leading to a big pressure drop and huge concentration gradients between the channel inlet to the outlet. Besides, in a single serpentine flow channel, the probability of flooding in higher current densities increases as all the generated water should be removed through only one channel. Watkins *et al.* [33] proposed multi-serpentine flow field by which the pressure drop and consequently the parasitic power required to pressurize the air will be minimized. This flow field ensures that the generated water will be removed by the gas flow and that no stagnant areas will form due to flooding at the cathode side. The output power of a stack with multi-serpentine flow field is reported to be 50% higher than that in a stack with single serpentine flow field [33].

In serpentine flow field, it is possible for the gas flow to pass through the diffusion layer from a high pressure leg of the channel to a low pressure one which may produce reactant gas short circuiting between the adjacent legs. To solve this problem, Rock [35] proposed a design which subdivides the channels into segments which are serially connected and each segment includes a single serpentine channel with short legs leading to a low pressure drop. The special design of this flow field decreases the flow bypassing in different parts.

(iv) Interdigitated flow field

In the conventional flow fields as described above, the reactant flow diffuses into the gas diffusion layer and the dominant flow is parallel to the cathode or anode surfaces. The molecular diffusion is slow, produces high concentration gradients and hinders the liquid water transfer through the gas diffusion layer. On the other hand, interdigitated flow field provides convective mass transfer and gas velocity normal to the surface of the electrodes leading to enhanced mass transport and liquid water removal in the porous gas diffusion [36]. This flow field consists of dead-ended flow paths built on bipolar plates through which the flow is forced to pass through the porous gas diffusion layer which develops the convection flow towards the anode and cathode catalyst layers. However, there is a large pressure drop for the gas flows. This flow field is attractive from this point of view that the catalyst particles are completely exposed to the reactants through the forced convection flow through the electrodes. In interdigitated flow field, the reactant concentrations reduce significantly along the flow channels leading to un-even reaction across the electrodes. To improve the mass transfer, Gurau *et al.* [37] proposed a design based on interdigitated flow field in which the volume of outlet channel is less than that of the inlet channel. Thus, the fluid flow rate into the outlet channel is increased leading to a better fluid removal. One of the approaches used to achieve such a condition is to make the outlet channel with a smaller depth than of the inlet channel.

2.1.3 Gas Diffusion Layer

Physical and electrical properties of gas diffusion layers (GDL) are crucial factors. The typical gas diffusion layers used in fuel cell applications have two layers. A substrate layer whose structure determines the mechanical strength and electrical conductivity of the layer and a micro porous layer (MPL) which significantly affects the permeability, porosity and roughness of the gas diffusion layer [38]. The treatment of the gas diffusion layer with polytetrafluoroethylene (PTFE) improves the water transport in the gas diffusion layer by increasing the hydrophobicity and permeability. On the other hand, it decreases the porosity of the porous structure of the gas diffusion layer. This is because PTFE blocks and narrows the pores of the gas diffusion layer.

Figure 2.2a presents the wide range of the porosity in commercial gas diffusion layers. Several researches have reported the porosity and pore size distribution of gas diffusion layers and the measurement methods for determining these parameters [38, 39]. El kharouf *et al.* [38] has measured the in-plane and through-plane permeability of the gas diffusion layers by the mercury intrusion method. The reported values indicate that the parameters effective on the permeability are the presence/absence of the MPL, the carbon fiber density, thickness and PTFE loading. The permeability values are presented in Fig. 2.2b.

a)

b)

Fig. 2.2 The porosity (a) and permeability (b) of commercial GDLs. Reproduced from Ref. [38] with permission of Elsevier.

2.1.4 Clamping Pressure

The clamping pressure affects the contact resistance between the GDL and bipolar plate. Figure 2.3 shows [38] the contact resistance as a function of the clamping pressure used to assemble the cells with straight fiber, felt fibers papers and woven fiber cloths. Too much pressure can cause permanent damage to the gas diffusion layers. The clamping pressure of 2MPa appears to be the optimized clamping pressure.

Fig. 2.3 Contact resistance as a function of clamping pressure. Reproduced from Ref. [38] with permission of Elsevier.

2.2 CO Poisoning Mitigation Approaches

2.2.1 Off-fuel cell CO Removal Technologies

(i) Catalytic methanation

Catalytic methanation, the reaction of CO and hydrogen fuel ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$), produces methane. It does not disturb the anodic reaction in PEM fuel cell. Besides, oxygen is not needed to be introduced into the fuel cell system. However, it is a high temperature process and consumes some of the hydrogen.

Rehmat and Randhava [40] compared some commercial catalysts such as Ru/ α - Al_2O_3 , Raney nickel and alumina-supported Ni catalysts and found that Ru was the most effective, followed closely by the Raney nickel-type catalyst.

Takenaka *et al.* [41] proposed Ni/ ZrO_2 and Ru/ TiO_2 as promising catalysts based on the screening experiment and concluded that the larger Ni and the smaller Ru was plausible for the high catalytic activity. They also showed that the CO concentration can be decreased from 0.5% to 20 ppm in the gases formed by the steam reforming of methane.

Echigo and Tabata [42] reported that the CO concentration below 10 ppm could be obtained only by multi-stage CO methanation over Ru/ Al_2O_3 .

There are some obstacles to be overcome for this process as follows [41, 42]:

- The temperature range leading to high CO conversion is very narrow even in the lab-scale experiments.

- The rapid consumption of hydrogen can be carried out via the CO₂ methanation in the absence of the fine temperature control.
- The inlet CO concentration should be low to reduce CO concentration satisfactorily.

(ii) Catalytic preferential CO oxidation

This reaction ($\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$) similar to catalytic methanation can be divided to two processes: 1) adsorption of CO molecules on a catalyst; 2) oxidation of the adsorbed CO molecules. Adsorption process is favored by low temperature while the oxidation part to be enhanced requires high temperature. It has been largely investigated; Co-Ni supported on activated carbon as the catalyst was reported to convert 99.5% of CO in hydrogen at temperature range of 130-150°C [43]. CO in a humidified hydrogen stream catalyzed on Ir/CoO_x-Al₂O₃/carbon was completely converted to CO₂ using oxygen to CO ratio of 1.5 at 75°C [44]. Chen *et al.* [45] could convert the entire CO in hydrogen rich stream to CO₂ using a 7% CuO/CeO₂ catalyst with a partial Ce lattice substitution with Zr⁴⁺ at 77°C. The lower the temperature the larger the reactor because at low temperatures the reaction rate is not reasonably high.

The carbon monoxide in the exit of the water–gas shift reactor can be removed over the oxidation catalyst with the oxygen supplied externally. Although the preferential oxidation (PROX) system requires the units to control the temperature and the flow rate of air, the smaller amounts of hydrogen can be consumed compared with those of the selective CO methanation.

Oh and Sinkevitch [46] compared various commercial catalysts for the PROX to be applied to fuel cell feed streams and reported that Ru/Al₂O₃ and Rh/Al₂O₃ were more selective than Pt/Al₂O₃. Since then, a number of catalysts more active for the CO oxidation than the H₂ oxidation have been reported, such as metal oxides (CoO_x, CuO and CeO₂), supported gold catalysts, and supported noble metal (Ru, Pt, and Rh) catalysts.

(ii.1) Metal oxides

CoO was reported to show the best performance among 3d transition metal oxides [47]. Supported cobalt oxide catalysts were also reported to be active for this reaction [48].

Among mixed metal oxides, CuO-CeO₂ has been reported to be quite active and intensively studied by several groups. The effect of preparation method [49], pre-treatment condition [50], promoter [51], and support [52] on the PROX has been reported. Its catalytic activity has been reported to be strongly dependent on the preparation methods including pre-treatment conditions. Although the addition of Co on CuO-CeO₂/g-Al₂O₃ has been reported to have the positive effect on the catalytic activity [53]. No promotional effect of noble metals such as Pt and Ru has been observed.

(ii.2) Supported gold catalysts

Supported gold catalysts have been reported to be quite active for the PROX especially at low temperatures [54, 55]. However, the selectivity for CO oxidation over H₂ oxidation decreased rapidly with increasing reaction temperature. Kandoi *et al.* [56] explained this observation based on the theoretical calculation. They found that H oxidation (OH formation) competed

with CO oxidation in PROX. The activation energy barrier for CO oxidation was calculated to be 0.18 eV on Au (1 1 1) and 0.96 eV on Pt (1 1 1), whereas the barrier for OH formation is 0.90 and 0.83 eV, respectively. The significantly weaker CO adsorption was calculated on Au at high temperature, which caused the substantial loss in the selectivity. Moreover, Au/Mn₂O₃ [57], Au/MO_x/Al₂O₃ (M = Mg, Mn), and Au/CeO₂ [58], have been reported to be active for the PROX.

Recently, an aqueous phase PROX system mediated via polyoxometalates over supported gold catalysts has been proposed to be quite selective. Because this reaction condition is quite different from the conventional case, further studies should be carried out to show its feasibility. The supported liquid-phase catalyst containing supported gold catalysts and a co-catalyst is claimed to remove high concentration of CO effectively at low temperatures [59].

(ii.3) Supported Pt-based catalysts

Various zeolites have been utilized as supports for Pt catalysts, such as A type zeolite [60], mordenite and X type zeolite [61].

Although lots of works have been conducted over Pt-based catalysts compared with other PROX catalysts, only a few catalysts have been reported to show a wide temperature window showing the acceptable CO conversion in a realistic condition over a long period of time. Until now, several catalyst systems have been characterized to reveal their superior catalytic activity to the conventional monometallic Pt catalysts. The carbon-supported Pt₃Sn catalyst has the lower activation energy for CO oxidation than that for H₂ oxidation, while Pt/Al₂O₃

catalyst has the similar activation energy for both reactions which are larger than those of Pt_3Sn catalysts [62].

Pt-Co/Y-ZrO_2 has been proposed to be one of active PROX catalysts after a careful pre-treatment [63]. This catalyst can reduce the CO concentration to below 10 ppm in the temperature range 380–423 K in the practical condition.

(ii.4) Supported Ru, Rh, and Ir catalysts

Supported Ru catalysts have been actively applied to the PROX system since Oh and Sinkevitch [46] reported that $\text{Ru/Al}_2\text{O}_3$ was the most active among commercial catalysts.

The supported Ru catalyst has been reported to be affected noticeably by the preparation parameters such as Ru precursors, reducing agents, and pre-treatment conditions [64]. Until now, $\text{Ru/Al}_2\text{O}_3$ catalyst can be considered to be the most promising based on the real operation data. However, there has been no report that the acceptable CO removal can be achieved with the high inlet CO concentration such as around 1 vol% in the real gas composition. Supported Ru catalysts have also some advantages over other supported noble metal catalysts because both oxidation and hydrogenation can be accomplished at once. Compared with supported Ru catalysts, supported Rh and Ir catalysts have been reported to be less selective for the PROX [64].

(iii) Water gas shift (WGS) reaction

Low temperature water gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) takes place at 200°C which is not so suitable for on-board applications.

2.2.2 On-board CO Removal

CO removal has been tried on-board with no pre-processing needed beforehand. PEM fuel cell application at high temperature (temperatures more than 200°C) is the first on-board approach to mitigate the CO poisoning which needs to have heating devices to heat up the introduced gases at desired temperatures.

The second approach is air or oxygen bleeding including introducing hydrogen with O_2 to the fuel cell. Oxygen reduces the CO poisoning by oxidizing the CO molecules adsorbed on the anode catalyst. This only can be done when the CO content of the low volume rate hydrogen stream is less than 50 ppm; obviously it cannot suitably remove the CO in hydrogen stream needed for a typical vehicle. Moreover, a malfunction in oxygen flow meters and controllers can lead to explosion.

Alloying Pt with another metal such as Ru, Fe or Mo has been investigated extensively to prepare CO tolerant catalysts [10, 18, 19, 21-24]. Among them, Pt-Ru alloys have been reported to be the most effective. Other unsupported or supported Pt-based alloy catalysts have also been demonstrated to exhibit high tolerance to CO poisoning. More information on the development of high-performance and cost-effective CO-tolerant anode electro-catalysts for PEM fuel cells can be found in the following section. However, these electrocatalysts can not eliminate the effect of CO completely.

2.2.2.1 Electrocatalysts for Enhanced CO Tolerance

A comprehensive review of the investigations performed in search of electrocatalysts with enhanced reformat tolerance for low temperature polymer electrolyte membrane (PEM) fuel cells are presented. Remarkable efforts have been made to attain improved catalytic activities and robustness by adding second element to Pt/C or third element to Pt-Ru/C, commercial catalysts for PEM fuel cell applications. The enhanced CO tolerance of the developed catalysts is strongly dependent on the type, composition and atomic ratios of the added elements/ groups, and type and structure of the support materials. The synthesis method of the catalysts also plays a remarkable role in the catalytic activity and stability since it determines the structure, morphology and size distribution of the catalyst nanoparticles, which are directly effective on the stability and activity. Choosing a proper synthesis method, inclusion of appropriate content of suitable promoters to Pt-based catalysts, and using a proper support material are the major requirements of an effective catalyst. The CO tolerance enhancement has been attributed to the bi-functional mechanism and electronic effects. Understanding the underlying mechanisms and the activity-structure correlations will shed a light in designing novel electrocatalysts via innovative routes for excellent robust CO tolerant electrocatalysts.

(i) Introduction

The presence of carbon monoxide (CO) as the most common impurity in the hydrogen stream degrades the performance of polymer electrolyte membrane fuel cells (PEMFC's) [14, 16, 19, 65]. It is well-known that one of the greatest obstacles in commercialization of PEMFC's is the high cost of the electrocatalysts and their susceptibility to impurities. Thus, a remarkable number of studies have focused on the synthesis and development of catalysts for PEM fuel

cells with enhanced CO tolerance to be used in the anode. In a conventional approach, Pt is alloyed with another element such as Ru to form Pt–Ru catalyst enhancing the CO tolerance of the catalyst. Another advantage of inclusion of a second or third element in the catalyst structure is that these novel materials reduce the high loading of Pt thus lower cost than Pt/C.

Pt-Ru/C is currently considered as the most promising catalyst commercially available to mitigate the CO poisoning in the anode of a PEM fuel cell [19]. However, there is still room for further improvement of the catalytic activity of the catalysts. A variety of carbon or non-carbon supported binary and ternary catalysts by inclusion of transition metals or some oxidative agents into the conventional Pt/C and PtRu/C with different structures and morphologies have been prepared and explored *via* different electrochemical and spectroscopic instruments such as rotating disk electrode, Infrared Reflection Absorption Spectroscopy (EC-IRAS), X-ray absorption spectroscopy (XAS) and differential electrochemical mass spectrometry (DEMS) for the enhanced catalytic activity towards CO oxidation and stability. These studies were focused on the catalysts composition and structure to attain superior CO tolerance and stability. Although none of the catalysts developed so far has been capable to eliminate the destructive effect of CO poisoning on PEM fuel cells performance, great efforts have been made to enhance it.

The high reformate tolerance of these electrocatalysts is usually attributed to the electronic [14, 16, 66] and bifunctional mechanisms [14, 67]. In the former, the electronic effects argue that the added element modifies the Pt electronic structure in a way that either the Pt–CO bond is weakened facilitating the CO oxidation by nearby OH groups, or the Pt–H₂O activation is improved making it possible for CO molecules to be directly oxidized on the Pt

sites. The electronic structure modification of Pt is related to the electron donation or back-donation of the added element. This modification reduces the impurities coverage leaving more vacant Pt sites for hydrogen oxidation. In the latter, the bifunctional mechanism, the electro-oxidation of CO is promoted through the formation of OH groups on oxophilic sites:

And then the spillover process of CO molecules to the vicinity of the sites occupied by OH species and CO oxidation:

The composition, morphology, size and structure of the catalyst particles affect the interactions formed between the reactants (H_2O , CO and H_2) and the catalyst determining the activity of the catalyst particles [68-72]. Furthermore, these factors influence the stability of the catalyst [73-75]. Therefore, a possible approach towards development of novel catalysts, as practiced routinely by many researchers, is varying the particles compositions, morphologies and sizes controlled by the synthesis method. Since there are many effective variables, a primary understanding of the chemical mechanisms and pathways is critical for a more efficient catalyst search. Thus, as a powerful tool to search for novel electrocatalysts with desired properties, numerical methods play an important role. First principles calculations based on the density functional theory (DFT) can be used to obtain the microscopic mechanisms through calculating the energetics and the reaction elementary pathways such as adsorption and activation energies of reactants, and products on the catalyst surface [76, 77]. Furthermore, the electronic densities and densities of electronic states of

each reaction stage on the catalyst surface can be analyzed to determine the parameters affecting the kinetics and energetics of the reaction. This provides a rational basis for designing novel electrocatalysts.

It is believed that by determining the effective parameters on the catalytic performance, mechanisms and pathways of the reaction on a catalyst, the design and development of novel catalysts with enhanced CO tolerance and stability will be achieved more efficiently. In order to provide a broad insight into the available literature and future directions, this study reviews the efforts made to develop and understand CO tolerant electrocatalysts and their tolerance mechanisms. The main objective is to illustrate the basic requirements of effective materials with enhanced catalytic activity and stability.

The structure of this section is as follows: the state-of-the-art electrocatalysts and the parameters that affect the CO tolerance and stability of the anode materials are elaborated. These parameters include: composition and structure of the catalysts, atomic ratio of the elements, catalyst support and preparation methods. Furthermore, the activity of the electrocatalysts is compared and approaches to improve the stability of the electrocatalysts are introduced. Pt based binary and ternary electrocatalysts developed by adding second or third elements to Pt/C are categorized to these groups: Pt- based binary alloy catalysts, Pt-based core-shell architecture, Pt-metal oxides/C, Pt based catalysts decorated with promoters, Pt-based ternary alloys and Pt-Ru-metal oxide/C. The activity towards CO electrooxidation presented by catalysts are compared with those of standard binary catalysts deployed in PEM fuel cells.

(ii) *State-of-the-art CO tolerant electrocatalysts*

The activity, stability, and selectivity of the CO tolerant electrocatalysts depend directly on the architecture, which is greatly affected by the composition and the synthesis conditions, including the preparation method, and the support [78-80]. In a conventional approach, other element(s) are added into the Pt/C structure to increase the CO tolerance. The stability and activity are also strongly dependent on the synthesis methods [78, 81, 82]. Significant efforts have been made in the development of CO tolerant electrocatalysts for PEM fuel cells leading to preparation of a large library synthesized with different methods and characterized with several electrochemical tests as summarized in Table 2.1.

(iii) Parameters that affect the CO tolerance of the electrocatalysts**(iii.1) Composition and structure of the catalysts****(iii.1.1) Composition**

Table 2.1 shows the electrocatalysts developed so far to enhance the CO tolerance of the deployed catalysts in PEM fuel cells operating at low temperatures. These include carbon supported Pt-based binary alloys, Pt-metal oxides, Pt-based binary core-shell structures, oxidative agent modified Pt-based materials, Pt-based ternary alloys, and PtRu-metal oxides as well as the non-Pt catalysts. Development of non-Pt electrocatalysts is of great interest because if the catalytic performance can be comparable with that of Pt-based electrocatalysts, significant economic impacts will be achieved.

The role of the elements added into the structure of Pt/C is to facilitate the CO oxidation on the catalyst surface via either the bifunctional mechanism or the ligand effect or a

combination of the two [68, 83]. The bifunctional mechanism improves the CO oxidation by the catalyst through forming a good dispersion of oxy-hydroxides on the catalyst surface. The effect of these groups is that the CO oxidation onset potential shifts to lower values. In fact, the added element modifies the adsorptive properties of the catalyst surface towards the water and thereby oxygen. Figure 2.4 illustrating the M–O bond energies for elements from different groups [84], enables one to prepare catalysts via including suitable oxophilic elements into the catalysts structure. Theoretically, the M–O bond energy should be around that of Pt–CO bond energy, which is ~590 kJ/mol. Therefore, Mo, Ru, Os, Sn, and Re are suggested to be appropriate elements to be added to the active surface phase of a catalyst.

The reformate tolerance of some binary and ternary catalysts including Pt-M (M= Ru, Mo, Fe, Co, Ni), PtRuMo/C, PtCoMo/C and PtRuPb/C electrocatalysts was investigated in a comprehensive research [85].

Table 2.1 List of the electrocatalysts developed for enhanced CO tolerance and the electrochemical tests carried out to characterize the performance.

Catalyst Architecture	Catalyst Formula	Electrochemical tests performed	Results and mechanisms	Ref's
Binary Alloys (Pt-M/C)	Pt-Ru/C	– PEM fuel cell operation at 85°C with H ₂ /x ppm CO – Test in 1 M H ₂ SO ₄ in a stream of H ₂ /x ppm CO	Pt-Ru/C exhibits significant CO and CO ₂ tolerance compared to Pt/C due to both electronic and bifunctional mechanisms.	[1-3] [10, 86]
	Pt-Mo/C	–PEM fuel cell operation at 85°C with H ₂ /x ppm CO –Test in 1 M H ₂ SO ₄ in a stream of H ₂ /x ppm CO	Pt-Mo/C performs much better (3-4 folds) than Pt-Ru/C. The dominating mechanism is the bifunctional mechanism. Stability is an issue.	[14, 22, 87, 88]
	Pt-Sn/C	–PEM fuel cell operation at 85°C with H ₂ /x ppm CO –Test in 0.5 M H ₂ SO ₄ in a stream of H ₂ /x ppm CO	Pt-Sn/C exhibits enhanced CO tolerance compared to Pt-Ru/C due to the electronic and bifunctional mechanisms. Stability is an issue.	[24, 66] [23, 89]
	Pt-Fe/C	–PEM fuel cell operation at 85°C with H ₂ /x ppm CO –Test in 0.5 M H ₂ SO ₄ in a stream of H ₂ /x ppm CO	Superior CO tolerance is observed due to formation of Pt-skin and electronic effect.	[65, 90, 91]
	Pt-Ni/C	- Test in 0.5 M HClO ₄ . -PEM fuel cell operation at 85°C with H ₂ /100ppm CO	Superior CO tolerance is observed compared to Pt/C.	[85, 92]
	Pt-W/C	–PEM fuel cell operation at 85°C with H ₂ /x ppm CO –Test in 0.5 M H ₂ SO ₄ in a stream of H ₂ /x ppm CO	Tungsten exhibits a co-catalytic activity for hydrogen oxidation in the presence of CO, although the effect is not as effective as that of Ru.	[65, 78, 93]
	Pt-Co/C	–Tests under PEMFC operating conditions –Test in 0.05 M H ₂ SO ₄ /0.1M HClO ₄ in a stream of H ₂ /x ppm CO.	Cobalt shifts the CO oxidation onset potential negatively. Stability is an issue.	[69, 85, 94]
	Pt-Ce/C	Both fuel cell (80°C) and electrochemical cell (0.5 M H ₂ SO ₄) were used.	Pt-CeO ₂ /C with 20% Ce content exhibited a very higher CO tolerant activity	[95]
	Pt-Pb/C	–Test in 0.1 M sulfuric acid solution.	Pt-Pb exhibits lower oxidation onset potential and a	[96, 97]

			higher CO tolerance compared to Pt.	
	PtSn@Pt	–Test in 0.5 M sulfuric acid solution saturated with CO.	The core-shell structure presents much higher CO tolerance compared to that of commercial E-TEK PtRu	[24]
Core-shell architecture	Pt ₃ Fe@Pt Pt@Fe _x O _y	–Test in 0.5 M H ₂ SO ₄ in a stream of H ₂ /x ppm CO.	Superior CO tolerance is observed due to formation of Pt-skin and electronic effect.	[91]
	Ru@Pt	–Test in at room temperature in 0.5 M HClO ₄	The CO oxidation onset potential is shifted negatively due to ligand effect.	[98]
	MoO _x @Pt	– Test in 0.5 M H ₂ SO ₄ at 298 K.	MoO _x @Pt core-shell nanoparticles exhibit significantly higher CO tolerance than that of PtRu alloy.	[22]
Pt-metal oxide (Pt-MO_x/C)	Pt-WO ₃ /C	–Test in 0.5 M H ₂ SO ₄ exposed to a stream of H ₂ /100 ppm CO at 80 °C. –Cyclic voltammetry in 0.5 M H ₂ SO ₄ and on-line mass spectrometry	Pt–Ru–WO ₃ /C presented excellent CO tolerance The CO oxidation onset potential is shifted negatively.	[99-103]
	Pt-M/nonPt (M= Ir, Pd, Ru)	–Test in 0.1 M HClO ₄	The mentioned catalysts exhibit improved CO tolerance.	[104]
Pt/non-carbon support	Pt/Ti _{0.7} W _{0.3} O ₂	– Test in 0.1 M H ₂ SO ₄	The unique CO-tolerant electrocatalytic activity of this catalyst as compared with commercial E-TEK PtRu/C catalysts is reported.	[105]
	Pt/WO _x	–Test in 0.5 M H ₂ SO ₄ . –Single cell operation at 80 °C.	The presence of Pt on the WO _x film shifted the oxidation onset potential to lower potentials compared to that of Pt.	[106, 107]
(Promoter+ Pt)/C	Rh(porphyrin)-PtRu/C	–Test in 0.1 M HClO ₄	(Rh(porphyrin)-PtRu/C) presented a significantly higher CO tolerance than that of PtRu/C.	[108]
	HPA-Pt/C	– Single cell operation at 80 °C.	Adding proper amount of HPA can improve the	[109,

			catalytic activity of the Pt anodes in a fuel cell fed with hydrogen/ CO mixture.	[110]
	Pt-Ru-Mo/C	– PEM fuel cell operation at 80°C. – PEM fuel cell operating at 75°C.	The performance of this catalyst was significantly better than that of those including Pt and Ru only.	[111, 112]
	Pt-Ru-Co/C	–Scanning electrochemical microscopy.	This catalyst exhibits enhanced CO tolerance.	[113]
	Pt-Ru-Ni/C	–Test in 0.5 M H ₂ SO ₄ and a PEM fuel cell.	Superior CO tolerance compared to Pt-Ru.	[92]
Pt-based ternary alloys	Pt-Ru-W/C	– PEM fuel cell operating at 75°C.	The catalyst prepared by colloidal method exhibits superior CO tolerance compared to that of E-TEK Pt-Ru.	[78]
	Pt-Ru-Pd/C	–Test in phosphoric acid at 180°C.	Exhibits improved CO tolerance compared to Pt-Ru/C.	[114]
	Pt-Ru-Sn/C	–PEM fuel cell operating at 75°C. –Test in 0.5M H ₂ SO ₄ .	Exhibits improved CO tolerance compared to Pt-Ru/C.	[115]
	Pt-Co-Mo/C	–PEM fuel cell operating at 85°C.	Superior CO tolerance compared to Pt-Ru.	[85]
	Pt-Ru-Ir/C	– Test in 0.5 M H ₂ SO ₄ and a PEM fuel cell.	Presents excellent CO tolerance compared to Pt-Ru/C.	[116]
PtRu-metal oxide (PtRu-MOx/C)	Pt-Ru-MoO _x /C	– PEM fuel cell operating at 80°C.	If includes 1wt% Mo, it presents excellent CO tolerance compared to Pt-Ru/C.	[67]
	Pt-Ru-WO _x /C	–Cyclic voltammetry (CV) and tests in a PEM fuel cell with H ₂ /1% CO –Test in 0.5 M H ₂ SO ₄ in a stream of H ₂ /100 ppm CO at 80°C.	Improved CO tolerance compared to that of PtRu is reported.	[117-119]
Non-noble catalysts	MoC _x /C	–Test in 0.5 M sulfuric acid solution	Capability to oxidize CO is reported.	[120]

Fig. 2.4 The metal oxygen bond dissociation energy in diatomic molecules as a function of group in the period [84]. Reprinted with permission from Ref. [84]. Copyright 1997, the Electrochemical Society.

(iii.1.2) Structure

The catalytic activities of electrocatalysts for PEM fuel cell applications are significantly affected by the structure and morphology of the catalysts. Depending on the preparation conditions, different molecular structures may form. They include alloys, intermetallic phases, core-shell structures and oxidative agents decorative Pt/C.

The enthalpies of formation of alloys are very small values, thus they can be unstable [96]. Electrochemical conditions such as high current densities can change the structure and

composition of the top layer of a PtRu alloy catalyst significantly [121]. In contrast, the crystalline structure of catalysts with ordered intermetallic structures are well-defined and normally possess high enthalpies of formation, which increases the stability of these materials compared to that of alloys [24, 96, 97]. The atomic scale electronic and geometric structures of intermetallic compounds can be well controlled and preserved. Furthermore, these structures have been reported to exhibit excellent electrocatalytic performance towards CO oxidation [24,122]. However, according to results of electrochemical experiments, intermetallic structures including non-noble elements such as Bi or Pb may not be stable at the electrode potentials as high as +0.80 V or beyond [123].

It was reported that the intermetallic structures can be converted to a core-shell one by applying a potential cycling on the catalyst while it is exposed to CO-saturated sulfuric acid solution [22, 24]. Catalysts with core-shell structures are also more stable and catalytically active compared to alloys. Figure 2.5 [22, 24] compares the polarization curves of the alloyed and core-shell structures of PtSn and PtMo with E-TEK PtRu tested in 0.5 molar sulfuric acid solution in the presence of 1000ppm CO balanced in hydrogen [22, 24]. Core-shell structure of $\text{MoO}_x\text{@Pt}$ exhibits the best catalytic activity towards the oxidation of H_2/CO mixture followed by the core-shell structure of PtSn@Pt . The cluster size and morphology can influence the CO tolerance of Pt-Ru/C electro-catalysts. Scott et al. [68] have reported that the basic mechanisms of CO oxidation are the same for different cluster sizes and morphologies. However, some changes are observed in the effectiveness of the catalysts with different cluster sizes and morphologies. According to their results, both the direct electronic and bifunctional mechanisms are active in CO tolerance.

Fig. 2.5 Polarization curves for electrooxidation of CO/H₂ mixtures (1000 ppm CO, balance H₂) on different PtSn and PtMo catalysts with comparisons to E-TEK Pt and PtRu catalysts (all catalysts contain 30% total metal loading). Curves were recorded at 298 K with 1 mVs⁻¹ scan rates and 1600 rpm rotation rates. Electrolyte: 0.5m H₂SO₄ solution. Reproduced from Ref. [22] and [24] with permission of the American Chemical Society and John Wiley and Sons, respectively.

This was reported in other studies, too [83]. The morphology and size of the clusters and Ru islands play a critical part in the relative importance of the mentioned mechanisms. The bifunctional mechanism dominates in the presence of mono-dispersed Ru islands, while ligand effect prevails in the presence of larger Ru islands. It is suggested that by tuning the particle size and morphology the dominating mechanism can be determined.

According to their X-ray absorption spectroscopy (XAS) measurements, at the Pt L₃ edge (XANES and EXAFS) carried out on three Pt_nRu's, two Pt_nMo's and a PtSn, only in the case of PtRu, the island size and metal oxidation state play a critical role in the electrocatalyst performance. It can be explained by the fact that at the corresponding working potential range, Sn and Mo islands on the surface involving those sites which are not alloyed with Pt

are completely oxidized. According to their results, the ligand effect follows this order: $\text{Ru} < \text{MoO}_x \approx \text{SnO}_x < \text{RuO}_x$. The strength of the Pt-OH and the Pt-CO bonds get stronger and weaker respectively as ligand effect (oxidation state of the metal) increases. In fact, Ru is a metal from the same group as Pt sharing common properties with Pt leading to a weak ligand interaction effect between Pt and an isolated Ru atom. However, Ru islands form bigger islands as a consequence of oxidation leading to different properties. On the other hand, Mo and Sn islands oxidize at lower potentials with the consequence of a strong ligand effect at all potentials. It is also suggested that the CO tolerance in hydrogen-rich reformat depends on the hydrogen replacement mechanism which is enhanced by the MO_x ligand effect which decreases the Pt-CO bond strength.

Herranz et al. [70] studied the effect of the crystal structure of PtSn intermetallic phases on the CO electrooxidation. Two samples including Pt_3Sn (fcc phase) and PtSn (hcp phase) supported on carbon were synthesized by controlled surface reactions. The prepared catalysts were characterized by several techniques such as XRD and high resolution TEM confirming the actual crystal structure of the sample. In each case, the characterization method results determine if the dominant phase available in the sample is either the hcp or the fcc PtSn phase. To assure that the only difference in the prepared PtSn samples is the crystal structure, the effect of particles size and metals loading should be eliminated. To achieve this purpose, the catalysts were characterized by extensive experiments making sure that all of the prepared catalysts have the same properties and the crystal structure is the only difference. The electrochemical tests, along with electrochemical coupled Infrared Reflection Absorption Spectroscopy (EC-IRAS) and differential electrochemical mass spectrometry (DEMS) were carried out to evaluate the catalytic performance of prepared catalysts towards the oxidation

of hydrogen/CO and methanol as the anode side feed of PEM fuel cells. The results showed that the catalytic performance of the fcc phase is higher than that of the hcp phase towards methanol oxidation due to the dilution effect of Sn sites on the catalyst surface which hinders the early stage methanol oxidation i.e., methanol dehydrogenation. However, the CO oxidation onset potentials were reported to be very close to each other, which show that the CO oxidation enhancement due to the OH groups nucleation by Sn sites does not depend on the metal loading.

It is observed that formation of an alloy is not a necessary condition for attaining effective CO oxidation activity [87]. It is possible to enhance the CO electro-oxidation of the Pt-based electrocatalysts by decorating the catalysts surface by other metals or groups [124-129]. The role of the added metal/ group is to promote the catalytic activity. Dubau et al. [71] reported that the Ru decorated Pt/C presents improved CO tolerance compared to PtRu/C alloy prepared with the same Pt/Ru atomic ratio. However, it is a must for the promoter to be in the vicinity of Pt sites in order to be effective for the CO electro-oxidation [71, 130].

In the following sections, the state-of-the-art catalysts developed for the anode side of PEM fuel cell operating at low temperature are listed and their structure-electrocatalytic performances are elaborated.

(iii.2) Atomic ratio of the elements

The atomic ratio of the constituent elements can affect the catalytic activity of the catalysts towards CO oxidation. Ianniello et al. [131] studied the CO oxidation on catalysts with different Ru contents through *in situ* infrared (FTIR) spectroscopy and differential electrochemical mass spectrometry (DEMS). According to their results, the CO oxidation

onset potential remains the same for all the samples. However, the peak potential for CO oxidation decreases by increasing Ru content. PtRu (1:1) has the lowest peak potential presenting the most appropriate composition which has been also reported in the research by Wasmus and Kuver [132].

In contrast to PtRu, Urian et al. [14] through polarization measurements of PtMo with alloying compositions in the range of 1:1 to 5:1 observed an invariance of anode polarization behaviour for electro-oxidation of hydrogen containing 50ppm CO. This implies that Mo has a unique property in effectively oxidizing the adsorbed CO layer and very small amount of it is required for CO tolerance.

Chen et al. [133] investigated the effect of the atomic ratio on the catalytic activity and CO tolerance of a series of $\text{Fe}_x\text{Pt}_{1-x}$ ($x=10, 15, 42, 54, 58$, and 63) bimetallic electrocatalysts towards oxidation of formic acid. According to their results obtained from CV, chronoamperometry and electrochemical impedance spectrometry experiments, the alloys composition affects the catalytic activity of the catalysts significantly. The activity increases in the sequence of $\text{Fe}_{63}\text{Pt}_{37} < \text{Fe}_{10}\text{Pt}_{90} < \text{Fe}_{58}\text{Pt}_{42} \approx \text{Fe}_{54}\text{Pt}_{46} < \text{Fe}_{42}\text{Pt}_{58}$. The maximum activity and stability was observed for $\text{Fe}_{42}\text{Pt}_{58}$. It was concluded that the maximum current density, the lowest oxidation onset potential and the most superior CO tolerance is exhibited by PtFe with atomic ratio of 1:1.

In the case of oxidative agents modified Pt-based electrocatalysts, the activity of the catalysts are strongly dependent on the content of the promoter. For instance, Lin et al. [95] through polarization and voltammetry experiments have found out that the hydrogen and CO

oxidation activity of Pt/C promoted by cerium is strongly influenced by the content of CeO₂. An optimum content of 20% was reported the appropriate amount of cerium to effectively enhance the CO oxidation. In fact, adding too much of the oxidative agent blocks a large portion of the Pt active sites.

(iii.3) Catalyst support

The primary goals of placing the active components of a catalyst onto a support material are to improve the dispersion of the active components and the mechanical and chemical stability of the catalyst. These goals are achievable by applying suitable supports and generating effective interactions between the active content and the support.

A suitable support for fuel cell applications is TiO₂, which possesses high stability in the acidic and oxidative environment [134, 135]. Although the electronic conductivity of titania is lower than that of carbon materials, it can be increased by aliovalent cation substitution. Tungsten was used as a support component by Wang et al. [105]. Pt was supported on Ti_{0.7}W_{0.3}O₂ nanoparticles (50 nm), which were synthesized using sol-gel method and platinized using impregnation and subsequent reduction technique. Electrochemical experiments indicate the unique CO-tolerant electrocatalytic activity of this catalyst as compared with commercial E-TEK PtRu/C catalysts.

Tungsten oxide, WO₃, has been used as a support material for Pt by Xiangzhi et al. [106] to study the performance of the catalyst, Pt/WO₃, which is a mesostructured electrocatalyst. The loading of Pt in the catalyst was as low as 7.5 wt% supported on tungsten oxide prepared using mesoporous silica by a simple one-step casting method. The catalytic activity of the

catalyst towards the oxidation of hydrogen and CO and the stability of the catalyst in acidic media were investigated. The experimental results indicated that the catalyst exhibits more than three times higher mass activity towards hydrogen oxidation, superior CO tolerance and improved stability compared to those of the commercial 20 wt% Pt/C. The high catalytic activity of the catalyst is related to the formation of the tungsten bronze, the high surface area and meso-porosity of the WO_3 as the support material. The mesoporosity of the support enhances the catalytic activity due to the more facile gas molecules transportation through the meso-porous support [136].

Thin-film WO_x electrodes deposited on GDL with and without Pt have been incorporated in polymer electrolyte membrane fuel cells by Wickman et al. [107]. In their work, the effect of applying WO_x as a Pt support with different thicknesses (0- 40 nm) with and without a 3 nm Pt top layer were prepared by thermal evaporation. XPS measurements showed that WO_3 is the species most likely to form during oxidation. On the other hand, platinum was found to be in a metallic state. SEM graphs shows that the WO_x covers efficiently the carbon particles in the micro-porous layer of the gas diffusion layer. The limiting current in the hydrogen oxidation reaction increases with the Pt surface area on thicker WO_x films. In addition, the presence of Pt on WO_x film shifted the oxidation onset potential to lower potentials compared to that of Pt. However, inclusion of WO_x increases the contact resistance of the electrode. According to their results, the electrochemical surface area (ECSA) was higher in the case of samples with Nafion, while in the absence of Nafion, a very low ECSA was obtained. This is attributed to the hydrophobic nature of the gas diffusion layer which reduces the wet-ability of Pt particles when Nafion is not included. However, in the presence of a layer of WO_x as the

platinum support, a high ECSA was observed even in the absence of Nafion. It is because of the increase of the gas diffusion layer wet-ability in the presence of WO_x . They reported that coating the samples of Pt on a WO_x layer with Nafion decreased the ECSA initially and further cycling deactivated the electrode. This might be due to WO_x dissolution which degrades the Nafion or poisons the Pt. This issue was not seen in a fuel cell environment which indicates that this issue happens only in the liquid electrolyte. In addition, the ECSA was almost the same value for both Pt and Pt on WO_x under the fuel cell environment. ECSA increased in the absence of Nafion for Pt on WO_x layers of 10 nm and thicker. The higher Pt utilization might be because of the proton conductivity of WO_x . According to their results, WO_x increases the Pt utilization for the hydrogen oxidation reaction and increases the CO tolerance.

Using a proper metallic support material with a compressive strain and ligand effect on the catalytic activity of Pt is a possible approach to develop CO tolerant electrocatalysts. Nilekar et al. [104] designed and evaluated a class of Pt-M (M=Ir, Pd, and Ru) monolayer supported on a non-Pt metal using a combination of density functional theory (DFT) calculations and voltammetry experiments. According to their results, the mentioned catalysts exhibit improved CO tolerance and might be suitable for the anode side of PEM fuel cells. These catalysts reduce both the anode overpotential in the presence of CO and the used Pt amount with the consequence of reducing materials cost. Using DFT calculations, they attributed the better CO tolerance of these catalysts to high repulsive interactions between CO molecules adsorbed on the surface which leads to weaker binding energy and lower coverage of CO than on pure Pt.

A critical factor in the design of CO tolerant catalysts is the placing location of the active materials onto the support material. CO molecules are possibly adsorbed by the support materials, thus placing the active materials deep within the support would guard the catalyst from poisoning. A possible modification would be the deposition of Pt deep in the support structure while the promoters are deposited close to the catalyst surface so that the CO molecules are removed before reaching of the hydrogen stream to Pt sides.

(iii.4) Preparation methods

The preparation of electrocatalysts includes two steps: a dispersion step and a subsequent reduction, the former being the determining step after which the final product particles structure and placement will be retained. Dispersion is achieved by impregnation, colloidal technique, co-precipitation, and deposition.

Götz and Wendt [78] prepared and compared the catalytic activity of ternary electrocatalysts including PtRuM/C (M= W, Mo and Sn) starting from PtRu/C prepared by impregnation and colloidal methods. Figure 2.6 shows the polarization curves of PEM fuels with the prepared catalysts operating at 75°C fed by a hydrogen stream including 150 ppm CO. It can be seen that for both impregnation and colloidal methods, PtRuW/C and PtRuSn/C exhibit the most superior activity at low ($<200 \text{ mA.cm}^{-2}$) and high ($>200 \text{ mA.cm}^{-2}$) current densities, respectively. Furthermore, The E-TEK PtRu/C catalyst presents a higher activity compared to all the ternary catalysts prepared by the impregnation method. This is supposedly attributed to the structure-activity correlation. E-TEK PtRu/C has a uniform alloy structure [122] as evidenced from XRD patterns, while according to the XRD pattern of the impregnated PtRu/C catalyst, phases of cubic platinum and hexagonal ruthenium structures are observed

implying that it still contains unalloyed platinum particles. These unalloyed sites can be modified by adding other elements but adding a second metal to a homogenized alloy will just block a part of the active area.

Furthermore, Fig. 2.6 shows that the catalysts synthesized by colloidal method are more active than those prepared by impregnation. It is because of the close contact among the elements in the catalyst prepared by colloidal method (developed by Bönnemann [137]) ensuring the formation of completely alloyed particles as observed in the case of PtRu/C. For the catalysts prepared by impregnation, the extent of contact or separation among elements is not known.

Fig. 2.6 Polarization curves of fuel cells operating on hydrogen containing 150ppm CO with the anode catalysts synthesized by impregnation and colloid methods [78]. Reproduced from Ref. [78] with permission of Elsevier.

Other authors have also stated that to synthesize electrocatalysts with more pronounced CO tolerance, it is essential for the promoter to be in close contact with the Pt sites occupied by CO molecules [68, 71, 130, 138]. Kim et al. [115] claimed that the conventional impregnation technique does not lead to a structure in which the interface between the promoter element, Sn, and Pt is formed effectively. To solve this issue, Kim et al. [115, 139] added Sn into the Pt structure using chemical vapor deposition (CVD) such that it was selectively deposited on the Pt and Ru surfaces instead of on the carbon support. Lim et al. [81] developed a new effective method to prepare well dispersed nano-sized PtSn/C catalysts synthesized by borohydride reduction and hydrothermal treatment. A slight shift in 2θ values of the Pt (2 2 0) peak of the PtSn/C catalysts was reported in the XRD pattern as the Sn content is increased, compared with those of the Pt/C catalyst, which suggests that PtSn alloy has been formed. HR-TEM results show average particle sizes of approximately 2.3 nm Pt-Sn particles on the carbon surface, which is in agreement with XRD data. According to the single-cell and accelerated durability tests carried out, the PtSn and Pt₃Sn/C catalysts shift the CO oxidation onset potential to lower values than that on the commercial Pt/C catalyst and also exhibit higher stability. The improved performance and reliability are attributed to the coexistence of PtSn alloys and Sn oxides.

Antolini [80] presented a comprehensive review on the preparation techniques and structural properties of Pt-Ru based ternary electrocatalysts used for PEM fuel cell applications.

Composite support is another preparation method used by Hou et al. [140] who synthesized PtRu-H_xMeO₃/C (Me= Mo and W) catalysts. The synthesis method is briefly preparing a composite support including H_xMeO₃ colloids on carbon and subsequent impregnation of Pt

and Ru metal salts reduced by formaldehyde. The superior CO tolerance of the synthesized catalyst is attributed to the spill-over of hydrogen and CO occurred on the transition-metal oxides facilitating the CO electro-oxidation in PEMFC anode. Martínez-Huerta et al. [82] innovated a new two-step method to develop PtRu–MoO_x/C nanoparticles through deposition of Pt and Ru nanoparticles on MoO_x/C prepared by colloidal method of Watanabe et al. [141]. They obtained excellent CO tolerance and smaller noble metal amounts usage by applying this method. The crystal structure of the intermetallic catalysts affects the catalytic performance towards CO electrooxidation. To prepare catalysts with the exclusive presence of crystal structures of nanoparticles, such as (fcc or hcp) controlled surface reaction modification can be used [70].

An important factor determining the catalytic activity of electrocatalysts towards CO and H₂ oxidation is the particle size. The formic acid method leads to formation of particles with very small average size (3nm) and consequently increasing the surface area [88]. The preparation methods of promoter decorated Pt/C catalysts synthesis are well explained in a review by Maillard et al. [87].

(iv) Catalytic activity of the catalysts towards CO oxidation

Making a realistic and meaningful comparison among the Pt-based electrocatalysts towards CO electro-oxidation is not an easy task because of the different preparation techniques applied, variable compositions and morphologies, and different experimental conditions. In our investigation, we have studied several binary and ternary electrocatalysts under PEM fuel cell operating conditions. Figure 2.7 shows the single cell potential-current curves for the catalysts (Pt-M (M= Ru, Mo, Fe, Co, Ni), PtRuMo/C, PtCoMo/C and PtRuPb/C) in an H₂/O₂ PEM fuel cell with anodes fed by hydrogen in the presence of 100ppm CO [85]. The anodic

catalyst loadings are 0.5 mg.cm^{-2} (60 wt %) for all cases. Electrochemical experiments carried out in this configuration provide direct comparison of the anode catalysts under realistic fuel cell operating conditions. The significant kinetic loss due to the presence of CO is obvious. The contributions of mass transport polarization are negligible and the ohmic polarization losses have approximately the same contribution for all the electrocatalysts considered in this study. To compare the catalytic activity of the electrocatalysts investigated by other researchers, the results from rotating disk electrode and single PEM fuel cell polarization curves measurement and cyclic voltammetry experiments are used, which is the most common technique applied to determine the catalytic activity towards hydrogen and carbon monoxide oxidation in acidic media.

Fig. 2.7 Single cell polarization curves for the catalysts (Pt-M (M= Ru, Mo, Fe, Co, Ni), PtRuMo/C, PtCoMo/C and PtRuPb/C) in an H₂/O₂ PEM fuel cell with anodes fed by hydrogen in the presence of 100ppm CO.

CO oxidation onset potential and current density at a certain potential measured from CV and polarization measurements are listed in Tables 2.2 and 2.3 illustrating the electrocatalysts kinetic parameters for CO oxidation. Comparing the information presented in Tables 2 and 3, it is observed that the catalytic activity of Pt/C is enhanced significantly by adding the transition metals.

Table 2.2 Kinetics parameters of CO electro-oxidation under fuel cell operating conditions.

Electrocatalyst	Fuel Cell		Ref.
	i (A.cm ⁻²)@ E	E_{onset}	
Pt/C ^a	0.16@0.7V	0.4	[14]
Pt-Ru/C ^a	0.21@0.7V	0.25	[3]
Pt-Mo/C ^a	0.35@0.7V	0.05	[3]
Pt-Sn/C ^b	0.05@0.7V	0.25	[78, 81]
Pt-Fe/C ^a	0.19@0.7V	0.42	[65]
Pt-Ni/C ^a	0.19@0.7V	0.41	[85]
Pt-W/C ^a	0.36@0.7V	0.41	[65]
Pt-Co/C ^a	0.2@0.7V	0.41	[85]
Pt-Ce/C ^c	0.8@ 0.41V	–	[95]
Pt/WO _x ^d	–	0.45	[107]
HPA-Pt/C	0.21@0.7V	0.3	[109]
Pt-Ru-Mo/C	0.34@0.7V	0.12	[85]
Pt-Ru-Ni/C ^d	0.91@0.7V	–	[72]
Pt-Ru-W/C ^b	0.08@0.7V	–	[78]
Pt-Ru-Sn/C ^b	0.12@0.7V	–	[78]
Pt-Ru-Ir/C ^d	0.67@0.7V	–	[116]
Pt-Ru-MoO _x /C	0.2@0.7V	0.22	[67]
Pt-Ru-WO _x /C ^f	0.1@0.7V	–	[119]

a 85°C, 100ppm CO/H₂- O₂, 0.3MPa

b H₂/150 ppm CO

c 80°C, 5ppm/H₂-air

d 80°C, 100 ppm CO/H₂- O₂, 0.2MPa

e 70°C, 100 ppm CO/H₂- O₂

f 75°C H₂/150 ppm CO

Table 2.3 The activity of the electrocatalysts.

Electrocatalyst	Activity		Ref.
	i at E	E_{onset}	
Pt-Ru/C ^a	0.25 mA.cm ⁻² @0.1V vs. SCE	0.05 V vs. SCE	[22]
Pt-Mo/C ^a	1.3 mA.cm ⁻² @0.1V vs. SCE	-0.05 V vs. SCE	[22]
Pt-Sn/C ^b	0.5 mA.cm ⁻² @0.1V vs. SCE	0.22 vs. RHE	[24]
Pt-Fe/C ^a	1.86 mA.cm ⁻² @0.1V vs. SCE	-0.2 vs. SCE	[91, 92]
Pt-Ni/C ^c	–	0.4vs. NHE	[92]
Pt-Ce/C ^b	0.5 mA.cm ⁻² @0.1V vs. RHE	0.64 vs. RHE	[95]
Pt-Pb/C ^d	–	~0.2 vs. RHE	[96]
PtSn@Pt ^b	2 mA.cm ⁻² @0.1V vs. SCE	-0.14 vs. SCE	[24]
Pt ₃ Fe@Pt ^a	1.85 mA.cm ⁻² @0.1V vs. SCE	0 vs. SCE	[91]
Pt@Fe _x O _y	–	–	–
Ru@Pt ^c	–	0.45vs. RHE	[98]
MoO _x @Pt ^a	2 mA.cm ⁻² @0.1V vs. SCE	-0.14 vs. SCE	[22]
Pt-WO ₃ ^b	–	0.12vs. RHE.	[100]
Pt-Ir/Ir ^e	–	0.55 vs. RHE.	[104]
Pt/Ti _{0.7} W _{0.3} O ₂ ^f	0.5 mA.cm ⁻² @0.2vs. RHE	0.05 vs. RHE	[105]
Rh(porphyrin)-PtRu/C ^g	50μA.cm ⁻² @0.3V	0.12 vs. RHE	[108]
MoC _x /C ^b	max current: 8.44 μA	0.63vs. RHE	[120]

a 0.5 M H₂SO₄, H₂/1000 ppm COb 0.5 M H₂SO₄, saturated with COc 0.5 M HClO₄, saturated with COd 0.1 M H₂SO₄, saturated with COe 0.1 M HClO₄, saturated with COf 0.1 M H₂SO₄ in the presence of 2% COg 0.1 M HClO₄ in the presence of 2% CO

(v) Stability of the catalysts in acidic media

As reviewed in this chapter, many efforts have been made to develop CO tolerant electrocatalysts with improved catalytic activity. The catalyst system currently acknowledged as the most promising anode material for PEM fuel cells is PtRu/C. Another important property of the anode catalysts for PEM fuel cell, which has not been researched significantly, is the stability of the electrocatalysts. Under PEM fuel cell operating conditions, the ions of the added metal leach out from the electrode leading to degradation and poor stability of the anode materials. PEM fuel cells degradation mechanisms and mitigation approaches are well reviewed in several studies [142-145]. The loss of the metal ions not only decreases the functionality of the anode and increases the anode overpotential, but also affects other parts of the cell. The dissolved ions cause membrane drying and cathode degradation, too. Although multimetallic anode materials for CO and methanol oxidation have been prepared which present superior catalytic activity, they should be studied under long term operational and potential cycling conditions.

Generally, electrocatalysts with ordered intermetallic structure are more stable compared to alloys because of their high enthalpies of formation [24, 96, 97]. However, according to results of electrochemical experiments, intermetallic structures including non-noble elements such as Bi or Pb may not be stable at the electrode potentials as high as +0.80 V or beyond [123]. Electrocatalysts with core-shell structure also possess a higher stability compared to those with alloy structures [22, 24, 98]. Ochal et al. [98] investigated the stability of Ru@Pt core-shell particles and reported the good reliability of this electrocatalyst. This is in agreement with the theoretical predictions [146].

Adding another metal to Pt as the PEM fuel cell catalyst improves the stability of the catalyst by hindering the agglomeration of Pt particles [75]. The oxides or carbides of some elements such as silicon [147], titanium [147-149], tungsten [107, 150], and cerium [95] are promising candidates for electrode materials to be used under fuel cell operating conditions. Although some of these materials suffer from low electronic conductivity because of the metal being in their highest oxidation state.

PtMo/C with alloy structure has been acknowledged for its excellent CO tolerance. However, this catalyst is unstable because of the high solubility of $\text{MoO}_3 \cdot x\text{H}_2\text{O}$ at low pH [73]. Lebedeva and Janssen [73] prepared binary PtMo via the reductive co-precipitation and studied electrochemical properties of the prepared catalyst. It is reported that X-ray photoelectron spectroscopy indicates that Mo is formed in its trioxide state, MoO_3 , while Pt is fully reduced to Pt^0 . This should be noted that their experimental results indicate that the bimetallic Pt-Mo/C catalysts are apparently unstable because Mo dissolves gradually and the catalyst suffers from a gradual loss of Mo. Therefore, stability is a critical factor in the development of new catalysts with improved CO tolerance. Martinez-Huerta et al. [92] also observed that Pt-Ni alloy is not stable as Ni is removed out of the surface under long term stability tests by cycling beyond 1V.

In contrast to PtMoO_3/C [73], PtWO_3/C is reported to be stable enough when exposed to 0.5M sulphuric acid solution and under continuous potential cycling between 0.05 and 0.8V vs. RHE at room temperature. However, other research studies have reported the slight solubility of the tungsten oxide at higher temperatures [150, 151].

Cheah et al. [74] coupling Monte Carlo (MC) simulation with an elementary kinetic model studied the effect of CO adsorption on Pt-Co nanostructure, activity and stability. The results obtained were compared with experiments indicating an agreement between the theoretical and experimental data. They reported that the nanoparticles size and composition strongly affect the HOR activity and stability. Simulations reveal that the cobalt dissolution is slowed down in the case of Pt-Co in short term operation because of the preferential CO adsorption on cobalt. However, in long-term operation, CO adsorption on PtCo reduces the catalyst activity leading to an increase in the electrostatic potential with the consequence of higher surface cobalt dissolution. Due to the cobalt dissolution, the Pt-Co activity degrades faster than that of Pt₃Co in long-term operation. This phenomenon is verified by performing electrochemical half cell experiments. The experimental results presented that there are more cobalt ions dissolving into the electrolyte when CO is present in the hydrogen feed.

2.3 Modeling of PEMFC Carbon Monoxide Poisoning

Carbon monoxide poisoning issue has been studied in the literature both numerically and experimentally. The CO poisoning simulation efforts may be classified into one dimensional and multidimensional model.

The model developed by Springer *et al.* [152] considering CO kinetics explained the effects of CO adsorption and reaction on the PEM fuel cell performance successfully. Zhang *et al.* [153] using a mass balance between the inlet and outlet of the PEM fuel cell calculated the CO consumption inside the fuel cell; however, the carbon monoxide and hydrogen concentrations variation along and across the anode flow channel have been neglected.

Baschuk and Li [5] examined the issue of carbon monoxide poisoning in PEM fuel cells. They investigated the carbon monoxide and hydrogen electrochemistry, the effect of CO poisoning on the cell performance, CO poisoning mitigation methods and models of CO poisoning. It is found that CO is adsorbed on the catalyst surface preferentially and poisons the hydrogen oxidation through blocking active sites.

Effect of reformat usage as the feed stock of PEM fuel cells has been investigated by Springer *et al.* [154], and Chan *et al.* [155]. Chan *et al.* combined the Bernardi and Verbrunge and Springer *et al.* works considering the CO kinetics in the anode. They investigated the effect of different operating parameters such as temperature, pressure, current density, hydraulic permeability and electro-permeability on the water self-sufficiency of PEM fuel cells. Superficial velocities of water in the MEA at different current densities were calculated and compared with those calculated by Bernardi and Verbrunge. In addition, they investigated the effect of CO poisoning on the polarization of the cell.

Baschuk *et al.* [156] developed a non-isothermal, multi-dimensional, mathematical model of a PEM fuel cell considering the oxygen reduction in the cathode side and detailed hydrogen and carbon monoxide kinetics in the anode. They solved the equations for the one dimensional case and calculated temperature distributions in different parts of the cell. In addition, they evaluated the susceptibility of the cell performance to the pressure. The results are in good agreement with the experimental data.

Zhou *et al.* [157] incorporating the Springer *et al.* [152] carbon monoxide adsorption kinetic equations and oxidation behavior into their previously developed 3D model simulated the CO

poisoning effect on the PEM fuel cell operation. Furthermore, they considered the inert gases dilution effect. The detailed carbon monoxide and hydrogen concentration profiles inside the anode are calculated. In works done by Springer *et al.* [152, 154] and Zhang *et al.* [153] the fuel cell chemical reactions variations have not been taken into account. The simulation results are also in a very good agreement with the experimental data by Divisek *et al.* [158].

Through a multi-dimensional model incorporating the PEMFC electrochemical reactions, transport phenomena and the anode side carbon monoxide poisoning related four chemical/electrochemical processes, Ju *et al.* [159] obtained a clear understanding of the CO poisoning mechanisms; the simulation results agree well with the experimental data available in the literature. In case of feed stock containing 50 and 100 ppm level of CO, the three distinctive regions of polarization curve showing the performance degrading effect of carbon monoxide in the anode side have been observed. Finally, based on their model, they could propose some methods to decrease the detrimental effects of CO poisoning on PEMFC.

Chapter 3 Experiments¹

3.1. The Role of Electronic Properties of Pt and Pt Alloys for Enhanced Reformate Electrooxidation in Polymer Electrolyte Membrane Fuel Cells

3.1.1. Overview

One major current challenge of PEM fuel cells deployment is to overcome the durability issue of the current anode materials which are susceptible to hydrogen impurities. To design stable and efficient catalysts with enhanced reformate tolerance, a comprehensive understanding of effective factors is essential. Through electrochemical tests, the catalytic performance and reformate tolerance of some binary and ternary catalysts including Pt-M (M= Ru, Mo, Fe, Co, Ni), PtRuMo/C, PtCoMo/C and PtRuPb/C electrocatalysts are studied focusing on the effective factors on reformate tolerance. The anode side is fed by H₂: CO (x ppm CO balanced in hydrogen) and H₂:CO₂ (50:50 molar ratio) under identical stoichiometry and operational conditions. Reformate as the PEM fuel cells anode side feedstock, typically contains a mole fraction of hydrogen in the range of 0.4- 0.75, with CO in the range of 50-100 ppm and CO₂ making up the balance. CO is well-known as a poison for hydrogen oxidation on platinum in the anode of a PEM fuel cell and a medium temperature phosphoric acid system. Besides, CO₂ has the potential of CO production through either a) a reverse water gas shift reaction [10-14] ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) which is the reduction of CO₂ at the operating temperature of PEM fuel cells of 80 °C or b) the electro-reduction of CO₂ through $\text{CO}_2 + \text{H}^+ \rightarrow \text{CO} + \text{H}_2\text{O}$ [15-

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Ehteshami, S.M.M., W.J. Zhou, and S.H. Chan, *Energy analysis of an electrolytic-based selective CO oxidation system for on-board pure hydrogen production*. International Journal of Hydrogen Energy, 2012.

17]; The poisoning level caused by CO_2 is beyond those accounted for by simple dilution [11-14]. Hence, on the way to develop new durable catalysts for impure hydrogen feedstock, the enhancement of the reformat oxidation should be considered over the whole range of industrial CO and CO_2 concentrations. PtRu alloy catalyst has been widely acknowledged as one of the most promising candidates for the anode side exposed to reformat feedstock [18, 19]. Although other bimetallic alloys, such as PtMo [20, 22] and PtSn [23, 24], have also shown good CO tolerance, even better than that shown by the PtRu alloys. However, on the contrary, it is observed that the CO_2 tolerance of PtRu/C is greater than that of PtMo/C [10, 14, 17]. Russell et al. [10] have shown that the decreased CO_2 tolerance of PtMo compared to PtRu is owing to the difference in the mechanisms of improved CO tolerance, compared to a Pt/C reference catalyst; at PtRu the mechanism is because of the water activation which occurs at Ru sites, while at PtMo the mechanism relies on the turn-over the Mo (IV/VI) redox couple.

Addition of the transition metals to Pt modifies the electronic properties and thus changes the binding energy and impurities coverage with the consequence of enhanced reformat tolerance. Enormous investigations have been done to develop CO tolerant binary and ternary catalysts by adding elements such as W, Mo, Co, Ni, Sn, Ir, Pd etc. to Pt/C and PtRu/C [18, 72, 78, 114-116, 132, 160, 161]. The added component either as Pt alloy or adsorbate layer on Pt, has a co-catalytic activity for CO oxidation. These works have attributed the effect of the added element to the modification of the bifunctional catalysis, electronic properties of Pt, lateral repulsive forces, and ensemble effects. So far, very few of the works have considered both CO and CO_2 issues and a comprehensive and consistent theory to correlate the enhanced

tolerance to the effective features is missing. In this study, it is suggested that a target anode catalyst which efficiently tolerates both CO and CO₂ in the hydrogen stream could be a Pt-based multi-component material in which: 1) there are sufficient oxophilic catalyst sites on the surface in the vicinity of Pt nano-particles, 2) the electronic structure of Pt is altered in a way that impurities are adsorbed less and weaker on Pt sites, and 3) yet the availability extent of Pt sites is enough for hydrogen oxidation, among the fuel molecules and between the fuel molecules and the catalyst surface.

Adding transition metal neighbors M (M = Fe, Co, Ni, Ru, Mo) [19, 72, 78, 91, 94] changes the Pt electronic properties which accordingly modifies the overall binding energy of simple adsorbates to the metal surface. Therefore, it is critical to comprehensively elaborate the role of electronic properties on the reformat tolerance of electrocatalysts to be able to design and develop catalysts with excellent activity and tolerance in the presence of CO and CO₂. Electronic properties modifications are explainable by combined ligand and strain effects caused by alloying Pt with the added element.

3.1.2. Catalyst preparation

The anode electrocatalysts used in this study including Pt/C and binary catalysts PtM (M=Ru,Co, Ni, Fe, Mo) are obtained from De Nora N.A., E-TEK division, Somerset, NJ. The ternary catalysts including PtRuM (M=Mo and Pb) are synthesized in-house. Micro-emulsions technique was used to synthesize the ternary catalysts. The details of the synthesis method can be found elsewhere [162, 163]. All the binary catalysts include 30% metal content and an atomic ratio of (1:1) for binaries (PtRu/C (1:1), PtMo (1:1), PtFe (1:1), PtNi(1:1),

PtCo(1:1)). The ternary electrocatalysts include 30% metal content and with the atomic ratio of (1:1:1) (PtRuMo (1:1:1), PtCoMo (1:1:1)). Another ternary catalyst has been developed and tested by our group which includes 30% PtRuPb with atomic ratio of (7:7:1). This catalyst exhibited fairly good performance for methanol oxidation. Here in this work, the reformate tolerance of this catalyst is studied to clarify the role of adding Pb in the reformate tolerance of PtRu/C. Pt/C was used as a control to compare the activity and tolerance of the binary and ternary catalysts with a standard. After washing and filtering the ternary catalysts supplies, they were dried at 100 °C overnight. The dried catalyst was reduced by heating to 300 °C in a tube furnace exposed to hydrogen stream. A loading of 0.5 mg cm⁻² of all catalysts were used to make the anode gas diffusion electrodes. The cathode side was the same in all experiments (a Pt/C electrode with loading of 0.5 mg cm⁻² from E-TEK division, Somerset,NJ). The anode electrodes were made by spraying the catalyst ink to reach a metal loading of 0.5 mg cm⁻². Nafion 112 was used to make MEAs using a standard hot pressing method.

3.1.3. Physical Characterizations

The carbon-supported core-shell nanoparticles are characterized by X-ray diffraction (XRD). The XRD patterns are collected using a Rigaku X-ray Diffractometer equipment with CuK α (wavelength 1.5418Å) filtered by a nickel filter. The samples are scanned within 10°<2 θ <90° and the recorded patterns are matched against the Joint Committee on Powder Diffraction Standards (JCPDS) data base files. The XRD results are presented in Table 3.1. Face centered cubic (FCC) lattices with very high degree of crystallinity are observed in the XRD results. As can be seen, alloying Pt with transition metals leads to a lowering of the lattice parameters

(and hence the Pt-Pt bond distance). The perturbation of the lattice parameters is significant for all the catalysts except for PtMo/C and PtRuMo/C. The particle sizes are in the range 25-39Å.

3.1.4. Catalyst Ink Preparation

The ionomer is added into the catalyst in the modified method of MEA fabrication which was used in the experiments. Because platinum can react with any strong oxidizer and organic materials, ionomer is not added into the catalyst directly. To avoid catalyst damage, water is added into the catalyst as the solvent before the Nafion is added. The carbon supported platinum is weighed and water is added to avoid the catalyst damage. Then Nafion is added to the solution with a 3:7 ratio. Isopropanol alcohol (IPA) is added into the solution; then, magnetic and ultrasonic stirring are applied to obtain a homogeneous and viscosity controlled catalyst ink.

Table 3.1 XRD results of the electrocatalysts considered in this study

Electrocatalyst	Lattice Type	Nominal atomic ratio	XRD Analysis		
			Lattice parameter/ Å	Pt-Pt bond distance/Å	Particle size/ Å
Pt/C	fcc	-	3.927	2.777	28
PtRu/C	fcc	1:1	3.890	2.751	35
PtMo/C	fcc	1:1	3.910	2.765	35
PtFe/C	bcc	1:1	3.829	2.707	39
PtNi/C	fcc	1:1	3.812	2.695	25
PtCo/C	fcc	1:1	3.904	2.760	34
PtRuPb/C	fcc	7:7:1	3.885	2.747	34
PtRuMo/C	fcc	1:1:1	3.91	2.765	25
PtCoMo/C	fcc	1:1:1	3.87	2.736	42

3.1.5. Membrane electrode assembly (MEA) Fabrication

Generally, there are two methods for preparing the catalyst layer and assembling it with the membrane. MEA fabrication is the commonly used title for the combination of membrane and catalyst layers. The first technique is depositing the catalyst onto the gas diffusion layer and then assembling it with the membrane by hot-pressing. The second method contains applying the catalyst layer onto the membrane. The gas diffusion layer will be added later.

The first method can be used in two ways. These two methods differ in the impregnation of electrolyte into the catalyst layer. In conventional method, the catalyst ink is first applied on the gas diffusion layer followed by sintering. Then the ionomer is spread onto the sintered gas diffusion layer; while in the modified method the ionomer solution is added into the catalyst ink and the ink will be then applied to gas diffusion layer. Finally, sintering is the last step. The benefit of the modified method is the easy control of Nafion content in the catalyst ink. There are some methods to deposit the catalyst ink either on the gas diffusion layer or membrane such as spreading, spraying, catalyst powder deposition, ionomer impregnation, electro-deposition, impregnation reduction, evaporative deposition, dry spraying, and painting. Although great progress has been made in catalyst layer fabrication, still some technical aspects should be considered in order to make future progress in this area. Maximizing the three phase interface of catalyst, membrane and voids, method of stabilizing the catalyst particles on the supporting media, and reducing the degradation of the catalyst layer are points to be taken into account.

To remove different impurities in the membrane, the membrane is treated with proper solutions. The membrane to be made from perfluoro-sulphonic acid needs a 5% aqueous hydrogen peroxide solution at the boiling point of the solution to eliminate organic impurities. Metallic impurities can be removed by immersion of the membrane in diluted sulfuric acid. The membrane is immersed in distilled water for several times after each immersion in hydrogen peroxide and sulfuric acid to clean any remaining hydrogen peroxide and acid residues.

Carbon paper is treated in a 30% polytetrafluoroethylene (PTFE) solution to increase its hydrophobicity. To improve the pore homogeneity of the gas diffusion layer, carbon powder solution is prepared and applied onto the PTFE treated carbon paper. Carbon powder and PTFE are added together with a 3:7 mixing ratio. Also, water, the same amount of PTFE, and Isopropanol alcohol (IPA), 30% of the water amount are added to control the solution viscosity followed by stirring in order to obtain homogeneity. The GDL then is dried in the ambient temperature. This step is done for several times to get loading around 3 mg/cm^2 . After drying for half a day, the GDL is heated in the furnace to be sintered at 400°C for around an hour.

The carbon powder layer applied on the treated carbon paper is considered as the micro-porous layer. The primary role of this layer is facilitating water transport from the cathode catalyst layer into the gas diffusion layer by producing much smaller water droplets. In addition, it improves the electrical contact between the porous media and the adjacent catalyst sites. The most important advantage of this layer is prevention of Pt particles used in the

catalyst layer to penetrate in the GDL and avoiding catalyst layer degradation. The catalyst ink is applied onto the GDL, sintered in the furnace at 130°C for half an hour. Membrane and the electrode are then hot pressed at 130°C with a pressure of $30\text{--}40\text{ kg/cm}^2$ for 90 seconds.

3.1.6. Electrochemical experiments

All MEAs were tested in a 5-cm^2 single cell fuel cell using a test station facility which allows control of humidification, cell temperature, gas flow rates, etc. A LabView[†] routine is used to as the interface program to record the polarization data from the cell using an HP 60501B 150 W electronic load module.

Before acquiring the polarization data, nitrogen flows through both sides of the cell to condition the MEAs by gradually increasing the humidification temperature from room temperature up to 85°C . After keeping the cell under these conditions for a few hours, the pressures of the anode and cathode sides are increased slowly to 3 and 5 atm, respectively. The half cell polarization of the as conditioned MEAs was measured after the gases were switched to saturated H_2 and O_2 and only those with less than $\pm 5\text{ mV}$ variation at 1 A cm^{-2} compared to a control electrode were used for subsequent measurements.

The operating temperature and the relative humidification of the cell were 85°C , 100%, respectively. Oxygen as the oxidant flow through the cathode side while 100ppm CO and 50% molar ratio of CO_2 balanced in hydrogen as the fuel flow through anode are used. In addition, the steady-state polarization measurements were also measured with anode gas compositions containing 50, 100 and 300 ppm of CO (balance H_2). The cyclic voltammetric

experiments were carried out using an Autolab potentiostat/galvanostat (PGSTAT-30, Ecochemie, Brinkman Instruments). Cyclic voltammetry was performed while pure H₂ was passed over the reference electrode (cathode side) and N₂ over the working electrode (anode side). All the experiments were repeated at least twice to ensure reproducibility.

Anode polarization of the hydrogen electrode in the presence of CO or similarly CO₂ ($E_{H_2/ads}$) as a function of current density was obtained from measurements of the electrode polarization (E_{H_2}) in the absence of CO or CO₂ with respect to a hydrogen reference electrode which was modelled by flowing hydrogen through the cathode side and considering the cell potential values in the presence ($V_{H_2/ads}$) and absence of CO or CO₂ (V_{H_2}), by using the expression:

$$E_{H_2/ads} = V_{H_2} - V_{H_2/ads} + E_{H_2} \quad (3.1)$$

The anode overpotential in the presence of impurities is calculated via the following equation at each current density:

$$\eta = [E_{H_2/ads} - (E_{H_2/ads})_{J=0}] \quad (3.2)$$

OCV was read 15 minutes after introducing fuel and oxidant into the cell to ensure reaching steady state. For fuel cells operating with hydrogen and air at 1 atm, OCV of above 0.9 V is acceptable.

3.1.7. Results and discussion

Figure 3.1 compares the single cell polarization curves for the catalysts (Pt-M (M= Ru, Mo, Fe, Co, Ni), PtRuMo/C, PtCoMo/C and PtRuPb/C) in an H₂/O₂ PEM fuel cell with anodes fed by hydrogen in the presence of 100ppm CO. The anode loadings are 0.5 mg. cm⁻² (60 wt %)

for all cases. Electrochemical experiments carried out in this configuration provide direct comparison of the anode catalysts under realistic fuel cell operating conditions. The big kinetic loss due to the presence of CO is obvious. The contributions of mass transport polarization are negligible and the ohmic polarization losses have approximately the same contribution for all the electrocatalysts considered in this study. Figure 3.1b shows the corresponding extra anode polarization due to the presence of 100ppm CO as defined in equation (3.2). Comparison of the single cell performance and the anode polarization curves presented in Figure 3.1 for the electrocatalysts considered in this study shows that the ternary electrocatalysts developed in this study (PtCoMo, PtRuMo, PtRuPb) exhibit superior CO tolerance compared to PtRu/C both of which are significantly higher than Pt/C. The CO tolerance of the ternary catalysts increases in the order: PtRuPb < PtRuMo < PtCoMo. The binary catalysts CO tolerance (except for PtMo/C which exhibits the best performance among all the catalysts (binaries and ternaries)) is lower than that of PtRu/C and increase in the order: PtNi < PtFe < PtCo < PtRu. Table 3.2 presents a more quantitative picture of the tolerance of the electrocatalysts considered in this study in the presence of CO and CO₂ comparing the kinetic parameters.

As can be seen in Fig. 3.1, PtMo/C exhibits the lowest anode overpotential in the presence of 100ppm CO. Although the turn-over of the Mo (IV/VI) redox couple plays an important role for CO stripping in PtMo sites, but generally the superior CO oxidation on Mo sites indicates that the oxy-hydroxides are efficiently and well dispersed on Mo surface leading to the effective electro-oxidation of CO adsorbed species and therefore more facile hydrogen oxidation.

Ru plays a similar role and in a second level after Mo produces oxy-hydroxide groups and oxidizes the CO adsorbed layer efficiently. An important fact is the big difference between the anode overpotential on Pt/C and those of these catalysts (PtM, M=Fe, Co and Ni) although their CO oxidation initiates at almost the same potential as that for Pt/C. This huge difference (~250mV) is attributed to the electronic properties of the alloyed catalysts.

It should be noted that the anode overpotential losses in these catalysts are comparable to that of PtRu. This suggests that the electronic properties modification in the case of PtCo/C, PtFe/C and PtNi/C are as effective as the oxy-hydroxides formation on the surface in PtRu/C. Ternary alloys including Mo (PtCoMo/C and PtRuMo/C) following the same trend exhibit low overpotentials. PtRuPb/C also shows a lower CO oxidation overpotential compared to PtRu/C implying the positive role of adding lead to the catalyst which is attributed to the electronic effect of lead. PtCoMo/C appears to be the best among the catalysts considered except for PtMo/C. PtCoMo/C benefits from both the oxy-hydroxide groups formed on Mo as well as the electronic modification due to Co.

Fig. 3.1 (a) Single cell polarization curves for the catalysts (Pt-M (M= Ru, Mo, Fe, Co, Ni), PtRuMo/C, PtCoMo/C and PtRuPb/C) in an H₂/O₂ PEM fuel cell with anodes fed by hydrogen in the presence of 100ppm CO. (b) Extra anode overpotential in the presence of 100ppm CO in hydrogen. the cathode side is fed with hydrogen.

The anode polarization profiles for the catalysts considered in this study as a function of varying CO concentration in the hydrogen feed in the range of 50-300 ppm are presented in Fig. 3.2 where the anode polarization profiles for the catalysts considered in this study as a function of varying CO concentration in the hydrogen feed in the range of 50-300 ppm are presented. The presented data are from a PEM fuel cell under 85°C cell temperature, 100% humidification and 60/50 psig for cathode and anode backpressures, respectively. As evident from the data, ternary catalysts exhibit superior CO tolerance compared with Pt and binaries. The variation of anode polarization is the highest in the case of Pt, and it increases in the order $M = \text{Ru} < \text{Co} < \text{Fe} < \text{Ni}$ in the case of binaries PtM and in the order $\text{MN} = \text{CoMo} < \text{RuMo} < \text{RuPb}$ in the case of ternaries.

Table 3.2 Electrode kinetic parameters for CO and CO₂ tolerance

Electrocatalyst	Current Density ($\text{A}\cdot\text{cm}^{-2}$) at 75 mV overpotential due to 50% CO ₂ in the hydrogen feed	Current Density ($\text{A}\cdot\text{cm}^{-2}$) at 100 mV overpotential due to 100ppm CO in the hydrogen feed
Pt/C	0.648	0.173
PtRu/C	0.695	0.215
PtMo/C	0.614	0.85
PtFe/C	0.55	0.173
PtNi/C	1.367	0.173
PtCo/C	1.372	0.173
PtRuPb/C	1.17	0.345
PtRuMo/C	0.472	0.39
PtCoMo/C	0.97	0.578

Fig. 3.2 Steady-state anode polarization for the catalysts (Pt-M (M= Ru, Mo, Fe, Co, Ni), PtRuMo/C, PtCoMo/C and PtRuPb/C) as a function of different CO concentrations available in hydrogen feed. H₂ [50ppm CO, circles; 100ppm CO, triangles; and 300ppm CO, squares].

In Figure 3.3, the anode potential loss of the catalysts in the presence of 50% of CO₂ molar ratio is presented. PtCo and PtNi exhibit superior CO₂ tolerance over the entire range of current densities. This behaviour is in contrast with that of Pt/C where the anode overpotential level at current densities lower than 0.4 A.cm⁻² is almost the same as that of PtNi/C and PtCo/C while at current densities higher than 0.4 A.cm⁻², the anode overpotential is significantly higher. The electrocatalysts including Mo sites exhibit significantly higher overpotentials compared to Pt/C especially at lower current densities. At higher current densities the overpotential has almost the same value as Pt/C. PtRu/C shows significantly

lower anode overpotentials as compared to the catalysts including Mo such as PtRuMo at current densities above 0.4 A.cm^{-2} . Furthermore, PtRuPb exhibits lower anode overpotential than PtRu over the whole current density range. The availability of Pt sites is a determining factor in the anode overpotential due to the presence of CO and CO₂ in the hydrogen feed. This has been discussed in an earlier publication [14]. In the case of catalysts where the number of available Pt sites is significantly higher than the other metals, the susceptibility of the catalyst to the impurities would be higher. It is explainable by the lower bonding energies and coverage of CO/CO₂ species on a surface with higher Pt d-band vacancy. According to Blyholder model [164], the bonding mechanism of CO and CO₂ to the metal surface is explained by σ -donation of electron density from CO/CO₂ to the metal and π -backdonation from the metal d-orbital to the gas. It is shown that the electron backdonation from the metal to the adsorbate increases the metal-carbon bond and decreases the C-O bond strengths with the consequence of stabilizing the coordinate bond. Therefore, as Pt d-band vacancy increases, less number of electrons from metal surface participates in the backbond leading to weaker adsorption of the gases on the surface. It is also argued that the CO₂/CO adsorption is enhanced at lower coordination step sites where the d-band vacancy or work function is higher [164, 165].

PtCoMo and PtFe exhibit high anode overpotentials. This high overpotential is due to the presence of Mo and to the different crystal structure of PtFe for the former and the latter, respectively. It has been shown that in the case of PtFe, following the surface alloy layer dissolution, a rearrangement of the remaining Pt occurs resulting in a Pt skin layer protecting the underlying bulk alloy from corrosion [166]. The composition and electronic properties of the surfaces of the different catalysts also play a crucial role in their activities towards reverse

water gas shift reaction, thereby leading to different performances in the presence of 50% molar ratio of CO_2 .

Fig. 3.3 Half cell polarization curves for the catalysts (Pt-M (M= Ru, Mo, Fe, Co, Ni), PtRuMo/C, PtCoMo/C and PtRuPb/C) in an H_2/O_2 PEM fuel cell with anodes fed by hydrogen in the presence of 50% molar ratio of CO_2 .

Another observation is that the anode overpotential of pure Pt in the presence of CO_2 at low current densities has around the same value of other electrocatalysts. This is explainable by this fact that at low current densities, the available Pt sites are sufficient to produce the current by hydrogen oxidation.

Figure 3.4 presents the cyclic voltammetry of the electrocatalysts sample PtRu, PtRuMo and PtRuPb anodes purged by three gas streams: 1) N_2 , 2) $\text{H}_2/100$ ppm CO, and 3) hydrogen in the presence of 60% molar ratio of CO_2 for an hour. These experiments were carried out in a

single PEM fuel cell with the anode and cathode sides purged with nitrogen and hydrogen, respectively. The operating conditions of the cell were 100% relative humidity and 80 °C.

In the case of electrocatalysts purged with N₂, the cyclic voltammograms of PtRu/C and PtRuPb/C have similar features. The hydrogen adsorption and desorption region is well defined in both cases. On the other hand, PtRuMo/C and PtCoMo/C present Mo features as described in previous studies [14]. A redox behavior is observed in the voltammogram of PtMo/C in the potential range of 0.4V-0.50 V versus reversible hydrogen electrode (RHE). This behavior is due to the presence of Mo. Mukerjee et al. have reported the change in oxidation state from Mo⁺⁵ to Mo⁺⁶ using in situ XANES spectroscopy at the Mo K edge for PtMo/C [14].

In the case of the voltammograms of the electrocatalyst studied including Mo (PtCoMo/C and PtRuMo/C) in the presence of CO, the carbon monoxide electro-oxidation initiates at lower potentials around 0.05 V. This is due to the presence of oxygenated groups on the Mo surface. The second peak occurs at approximately 0.65 V, which is due to the electro-oxidation of CO on Pt sites. This is in contrast with the voltammograms of PtRu/C and PtRuPb/C, where there is only a single peak due to CO electro-oxidation and happens at 0.4V and 0.3V, respectively.

As explained in the effect of CO₂ in reformat feedstock on the polarization data of the electrocatalysts in Fig. 3.3 the anode poisoning happens due to the formation of CO via the reverse water gas shift reaction. The cyclic voltammograms of the electrocatalysts exposed to the flow including 60% molar ratio of CO₂ in hydrogen stream show approximately the same

CO stripping peaks implying the poisoning effect of CO₂. During measurement of voltammograms in the presence of CO₂ in the hydrogen stream, nitrogen is purged onto the anode side while cathode side remains under a pure hydrogen flow. The operating conditions of the cell are the same as mentioned. There is a good match between the oxidation peaks happening at the same potential in the case of anode side fed by H₂/100ppm CO and hydrogen including 60% molar ratio of CO₂. This has been observed in prior studies, too [8, 38-40].

Fig. 3.4 Cyclic voltammograms for (a) PtRu, (b) PtRuMo (1:1:1 atomic ratio), (c) PtRuPb (7:7:1 atomic ratio, Pt:Ru:Pb) as a function of different anode gas feeds, 85 °C, 60/50 psi cathode, anode backpressure, 100% humidification condition.

Figure 3.5 represents the anode overpotential at the current density of 0.5 A.cm^{-2} due to the presence of 100ppm CO in the hydrogen feed versus the CO oxidation onset potential for the corresponding electrocatalyst. The anode overpotentials are measured and plotted versus the CO oxidation onset potential measured from the cyclic voltammetry experiments. Generally, the CO oxidation onset potential is the potential at which oxy-hydroxides commence to form on the electro-catalyst surface [14, 83, 86]. As can be seen, the anode overpotential due to 100ppm CO increases significantly against the CO oxidation onset potential following a linear trend indicating the significant effect of oxy-hydroxides formation on the CO oxidation. In contrast, no trend is identified for the anode overpotential due to 50% molar ratio of CO_2 . The CO oxidation onset potential in this case is the potential at which CO molecules produced from the CO_2 reverse water gas shift reaction start stripping off the surface. In fact, CO_2 tolerance not only is not related to the oxy-hydroxides but also too many oxy-hydroxide groups increase the anode overpotential. As can be seen in Fig. 3.5, PtMo/C exhibits the lowest anode overpotential in the presence of 100ppm CO. Although the turn-over the Mo (IV/VI) redox couple plays an important role for CO stripping in PtMo sites, but generally the superior CO oxidation on Mo sites indicates that the oxy-hydroxides are efficiently and well dispersed on Mo surface leading to the effective electro-oxidation of CO adsorbed species and therefore more facile hydrogen oxidation. In contrast, the anode overpotential of PtMo/C due to presence of 50% molar ratio of CO_2 is significantly higher than the other alloys. It is attributed to the suppression of the CO oxidation mechanism on Mo sites. Ru plays a similar role and in a second level after Mo produces oxy-hydroxide groups and oxidizes the CO adsorbed layer at 0.25V. Figure 3.5 also shows that, water molecules are activated at higher potentials on Fe, Co and Ni sites, around 0.4V, which reflects that the oxy-hydroxides are not

formed so effectively on these metals leading to an increase in higher potential losses in the presence of CO. An important fact is the big difference between the anode overpotential on Pt/C and those of these catalysts (PtM, M=Fe, Co and Ni) although their CO oxidation initiates at almost the same potential as that for Pt/C. This huge difference (~250mV) is attributed to the electronic properties of the alloyed catalysts. It should be noted that the anode overpotential losses in these catalysts are comparable to that of PtRu. This suggests that the electronic properties modification in the case of PtCo/C, PtFe/C and PtNi/C are as effective as the oxy-hydroxides formation on the surface in PtRu/C. Ternary alloys including Mo (PtCoMo/C and PtRuMo/C) following the same trend exhibit low overpotentials. PtRuPb/C also shows a lower CO oxidation overpotential compared to PtRu/C implying the positive role of adding lead to the catalyst which is attributed to the electronic effect of lead. PtCoMo/C appears to be the best among the catalysts considered except for PtMo/C. PtCoMo/C benefits from both the oxy-hydroxide groups formed on Mo as well as the electronic modification due to Co.

In brief, these examples suggest that electronic properties play an important role in the reformat tolerance of anode electro-catalysts. To clearly evaluate the effect of electronic properties on the reformat (including CO and CO₂ issues) tolerance of the electro-catalysts in our study, the effect of charge transfer between Pt and the added elements and the combined ligand and strain effects are considered.

Fig. 3.5 The anode overpotential at the current density of 0.5 A.cm^{-2} due to the presence of 100ppm CO in the hydrogen feed versus the CO oxidation onset potential for the corresponding electrocatalyst.

3.2. Electrolytic selective CO oxidation system to produce pure hydrogen

3.2.1. Electrolyzer/ Adsorber Materials and Fabrication

As mentioned earlier, the structure and the materials of the electrolyzer/adsorber is the same as the PEM fuel cell. The only difference is that an activated carbon electrode is deposited on the anode GDL and also the adsorber anode catalyst layer support is made of activated carbon. The loading of the electrolyzer cathode catalyst layer is 0.4 mgcm^{-2} while the catalyst loading of the anode side varies, the base case loading being 2 mg.cm^{-2} . Loadings of 0.5 mg.cm^{-2} and 1 mg.cm^{-2} are also studied to investigate the effect of catalyst loading on the

adsorption capacity. Standard temperature and pressure and 100% relative humidity were chosen as the operating conditions of the system.

3.2.2. PEMFC- Adsorber/Electrolyzer System Set Up

The set up used for on-site/board application CO removal as explained in chapter 1 operates at low temperature and pressure and applies polymer electrolyte membrane (PEM) reactors for the electrolytic process. The schematic of the set up is depicted in Fig. 1.3. The favorable operating conditions at which the system works are in contrast with those of existing multistage catalytic technologies, where high temperature is a requisite factor to achieve high CO conversion rates and therefore the conventional systems lead to more economic burden. The system includes two identical PEM reactors integrated in parallel with a PEM fuel cell. This configuration ensures that at any time, the supply of feedstock passes through one of the reactors (adsorber) while the other is being regenerated.

One may highlight the high cost of the catalyst loading. It should be noted that loadings lower than 2mg.cm^{-2} can also be used with reasonable breakthrough times as can be seen in Fig. 3.15.

The proposed system is highly suitable for on-board applications because it can operate at ambient temperatures and atmospheric pressures. It can also potentially be used as an off-board application to replace the traditional low temperature water-gas-shift reaction for CO removal. The actual set up used is shown in Fig. 3.6.

Fig. 3.6 the actual set up used.

The CO is accumulated on the surface of the electro-catalyst and eventually reaches the saturation point. The level of saturation is detected by an infrared based gas analyzer able to detect ppm level of CO. Once the saturation point is reached, the feedstock is switched over from the saturated adsorber to the fresh adsorber. The time interval of switching feedstock from one adsorber to the other is determined by amount of impurities in the feedstock as well

as the flow rate. The time during which the adsorber can produce hydrogen with less than 10ppm CO content is termed as breakthrough time here in this study. The regeneration step needs applying a form of energy to the system. In conventional technologies, it is carried out by applying thermal energy to the system introducing more complexities to the system. In an electrolytic system, the saturated adsorber is regenerated through an electro-chemical approach which is achieved by applying a potential from a source between the anode and cathode of the electrolyzer. The saturated adsorber now acts as an electrolyzer and removes the adsorbed impurities by electro-oxidizing the adsorbed molecules and, thereby, regenerates the saturated absorber. Applying the electrochemical approach brings about favorable operating conditions (low pressure and temperature) which are unique features of this approach and are in contrast with those of existing multistage catalytic technologies, where a high temperature is a perquisite factor to achieve high CO conversion rates. The low temperature requirement facilitates and favors the adsorption of impurities on the electro-catalysts; the faster is the reaction rate, the smaller is the volume of the reactor. The proposed system is highly suitable for on-board applications because it can be operated at ambient temperatures and atmospheric pressures. The system can also potentially be used as an off-board application to replace the traditional low temperature water-gas-shift reaction for CO removal.

A gas handling unit pre-processes the inlet of the analyzer as a safety filtering the liquid water and other solid particles present in the sample gas as shown in Fig.3.7. Three gas cylinders containing hydrogen with 100, 300 and 500 ppm carbon monoxide were used. They are the feedstock to investigate the CO removal efficiency of the electrolyzer/adsorber. The

calibration unit is the path through which the analyzer calibration is carried out using the zero and span gases.

The main goal of this section is to perform a parametric study of the adsorber and the EWGS electrolyzer. Experiments are carried out to investigate the adsorption capacity of the adsorber through measuring the breakthrough curves of the adsorber exposed to different feedstock flow rates ($40\text{--}200\text{ ml. min}^{-1}$) and CO concentrations (100, 300, and 500ppm CO).

Fig. 3.7 Schematic of the gas handling system

In addition, the optimized values for regeneration potential and time leading to the minimum fuel cell performance degradation are presented. With experimental studies and the theoretical investigations presented in Chapter 4, a deeper insight is provided into the selective CO

oxidation from a hydrogen stream in a PEM reactor by analyzing the influence of the operational variables and guidelines are provided for efficient application of the system.

3.2.3. Parametric Study of the adsorber

Systematic experiments are carried out to investigate the adsorption capacities through measuring the breakthrough curves of the adsorber with the four flow field types exposed to different feedstock flow rates (40, 80, 120, 160 and 200 mL min⁻¹) and CO concentrations. As a measure of the system performance, it is essential to have an insight of the adsorption capacity of the adsorber. The time taken for the concentration of the CO in the outlet to reach 10 ppm is measured and reported as the breakthrough time. The set up used to measure the breakthrough times is depicted in Fig. 3.8. It includes a gas analyzer with an Infra-Red detector to measure the CO and hydrogen concentrations before and after the adsorber.

Fig. 3.8 Setup for the measurement of the CO concentration at the outlet of the adsorber/electrolyzer

The focus is on the effect of different geometrical and operational parameters of the adsorber such as the gas flow field geometry, gas diffusion layer porosity and thickness, and catalysts loading on the adsorption capacity of the adsorber. Having obtained these correlations, one

Table 3.3 Bipolar plates geometrical specifications

	Multi-serpentine	Straight	Pin-type	Interdigitated
	flow field	flow field	flow field	flow field
Channel width/mm	1	1	1	1
Channel depth/mm	0.8	0.8	0.8	0.8
Shoulder width/mm	1	1	1	1
Plate thickness/mm	2.5	2.5	2.5	2.5
Plate dimensions/mm×mm	87×87	87×87	87×87	87×87
MEA/bipolar plate contact area (%)	47	41	22	41.5

can make adsorber with the best performance while using optimum amount of catalyst loading. Four different flow fields (straight, multi-serpentine, pin-type and interdigitated flow fields), gas diffusion fields with porosities of 0.74 and 0.78 and single metal catalyst (Pt) and alloyed (PtRu) supported onto two different supports including carbon black and activated carbon with metal loadings of 0.5, 1 and 2 mg.cm⁻² are investigated.

3.2.4. Bipolar plates and Membrane Electrode Assemblies (MEAs)

Four types of flow field geometries are used in the experiments which are pin-type, straight, multi-serpentine and interdigitated flow fields as shown in Fig. 3.9. The 4 step serpentine has been used in order to reduce machining time. Straight (parallel) and pin-type channels are ideal for the low-pressure drop design with the consequence of reducing the gases blower power and therefore parasitic losses. The bipolar plates design specifications and the MEA to bipolar plate contact area ratio are shown in Table 3.3.

The bipolar plates are made of graphite with 2.5 mm thickness, and channels are milled with a computer numerically controlled machine. Figure 3.10 shows a simplified schematic of the PEM reactor used.

Fig.3.9 the four types of flow fields studied: a) multi-serpentine pattern, b) straight pattern, c) pin-type pattern, and d) interdigitated pattern.

The end-plates are designed and fabricated in a way that the different flow fields are replaced conveniently. Silicon glue is used as the sealant material. As the experiments are carried out at room temperature, no heating systems are required. The MEA's are fabricated in house by an automatic spraying machine used to deposit the catalyst nanoparticles on the carbon paper and a hot press machine to assemble the electrodes and the proton conductive membrane. Two types of carbon papers are used in this research whose specifications are summarized in Table 3.4. Figure 3.11 shows the SEM graphs of the bare carbon papers and carbon papers deposited with Pt nanoparticles.

Fig. 3.10 The schematic of the PEM reactor used as the adsorber

To study the effect of the catalyst type, Pt/C and PtRu/C are used. Adding another metal to Pt changes the electronic properties of Pt which might change the adsorptive capacity of the catalyst.

Table 3.4 Specifications of the carbon papers

Type of	Thickness	Bulk Density	Overall	Permeability
Carbon paper	(μm)	($\text{g}\cdot\text{cm}^{-3}$)	Porosity	(D)
Ballard AvCarb® P75	250	0.45	74	5.7
Toray 060	205	0.4	78	9

In addition, the catalyst support can influence the ability of the electrode to adsorb impurities. To investigate the effect of the catalyst support, Pt nanoparticles supported onto two types of carbon, carbon black and activated carbon are studied. To compare the surface area and pore size distribution of the bare carbon black, and activated carbon particles as well as their Pt decorated samples, the nitrogen adsorption and desorption isotherms are obtained and the results are shown in Table 3.5 and Table 3.6, respectively.

The catalyst ink for electrodes with different gas diffusion layer electrodes was prepared by ultrasonically stirring of the supported catalyst (Pt/C or PtRu/C) and appropriate amounts of 5 wt% Nafion solution in a mixture of ultrapure water and isopropanol for 30 min. A Nafion 112 membrane (DuPont) was treated by boiling in 5% H_2O_2 for half an hour followed by boiling in 0.5 M sulfuric acid for another half an hour and finally boiling in ultrapure water for 1 h. The treated membrane was stored in ultrapure water. The conductance of this membrane is the highest among the nafion family as it is the thinnest.

Table.3.5 Characteristics of catalysts supports by N₂ adsorption/desorption

Sample	S_{BET}	S_{mi}	S_{me}	V_{mi}	V_{tot}	V_{me}	V_{me}/V_{tot}
	(m ² /g)	(m ² /g)	(m ² /g)	(cm ³ /g)	(cm ³ /g)	(cm ³ /g)	(%)
Carbon Black	235	89	145	0.05	0.33	0.26	78
Activated Carbon	1118	793	333	0.33	1.33	0.95	71

Table.3.6 Characteristics of catalysts by N₂ adsorption/desorption

Sample	S_{BET}	S_{mi}	S_{me}	V_{mi}	V_{tot}	V_{me}	V_{me}/V_{tot}
	(m ² /g)	(m ² /g)	(m ² /g)	(cm ³ /g)	(cm ³ /g)	(cm ³ /g)	(%)
Pt/C	108	31	77	0.01	0.17	0.15	88
Pt/AC	542	286	253	0.26	0.81	0.54	66

S_{mi} : The surface area of the micro-pores, i.e., pores with pore diameters of less than 2 nm

S_{me} : The surface area of the meso-pores , i.e., pores with pore diameters between 2 nm and 50 nm

V_{mi} : The volume of the micropores

V_{me} : The volume of the meso-pores

Fig. 3.11 SEM images of: a) bare Ballard carbon paper, b) bare Toray carbon paper, c) Ballard carbon paper decorated with Pt nanoparticles, and d) Toray carbon paper decorated with Pt nanoparticles.

The catalyst ink was sprayed in layers onto the carbon papers by the spraying machine. This machine assures a well distribution of the catalyst ink onto the carbon papers producing a homogeneous catalyst layer. Electrodes with desired loadings are made without any significant loss. The catalyst layer weight was confirmed by measurements of the electrode weight before spraying and after drying of the electrode. The cell is assembled using a uniform torque of 10 N.m.

3.2.5. Breakthrough curve measurement tests

Systematic experiments are carried out to investigate the adsorption capacities through measuring the breakthrough curves of the adsorber with the four flow field types exposed to different feedstock flow rate of 120 ml. min^{-1} and different CO concentrations including 100, 300 and 500ppm balanced in hydrogen. As a measure of the system performance, it is essential to have an insight of the adsorption capacity of the adsorber. The time taken for the concentration of the CO in the outlet to reach 10 ppm is measured and reported as the breakthrough time. The set up used to measure the breakthrough times is depicted in Fig. 3.8. It includes a gas analyzer with an Infra-Red detector to measure the CO and hydrogen concentration after the adsorber. The gases are supplied to the cell via a pressure cylinder regulated by pressure gauges. The feedstock flow rates are measured and controlled using a digital mass flow controller. The breakthrough curves were measured by the gas analyzer at the outlet of the adsorber. The analyzer is able to detect ppm level of CO available in the gas stream flowing through the CO sensor. The analog current output is recorded on a computer through a data logger. The current is proportional to the carbon monoxide concentration and therefore, the concentrations are calculated according to the recorded currents.

Studying the effect of different geometrical and operational parameters on the adsorber breakthrough time provides a guideline for making adsorber with the optimized performance. An in-house fabricated PEM reactor with a 50 cm^2 membrane electrode assembly (MEA) sandwiched between two graphite plates as the flow fields is used. Once the adsorber is saturated with CO at the end of a breakthrough measurement test, a potential of 0.9V is applied for 5 minutes (arbitrary time) to fully electro-oxidize the CO molecules adsorbed.

Subsequently the reactor is purged with nitrogen for at least 10 min to remove the CO₂ molecules from the reactor.

3.2.6. Optimizing the Regeneration Step

Two in-house fabricated PEM reactors are used. The reactors include a 50 cm² membrane electrode assembly (MEA) with metallic catalyst Pt supported on carbon with a loading of 2 mg.cm⁻² sandwiched between two graphite plates as the flow fields. Interdigitated flow field was used to prolong the contact between the catalyst and the CO molecules with the consequence of increasing the CO adsorption and breakthrough time. The fabrication process and structure of the reactors are the same as a PEM fuel cell. One fuel cell is used to simulate the adsorber/electrolyzer to purify the H₂ feed stream, while the other is used to investigate the fuel cell performance. The operating conditions of the adsorber/electrolyzer in all experiments are at 25°C, 1 atm, and 100% relative humidity. Pure CO and three gas mixture tanks, namely, 100, 300 and 500ppm CO balanced in hydrogen are used as CO sources for the investigation of the effect of CO removal in the EWGS processes.

To study the regeneration process of the adsorber, different potentials (regeneration potential, $V_{\text{reg}} = 0.7\text{-}1.4\text{V}$) are applied to the electrolyzer for different durations (regeneration time, $t_{\text{reg}} = 10\text{-}120\text{ s}$) and the breakthrough time in the next duty period is monitored. Constant potentials are applied through a potentiostat which plays the role of the power supply. In each case the current-time curve is measured along with the regeneration process. The objective of these experiments is to obtain the optimized values of the potential and time required for the electrolyzer to get regenerated so that the minimum fuel cell performance degradation

happens. Further, the regeneration current obtained in the regeneration experiments is used to validate the thermodynamic model results presented in section 4.2. In addition, the effect of the sequential regeneration on the adsorption capacity of the adsorber and fuel cell performance is investigated. The objective of these experiments is to investigate if the adsorption capacity of the catalyst nanoparticles will be affected by sequential regeneration over time.

3.2.7. Results and discussion

Figure 3.12 presents the breakthrough curves of the adsorber with different flow fields exposed to hydrogen flow in the presence of (a) 100, (b) 300 and (c) 500 ppm CO. As mentioned earlier, the area of MEA is 50cm^2 with a loading of 2mg.cm^{-2} Pt/C deposited on Toray carbon paper. The gas flow rate is 120 ml.min^{-1} and the measurements are done at ambient temperature and atmospheric pressure. Results indicate that the breakthrough time for all the three CO concentrations increases in this order: straight < pin-type < multi-serpentine < interdigitated. Straight flow field provides the shortest flow path among the flow fields which justifies the shortest breakthrough time presented by this flow field. Straight and pin-type flow fields are beneficial as they decrease the pressure drop. However, in the case of these two flow fields, gas flows tend to pass through paths with the least flow resistance which may cause dead volume and stagnant areas. This can disturb the uniformity of the gases distribution leading to the decrease of the contact between the gas molecules and the catalyst layer with the consequence of the decrease in breakthrough time. Serpentine flow field is claimed to improve the issues mentioned in straight and pin-type flow fields. In addition, this flow field produces a longer channel length leading to a big pressure drop between the

channel inlets to the outlet but favorably at the same time it increases the exposure time of the gas and catalyst surface.

a)

b)

c)

Fig. 3.12 The breakthrough curves of the adsorber with different flow fields exposed to hydrogen flow in the presence of 100, 300 and 500 ppm CO.

The gas flow is passed through the flow channels in the case of straight, pin-type and multi-serpentine flow fields and the contact between the gas molecules and the catalyst layer is because of the diffusion of the molecules through the catalyst layer. While, in the case of interdigitated flow field, the gas flow is forced through the catalyst layer which prolongs the contact between the catalyst and the CO molecules with the consequence of increasing the CO adsorption and breakthrough time. The breakthrough times of the adsorber of 50cm^2 area with different flow fields exposed to hydrogen flow in the presence of 100, 300 and 500 ppm CO are shown in Fig. 3.13. In all cases, a loading of 2mg.cm^{-2} Pt/C deposited on Toray carbon paper is used as the catalyst layer and the gas flow rate is 120 ml.min^{-1} .

To study the effect of gas diffusion layer porosity and morphology on the adsorption capacity of the adsorber, the breakthrough time of the adsorber with a Ballard carbon paper is measured. The time during which the adsorber can produce hydrogen with less than 10ppm CO content is termed as breakthrough time here in this study. Figure 3.14 presents the breakthrough times of the adsorber made with Ballard carbon paper of 50cm^2 area and the same catalyst loading (2mg.cm^{-2} Pt/C) with different flow fields exposed to hydrogen flow in the presence of 100, 300 and 500 ppm CO. Compared to the corresponding breakthrough times of the adsorber using Toray carbon papers, adsorbers with Ballard carbon paper have shorter breakthrough times. This is related to the effect of porosity of the gas diffusion media.

Fig.3.13 The breakthrough times of the adsorber with 2 mg.cm^{-2} loading of Pt/C on a 50cm^2 areas Toray carbon paper and with different flow fields exposed to hydrogen stream with a flow rate of 120 ml. min^{-1} in the presence of 100, 300 and 500 ppm CO.

As seen from SEM results in Fig. 3.11 and confirmed by the porosity data presented in Table 3.4, Toray carbon paper provides better gas transport which facilitates the contact between the catalyst nanoparticles and the CO molecules.

Fig. 3.14 The breakthrough times of the adsorber made with Ballard carbon paper of 50cm^2 area and the same catalyst loading (2mg.cm^{-2} Pt/C) with different flow fields exposed to hydrogen flow in the presence of 100, 300 and 500 ppm CO.

Figure 3.15 presents the breakthrough times of the adsorbers with catalyst loadings of 0.5 and 1 mg.cm^{-2} deposited on Toray carbon papers. The flow rate of the gas feed is 120 ml.min^{-1} . The breakthrough results of the adsorber with the same carbon paper with the loading of 2 mg.cm^{-2} are presented in Fig. 3.13 as discussed earlier. It can be seen that there is almost a linear correlation between the catalyst loading and the breakthrough time.

The effect of using Pt-based alloy catalyst such as PtRu/C on the adsorption capacity of the adsorber is studied, too. Figure 3.16 presents the breakthrough times of the adsorbers with PtRu/C catalyst loading of 2 mg.cm^{-2} deposited on Toray carbon papers. Compared to the

breakthrough times of adsorbers with the same loading of Pt/C sprayed on Toray carbon paper, no remarkable difference is observed. This implies that alloying Pt with Ru does not change the CO adsorption relative to pure Pt noticeably. This observation is in agreement with the density functional theory (DFT) calculations by Han and Ceder [167]. They concluded that alloying Pt with Ru increases the adsorption energy by 6 meV which is negligible compared to the Pt-Co bond strength which is around 1.7 eV. This is related to the difference of Pt and Ru lattice sizes ($R_{\text{Ru}} < R_{\text{Pt}}$) which induces a surface strain with the consequence of changing the electronic densities of Pt and increase in CO adsorption [168].

Fig. 3.15 The breakthrough times of the adsorbers with catalyst loadings of: a) 0.5, and b) 1 mg.cm⁻² deposited on Toray carbon papers.

The effect of the catalyst support is investigated by comparison between the adsorption times of adsorber with 2 mg.cm⁻² Pt/C as shown in Fig. 3.17 and those of adsorbers with 2 mg.cm⁻² Pt supported on activated carbon. Breakthrough times of adsorbers with catalyst particles supported on activated carbon are considerably longer than those supported on carbon black. This is related to the microstructure, porosity and the surface area of the two supports. Activated carbon is a high surface area carbon with 4-5 folds higher surface area compared to carbon black as indicated in Table 3.5. These factors influence the electrocatalyst nanoparticles dispersion on the carbon surface.

Fig. 3.16 The breakthrough times of the adsorbers with PtRu/C catalyst loading of 2 mg.cm^{-2} deposited on Toray carbon papers.

A good dispersion of the nanoparticles provides access to a larger number of active sites, therefore enhances the contact between the catalyst sites and the gas molecules with the consequence of improving the adsorption of impurities.

The results in Fig. 3.18 present the breakthrough data of the adsorber for hydrogen flow with 100, 300 and 500 ppm CO at 40, 80, 120, 160 and 200 ml.min^{-1} at ambient temperature and pressure. As mentioned earlier, the area of MEA is 50cm^2 with a loading of 2mg.cm^{-2} Pt/C deposited on carbon paper. The CO adsorption time can be prolonged by increasing the volume of the anode flow chamber and the exposure time. The results indicate that the proposed system may have the potential to enable a H_2 powered application, such as, a fuel cell vehicle, to operate for several hours before regeneration is required to remove the

adsorbed CO at ambient temperature and pressure. Figure 3.18b presents the corresponding experimental breakthrough curves for a feedstock flow rate of 120 ml.min^{-1} and for three CO

Fig 3.17 the breakthrough times of the adsorber with 2 mg.cm^{-2} loading of Pt/AC on a 50 cm^2 areas Toray carbon paper and with different flow fields exposed to hydrogen stream with a flow rate of 120 ml.min^{-1} in the presence of 100, 300 and 500 ppm CO.

concentrations (100, 300 and 500ppm) while Figure 18c shows the breakthrough curves for different flow rates of feedstock (40, 80, 120, 160, and 200 ml.min^{-1}) containing 100 ppm level of CO. Breakthrough time decreases with the flow rate as at a higher flow rate the contact between the gas and the catalyst surface is lower. At all these experiments, the flow fields, catalyst type/ loading and all other parameters are remained the same.

a)

b)

c)

Fig. 3.18 a) The breakthrough data of the adsorber for hydrogen flow with 100, 300 and 500 ppm CO at 40, 80, 120, 160 and 200 ml.min⁻¹ at ambient temperature and pressure. b) The corresponding experimental breakthrough curves for a feedstock flow rate of 120 ml.min⁻¹ and for three CO concentrations (100, 300 and 500ppm). c) Breakthrough curves for different flow rates of feed (40, 80, 120, 160, and 200 ml.min⁻¹) containing 100 ppm level of CO.

According to the model developed which is presented in section 4.2, the ideal current density to apply for the electrolytic process should be less than 0.2 A.cm⁻² so that the energy efficiency would be the highest possible (>80%). To investigate the effect of different potential ranges and regeneration times on the electrolyzer performance, a set of potential-time profiles are applied to an adsorber which has been exposed to the feedstock hydrogen and CO mixture and is at fully saturated condition. In each case, the potential is applied and the corresponding current curve is recorded. The current curve in the case of an adsorber which has been exposed to the feedstock containing 100ppm CO with a flow rate of 40 ml.min⁻¹ is shown in Fig. 3.19. The total CO adsorbed on the catalyst surface and the amount

of oxidized CO through the electrolytic process were calculated using (3.3) and (3.4) from the breakthrough curve ($0.279 \text{ mol.mg}^{-1}$) and current-time curve obtained from the regeneration process ($0.288 \text{ mol.mg}^{-1}$). A reasonable agreement ($\sim 3\%$ percentage error) is observed between these two values confirming that all the CO molecules adsorbed are electro-oxidized during the electrolytic step.

$$N_{ads} \cdot m_{cat} = \int_0^{T_{Brk}} \frac{(100-c)}{10^6} \cdot n_{inlet} dt \quad (3.3)$$

$$N_{elec.oxid.} \cdot m_{cat} = \int_0^{T_{reg}} i/nF \cdot dt \quad (3.4)$$

where N_{ads} , m_{cat} , $N_{elec.oxid.}$, T_{Brk} , c , n_{inlet} , T_{reg} , i , n , and F are the amount adsorbed (mol.mg^{-1}), , catalyst amount (mg), amount electro-oxidized (mol.mg^{-1}), breakthrough time (s), the concentration (ppm), flow rate at the inlet, current (A), number of electrons, and Faraday constant, respectively.

Figure 3.20 shows the adsorber maximum adsorption capacity decrease percentage in the next adsorption cycle after the specific regeneration conditions are applied during the electrolytic process. According to the results, the adsorption capacity decreases with regeneration time and potential applied till reaching a regeneration condition at and after which the decrease percentage is constant and minimum. To study the effect of electrochemical removal of CO from H_2 stream on the fuel cell performance, an experiment is carried out. In this experiment, a fully water vapor saturated hydrogen stream containing 300 ppm level of CO is introduced to the adsorber at a flow rate of 120 mLmin^{-1} . The adsorber operates at room temperature, and atmospheric pressure. Fig 3.21 shows the effects of CO removal on the performance of the PEM fuel cell.

Fig. 3.19 The current-time curve in the case of an adsorber which has been exposed to the feedstock containing 100ppm CO with a flow rate of 40 ml.min⁻¹

The fuel cell is polarized at a 0.2 A.cm⁻². The fuel cell voltage drops significantly as the hydrogen stream in the presence of 300ppm CO is fed into the fuel cell. The fuel cell is regenerated by applying a potential of 0.8V to the two sides and purged with nitrogen. The same gas stream is fed into the adsorber and the outlet of the adsorber is introduced to the fuel cell.

Fig. 3.20 The decrease percentage of the maximum adsorption capacity of a PEM reactor measured in two consecutive adsorption cycles. Between the two cycles, regeneration steps with different duration and potentials are applied.

As seen in Figure 3.21, the voltage remains at ~ 0.75 V for almost 50 minutes which is the same result reported through breakthrough experiments. This experiment was repeated for 8 times to study the effect of the sequential regeneration of the adsorber and if the regeneration might affect the adsorptive capacity of the catalyst particles. It is observed that the sequential regeneration does not affect the adsorber performance. To confirm this, the outlet concentration of the adsorber is measured by the CO analyzer using the set up depicted in Fig. 3.8. A fully water vapor saturated hydrogen stream containing 300 ppm level of CO is introduced to the adsorber at a flow rate of 120 mLmin^{-1} . The adsorber operates at room temperature, and atmospheric pressure. The breakthrough curve is measured and a regeneration process is carried out by applying a 0.8V potential for 2 minutes. This experiment is repeated for 8 times. Figure 3.21b shows the breakthrough curves of this

configuration with sequential regeneration confirming that the sequential regeneration doesn't affect the CO removal capacity of the adsorber.

Fig. 3.21 a) The effects of CO removal on the performance of the PEM fuel cell. b) The breakthrough curves of the adsorber exposed to H_2 with 300ppm CO at a flow rate of $120 \text{ ml} \cdot \text{min}^{-1}$ with sequential regeneration.

Chapter 4 Theoretical Investigations¹

This chapter includes the theoretical investigations carried out including the numerical simulation of the PEMFC performance incorporating the CO kinetics in the anode. A CO molecule could be adsorbed onto one or two Pt sites on the surface producing linear and bridged adsorption sites, respectively. In this model, linear and bridged- bonded adsorbed CO are considered to occur in parallel on Pt/C and PtRu/C catalysts. Furthermore, a thermodynamic-electrochemical model is developed to simulate the energy balance of the electrolyzer indicating that this process offsets the actual energy consumption because it produces extra hydrogen.

4.1 Computational Fluid Dynamics Simulation of PEM Fuel Cells Operating on Reformate

Carbon monoxide (CO) can extremely diminish the polymer electrolyte membrane fuel cell (PEMFC) performance since it is preferentially absorbed on the platinum catalyst layer blocking and reducing the number of catalyst sites available for the hydrogen oxidation reaction. In order to obtain a good insight of CO poisoning characteristics and remediate CO-poisoned PEMFCs, a two-dimensional, isothermal, and single phase CO poisoning numerical model taking into account the transport phenomena, electrochemical reactions and multi-component gas mixture transport is developed.

A schematic of a PEMFC is shown in Fig. 4.1. Linear and bridged- bonded adsorbed CO were considered to occur in parallel on Pt/C and PtRu/C catalysts. By performing computational fluid dynamics numerical simulations, this study clearly illustrates the

¹ This chapter has been partly published in:

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Ehteshami, S.M.M., W.J. Zhou, and S.H. Chan, *Energy analysis of an electrolytic-based selective CO oxidation system for on-board pure hydrogen production*. *International Journal of Hydrogen Energy*, 2012.

polymer electrolyte membrane fuel cell CO poisoning mechanism. A finite element based numerical procedure was used to solve the governing equations. The numerical results obtained are in good agreement with the experimental data obtained from the cell operating on reformat.

All the available models for CO poisoning simulations have considered the linear CO poisoning mechanism which solely cannot model the problem properly [152, 156-158]; hence, in this research a more accurate CO poisoning mechanism is applied considering the two types of the parallel CO oxidation possibilities for linear- and bridge-bonded adsorbed CO as reported by characterization techniques discussed earlier.

Fig. 4.1 Schematic of a PEM fuel cell

This study formulates an isothermal, two-dimensional and single phase, mathematical model of a PEM fuel cell with a detailed process of adsorption, desorption and electrochemical reaction of CO and H₂ in the anode catalyst layer and electrochemical reaction of O₂ in the cathode catalyst layer. Two types of the CO oxidation possibilities for linear- and bridge-bonded adsorbed CO were considered to occur in parallel on the highly

dispersed nanocrystalline Pt/C, PtRu/C catalysts. Additionally, the mathematical model incorporating CO poisoning is compared to published experimental data.

4.1.1 Theory

Figure 4.2 shows the schematic of the model geometry of a single fuel cell. The geometrical specifications of the cell components are presented in Table 4.1. The equations governing the transport phenomena in PEM fuel cell components are presented in the following.

4.1.1.1 Gas distribution electrodes

The flow in the porous media of the gas diffusion layers of the PEM fuel cell is modeled by Darcy's law where the pressure gradient is the driving force. The shear stress terms in the momentum equation are negligible in porous media since the walls of an individual pore prevent the transport of this momentum to the fluid outside of the pore. Darcy's law considers the homogenized porous and fluid media into one single medium and the detailed geometrical shape of the pore structure is not required. Based on the Darcy's law, the velocity vector is determined by the pressure gradient, the fluid viscosity, and the permeability of the porous media represented with the following equation:

$$u = -\frac{k_p}{\mu} \nabla p \quad (4.1)$$

Where u , k_p , μ , and p are the velocity vector, permeability of the porous media, viscosity of the fluid and pressure, respectively.

Fig. 4.2 Schematic of the model domain

At low densities, the multi-component gases diffusion can be well approximated by Maxwell–Stefan equation:

$$\nabla x_i = - \sum_{j=1}^N \frac{(x_j N_i - x_i N_j)}{c D_{ij}}, \quad i=1,2,3, \dots, N \quad (4.2)$$

Where D_{ij} , x_i , c , and N_i are the binary diffusivity of i and j , the mole fraction of component i , the concentration, x_i , and the molar flux vector of component i , respectively. The binary diffusivities obtained from experiment, D_{ij}^0 at atmospheric pressure, and reference temperature, T_0 shown in Table 4.1 can be used to predict the binary diffusivities at operating temperature and pressure according to equation (4.3) [169].

$$- - - \quad (4.3)$$

Due to the porosity of the electrode, the binary diffusivities should be corrected with the Bruggemann correlation:

Table 4.1 Properties and geometric parameters ^a

Parameter	Value	Unit
L_{Ch} , Channel length	0.5×10^{-3}	m
L_{Sh} , Shoulder length	0.5×10^{-3}	m
t_a , t_c , Anode and cathode GDL thickness	2.6×10^{-4}	m
t_{cat} , Anode and Cathode catalyst thickness	0.6×10^{-5}	m
t_m , membrane thickness	1.27×10^{-4}	m
ϵ , porosity of GDL and catalyst layers	0.6	-
T, temperature	358	K
p, pressure	1	atm
k_p , GDL permeability	1.76×10^{-11}	m^2
Inlet nitrogen/oxygen mole ratio	0.79/0.21	-
σ_{eff}^S , Electronic conductivity	570	$S\ cm^{-1}$
σ_m , Ionic conductivity of membrane	13.1	$S\ cm^{-1}$
μ_a , viscosity of anode gas	$1.378 \times 10^{-5} (T/298)^{1.02}$	Pa.s
μ_c , viscosity of cathode gas	$1.094 \times 10^{-5} (T/298)^{1.02}$	Pa.s
EW_m , membrane equivalent molecular weight	1.1	$kg\ mol^{-1}$
$pD_{O_2-H_2O}$, Binary diffusivity pressure product	0.7	$atm.\ cm^2\ s^{-1}$
$pD_{O_2-N_2}$, Binary diffusivity pressure product	0.56	$atm.\ cm^2\ s^{-1}$
$pD_{H_2O-N_2}$, Binary diffusivity pressure product	0.77	$atm.\ cm^2\ s^{-1}$
$pD_{H_2-H_2O}$, Binary diffusivity pressure product	0.91	$atm.\ cm^2\ s^{-1}$
pD_{H_2-CO} , Binary diffusivity pressure product	0.99	$atm.\ cm^2\ s^{-1}$
Reference exchange current density times area at the cathode	500	$A\ m^{-3}$
Oxygen reference concentration	3.39	$mol\ m^{-3}$
α , cathode transfer coefficient	2	-

^a most of the data from [155]

$$D_{ij}^{eff} = D_{ij} \epsilon^{1.5} \quad (4.4)$$

It should be noted here that to consider the effect of liquid water in different parts of the cell which is produced in the cathode catalyst layer, different values of water has been assumed to be produced and a factor has been used in calculating the effective diffusion coefficients;

The species conservation in the gas diffusion layers are solved with the following equation:

$$\nabla \cdot \left(-\rho \omega_i \sum \left(D_{ij} \nabla x_j + (x_j - \omega_j) \frac{\nabla p}{p} \right) + \rho \omega_i u \right) = 0 \quad (4.5)$$

Where the species, i are H_2 and H_2O for the anode side and O_2 , H_2O and N_2 for the cathode side, w the weight fraction, and ρ is the density of the gas mixture which is calculated by the following equation:

$$\rho = \frac{\sum_i x_i \cdot MW_i}{RT} p \quad (4.6)$$

In addition to species and momentum balances in the gas diffusion layers, the charge balance is solved in the electrodes with the following equation:

$$-\nabla \cdot (\sigma_{eff}^s \nabla \phi_s) = 0 \quad (4.7)$$

Where σ_{eff}^s and ϕ_s are the electric conductivity and the potential of the porous electrodes.

4.1.1.2 Membrane

The membrane is assumed to be impermeable to hydrogen, oxygen, and nitrogen. Hence, only protons and water are transported through the membrane and both obey the conservation of mass; in addition, the continuity equation is considered for the charge balance in the membrane.

$$-\nabla \cdot (\sigma_m \nabla \phi_m) = 0 \quad (4.8)$$

where φ_m and σ_m are the membrane potential and conductivity. The membrane conductivity is a function of the water content of the membrane λ , i.e., the concentration ratio of water to sulphonate group ($[\text{H}_2\text{O}]/[\text{SO}_3^-]$) in the membrane. The following experimental expression for the conductivity of Nafion membrane has been presented by Springer *et al.*[154]:

$$\sigma_{30} = 0.5139\lambda - 0.326, \quad \text{for } \lambda > 1 \quad (4.9)$$

where σ_{30} is the membrane conductivity [S/m] which is measured at 30°C ; the conductivity at the operating temperature then will be calculated using the following correlation:

$$\sigma_m = \exp \left[1268 \left(\frac{1}{303} - \frac{1}{T} \right) \right] \sigma_{30} \quad (4.10)$$

Three processes of water transport contribute to the mass flux of water in the membrane: flow of protons through electro-osmotic drag, concentration gradient leading to diffusion, and pressure gradient producing convection. These three factors lead to:

$$N_W = \frac{n_d I M_W}{F} - D_W \nabla c_W - c_W u_W \quad (4.11)$$

where c_W , D_W , F , I , M_W , and n_d are the mass concentration of water, the diffusion coefficient of water in the membrane, the Faraday's constant, the local current density vector, the molecular weight of water and the electroosmotic drag coefficient, respectively. The water velocity vector in the membrane, u_W can be obtained using the Darcy's law.

The water balance in the membrane at the steady state will be:

$$\nabla \cdot N_w = 0 \quad (4.12)$$

Where N_w is the net water flux vector. If the net water flux is from anode to cathode the value of N_w will be positive otherwise it will be negative.

Motupally *et al.* [170] has proposed a correlation for the membrane water diffusivity related to the temperature and water content of the membrane:

$$D_w = \begin{cases} 3.1 \times 10^{-7} \lambda [\exp(0.28\lambda) - 1] \exp(-2346/T), & \lambda \leq 3 \\ 4.17 \times 10^{-8} \lambda [1 + 161 \exp(-\lambda)] \exp(-2346/T), & \lambda > 3 \end{cases} \quad (4.13)$$

Like the water diffusivity of the membrane, the drag coefficient of water in the membrane, n_d also depends on the membrane water content. The drag coefficient is unity within $\lambda = 5$ to 14 and for water content below 5 a linear relation is assumed between the drag coefficient and water content since the drag coefficient must be zero at $\lambda = 0$ [171]. As the water content of the membrane goes up from 14 to 22, the drag coefficient in equilibrium with liquid water increases from 1 to 2.5.

$$n_d = \begin{cases} 0.2\lambda, & \text{for } \lambda < 5 \\ 1, & \text{for } 5 \leq \lambda \leq 14 \\ 0.1875\lambda - 1.625, & \text{for } \lambda > 14 \end{cases} \quad (4.14)$$

The water content itself is calculated after calculation of water concentration of the membrane using [172]:

$$\lambda = \frac{EW_m \cdot c_w}{\rho_m \cdot M_{H_2O}} \quad (4.15)$$

where ρ_m and EW_m are the density and the equivalent molecular weight of the membrane.

4.1.1.3 CO Kinetics

For CO poisoning modelling, participation of several kinds of poisoning species may be considered: the linear- and bridge-bonded adsorbed CO, and the linear-bonded CHO and COOH derivatives. As for the mechanism, three approaches may likely be used. In a first approach, the problem can be solved assuming the presence of only linear-bonded adsorbed CO, as proposed before [152]. In other approaches, the participation of the linear-bonded CO together with one of the other adsorbates at a time may be assumed. Finally, in the third approach, participation of two types of active sites for the adsorption and oxidation of both reactants (hydrogen and carbon monoxide) can be considered. Among these mechanisms only the third has led to results in good agreement with the experimental data of PtRu/C as supported by results obtained for Pt single crystals [173], and also by *in situ* nuclear magnetic resonance results on Pt/C at 0.35 V [174].

According to this discussion, CO poisoning effect modelling here in this work is carried out considering the linear and bridge-bonded adsorbed CO in which the linear- and the bridge-bonded CO are adsorbed in parallel. The hydrogen and CO adsorption and electro-oxidation processes are taken into account on two catalysts sites types; Pt or PtRu linearly and bridged bonded are shown by S_L and S_B , respectively. The following mechanisms were assumed for hydrogen and CO adsorption and electro-oxidation in the vicinity of the Pt/C and PtRu/C catalyst sites.

For linear adsorption sites:

For bridge adsorption sites:

Reactions (4.16) and (4.17), or (4.20) and (4.21) correspond to the hydrogen adsorption and oxidation which is called Tafel/Volmer mechanism, usually considered for the hydrogen oxidation reaction (HOR) in acid media [175]. Reactions (4.18) and (4.19) represent the CO adsorption on the catalyst surface. While, reactions (4.22) and (4.23) are responsible for the CO oxidation possibilities for linear- and bridge-bonded adsorbed CO, respectively. To simplify the mathematical treatment and minimize the number of variables, all steps involving CO were considered totally irreversible, and the rate constants for the hydrogen adsorption/desorption (k_{1L} , k_{-1L} , k_{1B} , k_{-1B}) and oxidation (k_{2L} , k_{-2L} , k_{2B} , k_{-2B}) steps were assumed to be the same in the linear and bridge sites. The time dependence of the degree of linear and bridged-bonded hydrogen coverage of hydrogen (θ_H^L , θ_H^B) and that of carbon monoxide (θ_{CO}^L , θ_{CO}^B) from the mass balance for reactions (16-19) and (20-23) are given by:

$$\left(\frac{d\theta_H^L}{dt}\right) = k_{1L}p_{H_2}(\theta_S^L)^2 - k_{-1L}(\theta_H^L)^2 - 2k_{2L}^\eta \theta_H^L + 2k_{-2L}^\eta \theta_S^L \quad (4.24)$$

$$\left(\frac{d\theta_H^B}{dt}\right) = k_{1B}p_{H_2}(\theta_S^B)^2 - k_{-1B}(\theta_H^B)^2 - 2k_{2B}^\eta \theta_H^B + 2k_{-2B}^\eta \theta_S^B \quad (4.25)$$

$$\left(\frac{d\theta_{CO}^L}{dt}\right) = k_{3L}p_{CO}\theta_S^L - k_{4L}^\eta \theta_{CO}^L \quad (4.26)$$

$$\left(\frac{d\theta_{CO}^B}{dt}\right) = k_{3B}p_{CO}(\theta_S^B)^2 - k_{4B}^\eta \theta_{CO}^B \quad (4.27)$$

where the rate constants $k_{2L}^\eta, k_{-2L}^\eta, k_{4L}^\eta$ are in A.cm^{-2} and p_{CO} and p_{H_2} are the partial pressures of hydrogen and carbon monoxide in the system expressed in atm. θ_S^L and θ_S^B are the fraction of surface sites free of linear and bridged adsorbed species; that is:

$$\theta_S^L = 1 - \theta_H^L - \theta_{\text{CO}}^L \quad (4.28)$$

$$\theta_S^B = 1 - \theta_H^B - \theta_{\text{CO}}^B \quad (4.29)$$

The dependence of k_{2L}^η and k_{2B}^η on the electrode overpotential (η) is expressed assuming an exponential polarization as given by the Tafel equation, that is:

$$k_{2L}^\eta = k_{2L} \exp\left(\frac{\eta}{b_2}\right), \quad k_{-2L}^\eta = k_{-2L} \exp\left(\frac{\eta}{b_2}\right) \quad (4.30)-(4.33)$$

$$k_{2B}^\eta = k_{2B} \exp\left(\frac{\eta}{b_2}\right), \quad k_{-2B}^\eta = k_{-2B} \exp\left(\frac{\eta}{b_2}\right)$$

Equations (4.30)-(4.33) are valid when $\eta \gg 50$ mV. For CO electro-oxidation reactions, the dependence of k_{4L}^η and k_{4B}^η on the electrode overpotential (η) is expressed assuming an exponential polarization as:

$$k_{4L}^\eta = k_{4L} \exp\left(\frac{\eta}{b_{4L}}\right) \quad (4.34)$$

$$k_{4B}^\eta = k_{4B} \exp\left(\frac{\eta}{b_{4B}}\right) \quad (4.35)$$

where k_{4L} and k_{4B} define the onset of the electro-oxidation process and b_{4L} and b_{4B} the dependence with the overpotential. These kinetic parameters are presented in Table 4.2.

The electro-oxidation current density contributions of linear and bridged bonded hydrogen and carbon monoxide were calculated from:

$$j_H^L = 2(k_{2L}^\eta \theta_H^L - k_{-2L}^\eta \theta_S^L), \quad j_H^B = 2(k_{2B}^\eta \theta_H^B - k_{-2B}^\eta \theta_S^B) \quad (4.36)-(4.39)$$

$$j_{CO}^L = 2k_{4L}^\eta \theta_{CO}^L, \quad j_{CO}^B = 2k_{4B}^\eta \theta_{CO}^B$$

Finally, the total current for the hydrogen (j_{HT}) and CO (j_{CO}) oxidations was calculated from:

$$j_{HT} = (1 - f)j_H^L + fj_H^B \quad (4.40)$$

$$j_{CO} = (1 - f)j_{CO}^L + fj_{CO}^B \quad (4.41)$$

where f is the fraction of the total surface corresponding to bridge-bonding sites. At the anode, the source terms for hydrogen molecules and protons are $-j_a/(2Fc)$, and $j_a/(Fc)$, respectively where j_a is the summation of total current produced by electro-oxidation of hydrogen and carbon monoxide. While to obtain the local current density distribution at the cathode catalyst region, the Butler-Volmer kinetic equation is used:

$$j_c = (ai_0^{ref})_c \left(\frac{c_{O_2}}{c_{O_2 ref}} \right) \times \left[\exp \left(\frac{\alpha_a^c}{RT} \eta_c \right) - \exp \left(\frac{\alpha_c^c}{RT} \eta_c \right) \right] \quad (4.42)$$

Table 4.2 Kinetic parameters for hydrogen and carbon monoxide oxidation

Parameter	Value	Unit
$k_{1L} = k_{1B}$	40	A atm ⁻¹ cm ⁻²
$k_{-1L} = k_{-1B}$	8	A cm ⁻²
$k_{2L} = k_{2B}$	3	A cm ⁻²
$k_{-2L} = k_{-2B}$	2.1	A cm ⁻²
b_2	140	mV dec ⁻¹
Pt/C $k_{3L}=k_{3B}$	10	A atm ⁻¹ cm ⁻²
k_{4L}	3.5×10^{-7}	A atm ⁻¹ cm ⁻²
k_{4B}	2.6×10^{-5}	A atm ⁻¹ cm ⁻²
PtRu/C $k_{3L}=k_{3B}$	10	A atm ⁻¹ cm ⁻²
k_{4L}	7.5×10^{-7}	A atm ⁻¹ cm ⁻²
k_{4B}	9×10^{-6}	A atm ⁻¹ cm ⁻²
b_{4L}	230	mV dec ⁻¹
b_{4B}	1300	mV dec ⁻¹
f	0.1	-

where $(ai_0^{ref})_c$ is the reference exchange current density times area at the cathode, η the activation overpotential, and α is the transfer coefficient. The cathode activation overpotential is defined as:

$$\eta = \varphi_s - \varphi_m - V_{oc} \quad (4.43)$$

where V_{oc} is the thermodynamic open circuit potential for the overall cell reaction and is calculated using the Nernst law [154]:

$$V_{oc} = 1.229 - 0.9 \times 10^{-3}(T-298) + 2.3 \frac{RT}{4F} \log(p_{H_2}^2 p_{O_2}) \quad (4.44)$$

4.1.1.4 Boundary Conditions

Figure 4.2 shows the schematic of the numerical domain. For the above mathematical model the following boundary conditions are taken into account. The gas pressure and concentrations of anode and cathode gaseous species at the interfaces 1 and 8, between anode and cathode channels and gas diffusion layers, are set equal to the inlet conditions. Interfaces 2 and 9, between the anode and cathode shoulders and the gas diffusion layers are considered to be impermeable to gases; therefore, at these interfaces, fluxes of gaseous species normal to the interface are set to zero. The electric potential for these interfaces are set to zero and the applied cell potential, respectively. At interfaces 3 and 7, between the gas diffusion layers and the catalyst layers, continuous electronic current and gaseous normal fluxes are considered. Protons flux at these interfaces is set to zero at these interfaces because no ionic current is available in the gas diffusion layer. The boundary conditions for interfaces 4 and 5, between the catalyst layers and membrane, are continuous ionic current and zero gases flux and electronic current. Symmetry conditions are used for all the other boundaries which are not labelled in Fig.4.2.

For comparison purposes, the simulations are carried out considering the linear CO adsorption (equations (4.16)-(4.19)) only, too. The conservation equations used for this case are the same; the only difference is that the hydrogen and CO oxidation terms should be calculated from the conventional CO poisoning mechanism used in the literature of PEM fuel cells CO poisoning simulation [152, 155, 156]. Using the COMSOL multi-physics, the governing equations in the different regions of the fuel cell are solved simultaneously to ensure the coupling of the flow, species, overpotential and current density.

4.1.1.5 Numerical Procedure

The chemical engineering module of COMSOL multi-physics which is a finite element method based package was used to solve the system of the governing equations. The geometrical parameters and transport properties used in the simulation are shown in Table 4.1. Triangular mesh elements are used for two-dimensional geometries in COMSOL. The computational mesh for the simulations is shown in Fig. 4.3. Twenty thousand mesh elements provided accurate enough results and the solution obtained was found to be independent of the grid size. Stationary non-linear solver under the solver parameters menu with Direct (UMFPACK) linear system solver were used. To enhance the convergence, the model was initially solved for the potential fields using proper initial values. Proper initial value means the value of a parameter close to the final solution as chosen by the user in a way that the solution converges faster. The obtained solution was used as the initial value to solve for all other variables. The convergence criterion for the iterations was set to 1×10^{-5} . Polarization curves were obtained by changing the cell potential. The run time for each cell voltage varied between 90-600s on a dual core Intel 2G-RAM.

Fig. 4.3 Computational mesh for two dimensional PEMFC

4.1.2 Results and Discussion

A series of computation simulations were performed using the two dimensional fuel cell model. Kinetic parameters for hydrogen and carbon monoxide oxidation taken from [176] are listed in Table 4.2. The simulations are done at 85°C and 1 atm to make the substantiation of the simulations with the experimental data [177] a possibility. Figure 4.4 shows the effect of different CO concentrations on the performance of the PEM fuel cells with Pt/C and PtRu/C performance operating in the base case conditions. The significance of CO poisoning can be clearly seen; the large voltage drop at a CO concentration of 20 ppm is evident for both cases. Anyways, the performance degradation for the Pt/C is the most significant. It can be explained as: for relatively low current densities ($I < 0.4 \text{ A/cm}^2$), only a small anode overpotential exists for the electro-oxidation of hydrogen to provide the current density; this is due to fast kinetics of the hydrogen electro-oxidation although only a small fraction of catalyst sites are available for hydrogen oxidation. For intermediate current densities, which is characterized by the sharp increase in anode overpotential ($0.3 < I < 0.5 \text{ A cm}^2$), the required anode overpotential to supply the requisite current density increases as the small number of available sites are insufficient for hydrogen electro-oxidation to be carried out at a suitably fast pace. At these current

densities, however, the anode overpotential is insufficient to bring about significant electro-oxidation of CO to free up the catalyst sites for hydrogen adsorption.

a)

b)

Fig. 4.4 the effect of different CO concentrations on the PEM fuel cell performance for a) Pt/C and b) PtRu/C

For high current densities ($I > 0.5 \text{ A/cm}^2$), a correspondingly large anode overpotential is required for hydrogen electro-oxidation, at the same time, the presence of the large overpotential enables CO electro-oxidation to take place relatively fast, resulting in the freeing of catalyst sites for hydrogen adsorption. This explains the subsequent gradual leveling of the anode overpotential as current density is increased beyond 0.4 A/cm^2 .

It is observed that the onset of CO oxidation process occurs at different potentials, at 0.4 V for Pt/C and 0.1 V for PtRu/C depending on the nature of the electrode material; the onset of this reaction occurs first for PtRu/C followed by Pt/C. The different polarization behaviours observed for various catalysts in the presence of CO may be attributed to different mechanisms for the CO poisoning effect. The electro-oxidation of CO occurrence explains very satisfactorily many of the CO tolerance factors for the alloy catalysts, although very important, it is not the only factor responsible for the CO tolerance effect. Other contributors can be changes promoted by the alloyed materials on the thermodynamics and the kinetics of the CO adsorption process.

As Figure 4.5 compares the predicted polarization curve and the experimental data of the cell with Pt/C catalyst layer from Lee *et al.* [177] for the three base cases at 20, 50 and 100 ppm level of CO; there is a good agreement between the model and experimental data; the difference at the high current density end is due to the single phase model ignoring the hindering effect of liquid water produced in the cathode catalyst layer by the oxygen reduction which sometimes may be more than the amount of liquid water that can be transported out of the cell by the oxidant gas stream.

The distribution of CO concentration across the anode catalyst layer for current densities of 0.25 A/cm^2 and 0.6 A/cm^2 with 100 ppm CO in the anode feedstock is shown Figure

4.6. At the current density of 0.25 A/cm^2 , the concentration of CO decreases only slightly from 100 ppm to 90ppm due to the small rate of CO oxidation which shows that the contribution of CO oxidation in the current density produced is too low; while, for the current density of 0.6 A/cm^2 the overpotential is high enough to oxidize all the CO.

Figure 4.7 shows the current contribution of hydrogen and carbon monoxide electro-oxidation on Pt/C and PtRu/C at 50 ppm CO. As can be seen, the maximum current density produced by CO oxidation is 300 mA cm^{-2} which is too low in comparison to hydrogen oxidation reaction current that can reach as high as 2 A cm^{-2} . It is also observed, as mentioned before, that the onset of the CO electro-oxidation is shifted from 0.4 V for Pt/C to 0.1 for PtRu/C; this phenomenon has been reported by other cyclic voltammetric response as well [4].

Fig . 4.5 Comparison of the predicted polarization curve and the cell experimental data of Lee *et al.* [15]

Figure 4.8 shows the hydrogen and carbon monoxide coverage ratios across the anode catalyst layer made of Pt/C for the same current densities and with 100 ppm CO present in the anode inlet gas. At current density of 0.25 A/cm^2 , increases from 0.95 to 0.965 and then decreases to 0.961 because of CO concentration decrease due to CO oxidation; while for the 0.6 A/cm^2 case, the high rate CO oxidation decreases the CO coverage leading to more catalyst sites available for the hydrogen molecules.

Fig.4.6 The distribution of CO concentration across the anode catalyst layer for current densities of 0.25 A cm^{-2} and 0.6 A cm^{-2} with 100 ppm CO in the anode feedstock

Figure 4.9 shows the fraction of catalyst sites bonded linearly or bridged with CO molecules for the same conditions discussed for Figure 4.8. This shows that the bonding mode of the adsorbed CO molecules is dependent on the CO coverage, and the linear CO sites increase with increasing the CO coverage; this is in agreement with the work done by Chang *et al.* [178] using IR spectroscopy for CO adsorbed on Pt catalyst sites. The adsorbed CO bonding state may be affected by other factors like the surface smoothness and the potential of the electrode as have been reported in the literature; however, under any conditions, CO molecules have the tendency to be adsorbed linearly at high coverage.

Fig. 4.7 The current contribution of hydrogen and carbon monoxide electro-oxidation on Pt/C and PtRu/C at 50 ppm CO

Fig. 4.8 The fraction (θ) of anode catalyst sites occupied by hydrogen and carbon monoxide

10ppm CO level has shown negligible reduction in PEMFC performance which agrees with the experimental data available in the literature.

Fig. 4.9 The fraction (θ) of anode catalyst sites bonded linearly or bridged with CO molecules at 0.6 A cm^{-2}

4.2 Thermodynamic Modeling of the Electrolytic CO oxidation System

4.2.1 Thermodynamic model

The schematic of the plant considered in the thermodynamic modeling is shown in Fig. 4.10. The model is similar to the one described in earlier works [179, 180] where the authors modeled the water electrolysis to produce hydrogen and oxygen. In contrast, the focus of the model developed in this dissertation is the electrochemical water-gas shift reaction to electro-oxidize CO in the electrolytic selective CO oxidation. The details of the reactions are presented in equations (4.45) - (4.48). During the EWGS operation, electricity is supplied to the electrolyzer to initiate the electrochemical reactions. The wet

mixture of hydrogen and CO flow introduced to the adsorber provides water molecules required for the electrolytic CO electro-oxidation. The feedstock is fed to the adsorber at ambient operating conditions i.e., room temperature (30°C) and 1atm. The purified hydrogen exits the adsorber and enters the fuel cell. The hydrogen gas produced at the anode through electro-reduction of protons is an additional amount of hydrogen generation, which is added to the hydrogen line fed to the fuel cell. In fact, 1 mole of hydrogen will be generated at the anode side of the electrolyzer for one mole CO adsorbed at the cathode side. The overall adsorber/ electrolyzer system reaction is that CO, H₂O plus electricity turn to H₂.

4.2.2 Energy efficiency

In this section, a quantitative energy analysis is presented evaluating the thermodynamic performance of the adsorber/ electrolyzer system. As the first step, it is necessary to calculate the theoretical energy demand for EWGS reaction. The total energy demand for this reaction can be calculated as:

Fig. 4.10 The schematic of the plant considered in the thermodynamic modeling

$$\Delta H = \Delta G + T\Delta S \quad (4.49)$$

where the Gibb's free energy change (ΔG), is the electrical energy demand and $T\Delta S$ is the thermal energy demand (J/mol H_2). The thermal energy demand is eliminated in this study as no thermal input is used and the total required energy for the electrolytic process is provided by electrical energy. This total energy demand is the theoretical energy required for electrolytic CO oxidation without considering losses. In reality, losses are unavoidable affecting the system performance. Therefore, the performance of the system can be evaluated in terms of energy efficiency (η_{en}) defined as:

$$\eta_{en} = \frac{\dot{N}_{H_2,gen} \cdot LHV_{H_2}}{Q_{electric}} \quad (4.50)$$

Where LHV_{H_2} , $\dot{N}_{H_2,gen}$ and $Q_{electric}$ are the hydrogen lower heating value, the outlet flow rate of generated hydrogen and the rate of electric energy input for the electrolyzer, respectively; The outlet flow rate of generated hydrogen can be determined by:

$$\dot{N}_{H_2,gen} = \frac{J}{2F} = \dot{N}_{CO,reacted} = \dot{N}_{H_2O,reacted} \quad (4.51)$$

where J is the current density, F is the Faraday constant and $\dot{N}_{CO,reacted}$, $\dot{N}_{H_2O,reacted}$ are the rate of CO and H_2O reacted in the electrolytic process.

4.2.3 Thermodynamic-electrochemical modeling of the EWGS electrolyzer

The energy involved in the EWGS electrolyzer operation can be evaluated by applying some modifications on the electrochemical model developed by Ni et al. [180]. The electric energy is calculated from the equation (4.52) to consider for the gibb's free energy difference between the reactants and products.

$$Q_{electric} = JV \quad (4.52)$$

$$V = V_0 + \eta_{act,a} + \eta_{act,c} + \eta_{ohmic} \quad (4.53)$$

Where V_0 is the reversible potential, which in the case of EWGS electrolyzer is 0.11 V as obtained from standard potential tables [181]; $\eta_{act,a}$, $\eta_{act,c}$, and η_{ohmic} are the overpotentials due to the anode and cathode activations and the electrolyte ohmic resistance, respectively which are calculated from equations (4.54) and (4.55).

$$\eta_{act,i} = \frac{RT}{F} \sinh^{-1} \left(\frac{J}{2J_{0,i}} \right) = \frac{RT}{F} \ln \left[\frac{J}{2J_{0,i}} + \sqrt{\left(\frac{J}{2J_{0,i}} \right)^2 + 1} \right], \quad i = a, c \quad (4.54)$$

$$\eta_{ohm} = JR_{membrane} \quad (4.55)$$

Where $R_{membrane}$, R , T , and $J_{0,i}$ are the ohmic resistance of the proton conductive membrane, gas constant, temperature and exchange current density, respectively. $R_{membrane}$ and $J_{0,i}$ are given by equations (4.56) and (4.57).

$$R_{membrane} = \int_0^L \frac{dx}{\sigma(x)} = \int_0^L \frac{dx}{[0.5139\lambda(x) - 0.326] \exp \left[1268 \left(\frac{1}{303} - \frac{1}{T} \right) \right]} \quad (4.56)$$

$$J_{0,i} = J_i^{ref} \exp \left(-\frac{E_{act,i}}{RT} \right), \quad i = a, c \quad (4.57)$$

Where L , $\sigma(x)$, $\lambda(x)$, J_i^{ref} and E_{act} are the thickness, conductivity, and water content of the membrane and reference exchange current density. The water content of the membrane is calculated from equation (4.58).

$$\lambda(x) = \frac{\lambda_a - \lambda_c}{L} x + \lambda_c \quad (4.58)$$

As the current densities applied are not too high (i.e. $J < 1 \text{ A/cm}^2$), the concentration overpotentials are neglected.

4.2.4 Results and discussion

4.2.4.1 Model validation

The electrochemical model developed here is used to simulate electrolytic characteristics of the EWGS electrolyzer. The experimental data obtained from regeneration experiments are used to validate the model results. The electrolyte used in the experiments is Nafion 112, a perfluorosulfonic (PFSA) proton conducting polymer which is widely used as electrolyte in PEM fuel cells and electrolyzers. The thickness of this kind of electrolyte is 50 μm . Platinum is used as the electrode catalyst. The values of exchange current density for anode and cathode are 5×10^{-5} and 10 A.m^{-2} at 353 K, respectively. Substituting these values in equation (4.57), the exchange current densities at room temperature are calculated. The electrolytic WGS reaction is conducted at atmospheric pressure. Typical values of the parameters used in the thermodynamic modeling are presented in Table 4.3.

The simulated polarization curves of the EWGS electrolysis are compared with experimental data obtained in the regeneration studies as shown in Fig 4.11. The modeling results are in reasonable agreement with experimental data, indicating the validity of the present model.

Fig. 4.11 Comparison between the simulated and experimental data of the polarization curves of the EWGS electrolysis

Table 4.3 Typical values of the parameters used in the thermodynamic modeling

Parameter	Value
Operating Pressure (atm)	1
Operating Temperature (K)	303
Anode Activation Energy (kJ/mol)	76
Cathode activation Energy(kJ/mol)	18
Anode water content	14
Cathode water content	10
Membrane thickness (μm)	50

It is found that the cell potential increases rapidly in the current density range of $J < 0.2 \text{ A.cm}^{-2}$. As current density exceeds this value, the cell potential increases slightly with current density. The ohmic and activation losses are investigated as shown in Figure 4.12 in order to fully understand the electrochemical performance of the EWGS electrolyzer. The ohmic loss is relatively small compared to other losses and as can be seen increased slightly with current density. The low value of the ohmic loss is because of the high ionic conductivity of the membrane at typical humidity.

Although the cathode activation overpotential is larger than the ohmic loss, it is much smaller than that of the anode side. This is because of the faster reaction of proton reduction at Pt cathode surface (equation (4.48)). The anode activation loss exhibits a sudden increase at current densities less than 0.2 A.cm^{-2} , and then a steady increase with current density for values bigger than 0.2 A.cm^{-2} . As it can be seen, the anode activation overpotential which is due to water partial electrolysis (equation (45)) dominates the total potential loss shown in Figure 4.12. In the real system, the anode overpotential is due to carbon corrosion and water electrolysis.

Fig. 4.12 The contributions of ohmic loss, and cathode and anode activation overpotentials of the electrolysis process

Figure 4.13a presents the effect of current density on the energy efficiency of the EWGS electrolyzer system at a temperature of 303 K. Energy efficiency decreases at a decreasing rate with current density. To understand the phenomena more clearly, the electrical energy input and the energy output in the generated hydrogen are also compared in Figure 4.13a. The change rate of the energy input and output are different with increasing current density. The electrical energy demand increases significantly with increasing current density while the energy output increases linearly with current density. The energy efficiency decreases with current density as shown in Figure 4.13a as the rate of energy

input (electrical energy) increase with current density is higher than that of the energy output (H_2 produced).

One important point about this model is that the focus is on the thermodynamic-electrolytic characteristics of the EWGS electrolyzer system without inclusion of the electrical energy supply method. It can be used for energy analysis of any electrolytic hydrogen production system driven by renewable energy such as solar or wind power.

The effect of operating temperature on the energy efficiency of the EWGS electrolyzer plant is shown in Figure 4.13b at typical working temperatures of 298, 303, 323 and 353 K. The results show that the higher the temperature the higher the energy efficiency. At higher operating temperature, the electrodes of EWGS electrolyzer are more reactive leading to lower activation losses due to higher exchange current density explained by Equation (4.14). Decrease in the activation overpotentials reduces the cell potential with the consequence of a decrease in the electrical energy input.

Fig. 4.13 a) The effect of current density on the energy efficiency of the EWGS electrolyzer system at a temperature of 30 °C. b) The effect of operating temperature on the energy input and the energy efficiency of the EWGS electrolyzer plant.

Chapter 5 Conclusions and Future Works

In this chapter, the concluding remarks of this research are presented and some ideas are suggested for future research. This dissertation presents a fundamental insight into the CO poisoning issue in polymer electrolyte membrane fuel cells. In addition, it provides mitigation approaches for this issue. The possible approaches to solve the CO poisoning of PEM fuel cells can be categorized to two main technologies: on-fuel cell and off-fuel cell approaches. A combination of electrochemical studies and numerical simulations are carried out to understand the mechanism of CO poisoning. Furthermore, the merit and affectivity of two different approaches to mitigate this issue are investigated. First, electrochemical studies are performed to investigate the CO tolerance of some binary and ternary Pt-based alloys incorporated in a PEMFC. Second, an electrolytic-based selective CO oxidation system for on-board pure hydrogen production is introduced. Such a system adsorbs CO and other impurities and removes them via electrochemical water gas shift reaction. The electrolytic process (regeneration) and geometrical parameters of the adsorber are optimized with the effort of completely removing the adsorbed CO molecules. Furthermore, a thermodynamic-electrochemical model is developed to simulate the energy balance of the electrolyzer indicating that this process offsets the actual energy consumption because it produces extra hydrogen. Thermodynamically, removing CO by electricity is more efficient than by heat which leads to high energy efficiencies (>80%). Such a study on CO poisoning fundamentals and mitigation approaches are expected to provide a complete understanding of the issue, electrocatalysts requirements, and finally design of novel approaches to solve this issue.

5.1 Concluding remarks for CO poisoning modeling

A finite element based computational fluid dynamics method was used successfully to simulate the performance leading to a better understanding of the phenomena occurring inside the PEM fuel cell operating on reformat. The model can predict not only the polarization curves of the cell but also the distribution of the reactants and products inside the cell with Pt/C and PtRu/C catalyst layers. The predicted results are in good agreement with the experimental data. The model provides a good understanding on the CO kinetics effects on the cell performance. It is found that the CO hinders the hydrogen oxidation in reaction sites; the significance of CO poisoning is evident at a CO concentration of 20 ppm for both Pt and PtRu catalysts.

It is observed that the onset of CO oxidation process occurs at different potentials at 0.4 V for Pt/C and 0.1 V for PtRu/C; the onset of this reaction occurs first for PtRu/C followed by Pt/C which shows the higher CO tolerance of PtRu catalyst. The electro-oxidation of CO occurrence explains very satisfactorily many of the CO tolerance factors for the alloy catalysts, although very important, it is not the only factor responsible for the CO tolerance effect. Other contributors are the changes promoted by the alloyed materials on the thermodynamics and the kinetics of the CO adsorption process.

Modeling the performance of PEM fuel cells with different kind of binary and ternary electrocatalysts could be the topic for future research.

5.2 Concluding remarks for development of novel CO tolerant Electrocatalysts

Through efforts made in the development of catalysts with excellent CO tolerance and stability, enormous progress has been made in catalyst synthesis techniques, and understanding the effective parameters which enhance the catalytic activity and stability.

Choosing a proper synthesis method, inclusion of appropriate content of suitable promoters in Pt-based catalysts, and using a proper support material seem to be the major requirements of an effective catalyst. Optimizing the synthesis conditions, the amount of each component in the catalyst and metal-support interactions to reach the highest catalytic activity and stability would be the most crucial efforts for the future research.

It is essential to add appropriate amounts of elements to Pt/C or PtRu/C which enhance the catalytic activity through the bifunctional mechanism and electronic effects. Mo, Ru, Os, Sn, and Re are suggested to be appropriate elements which create oxophilic groups on the catalyst surface facilitating the CO electrooxidation through bifunctional mechanism. In addition, all transition metals change the electronic properties of the electrocatalysts nanoparticles via electron transfer between the Pt and the added element in a way that the Pt–CO bond weakens leading to a decrease in CO coverage, and thereby enhancing the catalytic performance.

The catalytic activities of electrocatalysts for PEM fuel cell applications are significantly affected by the structure and morphology of the catalysts. Depending on the preparation conditions, different molecular structures form including alloys, intermetallic phases, core-shell structures and oxidative agents decorative Pt/C.

The crystalline structure of catalysts with ordered intermetallic architectures is well-defined and normally possesses high enthalpies of formation, which increases the stability of these

materials compared to that of alloys. In addition, the cluster size and morphology can influence the catalytic activity of the electrocatalysts towards CO electrooxidation. For instance, the morphology and size of the clusters and Ru islands play a critical part in the relative importance of the mentioned mechanisms. Controlling the catalysts structure and morphology and understanding the structure-activity correlations are of great importance in designing novel CO tolerant electrocatalysts with superior performance.

It is observed that formation of an alloy is not a necessary condition for attaining effective CO oxidation activity. It is possible to enhance the CO electro-oxidation of the Pt-based electrocatalysts by decorating the catalysts surface by other metals or groups. The role of the added metal/ group is to promote the catalytic activity. In addition, it is a must for the promoter to be in the vicinity of Pt sites in order to be effective for the CO electro-oxidation

The atomic ratio of the elements plays an important role in the catalytic activity. It is concluded that for bimetallic electrocatalysts such as PtRu, PtFe and PtW the maximum activity and the most superior CO tolerance is exhibited by those with atomic ratio of 1:1. In the case of oxidative agents modified Pt-based electrocatalysts, the activity of the catalysts are strongly dependent on the content of the promoter. An optimum content of the promoter must be added to the Pt/C to effectively enhance the CO oxidation. In fact, adding too much of the oxidative agent would block a large portion of the Pt active sites.

The primary goals of placing the active components of a catalyst onto a support material are to improve the dispersion of the active components and the mechanical and chemical stability of the catalyst. These goals are achievable by applying suitable supports and generating effective interactions between the active content and the support.

The preparation technique plays a crucial role in the catalytic structure and thus the activity. Colloidal method has been widely acknowledged as the appropriate synthesis method producing a close contact among the elements in the catalyst which ensures the formation of completely alloyed particles. Other techniques such as vapour deposition and borohydride reduction have also been applied to produce excellent and effective contact among the elements. An important factor determining the catalytic activity of electrocatalysts towards CO and H₂ oxidation is the particle size. Effective reducing agents such as sodium borohydride and formic acid have been used to form particles with very small average size (<3nm) and consequently increasing the surface area.

It is concluded that by taking into account the effective parameters on the catalytic performance, and stability, and understanding the mechanisms and pathways of the reaction on a catalyst, the design and development of novel catalysts with enhanced CO tolerance and stability will be achieved more efficiently. On this note, the role of numerical chemistry specifically DFT calculations as a powerful tool should be well acknowledged.

In this dissertation, using a combination of experimental and theoretical XAFS analysis, the reformate tolerance of some binary and ternary catalyst (Pt-M (M= Ru, Mo, Fe, Co, Ni), PtRuMo/C, PtCoMo/C and PtRuPb/C) are systematically examined and correlated to the electronic properties of the catalyst caused by alloying Pt with transition metals. Among these electrocatalysts the ternary catalyst PtCoMo/C exhibits the best performance for reformate oxidation. Both CO and CO₂ issues are considered in the electrochemical experiments. The CO tolerance is the highest for PtMo/C followed by PtCoMo/C, PtRuMo/C, PtRuPb/C,

PtRu/C, PtCo/C, PtFe/C, PtNi/C and Pt/C while the CO₂ tolerance increases in the order: PtCo, PtNi> PtRuPb> PtRu> PtCoMo> PtRuMo> PtFe> Pt> PtMo.

It is shown that the improvements in the reformat tolerance are attributed to three factors: available Pt sites, OH groups formation on the surface and the electronic properties of the electrocatalyst. Cyclic voltammetry experiments show that there is a linear correlation between the CO oxidation onset potential and the anode overpotential. PtMo, PtRuMo and PtCoMo exhibit deep decreases in anode overpotential due to the presence of CO compared to others highlighting the vital role of Mo in CO oxidation. This crucial effect is due to the efficient and effective formation of OH groups on Mo leading to immediate oxidation of adsorbed CO species on the surface. On the other hand, catalysts including Mo exhibit very high anode overpotential in the presence of CO₂ in the hydrogen feed. This is attributed to the suppression of superior CO oxidation by Mo sites at higher current densities.

The roles of electronic properties on the reformat tolerance is significant. The correlations between the alloys' reformat tolerance and the modification of Pt electronic properties is elucidated via two important factors Pt d-band vacancy and Pt d-band centre. It is shown here quantitatively that the higher the Pt d-band vacancy the lower the impurities adsorption and coverage on the surface and therefore leading to lower anode overpotentials. On the other hand, the lower the Pt d-band centers the lower the CO/CO₂ coverage and therefore anode overpotential. Understanding the effect of electronic properties on the reformat tolerance produces a bright perspective to design and develop new catalysts with enhanced reformat tolerance and excellent activity.

Density functional theory (DFT) calculation for development of novel electrocatalysts with enhanced CO tolerance is a topic for future research.

5.3 Concluding remarks for the electrolytic CO oxidation system for production of pure hydrogen

5.3.1 Parametric study to obtain the maximum adsorption capacity

A parametric study is carried out to provide guidelines for designing a PEM reactor used as a gas clean-up system for production of pure hydrogen for fuel cells or other applications. The focus is on the effect of different geometrical and operational parameters of the adsorber such as the gas flow field geometry, gas diffusion layer porosity and thickness, catalysts and catalyst supports type and loading on the adsorption capacity of the adsorber. Having obtained these correlations, one can make adsorber with the best performance while using optimum amount of catalyst loading. To achieve this purpose, four different flow fields (straight, multi-serpentine, pin-type and interdigitated flow fields), gas diffusion fields with porosities of 0.5 and 0.7 and single metal catalyst (Pt) and alloyed (PtRu) supported onto two different supports including carbon black and activated carbon with metal loadings of 0.5, 1 and 2 mg.cm^{-2} are studied.

Results indicate that the breakthrough time for all the three CO concentrations increases in this order: straight < pin-type < multi-serpentine < interdigitated. In the case of interdigitated flow field, the gas flow is forced through the catalyst layer which prolongs the contact between the catalyst and the CO molecules with the consequence of increasing the CO adsorption and breakthrough time. Compared to the corresponding breakthrough times of the adsorber using Toray carbon papers, adsorbers with Ballard carbon paper have shorter

breakthrough times. This is related to the effect of porosity of the gas diffusion media. It is also found out that there is almost a linear correlation between the catalyst loading and the breakthrough time. In addition, compared to the breakthrough times of adsorbers with the same loading of Pt/C sprayed on Toray carbon paper, no remarkable difference is observed when PtRu/C is used as the catalyst. This implies that alloying Pt with Ru does not change the CO adsorption relative to pure Pt noticeably. Furthermore, breakthrough times of adsorbers with catalyst particles supported on activated carbon are considerably longer than those supported on carbon black. This is related to the microstructure, porosity and the surface area of the two supports.

5.3.2 Energy analysis of the electrolytic CO oxidation system

In this study, an energy analysis and parametric study are performed on the electrolytic-based selective CO oxidation system for on-board/site pure hydrogen production. An electrochemical-thermodynamic model is developed to simulate the hydrogen production and CO removal through an electrochemical water-gas shift (EWGS) reaction on the catalyst layer of a PEM reactor. The model takes into account the electrolytic process at the electrolyzer. The predicted results are in reasonably good agreement with the data obtained from the experiments.

The adsorption capacity of a PEM reactor adsorber/ EWGS electrolyzer concept was investigated in details. The CO gas molecules were adsorbed physico-chemically on the catalyst (Pt/C) surface with a metal loading of 2 mg.cm^{-2} supported on a carbon paper with 50 cm^2 area. The breakthrough curves were obtained for different concentrations of CO present

in the hydrogen stream (100, 300, and 500ppm CO) and feed flow rates (40, 80, 120, 160 and 200 ml.min⁻¹). The results indicate that the proposed system may have the potential for portable or mobile applications, such as, a fuel cell vehicle, to operate for a certain duration before regeneration is required to remove the adsorbed CO in the adsorber. Through an extensive experiment, the optimum regeneration parameters have been obtained. $t_{reg}=100$ sec and $V_{reg}=0.7$ V are considered as the optimal regeneration conditions at which the capacity decrease level is minimum. In addition, the electrical energy demand and efficiency for the electrolysis were calculated at different operating temperatures and current densities. As expected, the model showed that the electrical energy input required for the electrolysis decreases with increase in temperature and the energy efficiency decreases with increase in current density. This decrease is significant for current densities less than 0.2 A.cm⁻². In fact, according to the developed model, the ideal applied current density for the electrolytic process should be less than 0.2 A.cm⁻² so that the energy efficiency would be the highest possible (>80%). Furthermore, the long term performance of the system under sequential regeneration conditions show that the adsorber adsorption capacity was not affected at all implying that the electrolytic-based selective CO oxidation system is a promising approach to produce pure hydrogen for on-board/site applications.

Investigating the effect of applying different types of electric inputs on the regeneration step is a topic for future research. In this study, using a power generator which is able to produce different types of voltage profiles, triangular and sinusoidal and so on will be applied to regenerate the adsorber. It is possible that applying different voltage profiles enhances the efficiency of the regeneration step.

The adsorption of CO on noble catalysts such as platinum (Pt) and palladium (Pd) is well researched. In fact, noble catalysts adsorb CO preferentially at different temperatures. However, only handful of research studies focusing on non-noble catalysts for CO adsorption and electro-oxidation specifically in a hydrogen-rich environment. Basically, the acidic atmosphere by the ionomer restricts the candidates of non-platinic materials from application. The stability for the redox potential and fuel atmosphere also affects the material choice. Among the trial materials, transition metal carbides and promoted oxides are successfully developed for methanol and hydrogen oxidation. However, the performance of non-platinic catalysts is reported to be much lower than that of the platinum.

Developing design criteria for non-noble catalysts such as cobalt (Co), nickel (Ni), their alloys, and alkali metal doped NiCo using the first-principles for CO adsorption and electro-oxidation at low temperatures is another topic for future research. Development of novel catalysts with enhanced stability and activity comparable with Pt address the issue of the system cost.

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