

Synthesis and Characterization of Bimetallic Platinum Nanoparticles for use in Catalysis

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the Degree of Doctor of Philosophy.**

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DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the Degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

Signature of candidate

.....day of2015

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ABSTRACT

Bimetallic platinum nanoparticles were synthesized for application as anode catalysts for low temperature fuel cells such as direct methanol fuel cells (DMFCs). Two distinct synthesis procedures were used; namely conventional synthesis with post-synthesis heat treatment, and secondly polyol microwave-irradiation without further heat-treatment. The aim was to synthesize interesting and novel bimetallic nanostructures and relate their shape and morphologies to their methanol oxidation reaction (MOR) activities and their CO tolerance.

Due to the high cost of the conventional synthesis processes as well as their use of harmful solvents, microwave-irradiation was explored as a possible synthesis procedure. It is a greener and more environmentally friendly approach with possibilities of mass production of the nanoparticles. For both the synthesis procedures, the reducing agent, the precursor salts, surfactants, pH of the solution and molar ratios were varied to determine the effect on the shape, size and ultimately the electrocatalytic activities of the Pt-Co and Pt-Ni nanoparticles.

For the conventional synthesis procedure, the main parameter of comparison was the strength of the reducing agents, where NaBH_4 and N_2H_4 were used under the same reaction conditions. In this study, the strength of the reducing agent affected the properties of the Pt-Co and Pt-Ni nanoparticles, such that, the stronger the reducing agent, the higher the degree of alloying and the more electrocatalytically active the materials. The drawback in the conventional synthesis was however low

current outputs, in the microamps range, which necessitates a need to explore other synthesis procedures.

Microwave-irradiation was thus used as an alternative synthesis procedure in an attempt to produce more active bimetallic platinum nanoparticles. Different reaction parameters were changed in this process to optimize the synthesis process, namely the pH of the solution, the amount of surfactant and the Pt-Ni molar ratio. In changing the reaction parameters, there was an observed change in the structure of the nanoparticles, with an average size in the order of 5 nm and different MOR activities. Furthermore, it was found that the activity was highest for the optimum amount of PVP and NaOH concentration of 500 mg and 1.0 M NaOH. In general, the MW synthesized nanoparticles achieved current values in the microamps to amps range, making it a more attractive synthesis procedure compared to the conventional method.

The CO tolerance of the materials is an important aspect, as one of the main drawbacks of the commercial application of fuel cells is the propensity of Pt to get poisoned by CO during the methanol dissociation process. Therefore CO stripping measurements were performed on the MW-irradiated catalysts. The catalysts produced in this work showed good resistance towards CO. In general, the behaviours of the catalysts were dependent on the amount of surfactant and the molar ratio of the starting solution. The mechanism of CO tolerance in this case was determined as the bifunctional model, where the Ni-oxide and Ni-hydroxide species donate O to the electrooxidation of CO to CO₂. In conclusion, the study of microwave-irradiated bimetallic nanoparticles performed here, resulted in highly active catalysts, which are even more active than commercial Pt/C nanoparticles.

PUBLICATIONS AND PRESENTATIONS ARISING FROM THIS THESIS

Publications

1. **N.R. Mathe**, M.R. Scriba, J.E. Olivier, N.J. Coville, "*TEM and EELS studies of microwave-irradiation synthesis of bimetallic platinum nanocatalysts*", **Institute of Physics: Conference Series 522 (2014) 012066.**
2. **N.R. Mathe**, M.R. Scriba, N.J. Coville, "*Methanol Oxidation Reaction activity of Microwave-irradiated and Heat-treated Pt/Co and Pt/Ni Nano-Electrocatalysts*", **International Journal of Hydrogen Energy 39, (2014), 18871 - 18881**
3. **N.R. Mathe**, M.R. Scriba, N.J. Coville, "*The Effect of Reducing Agents on the Electronic, Magnetic and Electrocatalytic Properties of Thiol-Synthesized Pt/Co and Pt/Ni Electrocatalysts*", **Electrocatalysis, (2014), doi:10.1007/s12678-014-0241-y. Available Online.**
4. **N.R. Mathe**, M.R. Scriba, N.J. Coville, "*Microwave-irradiation Polyol Synthesis of PVP-protected Pt/Ni Electrocatalysts for Methanol Oxidation Reaction*", **Journal of Power Sources (2014), In process.**
5. **N.R. Mathe**, M.R. Scriba, N.J. Coville, "*FTIR and UV-VIS Study of Microwave-Irradiation Polyol Synthesized Pt/Ni Nano-Electrocatalysts*", **Electrochemistry Communications (2014). In process.**

Conferences

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5. 4th NanoAfrica Conference, 2012, University of the Free State, Bloemfontein, South Africa. **Oral**
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LIST OF ABBREVIATIONS

Ag – silver

AgCl – silver chloride

At.% - atomic percentage

BE – binding energy

BET – Brunauer, Emmett and Teller

CH₂OH – methanol

C – carbon

CO₂ – carbon dioxide

CO – carbon monoxide

Co – cobalt

CoCl₂ – cobalt chloride

CV – cyclic voltammetry

DFAFC – direct formic acid fuel cells

DMFC – direct methanol fuel cells

E_a – activation energy

ECSA – electrochemically active surface area

EELS – electron energy loss spectroscopy

EG – ethylene glycol

eV – electron volt

FE-SEM – field emission scanning electron microscope

FT-IR – fourier-transformed infra-red spectroscopy

FCC- face centred cubic

Fe – iron

GC – glassy carbon electrode

H₂PtCl₆ – chloroplatinic acid

H₂SO₄ – sulphuric acid

HCP – hexagonal closed packing

HT – heat treatment

H₂ – hydrogen

H₂O – water

mA/cm² – milliamps per square centimetre

mA/mg Pt – milliamps per milligrams of platinum

M – transition metal

M-O – transition metal oxide

M-OH – transition metal hydroxide

MOR – methanol oxidation reaction

mV/s – millivolts per second

MW – microwave

N₂ – nitrogen

N₂H₄ – hydrazine hydrate

NaBH₄ – sodium borohydride

NaOH – sodium hydroxide

NHE – normal hydrogen electrode

Ni – nickel

NiCl₂ – nickel chloride

ODT – octadecanethiol

OH – hydroxide

ORR – oxygen reduction reaction

PEMFC – polymer electrolyte membrane fuel cells

Pt – platinum

Pt-Co – platinum cobalt

Pt-Ni – platinum nickel

PVP – polyvinylpyrrolidone

Ru – ruthenium

S - sulphur

S-A – surface area

SA – South Africa

SEM – scanning electron microscope

STEM – scanning transmission electron microscope

THF – tetrahydrofuran

XPS – x-ray photoelectron spectroscopy

XRD – x-ray diffraction

V – Voltage

CHAPTER 1: INTRODUCTION

1.1. Background and motivation

In South Africa, the main source of energy is coal, followed by oil and gas. Over the last few decades there has been a drive to develop alternative energy devices in order to decrease the SA's dependence on fossil fuels as a source of energy. This has led to research in the development of other energy sources and one of these is the fuel cell.

A particular class of fuel cells is the polymer electrolyte membrane fuel cells (PEMFCs). PEMFCs can be categorised into direct hydrogen fuel cells (DHFC), direct methanol fuel cells (DMFC), direct formic acid fuel cells (DFAFC), etc. These devices convert chemical energy stored in fuel molecules into electrical energy [1]. The polymer-electrolyte, H_2 /air and direct methanol fuel cells find application in portable power and residential applications [2-4]. Even though there is substantial research activities performed in this field, the wide spread application of fuel cells as alternative energy devices is still lacking. Factors affecting this development include the high cost of the platinum (Pt) catalyst, the slow kinetics of some of the reactions (specifically the methanol oxidation reaction) and the propensity of Pt to be poisoned by carbon monoxide (CO) during the reaction [5-7].

Therefore this thesis study will attempt to develop new catalysts to alleviate the problem of the high cost of the anode catalyst materials and improve the CO poisoning resistance of the Pt.

1.2. Research hypothesis

In this work, the hypothesis investigated is that the size and morphology of bimetallic anode catalysts and the synthesis procedures needed to make the catalysts will affect the electrocatalytic activity of the bimetallic platinum nanoparticles.

Noble metals, e.g. platinum, dispersed on high surface area supports, are currently the most used electro-catalysts for applications in fuel cell systems [8, 9]. Catalysts are not uniform structures; they exhibit varying particle size distributions, lattice defects and dislocations [10]. The lattice surface activity, particle clustering, particle size and size distribution effects are known to influence the catalytic activities of nanoparticles. In adding transition metals such as nickel (Ni) or cobalt (Co) to Pt, non-traditional structures may be formed arising from the different metal mixing process.

An enhancement in the catalytic activity of bimetallic platinum compared to pure platinum has been reported [2, 11, 12]. The source of the enhancement found in these bimetallic platinum catalysts is suggested to be due to different factors such as the decreased Pt-Pt interatomic distance, the presence of the alloying metal oxides and hydroxides, particle shape and size effects, as well as the particle size distribution. The aim of the present research is to add information as to the source

of the catalytic enhancement in two specific platinum metal-to-metal mixtures, i.e. those containing Co or Ni.

1.3. Objectives of the research

This research aims to address the question of how the size, morphology and synthesis procedures affect the electrocatalytic activity of platinum nanostructures made with Co or Ni. The main focus in synthesizing the nanoparticles will be on the production of different nanostructures focusing on the control in the size and shape of the nanoparticles by varying the synthesis parameters to obtain new structures. Microwave-irradiation was used to explore in detail the production of Pt-Co and Pt-Ni nanoparticles. Microwave heating provides more uniform heating, the potential for mass production of the catalysts, and shorter synthesis periods when compared to the known conventional synthesis methods.

1.4. Thesis outline

- **Chapter 2**

Literature is reviewed in this chapter. Since the focus of the study relates to the development of electrocatalysts for direct methanol fuel cells, this chapter provides the framework information on different synthesis procedures used to synthesize Pt-Co and Pt-Ni catalysts by conventional method and a microwave-

irradiation synthesis procedure. Information is provided on the bimetallic metal structures studied in this work (Pt-Co and Pt-Ni).

- **Chapter 3**

The synthesis procedures used in this work as explained in detail. This chapter also outlines the different characterization techniques used to determine the structural, morphological, and electronic and electrocatalytic properties of the synthesized nanoparticles.

- **Chapter 4**

In this chapter, the conventional thermal synthesis procedure used to produce Pt-Co and Pt-Ni nanoparticles is described. The focus of this chapter was to evaluate the effect of the different reaction parameters such as reducing agents, molar ratios and capping agents on the overall properties of the nanoparticles. This was done in order to establish the effect that these parameters have on the properties of the nanoparticles. The emphasis was on the electrocatalytic activity of the materials in the methanol oxidation reaction (MOR).

- **Chapter 5**

A new synthesis procedure using microwave-irradiation to make Pt-Co and Pt-Ni nanoparticles was explored and compared with the conventional synthesis procedure. The new catalysts were tested as electrocatalysts for the methanol oxidation reaction.

- **Chapter 6**

The chapter focused on the microwave-irradiation synthesis of Pt-Co and Pt-Ni nanoparticles for use as anode catalysts for the methanol oxidation reaction. The synthesis procedure was optimized by varying different reaction parameters such as; the amount of surfactant, precursor salt molar content, and the NaOH concentration.

- **Chapter 7**

One of the main drawbacks of using Pt as an electrocatalyst for methanol fuel cells is the poisoning the metal by carbon monoxide, a by-product of the methanol oxidation reaction. In this chapter the CO stripping technique was used to determine the effect of CO on the catalytic activity of the materials synthesized in chapter 6.

- **Chapter 8**

The overall conclusions of the study are made in this chapter. Future work suggestions were mentioned.

References

1. Peng, Z. and H. Yang, *Designer platinum nanoparticles: Control of shape, composition in alloy, nanostructure and electrocatalytic property*. Nano Today, 2009. **4**: p. 143 - 164.
2. Arico, A.S., et al., *An XPS study on oxidation states of Pt and its alloys with Co and Cr and its relevance to electroreduction of oxygen*. Applied Surface Science, 2001. **172**: p. 33 - 40.

3. Tao, F., et al., *Reaction-Driven Restructuring of Rh-Pd and Pt-Pd Core-Shell Nanoparticles*. Science, 2008. **322**: p. 932 - 934.
4. Vinodgopal, K., et al., *Sonochemically Prepared Platinum-Ruthenium Bimetallic Nanoparticles*. Journal of Physical Chemistry Letters B, 2006. **110**: p. 3849 - 3852.
5. Antolini, E., J.R.C. Salgado, and E.R. Gonzalez, *The methanol oxidation reaction on platinum alloys within the first row transition metals. The case of Pt-Co and Pt-Ni alloy electrocatalysts for DMFCs : A short review*. Applied Catalysis B: Environmental, 2006. **63**: p. 137 - 149.
6. Gasteiger, H.A., N.M. Markovic, and P.N. Ross, *H₂ and CO Electrooxidation on Well-Characterized Pt, Ru, and Pt-Ru. 1. Rotating Disk Electrode Studies of the Pure Gases Including Temperature Effects*. Journal of Physical Chemistry, 1995. **99**: p. 8290 - 8301.
7. Iwasita, T., *Methanol and CO Electrooxidation*, in *Handbook of Fuel Cells - Fundamentals, Technology and Applications*, W. Vielstich, H.A. Gasteiger, and A. Lamm, Editors. 2003, John Wiley & Sons. p. 603 - 624.
8. Teng, X., et al., *Platinum-Maghemite Core-Shell Nanoparticles Using a Sequential Synthesis*. Nano Letters, 2003. **3**(2): p. 261 - 264.
9. Zhang, X. and K.-Y. Chan, *Water-in-Oil Microemulsion Synthesis of Platinum-Ruthenium Nanoparticles, Their Characterization and Electrocatalytic Properties*. Chemistry of Materials, 2003. **15**: p. 451 - 459.
10. Muraviev, D.N., et al., *Cation-exchange membrane as nanoreactor: Intermatrix synthesis of platinum-copper core-shell nanoparticles*. Reactive & Functional Polymers, 2007. **67**: p. 1612-1621.
11. Mukerjee, S., *Particle size and structural effects in platinum electrocatalysts*. Journal of Applied Electrochemistry, 1990. **20**: p. 537 - 548.
12. Colon-Mercado, H.R. and B.N. Popov, *Stability of platinum based alloy cathode catalysts in PEM fuel cells*. Journal of Power Sources, 2006. **155**: p. 253 - 263.

CHAPTER 2: LITERATURE REVIEW OF BIMETALLIC PLATINUM NANOPARTICLES AS DIRECT ALCOHOL FUEL CELL ELECTROCATALYSTS

In recent years there has been a drive to manufacture alternative energy devices with fuel cells playing a big role in the process. This chapter will explore the current literature available in the study of fuel cells with the focus being on the synthesis and use of bimetallic platinum nanoparticles as anode electrocatalysts for direct methanol fuel cells (DMFCs).

2.1. Introduction

Fuel cells are energy conversion devices that possesses the ability to convert chemical energy into electrical energy using fuel sources such as hydrogen, methanol and hydrocarbons and in doing so to produce CO_2 and H_2O as the by-products [1, 2] in the process. These electrochemical devices consist of an electrolyte solution between two electrodes, the anode and cathode [3]. The ions generated during the oxidation or reduction reactions are then transported from one electrode to another through the insulating electrolyte.

The performance and durability of low temperature fuel cells depend on the catalysts used [4]. Platinum (Pt) has good catalytic activity towards the oxygen reduction reaction (ORR) [5] and methanol oxidation reaction (MOR) [6]. This is because

platinum is a corrosion resistant metal that can withstand the harsh acidic environment of fuel cells [7]. Though direct methanol fuel cells have attracted attention as portable power source devices, the high costs of platinum catalysts and catalyst poisoning still pose a big problem. To make fuel cells more viable, research has been driven towards alloying the platinum with transition metals such as ruthenium [8, 9], cobalt [10, 11], and nickel [12]. These metals are less expensive and have shown some good resistance to carbon monoxide (CO) poisoning [8, 13].

This area of research is driven by the need for larger surface area catalysts, usually obtained by adding the catalysts to appropriate supports [5]. However, the use of unsupported nanocatalysts was studied by Antolini and Perez, where they observed improved long-term stability during operation, compared to carbon-supported catalysts which suffer from corrosion and sintering [2]. An important characteristic of fuel cell electrocatalysts is their ability to resist CO, which is a product of the alcohol oxidation reaction, i.e., the dissociative chemisorption of the alcohol used [7]. Furthermore, the increase in the fuel cell efficiency is dependent on a number of issues such as the slow kinetics of the reaction involving Pt and its high cost. As mentioned, the high price and in-process consumption of Pt electrocatalysts limits the widespread use of fuel cells. To solve this problem researchers have either developed new and more cheaper catalysts or optimized the properties of current electrocatalysts to minimize their consumption [14].

Catalysis is a surface process where the catalytic activity is directly related to the size, shape and surface roughness of the catalyst. Therefore, determining the shape and atomic arrangement in the crystal planes forming the surfaces is important in understanding their catalytic behaviour [15]. For electrocatalysts, it is important to determine the electrocatalytic active surface area (ECSA) in order to fully understand

the activity of a particular catalyst. Though a lot of research has been undertaken in the synthesis of metal nanoparticles for catalysis, the growth mechanism of nanoparticles is however not clearly understood [16]. Factors such as change in surface structure, surface free-energy, oxygen interaction with the alloying element, the interatomic spacing in the alloy and its work function, alter the electrochemical characteristics of the platinum metal [17]. This in turn will affect the electrocatalytic activity of the nanoparticles.

The aim of this chapter is to review the current fuel cell electrocatalyst literature by discussing both supported and unsupported bimetallic platinum electrocatalysts. The focus was on the various synthesis procedures used.

2.2. Supported and unsupported Platinum (Pt) electrocatalysts

In the early 1960s unsupported platinum catalyst were the first to be used for low temperature fuel cells [2], followed by carbon supported catalysts with Pt particle sizes in the range of 2 – 4 nm in the 1980s – 1990s. These advances promised to lead to generally lower catalyst loadings (low cost), while fulfilling the performance and durability required of a fuel cell [18]. Markovic et al. showed that the carbon-supported Pt catalysts were high performance materials in H_2/O_2 fuel cells with very low Pt loadings ($0.1 - 0.2 \text{ mg/cm}^2$) [6]. In contrast, Liu et al., have reported that direct alcohol fuel cell (DAFC) anodes typically have Pt loadings of several mg/cm^2 when unsupported PtRu was used [19]. The higher specific surface area of the

supported catalyst was determined to be the reason for the higher catalytic activity relative to the unsupported catalysts [2]. There is however a drawback: these supported catalysts suffers from coarsening and corrosion of the carbon support in the harsh acid electrolyte, and this leads to loss in surface area and decreased catalyst durability [20, 21].

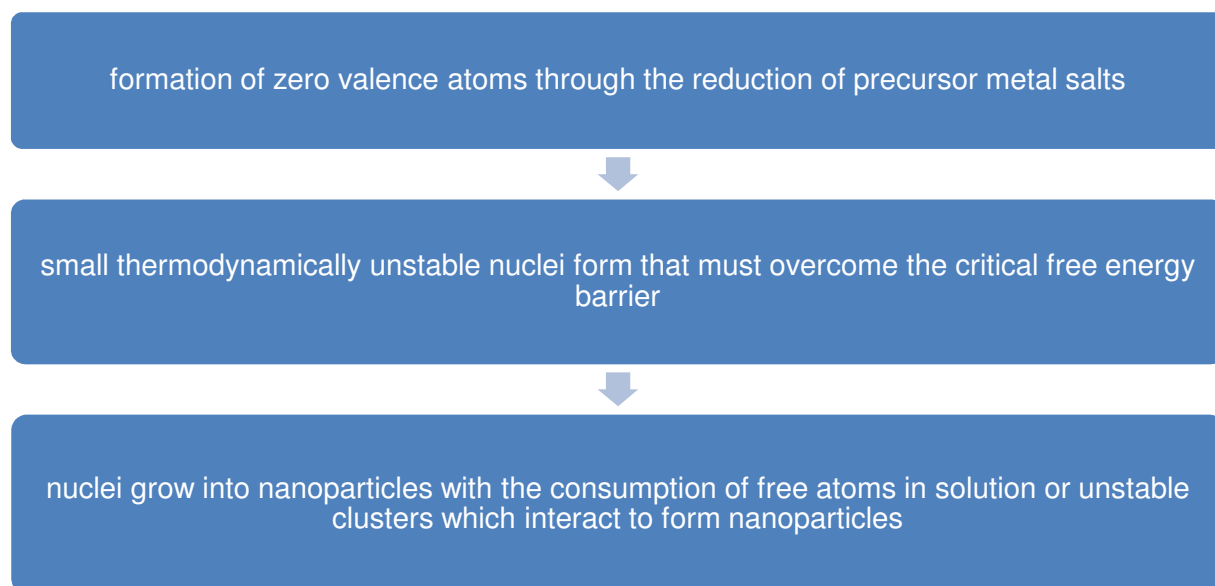
In recent years there has been increased interest in the use of unsupported Pt catalysts which are known to provide improved long-term stability when compared to the carbon-supported catalysts during fuel cell operations because the issue of the carbon corrosion is eliminated [2]. For instance, Arico et al. [22], determined that in DMFCs the use of unsupported catalysts allow for very thin catalyst layers to be used (2 mg/cm^2 loadings) leading to a reduction in the electrical resistivity. This is said to facilitate the migration of the reacting species through the catalyst layers. Since a goal of this study is the improvement of the catalytic activity of Pt-Co and Pt-Ni nanoparticles, advances in the synthesis and use of these bimetallic electrocatalysts will be reviewed.

2.2.1. Bimetallic platinum electrocatalysts (Pt-Ni and Pt-Co)

Bimetallic nanoparticles are materials that consists of two metals alloyed together to form a new structure. In these systems, the properties of the two metals are combined resulting in an enhancement in their overall properties due to the synergistic effect [23]. Alloying also affects the Pt electronic structure which in turn affects the hydrogen and methanol oxidation activities in the fuel cells [5]. A study by

Watanabe et al. [24] revealed a modification of the Pt d-band vacancy due to alloying and the effect it had on the Pt electronic structure. For instance, adding the Ni (fcc, $a = 3.52 \text{ \AA}$) or Co (hcp, $a = 2.52 \text{ \AA}$) atoms to the Pt (fcc, $a = 3.92 \text{ \AA}$) lattice resulted in lattice contractions and thus a modification in the structure. The introduction of alloying components with smaller lattice parameters caused the Pt lattice to contract, which led to a reduction in the nearest neighbour distance [25]. This resulted in an optimum Pt-Pt spacing, while maintaining good platinum electronic properties [26], which is the main reason for the higher MOR activity observed in bimetallic platinum electrocatalysts when compared to monometallic Pt catalysts.

The growth mechanism of the nanoparticles can be modified by varying reaction parameters to control the shape and minimize surface energies by forming specific crystal facets [2]. Traditional shapes such as the tetrahedron, cube and truncated tetrahedron can be predicted for face centred cubic (fcc) crystals. On the other hand, the introduction of defects can break down the crystal symmetry resulting in the formation of shapes with reduced symmetry such as nanorods, plates as well as multipods [2]. Scheme 2.1 illustrates the factors affecting the shape and size of platinum nanoalloys produced in solution through the nucleation and growth processes [25].



Scheme 2.1. A schematic of the formation of nanoparticles in solution [25].

The key to achieving the desired shape is through either the promotion or inhibition of a selective surface growth or the relative stability of the surfaces. Therefore through shape-controlled synthesis, the issues of the shape of the nanoparticles can be addressed that can lead to specific set of nanocrystal facets [2].

A focus in developing electrocatalysts has been to synthesize materials that are both cheaper, and mostly resistant to CO poisoning [8]. This has been achieved through alloying platinum with transition metals such as nickel (Ni) [27], cobalt (Co) [28], iron (Fe) [29] and ruthenium (Ru) [30]. These alloy structures are known to have enhanced catalytic activity when compared to pure platinum, and they are more resistant to CO poisoning [1]. Table 2.1 shows work that has already been done in regards to platinum electrocatalysts alloyed with Co and Ni.

Table 2.1. Bimetallic platinum electrocatalysts for methanol oxidation and oxygen reduction reactions.

Catalyst	Synthesis procedure	Catalyst shape	Reaction	Reference
Pt-Ni	Co-reduction	Spherical	MOR	Park 2002 [31]
Pt-Ni/C	Commercial		ORR	Murkerjee 1995 [32]
Pt-Co	Microemulsion	Spherical	MOR	Zhang 2004 [33]
Pt-Co/C	Commercial		ORR	Murkerjee 1995 [32]
Pt ₃ Co	UHV		ORR	Stamenkovic 2002 [34]
Pt ₃ Ni	Conv.metal		ORR	Stamenkovic 2003 [35]
Pt-Co			ORR	Watanabe 1994 [24]
Pt-Ni	Commercial	Spherical	ORR	Paulus 2002 [10]
Pt-Co	Commercial	Spherical	ORR	Paulus 2002 [10]
Pt-Co/C	Commercial		MOR	Page 2000 [36]
Pt-Ni/C	Commercial		MOR	Page 2000 [36]
Pt-Co	Impregnation	Spherical	ORR	Salgado 2004 [11]
Pt-Ni	Microwave	Spherical	CO oxidation	Abdelsayed 2009 [37]
Pt-Ni	Microwave	Spherical	MOR	Deivaraj 2003 [38]
CNT/Pt-Co	Microwave	Spherical	CV	Hsieh 2012 [39]
Pt-Ni	Electrochemical deposition	1-D rods	MOR	Wu 2013 [40]
Pt-Ni/C	High temperature synthesis	Core-shell	MOR	Kang 2013 [41]

***ORR = oxygen reduction reaction, MOR = methanol oxidation reaction, CO = carbon monoxide, CNT = carbon nanotubes, CV = cyclic voltammetry.**

The challenge in synthesizing electrocatalysts is to generate the active sites that involve both platinum and the alloying metal, such that the metals are close enough to interact with each other and to modify the electrocatalytic activity [42]. Alloying Pt with Co and Ni metals have presented methanol-tolerant cathode materials that can act as anode materials with improved MOR for DMFC activities [28]. These two transition metals possess the ability to enhance the MOR activity by promoting C-H bond cleavage at low potentials. The presence of Co or Ni oxides on the surface also provides an oxygen source for CO oxidation.

In studying the intrinsic catalytic activity of Pt₃Co and Pt₃Ni alloys, Stamenkovic et al., [34], demonstrated that the ability to make a controlled and well-characterized arrangement of two elements in the electrode surface region is essential to understanding the kinetics of the reactions [35]. Thus, the behaviour of bimetallic nanoparticles in electrocatalysis can be split into two effects; the electronic effect and the geometric effect [43]. The interplay between these factors is said to be the source of enhancement of the Pt-M alloys, though their effect on the chemisorption of OH species from the electrolyte also affects the catalytic activity. One of the major drawbacks in the alloying of platinum with transition metals is the leaching of metal atoms during the harsh acidic conditions used in fuel cells [44]. This leaching is thought to increase the surface roughness and thus the electrocatalytically active surface area (ECSA), though Ralph and Hogarth [44], found that the ECSA was reduced by leaching. This change in activity could result from grain size enlargement and particle agglomeration. The ECSA of the Pt/C can be estimated using the integrated charge in the H₂ desorption region.

2.2.2. Synthesis of bimetallic nanoparticles

There exist different synthesis procedure to make bimetallic nanoparticles in various forms such as powder, liquid dispersion and thin films. The two general approaches to produce metal nanoparticles are, (i) the top-down procedures, where the nanoparticles are forged from bulk materials using mechanical procedures, and (ii) the bottom-up procedures which involve the use of metal precursors to produce the atoms used to build the nanoparticle structures [45]. The top-down techniques suffer from the need to remove large amounts of material, while the bottom up techniques suffer from poor monodispersity due to the need to arrest growth at the same point for all the nanoparticles [46]. Therefore, the properties of the metal nanoparticles depend on the synthesis parameters involved in each method [47].

Suitable bottom-up synthesis methods used to make electrocatalysts include colloidal and electrochemical synthesis, alcohol reduction, microwave irradiation [48] [49], reverse micellization [50], photoreduction and metal organic chemical vapour deposition procedures [51]. However, amongst these methods the surfactant-stabilized colloidal method allows for good particle size control [52, 53] as well as the synthesis of different structures such as core-shell, intermetallic and heterostructures [23], see Fig. 2.1. The core-shell structure (Fig. 2.1a) is formed when the atoms of the 2nd metal deposits as a shell onto the 1st metal, the island structure (Fig. 2.1b) occurs when the second metal only deposits on specific facets while the intermetallic structure (Fig. 2.1c) results from the diffusion of the atoms of the alloying metal into the lattice of the first metal. By controlling the capping agent, reducing agent and solvents, the shape and size of Pt nanoparticles can thus be controlled [54].

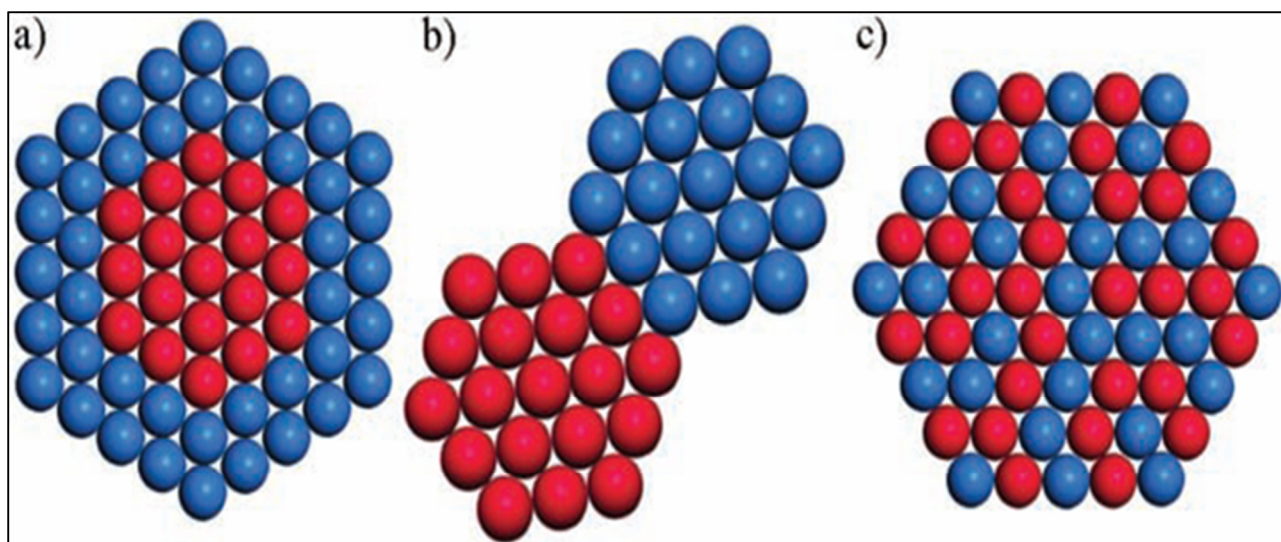


Fig. 2.1. The different structures that can be obtained when mixing two metals (a) core-shell, (b) heterostructure (island structure) and (c) an intermetallic (alloy) structure.

Though the synthesis procedures to make nanoparticles are well studied, the drawback in their mass production includes the relatively high costs to synthesize and their instability towards oxidation and agglomeration [47]. Therefore more cost-effective methods have been explored for the mass production of nanoparticles, and one of these is to use microwave irradiation as an alternative synthesis procedure.

2.2.2.1. Microwave-irradiation (MW) polyol synthesis procedure

Because the above-mentioned synthesis procedures involve the use of volatile solvents, efforts have been made to develop more eco-friendly technologies for the industrial synthesis of nanoparticles [46, 55]. Microwave-irradiation heating has been a focus for researchers in the last decade because it offers more rapid and uniform

heating [48, 56, 57], without the use of harmful reducing agents such as NaBH_4 [46]. The versatility of this approach, [58], and its potential for mass production of nanoparticles, in view of their utilization as magnetic and catalytic materials, makes the method particularly attractive [47, 48].

Microwaves are electromagnetic waves, which contain electric and magnetic field components. They are a portion of the electromagnetic spectrum with frequencies in the range of 300 MHz to 300 GHz [49]. When the microwaves penetrate and propagate through a dielectric solution or suspension, the internal electric fields generated within the exposed volume induces translational motions of free or bound charges such as electrons or ions. The fields can also rotate charge complexes such as dipoles [59]. The energy dissipation in the core of materials allows for a much more regular heat distribution when compared to conventional heating procedures [48, 49]. The main feature of the microwave-irradiation of metal precursors in solution is that the reduction reaction occurs in the solution rather than in the solid state, thus the metal particles are formed by nucleation and growth from solution [49].

In recent years, the use of microwave-irradiation (MW) in synthesis has made great progress in organic reactions, molecular sieve preparation, the synthesis of inorganic complexes and in radio-pharmaceuticals. MW have also been used in analytical chemistry [60]. In microwave synthesis, the polyol process is the most common procedure used for the production of nanoparticles. The polyol (ethylene glycol) first acts as a solvent for the precursor salts because of its high dielectric constant. The dielectric constant (41.4 at 25 °C) and dielectric loss of ethylene glycol are high, and hence rapid heating occurs under microwave-irradiation [59]. At a temperature of 180 °C, the polyol works as a reducing agent for a metal precursor salts, resulting in

nanoparticles formation [61, 62]. The mechanism of formation for nanoparticles in ethylene glycol occurs in a series of steps: the dissolution of the precursor salts, reduction of the salts by the polyol at high temperatures and finally the nucleation and growth of the metal nanoparticles [63, 64].

Microwave effects can be categorized into both thermal (caused by the temperature regime created by the microwave dielectric heating) and non-thermal effects (the inherent characteristics of microwaves other than the thermal effects) [45]. Though it was initially said that non-thermal effects were the dominating factor, it is now generally accepted that the thermal effects is the main contributing heating factor. Tu et al. [60], determined that the thermal effects are more prominent, as the formation mechanism is said to be the same as found using the conventional heating methods. The uniform heating provided by a microwave synthesis results in the formation of homogeneous nanostructures [65].

The main advantages of microwave heating over conventional heating include, uniform and rapid heating resulting in the formation of novel phases, selective formation of phases, as well as the formation of smaller and more homogeneous structures [49]. During the microwave irradiation of liquid samples, temperature and concentration gradients can be avoided, providing a uniform environment for nucleation.

2.2.2.2. Nanoparticle surface properties

In the synthesis of nanostructured materials, it is important to understand the effect of surface segregation, i.e. the enrichment of one element on the surface relative to the bulk structure. This is needed in order to relate the surface properties to the catalytic activity [28]. However, nanoparticle segregation is very little studied [34]. Shulka et al., [66], used XPS to determine that there was surface enrichment of the Pt metal in a Pt-Co/C system. The surface Pt atomic ratio of 0.84 vs. 0.72 in the bulk structure and Pt-Ni/C 0.86 vs. 0.64 was obtained by high temperature annealing. This was also observed by Paulus et al., who determined that 70% and 58% of the Pt is on the surface in Pt₃Ni [31] and Pt₃Co systems, respectively [10].

For Pt-M structures, some unreacted M species are also present, and this depends on the synthesis method used and the degree of alloying. The XPS data reported by Park et al., revealed the presence of Pt₃M, PtO, MO on the surface of Pt-Ni nanoparticles [31]. They observed that the shift in the XPS binding energy of Pt in Pt-Ni alloys resulted from the modification of the electronic structure of platinum by electron transfer from the Ni to the Pt atoms [28]. Furthermore, using XPS, Shulka et al. revealed the presence of PtO species in the Pt-Co system, though the concentration was lower than in Pt-Ni system [66]. The choice of the reduction technique, time and capping agent therefore determine the shape, size and surface oxidation properties of the resulting nanoparticles [46].

Since the main application for the catalysts developed in this work is for used as fuel cells with the reactions of interest being the methanol oxidation reaction (MOR) (a more detailed discussion of the MOR follows). Also, the ability for the catalysts to resist carbon monoxide (CO) poisoning will also be discussed.

2.3. Electrocatalytic activity of Platinum catalysts

2.3.1. Methanol oxidation reaction (MOR) activity of platinum electrocatalysts

Methanol as a source of fuel in fuel cell systems has advantages over hydrogen because it is cheaper, is easily handled, transported, and stored and also has a high theoretical energy density [7, 67]. The methanol oxidation reaction is a slow reaction that requires multiple active sites for the adsorption of methanol which can donate OH species for the desorption of the adsorbed methanol residues (see Fig. 2.3) [68]. Platinum electrodes are the most used methanol oxidation electrocatalysts in a fuel cell system [69]. In most cases, the platinum is alloyed with other transition metals to prevent the formation of the CO layer on the electrodes, and to enhance the MOR catalytic activity. Lamy et al. studied different binary and ternary Pt-Ru alloys systems, where the Pt-Ru-Mo ternary alloy showed the highest activity [7].

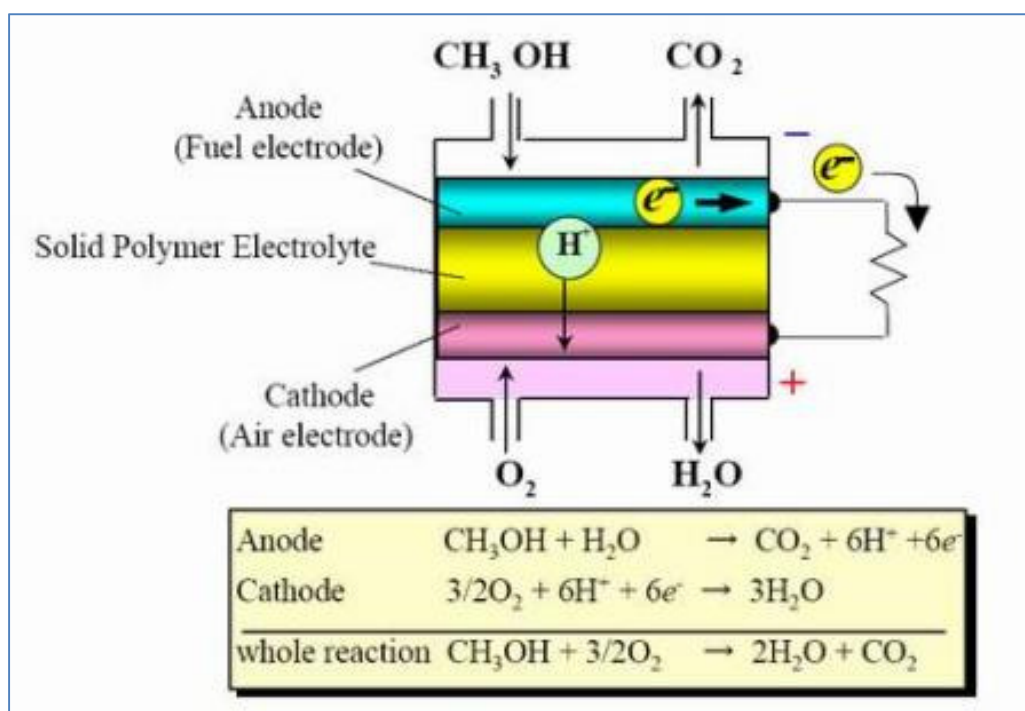
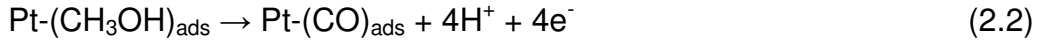


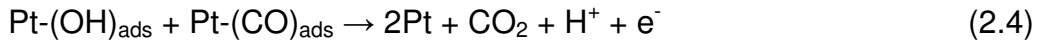
Figure 2.2. A schematic demonstration of a direct methanol fuel cell. Source: www3.toshiba.co.jp/ddc/eng/dmfc/about.htm.

The mechanism of direct methanol fuel cell operation is as follows (see Fig. 2.2): first the methanol fuel solution is added to the anode side of the cell, and then this solution is broken down into protons and electrons with CO_2 as the by-product. The electrons are then guided out of the fuel cell to form an electric current. The final step of the operation is the cathode reaction of the proton and electrons to form water. The first process is the methanol adsorption process, which occurs at potentials of around 0.2 V (Eq. 2.1 – 2.2) because the methanol requires several free binding sites, which are freed from the hydrogen detachment [70]. The dissociation of water then takes place at 0.4 – 0.5 V for pure Pt electrodes, which acts as the oxygen donor of the reaction.

The electrooxidation of methanol on the platinum electrode occurs as follows:

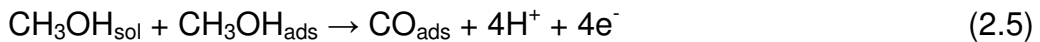


This adsorbed CO can be removed by the reaction with OH_{ads} (Eqs. 2.3), produced by the dissociation of the water molecules [42]:



The main product from this reaction is CO_2 (Eq. 2.4), with the presence of some carbonaceous species such as formaldehyde, formic acid and methyl formate. These species affect the fuel cell efficiency [71]. The CO_2 is formed by reaction between the CO- and O-species (from OH), aided by the alloying metal. In the reaction, the CO poisoned platinum is regenerated, consistent with the bifunctional model theory [6, 9, 36]. The ligand model dictates that the change in the electronic properties of the Pt is induced by the alloying metal. This makes the Pt atoms more susceptible for OH adsorption during the dissociative adsorption in the methanol reaction [70]. Therefore, to increase the fuel cell resistance against CO poisoning, it is important to have a catalyst that is efficient for C-C bond cleavage [72].

The MOR reaction mechanism for Pt-M electrocatalysts was proposed by Gasteiger et al., [8], and Markovic et al.,[6]:



The reaction pathways in Eqs. 2.5 – 2.6 show that the oxidation of methanol occurs on both the Pt and M sites, and that CO_{ads} is the product of the dehydrogenation in the methanol step (Eq. 2.5, intermediate step). For $\text{M} = \text{Ru}$, studies done have revealed that the mechanism of catalysis is consistent with the bifunctional model [6]. The Pt sites act as the adsorption and dehydrogenation centres producing various adsorbed carbonaceous species. The nucleation of oxygen containing species at the Ru-sites occurs at 0.2 - 0.3 V lower than found on a pure Pt surface. Some of the carbonaceous species are intermediates and are preferentially oxidized at these Ru sites by the Ru surface diffusion from the adsorption centres. For Pt-Co catalysts in alkaline medium, the dehydrogenation step (Eq. 2.5) occurs at lower potentials and Eqs. 2.6 – 2.8 occurs at much higher potentials, as mentioned by Zhang et al. [33]. For MOR it was suggested that a small amount of activation energy is required and it was attributed to the electronic interaction of the Pt and M, and the change in the Pt lattice parameter due to the addition of the M (Co, Ni, Ru, Au) atoms [68]. This is because the presence of the alloying metals is known to result in lattice contraction and production of a favourable Pt-Pt distance [1].

2.3.2. Carbon monoxide (CO) electro-oxidation

Numerous mechanisms for the MOR have been proposed. These include the bifunctional model, ligand model, synergistic effect and the oxide formation model [1]. In the bifunctional model, the oxygenated surface is created by H_2O dissociation at the M-sites which occurs at lower potentials (0.2 V, NHE) when compared to Pt. This H_2O dissociation promotes the oxidation of adsorbed CO to CO_2 and leads to a

decrease in CO poisoning. Therefore, the presence of the oxygenated M-sites increases the CO tolerance of the Pt electrocatalysts [73, 74]. This occurs because the OH species, have a preference for M-sites than Pt sites [75, 76]. In contrast, the ligand model requires that the presence of M changes the chemical properties of Pt at the surface. This leads to weakening of the Pt-CO bond and which minimizes CO poisoning. Therefore the role of the second metal in MOR is to promote the cleavage of the C-C bond and to improve the removal of the CO species adsorbed onto the active Pt sites [1, 28].

The mechanism of CO oxidation is said to occur via the Langmuir-Hinshelwood reaction mechanism (expansion of Eq. 2.8 above). To prevent the formation of a CO layer on the electrodes, one can either alloy the Pt with more CO resistant metals or decrease the potential at which the CO forms at the surface to unblock the Pt active sites [77]. During CO adsorption, the electrons are donated from the 5d orbital of the Pt atom, whilst the electrons are back-donated into the CO $2\pi^*$ orbital. This back-donation is said to increase with the decrease in platinum particle size resulting in stronger adsorbed CO. This leads to a higher overpotential, and poisoned electrodes [69]. Leger et al., determined that the CO overpotential can be reduced by alloying with Ru, which activated the water molecule at a lower potential, i.e., 0.35 V compared to 0.60 V for a pure Pt electrode [42].

The use of Pt-Co and Pt-Ni as fuel cell electrocatalysts has been extensively studied to determine their activity towards the MOR [28, 36]. It was determined that Pt-Co and Pt-Ni were more reactive than some commercial Pt/C and Pt-Ru/C and Pt-Co/C electrocatalysts. This was supported by the work by Zhang [33], Chi [78] and Park [31]. Though the high M content enhanced the MOR by an electronic effect and the presence of higher amounts of MO species, the lower M content reduced the

methanol oxidation through an ensemble effect where the dilution of the active component with the catalytically inert metal reduced the methanol adsorption [28].

2.4. Conclusions

The use of unsupported Pt nanoparticles as fuel cell catalysts has led to extensive research into fuel cells as alternative energy devices. This is because of their durability and stability. However, the use of Pt had drawbacks such as low surface area and high catalyst loading, and this has made the general use of fuel cells as alternative energy devices very expensive. Therefore research in this study was performed towards decreasing the costs of the fuel cell catalysts by alloying the Pt with first-row transition metals which have proved to be more active than Pt in some instances. This enhancement in the catalytic activity was proposed by many authors to be due to both the geometric and electronic properties associated with the modification of the Pt-Pt bond by the introduction of the alloying metals atoms into the Pt lattice. Another main focus for research in fuel cells is to provide solutions that will alleviate the CO poisoning that occurs during MOR, since CO is a product of the methanol oxidation reaction. The presence of the alloying metal in Pt has been shown to provide more resistance to CO poisoning by the bifunctional or the ligand model which explains the formation of CO₂ from CO. Both these mechanisms rely on the presence of M-O and M-OH species which donate O atoms to CO to form CO₂. To fully understand the kinetics of the reactions, it is essential to synthesize Pt-M electrocatalysts where the arrangement of the two metals is clearly characterized.

References

1. Lim, D.-H., W.-D. Lee, and H.-I. Lee, *Highly dispersed and Nano-sized Pt-based Electrocatalysts for Low-temperature Fuel Cells*. Catalysis Survey Asia, 2008. **12**: p. 310 - 325.
2. Antolini, E. and J. Perez, *The renaissance of unsupported nanostructured catalysts for low-temperature fuel cells: from the size to the shape of metal nanostructures*. Journal of Materials Science, 2011. **46**: p. 4435 - 4457.
3. Ramani, V., *Fuel Cells*. The Electrochemical Society : Interface, 2006. **15**: p. 41 - 44.
4. Antolini, E. and E.R. Gonzalez, *Ceramic materials as supports for low-temperature fuel cell catalysts*. Solid State Ionics, 2009. **180**: p. 746 - 763.
5. Antolini, E., *Formation of carbon-supported PtM alloys for low temperature fuel cells: a review*. Materials Chemistry and Physics, 2003. **78**: p. 563 - 573.
6. Markovic, N.M., et al., *Electro-Oxidation Mechanisms of Methanol and Formic Acid on Pt-Ru alloy surfaces* Electrochimica Acta, 1995. **40**: p. 91 - 98.
7. Lamy, C., et al., *Recent advances in the development of Direct Alcohol Fuel Cell (DAFC)*. Journal of Power Sources, 2002. **105** p. 283 - 296.
8. Gasteiger, H.A., N.M. Markovic, and P.N. Ross, *H₂ and CO Electrooxidation on Well-Characterized Pt, Ru, and Pt-Ru. 1. Rotating Disk Electrode Studies of the Pure Gases Including Temperature Effects*. Journal of Physical Chemistry, 1995. **99**: p. 8290 - 8301.
9. Gojkovic, S.L., T.R. Vidakovic, and D.R. Durovic, *Kinetic study of methanol oxidation on carbon-supported PtRu electrocatalyst*. Electrochimica Acta, 2003. **48**: p. 3607 - 3614.
10. Paulus, U.A., et al., *Oxygen reduction on carbon-supported Pt-Ni and Pt-Co alloy catalysts*. Journal of Physical Chemistry B, 2002. **106**: p. 4181 - 4191.
11. Salgado, J.R.C., E. Antolini, and E.R. Gonzalez, *Structure and activity of carbon-supported Pt-Co electrocatalysts for Oxygen Reduction*. Journal of Physical Chemistry B, 2004. **108**: p. 17767 - 17774.
12. Travitsky, N., et al., *Pt, PtNi- and PtCo-supported catalysts for oxygen reduction in PEM fuel cells* Journal of Power Sources, 2006. **161**: p. 782 - 789.
13. Iwasita, T., *Methanol and CO Electrooxidation*, in *Handbook of Fuel Cells - Fundamentals, Technology and Applications*, W. Vielstich, H.A. Gasteiger, and A. Lamm, Editors. 2003, John Wiley & Sons. p. 603 - 624.
14. Bensebaa, F., et al., *Microwave synthesis of polymer-embedded Pt-Ru catalyst for direct methanol fuel cell*. Journal of Physical Chemistry, 2005. **109**: p. 15339 - 15344.
15. Ahmadi, T.S., et al., *"Cubic" collodail platinum nanoparticles*. Chemistry of Materials, 1996. **8**: p. 1161 - 1163.
16. Mpourmpakis, G. and D.G. Vlachos, *Growth Mechanisms of Metal Nanoparticles via First Principles*. Physical Review Letters, 2009. **102**(15): p. 155505.
17. Jalan, V. and E.J. Taylor, *Importance of interatomic spacing in catalytic reduction of oxygen in phosphoric acid*. Journal of Electrochemical Society, 1983. **130**(11): p. 2299 - 2302.

18. Costamagna, P. and S. Srinivasan, *Quantum jumps in the PEMFC science and technology from the 1960s to the year 2000 Part I. Fundamental scientific aspects*. Journal of Power Sources, 2001. **102**: p. 242 - 252.
19. Liu, L., et al., *Carbon supported and unsupported Pt±Ru anodes for liquid feed direct methanol fuel cells*. Electrochimica Acta, 1998. **43**: p. 3657 - 3663.
20. Stevens, D.A. and J.R. Dahn, *Thermal degradation of the support in carbon-supported platinum electrocatalysts for PEM fuel cells*. Carbon, 2005. **43**: p. 179 - 188.
21. Maass, S., et al., *Carbon support oxidation in PEM fuel cell cathodes*. Journal of Power Sources, 2008. **176**: p. 444 - 451.
22. Arico, A.S., et al., *Effect of carbon-supported and unsupported Pt-Ru anodes on the performance of solid-polymer-electrolyte direct methanol fuel cells*. Journal of Applied Electrochemistry, 1999. **29**: p. 671 - 676.
23. Wang, D. and Y. Li, *Bimetallic nanocrystals: liquid-phase synthesis and catalytic applications*. Advanced Materials, 2011. **23**: p. 1044 - 1060.
24. Watanabe, M., et al., *Activity and stability of ordered and disordered Co-Pt alloys for phosphoric acid fuel cells*. Journal of Electrochemical Society, 1994. **141**: p. 2659.
25. Peng, Z. and H. Yang, *Designer platinum nanoparticles: Control of shape, composition in alloy, nanostructure and electrocatalytic property*. Nano Today, 2009. **4**: p. 143 - 164.
26. Min, M., et al., *Particle size and alloying effects of Pt-based alloy catalysts for fuel cell applications*. Electrochimica Acta, 2000. **45**: p. 4211 - 4217.
27. Park, K.-W., et al., *Chemical and electronic effects of Ni in Pt/Ni and Pt/Ru/Ni alloy nanoparticles in methanol electrooxidation*. Journal of Physical Chemistry B, 2002. **106**: p. 1869-1877.
28. Antolini, E., J.R.C. Salgado, and E.R. Gonzalez, *The methanol oxidation reaction on platinum alloys within the first row transition metals. The case of Pt-Co and Pt-Ni alloy electrocatalysts for DMFCs : A short review*. Applied Catalysis B: Environmental, 2006. **63**: p. 137 - 149.
29. Li, W., Q. Xin, and Y. Yan, *Nanostructured Pt-Fe/C cathode catalysts for direct methanol fuel cells: The effect of catalyst composition*. International Journal of Hydrogen Energy, 2010. **35**: p. 2530 - 2538.
30. Kuk, S.T. and A. Wieckowski, *Methanol electrooxidation on platinum spontaneously deposited on unsupported and carbon-supported ruthenium nanoparticles*. Journal of Power Sources, 2005. **141**: p. 1-7.
31. Park, K.-W., et al., *Chemical and electronic effects of Ni in Pt/Ni and Pt/Ru/Ni Alloy nanoparticles in methanol electrooxidation*. Journal of Physical Chemistry B, 2002. **106**: p. 1869 - 1877.
32. Mukerjee, S., et al., *Effect of Preparation Conditions of Pt Alloys on Their Electronic, Structural, and Electrocatalytic Activities for Oxygen Reduction-XRD, XAS, and Electrochemical Studies*. Journal of Physical Chemistry, 1995. **99**: p. 5477 - 4589.
33. Zhang, X., K.-Y. Tsang, and K.-Y. Chan, *Electrocatalytic properties of supported platinum-cobalt nanoparticles with uniform and controlled composition*. Journal of Electroanalytical Chemistry, 2004. **573**: p. 1 - 9.
34. Stamenkovic, V., et al., *Surface Composition Effects in Electrocatalysis: Kinetics of Oxygen Reduction on Well-Defined Pt₃Ni and Pt₃Co Alloy Surfaces*. Journal of Physical Chemistry B, 2002. **106**: p. 11970 - 11979.

35. Stamenkovic, V., et al., *Surface segregation effects in electrocatalysis: kinetics of oxygen reduction reaction on polycrystalline Pt₃Ni alloy surfaces*. Journal of Electroanalytical Chemistry, 2003. **554 - 555**: p. 191 - 199.
36. Page, T., et al., *A study of methanol electro-oxidation reactions in carbon membrane electrodes and structural properties of Pt alloy electro-catalysts by EXAFS*. Journal of Electroanalytical Chemistry, 2000. **485**: p. 34 - 41.
37. Abdelsayed, V., et al., *Microwave synthesis of bimetallic nanoalloys and CO oxidation on Ceria-supported nanoalloys*. Chemistry of Materials, 2009. **21**: p. 2825–2834.
38. Deivaraj, T.C., W. Chena, and J.Y. Lee, *Preparation of PtNi nanoparticles for the electrocatalytic oxidation of methanol*. Journal of Materials Chemistry, 2003. **13**: p. 2555 - 2560.
39. Hsieh, C.-T., et al., *Deposition and activity stability of Pt–Co catalysts on carbon nanotube-based electrodes prepared by microwave-assisted synthesis*. Journal of Power Sources, 2012. **199**: p. 94 - 102.
40. Wu, P., et al., *Composition- and aspect-ratio-dependent electrocatalytic performance of one-dimensional aligned Pt-Ni nanostructures* Journal of Physical Chemistry C, 2013. **117**: p. 19091 - 19100.
41. Kang, J., et al., *Effect of Ni core structure on the electrocatalytic activity of Pt-Ni/C in methanol oxidation*. Materials, 2013. **6**: p. 2689 - 2700.
42. Leger, J.-M., *Preparation and activity of mono- or bi-metallic nanoparticles for electrocatalytic reactions*. Electrochimica Acta, 2005. **50**: p. 3123 - 3129.
43. Song, C. and J. Zhang, *Electrocatalytic oxygen reduction reaction, in PEM, Fuel Cells Electrocatalysts and Catalysts Layers : Fundamental and Applications*, J. Zhang, Editor 2008, Springer. p. 89 - 134.
44. Ralph, T.R. and M.P. Hogarth, *Catalysis for Low Temperature Fuel Cells*. Platinum Metals Review, 2002. **46**: p. 3 - 14.
45. Yu, W., W. Tu, and H. Liu, *Synthesis of nanoscale platinum colloids by microwave dielectric heating*. Langmuir, 1999. **15**: p. 6 - 9.
46. Mallikarjuna, N.N. and R.S. Varma, *Microwave-assisted shape-controlled bulk synthesis of noble nanocrystals and their catalytic properties*. Crystal Growth and Design, 2007. **7**(4): p. 686 - 690.
47. Bensebaa, F., et al., *Tunable platinum-ruthenium nanoparticle properties using microwave synthesis*. Journal of Materials Chemistry, 2004. **14**: p. 3378 - 3384.
48. Tu, W. and H. Liu, *Continuous synthesis of colloidal metal nanoclusters by microwave irradiation*. Chemistry of Materials, 2000. **12**: p. 564 - 567.
49. Grace, A.N. and K. Pandian, *One pot synthesis of polymer protected Pt, Pd, Ag and Ru nanoparticles and nanoprisms under reflux and microwave mode of heating in glycerol - A comparative study*. Materials Chemistry and Physics, 2007. **104**: p. 191 - 198.
50. Lai, L.-B., D.-H. Chen, and T.-C. Huang, *Preparation and characterization of Ti-supported nanostructured Pt electrodes by electrophoretic deposition*. Materials Research Bulletin 2001. **36**: p. 1049 - 1055.
51. Serp, P., et al., *Novel carbon supported material: highly dispersed platinum particles on carbon nanospheres*. Journal of Materials Chemistry, 2001. **11**: p. 1980 - 1981.
52. Zoval, J.V., et al., *Electrochemical Preparation of Platinum Nanocrystallites with Size Selectivity on Basal Plane Oriented Graphite Surfaces*. Journal of Physical Chemistry B, 1998. **102**: p. 1166 - 1175.

53. Liu, Z., et al., *Preparation and characterization of Pt/C and Pt Ru/C electrocatalysts for direct ethanol fuel cells*. Journal of Power Sources, 2005. **149**: p. 1 - 7.
54. Subhramannia, M. and V.K. Pillai, *Shape-dependent electrocatalytic activity of platinum nanostructures*. Journal of Materials Chemistry, 2008. **18**: p. 5858 - 5870.
55. Zhu, Y.-J., et al., *Microwave-assisted synthesis of single-crystalline Tellurium nanorods and nanowires in ionic liquids*. Angewandte Chemie, 2004. **116**: p. 1434 - 1438.
56. Kundu, P., et al., *Ultrafast microwave-assisted route to surfactant-free ultrafine Pt nanoparticles on graphene: synergistic co-reduction mechanism and high catalytic activity*. Chemistry of Materials, 2011. **23**: p. 2772 - 2780.
57. Pan, R., et al., *Preparation and catalytic properties of platinum dioxide nanoparticles: A comparison between conventional heating and microwave-assisted method*. Chemical Engineering Journal, 2009. **153**: p. 206 - 210.
58. Vollath, D. and D.V. Szabó, *The microwave plasma process - a versatile process to synthesize nanoparticulate materials*. Journal of Nanoparticle Research, 2006. **8**: p. 417 - 428.
59. Komarneni, S., et al., *Microwave-polyol process for Pt and Ag nanoparticles*. Langmuir, 2002. **18**: p. 5959 - 5962.
60. Tu, W. and H. Liu, *Rapid synthesis of nanoscale colloidal metal clusters by microwave irradiation*. Journal of Materials Chemistry, 2000. **10**: p. 2207 - 2211.
61. Ramulifho, T., et al., *Fast microwave-assisted solvothermal synthesis of metal nanoparticles (Pd, Ni, Sn) supported on sulfonated MWCNTs: Pd-based bimetallic catalysts for ethanol oxidation in alkaline medium*. Electrochimica Acta, 2012. **59**: p. 310 - 320.
62. Mabena, L.F., et al., *Ruthenium supported on nitrogen-doped carbon nanotubes for the oxygen reduction reaction in alkaline media*. Fuel Cells, 2012. **12**: p. 862 - 868.
63. Viau, G., et al., *Preparation and microwave characterization of spherical and mono-disperse Co-Ni particles*. Journal of Magnetism and Magnetic Materials, 1995. **140 - 144**: p. 377 - 378.
64. Fievet, F., J.P. Lagier, and M. Figlarz, Mater. Res. Bull., 1989. **32 - 33**: p. 29.
65. Viau, G., F. Fievet-Vincent, and F. Fievet, *Nucleation and growth of bimetallic CoNi and FeNi monodisperse particles prepared in polyols*. Solid State Ionics, 1996. **84**: p. 259 - 270.
66. Shukla, A.K., et al., *An XPS study on binary and ternary alloys of transition metals with platinized carbon and its bearing upon oxygen electroreduction in direct methanol fuel cells*. Journal of Electroanalytical Chemistry, 2001. **504**: p. 111 - 119.
67. Reddington, E., et al., *Combinatorial Electrochemistry: A Highly Parallel, Optical Screening Method for Discovery of Better Electrocatalysts*. Science, 1998. **280**: p. 1735 - 1737.
68. Wang, K., et al., *On the Reaction Pathway for Methanol and Carbon Monoxide Electrooxidation on Pt-Sn alloy versus Pt-Ru alloy surfaces*. Electrochimica Acta, 1996. **41**: p. 2587 - 2593.
69. Tang, Z., D. Geng, and G. Lu, *Size-controlled synthesis of colloidal platinum nanoparticles and their activity for the electrocatalytic oxidation of carbon monoxide*. Journal of Colloid and Interface Science, 2005. **287**: p. 159 - 166.

70. Iwasita, T., *Electrocatalysis of methanol oxidation*. Electrochimica Acta, 2002. **47**: p. 3663 - 3674.
71. Korzeniewski, C. and C.L. Childers, *Formaldehyde Yields from Methanol Electrochemical Oxidation on Platinum*. The Journal of Physical Chemistry B, 1998. **102**: p. 489 - 492.
72. Antolini, E., *Platinum-based ternary catalysts for low temperature fuel cells Part I. Preparation methods and structural characteristics*. Applied Catalysis B: Environmental, 2007. **74**: p. 324 - 336.
73. Yajima, T., et al., *Adsorbed water for the electro-oxidation of methanol at Pt-Ru alloy*. Chemical Communications, 2003: p. 828 - 829.
74. Tong, Y., et al., *An NMR Investigation of CO Tolerance in a Pt/Ru Fuel Cell Catalyst*. Journal of American Chemical Society, 2002. **124**: p. 468 - 473.
75. Liu, R., et al., *Potential-Dependent Infrared Absorption Spectroscopy of Adsorbed CO and X-rayPhotoelectron Spectroscopy of Arc-Melted Single-Phase Pt, PtRu, PtOs, PtRuOs, and Ru Electrodes*. Journal of Physical Chemistry B, 2000. **104**: p. 3518 - 3531.
76. Antolini, E., J.R.C. Salgado, and E.R. Gonzalez, *Carbon supported Pt75M25 (M= Co, Ni) alloys anode and cathode electrocatalysts for direct methanol fuel cells*. Journal of Electroanalytical Chemistry, 2005. **580**: p. 145 - 154.
77. Arenz, M., et al., *The Effect of the Particle Size on the Kinetics of CO Electrooxidation on High Surface Area Pt Catalysts*. Journal of American Chemical Society, 2005. **127**: p. 6819 - 6829.
78. Chi, N., K.-Y. Chan, and D.L. Phillips, *Electrocatalytic oxidation of formic acid by Pt/Co nanoparticles*. Catalysis Letters, 2001. **71**: p. 21 - 26.

CHAPTER 3: MATERIALS SYNTHESIS AND CHARACTERIZATION

In this chapter, the production processes utilized to synthesize nanoparticles for this study, as well as the techniques used for their characterization will be discussed.

3.1. Catalyst Synthesis

Two distinctively different methods, namely conventional chemical synthesis and microwave-assisted (MW) synthesis were used. These processes were chosen specifically to compare the new and much easier microwave route with the conventional methods. A brief description of the precursors is summarized in Table 3.1.

3.1.1. Materials

$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (99%), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (97%), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (99%), ethylene glycol (EG, $\geq 99.5\%$), 1-octadecanethiol (ODT, 98%), polyvinylpyrrolidone (MW 40,000, PVP-40), sodium borohydride (NaBH_4 , 95%), hydrazine hydrate (N_2H_4 , 65%), tetrahydrofuran (THF, 99.9%) and sodium hydroxide pellets (NaOH), were purchased from Sigma Aldrich and used as received without further modification or purification.

Table 3.1. Summary of the parameters for the synthesis of bimetallic platinum nanoparticles

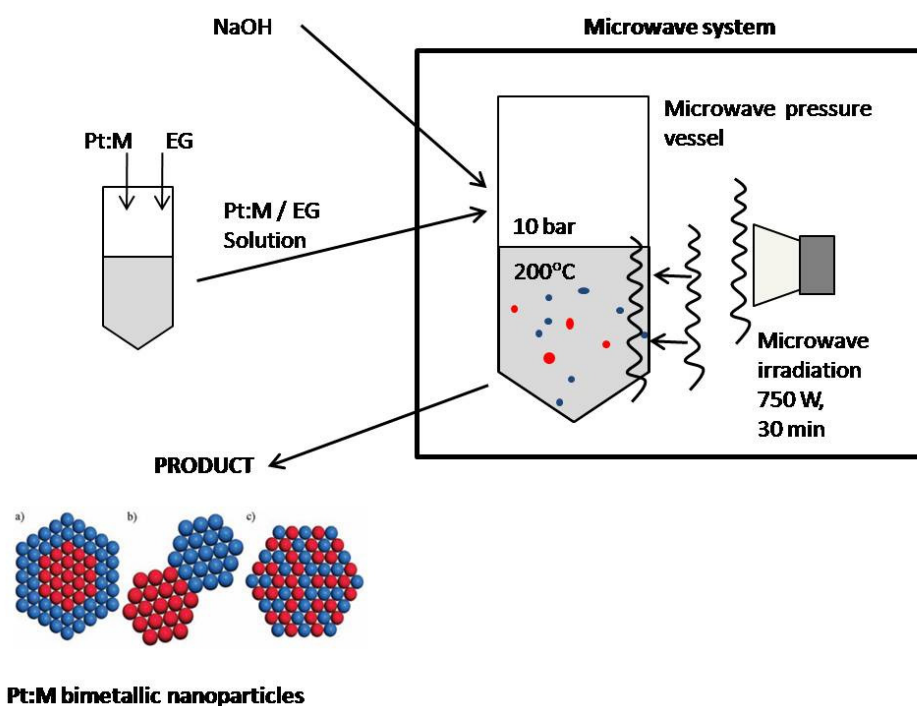
Synthesis method	Platinum precursors	Alloy metal precursors	Capping agents	Reducing agents	Solvents
Conventional	H_2PtCl_6	CoCl_2	ODT	NaBH_4	THF
		NiCl_2	PVP	N_2H_4	
Microwave	H_2PtCl_6	CoCl_2	PVP	EG	EG/ H_2O
		NiCl_2			

3.1.2. Conventional synthesis method

In this method, the synthesis was carried out at room temperature using the precursor salts, surfactants, capping agents and solvents in Table 3.1. The procedure was adapted from Yee et al. [1], for the synthesis of thiol-protected platinum nanoparticles, however different reducing agents, namely NaBH_4 and N_2H_4 , were used here. The reaction conditions such as molar ratio and reducing agents were varied to determine the effect on the properties of the nanoparticles. Metal precursor salts were dissolved in THF together with the surfactant and stirred overnight. The solutions were then reduced with either sodium borohydride (NaBH_4) or hydrazine hydrate (N_2H_4). The exact amounts of reagents as well as the resulting properties of nanoparticles will be discussed in Chapter 4 and 5. In this conventional synthesis procedure, the synthesis reaction takes place at room temperature (25 °C), with further heat treatment of the nanoparticles powders at 150 – 200 °C.

3.1.3. Microwave-assisted synthesis

The microwave-irradiation synthesis procedure was adapted from work by Yu et al. [2], where they used a domestic microwave oven. In this work a commercial Anton Paar M300 microwave reactor was used, which gives more control over the temperature and pressure of the reaction. The microwave-irradiation synthesis procedure was discussed in detail in Chapter 2, section 2.4.2. For this synthesis procedure, precursor salts and surfactant (see Table 3.1) were dissolved in ethylene glycol (EG) for 2 hours. The solutions were then poured into 60 ml teflon vessels and placed in an Anton Paar microwave reactor (M300) set to 200 °C, and 750 W for a reaction time of 30 minutes (schematic 3.1). For microwave-irradiation, the effect of the capping agent, pH and molar ratio were evaluated. The results for this synthesis procedure will be discussed in Chapter 5 and 6.



Schematic 3.1. Demonstration of the microwave-irradiation synthesis procedure of bimetallic platinum nanoparticles.

Characterization of the nanoparticles is important in understanding their properties and determining their behaviour in different applications. Therefore the rest of this chapter will discuss the different characterization techniques used in this work.

3.2. Structural Characterization

In order to fully understand the behavior of the nanoparticles, it is important to determine their structural morphologies, size and crystalline structure. For this purpose a transmission electron microscopy (TEM), scanning electron microscopy (SEM) and x-ray diffraction (XRD) were used. Each will be discussed briefly below.

3.2.1. Transmission Electron Microscope (TEM)

All the nanoparticles were investigated using two distinctive TEM techniques. For size and morphology determination, ordinary TEM images were collected using a JEOL TEM 200 at 200kV, fitted with a Gatan CCD camera. Secondly, electron energy loss spectroscopy (EELS) and scanning transmission electron microscope (STEM) were performed on a JEOL ARM 200F, both at 200 kV. EELS measures the energy distribution of the inelastically scattered electrons that interact with the sample [3]. This technique has been used to study the chemistry and physics of solid surfaces and it is also capable of high spatial resolution. For bimetallic nanoparticles, the technique was used to map the metal-metal distribution based on the differences

in the electron densities of the materials [4, 5]. To process the images and calculate the particle size, the ImageJ^(R) software with statistical analysis was used.

Sample preparation for TEM: For effective TEM imaging, the samples must be less than 100 nm thick for the electron beam to pass through. When analyzing powders, a small amount of the sample is dispersed in absolute ethanol and sonicated for 2 – 5 minutes. A carbon coated Cu grid is then immersed in the solution for 5 seconds and dried at room temperature for 30 minutes before inserting into the TEM. X-rays striking the detector trigger electron-hole pairs on the sample. These are collected and the energy converted to a spectrum or images. Each element possesses specific energy resolution, this influences the ability of the technique to tell atoms apart especially light atoms.

3.2.2. Scanning Electron Microscopy (SEM)

Two scanning electron microscopes were used to obtain surface images and determine the elemental composition of the nanoparticle agglomerates. These were a JEOL SEM 2100 and a Carl Zeiss Auriga FIB-SEM, both used in imaging and EDS mode. As with the TEM, SEM works with an electron gun as a light source with condenser lenses and objective lenses present in the system. A fine beam of electrons is scanned across the surface of the specimen with a detector monitoring the intensity of the secondary signal from the sample [6].

3.2.3. X-ray diffraction (XRD)

A Pan'Analytical X-ray diffractometer, K_{α} was used to determine the structure of condensed matter on an atomic scale [7]. Especially, information on the crystal structure of the bimetallic nanoparticles will play an important role in understanding their electronic and magnetic catalytic properties. Here, x-ray powder diffraction was used to determine the crystallinity, crystallite size, lattice parameter and different phases that are formed in the metal nanoparticles. Approximately 2 g of nanoparticle powder was loaded onto a stainless steel sample holder and inserted into the XRD chamber. The X-rays were scanned from $2\theta = 20 - 80^{\circ}$ at a scan rate of 0.0445°/s.

The crystalline sizes of the nanoparticles were calculated using the Scherrer equation (Eq.3.1) [8].

$$D = \frac{0.94\lambda_{K\alpha}}{\beta_{2\theta}\cos\theta_B} \quad (3.1)$$

In this equation, D is the crystalline size (nm), θ_B is the angle of the (111) peak, β is the full-width-half maximum (FWHM) of the (111) peak, and λ is the Cu K_{α} wavelength (1.5405 Å) [9, 10].

3.2.4. BET surface area measurements

A BET Micrometrics TriStar II 3020 surface area porosity system was used to determine the surface area (m^2/g) of the nanoparticles. Such information can be used to understand the behaviour of the materials in different applications, such as

catalysis. In this case all samples were degassed with nitrogen overnight at 90°C before measurements commenced.

3.3. Compositional Characterization

In addition to investigating the morphology of the nanoparticles, it is important to determine the elemental composition and oxidation states of the materials. As these bimetallic nanoparticle structures are intended for catalysis, a quantitative analysis of their surface as well as bulk composition will be important. For this reason XPS was used and will now be discussed briefly.

3.3.1. X-ray photoelectron spectroscopy (XPS)

Due to the bimetallic nature of the nanoparticles in this work, it is important to determine their surface oxidation state as well as the different species that are formed during the reaction. X-ray photoelectron spectroscopy (XPS) is a technique suitable to determine these properties at a surface penetration depth of about 5 nm. The system used was a PHI 5000 Versaprobe – Scanning ESCA microprobe with an Al monochromator X-ray beam, at 25 W and 15 kV, with pass energy of 11.8 eV for individual elements. Peak correction was done using carbon peak shifting of Multipak^(R) software before curve fitting.

3.4. Electrochemical Characterization

The nanoparticles prepared in section 3.1 were analyzed for their electrocatalytic activity using an electrochemical cell. The electrocatalytic activity was tested in acid (section 3.4.2) and alcohol (section 3.4.3 and 3.4.4) electrolytes.

3.4.1. Electrochemical cell

For cyclic voltammetry a Metrohm Autolab (PGSTAT302N, VA366 stand) single electrochemical cell system (see Fig. 3.1) was used, to determine the electrocatalytic activity of the synthesized nanoparticles. It consists of a reference electrode (Ag/AgCl), counter electrode (Pt rod) and the working electrode (0.0314 cm², polished glassy carbon).

Working electrode preparation: A sample of the nanoparticle powder (0.020 g), Nafion (80 μ l), and isopropanol (40 μ l) were mixed and sonicated for approximately 2 hours in a vial, to form an ink. A 2.0 μ l aliquot of the ink was then deposited onto a polished glassy carbon (GC) electrode, which was dried at 90 °C for 1 hour. The two electrolyte solutions were 40 ml of 0.5 M H₂SO₄ (section 3.4.2) or 0.5 M H₂SO₄ + 1.0 M CH₃OH (section 3.4.3 and 3.4.4), and these were purged with N₂ for 30 minutes prior to each measurement. All the voltammograms presented in further sections were recorded for the 10th scan.

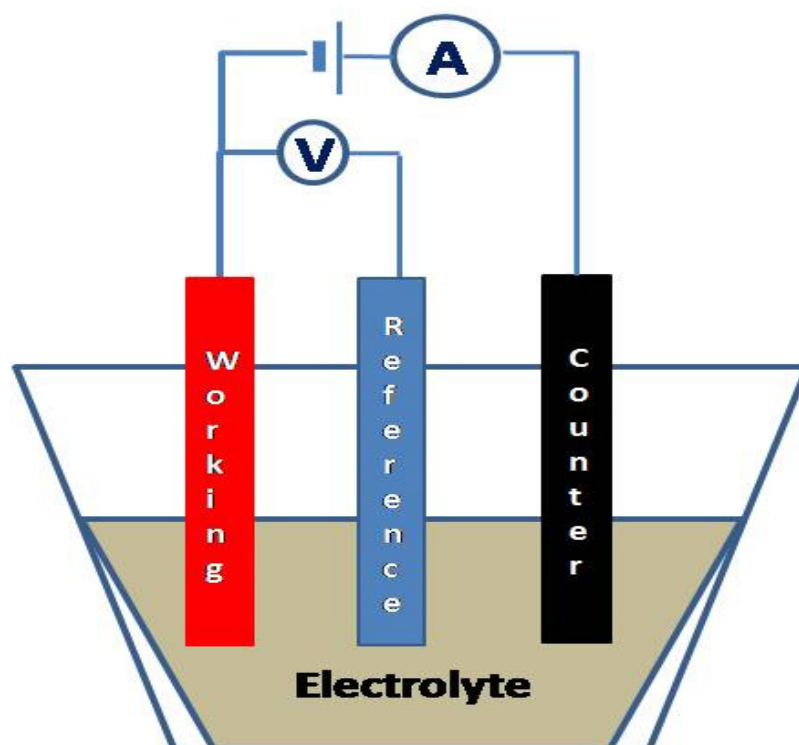


Figure 3.1. Illustration of a 3-electrode electrochemical cell where the reference electrode is Ag/AgCl, and the counter electrode (Pt-rod) and the working electrode is a polished glassy carbon electrode with catalyst ink deposited.

3.4.2. Cyclic voltammetry

Cyclic voltammetry (CV) was performed to determine the electrocatalytic activity, the electrochemical active surface area (ECSA), and the H₂ adsorption/desorption properties of the catalysts [11]. The behaviour of the catalysts in acid electrolyte was measured in a half-cell apparatus (described in section 3.4.1). The working electrode was a modified glassy carbon with the catalyst ink deposited.

The ECSA was calculated using the following equation:

$$ECSA = Q_H / [Pt] \times 0.21 \quad 3.2$$

Where: Q_H is the charge intergrated from the H_2 desorption peak area (mC/cm^2), $[Pt]$ is the total platinum metal loading (g/cm^2) and 0.21 is the charge required to oxidise a monolayer of H_2 on Pt (mC/cm^2) [12].

Voltammetry measurements were performed at a scan rate of 10 mV/s with scan potential from 0 – 1.2 V. In Fig. 3.2 a typical voltammogram of a platinum (Pt) catalyst in acid electrolyte is presented. The different regions/peaks shown on the graph are: H_2 adsorption/desorption (-0.2 – 0.1 V), Pt-oxide formation/reduction (0.65V and 0.50 V), as well as the capacitive region (0.8 – 1.1 V). The voltammograms of the nanoparticle catalysts prepared in this work will be discussed in Chapter 4 – 7.

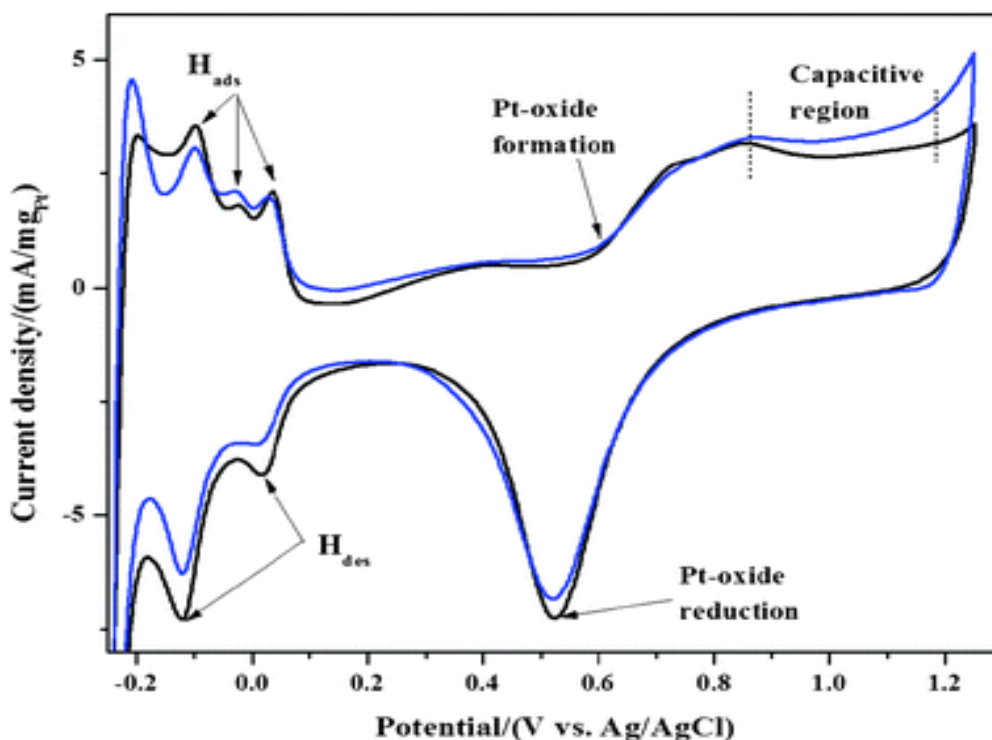


Figure 3.2. Typical voltammograms of Pt in acid electrolyte to demonstrate the peak positions and the accompanying reactions. The image was reproduced from Physical Chemistry Chemical Physics, 2012, 14, 4463 – 4474, [13]. With permission from Royal Society of Chemistry.

3.4.3. Methanol Oxidation Reaction (MOR)

Methanol was also used as an electrolyte with nitrogen saturation to determine the activity of the catalysts towards the methanol oxidation reaction. As an example, a typical voltammogram PtRu/C nanoparticles is presented in Fig. 3.3. The MOR peaks can be seen where methanol oxidation occurs in the forward scan (I_f) and in the reverse scan (I_b) the carbonaceous species such as formaldehyde and carbon monoxide formed in the methanol dissociation reaction are removed [12, 14].

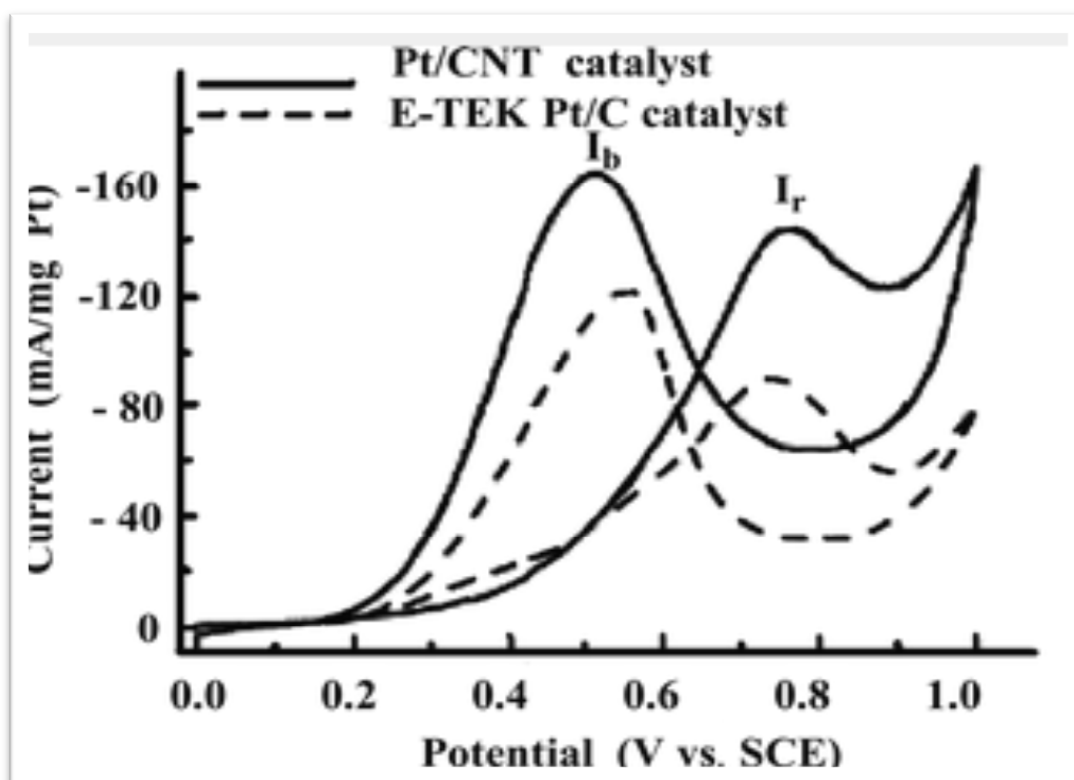


Figure 3.3. MOR voltammograms of PtRu/C nanoparticles showing typical oxidation and reduction peaks. The image was reproduced from Journal of Physical Chemistry B, 2005, 109, 22212 – 22216, [15], with permission from American Chemical Society.

3.4.4. Chronoamperometry measurements

Chronoamperometric experiments are current vs. time measurements which determine the time dependence of the current, [16], at a steady potential (0.5 V). These measurements were performed in the alcohol electrolyte over a time period of 1200 s at a scanning rate of 10 mV/s.

References

1. Yee, C., et al., *One-phase synthesis of thiol-functionalized platinum nanoparticles*. Langmuir, 1999. **15**: p. 4314 - 4316.
2. Yu, W., W. Tu, and H. Liu, *Synthesis of nanoscale platinum colloids by microwave dielectric heating*. Langmuir, 1999. **15**: p. 6 - 9.
3. Egerton, R.F., *Electron energy-loss spectroscopy in the TEM*. Reports on Progress in Physics, 2009. **72**: p. 016502.
4. Mathe, N.R., et al., *TEM and EELS studies of microwave-irradiation synthesis of bimetallic platinum nanocatalysts*. Journal of Physics: Conference Series, 2014. **522**: p. 012066.
5. Mathe, N.R., M.R. Scriba, and N.J. Coville, *Methanol oxidation reaction activity of microwave-irradiated and heat-treated Pt/Co and Pt/Ni electrocatalysts*. International Journal of Hydrogen Energy, 2014. **39**: p. 18871 - 18881.
6. Chescoe, D. and P.J. Goodhew, *The operation of transmission and scanning electron microscopes*. Royal Microscopical Society: Microscopy Handbooks 20. 1990: Oxford University Press.
7. Barrett, C.S., et al., *Advances in X-ray analysis*. Proceedings of the Third Annual Conferences on Applications of X-ray Analysis. 1994, Denver, Colorado: Plenum Press.
8. Liu, Z., et al., *Carbon-supported Pt and PtRu nanoparticles as catalysts for a direct methanol fuel cell*. Journal of Physical Chemistry B, 2004. **108**: p. 8234 - 8240.
9. Park, K.-W., et al., *Chemical and electronic effects of Ni in Pt/Ni and Pt/Ru/Ni alloy nanoparticles in methanol electrooxidation*. Journal of Physical Chemistry B, 2002. **106**: p. 1869-1877.
10. Punyawudho, K., et al., *Comparison of different methods for determination of Pt surface site concentrations for supported Pt electrocatalysts*. Electrochimica Acta, 2010. **55**: p. 5349 - 5356.

11. Min, M., et al., *Particle size and alloying effects of Pt-based alloy catalysts for fuel cell applications*. *Electrochimica Acta*, 2000. **45**: p. 4211 - 4217.
12. Huang, H.J., D.P. Sun, and X. Wang, *PtCo alloy nanoparticles supported on graphene nanosheets with high performance for methanol oxidation*. *Chinese Science Bulletin*, 2012. **57**: p. 3071 - 3079.
13. Tabet-Aoul, A. and M. Mohamedi, *Interrelated functionalities of hierarchially CNT/CeO₂/Pt nanostructured layers: synthesis, characterization and electroactivity*. *Physical Chemistry Chemical Physics*, 2012. **14**: p. 4463 - 4474.
14. Iwasita, T., *Methanol and CO Electrooxidation*, in *Handbook of Fuel Cells - Fundamentals, Technology and Applications*, W. Vielstich, H.A. Gasteiger, and A. Lamm, Editors. 2003, John Wiley & Sons. p. 603 - 624.
15. Georgakilas, V., et al., *Decorating carbon nanotubes with metal or semiconductor nanoparticles*. *Journal of Materials Chemistry*, 2007. **17**: p. 2679 - 2694.
16. Cohen, J.L., D.J. Volpe, and H.D. Abruna, *Electrochemical determination of activation energies for methanol oxidation on polycrystalline platinum in acidic and alkaline electrolytes*. *Physical Chemistry Chemical Physics*, 2007. **9**: p. 49 - 77.

CHAPTER 4: THE EFFECT OF REACTION PARAMETERS ON THE NUCLEATION AND GROWTH OF BIMETALLIC PLATINUM NANOPARTICLES

The synthesis and characterization of platinum-cobalt (Pt-Co) and platinum-nickel (Pt-Ni) nanoparticles using a conventional room temperature procedure is discussed in this chapter. Different reaction parameters were varied to determine the effect they will have on the size, shape, oxidation states as well as the electrocatalytic properties of the catalysts.

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4.1. Introduction

Due to their unique physical and chemical properties, platinum (Pt) nanoparticles have attracted a lot of attention in the electronic, catalysis and pharmaceutical industries within the last few decades. However, there are limitations to the application of nanoparticles in various fields because of their tendency to aggregate [1]. Without stabilization the nanoparticles aggregate and lose their unique shape and properties [2-4]. Another issue is that at the nanometre scale, the surface area and the surface energy increase and this could induce metal phase changes in the

nanoparticles [5]. Also, the introduction of a second metal into the Pt lattice at the nanoscale, results in non-classical thermodynamic mixing of the two metals. Therefore, phase diagrams based on bulk alloy systems cannot be directly applied to nanoalloys as the surface energies are different [6].

The synthesis of bimetallic nanoparticles is complex since the control of the composition, size and size distribution of the two component metals is difficult to predict. When two metal salts are simultaneously reduced, the reducing agent affects the reduction kinetics of the metals differently and also controls the crystallinity of seeds formed in the nucleation stage [7]. Metal precursor reduction is also influenced by a variety of parameters that impact on the physical and chemical properties of the resulting bimetallic particles [8]. The size and growth of nanoparticles is determined by reaction parameters such as temperature, surfactants, metal molar ratio, and reducing agent.

Depending on the mixing pattern of the two metals, there are 3 possible structures that can be formed. These are; core-shell, alloy or intermetallic and heterostructures [2, 9, 10]. The core-shell nanoparticles are formed by nuclei-based methods, whereas the alloy or intermetallic nanoparticles are formed by co-reduction methods [7]. If the two different metals show a separate nucleation and growth process, and if they share a mixed interface during growth, then a heterostructure will be formed. The activation energy for nucleation is usually higher than the activation energy for the growth process [11]. This makes it more difficult to nucleate metal nanoparticles than to grow them. The formation mechanism affects the structure and size of the bimetallic nanoparticles and these parameters impact on their catalytic, electronic and magnetic properties [12, 13].

The concentration of additives, such as capping agents or surfactants that are needed to stabilize the nanoparticles formation, contributes towards the growth mechanism and the morphology of the bimetallic nanoparticles [14]. These additives result in the introduction of lattice defects, and preferential site coverage giving rise to non-traditional structures, e.g. multipods, nanorods, planar structures, etc [15]. The absence of surfactants makes it difficult to separate the nucleation and growth processes and to prevent the particles from aggregating. Surfactants such as octanethiol, dodecanethiol, octadecanethiol and hexadecanethiol have been used to synthesize surfactant-stabilized platinum nanoparticles, producing monolayer protected platinum clusters [16, 17]. At a later time, the removal of these surfactants from the metal nanoparticle is required to produce an active catalytic surface.

An important factor in the synthesis of alloy nanostructures is the availability of zero-valence state solutes corresponding to the metals in solution during the reaction. Peng and Yang [5], determined that the solute atoms of platinum and a second metal, eg. Ru, Co, Ni, Fe, must be simultaneously present in solution, at both the nucleation and growth stages, and at the required concentration in order to produce alloy structures. Platinum ions are easily reduced [18], but this is not the case for other transition metals, which require the use of strong reducing agents like sodium borohydride, hydrazine, hydrogen etc. [19, 20]. When strong reducing agents such as NaBH_4 and N_2H_4 are used, the differences in the electron affinities of the transition and noble metals dominates the reduction process [21].

In this chapter, reaction parameters such as the metal molar ratio and reducing agent (NaBH_4 , N_2H_4) were varied to determine the effect they will have on the bulk and surface properties of platinum-cobalt (Pt-Co) and platinum-nickel (Pt-Ni) nanoparticles. The effects of the reducing agents on these types of bimetallic

nanoparticles and their properties have been studied by our group. [22], and this chapter further elaborates on our earlier work. These bimetallic nanoparticles have also been studied by Antolini et al, Zhang et al and Park et al, for use as fuel cell catalysts [23-25]. The earlier study (Chapter 2) is compared with the current study. Pt-Ni and Pt-Co were chosen because Ni and Co can modify Pt electrocatalysts, and improve methanol oxidation reactions [26]. It is proposed that this is achieved by lowering the electron binding energy in platinum through the alloying process [27].

It is known that Pt suffers from carbon monoxide (CO) poisoning, which is one of the by-products of the methanol dissociation process [28]. Not only does the addition of a cheaper transition metal (Co or Ni) lead to a decrease in the catalyst costs, but the second metal can also provide an oxygen source to convert CO into CO₂, which decreases the ability of the catalysts to be poisoned by CO [23, 25]. The work undertaken in this chapter using the conventional synthesis procedure was performed in order to compare with other studies available, but mostly to provide reference data for the synthesis of the Pt-Co and Pt-Ni nanoparticles by the new microwave-irradiation synthesis procedure discussed in Chapter 5 and 6.

4.2. Experimental Procedure

4.2.1. Materials

All the chemicals were purchased from Sigma Aldrich and were used as received without any further modification or purification. They were: H₂PtCl₆.6H₂O (99%), NiCl₂.6H₂O (97%), CoCl₂.6H₂O (99%), sodium borohydride (NaBH₄, 95%), hydrazine

hydrate (N_2H_4 , 65%), 1-octadecanethiol (ODT, 98%), and tetrahydrofuran (THF, 99.9%).

4.2.2. Synthesis of nanoparticles

The nanoparticles were synthesized by NaBH_4 or N_2H_4 reduction of the precursor salts of Pt and Co or Ni in a THF solution using ODT as the capping agent. Different molar ratios of Pt:M salts (1:0.5, 1:1 and 1:3) were dissolved in THF together with ODT (500 mg) and the resulting solutions were stirred for 18 hours. Then a 10 ml solution of 1.0 M NaBH_4 or 65% N_2H_4 was added dropwise and the solutions were further stirred for 2 hours. The resulting solutions were centrifuged to remove the liquid, after which they were washed with a 50/50 H_2O /ethanol solvent mixture and centrifuged four times to remove unreduced precursors and contaminants. The precipitates were dried at room temperature overnight and further heat-treated at 150 – 200 °C for 4 hours. The samples are denoted as such: Pt-M-(x:y)-B for NaBH_4 and Pt-M-(x:y)-H for N_2H_4 , where x = the moles of Pt and y = moles of Co or Ni.

4.2.3. Characterization

Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2100 microscope installed with a Gatan CCD camera device. The powder X-ray diffraction (XRD) data were collected on the PANalytical X'Pert Pro X-ray diffraction system. X-ray photoelectron spectra (XPS) of the catalysts were recorded on a PHI

5000 Versaprobe – Scanning ESCA microprobe. The system uses an Al monochromator X-ray beam at 25 W and 15 kV, with pass energy of 11.8 eV for individual elements. Peak correction was done using the carbon peak (C-1s) shift before curve fitting by the use of Multipak^(R) software. A BET Micrometrics TriStar II 3020 Surface area porosity system was used to determine the surface area of the catalysts, with degassing overnight at 90°C before measurements. The solutions were centrifuged with a Rotorfix 32A at 40 X 100 RPM for 15 minutes.

4.2.4. Cyclic voltammetry

Cyclic voltammetry was used to determine the electrocatalytic activity of the synthesized nanoparticles. A Metrohm Autolab single electrochemical cell system with scanning potential from 0 – 1.2 V and 10 mV/s scan rate was used. It consists of a reference electrode (Ag/AgCl), counter electrode (Pt rod) and the working electrode (0.0314 cm² polished glassy carbon). The catalyst powder sample (0.020 g), Nafion (80 µl), and isopropanol (40 µl) were sonicated for approximately 2 hours to form an ink. The ink (2.0 µl) was then deposited onto a polished glassy carbon (GC) electrode which was dried in an oven at 90°C for 1 hour. The electrolyte solutions, made of 40 ml of 0.5 M H₂SO₄ or 0.5 M H₂SO₄ + 1.0 M CH₃OH, were purged with N₂ for 30 minutes prior to each measurement. All the voltammograms presented were recorded for the 10th scan.

4.3. Structural and compositional analysis

The synthesized nanoparticle powders were characterized to determine their structural, compositional and electrocatalytic properties using the techniques mentioned above.

4.3.1. Effect of molar ratio on the structure of the nanoparticles

The size and shape of bimetallic nanoparticles can be controlled by changing the molar ratio of the metal precursors [7]. Therefore the molar contents of NaBH₄-reduced Ni, Pt and Co precursors were varied to determine the effect this would have on the shape, size and ultimately the catalytic activity of the materials. The results from the XRD study of Pt-Co mixtures are shown in Fig. 4.1a. The Pt (111), (200) and (220) diffraction peaks were present at 39.78°, 46.46° and 67.75° respectively (Fig. 4.1 and Table 4.1). The patterns are indicative of a typical face-centred cubic (fcc) Pt lattice structure [29]. When the cobalt (Co) was added into the Pt, there was a shift in the (111) peak to 40.23°, 40.99° and 40.39° for the 1:0.5, 1:1 and 1:3 molar ratios respectively. The increase in 2 θ values is indicative of the incorporation of the smaller Co atoms (2.50 Å) into the crystal lattice of Pt (3.92 Å) leading to lattice contractions and possible formation of an alloy structure [30]. This was more noticeable for the higher Co content samples, i.e. 1:1 and 1:3 molar ratios.

Peak broadening was observed after the incorporation of the Co into the Pt lattice due to possible formation of clusters or a decrease in particle size. The presence of diffraction peaks due to Co or Co-oxide hexagonal close-packed (hcp) structures, was not observed [29, 31], and suggest Co is present in an amorphous phase. The crystallite sizes were calculated using the Scherrer equation (Table 4.1).

Table 4.1. The size of the nanoparticles determined from TEM and XRD (N₂H₄)

Reducing agent	Sample name	TEM (nm)	XRD (nm)	(111) peak (2θ)	d-spacing (nm)
NaBH₄	Pt 1:0	7	8	39.78	2.259
	Pt-Co 1:0.5	10	7	40.23	2.240
	Pt-Co 1:1	8	5	40.99	2.200
	Pt-Co 1:3	5	5	40.39	2.231
	Pt-Ni 1:0.5	14	13	40.18	2.242
	Pt-Ni 1:1	8	5	40.41	2.230
	Pt-Ni 1:3	6	6	40.53	2.224
N₂H₄	Pt 1:0	7	8	39.91	2.257
	Pt-Ni 1:0.5	9	10	40.30	2.231
	Pt-Ni 1:1	7	9	40.08	2.248
	Pt-Ni 1:3	6	5	40.71	2.215

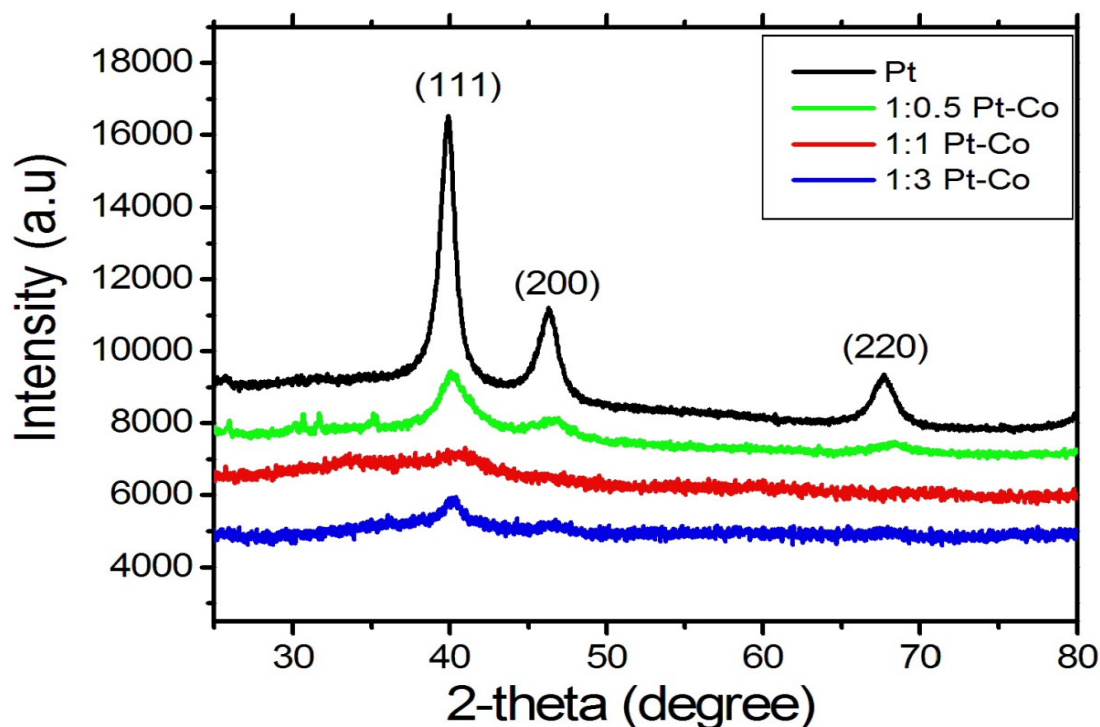
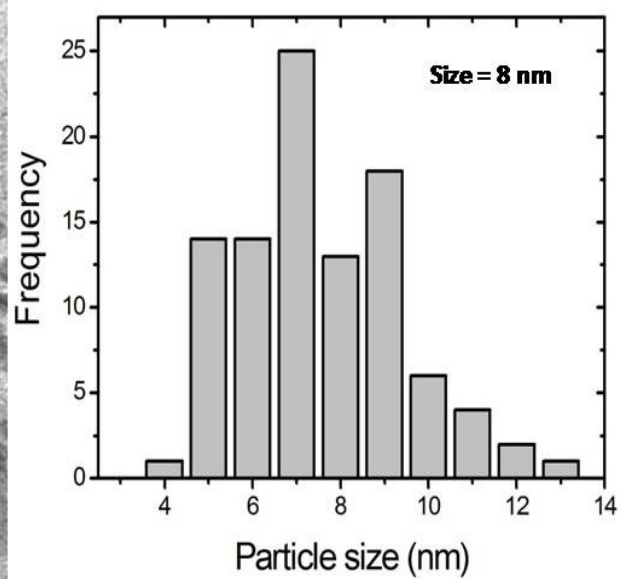
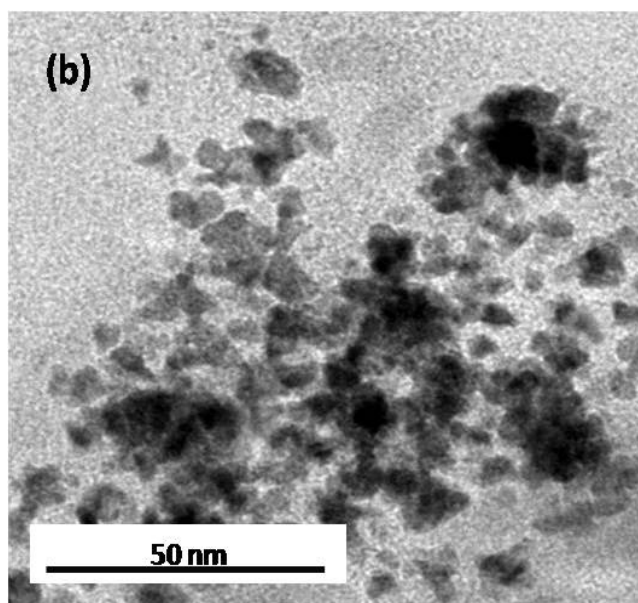
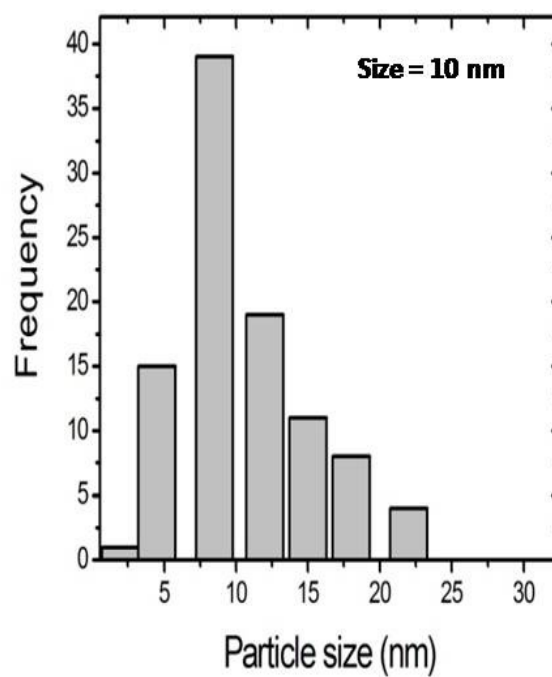
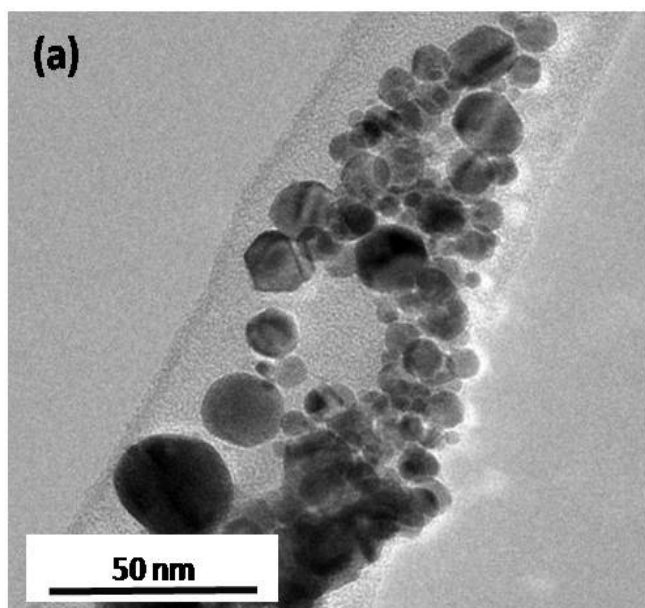


Figure 4.1. X-ray diffraction spectra of (a) Pt-Co nanoparticles synthesized using NaBH_4 .

The TEM images of the Pt-Co samples are presented in Fig. 4.2, together with their particle size distribution. For Pt-Co-(1:0.5)-B (Fig. 4.2a), a wide size distribution of nanoparticles with different shapes which were predominantly spherical, with some octahedral and oval shapes, was observed. The average size was determined as 10 nm with little clustering observed in the structures. In contrast, randomly dispersed nanoparticles were obtained for the Pt-Co-(1:1)-B sample (Fig. 4.2b) with an average particle size of 8 nm and a broad size distribution. The morphology showed a flat leaf-like structure with small agglomerates and irregular shapes. At a higher Co content (Pt-Co-(1:3)-B, Fig. 4.2c), smaller nanoparticles (5 nm) with irregular but mostly spherical shapes were obtained. These results show that the amount of Co in the Pt lattice creates differences in the structure and size of the nanoparticles.



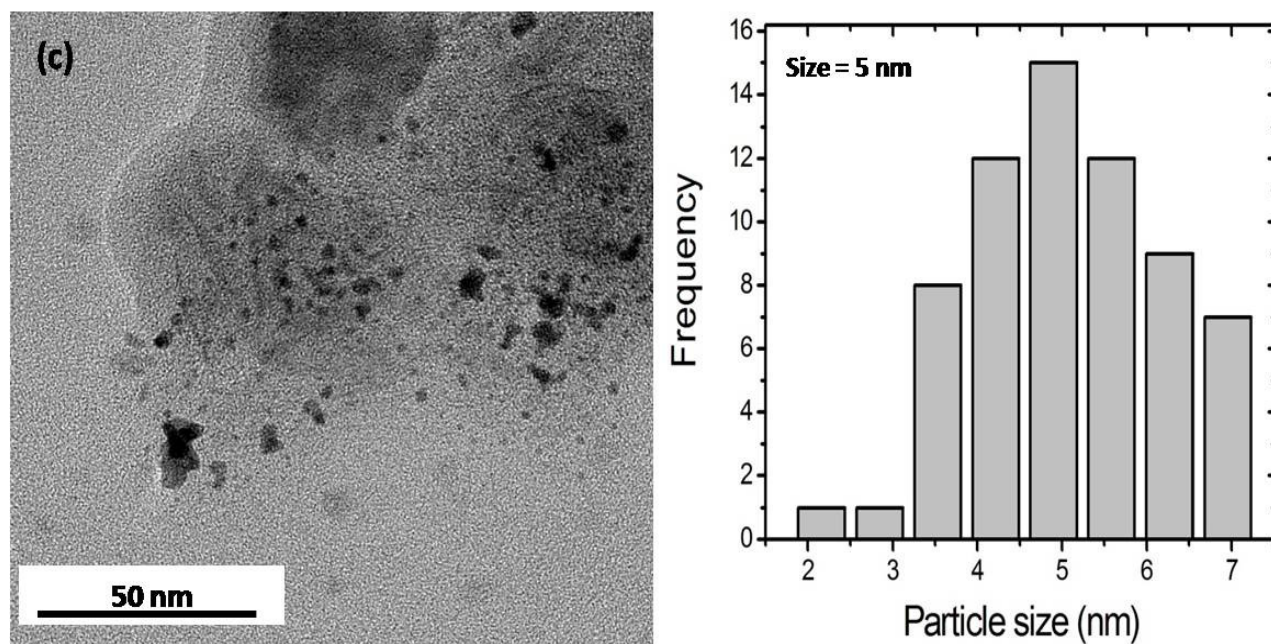


Figure 4.2. TEM images of Pt-Co nanoparticles at different molar ratios (a) 1:0.5, (b) 1:1 and (c) 1:3.

4.3.2. The effect of the alloying metal – Pt-Ni

In changing the alloying metal from cobalt (Co) to nickel (Ni), a change in the structure and particle size of the nanoparticles was noted. Fig. 4.3 shows the X-ray diffraction peaks of NaBH_4 -reduced Pt-Ni nanoparticles and monometallic Pt. No Ni or NiO diffraction peaks were observed. There was a general shift in the (111) peak of Pt at 39.87° to 40.18° , 40.41° and 40.53° after addition of Pt for the samples with 1:0.5, 1:1, and 1:3 Pt:Ni molar ratios. As the amount of Ni increased, the peaks broadened and diminished at high 2θ values. As with Co, such behaviour has been attributed to the incorporation of the small Ni ($3.52 \text{ \AA}$) atoms into the lattice of the Pt ($3.92 \text{ \AA}$) resulting in lattice contraction [29]. The calculated crystallite size from XRD structures are presented in Table 4.1.

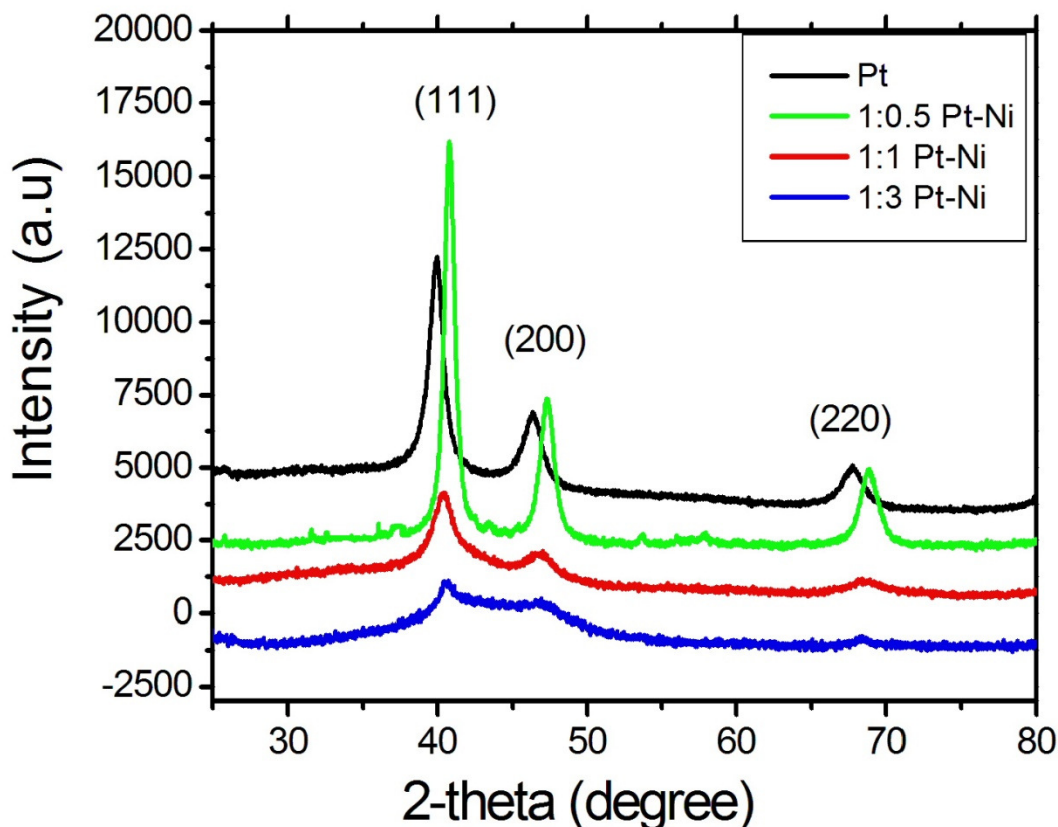
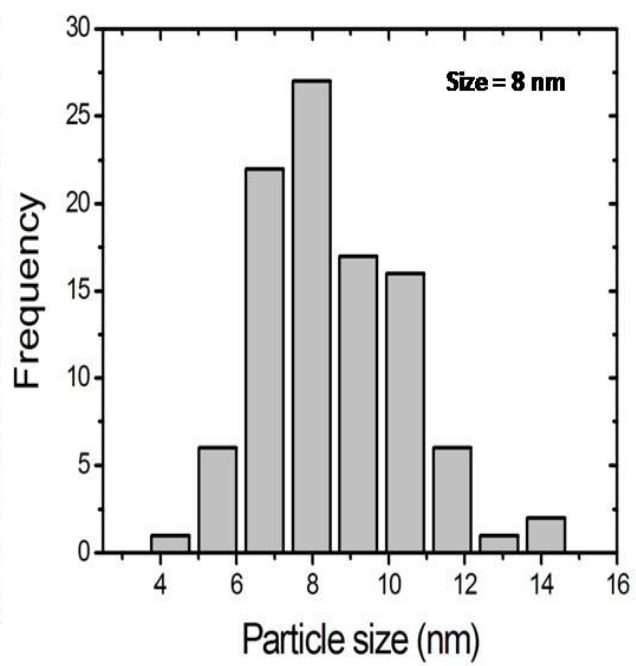
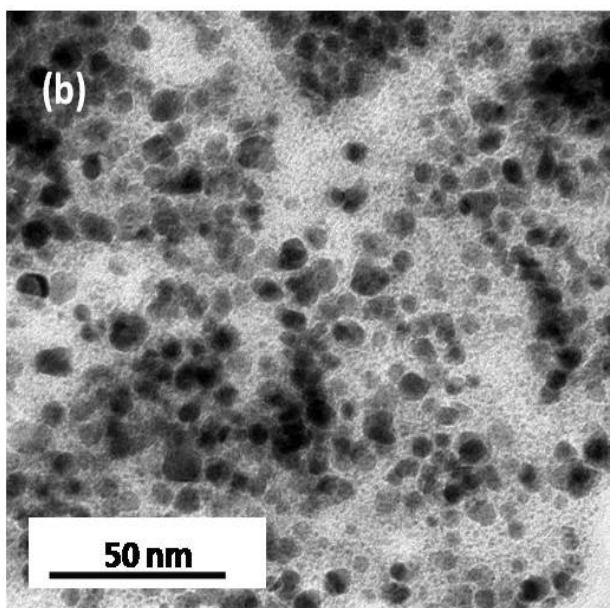
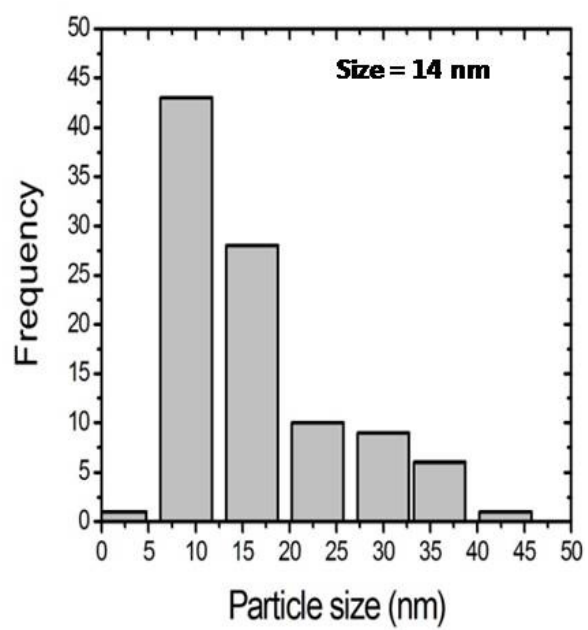
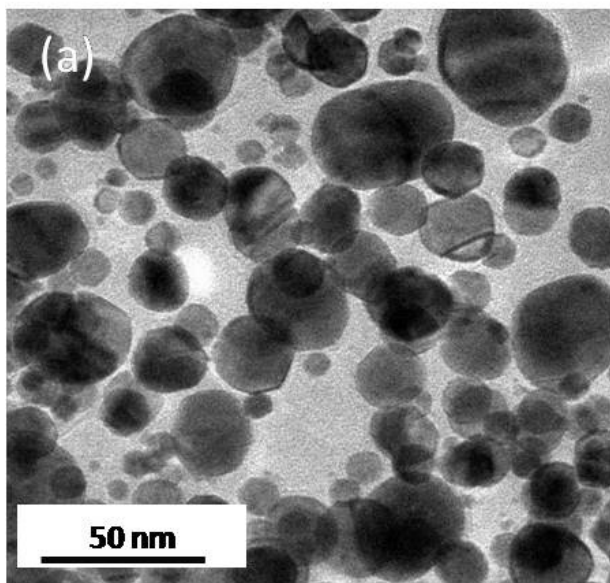


Figure 4.3. X-ray diffractograms of Pt-Ni nanoparticles synthesized using NaBH_4 .

Fig. 4.4 represents the TEM images of the Pt-Ni nanoparticles made with different molar ratios, together with their particle size distributions. For the Pt-Ni-(1:0.5)-B sample (Fig. 4.4.a) a large particle size distribution was observed with particles showing a morphology that is similar to what was obtained for Pt-Co-(1:0.5)-B (Fig. 4.2a). The average size of 14 nm was obtained for these nanoparticles. On the other hand, the Pt-Ni-(1:1)-B nanoparticles (Fig. 4.4b) show randomly dispersed nanoparticles with an average size of 8 nm. As the amount of Ni in the nanoparticles was further increased in Pt-Ni-(1:3)-B (Fig. 4.4c), small clustered nanoparticles were observed with a narrow size distribution and an average particle size of 6 nm.



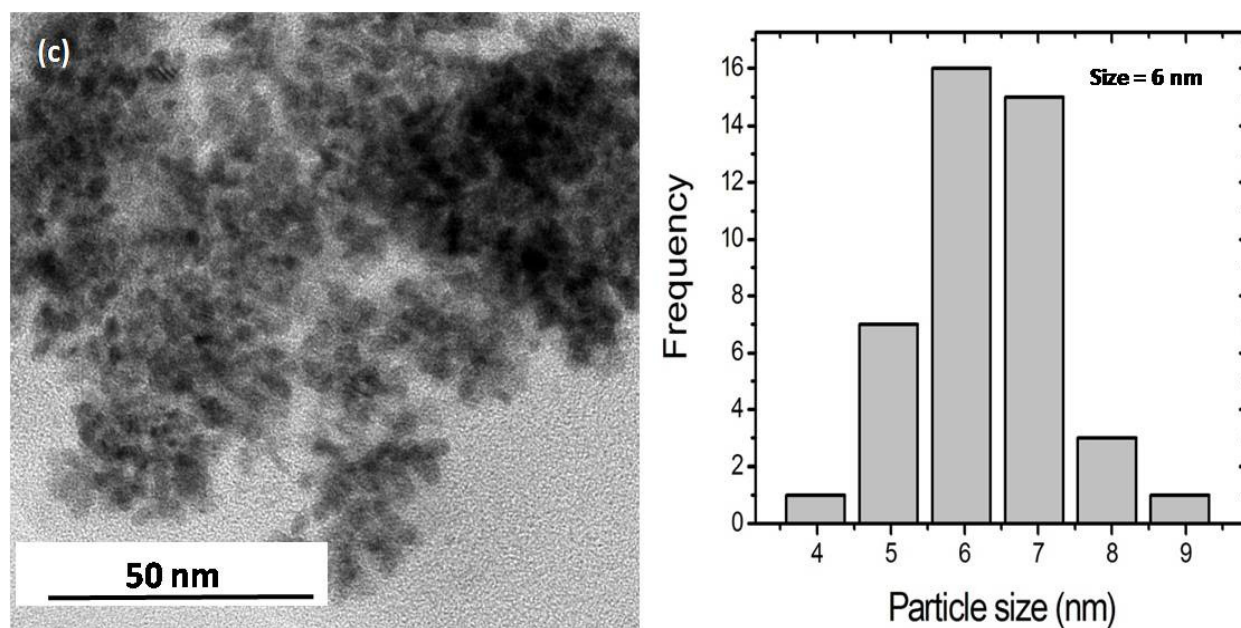


Figure 4.4. TEM images and size distribution of Pt-Ni nanoparticles (a) 1:0.5. (b) 1:1 and (c) 1:3.

It thus can be concluded from the molar ratio studies that changing this parameter results in alloys with different crystalline structures, morphologies and sizes of the nanoparticles. There is a clear shift in the 2θ values of the Pt-Co and Pt-Ni samples compared to the Pt (111) peak as reported in the literature which appears at $2\theta = 39.78^\circ$, indicating that alloying is occurring in the samples [32]. The broadening of the peaks is consistent with the reduction of particle size as found in the TEM studies. It is to be noted that Park et al. [25] and Deivaraj et al. [32] have reported that the formation of surface oxide (CoO and NiO) could result in amorphous structures and the absence of the Co or Ni respective metal XRD signature peaks. The types of nanoparticles obtained for the 1:0.5 samples, for both Pt-Co and Pt-Ni, were similar indicating that as predicted, the Ni and Co have similar surface energies and thus might result in similar structures under certain reaction conditions.

The activation energy for alloy formation increases with an increase in the metal atomic radius. This is consistent with the determining step for alloying being the diffusion of the second metal into the lattice of the platinum [11]. However, the alloy could be formed during precipitation and thus diffusion could be negligible. To further understand the effect of reaction parameters on the structure and size of the nanoparticles, the reducing agent was changed to N_2H_4 (hydrazine hydrate) when Pt was alloyed with Ni.

4.3.3. The effect of reducing agent – N_2H_4

As with the NaBH_4 -reduced Pt-Ni samples, the (111) peak positions also shifted for the Pt-Ni- N_2H_4 nanoparticles (Fig. 4.5). The peaks shifted to 40.30° , 40.08° and 40.71° for the 1:0.5, 1:1 and 1:3 molar ratios, respectively. Again the addition of the secondary metal has an effect on the crystal structure of Pt. The peak position and crystalline sizes, calculated using the Scherrer equation, for the samples are presented in Table 4.1. It should be noted when N_2H_4 is used as the reducing agent; sharper peaks were obtained compared to the broader peaks shown in Fig. 4.3 for the NaBH_4 -reduced samples.

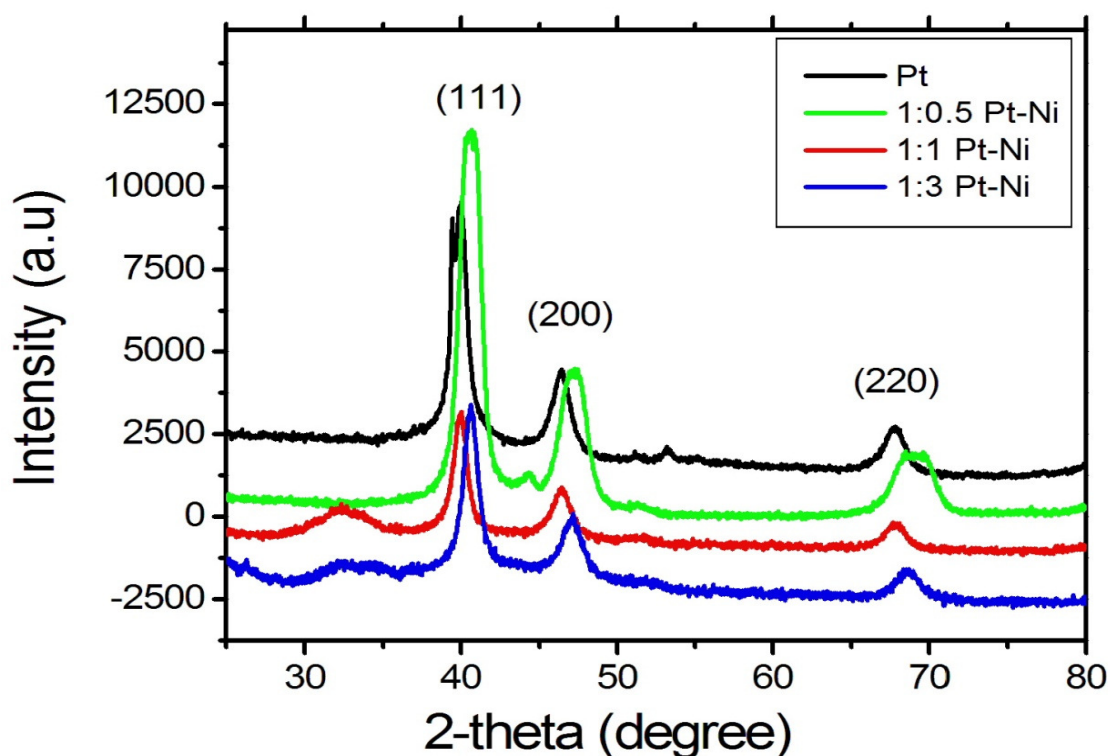


Figure 4.5. XRD spectra of (a) Pt-Co and (b) Pt-Ni nanoparticle synthesized using N_2H_4 .

In alloying platinum with nickel, different morphologies and particle size were obtained. At a low Ni molar content Pt-Ni-(1:0.5)-H (Fig. 4.6a), the nanoparticles form agglomerates to minimize surface energy. The average particle size of these nanoparticles was 9 nm. For the Pt-Ni-(1:1)-H sample (Fig. 4.6b), these nanoparticles were small, spherical and randomly dispersed with an average particle size 7 nm. Fig. 4.6c shows the Pt-Ni-(1:3)-H nanoparticles, which comprised of large spherical agglomerates (~45 nm) made up of smaller nanoparticles (6 nm).

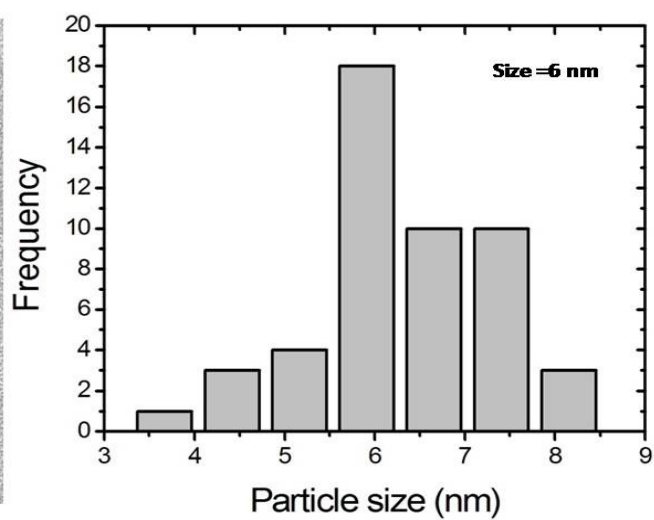
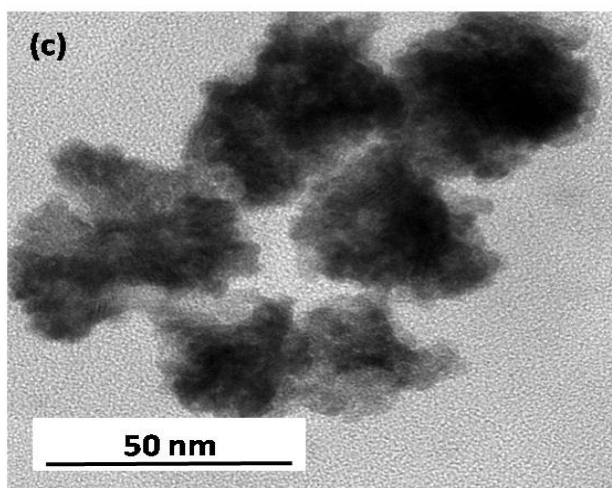
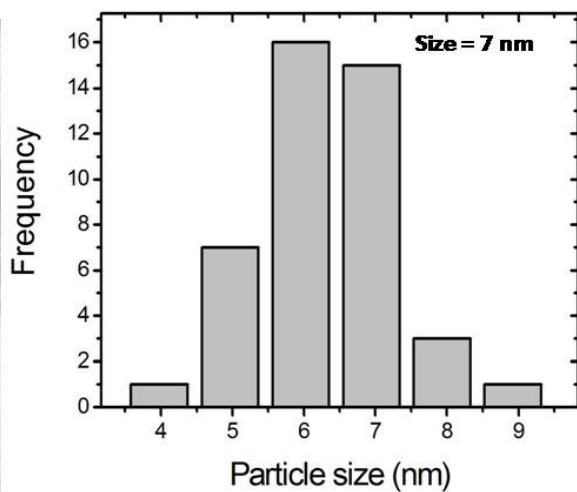
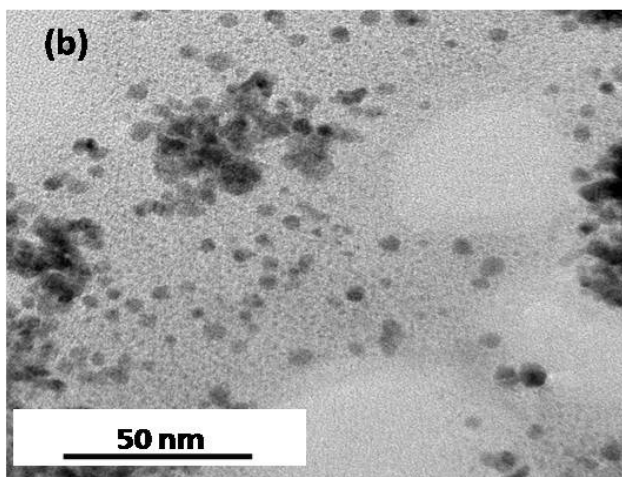
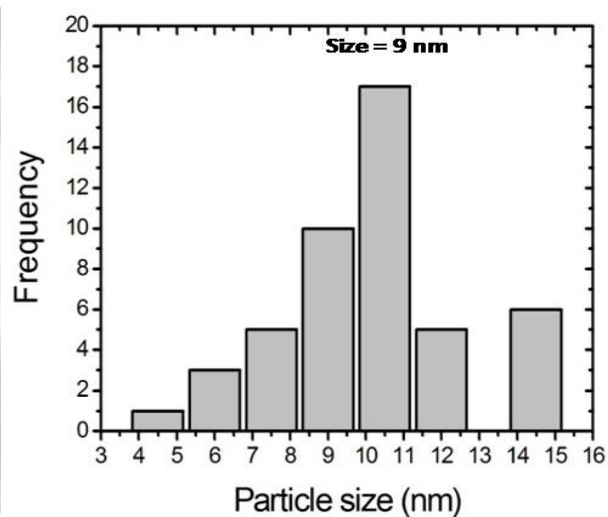
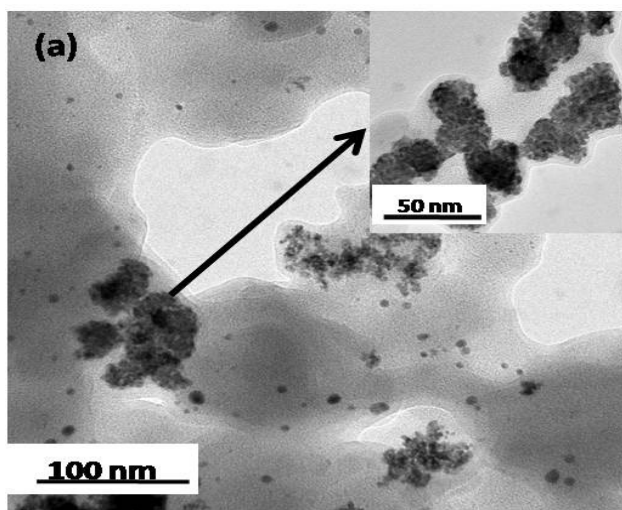


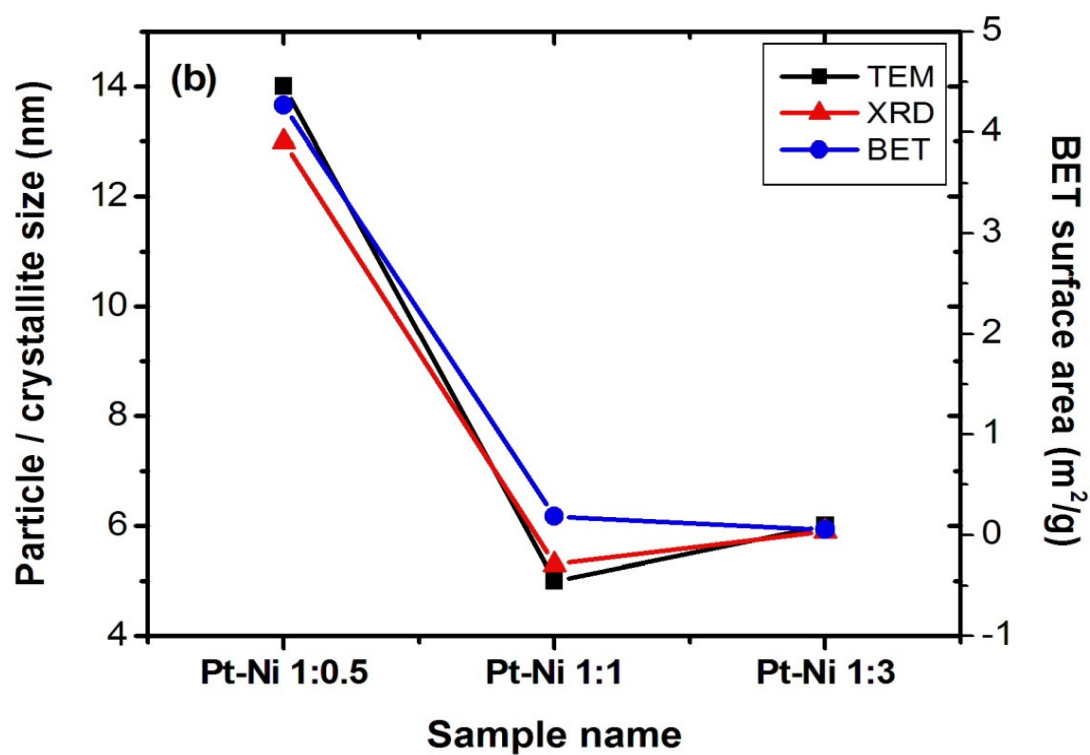
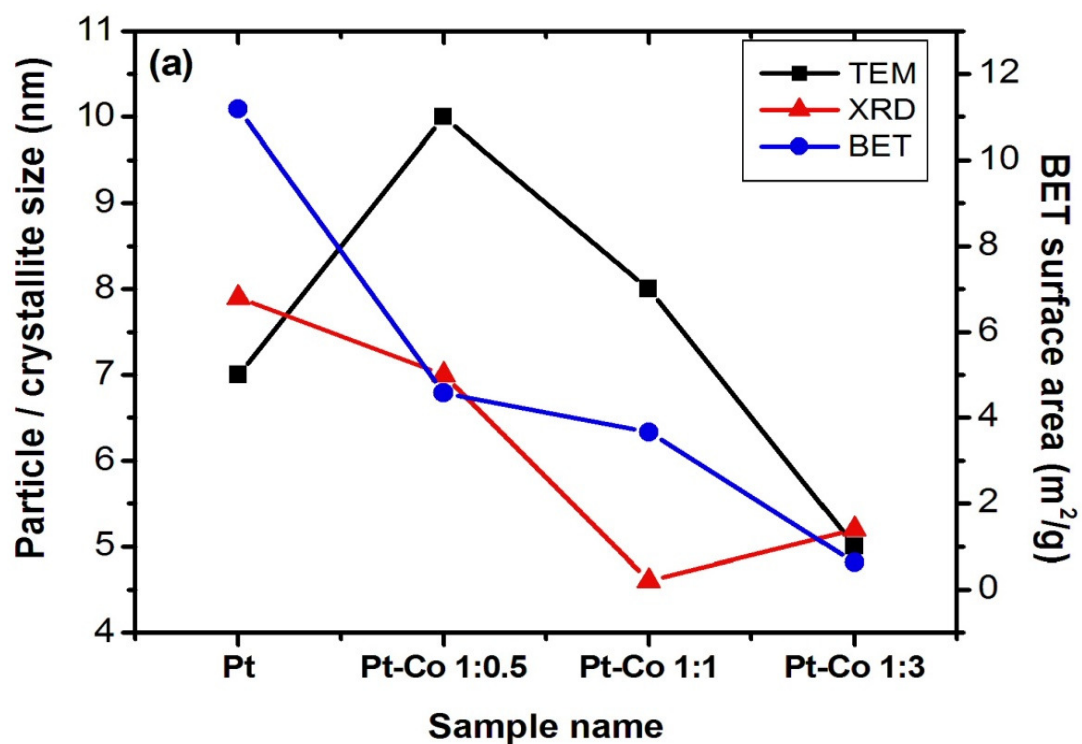
Figure 4.6. TEM images of Pt-Ni nanoparticles prepared with ODT and hydrazine hydrate, (a) 1:0.5, (b) 1:1 and (c) 1:3.

The rate of the reduction of the metals is related to the molar ratio because the particle size, calculated from TEM images, changes with an increase in the amount of the alloying metal. It has been determined that the stronger reducing agents results in smaller sized nanoparticles, whereas a weak reducing agent results in larger nanoparticles [7].

In summary, there was a general decrease in the crystalline size of the bimetallic nanoparticles when compared to monometallic Pt, observed for both reducing agents and for different molar ratios of the two metals. The shift of the (111) peaks to higher 2θ values indicates formation of an alloy structure due to the lattice contraction observed (d-spacing values).

4.3.3. Surface area (SA) measurements

These measurements were performed to determine the change in surface area with a change in the molar ratio. The data shown in graphical form in Fig, 4.7 for the Pt-Co and Pt-Ni samples showed that the surface area decreased with an increase in the amount of the transition metals in the solution.



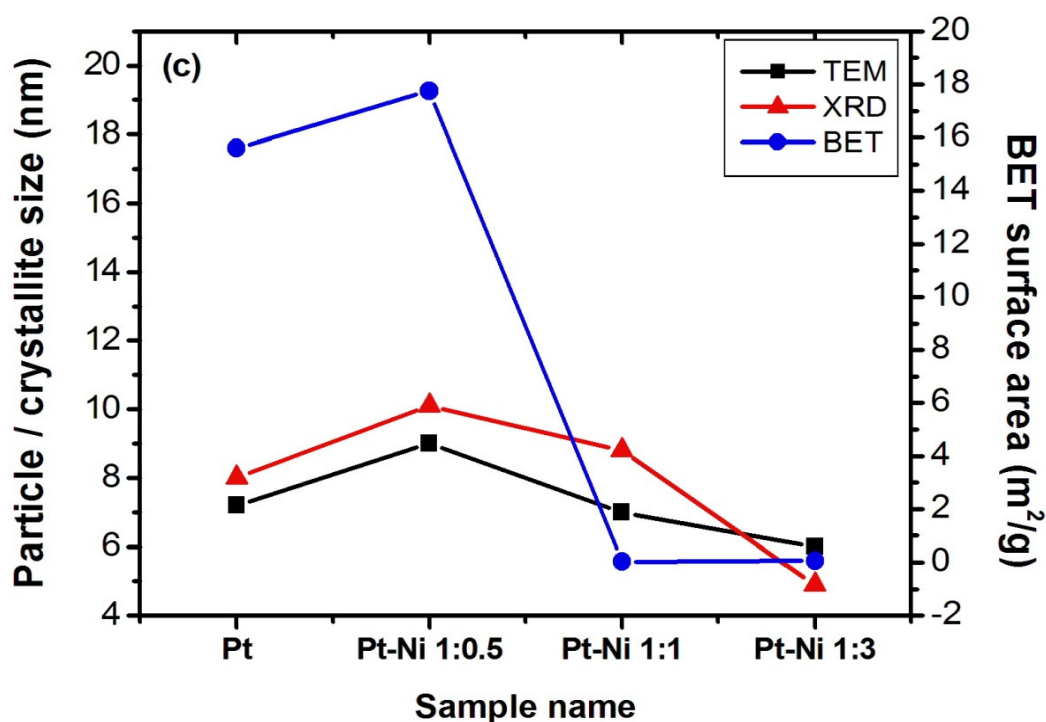


Figure 4.7. The surface area measurements of (a) Pt-Co-B, (b) Pt-Ni-B and (c) Pt-Ni-H samples.

TEM images in general showed smaller nanoparticles at higher Co and Ni content leading to the assumption that these samples should have a larger surface area.

The trends observed were:

- NaBH_4 and N_2H_4 reduced nanoparticles showed a decrease in surface area with an increase in Co/Ni content.
- XRD crystallite size presented a small decrease as the amount of M content in Pt is increased, indicating some degree of alloying.
- For the N_2H_4 reduced nanoparticles, there was a general decrease in the TEM particle size for the higher molar ratio samples (i.e. 1:3).

4.4. X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed on the Pt-Co and Pt-Ni nanoparticles to determine the surface oxidation states of the metals and the type of metal oxide/hydroxide species present. To achieve this, both the XPS full scans on the nanoparticles and the individual Pt-4f, Co-2p and Ni-2p scans were analyzed. Since the penetration depth in the XPS measurements is ~ 2.0 nm [33], the XPS data only gives information about the surface profile and not the bulk structure composition.

4.4.1. The effect of molar ratio and alloying metal

The NaBH_4 -reduced Pt-Co and Pt-Ni nanoparticles will be discussed first. The surface atomic concentrations of the nanoparticles were determined from the XPS full elemental scans (see Table 4.2). The Pt-Co-(1:0.5)-B and Pt-Ni-(1:0.5)-B samples contained very low amounts of Co/Ni on the surface suggesting Pt segregation. A low ratio is to be expected as the samples contained a larger amount of Pt in the synthesis procedures. In contrast, the Pt-Co-(1:1)-B presented surface segregation of Co. The presence of sulphur in the XPS scan was attributed to the octadecanethiol capping agent used, which has a thiol-containing functional group [34]. Since the atomic concentration of S is reasonably similar (2 – 6.2 at.%), its effect on the properties have been considered not to affect the discussion to follow [22].

Table 4.2. Atomic ratio of Pt-M species present on the nanoparticle surface from XPS. (The presence of carbon is attributed to residues from the synthesis process and the XPS carbon substrate)

Sample	Molar ratio	Pt (at.%)	Co/Ni (at.%)	Pt:M	C (at.%)	O (at.%)	S (at.%)
Pt-NaBH ₄	1:0	2.2	0	-----	86.4	5.3	6.2
Pt-Co-	1:0.5	1.6	0.6	1:0.4	90.3	2.2	5.3
NaBH ₄	1:1	1.3	9.7	1:7.5	61.2	25.7	2.2
	1:3	1.0	1.0	1:1	88	5.0	3.0
Pt-Ni-	1:0.5	3.1	0.2	1:0.06	79.1	15.1	2.5
NaBH ₄	1:1	2.9	2.2	1:0.75	86.2	5.1	3.6
	1:3	1.0	0.5	1:0.5	85	8.0	3.0

Fig. 4.8 shows the Pt-4f spectrum of the monometallic Pt-NaBH₄ sample, with no Co or Ni added. The spectrum showed a typical Pt-4f doublet which was deconvoluted into 4 peaks representing metallic Pt, and Pt oxides or hydroxides. Literature reported Pt-4f peaks for Pt⁰ (71.2 and 74.5 eV), PtO (72.4 and 75.7 eV) and Pt(OH)₂ (72.6 and 75.9 eV) were used as reference data [29, 35, 36]. The peaks in Fig. 4.8, observed at 71.0 and 74.3 eV (3.3 eV separation between the two peaks), were assigned to Pt⁰ and those at 72.3 and 75.6 eV were assigned to Pt(OH)₂ [36] (Table 4.3). The ratio of Pt⁰ to Pt(OH)₂ was 1:7 (calculated from relative peak intensities) with the Pt(OH)₂ species dominating the surface of the material.

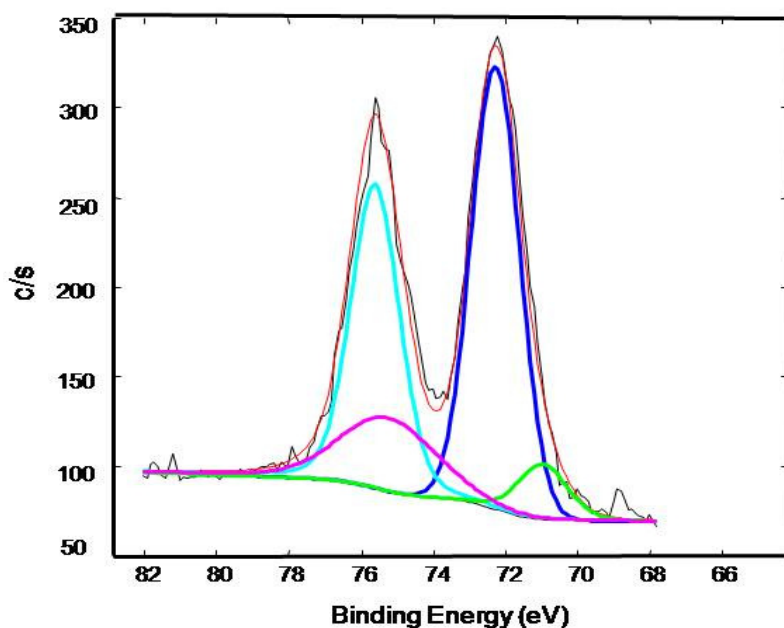


Figure 4.8. Pt-4f X-ray photoelectron spectra of monometallic platinum nanoparticles synthesized with NaBH₄.

The Pt-4f spectrum of the Pt-Co samples (reduced with NaBH₄) are presented in Fig. 4.9 with the Pt-Co-(1:1)-B peaks shown in Fig. 4.9a; the spectra for the rest of the samples are shown overlayed in Fig 4.9b. The Pt-4f_{7/2} peak positions representing Pt, PtO and Pt(OH)₂ are shown in Table 4.3. The binding energy (BE) peak separation for the Pt-4f doublet was 3.33 eV for the higher BE peak [36]. Peaks were observed at 71.1 eV (Pt⁰), 72.3 eV (Pt(OH)₂) for the Pt-Co-(1:0.5)-B and 72.1 eV (PtO) and 72.5 eV (Pt(OH)₂) for Pt-Co-(1:1)-B and 70.9 eV (Pt⁰) and 72.2 eV (Pt(OH)₂) for the Pt-Co-(1:3)-B samples. The ratio of the Pt⁰/Pt^{II} peaks were 1:1.7, 1:0.4 and 1:3 for the Pt-Co-(1:0.5)-B, the Pt-Co-(1:1)-B and the Pt-Co-(1:3)-B samples respectively. This was because Pt-Co-(1:0.5) contained a higher molar content of Pt from the synthesis process. The peak characteristics for Pt-Co-(1:0.5)-B was similar to Pt-(1:0)-B due mainly to the low content of Co in this sample. At a higher molar ratio, the surface was covered mostly by Pt-oxide and hydroxide

species. For bulk Pt-Co alloys, a shift in the Pt-4f BE has been observed and it has been attributed to the change in the electronic structure of Pt brought about by the addition of Co atoms [37]. This was also observed in the Pt-Co-(1:3)-B sample which contained larger amounts of Co compared to the Pt-Co-(1:0.5)-B sample. Therefore, analysis of the Pt-Co nanoparticles revealed that Pt-oxide and hydroxide species dominated on the surfaces.

Table 4.3. The binding energies and relative intensities of Pt species observed from Pt-4f_{7/2} XPS spectra for nanoparticles prepared NaBH₄ (Fig. 4.9 and Fig. 4.10).

Sample	Pt-4f_{7/2} BE (eV)	O-1s BE (eV)	Co-2p_{3/2} BE (eV)	Ni-2p_{3/2} BE (eV)
Pt	71.0 (12.5) 72.3 (87.5)	---		
Pt-Co-1:0.5	71.1 (12.2) 72.3 (87.8)	531.8 (58.0) 532.6 (42.0)	778.2 (56.6) 781.0 (33.8) 785.4 (9.60)	
Pt-Co-1:1	72.1 (28.2) 72.5 (71.8)	531.4 (53.5) 532.9 (30.6) 535.8 (15.9)	778.6 (17.5) 781.4 (33.8) 784.4 (48.7)	
Pt-Co-1:3	70.9 (25.0) 72.2 (75.0)	529.6 (4.5) 531.2 (71.9) 532.2 (23.6)	779.5 (44.0) 781.2 (38.8) 783.6 (17.2)	
Pt-Ni-1:0.5	71.0 (12.5) 72.3 (87.5)	531.2 (45.2) 532.2 (52.9) 533.1 (1.90)		852.8 (69.6) 854.5 (29.8) 857.6 (0.60)
Pt-Ni-1:1	70.6 (11.8) 72.3 (88.2)	531.8 (46.2) 532.1 (53.8)		853.1 (45.6) 855.4 (37.3) 856.5 (17.1)
Pt-Ni-1:3	70.9 (12.7) 72.2 (87.3)	529.5 (2.40) 531.3 (50.0) 532.2 (47.6)		853.9 (54.1) 855.1 (25.9) 856.9 (20.0)

() represent the relative peak intensities

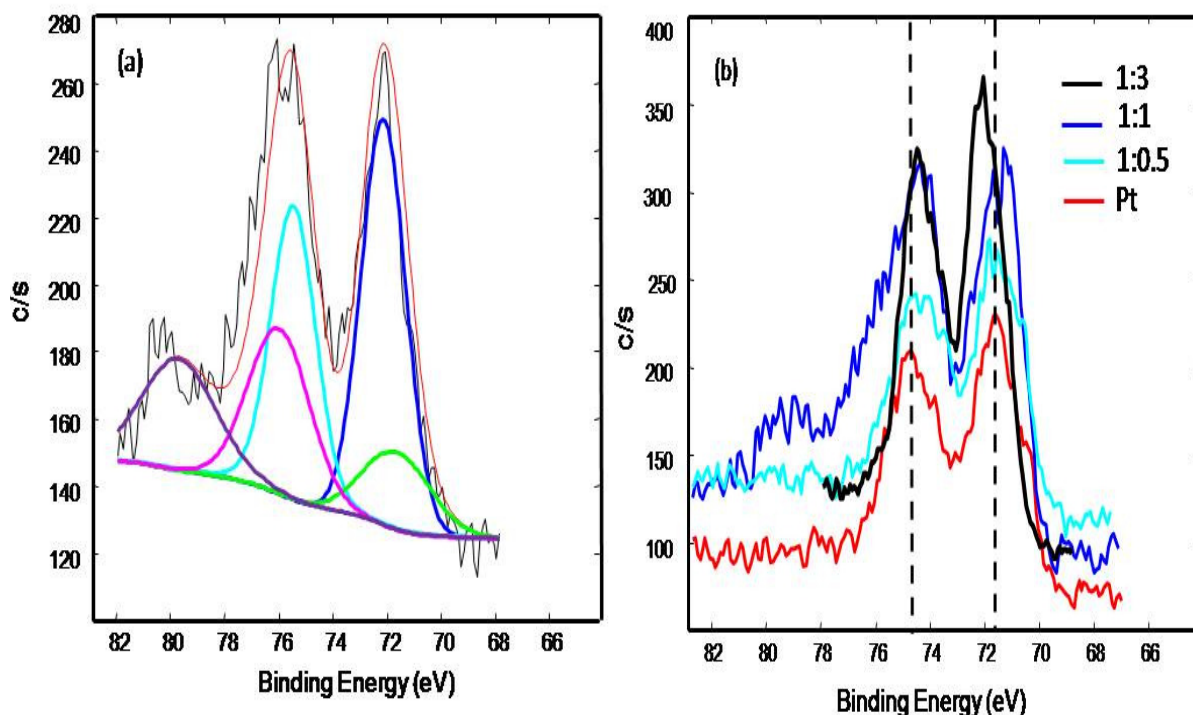


Figure 4.9. XPS spectra of (a) fitted Pt-Co 1:1 and (b) Pt-Co at different molar ratios synthesized using NaBH_4 .

The Pt-Ni samples (Fig. 4.10) showed the presence of Pt^0 at 71.0 eV for Pt-Ni-(1:0.5)-B, 70.6 eV for Pt-Ni-(1:1)-B and 70.9 for Pt-Ni-(1:3)-B, as well as $\text{Pt}(\text{OH})_2$ at 72.3 eV, 72.3 eV and 72.2 eV for the Pt-Ni-(1:0.5)-B, Pt-Ni-(1:1)-B and Pt-Ni-(1:3)-B, respectively (see table 4.3). As with the Pt-Co samples, the ratio of the $\text{Pt}^0/\text{Pt}^{\text{II}}$ species present on the surface was determined to be 1:7 for Pt-Ni-(1:0.5)-B, 1:7.5 for Pt-Ni-(1:1)-B and 1:7 for the Pt-Ni-(1:3)-B nanoparticles. Thus it is apparent that the surfaces of the Pt-Ni samples were dominated by Pt-hydroxide species. The oxide species on the surface of the nanoparticles were further evaluated by analysing their O-1s spectra.

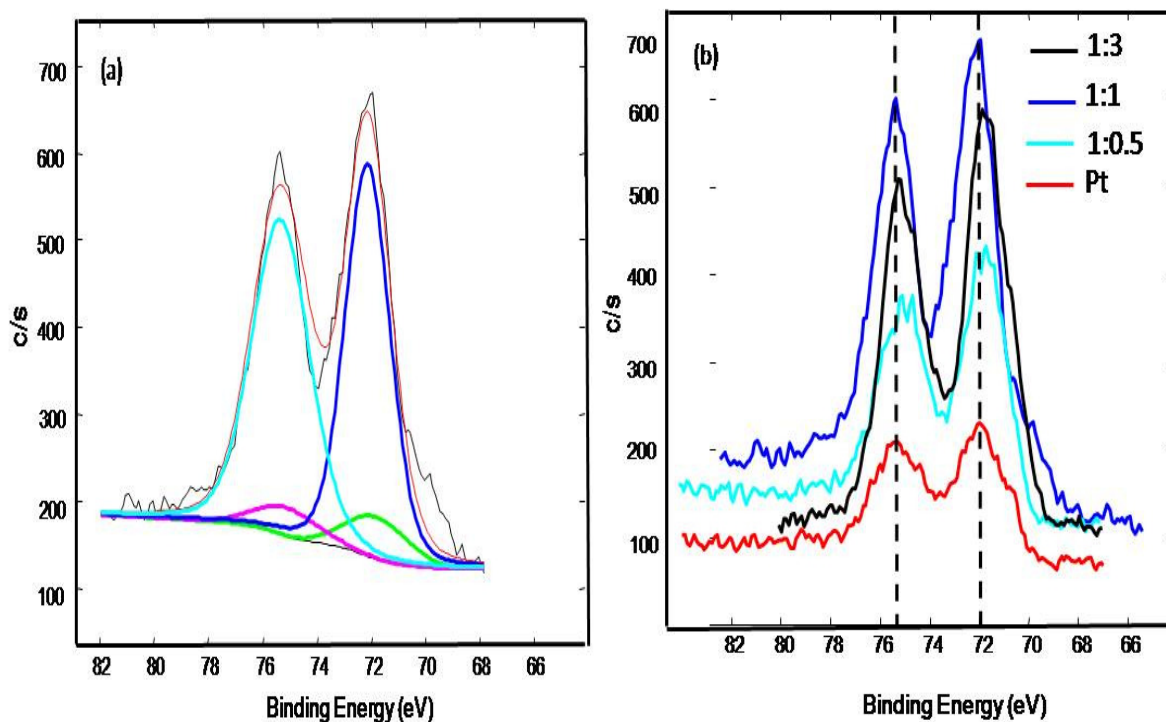
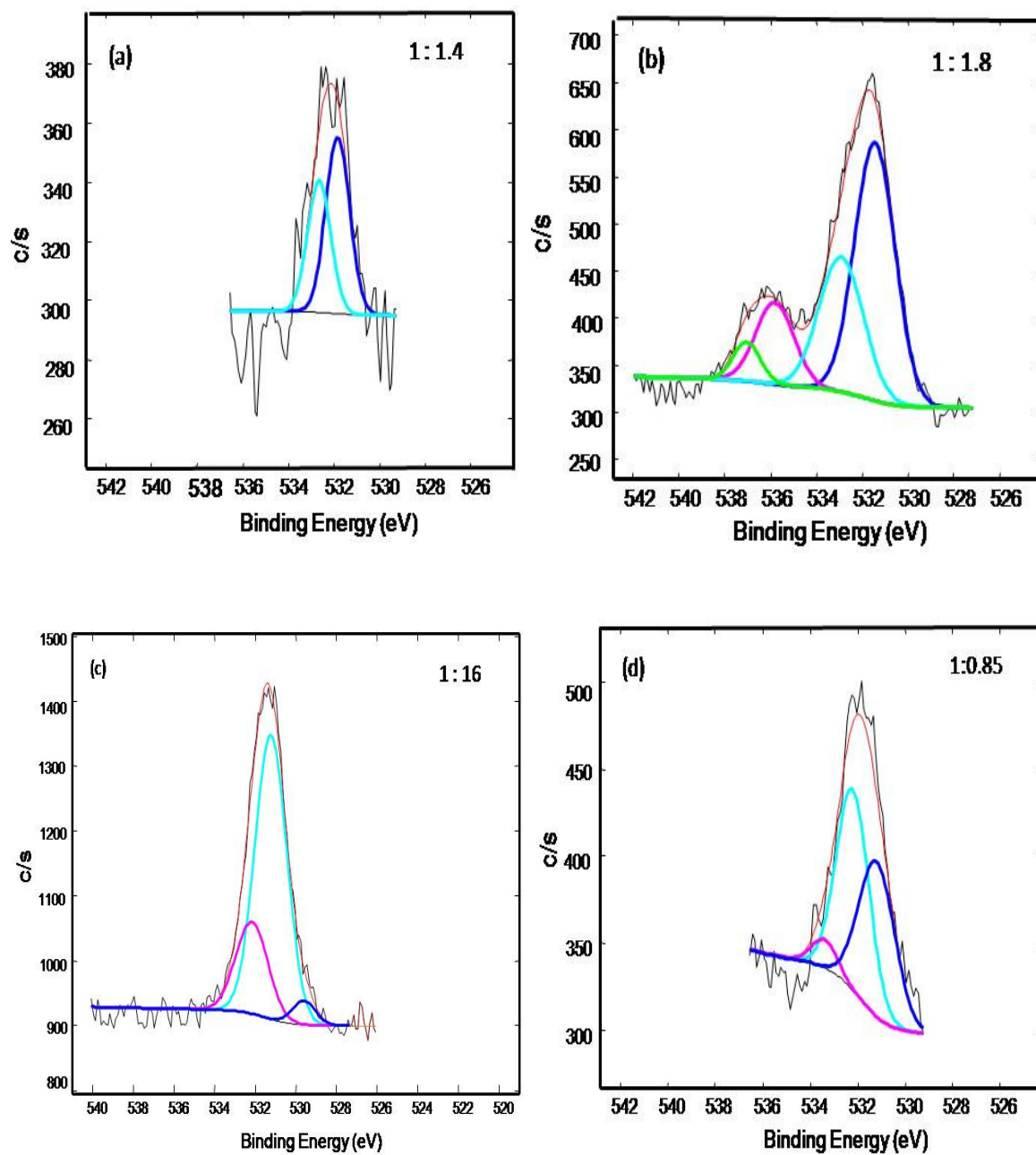


Figure 4.10. XPS spectra of (a) Pt-Ni 1:1 and (b) overlay of the molar ratio synthesized using NaBH_4 .

O-1s spectra

The O-1s spectra of the Pt-Co-B and Pt-Ni-B nanoparticles are presented in Fig. 4.11 and Table 4.3. The reported literature peaks for O-species attached to M (M = metal) varied with the type of O species present viz: M-O (529.79 eV), M-(OH) (531.07 eV), M-(H_2O) (533.5 eV) [38, 39]. The O-1s data revealed the presence of M-O (529.6 eV), M-OH (531.4, 531.8, 531.8 and 531.2 eV) and M-(H_2O) (532.9, 532.6, 532.1 and 532.2 eV) for the samples in Fig. 4.11 a – f, respectively (Table 4.3). The peak observed in Fig. 4.11b for the Pt-Co-(1:0.5)-B sample at 535.8 eV were reported at 535 – 537 eV for H_2O molecules on Pt/carbon nanofibres [40]. The ratio of these two O-species (i.e. the 1st and 2nd O peaks) is shown in the insert on the images where the Pt-Co samples presented more M-(H_2O) on the surface, and

the Pt-Ni samples showed M-OH dominance on the surface. There was a clear absence of M-O peaks, except for the 1:3 molar ratio samples, which is in agreement with what was obtained for the Pt-4f spectra where no metal oxide was detected on the surface.



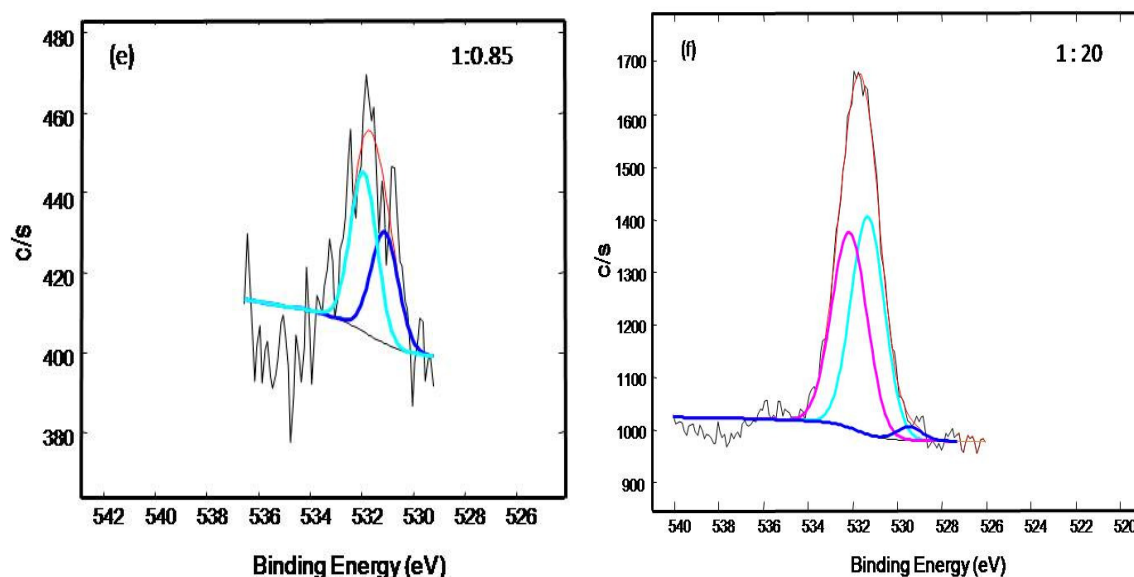


Figure 4.11. O-1s XPS spectra of Pt-Co, (a) 1:0.5, (b) 1:1, (c) 1:3 and Pt-Ni, (d) 1:0.5, (e) 1:1 and (f) 1:3 molar ratios nanoparticles synthesized using NaBH_4 .

Co/Ni-2p spectra

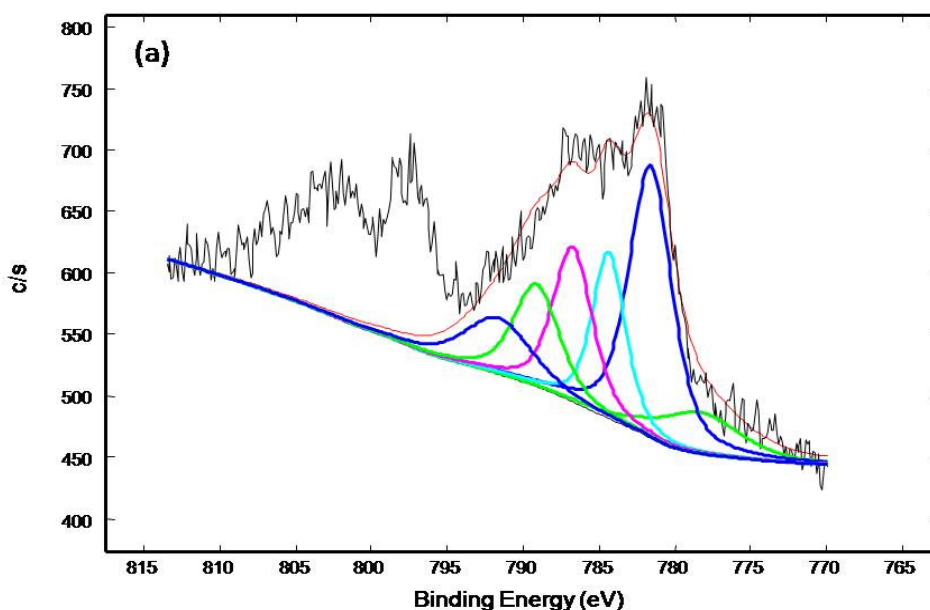
Co-2p (Fig. 4.12a) and Ni-2p (Fig. 4.12b) peaks were also analysed as they are associated with the alloying metals. The peak positions of the Co-2p_{3/2} and Ni-2p_{3/2} are shown in Table 4.3.

The Co-2p_{3/2} spectra were deconvoluted to show peaks corresponding to the Co⁰, CoO and Co(OH)₂ species. In literature, typical Co species are, Co⁰ (778.3 and 793.2 eV), CoO (780.4 and 795.8 eV) and CoOOH (781.4 and 796.6 eV) [24, 41]. Besides the satellite peaks caused by X-rays and energy loss peaks, there are photoelectron satellite peaks due to shake-up, multiplet splitting, and configuration interaction [36]. These often appear on the high binding energy side of the main peaks.

Metallic Co was present in all three Pt-Co samples at Pt-Co-(1:0.5)-B, Pt-Co-(1:1)-B and Pt-Co-(1:3)-B, 778.2, 778.6 and 779.5 eV respectively (note the shift for the Pt-

Co-(1:3)-B)) sample. The peaks at 781.0, 781.4 and 781.3 eV were assigned to CoOOH with satellite peaks at 785.4 eV, 784.4 and 783.6 eV for Pt-Co-(1:0.5)-B, Pt-Co-(1:1)-B and Pt-Co-(1:3)-B samples respectively. The ratio of the two species was 1:0.6 (Pt-Co-(1:0.5)-B), 1:1.9 (Pt-Co-(1:1)-B) and 1:0.25 (Pt-Co-(1:3)-B), where at lower Pt content the hydroxide species showed higher surface coverage. The Co-hydroxide species dominate on the surface of the materials when Co is added into the system.

The Ni-2p_{3/2} spectrum for Pt-Ni-(1:1)-B (Fig. 4.12b) was deconvoluted and fitted with 4 peaks. Traditional peaks for Ni-2p are associated with Ni⁰ (852.7 and 870.2 eV), Ni(OH)₂ (853.7 and 870.9 eV) and NiOH (854.6 and 871.8 eV) with satellite peaks found at higher binding energies [39]. The peaks obtained in this work were assigned to Ni⁰ (852.7 eV) and Ni(OH)₂ (854.5 eV) in a 1:1 ratio for Pt-Ni-(1:0.5)-B, and NiO (853.2 eV) and Ni(OH)₂ (854.2 eV) in a 2.5:1 ratio for Pt-Ni-(1:1)-B, and NiO (853.9 eV) and Ni(OH)₂ (855.1 eV) in a 2:1 ratio. As with the Co-2p peak analysis, the higher the concentration of Ni in the alloy, the higher the Ni-hydroxide concentration on the surface of the nanoparticles.



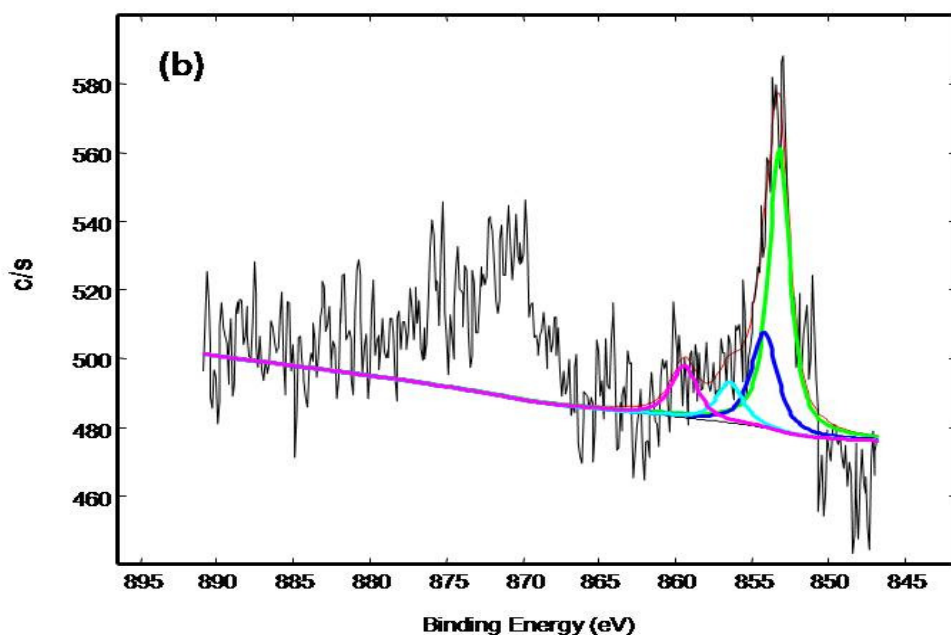


Figure 4.12. X-ray photoelectron spectra of NaBH_4 -reduced PtM nanoparticles, (a) Co-2p and (b) Ni-2p.

It is important to note that the co-reduction synthesis procedure resulted in atomic surface compositions that are different from the input molar ratios. In general, PtO species dominates on the surface suggesting preferential reduction of Co or Ni that act as nuclei for the Pt reduction. The amounts of surface species appear to depend on the molar ratio and not necessarily on the type of alloying metal used.

Further surface analysis was undertaken of the Pt-Ni nanoparticles reduced with N_2H_4 (Pt-4f, O-1s and Ni-2p), which are presented in section 4.4.2.

4.4.2. The effect of the reducing agent

In changing the reducing agent from NaBH_4 to N_2H_4 , the surface properties of the nanoparticles are expected to change. Compared to the NaBH_4 -reduced samples, the N_2H_4 reduced samples show a smaller amount of Pt on the surface (see table 4.4). This can be attributed to the higher reduction potential of NaBH_4 compared to N_2H_4 [42].

Table 4.4. Atomic ratio of Pt-M species present on the nanoparticles surface from XPS. (The presence of carbon is attributed to residues from the synthesis process and the XPS carbon substrate)

Sample	Molar ratio	Pt (at.%)	Ni (at.%)	Pt:Ni	C (at.%)	O (at.%)	S (at.%)
Pt- N_2H_4	1:0	1.3	0	1:0	92.4	1.8	4.6
Pt-Ni- N_2H_4	1:0.5	1.6	0.1	1:0.06	91.1	3.2	4.2
	1:1	1.2	0.1	1:0.08	93.6	0.1	5.2
	1:3	0.5	1.0	1:2	90	3.0	4.0

In Fig. 4.13 the Pt-4f spectrum of monometallic Pt reduced with N_2H_4 is presented. The spectrum shows a typical Pt-4f doublet which was deconvoluted into 4 peaks; two for Pt^0 (71.8 and 75.1 eV) and two for PtO (72.7 and 76.0 eV) (see table 4.5). The Pt^0 : PtO ratio was 1:13, and no hydroxide species were observed. This is in contrast with the results obtained for NaBH_4 -reduced monometallic Pt where, instead $\text{Pt}(\text{OH})_2$ was present on the surface of the nanoparticles. For both samples the amount of Pt^0 on the surface was less than PtO and $\text{Pt}(\text{OH})_2$.

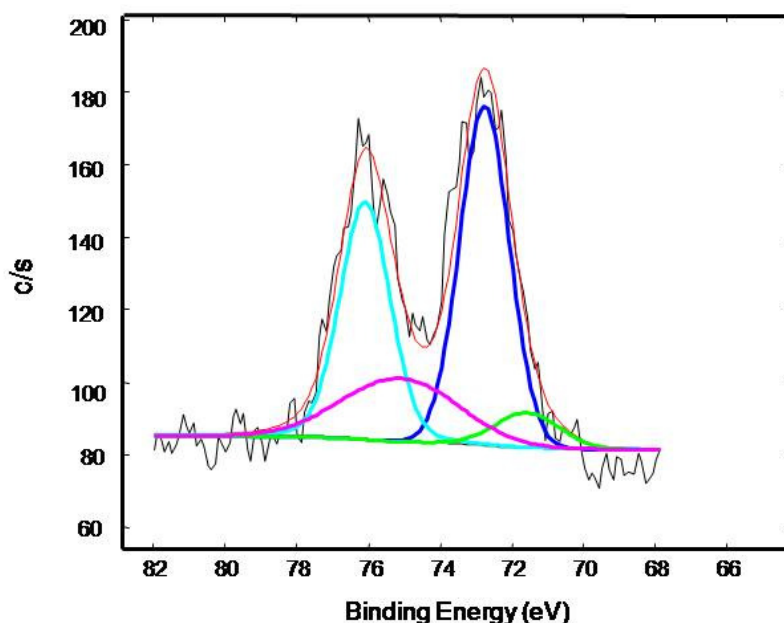


Figure 4.13. Pt-4f X-ray photoelectron spectra of monometallic platinum nanoparticles synthesized with N_2H_4 .

Pt-4f spectra for Pt-Ni samples are also presented in Fig. 4.14 and Table 4.5. Fig. 4.14a shows the deconvoluted peaks for the Pt-Ni-(1:1)-H sample and Fig. 4.14b show all of the Pt-4f spectra for the N_2H_4 -reduced Pt-Ni samples. The Pt-Ni-(1:1)-H peaks were deconvoluted, revealing 4 peaks that represent the two Pt species. The species present were determined to be $Pt(OH)_2$ (72.3 and 75.6 eV) and PtO (72.9 and 76.3 eV) in a 2.5:1 molar ratio. As with the previous Pt-4f analysis, the hydroxide species were dominant on the surface of the nanoparticles. For the Pt-Ni-(1:0.5)-H sample the peaks were observed at 71.4 and 74.8 eV assigned to Pt^0 , and 72.1 and 75.4 eV assigned to $Pt(OH)_2$. The peaks observed for Pt-Ni-(1:3)-H sample were also assigned to Pt^0 (71.4 and 74.7 eV) and $Pt(OH)_2$ (72.3 and 75.6 eV). The amount of the hydroxide species on the surface of the nanoparticles was 2.5 times more than that of the metallic Pt.

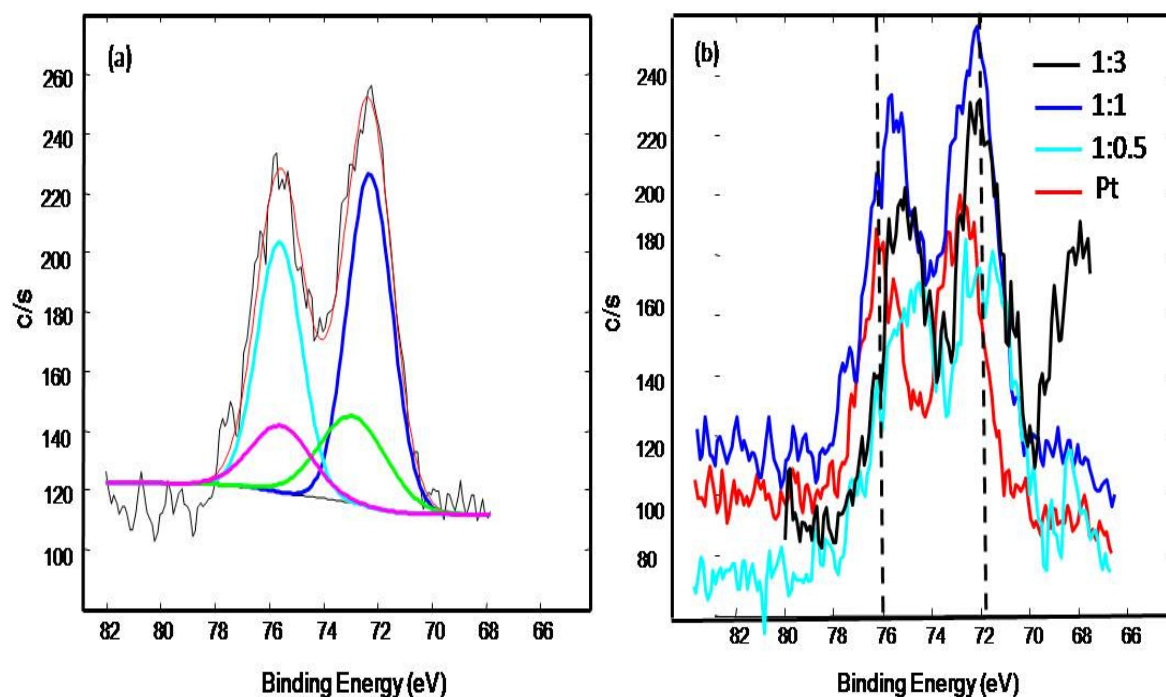


Figure 4.14. Pt-4f X-ray photoelectron spectra of (a) Pt-Ni 1:1 and (b) overlay of the Pt-Ni nanoparticles prepared by N_2H_4 .

The hydroxide species is the dominant species on the various samples. The O-1s spectra of the nanoparticles were further analyzed below to provide information on the surface oxide species.

O-1s spectra

The O-1s spectra of the N_2H_4 -reduced nanoparticles are shown in Fig. 4.15 and Table 4.5. The observation from these spectra confirms that there exist more M-OH (531.1 eV) species than M-O (529.7 eV) on the surface of the materials.

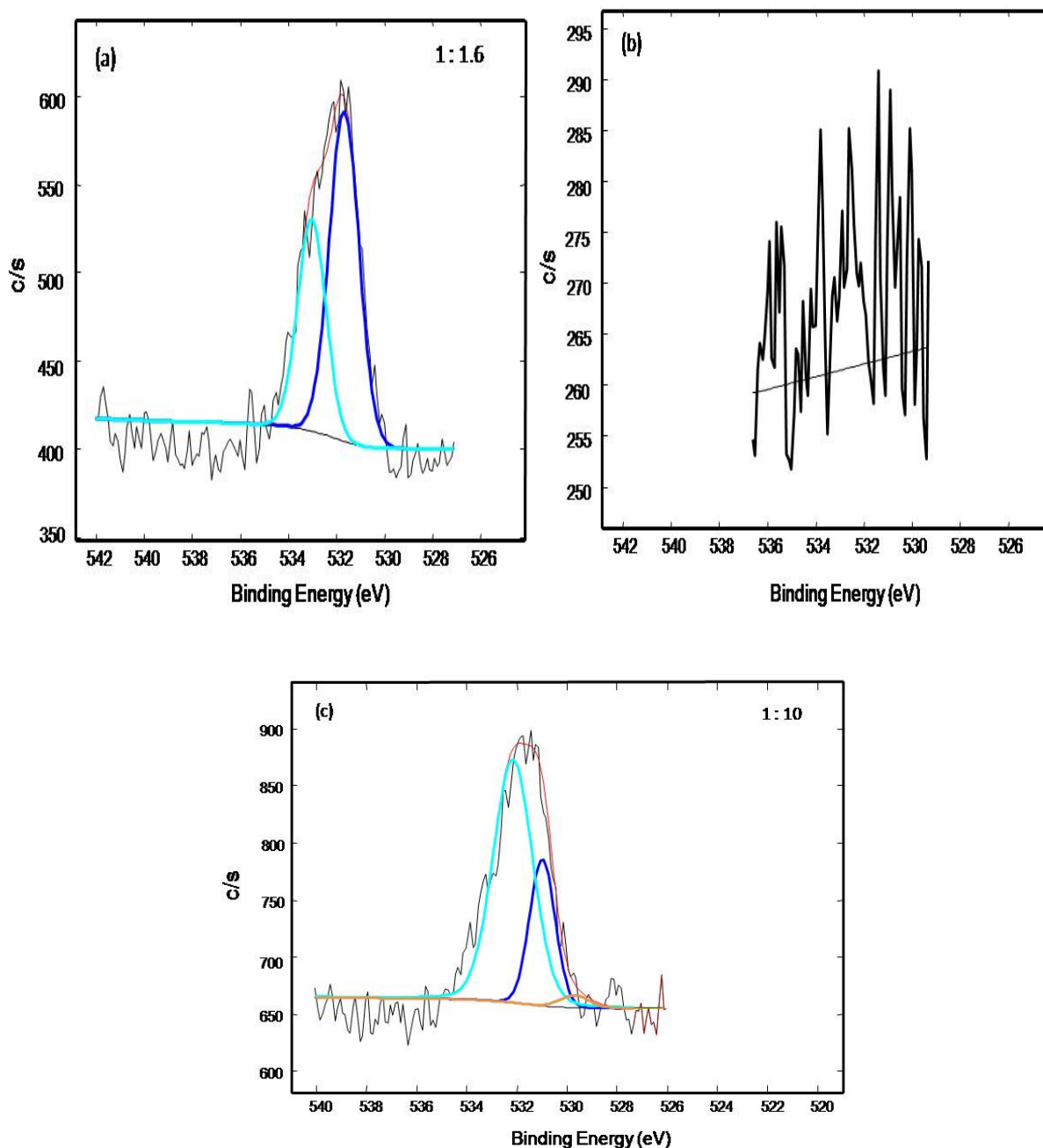


Figure 4.15. O-1s XPS spectra of Pt-Ni (a) 1:0.5, (b) 1:1 and (c) 1:3 nanoparticles synthesized using N₂H₄.

In Fig. 4.15a, the O-1s spectra of Pt-Ni-(1:0.5)-H is presented and also contain 2 peaks assigned to M-(OH) (531.7 eV) and M-(H₂O) (532.0 eV) in a 1.6:1 ratio, and M-O (529.7 eV) and M-OH (531.0) in a 1:10 ratio. There were no defined O-1s peaks for the Pt-Ni-(1:1)-H samples (Fig. 4.15b) which indicates a low concentration of O

(0.1at.%) on the surface of this sample (see table 4.4). Analysis of these spectra also confirmed that the surface is covered in metal oxide species with some adsorbed oxygen and water molecules [41].

Table 4.5. The binding energies and relative intensities of the species observed from Pt-4f, O-1s and Ni-2p XPS spectra for nanoparticles prepared with N₂H₄.

Sample	Pt-4f_{7/2} BE (eV)	O-1s BE (eV)	Ni-2p_{3/2} BE (eV)
Pt	71.8 (7.20) 72.7 (92.8)	-----	
Pt-Ni-1:0.5	71.0 (65.2) 72.3 (34.8)	531.5 (45.0) 532.4 (38.5) 533.4 (16.5)	853.8 (2.30) 855.9 (72.2) 857.6 (25.5)
Pt-Ni-1:1	72.3 (71.9) 72.9 (28.1)	-----	853.2 (4.10) 854.3 (69.5) 856.4 (26.4)
Pt-Ni-1:3	71.4 (18.7) 72.3 (81.3)	529.7 (2.60) 531.0 (26.3) 532.2 (71.1)	853.9 (68.6) 856.1 (24.6) 857.2 (6.80)

() represent the relative peak intensities

Ni-2p spectra

The Ni-2p spectra of the N₂H₄-reduced Pt-Ni nanoparticles are shown in Fig. 4.16 and Table 4.5. The Pt-Ni-(1:0.5)-H sample exhibited both Ni(OH)₂ (853.8 eV) and NiOH (855.9 eV) species as well as satellite peak at 857.6 eV. The amount of hydroxide species was 32 times that of the oxide species. The species obtained for Pt-Ni-(1:1)-H were Ni(OH)₂ (853.2 eV), NiOH (854.3 eV) with satellite peaks at 856.4 eV. The amount of Ni(OH)₂ in this case was 16 times less than that of the adjacent

peak at 854.3 eV. As the amount of Ni is increased further (Pt-Ni-(1:3)-H), the peaks were observed at 853.9 eV (NiO) and 856.1 eV (Ni(OH)₂) with the oxide species dominating the surface.

Thus it is apparent that in using the conventional metal reduction procedure, there is a preference towards the formation of hydroxide species over the oxide species on the surface.

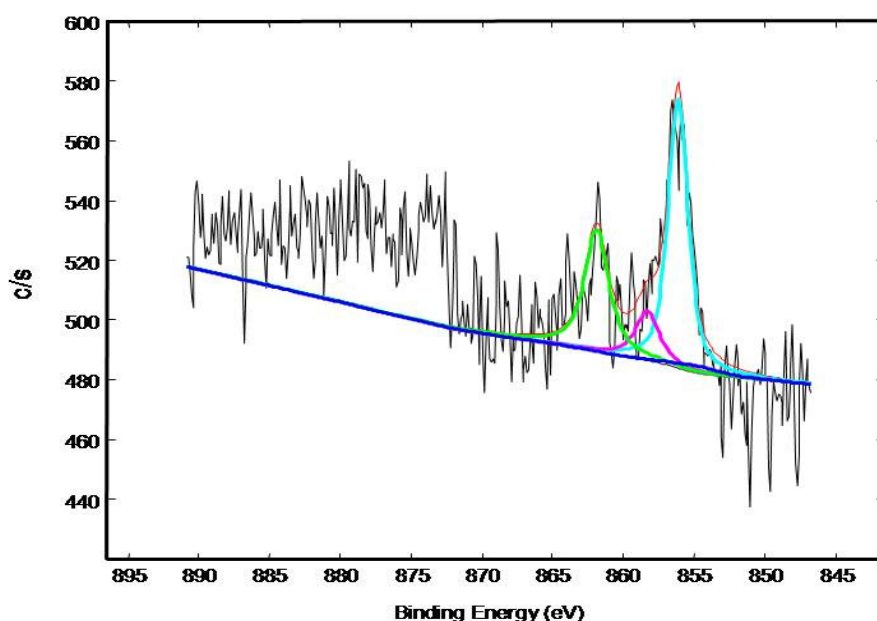


Figure 4.16. Ni-2p X-ray photoelectron spectra of N₂H₄-reduced nanoparticles with 1:1 molar ratio.

The information obtained from the XPS data for the Pt-Co and Pt-Ni nanoparticles can be summarized as follows:

- All the samples showed the presence of metallic Pt on the surface, the relative amounts differed with the two different reducing agents where the strong reducing agent (NaBH₄) showed higher levels of Pt than the weaker reducing agents (N₂H₄).

- The amount of hydroxide bound to the Pt, Co or Ni found on the surfaces of Pt/Co and Pt/Ni was greater than the oxide species. This was also confirmed by O-1s spectra where only M-OH species were dominant.
- Increasing the M (Co/Ni) molar ratio resulted in the presence of more M-OH species on the surface of the nanoparticles.
- There was Pt segregation for both metals at higher Pt to Co or Ni molar ratios, i.e. for the Pt-M-(1:0.5) nanoparticles.

Though there are oxides/ hydroxides present for all the samples as determined by XPS analysis, metal oxide species were not observed in the XRD spectra, instead the Pt retained its fcc lattice structure. It can be assumed that the higher oxidation states of Ni and Co atoms are concentrated on the surface of the nanoparticles without forming part of the Pt lattice [24].

The presence of surface oxides and hydroxides of Ni and Co, could provide an oxygen source and lead to an increase in the electrocatalytic activity of the nanoparticles particularly for the methanol oxidation reaction (MOR) [43, 44]. The electrocatalytic activities of these nanoparticles were tested in an acid and alcohol electrolyte to evaluate this possibility.

4.5. Electrochemical activity

4.5.1. Cyclic voltammetry

Cyclic voltammetry was used to determine the electrocatalytic activity of the Pt-Co and Pt-Ni samples in 0.5 M H_2SO_4 electrolyte solution after purging with N_2 for 30 minutes. The conventionally synthesized electrocatalysts in this chapter did not exhibit defined hydrogen adsorption/desorption regions (0 – 0.4 V). They presented a large double layer region, as observed by Spinacé et al. for PtRu/C electrocatalysts prepared by deposition of Pt on carbon-supported Ru nanoparticles [45]. The voltammograms of the Pt-Co nanoparticles in NaBH_4 (Fig. 4.17) showed a change in the electrocatalytic behaviour of the nanoparticles in an acidic electrolyte with change in the Pt/Co or Pt/Ni molar ratio. There was a decrease in the current density with an increase in Co, with the Pt-Co-(1:3)-B sample giving the lowest current density output over the same potential range. This behaviour is independent of the atomic concentration of the Pt and Co on the surface of the nanoparticles as obtained from XPS data (see table 4.2 and 4.4).

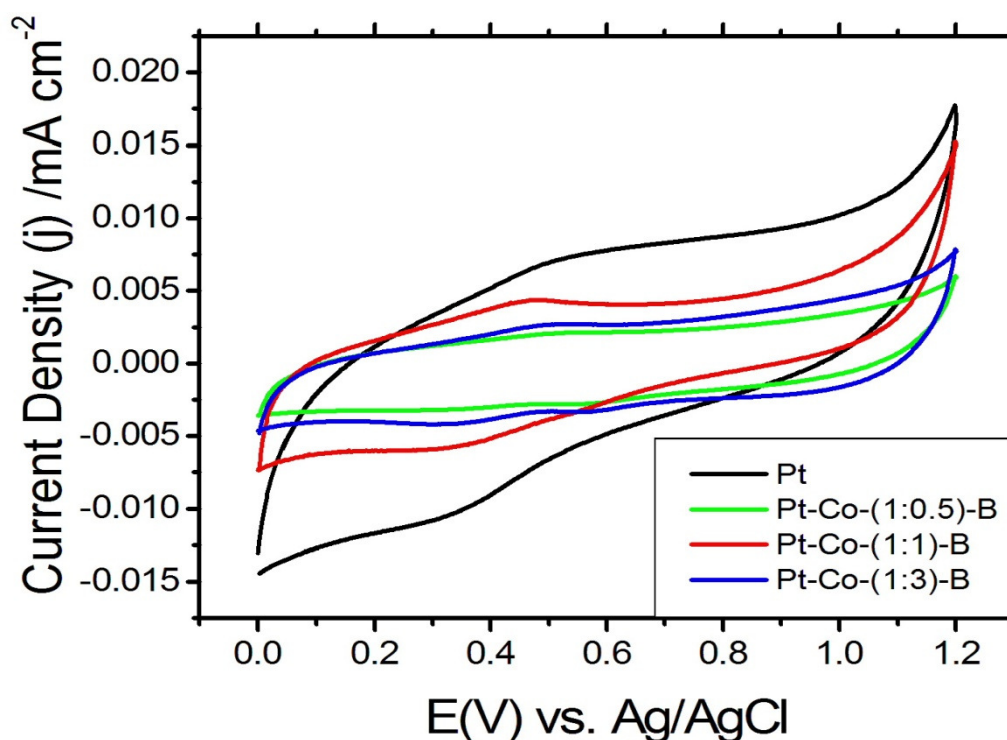


Figure 4.17. Cyclic voltammograms of Pt-Co nanoparticles synthesized with (a) NaBH_4 and (b) N_2H_4 in 0.5 M H_2SO_4 at 10 mV/s.

On the other hand, the Pt-Ni- NaBH_4 catalysts (Fig. 4.18a) exhibited completely different behaviour where the Pt-Ni-(1:1)-B sample showed typical PtO reduction/oxidation peaks, [46], at 0.9 V and 0.5 V respectively. The Pt-Ni-(1:0.5) and Pt-Ni-(1:3) samples as well as Pt-Ni-(1:0)-B showed little activity in the acid electrolyte. This behaviour of nearly identical CV profiles suggests that the electrocatalytic properties of these materials in acidic medium is not highly affected by the change in molar ratio of the bimetallic nanoparticles [47].

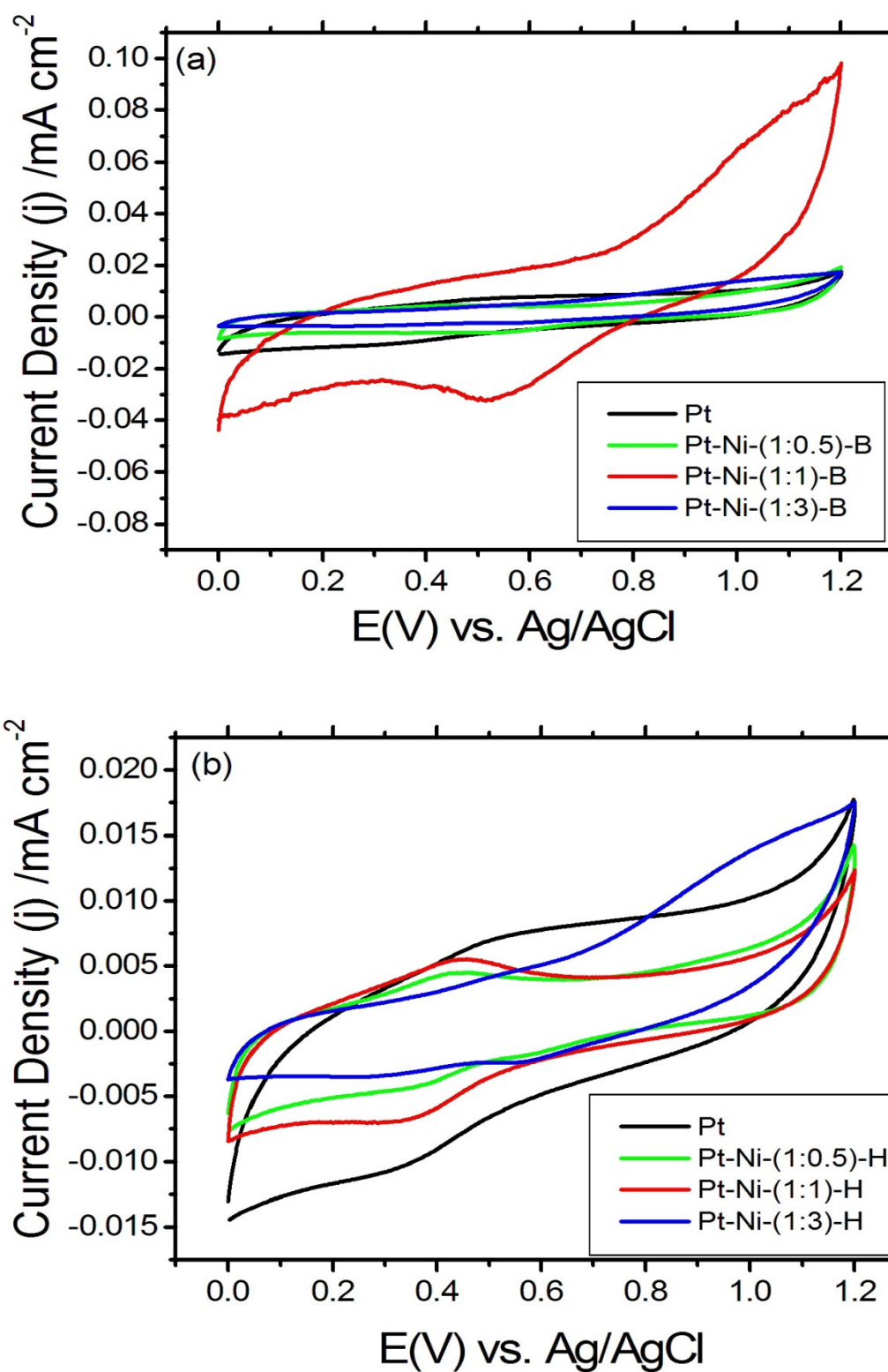


Figure 4.18. Voltammograms of Pt-Ni nanoparticles, (a) NaBH₄ and (b) N₂H₄ in 0.5 M H₂SO₄ at 10 mVs.

For the Pt-Ni samples reduced with N_2H_4 , little activity was observed for all the samples (Fig. 4.18b). The current density of the Pt-Ni-(1:0)-H was the highest and subsequently decreased with the addition of Ni. It should be noted that all the samples above did not exhibit H_2 adsorption/desorption peaks, [48], as well as any double-layer capacitance. This behaviour is consistent with the TEM study which showed large and dispersed nanoparticles. This in turn results in a less active catalyst in an acidic medium.

Therefore the catalysts were tested in an alcohol (methanol) electrolyte, i.e. 0.5 M H_2SO_4 + 1.0 M CH_3OH , to evaluate the current response to applied voltage (0 – 1.2 V) for the various samples.

4.5.2. Methanol oxidation reaction (MOR) analysis

The methanol oxidation activity of the catalysts was tested using the same set-up as above but in an alcohol electrolyte (0.5 M H_2SO_4 + 1.0 M CH_3OH). The resulting voltammograms in methanol for the Pt-Co catalysts prepared with NaBH_4 are presented. In Fig. 4.19, there was no observed MOR activity for the monometallic Pt, (i.e. Pt) as well as the Pt-Co-(1:1)-B samples. This can be attributed to a number of factors including the lack of Co-oxide species on the surface of these catalysts (observed from XPS analysis) which are needed for enhancement in the electrocatalytic activity. On the other hand, the Pt-Co-(1:0.5) and Pt-Co-(1:3) catalysts exhibited typical MOR behaviour as seen by the methanol oxidation peak, I_f , observed in the forward scan (0.63 V, 0.015 mA/cm^2 and 0.62 V, 0.025 mA/cm^2)

as well as the reverse peak, I_b , (0.47 V, 0.008 mA/cm² and 0.49 V, 0.016 mA/cm²) for the 1:0.5 and 1:3 molar ratios respectively (see Table 4.6).

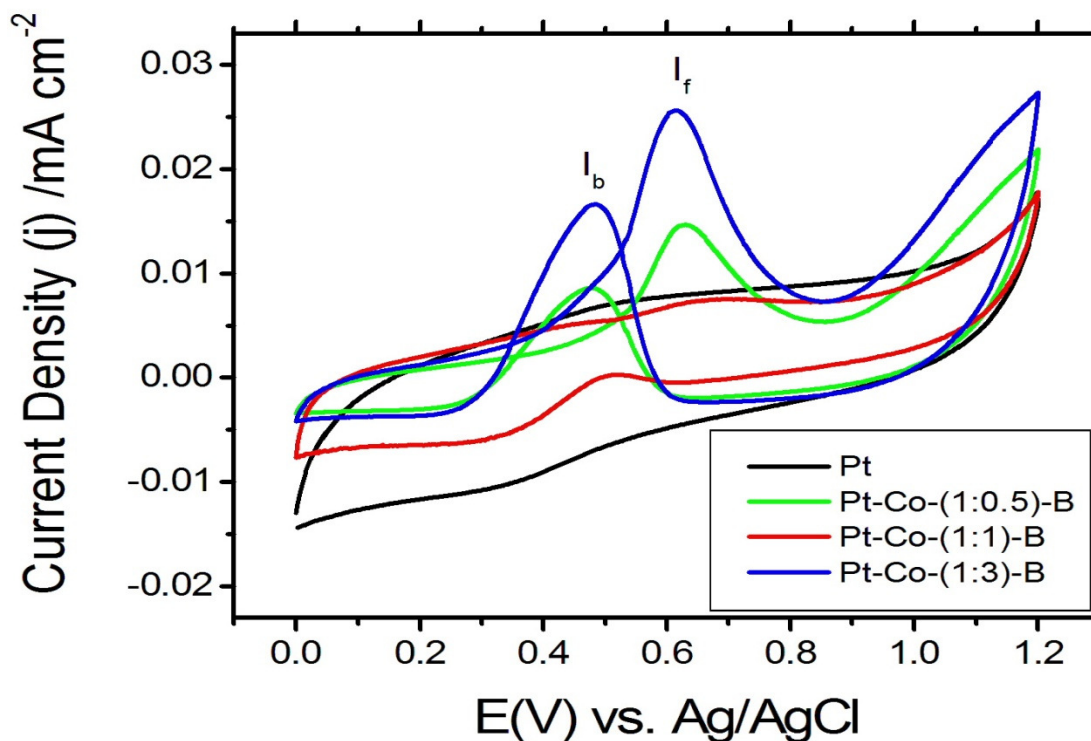


Figure 4.19. MOR voltammograms of NaBH₄-reduced Pt-Co nanoparticles in 0.5 M H₂SO₄ + 1.0 M CH₃OH electrolyte solution.

The onset potentials for methanol oxidation were observed at potentials of 0.39 (Pt-Co-1:0.5) and 0.45 V (Pt-Co-1:3). These values should be low if methanol is to adsorb onto the surface of the catalysts [34]. These values are positively shifted compared to the bulk Pt electrode, where the onset potential is at 0.2 V [49]. The onset potential can also be correlated with the activation energy of the reaction (E_a), where the lower the onset potential, the lower the energy of activation needed for MOR [50]. Therefore in comparing the two Pt-Co catalysts, it is seen that MOR occurs easily for the low Co content (1:0.5) sample compared to the higher Co molar ratio (1:3) catalyst. This result suggests that in adding the Co into the Pt lattice, the

ability of the catalysts to adsorb methanol is hindered. This results was also reported by Chan et al. [24], where they observed higher activity at an optimum molar ratio of 1:0.5 for Pt-Co nanoparticles. They attributed this effect to the changes in the electronic properties of Pt at higher molar ratios as well as the formation of Co oxides on the nanoparticles surface.

Table 4.6. Peak parameters of MOR voltammograms for the Pt-Co nanoparticles reduced with NaBH₄.

Sample	Ratio	E _{onset}	E _f (V)	I _f (mA/cm ²)	E _b (V)	I _b (mA/cm ²)	I _f /I _b	I(mA/mgPt)
Pt-Co	1:0.5	0.39	0.63	0.015	0.47	0.008	1.9	0.115
	1:3	0.45	0.62	0.025	0.49	0.016	1.6	0.023

The ratio of forward the anodic peak current (I_f) to the reverse peak current (I_b) is used to determine the tolerance of the catalysts to poisonous carbon-containing species that are formed during the methanol break-down process [51, 52]. For the catalysts in this section, the I_f/I_b values were calculated as 1.9 and 1.6 for the Pt-Co-(1:0.5)-B and Pt-Co-(1:3)-B catalysts respectively. This indicates that the catalysts possess a good ability to remove carbonaceous species. In order for the catalyst to be commercially viable, there is a need to determine the mass current density, i.e. current output per mass of Pt loading (mA / mg Pt) [34, 53]. The mass current density was calculated as 0.115 and 0.023 mA / mg Pt for the 1:0.5 and 1:3 molar ratios, respectively, showing the superiority of the Pt-Co-(1:0.5)-B catalyst. This together with the onset potentials shows that the lower Co content catalysts exhibit the best behaviour.

The electrocatalytic behaviour exhibited by the Pt-Ni samples was recorded and found to be different in that there was clear activity for methanol oxidation for the catalysts prepared with both NaBH_4 (Fig. 4.20a), and N_2H_4 (Fig. 4.20b and Table 4.7). The Pt-Ni-(1:1)-B sample showed the most activity when compared to the other samples reduced with NaBH_4 (Fig. 4.20a) with peak current density observed at 0.25 mA/cm^2 compared to 0.022 mA/cm^2 and 0.035 mA/cm^2 for Pt-Ni-(1:0.5)-B and Pt-Ni-(1:3)-B respectively (shown in the insert image). There was no methanol oxidation activity observed for the Pt sample. The onset potentials for the 3 samples were found to be; 0.38 V (1:1), 0.45 V (1:0.5) and 0.36 V (1:3) (table 4.6), indicating that the Pt-Ni-(1:3)-B catalyst was better at adsorbing methanol. As for the Pt-Co samples, the mass current density of the samples was calculated and the observed trend was found to be: $0.14 \text{ mA/mg Pt (1:1)} > 0.033 \text{ mA/mg Pt (1:3)} > 0.026 \text{ mA/mgPt (1:0.5)}$. The ratio of I_f/I_b was 1.70, 1.78 and 1.46 for molar ratios of 1:0.5, 1:1 and 1:3 respectively, which all indicate the catalysts have a good ability to remove carbonaceous species that block the catalytically active sites [34].

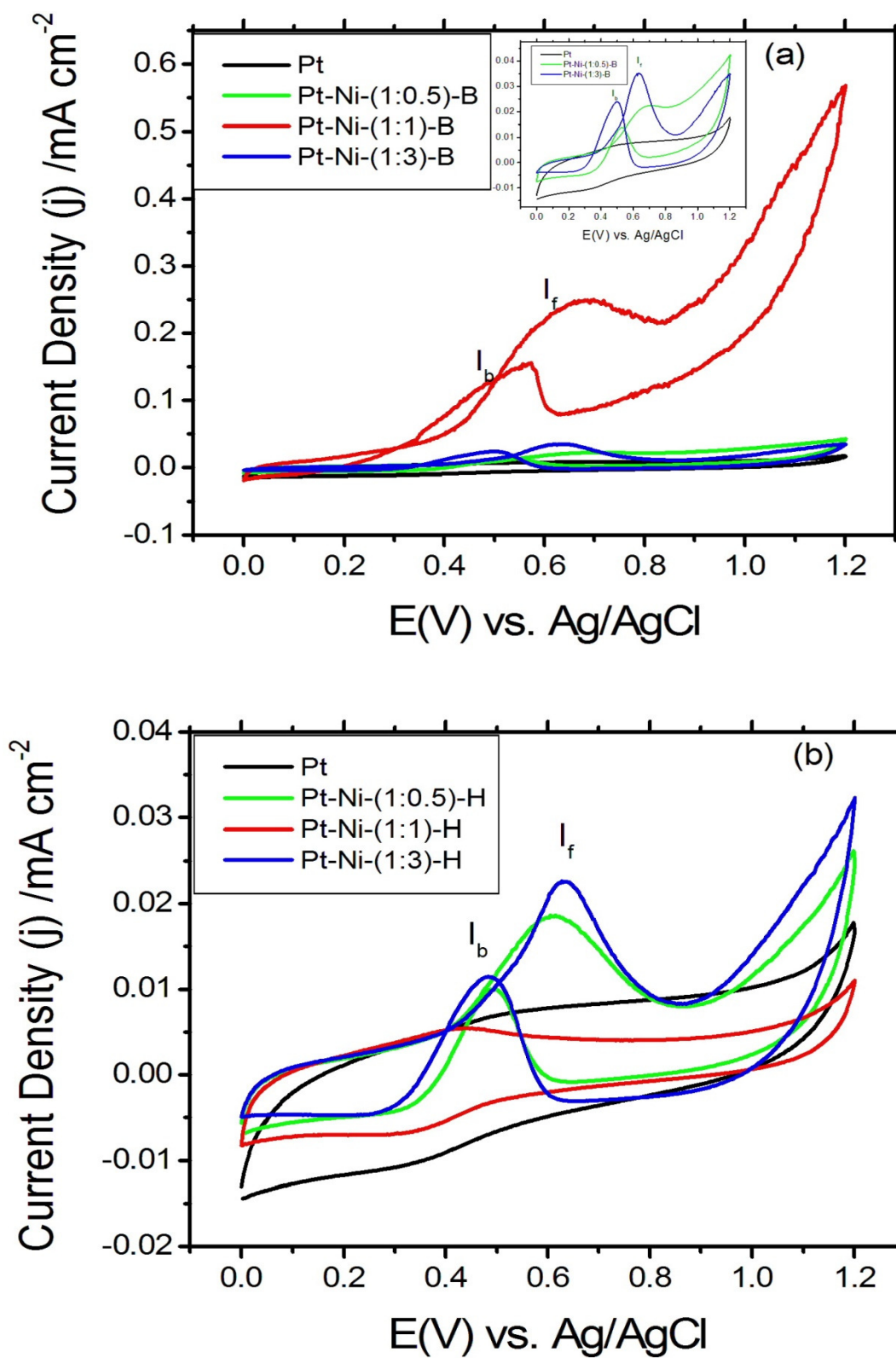


Figure 4.20. MOR voltammograms of Pt-Ni nanoparticles, (a) NaBH_4 and (b) N_2H_4 .

Fig. 4.20b shows the methanol oxidation voltammograms of Pt-Ni-N₂H₄ reduced nanoparticles. There was no MOR activity observed for the Pt-Ni-(1:1)-H catalyst which is in contrast to what was obtained for the Pt-Ni-(1:1)-B sample. The low activity observed for Pt-Ni-(1:1)-H is related to the low concentration of oxygen obtained from XPS analysis. The onset potentials of the active catalysts, i.e. using 1:0.5 and 1:3 molar ratios, were observed at 0.39 V and 0.42 V respectively (see Table 4.7) indicating similar methanol adsorption behaviour. The peak current densities of both active N₂H₄-reduced Pt-Ni samples was 10 times less than Pt-Ni-(1;1)-B which shows that the N₂H₄-reduced catalysts were inferior to the NaBH₄-reduced catalyst. This is also seen by the lower mass current densities of these catalysts, viz, 0.027 mA/mgPt and 0.043 mA/mgPt for the 1:0.5 and 1:3 molar ratios in comparison to NaBH₄-reduced catalysts.

The peak current ratios of the forward and reverse scan were also calculated (see table 4.7) and determined to be 1.8 (Pt-Ni-(1:0.5)-H) and 2.1 (Pt-Ni-(1:3)-H), signalling the ability of these catalysts to remove carbonaceous species formed in the forward scan reactions.

Table 4.7. Peak parameters of MOR voltammograms for the Pt-Ni nanoparticles reduced with NaBH₄ and N₂H₄.

Sample	Ratio	E _{onset}	E _f (V)	I _f (mA/cm ²)	E _b (V)	I _b (mA/cm ²)	I _f /I _b	I(mA/mgPt)
NaBH₄	1:0.5	0.45	0.67	0.022	0.53	0.013	1.70	0.026
	1:1	0.38	0.67	0.25	0.56	0.14	1.78	0.14
	1:3	0.36	0.63	0.035	0.50	0.024	1.46	0.033
N₂H₄	1:0.5	0.39	0.61	0.018	0.49	0.010	1.8	0.027
	1:3	0.42	0.63	0.023	0.48	0.011	2.10	0.043

4.5.3. Chronoamperometry measurements

The current vs. time behaviour of the catalysts is presented in Fig. 4.21. These measurements were performed in order to determine the long term stability of the catalysts, under a steady potential (0.5 V) in an alcohol electrolyte. The polarization current for all the curves showed an initial sharp increase from $t = 0$ for approximately 30 s before changes in their behaviour. This sharp increases can be caused by the formation of intermediate species during MOR [54], which poison the catalysts. It was observed that when using the different alloying metals, the chronoamperometric behaviour was completely different. The Pt-Co catalysts (Fig. 4.21a) show a steep decline in current after 30 s which stabilizes after 950 s. This is in contrast to the Ni catalysts, which did not exhibit a decline in current, but produced a steady current after 25 s.

This behaviour indicates that the Pt-Ni nanostructures possessed higher electrocatalytic stability when compared to Pt-Co. The effect of molar ratio was not examined. It should also be noted that the anodic current of the Pt-Co catalyst was higher than both Pt-Ni samples which possessed similar currents. Therefore the current at 1200 s was calculated for the Pt-Co as 42.0 % of initial current (Fig. 4.21a).

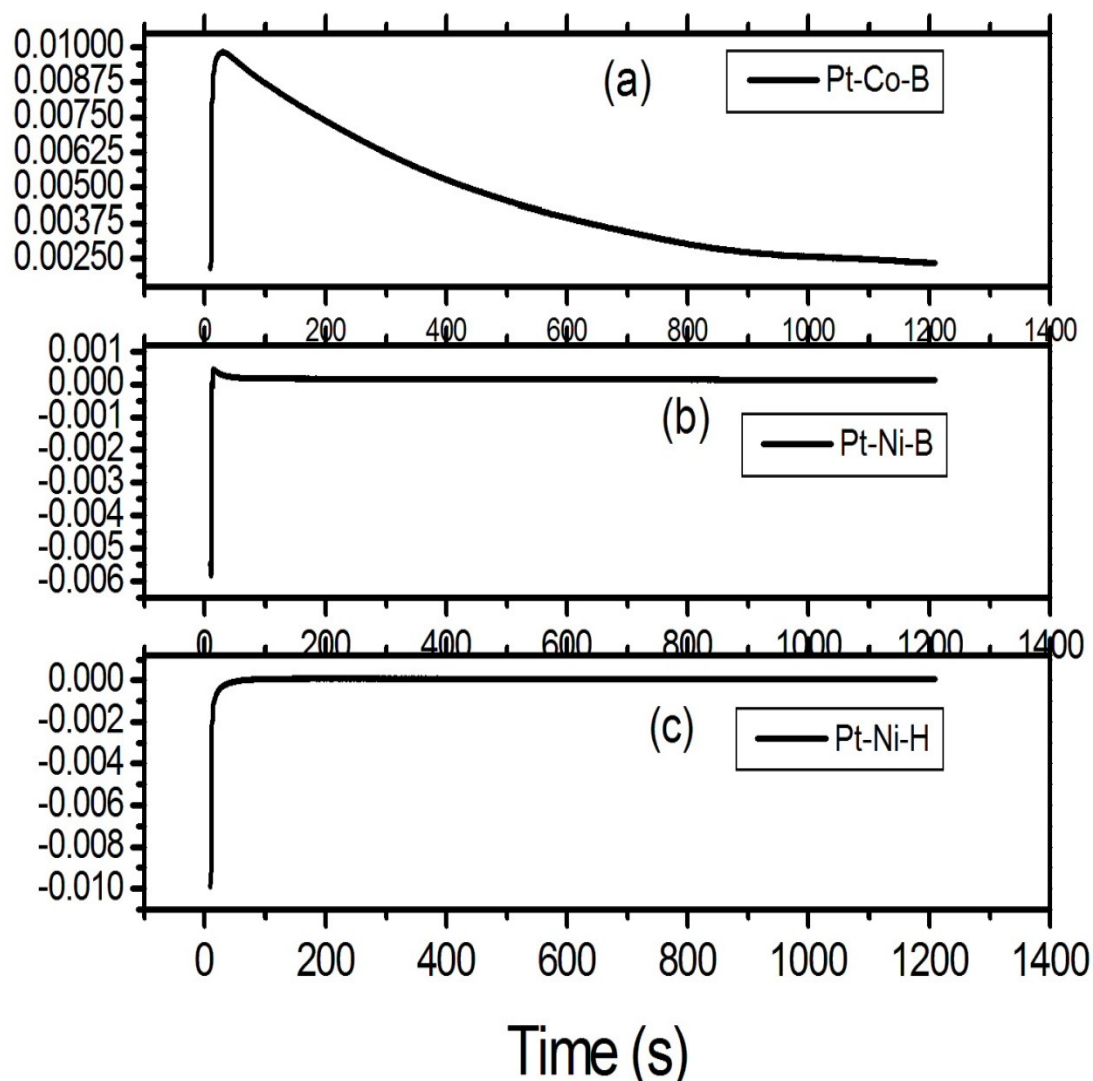


Figure 4.21. The chronoamperometry curves for (a) Pt-Co-B, (b) Pt-Ni-B and (c) Pt-Ni-H electrocatalysts using the 1:0.5 molar ratio.

4.6. Conclusion

Bimetallic Pt-Co and Pt-Ni nanoparticles were obtained using a co-reduction synthesis procedure. A trend was observed where the particle / crystallite sizes decreased as the amount of the alloying metal increased and when the reductant

strength was lower. This makes them more susceptible to particle agglomeration. The change in molar ratio also affects the nucleation and growth process and different morphologies were obtained for both the Pt-Co and Pt-Ni nanoparticles. The XRD spectra showed that the Pt (111) peaks at $2\theta \sim 40^\circ$ were observed even after the addition of Ni and Co into the solution, suggesting the formation of a Pt alloy structure. The lack of Co or Ni XRD peaks can also be attributed to the formation of amorphous Co or Ni phases. This was more prominent for the N_2H_4 -reduced nanoparticles in comparison to the NaBH_4 -reduced nanoparticles. XPS studies revealed that the surface atomic concentration of the catalysts is less dependent of an initial molar ratio but is greatly dependent on the type of reducing agent that was used. The general behaviour was that the Pt atomic percentage decreased with an increase in the alloying metal content.

The addition of the second metal resulted in predominant the formation of metal hydroxide species and less of metal oxide species. The catalysts showed poor MOR activity, especially the Pt-Co samples regardless of the reducing agent used. However, the Pt-Ni samples did exhibit some activity towards MOR for both the NaBH_4 and N_2H_4 -reduced nanoparticles.

Therefore these studies reveal that reaction parameters such as reducing agents and alloying metal influence the bulk and surface properties of the nanoparticles. Though the catalysts reported in this chapter are active, they exhibited low current output. Therefore, the need for other synthesis procedures to generate higher current outputs is needed. Approaches to advance this possibility are described in Chapter 5 -6.

References

1. Leonard, B.M., N.S.P. Bhuvanesh, and R.E. Schaak, *Low-temperature polyol synthesis of AuCuSn₂ and AuNiSn₂: using solution chemistry to access ternary intermetallic compounds as nanocrystals*. Journal of American Chemical Society, 2005. **127**: p. 7326 - 7327.
2. Alayoglu, S. and B. Eichhorn, *Rh-Pt bimetallic catalysts: synthesis, characterization, and catalysis of core-shell, alloy, and monometallic nanoparticles*. Journal of American Chemical Society, 2008. **130**: p. 17479 - 17486.
3. Dai, J., et al., *PtCo/Au nanocomposite: synthesis, characterization and magnetic properties*. Physica E, 2007. **39**: p. 271 - 276.
4. Bala, H., et al., *Preparation and characteristics of calcium carbonate/silica nanoparticles with core-shell structure*. Colloids and Surfaces A: Physicochem. Eng. Aspects, 2007. **294**: p. 8–13.
5. Peng, Z. and H. Yang, *Designer platinum nanoparticles: Control of shape, composition in alloy, nanostructure and electrocatalytic property*. Nano Today, 2009. **4**: p. 143 - 164.
6. Tao, F., et al., *Reaction-Driven Restructuring of Rh-Pd and Pt-Pd Core-Shell Nanoparticles*. Science, 2008. **322**: p. 932 - 934.
7. Wang, D. and Y. Li, *Bimetallic nanocrystals: liquid-phase synthesis and catalytic applications*. Advanced Materials, 2011. **23**: p. 1044 - 1060.
8. Bradley, J.S., et al., *Surface spectroscopic study of the stabilization mechanism for shape-selectively synthesized nanostructured transition metal colloids*. Journal of the American Chemical Society, 2000. **122**(19): p. 4631-4636.
9. Toshima, N. and T. Yonezawa, *Bimetallic nanoparticles - novel materials for chemical and physical applications*. New Journal of Chemistry, 1998: p. 1179 - 1201.
10. Peng, Z. and H. Yang, *Designer platinum : control of shape, composition in alloy, nanostructure and electrocatalytic properties*. Nano Today, 2009. **4**: p. 143 - 169.
11. Antolini, E., *Formation of carbon-supported PtM alloys for low temperature fuel cells: a review*. Materials Chemistry and Physics, 2003. **78**: p. 563 - 573.
12. Luo, J., et al., *Ternary alloy nanoparticles with controllable sizes and composition and electrocatalytic activity*. Journal of Materials Chemistry, 2006. **16**(17): p. 1665-1673.
13. Chui, Y.H. and K.-Y. Chan, *Distribution of platinum and cobalt atoms in a bimetallic nanoparticle*. Chemical Physics Letters, 2005. **408**: p. 49 - 53.
14. Lim, B., et al., *Twin-induced growth of palladium-platinum alloy nanocrystals*. Angew. Chem. Int. Ed, 2009. **48**: p. 6304.
15. Antolini, E. and J. Perez, *The renaissance of unsupported nanostructured catalysts for low-temperature fuel cells: from the size to the shape of metal nanostructures*. Journal of Materials Science, 2011. **46**: p. 4435 - 4457.
16. Sen, F. and G. Gokagac, *Activity of carbon-supported platinum nanoparticles toward methanol oxidation reaction: role of metal precursor and a new*

- surfactant, *tert*-octanethiol. *Journal of Physical Chemistry*, 2007. **111**: p. 1467 - 1473.
17. Tu, W., et al., *Interface effect on the electronic structure of alkanethiol-coated platinum nanoparticles*. *Journal of Physical Chemistry B*, 2003. **107**: p. 10134 - 10140.
 18. Mukerjee, S., *Particle size and structural effects in platinum electrocatalysts*. *Journal of Applied Electrochemistry*, 1990. **20**: p. 537 - 548.
 19. Singh, S.K. and Q. Xu, *Bimetallic Ni-Pt nanocatalysts for selective decomposition of hydrazine in aqueous solution to hydrogen at room temperature for chemical hydrogen storage*. *Inorganic Chemistry*, 2010. **49**: p. 6148–6152.
 20. Liang, H.-P., et al., *Angewandte Chemie Int. Ed.*, 2004. **43**: p. 1540 –1543.
 21. Wang, D., Q. Peng, and Y. Li, *Nanocrystalline intermetallic and alloys*. *Nano Research*, 2010. **3**: p. 574 - 580.
 22. Mathe, N.R., et al., *The effect of reducing agents on the electronic, magnetic and electrocatalytic properties of thiol-capped Pt/Co and Pt/Ni nanoparticles*. *Electrocatalysis*, 2014. doi:10.1007/s12678-014-0241-y.
 23. Antolini, E., J.R.C. Salgado, and E.R. Gonzalez, *The methanol oxidation reaction on platinum alloys with the first row transition metals. The case of Pt–Co and –Ni alloy electrocatalysts for DMFCs: A short review*. *Applied Catalysis B: Environmental*, 2006. **63**: p. 137 - 149.
 24. Zhang, X., K.-Y. Tsang, and K.-Y. Chan, *Electrocatalytic properties of supported platinum–cobalt nanoparticles with uniform and controlled composition*. *Journal of Electroanalytical Chemistry*, 2004. **573**: p. 1 - 9.
 25. Park, K.-W., et al., *Chemical and electronic effects of Ni in Pt/Ni and Pt/Ru/Ni alloy nanoparticles in methanol electrooxidation*. *Journal of Physical Chemistry B*, 2002. **106**: p. 1869-1877.
 26. Antolini, E., J.R.C. Salgado, and E.R. Gonzalez, *The methanol oxidation reaction on platinum alloys within the first row transition metals. The case of Pt-Co and Pt-Ni alloy electrocatalysts for DMFCs : A short review*. *Applied Catalysis B: Environmental*, 2006. **63**: p. 137 - 149.
 27. Antolini, E., J.R.C. Salgado, and E.R. Gonzalez, *The methanol oxidation reaction on platinum alloys with the first row transition metals. The case of Pt-Co and Pt-Ni alloy electrocatalysts for DMFCs : A short review*. *Applied Catalysis B : Environmental*, 2006. **63**: p. 137 - 149.
 28. Iwasita, T., *Methanol and CO Electrooxidation*, in *Handbook of Fuel Cells - Fundamentals, Technology and Applications*, W. Vielstich, H.A. Gasteiger, and A. Lamm, Editors. 2003, John Wiley & Sons. p. 603 - 624.
 29. Guo, J.W., et al., *Preparation and characterization of a PtRu/C nanocatalyst for direct methanol fuel cells*. *Electrochimica Acta*, 2005. **51**: p. 754 - 763.
 30. Huang, H.J., D.P. Sun, and X. Wang, *PtCo alloy nanoparticles supported on graphene nanosheets with high performance for methanol oxidation*. *Chinese Science Bulletin*, 2012. **57**: p. 3071 - 3079.
 31. Zhang, X. and K.-Y. Chan, *Microemulsion synthesis and electrocatalytic properties of platinum–cobalt nanoparticles*. *Journal of Materials Chemistry*, 2003. **12**: p. 1203–1206.
 32. Deivaraj, T.C., W. Chena, and J.Y. Lee, *Preparation of PtNi nanoparticles for the electrocatalytic oxidation of methanol*. *Journal of Materials Chemistry*, 2003. **13**: p. 2555 - 2560.

33. Castle, J.E., *Use of "shake-up" satellites in photoelectron spectra for analysis of oxide layers on metals*. Nature Physical Science, 1971. **234**: p. 93 - 95.
34. Ramulifho, T., et al., *Fast microwave-assisted solvothermal synthesis of metal nanoparticles (Pd, Ni, Sn) supported on sulfonated MWCNTs: Pd-based bimetallic catalysts for ethanol oxidation in alkaline medium*. Electrochimica Acta, 2012. **59**: p. 310 - 320.
35. Arico, A.S., et al., *An XPS study on oxidation states of Pt and its alloys with Co and Cr and its relevance to electroreduction of oxygen*. Applied Surface Science, 2001. **172**: p. 33 - 40.
36. Ikeo, N., et al., *Handbook of X-ray Photoelectron Spectroscopy*. 1991: JEOL UK.
37. Toda, T., et al., *Enhancement of the electroreduction of oxygen on Pt alloys with Fe, Ni, and Co*. J. Electrochem. Soc., 1999. **146**: p. 3750.
38. Casella, I.G., M.R. Guascito, and M.G. Sannazzaro, *Voltammetric and XPS investigations of nickel hydroxide electrochemically dispersed on gold surface electrodes*. Journal of Electroanalytical Chemistry, 1999. **462**: p. 202 - 210.
39. Biesinger, M.C., et al., *Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni*. Applied Surface Science, 2011. **257**: p. 2717 - 2730.
40. Boudou, J.P., et al., *Oxygen plasma modification of pitch-based isotropic carbon fibres*. Carbon, 2003. **41**: p. 41 - 56.
41. Biesinger, M.C., et al., *X-ray photoelectron spectroscopic chemical state quantification of mixed nickel metal, oxide and hydroxide systems*. Surface and Interface Analysis, 2009. **41**: p. 324 - 332.
42. Kumar, A., et al., *Facile synthesis of size-tunable copper and copper oxide nanoparticles using reverse microemulsion*. RCS Advances, 2013. **3**: p. 5015 - 5021.
43. Goodenough, J.B., et al., *Intraalloy Electron Transfer and Catalyst Performance: A Spectroscopic and Electrochemical Study*. Chemistry of Materials, 1989. **1**: p. 391 - 398.
44. Park, K.-W., et al., *Chemical and electronic effects of Ni in Pt/Ni and Pt/Ru/Ni Alloy nanoparticles in methanol electrooxidation*. Journal of Physical Chemistry B, 2002. **106**: p. 1869 - 1877.
45. Spinacé, E.V., A.O. Neto, and M. Linardi, *Electro-oxidation of methanol and ethanol using PtRu/C electrocatalysts prepared by spontaneous deposition of platinum on carbon-supported ruthenium nanoparticles*. Journal of Power Sources, 2004. **129**: p. 121–126.
46. Tabet-Aoul, A. and M. Mohamedi, *Interrelated functionalities of hierarchially CNT/CeO₂/Pt nanostructured layers: synthesis, characterization and electroactivity*. Physical Chemistry Chemical Physics, 2012. **14**: p. 4463 - 4474.
47. Sakar, A., A.V. Murugan, and A. Manthiram, *Pt-encapsulated Pd-Co nanoalloy electrocatalysts for oxygen reduction reaction in fuel cells*. Langmuir, 2009. **26**: p. 2894 - 2903.
48. Guzman-Blas, R., et al., *Vulcan/Pt/Fe catalysts prepared by impregnation using EDTA for direct methanol fuel cells, direct ethanol fuel cells, and polymer electrolyte membrane fuel cells*. Smart Grid and Renewable Energy, 2013. **4**: p. 1 - 9.

49. Frelink, T., W. Visscher, and J.A.R.v. Veen, *Particle size effect of carbon-supported platinum catalysts for the electrooxidation of methanol*. Journal of Electroanalytical Chemistry, 1995. **382**: p. 65 - 72.
50. Geng, D. and G. Lu, *Dependence of onset potential for methanol electrocatalytic oxidation on steric location of active centre in multicomponent electrocatalysts*. Journal of Physical Chemistry C, 2007. **111**: p. 11897 - 11902.
51. Wu, Y.-N., et al., *High-performance Pd@PtRu/C catalyst for the anodic oxidation of methanol prepared by decorating Pd/C with a PtRu shell*. Journal of Power Sources, 2013. **224**: p. 66 - 71.
52. Wu, P., et al., *Composition- and aspect-ratio-dependent electrocatalytic performance of one-dimensional aligned Pt-Ni nanostructures* Journal of Physical Chemistry C, 2013. **117**: p. 19091 - 19100.
53. Wang, H., et al., *Pt decorated PdFe/C: Extremely high electrocatalytic activity for methanol oxidation*. International Journal of Electrochemical Science, 2012. **7**: p. 3390 - 3398.
54. Basri, S., et al., *Novel anode catalysts for direct methanol fuel cells*. The Scientific World Journal, 2014. **2014**: p. 547604.

CHAPTER 5: METHANOL OXIDATION REACTION ACTIVITY OF MICROWAVE-IRRADIATED AND HEAT-TREATED Pt/Co AND Pt/Ni NANO-ELECTROCATALYSTS

Due to the low current outputs observed for the conventional synthesis nanoparticles in Chapter 4, there was a need to explore other synthesis procedures in obtaining more active catalysts. Microwave-irradiation is a procedure that has gained success in recent years and this chapter will compare the microwave-synthesized and conventionally-synthesized nanoparticles.

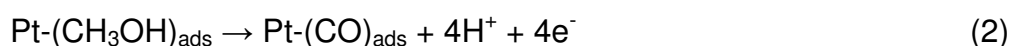
This work has been published: ***N.R. Mathe, M.R. Scriba, N.J. Coville, Methanol oxidation reaction activity of microwave-irradiated and heat-treated Pt/Co and Pt/Ni nano-electrocatalysts, International Journal of Hydrogen Energy, 39, (2014), 18871 – 18881.***

5.1. Introduction

Recent interest in fuel cells as alternative energy devices have resulted in a substantial increase in their study, especially direct methanol fuel cells (DMFCs) [1-3]. This is because methanol has advantages over hydrogen as a fuel source as it is cheap, is easy to handle, transport and store, and it also has a high theoretical energy density [1, 4]. The most commonly used catalyst in DMFCs is platinum (Pt). However, the use of Pt has drawbacks that include the high cost of Pt [5], as well as

the propensity for Pt to be poisoned by carbon monoxide (CO), which is one of the carbonaceous species formed during the methanol dissociation process [6, 7]. A general remedy to this problem is to alloy Pt with cheaper transition metals such as nickel [8], cobalt [5], iron [9] and ruthenium [10]. In addition to lowering the overall costs, these metals also increase the CO tolerance of the Pt catalysts.

To achieve further success in the use of Pt-alloy catalysts, it is important to understand the mechanism of CO poisoning in the methanol oxidation reaction (MOR). The first reaction (Eq. 1) in MOR is methanol adsorption on the catalyst to give $\text{Pt-(CH}_3\text{OH)}_{\text{ads}}$, which occurs at potentials of around 0.2 V and requires several free Pt binding sites [11]. The $\text{Pt-(CH}_3\text{OH)}_{\text{ads}}$ is then broken down to produce $\text{Pt-(CO)}_{\text{ads}}$ (Eq. 2) and carbonaceous species such as CO, formic acid and formaldehyde [12]. The dissociation of water then takes place at 0.4 – 0.5 V on pure Pt electrodes, where the H_2O molecule acts as the oxygen donor for the reaction. The electro-oxidation of methanol on the platinum electrode occurs as follows:



This adsorbed CO is then removed by the reaction with OH_{ads} (Eqs. 3 – 4), produced by the dissociation of the water molecules [13]:



The overall reaction yields 6e^- and 6H^+ for each adsorbed molecule of CH_3OH [7], as well as CO_2 , formed by the surface reaction between the CO- and O-species

(from OH) (Eq. 4). These formed carbonaceous species can block the catalytically active sites and affect the overall efficiency of the catalysts [6, 12].

Numerous mechanisms have been proposed to explain the enhancement in the activity of the methanol oxidation reaction (MOR) through the addition of the alloying of transition metals. These include the bifunctional model [14], the ligand model, the synergistic effect model and the oxide formation model [15]. For example, in the bifunctional model, an oxygenated surface is created by H₂O dissociation at the metal alloy sites which are at lower potentials (0.2 V, NHE) when compared to monometallic Pt sites. This promotes the oxidation of adsorbed CO to CO₂, decreasing the amount of CO present, thus resulting in the improvement of the metal CO tolerance [16, 17]. In the ligand model the alloying metal changes the chemical properties of Pt at the surface, weakening the Pt-CO_{ads} bond and minimizing CO poisoning [7, 18-20].

The effect that the addition of Co [2, 5] and Ni [8, 14] have on the electrocatalytic activity of Pt is well researched. Paulus et al. [21] studied the catalytic activity of Pt₃Ni and Pt₃Co bulk alloy catalysts with emphasis on the alloy surface properties. They found that Pt₃Co had an improved activity when compared to Pt₃Ni and Pt alone, though they did not perform CO poisoning studies. The same was also observed by Antolini et al. [2] and Zhang et al. [22] for Pt-Co electrocatalysts, and Kang et.al [3], and Deivaraj et.al [8] for Pt-Ni electrocatalysts in MOR. When Co and Ni atoms are added to Pt, they modify the Pt face centred cubic (fcc) lattice and improve oxidation reactions by lowering the electron binding energy in Pt [2]. The Co (-0.28 V) and Ni (-0.26 V) redox potentials are very close to each other [23] and are lower than that of Pt (0.73 V) which indicates the higher reduction ability of Pt. These two transition metals possess the ability to enhance the MOR activity by promoting

C-H bond cleavage at low potentials [24]. The presence of Co or Ni oxides on the surface also provides an oxygen source for CO oxidation in the bifunctional model.

In the work presented here, we demonstrate the methanol oxidation behaviour of Pt-Co and Pt-Ni nanoparticles synthesized using a conventional synthesis procedure entailing heat-treatment and a microwave-irradiation synthesis process. The aim was to evaluate the role of the synthesis strategies on the production of Pt catalysts alloyed with Co and Ni and to evaluate the activity and resistance to CO poisoning of the new alloys. The atomic ratio of metals used in synthesizing these nanoparticles was 1:1 (Pt: Co/Ni) to reduce the amount and therefore the cost of Pt needed to obtain enhanced catalytic activity.

5.2. Experimental Procedure

5.2.1. Materials

H₂PtCl₆.6H₂O (99%), NiCl₂.6H₂O (97%), CoCl₂.6H₂O (99%), ethylene glycol (EG, ≥ 99.5%), polyvinylpyrrolidone (MW 40,000, PVP-40), NaBH₄ (95%), isopropanol (99.5+%), Nafion (5wt%, 45% water) and tetrahydrofuran (THF, 99.9%) were purchased from Sigma Aldrich and used as received without further modification or purification.

5.2.2. Heat-treatment (HT) synthesis

PVP-40 (500 mg; 0.0125 mmol), CoCl_2 (250 mg; 1.05 mmol) or NiCl_2 (250 mg; 1.05 mmol) and H_2PtCl_6 (545 mg; 1.05 mmol) were dissolved in THF (10 ml) and stirred for 18 hours. NaBH_4 (1.0 M, 10 ml) was added drop wise to this solution to reduce the metal precursors. The mixture was further stirred for 2 hours before centrifuging and washing with a 50/50 distilled water/ethanol mixture four times, and then the precipitates were air-dried at room temperature overnight. The resulting powders were heat-treated at 150 °C (Pt-Co) and 200 °C (Pt-Ni) for 4 hours to remove low boiling contaminants and capping agents. These samples will be referred to as Pt-Co-HT and Pt-Ni-HT (HT = heat treatment). For this procedure, platinum nanoparticles were also synthesized without the addition of Co or Ni for comparison.

5.2.3. Microwave-irradiation (MW) synthesis

PVP-40 (500 mg; 0.0125 mmol), CoCl_2 (250 mg; 1.05 mmol) or NiCl_2 (250 mg; 1.05 mmol) and H_2PtCl_6 (545 mg; 0.0125 mmol) were dissolved in EG (60 ml) and stirred for 2 hours before adding NaOH (1.0 M, 10 ml). The two solutions, which contained Pt:M (M = Co or Ni) in a 1:1 molar ratio, were poured into Teflon reaction vessels and irradiated with microwaves in an Anton Paar M300 reactor (temperature = 200 °C, power = 750 W, time = 30 minutes). The microwave irradiated solutions were centrifuged and the precipitate washed and re-centrifuged with 50/50 distilled water/ethanol mixture 4 times before air-drying at room temperature overnight. No further heat treatment was performed on the resulting nanoparticle powders. These

samples will be referred to as Pt-Co-MW and Pt-Ni-MW (MW = microwave irradiated). Note that the samples were all prepared with a 1:1 M ratio of Pt:M (where M represents either Co or Ni)

5.2.4. Characterization

The size and shape of the nanoparticles was determined using the Carl Zeiss Auriga FE-SEM in imaging mode and a TEM JEOL JEM-2100 microscope. The powder X-ray diffraction (XRD) data were collected on the PANalytical X'Pert Pro X-ray diffraction system. Electron energy loss spectroscopy (EELS) and scanning transmission electron microscopy (STEM) measurements were performed on a JEOL ARM 200F at 200 kV. X-ray photoelectron spectra (XPS) of the catalysts were recorded on a PHI 5000 Versaprobe – Scanning ESCA microprobe. The system uses an Al monochromator X-ray beam at 25 W and 15 kV, with pass energy of 11.8 eV for individual elements. Peak correction was done using the carbon peak shift before curve fitting by use of Multipak^(R) software. A BET Micrometricis TriStar II 3020 surface area porosity system was used to determine the surface area of the catalysts, with degassing overnight at 90 °C before measurements were taken.

5.2.5. Electrochemical measurements

Cyclic voltammetry was used to determine the electrocatalytic activity of the synthesized nanoparticles. A Metrohm Autolab single electrochemical cell system

with scanning potential from 0 – 1.2 V and 10 mV/s scan rate was used. The system consists of a reference electrode (Ag/AgCl), counter electrode (Pt rod) and the working electrode (0.0314 cm² polished glassy carbon).

A samples of the nanoparticles powder (2.0 mg), Nafion (80 µl), and isopropanol (40 µl) were sonicated for approximately 2 hours to form an ink. The ink (2.0 µl) was then deposited onto a polished glassy carbon (GC) electrode which was dried at 90°C for 1 hour. The electrolyte solutions, made of 40 ml of 0.5 M H₂SO₄ or 0.5 M H₂SO₄ + 1.0 M CH₃OH, were purged with N₂ for 30 minutes prior to each measurement. All the voltammograms presented were recorded for the 10th scan.

5.3 Results and Discussion

In order to understand the reactivity of the catalysts produced, their crystal structure was determined by XRD and their morphology by TEM and SEM. As catalysis is a surface process, special attention was given to XPS, which gives an indication of the surface oxidation states in the outer 2 – 3 nm of the alloy nanoparticles. This information will be valuable for analysis and understanding the electrocatalytic activity of these nano-catalysts.

5.3.1. XRD analysis

X-ray diffraction spectra of the prepared nanoparticles are shown in Fig. 5.1. The Pt (Fig. 5.1a) presented typical platinum face centered cubic (fcc) reflections/peaks at 39.93° (111), 46.46° (200) and 67.58° (220) [8, 25]. Broadening of all peaks after the addition of the Co or Ni is to be noted (Table 5.1, calculated using the Scherrer equation) suggesting a reduction in the Pt particle size on synthesis of new materials. The observed broadening could also be due to the amorphous nature of the catalysts [5, 8].

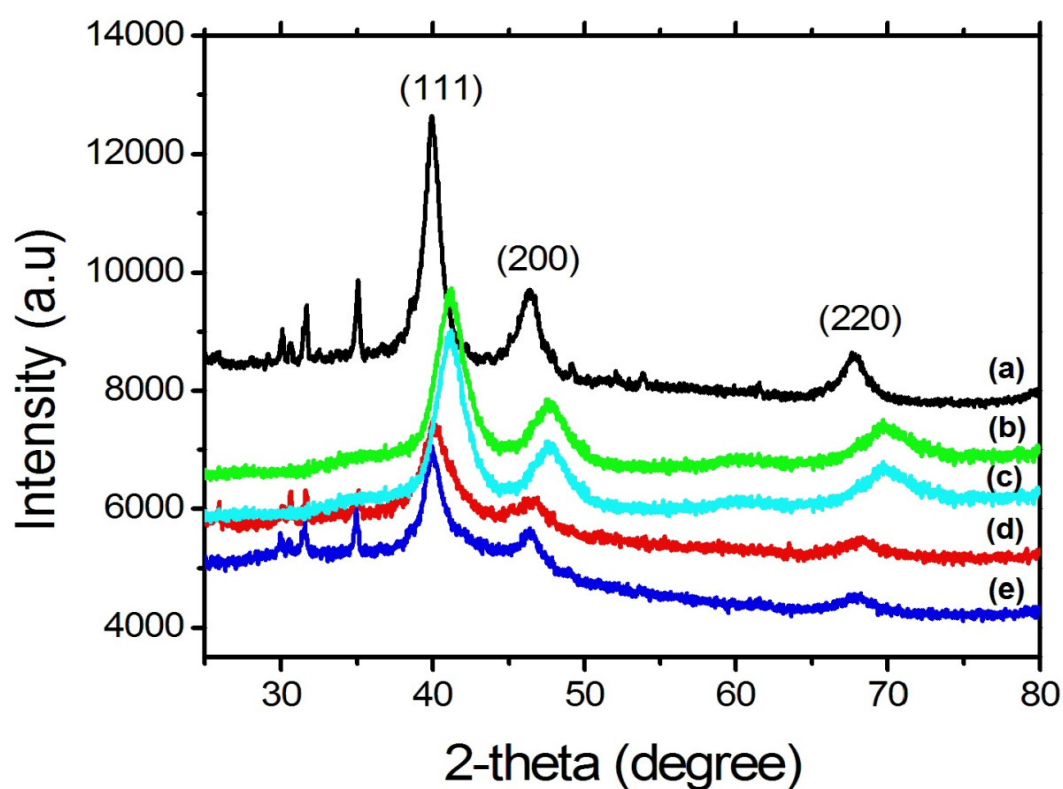


Figure 5.1. X-ray diffractograms of (a) Pt, (b) Pt-Co-MW, (c) Pt-Ni-MW, (d) Pt-Co-HT and (e) Pt-Ni-HT.

Table 5.1. The XRD data obtained from Fig. 5.1.

Sample	Peak (111) (2θ)	Crystallite size (nm)	Lattice parameter (Å)
Pt	39.93	8.39	2.254
Pt-Co-HT	40.15	3.74	2.244
Pt-Co-MW	41.18	4.56	2.190
Pt-Ni-HT	40.01	5.87	2.252
Pt-Ni-MW	41.17	4.65	2.191

The peak positions for the HT samples showed little change after the addition of Co (40.15°) or Ni (40.01°) suggesting little alloying has occurred for this synthesis procedure. However, the MW synthesized samples showed substantial peak shifts (41.18° for Pt-Co-MW and 41.17° for Pt-Ni-MW) which indicate the incorporation of the smaller Ni and Co atoms into the crystal lattice of the Pt resulting in lattice contractions [26]. The contraction brings about a favourable Pt-Pt distance [27] in modifying the electronic structure of the Pt.

Please note that the peaks observed at $2\theta = 30 - 36^\circ$ are not traditional Pt, Co or Ni peaks. These were seen only for the HT synthesized samples (Fig. 5.1a,b&e) and they were not present for the microwave-irradiated samples. They can be attributed to residual PVP ligands surface coverage of the nanoparticles.

5.3.2. SEM and TEM analysis

SEM images of the Pt-Co and Pt-Ni samples, made by HT and MW methods, are presented in Fig. 5.2 and 5.3, respectively. The image of the Pt-Co-HT

nanoparticles, (Fig. 5.2a), showed a material with a compact, layered microstructure and with some small nanoparticles on the surface; in contrast the images of the Pt-Ni-HT (Fig. 5.2b) showed a porous structure made of particles with varying shapes and sizes.

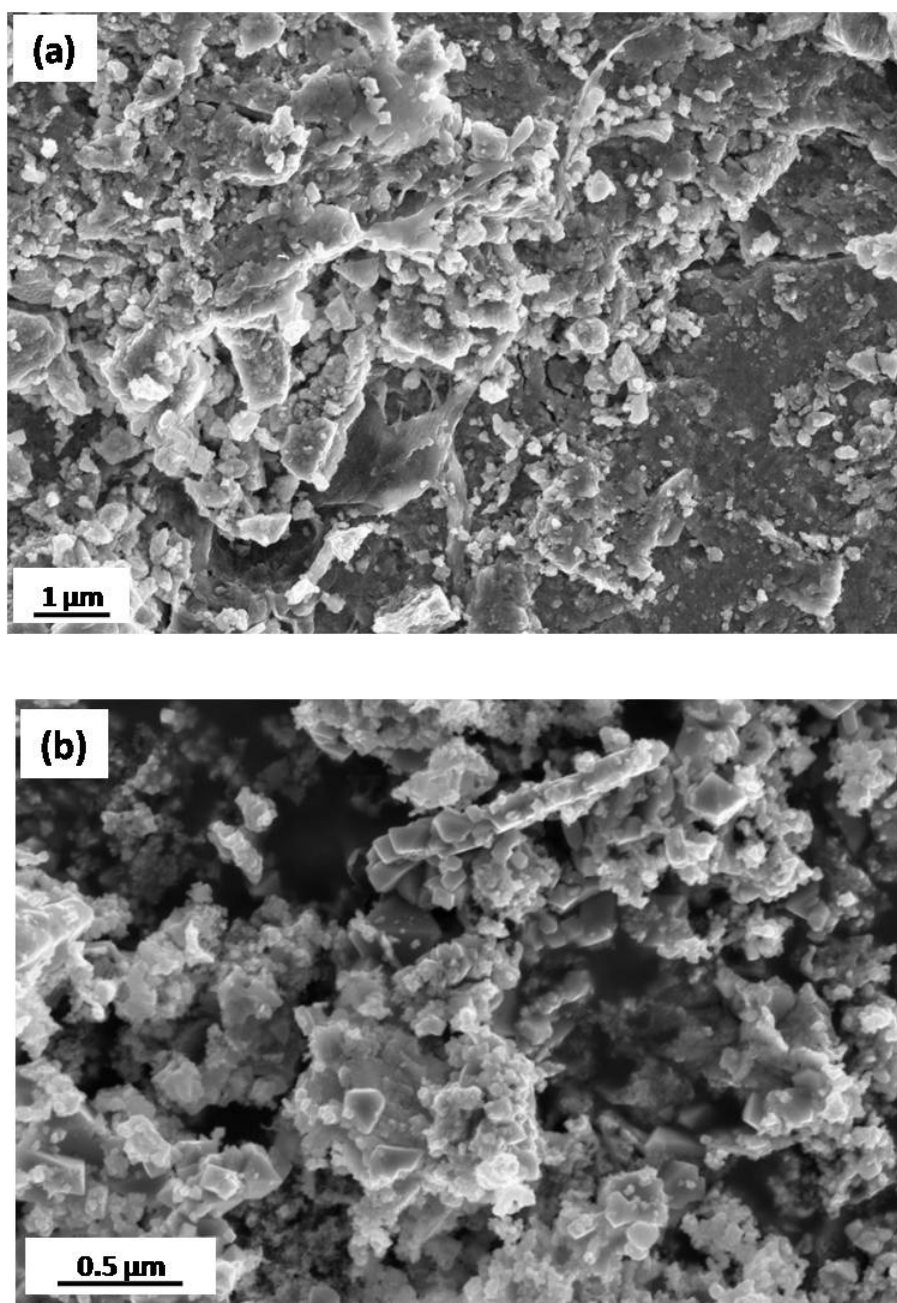
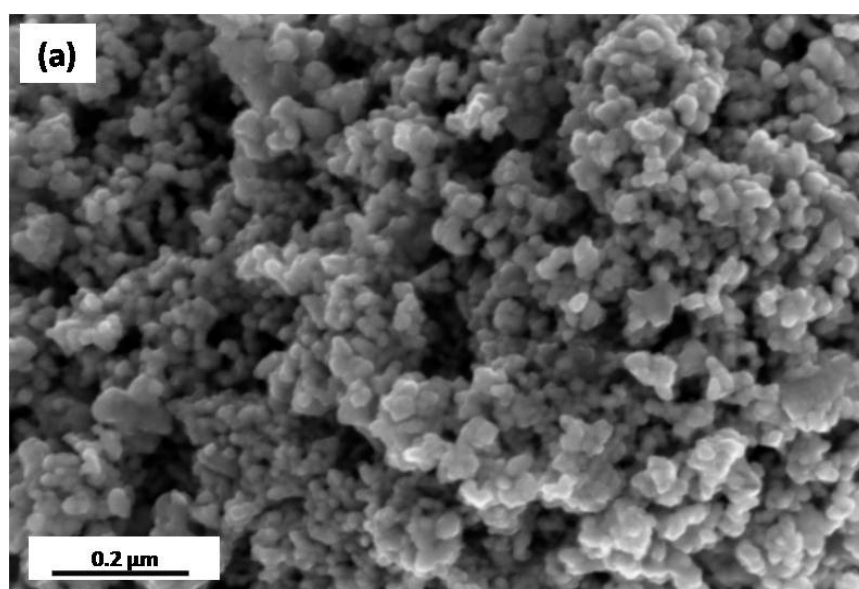


Figure 5.2. The SEM images of the heat-treated (HT), (a) Pt-Co and (b) Pt-Ni nanoparticles.

Pt-Co-MW nanoparticles had a structure made up of many spherical and near spherical shaped particles with a narrow size distribution (Fig. 5.3a) while the Pt-Ni-MW material (Fig. 5.3b) has a structure also made up with discrete particles but with a greater variety of shapes and range of sizes. It thus appears that the HT and MW Pt-Co samples have quite different morphologies; on the other hand, the HT and MW Pt-Ni morphologies show similarities. The observed differences indicate that the morphology of the resulting nanoparticles depends on the type of synthesis procedure used as well as the alloying metal.



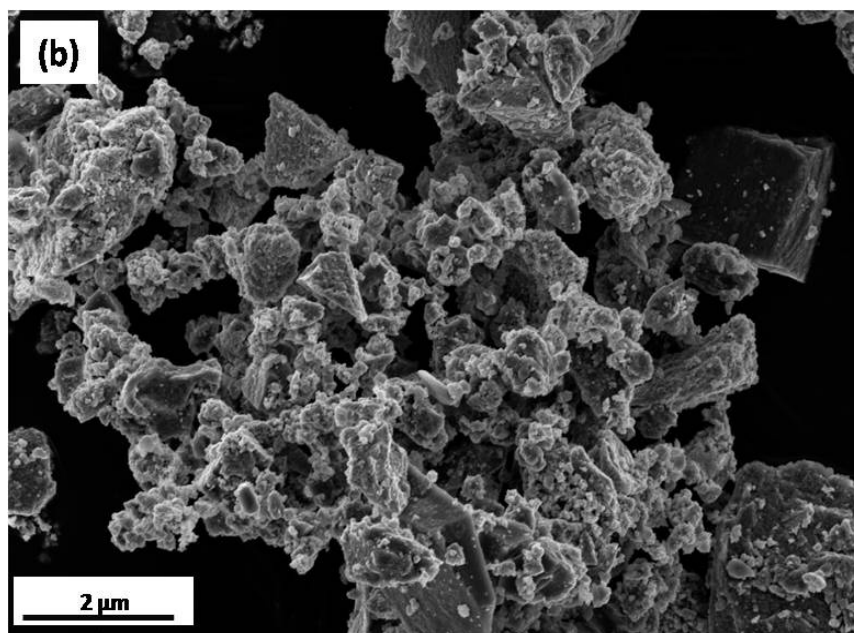


Figure 5.3. SEM images of microwave synthesized, (a) Pt-Co and (b) Pt-Ni nanoparticles.

TEM analysis was also used to investigate the shape and size of the nanoparticles (Figs. 5.4 & 5.5). A TEM image of spherical particles of Pt-Co-HT is shown in Fig. 5.4a and they appear to be made up of heterogeneous components while Pt-Ni-HT particles (Fig. 5.4b) formed agglomerated chain like structures from smaller almost bead like components (~ 5 - 10 nm).

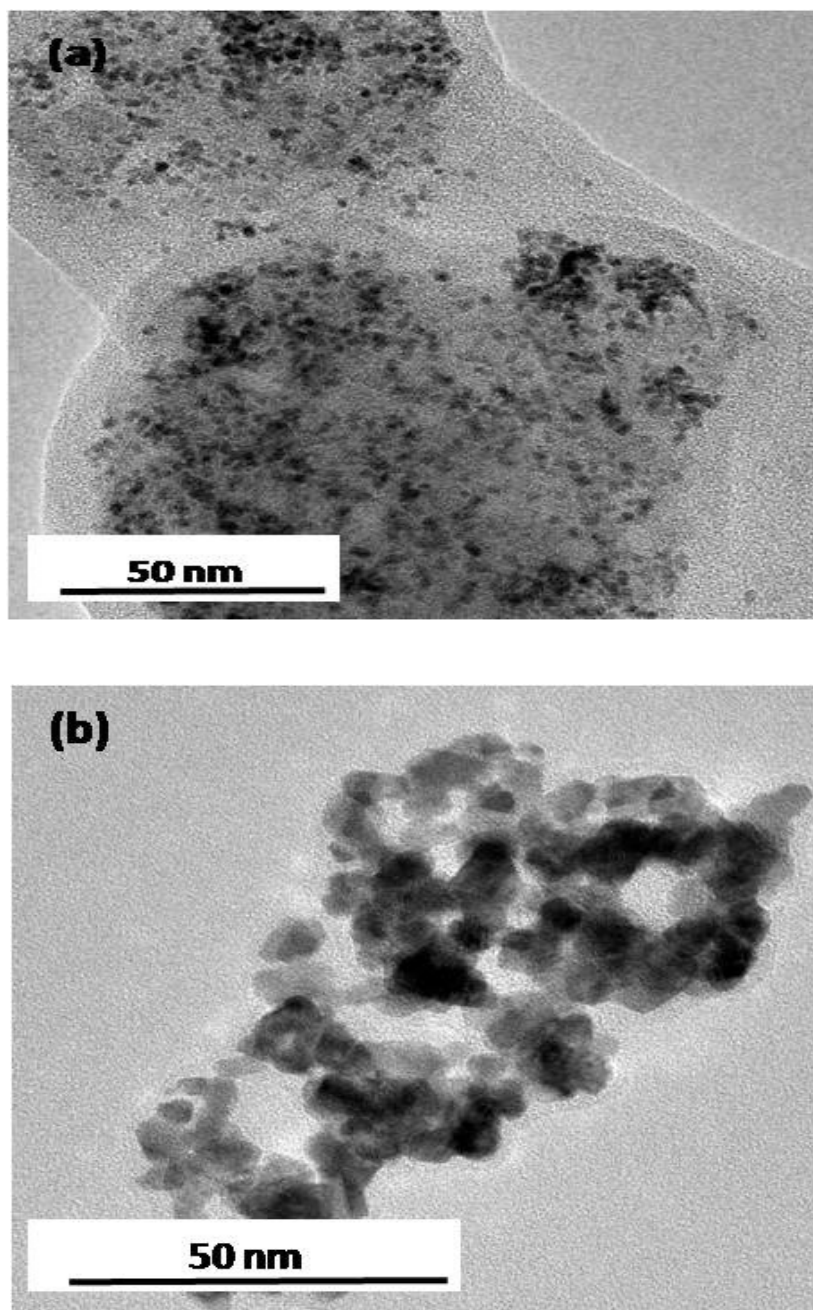


Figure 5.4. TEM images of the conventionally synthesized and heat-treated, (a) Pt-Co and (b) Pt-Ni nanoparticles.

Similarly, both the microwave-irradiated samples, (Fig. 5.5 (a) and (b)), exhibited a network of bead like nanoparticles forming a nanostructure of agglomerates with a high level of porosity. The TEM images of Pt-Co-HT, Pt-Co-MW and Pt-Ni-MW show similar morphologies. The chain-link-like structures observed should provide a large

and porous surface area with available Pt sites for methanol adsorption to aid the methanol oxidation reaction [28].

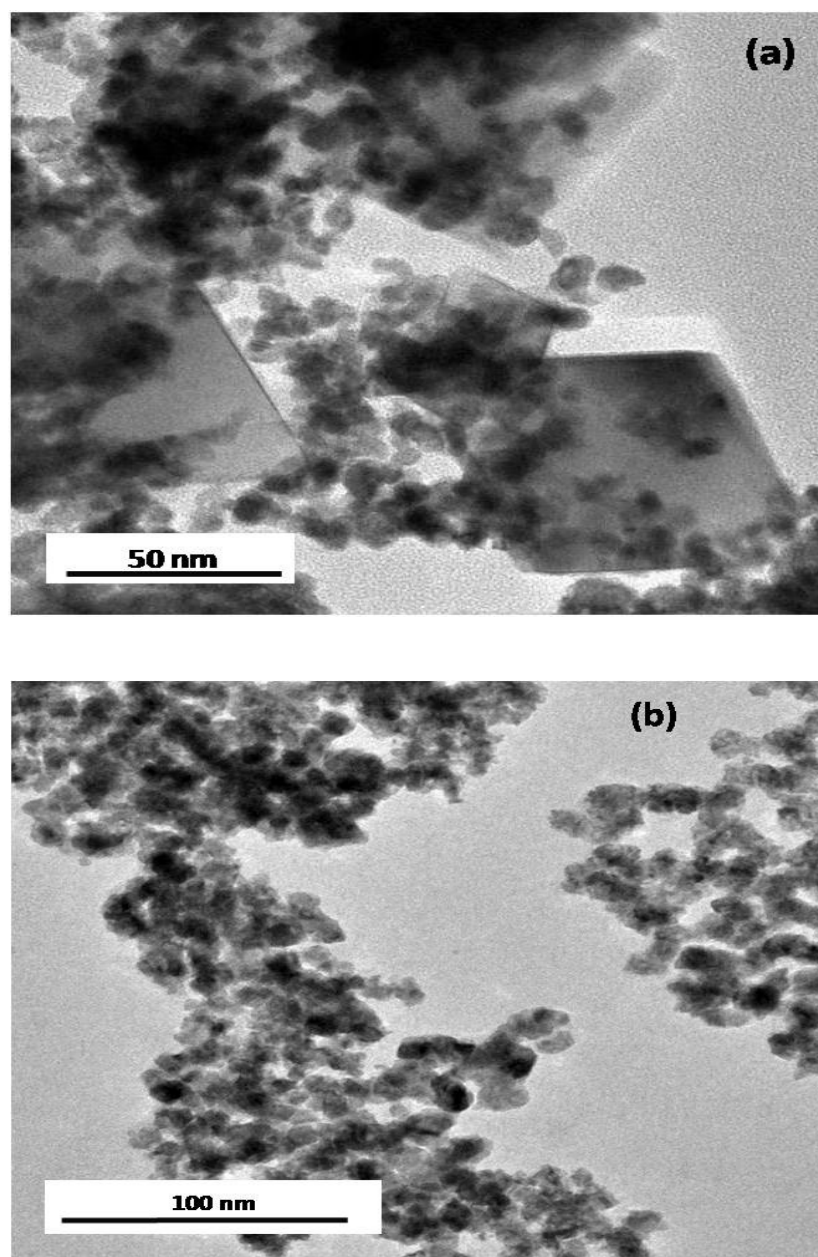


Figure 5.5. The TEM images of microwave synthesized, (a) Pt-Co and (b) Pt-Ni nanoparticles.

Microwave-irradiated Pt-Co and Pt-Ni samples were further characterized with HR-TEM and EELS mapping (Supporting information Fig 4.6b,c and 4.7b,c) to determine the type of alloy structures formed. Fig. 4.6a shows a STEM image and the corresponding EELS maps filtered for Pt (Fig. 4.6b) and Co (Fig. 4.7c) for the Pt-Co-MW nanoparticles.

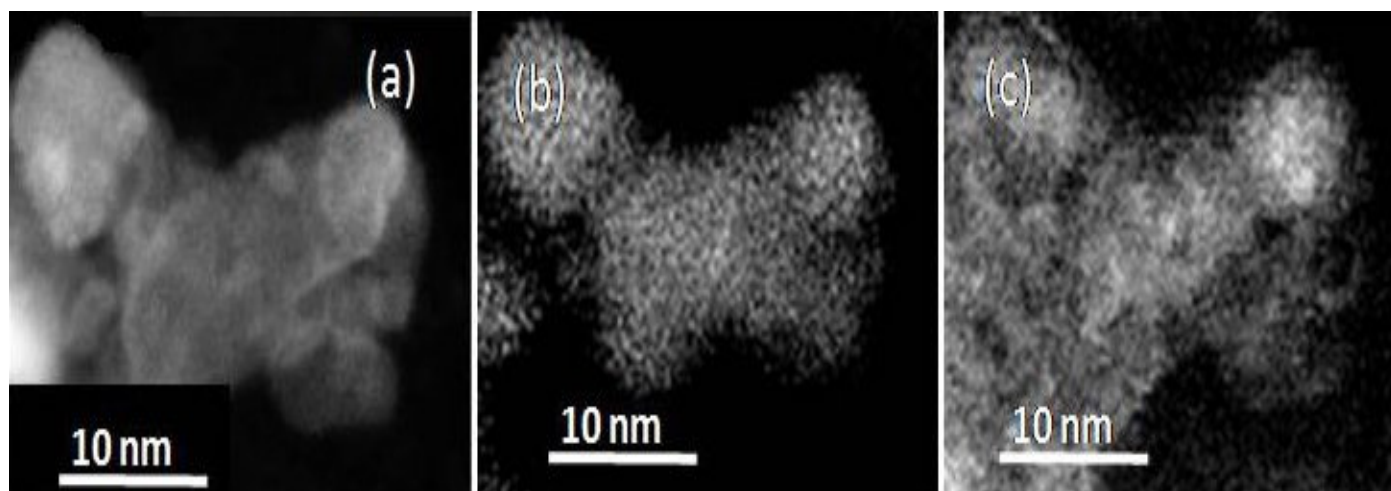


Figure 5.6. Energy-filtered EELS maps of the microwave-synthesised samples; (a) survey image,(b) Pt map and (c) Co map obtained from Pt-Co nanoparticles.

The EELS maps show that both metals are present throughout the nanoparticles and clusters. However, while the Pt appears to be homogeneously dispersed the Co appears to have a more heterogeneous dispersion. This suggests that the co-reduction process used here is producing a material with varying concentrations of Pt and Co in the sample due to different Co and Pt precipitation rates. In Fig. 5.7 the equivalent EELS images of the Pt-Ni sample are shown. The images showed a more uniform overlay of the Pt (Fig. 5.7b) and Ni (Fig. 5.7c) atoms in the sample. In this instance it appears that the Ni is dispersed but the Pt is more localised in some areas than in others.

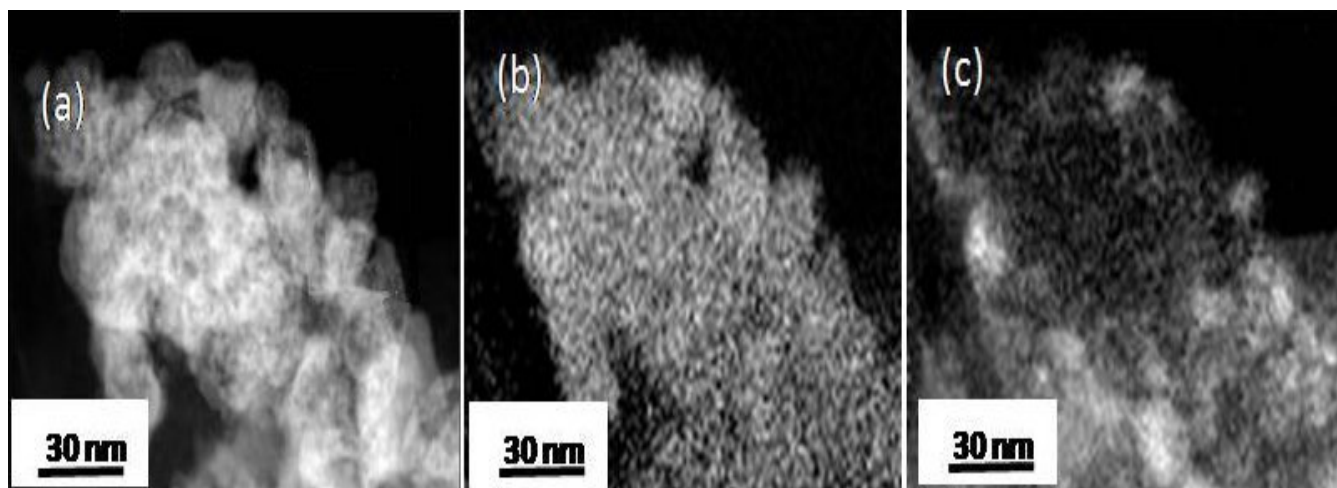


Figure 5.7. Energy-filtered EELS maps of microwave-synthesized Pt-Ni nanoparticles; (a) survey image, (b) Pt map and (c) Ni map.

BET measurements were performed on both the heat-treated and microwave-irradiated samples (Table 5.2). The BET surface areas of the heat-treated samples were generally larger than those found for the microwave-synthesized samples, with the Pt-Co-HT having the highest surface area. This can be correlated to the morphology of this sample as seen in TEM studies (Fig. 5.2b), which showed a sheet-like structure.

Table 5.2 BET surface area, pore volume and pore sizes of bimetallic nanoparticles.

Sample	BET (m²/g)	Pore volume (cm³/g)	Pore size (nm)
Pt-Co-HT	61	0.345	22.6
Pt-Co-MW	31.0	0.018	24.4
Pt-Ni-HT	23.4	0.058	9.42
Pt-Ni-MW	14.0	0.016	4.74

5.3.3. X-ray photoelectron spectroscopy (XPS) analysis

XPS was used to determine the oxidation states and atomic concentrations of the nanoparticles (Figure 5.8 and Table 5.3). The HT and MW synthesized nanoparticles presented dramatic differences in their surface atomic concentration of the second metal (Co, Ni) compared to the bulk values [29]. The data suggest that at the surface, very little alloying of the metals has occurred for the HT samples but may have occurred for the MW samples, consistent with the bulk measurements made from XRD analysis.

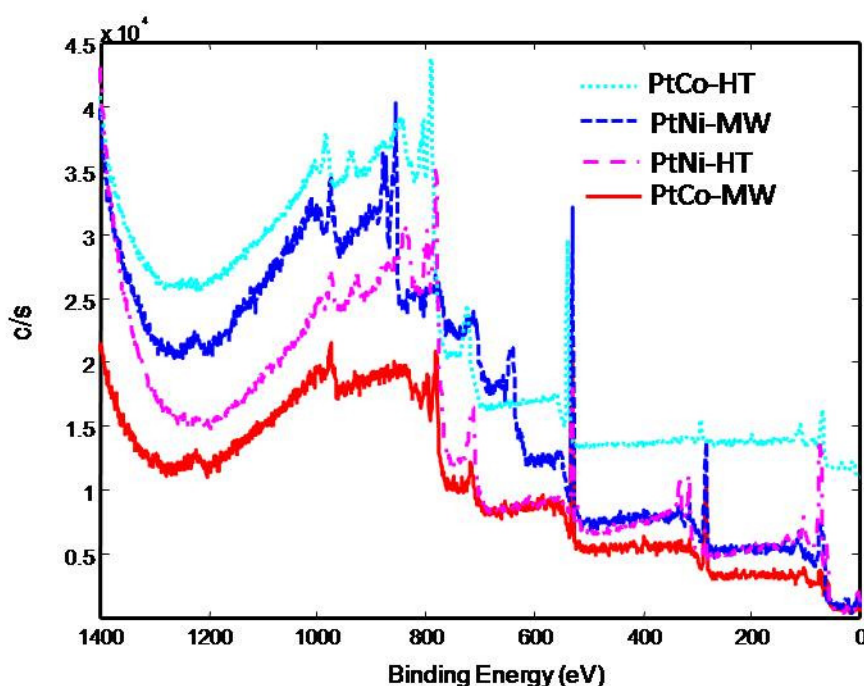


Figure 5.8. Full scan XPS spectra of the Pt-Co and Pt-Ni nanoparticles synthesized using heat-treatment and microwave-irradiation.

Table 5.3. Atomic ratio of Pt-M species present on the nanoparticle surface from XPS

Sample	Pt (at.%)	Co/Ni (at.%)	C (at.%)^a	O (at.%)
Pt-Co-HT	0.2	33.9	16.1	49.8
Pt-Co-MW	6.0	22.0	37.0	35.0
Pt-Ni-HT	10.5	0.1	27.0	62.5
Pt-Ni-MW	5.0	19.0	36.0	40.0

^a The presence of carbon is attributed to residues from the synthesis process and the XPS carbon substrate.

For the microwave-irradiated samples, the atomic percentage of Pt and Co or Ni on the surface was similar (5 at.% Pt, 19 at.% Ni for Pt-Ni-MW and 6 at.% Pt, 22 at.% Co for Pt-Co-MW), indicating a similar 1/4 Pt/M atomic ratio for both samples. Thus, together with the EELS data, these observations suggest that the microwave-irradiation reduction process for both metals is similar. The alloy formed on the surface is quite different to the known Pt₃M alloy structure [21, 30]. In contrast, the heat-treated samples showed entirely different reduction behaviour. The Pt-Co-HT showed preferential Co atom surface segregation (33.9 at %) and little surface Pt (0.2 at.%) while the Pt-Ni-HT exhibited Pt atom surface segregation (10.5 at.%) and little Ni (0.1 at.%) on the surface. Also to be noted are the high levels of surface oxygen (O) observed in the Pt-Co-HT nanoparticles (Table 5.3), indicative of metal surface oxidation (see Fig 5.9, 5.10, O-1s spectra).

Pt-Co XPS data. The literature Pt-4f peak is a doublet (ratio 4/3) with Pt(0) species appearing at 71.2 and 74.5 eV, PtO at 72.4 and 75.7 eV and Pt(OH)₂ at 72.6 and 75.9 eV, [31-34]. The Pt-4f XPS spectrum for Pt-Co-MW is shown in Figure 5.9b and revealed 2 peaks only corresponding to Pt(II) (Table 5.4). Analysis of Pt-4f in Pt-Co-

HT (Fig. 5.9a) was not possible due to the low surface concentration of the Pt (0.2 at.%), even though the O-1s XPS spectrum showed two peaks at 529.6 eV and 531.3 eV, corresponding to M-O and M-OH species (ratio 2/3) (Fig. 5.10a) [35].

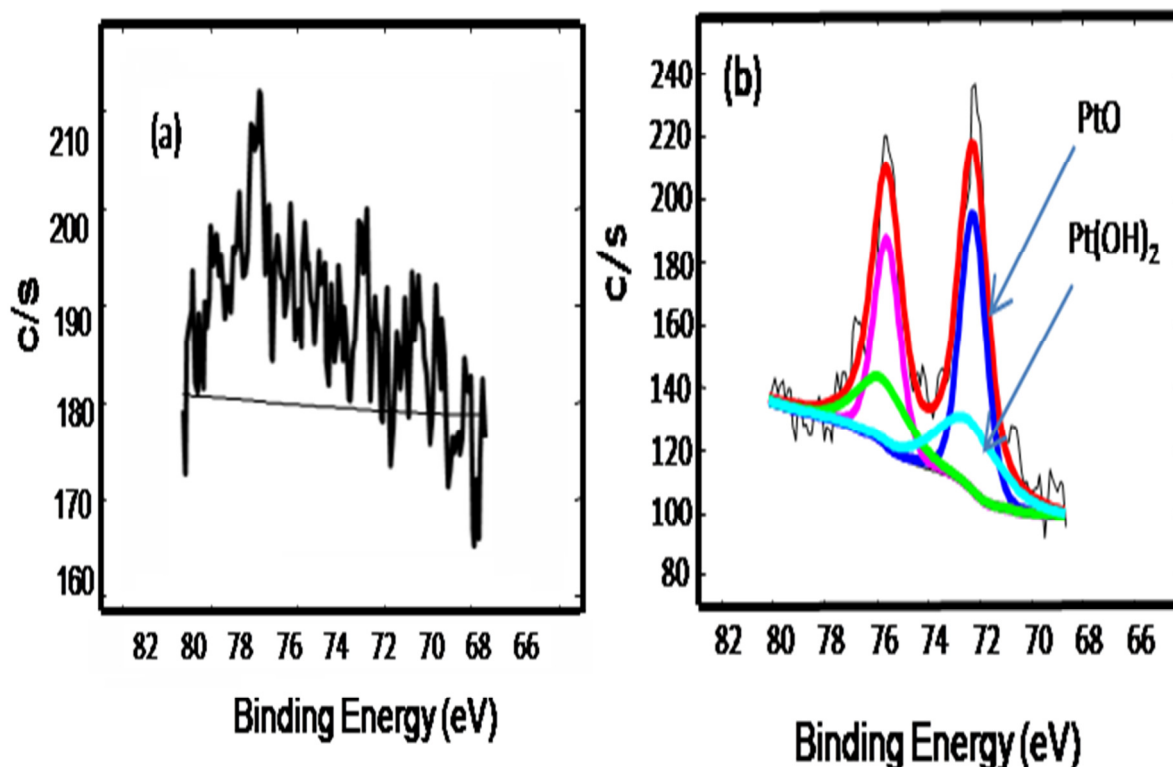


Figure 5.9 The deconvoluted Pt-4f X-ray photoelectron spectra for Pt-Co nanoparticles formed by (a) heat treatment and (b) microwave-irradiation.

Because there was no Pt was detected on the surface of the Pt-Co-MW material (Figure 5.9b), the peaks are thus associated with oxidized Co species (Fig 5.10b). The Pt-Co-MW Pt-4f spectrum presented clear peaks (Fig. 5.9b) which were deconvoluted to reveal Pt(II) species at 72.27 eV (Pt(OH)_2) and 72.41 eV (PtO) (see Table 5.4). the Pt-Co-MW spectrum also had two O-1s peaks (529.8 eV and 531.7 eV) in a 2/3 ratio. Since Co and Pt are both on the surface, the O and OH groups must be bound to both metal ions.

Table 5.4. Pt-4f binding energies and relative intensities of the present species.

Sample	Species	Binding Energies (eV) 4f _{7/2}	Binding Energies (eV) 4f _{5/2}	Relative Intensity (%)
Pt-Co-MW	Pt(OH) ₂	72.27	75.66	61.1
	PtO	72.41	75.74	38.6
Pt-Ni-HT	Pt ⁰	70.73	74.06	66.1
	Pt(OH) ₂	71.73	75.06	33.9
Pt-Ni-MW	Pt(OH) ₂	72.23	75.56	55.4
	PtO	73.20	76.53	44.5

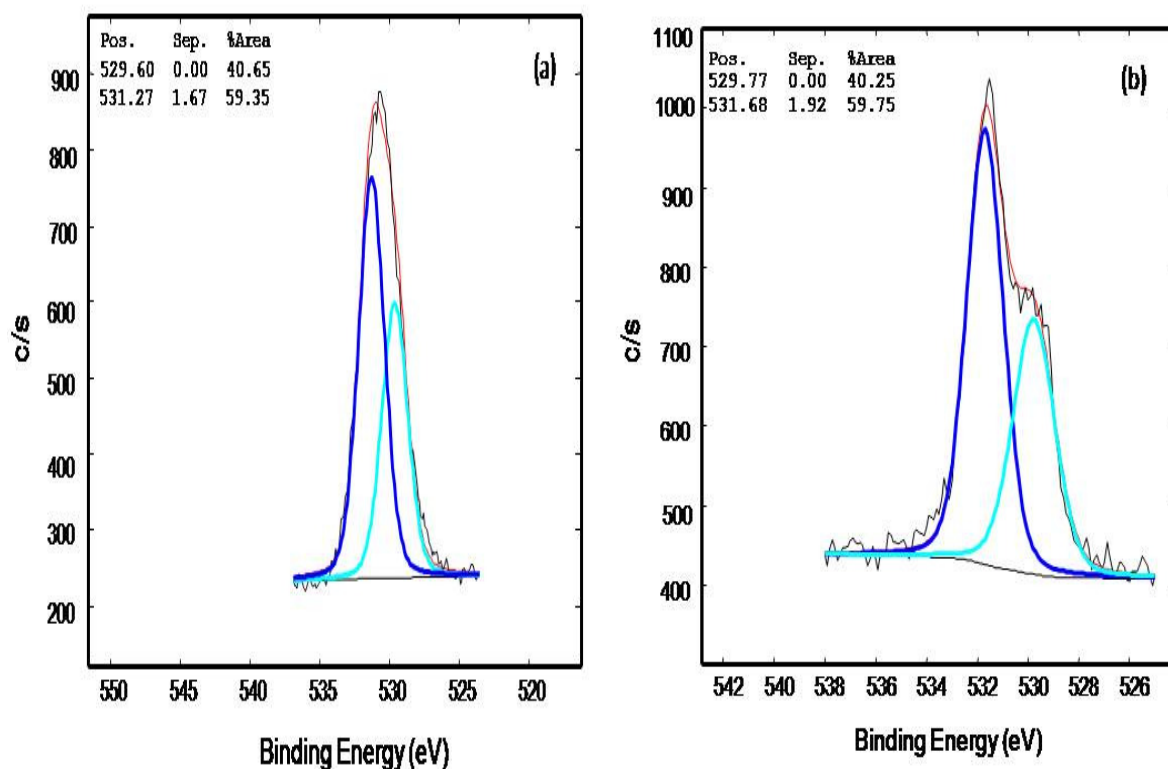
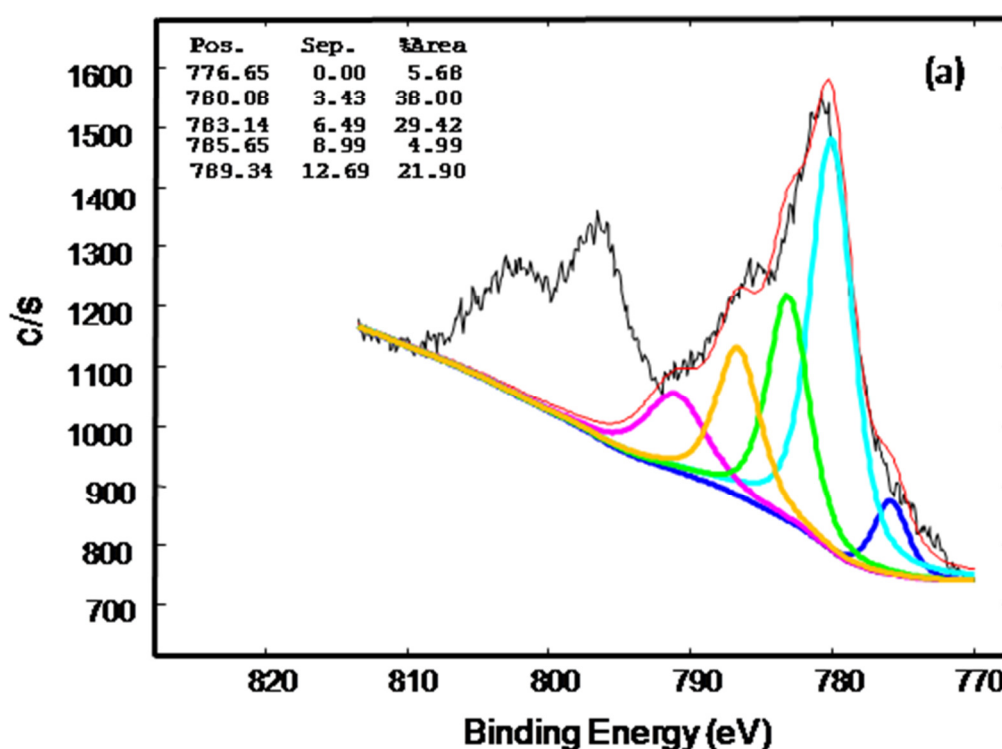


Figure 5.10. XPS O-1s spectra of (a) Pt-Co-HT and (b) Pt-Co-MW. The peak positions revealed the presence of Co-oxide and Co-hydroxide species resulting from lattice oxide and hydrated oxides.

The XPS Co-2p peak corresponding to Co⁰ (778.1 and 793.3 eV), Co-OH (781.1 and 796.3 eV) and Co-O (780.2 and 795.4 eV), [32, 36], are well documented in the literature. The Co-2p_{3/2} peaks were deconvoluted using a method reported by

Biesinger et al. [36, 37] to obtain the species that are present in both the Pt-Co samples [38]. Both the HT (Fig. 5.11a) and MW (Fig. 5.11b) samples have peaks associated with Co-O (780.08 and 780.08 eV) and Co-OH (785.65 and 786.67 eV) respectively, but the ratios are difficult to evaluate for Co. Further the ability to differentiate CoO from Co₃O₄ is not possible [36]. The absence of metallic Co (778.3, 793.5 eV) in both samples is apparent (see Table 5.4).



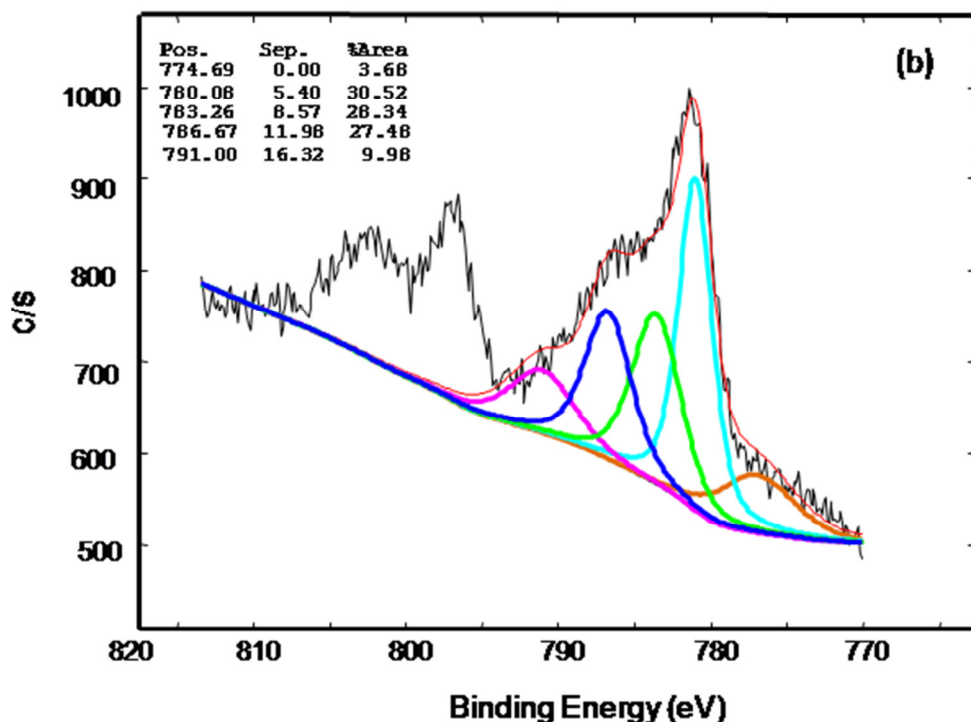


Figure 5.11. Co-2p XPS deconvoluted spectra of (a) heat-treated and (b) microwave-irradiated Pt-Co nanoparticles.

Interestingly the Co XPS data show similar Co species on the surface for both the HT and MW prepared samples, similar to what was observed from the O-1s XPS data. This indicates the samples show a preference for OH species and that the Pt has little effect on the type of Co species formed on the surface, although it does affect the Co bonding interaction (see O-1s XPS data).

Pt-Ni XPS data. The Pt-4f spectrum of Pt-Ni-HT (Fig. 5.12a) showed the presence of metallic Pt⁰ (70.73 eV, 74.06 eV) and Pt-O/Pt-(OH)₂ (71.73 eV, 75.06 eV), in a 2/1 ratio, implying the majority of the Pt was in reduced, not oxidised form. Due to the low Ni atomic concentration (0.1 at.%), a useful Ni spectrum was not obtained.

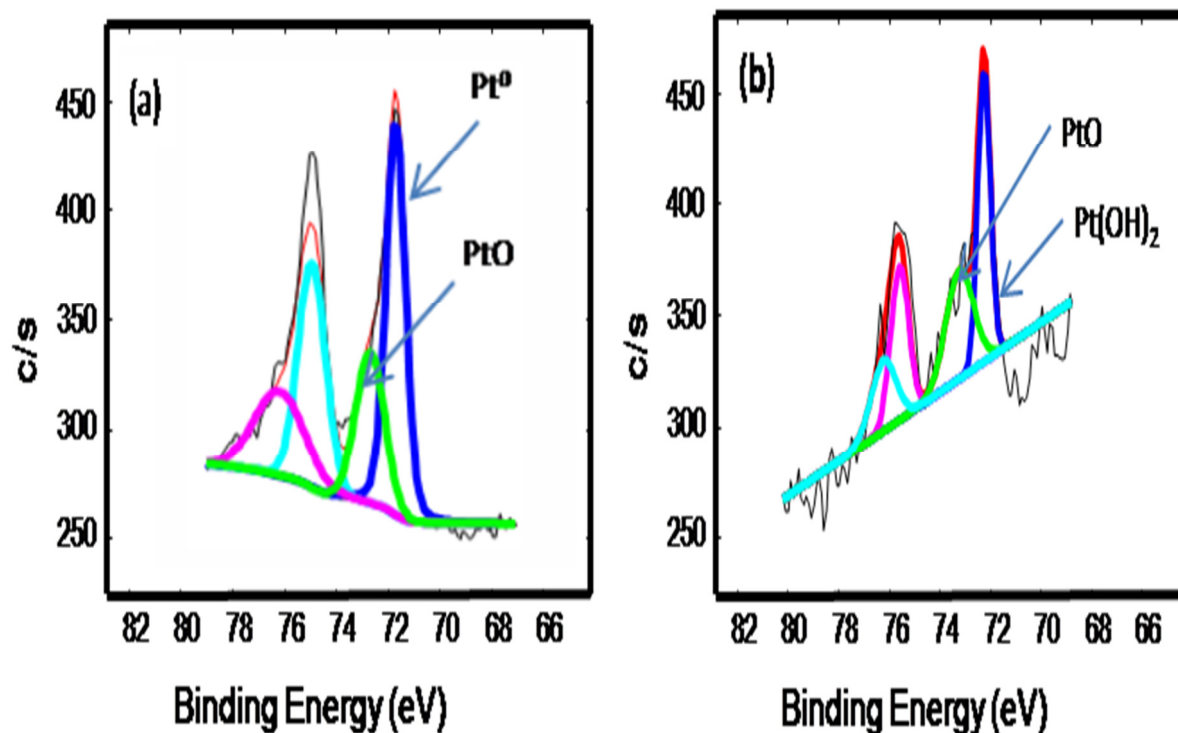


Figure 5.12. Deconvoluted Pt-4f XPS spectra of (a) heat-treated and (b) microwave-irradiated Pt-Ni nanoparticles.

As for the Pt-Ni-MW (Fig. 5.12b), the spectrum was deconvoluted into two sets of doublet peaks. These peaks correspond to those associated with Pt-OH (72.23 eV, 75.56 eV) and Pt-O (73.20 eV, 76.53 eV); with no Pt^0 species observed, as with the Pt-Co-MW nanoparticles. The shift to higher binding energies, i.e. to 73.20 eV could be due to a high oxygen concentration on the Pt [39]. Bensebaa et al. [40] attributed this binding energy shift to the presence of the high Pt oxidation states on the surface of nanoparticles. Wu et al. [25] and Li et al. [41] postulated that the shift was due to the interactions between the Pt and Ni resulting in a shift in the Pt d-band centres.

The O-1s spectra for the Pt-Ni nanoparticless are shown in Fig 5.13. The Pt-Ni-HT (Fig. 4.13a) data indicate three peaks corresponding to M-O (531.9 eV), M-OH (531.2 eV) and M(H₂O) (532.6 eV) [35]. Since the Pt-Ni-HT sample had very little surface Ni (Table 5.4), the peaks can be assigned to Pt-O and Pt-OH (ratio ca. 1/1). The Pt-Ni-MW nanoparticles contained both Ni and Pt on the surface (Table 4.3) and the O-1s XPS peaks must be associated with both Ni and Pt. It is clear from the spectrum (Fig 4.13b) that the surface O is dominated by OH species (M-OH/M-O ratio = 3/1).

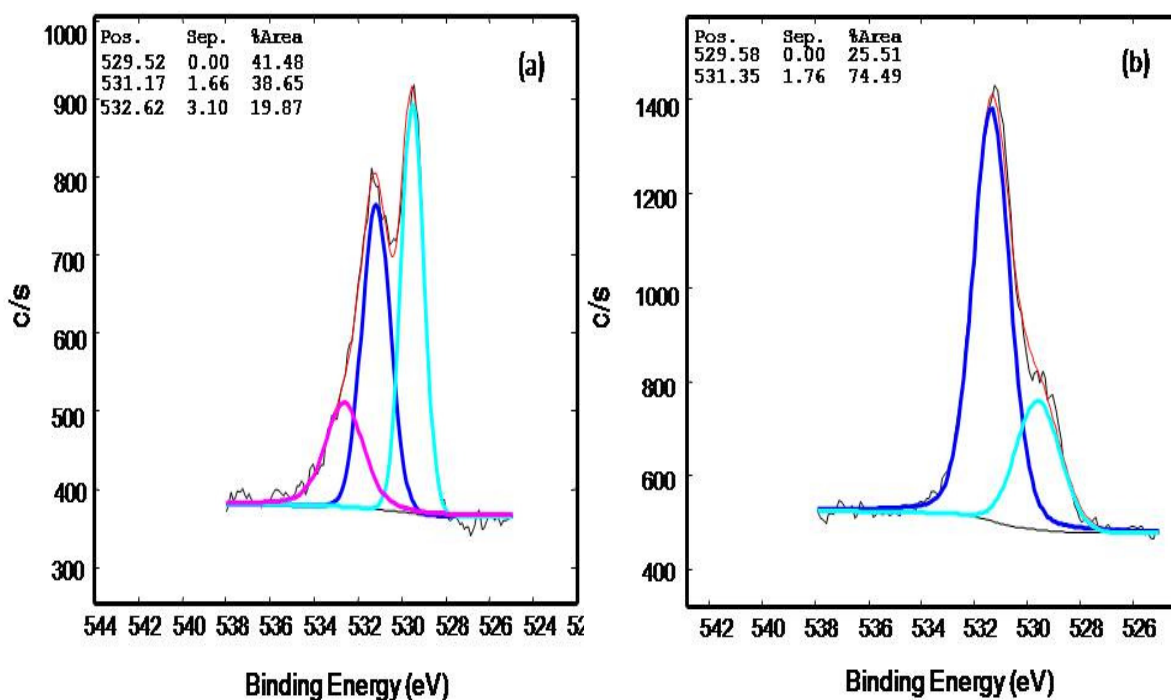
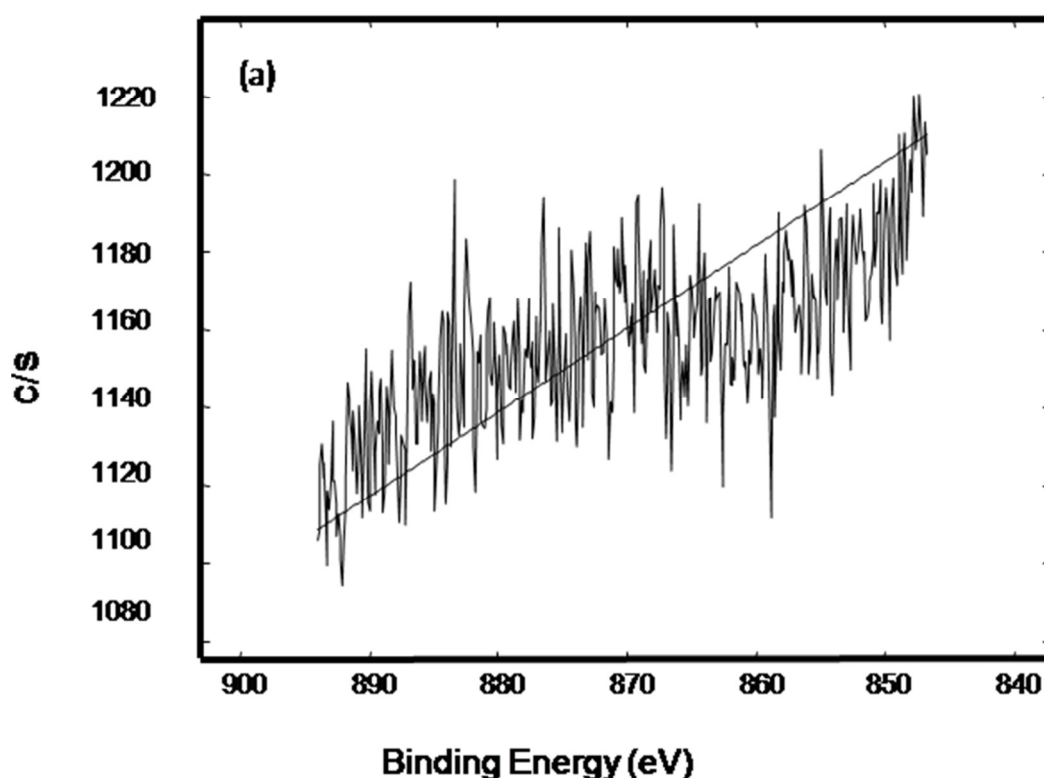


Figure 5.13. XPS O-1s spectra of (a) Pt-Ni-HT and (b) Pt-Ni-MW. The peak positions showed the Ni-oxide and Ni-hydroxide species from lattice oxide as well as the hydrate oxide. The 3rd peak at 532.62 in Pt-Ni-HT comes from organic oxygen.

The relative amounts and the oxidation states of Ni in the Pt-Ni samples were also determined using the Ni-2p spectra (Fig. 5.14). Literature Ni-2p peaks corresponding to Ni⁰ (852.6 and 869.8 eV), Ni(OH)₂ (854.9 and 872.1 eV) and NiO (853.7 and 87.09 eV), [14, 38] have been reported [31]. No defined Ni-2p XPS peaks for Pt-Ni-HT (Fig. 5.14a) were observed due to the low atomic concentration of Ni on the surface of this sample (0.1 at.%). On the other hand, Pt-Ni-MW (Fig. 5.14b) exhibited typical major peak (Ni-2p_{3/2}) and its satellite [40] which was further deconvoluted into six peaks. Analysis of oxidized Ni XPS data is non-trivial and in this instance the peaks can be ascribed to a mixture of Ni-O/Ni-OH peaks [37]. The major peak at 855.6 eV was assigned to Ni-OH which was consistent with the O-1s data, where Ni-OH species dominated.



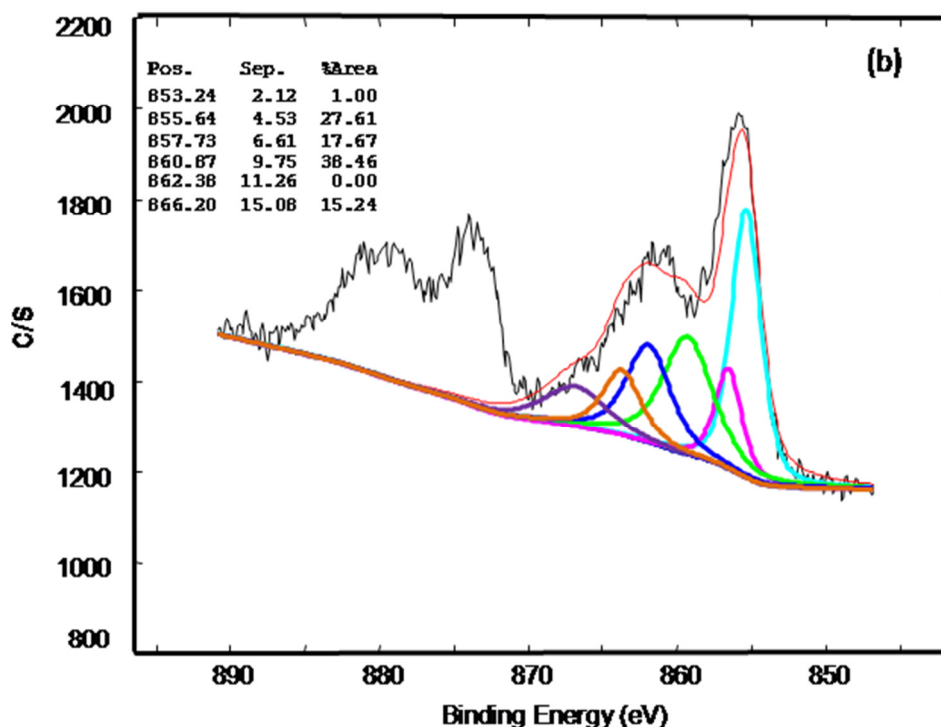


Figure 5.14. Ni-2p deconvoluted XPS spectra for the (a) heat-treated and (b) microwave-irradiated the Pt-Ni nanoparticles.

Summary of XPS data. The XPS data clearly indicate major differences for both synthesis procedures. Since the surface concentrations of the metals and metal oxidized species will impact on their electrochemical activity, it is worthwhile summarizing the findings prior to describing their electrochemical studies. XPS studies revealed the following information: (i) microwave irradiation generates alloys made of Pt and Co (or Ni) oxides, not the metallic species; (ii) the same surface features are found for both MW samples (Pt-Co and Pt-Ni) in which Pt/Co or Pt/Ni surface ratios are both about 1/4; (iii) the thermally treated samples yield materials with either a Pt metal rich surface (Ni) or a Pt poor surface (Co).

5.4. Cyclic voltammetry (CV)

In order to determine the electrocatalytic activity of the synthesized nanoparticles, their current response to applied voltage was tested using a 3-electrode electrochemical cell at potential 0 – 1.2 V and 10 mV/s scanning rate in 0.5 M H₂SO₄ electrolyte. The voltammograms of the Pt-Co nanoparticles prepared by both methods are shown in Fig. 5.15. CV analysis of the monometallic Pt sample (prepared at room temperature with no alloying metal added) showed no activity in the acid electrolyte. This inactivity in acid electrolyte was also observed by Nikles et al. [42], who determined that the catalytically active sites were blocked by surfactant which was bound on the surface of the nanoparticles. It is assumed this occurred here as well.

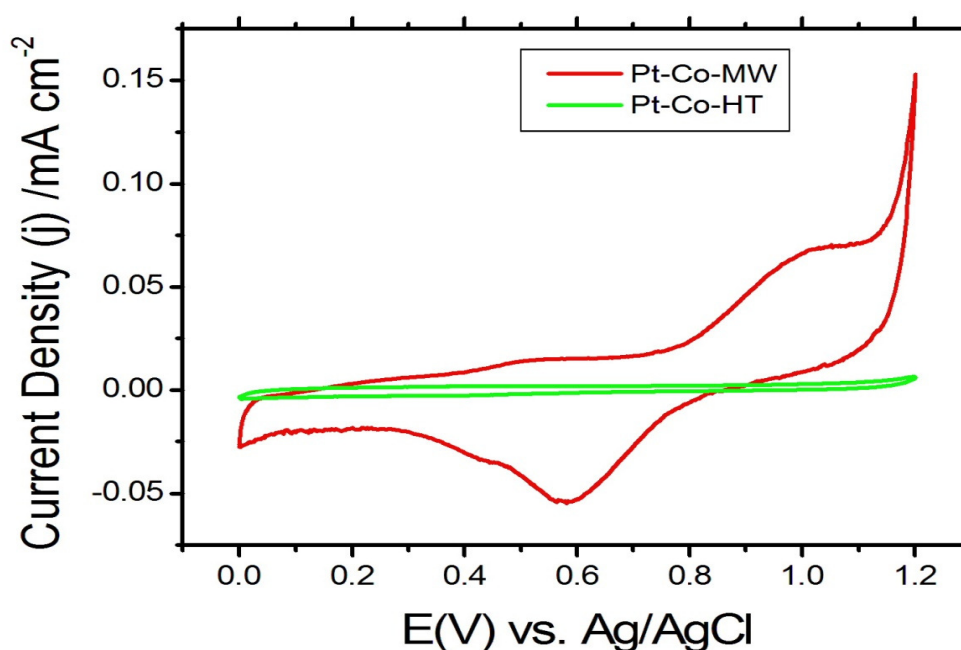
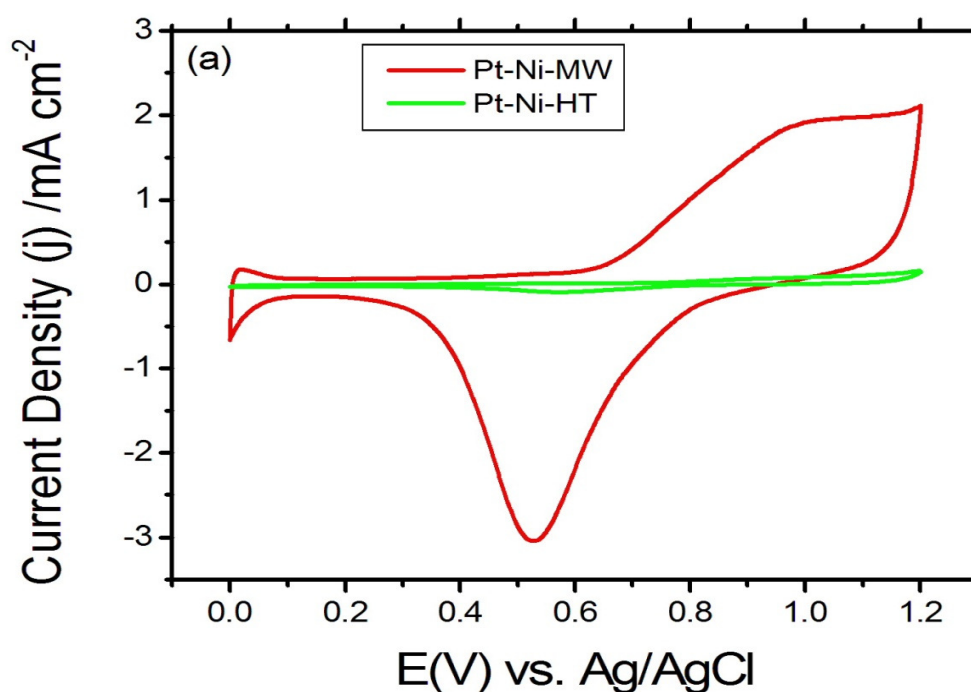


Figure 5.15. Cyclic voltammograms of (a) both Pt-Co sample and monometallic Pt. (Measurements were performed in 0.5 M H₂SO₄ at 10 mVs after purging with N₂ for 30 minutes).

The microwave-irradiated sample (Pt-Co-MW) exhibited peaks that are consistent with Pt electrocatalyst activity in acidic medium with Pt oxidation (0.99 V) and PtO reduction (0.60 V) peaks, and an onset potential of 0.75 V. This catalytic activity can be explained by the presence of surface ratio of Pt to Co (1:4). However, no typical Pt oxidation/reduction peaks were observed for the Pt-Co-HT sample, due to the low amount of alloyed Pt (0.2 at.%) and the large amount of inactive Co (33.9 at.%) present on the surface of these nanoparticles.

Both the Pt-Ni catalysts showed typical electrocatalytic activity in the acid electrolyte, with the current density of the Pt-Ni-HT (Fig. 5.16b) sample was only a tenth of that of the Pt-Ni-MW (Fig. 5.16a) sample. The Pt oxidation peaks were observed at 0.94 V and 0.95 V in the forward scan and the Pt reduction peaks at 0.52 V and 0.58 V in the reverse scan for the MW and HT samples respectively. Furthermore, the onset potential for the MW sample was at 0.72 V and that of the HT sample at 0.65 V.



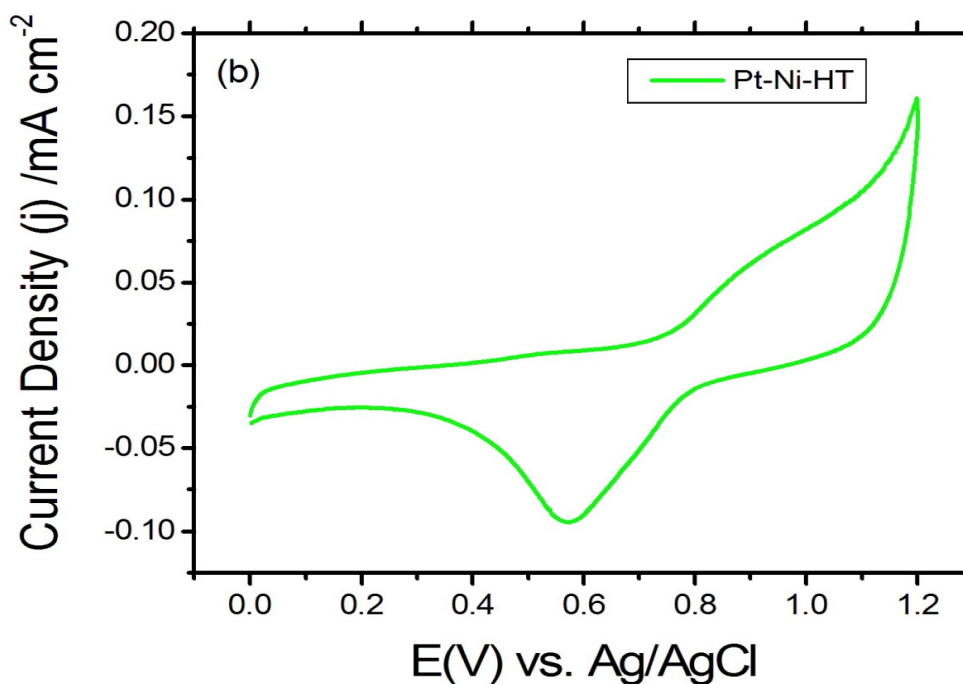


Figure 5.16. Cyclic voltammograms of (a) Pt, Pt-Ni-MW and Pt-Ni-HT and (b) the expanded scale of the Pt-Ni-HT sample. (Measurements performed in 0.5 M H₂SO₄ at 10 mVs after purging with N₂ for 30 minutes).

The electrochemical active surface areas (ECSA) of the nanoparticles were calculated by integrating the charge under the H₂ desorption areas. (See equation 3.2). The values were determined to be: 0.0046 m²/g Pt (Pt-Co-MW) < 0.028 m²/g Pt (Pt-Ni-HT) < 0.046 m²/g Pts (Pt-Ni-MW). This is to be expected as the ECSA is related to the surface concentration of oxides/hydroxides seen from XPS studies.

Nickel has been said to segregate on the surface of bimetallic nanoparticles, forming oxides and hydroxides [24], which are ideal for fuel cell electrocatalysts in that they enhance the overall catalytic activity through the donation of the O⁻ to oxidise the CO species to CO₂ during the methanol oxidation reaction [7]. The presence of the double-layer (observed at 0.1 – 0.3 V in Fig. 5.16a, Pt-Ni-MW) is also consistent with the presence of metal hydroxides and other surface oxides in

the nanoparticles [43]. Pt-Hi-HT (Fig. 5.16b) possessed the highest BET surface area, but contained only 0.1 Ni at.% on the surface; thus its behaviour approached that of monometallic Pt which was also determined to be inactive. Therefore it can be said that the presence of the alloying metal, that contains oxides and hydroxide species, contributes towards the enhancement in catalytic activity of the nanoparticles [3, 27, 44].

To further analyze the electrocatalytic activity of the catalysts they were tested for methanol oxidation activity in an alcohol electrolyte.

5.5. Methanol Oxidation Reaction (MOR)

The Pt-Co and Pt-Ni materials were tested as fuel cells electrocatalysts in direct methanol fuel cells (DMFCs) in a 0.5 M H_2SO_4 + 1 M CH_3OH electrolyte vs. an Ag/AgCl reference electrode (under the same reaction conditions in section 5.4). The voltammograms for the Pt-Co nanoparticles are shown in Fig. 5.17. There was no activity observed for the monometallic Pt nanoparticles, as seen in the acid electrolyte measurements. This could be due to the presence of PVP on the surface of these nanoparticles, confirmed by FT-IR studies which showed peaks associated with PVP [45]. This inactivity of Pt in methanol was also observed by Liu et al. [46] for Pt/C catalysts covered with a shell of thiol molecules. This is in contrast to Pt studies for MOR which show some electrocatalytic activity [47, 48].

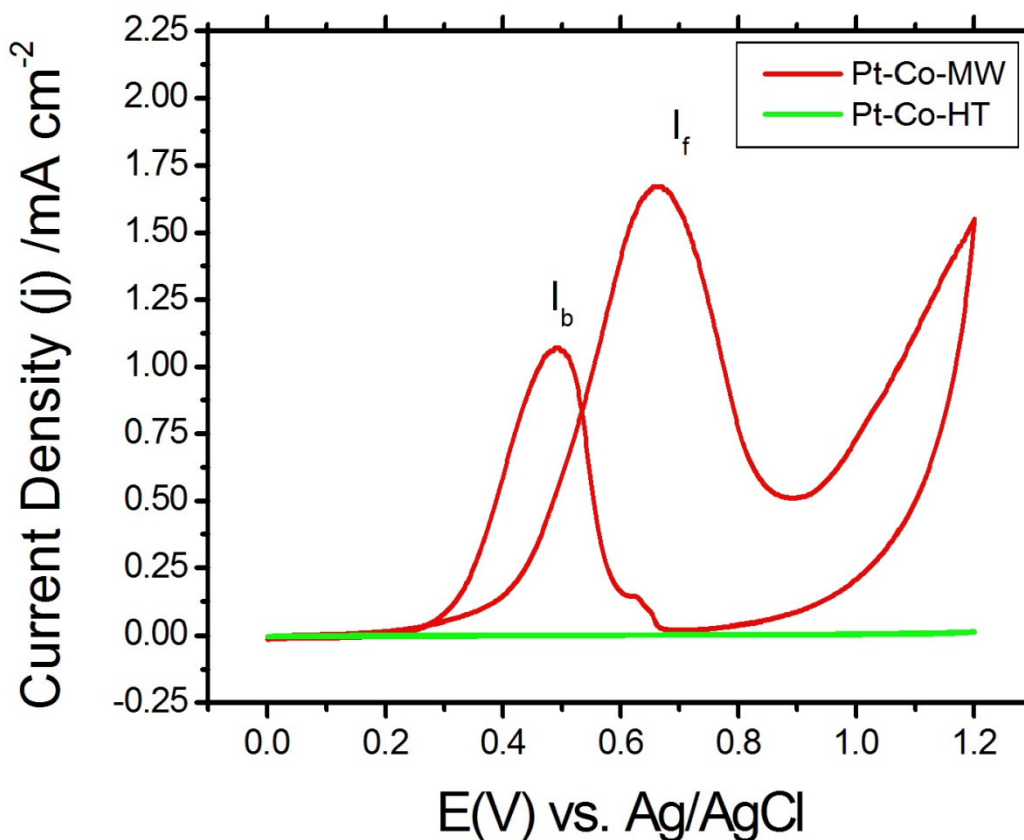


Figure 5.17. Methanol oxidation voltammograms of Pt-Co nanoparticles synthesized with microwave-irradiation and conventional procedure. (Measurements performed in 0.5 M H₂SO₄ + 1M CH₃OH at 10 mVs after purging the solution with N₂ for 30 minutes).

As observed in acid electrolyte tests, no MOR activity was observed for the Pt-Co-HT sample. The Pt-Co-MW nanoparticles in contrast exhibited electrocatalytic activity towards methanol oxidation with anodic peaks present in the forward (0.66 V) and reverse (0.48 V) scans. The reactivity of the catalysts is readily related to the structure and surface properties of the nanoparticles, where the poor performance of the Pt-Co-HT can be related to the non-availability of Pt surface sites for the methanol to adsorb in the first stage of the MOR (see Eq. 1).

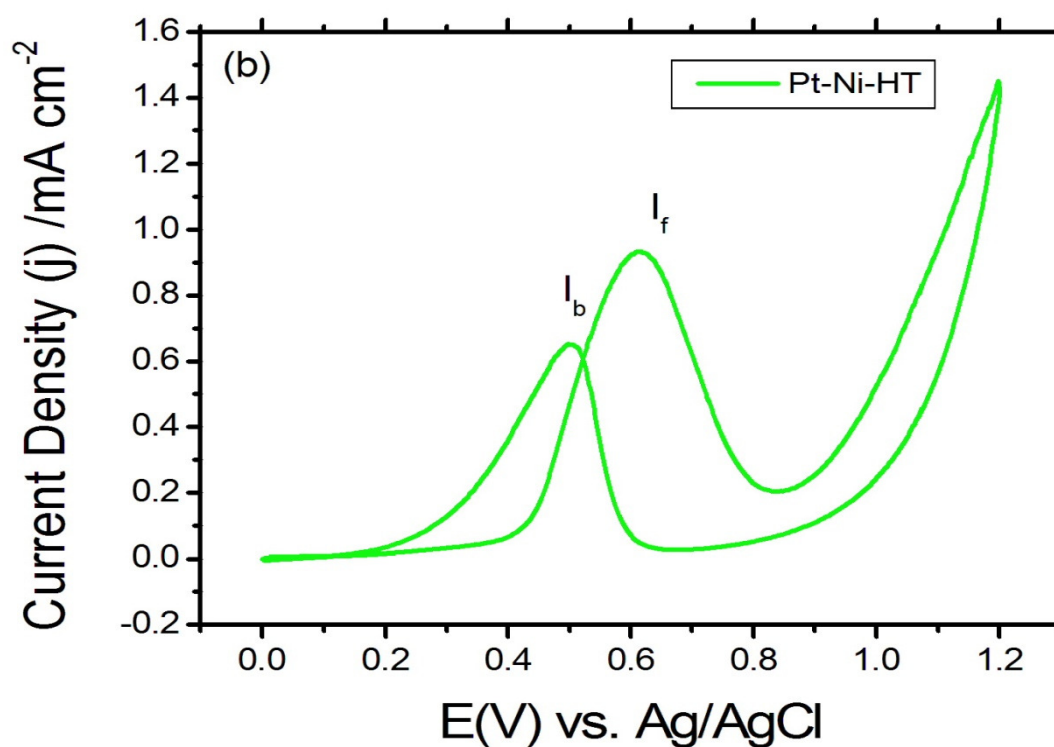
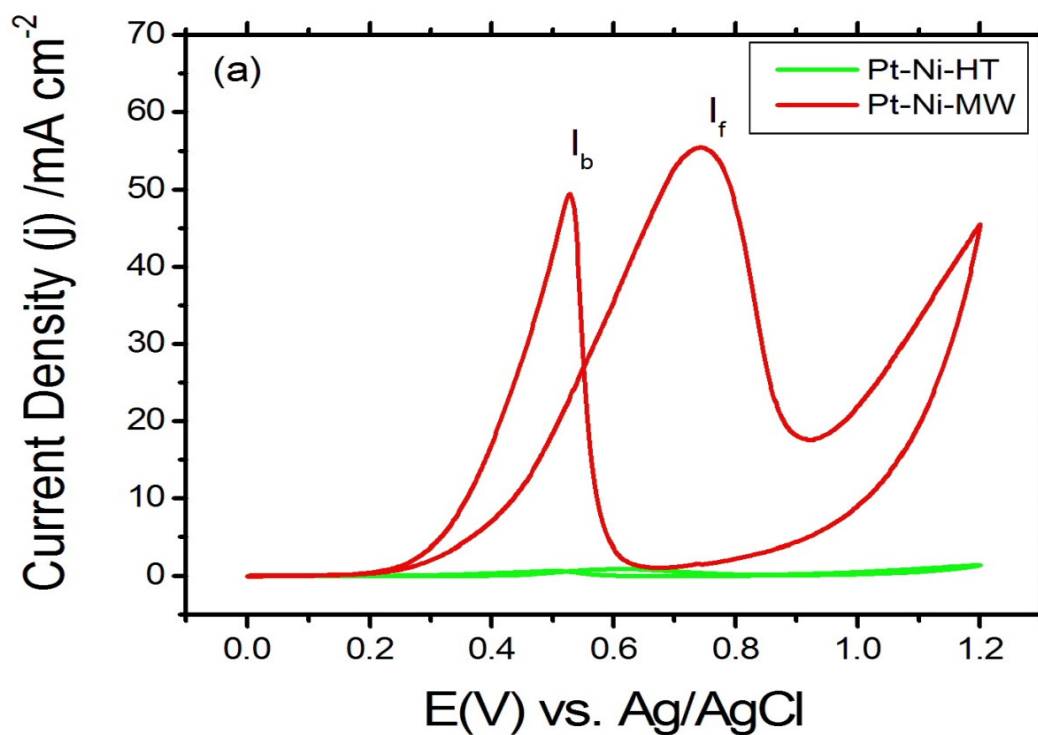


Figure 5.18. Methanol oxidation voltammograms of (a) both Pt-Ni MW and HT samples and (b) the HT sample with expanded scale. (Measurements done in 0.5 M H_2SO_4 + 1M CH_3OH at 10 mVs).

On the other hand, the behaviour of the Pt-Ni samples, MW (Fig.5.18a) and HT (Fig. 5.18b), was consistent with the results obtained in the acid electrolyte experiments. The onset potentials for these catalysts were observed at 0.22 V (MW) and 0.19 V (HT), with the forward anodic peaks at 0.74 V and 0.61 V, and the reverse peaks at 0.53 V and 0.49 V for the MW and HT samples respectively (see Table 5.5). The presence of these peaks is typical of electrocatalysts that are active for methanol oxidation [7]. The onset potential of the methanol oxidation reaction occurs at 0.26 V for the commercial PtC/E-ETEK catalyst [9]. Ideally the onset potential should occur at lower potential (0.20 V) to avoid the slow kinetics of the methanol oxidation reaction [6, 7].

A lower onset potential is also a sign of the ability of the catalyst to adsorb methanol during MOR [43, 44]. For the Pt-Co and Pt-Ni samples produced in this work the onset potential ranged from 0.19 – 0.26 V, thus this shows their good ability to adsorb methanol. The magnitude of the methanol oxidation onset potentials was as follows: Pt-Ni-HT (0.19) < Pt-Ni-MW (0.22) < Pt-Co-MW (0.27), where the Pt-Ni-HT showed the lowest onset potential. The onset potential of the materials can be related to the activation energy (E_a) of the methanol oxidation reaction of the catalysts [34], where the lower the onset potential, the smaller the required energy input for methanol oxidation.

However, the peak current for these samples were different which showed that the MW sample (55.4 mA/cm^2) was ~ 60 times higher than that obtained for the HT sample (0.92 mA/cm^2). The reason for this difference in peak current for the same molar composition Pt-Ni samples was ascribed to the absence of Ni on the surface of the HT sample (0.1 at.%) as compared to the Ni covered MW sample surface (19.0 at.%). Thus while monometallic Pt can be active for methanol oxidation, [14],

our data suggest that the presence of Co and Ni on the surface of the nanoparticles does contribute towards the general enhancement in electrocatalytic activity of the catalyst. The ratio of the forward peak current (I_f) to the reverse peak current (I_b), i.e. I_f/I_b , gives information on the efficiency of the catalyst in removing species such as CO and formaldehyde that are formed in the forward scan of the reaction [5-7]. These species block the catalytically active sites of the nanoparticles [6] and a good catalyst has a high ratio. The order of these peak ratios (I_f/I_b) obtained here was: Pt-Co-MW (1.58) > Pt-Ni-HT (1.44) > Pt-Ni-MW (1.14), showing that the microwave-synthesized Pt-Co-MW is best at removing the species that block the catalytic sites.

Table 5.5 Peak parameters of the Methanol Oxidation Reaction voltammograms.

Sample	Procedure	E_{onset} (V)	E_f (V)	I_f (mA cm^{-2})	E_b (V)	I_b (mA cm^{-2})	I_f/I_b	I (mA/mg Pt)
PtCo	HT	-----	-----	-----	-----	-----	-----	-----
	MW	0.27	0.66	1.68	0.48	1.06	1.58	0.085
PtNi	HT	0.19	0.61	0.92	0.49	0.64	1.44	0.047
	MW	0.22	0.74	55.4	0.53	48.5	1.14	2.81

The good activity of the Pt-Ni-MW catalyst was further supported by mass current density calculations (Table 5.5). The mass current density is described as the current output per mg of Pt catalyst loading on the glassy carbon electrode (mA/mg Pt) [9]. Mass current density data gave the following results; Pt-Ni-MW (2.81) > Pt-Co-MW (0.085) > Pt-Ni-HT (0.047) > Pt-Co-HT. The current density of our Pt-Ni-MW catalyst (2.81 mA/mg Pt) was found to be comparable to work done on other bimetallic electrocatalysts under the same reaction conditions e.g. Tripković et al. [48] for PtRu

nanoparticles (1.4 mA/mg Pt). This is an important finding as the current output based on the Pt catalyst loading, has implications in the commercial application of fuel cell [3, 9].

Overall, the order of activity when all factors are considered is Pt-Ni-MW > Pt-Co-MW > Pt-Ni-HT. It can be seen that the MW method leads to MOR enhancement due to; (i) the alloy formation, (ii) the metal oxide and hydroxide species, and (iii) the 1/4 Pt/M surface ratio produced by microwave-irradiation, as determined from XPS studies. The order can be correlated to the lattice parameters of the samples as calculated from XRD data (Table 5.1), where the lower the parameter the higher the degree of alloying. This has been said to relate to an increase in the methanol electrooxidation activity of the catalysts, which is in agreement with work done by Lu et al. [34]. They determined that a favourable Pt-Pt distance led to an increase in the number of Pt-M neighbours.

5.6. Chronoamperometry measurements

The long term stability of the Pt-Ni-MW catalyst (Fig. 5.19) was determined using chronoamperometry in an alcohol electrolyte. The time versus current measurement was used to calculate the current decay with time at a steady potential (0.5 V). After the 1200 s, the current density percentage was ~33.3% of the initial current ($t = 0$ s). The rate of current decay can be used to determine the ability of the catalyst to tolerate carbonaceous species formed in the methanol dissociation process [7, 49].

Therefore based on the current after 1200s it can be said that this catalyst showed good resistance to CO and intermediate poisoning [49].

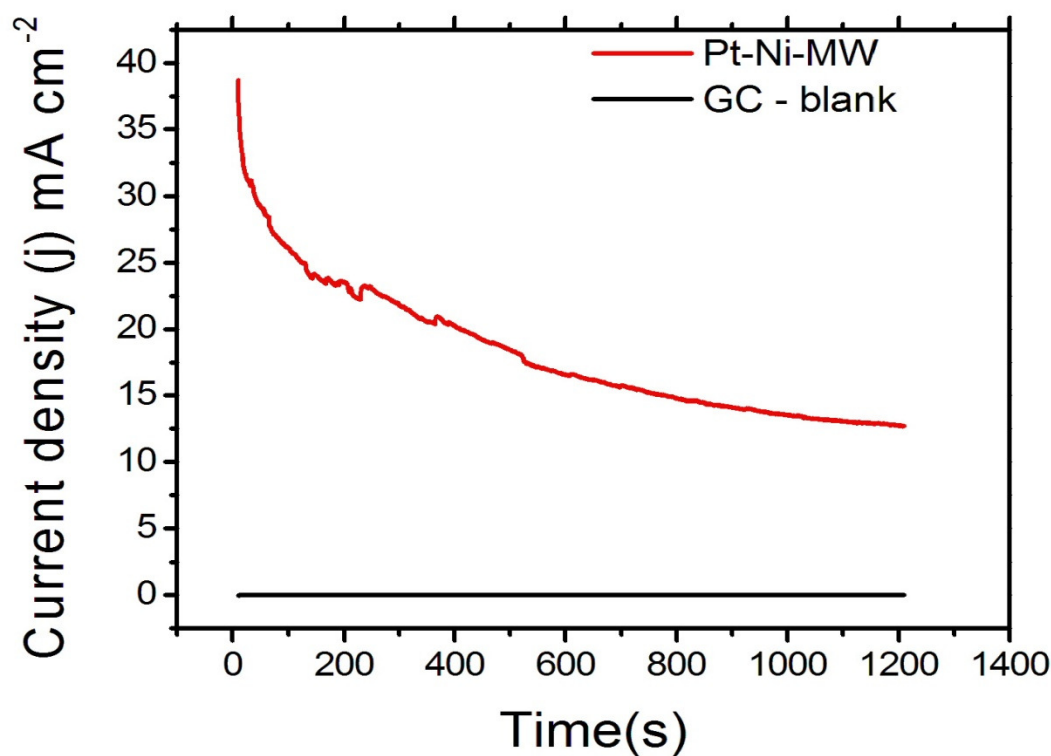


Figure 5.19. Chronoamperometry curve of the Pt-Ni-MW nanoparticles in 0.5 M H₂SO₄ + 1M CH₃OH at 10 mVs.

Studies on bimetallic catalyst that have been supported are in general agreement with the data found for the unsupported catalyst used in this study. Thus, the increased activity of Pt-Ni nanoparticles synthesized by microwave-irradiation was also observed by Deivaraj et al. [24], who obtained small Pt-Ni nanoparticles on a carbon support. In another study, Ozoemena, et al. [6] reported on carbon supported Pd-Ni prepared by microwave-irradiation, and showed that the presence of Ni-OH species contributed to the enhancement in the catalytic activity. Their data was consistent with the bifunctional model reaction mechanism.

In this work, the presence of the anodic reverse peak, indicated the reduction and regeneration of the PtO species formed during the forward scan [6]. As was mentioned by Marković et al. [50] and Gorjković et al. [51], this means that the alloying of Pt with Co or Ni leads to the donation of O-species to CO to form CO₂ during the electro-oxidation of CO. The donation of the O-species by the alloyed metal is associated with the bifunctional model (see Schmidt et al. [52]).

5.6. Conclusion

Electrocatalytically active Pt-Ni and Pt-Co nanoparticles for use in fuel cells were synthesised by a microwave-irradiation procedure. In comparison, nanoparticles synthesized conventionally, with the same precursors and surfactants were less active. The increased activity of MW nanoparticles, on addition of Co or Ni, was found to relate to the surface area and a decrease in the Pt lattice parameter revealing a favourable Pt-Pt atomic distance for MOR. XPS data analysis showed that more active catalysts (Pt-Co-MW and Pt-Ni-MW) contained a mixture of Pt and Ni (or Co), and also possessed higher Ni oxide and hydroxide concentrations. The MOR peak analysis indicated that the mechanism of methanol oxidation follows the bifunctional model, where the alloying metal donates O-species to the CO to form CO₂. The superiority of the Pt-Ni-MW catalyst in comparison to its HT counterpart can be attributed to the alloy formation resulting from the microwave-irradiation process. As expected, due to the high surface concentration of inactive Co, the Pt-Co-HT samples showed no activity for MOR.

References

1. Peng, Z. and H. Yang, *Designer platinum : control of shape, composition in alloy, nanostructure and electrocatalytic properties*. Nano Today, 2009. **4**: p. 143 - 169.
2. Wang, D., T. Xie, and Y. Li, *Nanocrystals: Solution-based synthesis and applications as nanocatalysts*. Nano Research, 2009. **2**(1): p. 30-46.
3. Antolini, E. and J. Perez, *The renaissance of unsupported nanostructured catalysts for low-temperature fuel cells: from the size to the shape of metal nanostructures*. Journal of Materials Science, 2011. **46**: p. 4435 - 4457.
4. Tu, W. and H. Liu, *Continuous synthesis of colloidal metal nanoclusters by microwave irradiation*. Chemistry of Materials, 2000. **12**: p. 564 - 567.
5. Gao, Y., et al., *Evidence of monolayer assembly of poly(vinylpyrrolidone) on the surface of silver nanowires*. Journal of Physical Chemistry B, 2004. **108**: p. 12877 - 12881.
6. Yee, C.K., et al., *Novel one-phase synthesis of thiol-functionalized gold, palladium, and iridium nanoparticles using superhydride*. Langmuir, 1999. **15**: p. 3486 - 3491.
7. Yee, C., et al., *One-phase synthesis of thiol-functionalized platinum nanoparticles*. Langmuir, 1999. **15**: p. 4314 - 4316.
8. Mathe, N.R., M.R. Scriba, and N.J. Coville, *Methanol oxidation reaction activity of microwave-irradiated and heat-treated Pt/Co and Pt/Ni electrocatalysts*. International Journal of Hydrogen Energy, 2014. **39**: p. 18871 - 18881.
9. Zhu, Y.-J., et al., *Microwave-assisted synthesis of single-crystalline Tellurium nanorods and nanowires in ionic liquids*. Angewandte Chemie, 2004. **116**: p. 1434 - 1438.
10. Komarneni, S., et al., *Microwave-polyol process for Pt and Ag nanoparticles*. Langmuir, 2002. **18**: p. 5959 - 5962.
11. Yu, W., W. Tu, and H. Liu, *Synthesis of nanoscale platinum colloids by microwave dielectric heating*. Langmuir, 1999. **15**: p. 6 - 9.
12. Vollath, D. and D.V. Szabó, *The microwave plasma process - a versatile process to synthesize nanoparticulate materials*. Journal of Nanoparticle Research, 2006. **8**: p. 417 - 428.
13. Grace, A.N. and K. Pandian, *One pot synthesis of polymer protected Pt, Pd, Ag and Ru nanoparticles and nanoprisms under reflux and microwave mode of heating in glycerol - A comparative study*. Materials Chemistry and Physics, 2007. **104**: p. 191 - 198.
14. Bensebaa, F., et al., *Microwave synthesis of polymer-embedded Pt-Ru catalyst for direct methanol fuel cell*. Journal of Physical Chemistry, 2005. **109**: p. 15339 - 15344.
15. Mathe, N.R., et al., *TEM and EELS studies of microwave-irradiation synthesis of bimetallic platinum nanocatalysts*. Journal of Physics: Conference Series, 2014. **522**: p. 012066.
16. Ramulifho, T., et al., *Fast microwave-assisted solvothermal synthesis of metal nanoparticles (Pd, Ni, Sn) supported on sulfonated MWCNTs: Pd-based bimetallic catalysts for ethanol oxidation in alkaline medium*. Electrochimica Acta, 2012. **59**: p. 310 - 320.

17. Long, N.V., et al., *Effets of heat treatment and poly(vinylpyrrolidone) (PVP) polymer on electrocatalytic activity of polyhedral Pt nanoparticles towards methanol oxidation*. Coll. Poly. Sci., 2011. **289**: p. 1373 - 1386.
18. Wang, D. and Y. Li, *Bimetallic nanocrystals: liquid-phase synthesis and catalytic applications*. Advanced Materials, 2011. **23**: p. 1044 - 1060.
19. Xu, W., et al., *Microwave-assisted synthesis of nickel nanoparticles*. Materials Letters, 2008. **62**: p. 2571 - 2573.
20. Bensebaa, F., et al., *Tunable platinum-ruthenium nanoparticle properties using microwave synthesis*. Journal of Materials Chemistry, 2004. **14**: p. 3378 - 3384.
21. Deivaraj, T.C., W. Chena, and J.Y. Lee, *Preparation of PtNi nanoparticles for the electrocatalytic oxidation of methanol*. Journal of Materials Chemistry, 2003. **13**: p. 2555 - 2560.
22. Ahrenstorf, K., et al., *Colloidal synthesis of NixPt1-x nanoparticles with tuneable composition and size*. Small, 2007. **3**(2): p. 271 - 274.
23. Mathe, N.R., et al., *The effect of reducing agents on the electronic, magnetic and electrocatalytic properties of thiol-capped Pt/Co and Pt/Ni nanoparticles*. Electrocatalysis, 2014. doi:10.1007/s12678-014-0241-y.
24. Park, K.-W., et al., *Chemical and electronic effects of Ni in Pt/Ni and Pt/Ru/Ni Alloy nanoparticles in methanol electrooxidation*. Journal of Physical Chemistry B, 2002. **106**: p. 1869 - 1877.
25. Yang, H., et al., *Structure and electrocatalytic activity of carbon-supported Pt-Ni alloy nanoparticles towards oxygen reduction reaction*. Journal of Physical Chemistry B, 2004. **108**: p. 11024 - 11034.
26. Arico, A.S., et al., *An XPS study on oxidation states of Pt and its alloys with Co and Cr and its relevance to electroreduction of oxygen*. Applied Surface Science, 2001. **172**: p. 33 - 40.
27. Guo, J.W., et al., *Preparation and characterization of a PtRu/C nanocatalyst for direct methanol fuel cells*. Electrochimica Acta, 2005. **51**: p. 754 - 763.
28. Park, K.-W., et al., *Chemical and electronic effects of Ni in Pt/Ni and Pt/Ru/Ni alloy nanoparticles in methanol electrooxidation*. Journal of Physical Chemistry B, 2002. **106**: p. 1869-1877.
29. Biesinger, M.C., et al., *Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni*. App. Surf. Sci., 2011. **257**: p. 2717 - 2730.
30. Casella, I.G., M.R. Guascito, and M.G. Sannazzaro, *Voltammetric and XPS investigations of nickel hydroxide electrochemically dispersed on gold surface electrodes*. Journal of Electroanalytical Chemistry, 1999. **462**: p. 202 - 210.
31. Grosvenor, A.P., et al., *New interpretations of XPS spectra of nickel and oxides*. Surface Science, 2006. **600**: p. 1771 - 1779.
32. Biesinger, M.C., et al., *X-ray photoelectron spectroscopic chemical state quantification of mixed nickel metal, oxide and hydroxide systems*. Surface and Interface Analysis, 2009. **41**: p. 324 - 332.
33. Castle, J.E., *Use of "shake-up" satellites in photoelectron spectra for analysis of oxide layers on metals*. Nature Physical Science, 1971. **234**: p. 93 - 95.
34. Kim, K.S. and N. Winograd, *X-ray photoelectron spectroscopic binding energy shifts due to matrix in alloys and small supported metal nanoparticles*. Chemical Physics Letters, 1975. **30**: p. 91-95.

35. Zhao, J., et al., *Microwave polyol synthesis of Pt/C catalysts with size-controlled Pt particles for methanol electrocatalytic oxidation*. Journal of Materials Science, 2006. **41**: p. 5514 - 5518.
36. Mabena, L.F., et al., *Ruthenium supported on nitrogen-doped carbon nanotubes for the oxygen reduction reaction in alkaline media*. Fuel Cells, 2012. **12**: p. 862 – 868.
37. Frelink, T., W. Visscher, and J.A.R.v. Veen, *Particle size effect of carbon-supported platinum catalysts for the electrooxidation of methanol*. Journal of Electroanalytical Chemistry, 1995. **382**: p. 65 - 72.
38. Gasteiger, H.A. and M.M. Markovic, *Just a dream - or future reality*. Science, 2009. **324**: p. 48 - 49.
39. Park, S., Y. Xie, and M.J. Weaver, *Electrocatalytic pathways on carbon-supported platinum nanoparticles: comparison of particle-size-dependent rates of methanol, formic acid, and formaldehyde electrooxidation*. Langmuir, 2002. **18**: p. 5792 - 5798.
40. Mu, Y., et al., *Controllable Pt nanoparticle deposition on carbon nanotubes as an anodic catalyst for direct methanol fuel cells*. Journal of Physical Chemistry B, 2005. **109**: p. 22212 - 22216.
41. Sun, S., et al., *Single-atom catalysis using Pt/graphene achieved through atomic layer deposition*. Scientific Reports, 2013. **3**: p. 1775.
42. Yung, T.-Y., J.-Y. Lee, and L.-K. Liu, *Nanocomposite for methanol oxidation: synthesis and characterization of cubic Pt nanoparticles on graphene sheets*. Science and Technology of Advanced Materials, 2013. **14**: p. 035001.
43. Okamoto, H., W. Kon, and Y. Mukouyama, *Five current peaks in voltammograms for oxidation of formic acid, formaldehyde and methanol on platinum*. Journal of Physical Chemistry B, 2005. **109**: p. 15659 - 15666.
44. Murthy, A. and A. Manthiram, *Application of derivative voltammetry in the analysis of methanol oxidation reaction*. The Journal of Physical Chemistry C, 2012. **116**: p. 3827 - 3832.
45. Antolini, E., J.R.C. Salgado, and E.R. Gonzalez, *The methanol oxidation reaction on platinum alloys within the first row transition metals. The case of Pt-Co and Pt-Ni alloy electrocatalysts for DMFCs : A short review*. Applied Catalysis B: Environmental, 2006. **63**: p. 137 - 149.
46. Iwasita, T., *Methanol and CO Electrooxidation*, in *Handbook of Fuel Cells - Fundamentals, Technology and Applications*, W. Vielstich, H.A. Gasteiger, and A. Lamm, Editors. 2003, John Wiley & Sons. p. 603 - 624.

CHAPTER 6: MICROWAVE-IRRADIATION POLYOL SYNTHESIS OF THE PVP-PROTECTED BIMETALLIC PLATINUM ELECTROCATALYSTS FOR METHANOL OXIDATION REACTION (MOR)

Due to the high electrocatalytic activity observed for the microwave-irradiated Pt-Ni samples in Chapter 5, a more comprehensive study of the microwave-irradiation process was performed in this chapter. This was to determine the effect that the different reaction parameters have on the electrocatalytic activity of the nanoparticles.

This work will be submitted for publication: ***N.R. Mathe, M.R. Scriba and N.J. Coville, Microwave-Irradiation Polyol Synthesized PVP-Protected Pt/Ni Nano-Electrocatalysts for Methanol Oxidation Reaction, Journal of Power Sources, 2014, In Process.***

6.1. Introduction

For decades, efforts have been made to prepare nanosized metal colloids and clusters with a narrow size distribution [1-4], but the production of the desired structures is still a huge challenge for researchers. The properties of the nanoparticles are controlled by their shape and size [5]. Therefore, it is important to control the morphologies of the nanoparticles in order to obtain the desired

properties. Many conventional chemical synthesis procedures have been used and these include chemical reduction which involves the use of volatile organic solvents and strong reducing agents [6-8]. These volatile organic reagents evaporate into the atmosphere resulting in the release of harmful chemicals into the environment. Therefore the introduction of cleaner, environmentally accepted and alternative synthetic technologies have become an important area of research [9].

Very recently, some new greener approaches to the generation of bimetallic metal nanoclusters were reported in the literature, and one of these techniques is microwave-irradiation (MW) (see Chapter 3 for detailed information on the MW process) [4, 10]. Microwave heating is an alternative to thermal heating. Since the introduction of microwave-irradiation as a synthesis procedure, much research using this technique has been conducted on organic reactions as well as in analytical chemistry [11].

Microwaves (MW's) are a portion of the electromagnetic spectrum [11, 12]. The heating effect associated with microwave dielectric heating results from dipolar polarization. This energy dissipation in the core of the material during heating results in a more regular heat distribution in a solvent compared to conventional heating [13]. It is reported that during the reaction, the microwaves penetrate the reaction solution resulting in a homogeneous and simultaneous fast heating. This effect eliminates the presence of a heat gradient observed in most conventional heating processes. This has made MW a very popular non-conventional energy source for the synthesis of nanoparticles [4, 11, 14].

The versatility of the microwave-irradiation approach and its potential for mass production of nanoparticles [4], for magnetic and catalytic materials, makes it

particularly attractive. Microwave effects can be divided into two categories: the thermal effects and the non-thermal effects. The thermal effects are caused by the temperature regime created by microwave dielectric heating; the latter caused by the inherent characteristics of microwaves other than the thermal effects [10]. The non-thermal effects contribute to the overall heating in the MW, though it is generally accepted that thermal effects are the main contributing factor [11].

We have recently demonstrated the superiority of MW-irradiation synthesis compared to conventional synthesis in developing electrocatalysts for fuel cell applications [8]. Therefore this chapter will focus on changing the reaction parameters in order to develop catalysts with improved current output. The molar ratio of the alloying metal, amount of capping agent and pH of the synthesis solutions were varied to determine the likely effect these parameters have on the shape, size and surface properties of the nanoparticles. These will ultimately affect the electrocatalytic activity, specifically for methanol oxidation reaction (MOR) of the nanoparticles.

6.2. Synthesis Procedure

6.2.1. Materials

H₂PtCl₆.6H₂O (99%), NiCl₂.6H₂O (97%), ethylene glycol (EG, ≥ 99.5%), polyvinylpyrrolidone (MW 40,000, PVP-40), isopropanol (99.5+%), and Nafion

(5wt%, 45% water) were purchased from Sigma Aldrich and used as received without further modification or purification.

6.2.2. Method

The synthesis procedure used was adapted from work by Yu et al. [11], where they used as domestic 2540 MHz microwave oven. Our method used a commercial Anton Paar M300 microwave reactor system with more control of the reaction parameters such as; temperature, pressure and power (see Chapter 3, section 3.1.2). The samples were prepared using metal precursor salts: $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (500mg), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (250 mg), with ethylene glycol (60 ml) as both the solvent and reducing agent. The precursor salts and PVP were stirred in EG for 2 hours until completely dissolved. Then the mixture was poured into Teflon microwave vessels and placed in an Anton Paar M300 microwave oven. The microwave parameters used were: temperature = 200 °C, power = 750 W, time = 30 min. To control the size and agglomeration of the nanoparticles, PVP (polyvinylpyrrolidone) was used as the capping agent. NaOH was used to control the pH of the solutions and thus increase the reduction rate of the EG. EG acted as a solvent and reducing agents at temperatures above 180 °C [8, 15, 16].

Reaction variable used included:

Surfactant. The amount of surfactant (PVP) was varied for the Pt-Ni-(1:1) catalysts, (1000 mg, 750, 500, 250 and 0 mg PVP). The PVP was used as both a stabilizer and to control the shape of the Pt nanoparticles [17].

pH. The NaOH concentration was varied at 0.5 M, 1.0 M and 2.0 M NaOH using the 1:1 Pt:Ni molar ratio and 500 mg PVP for all the samples.

Molar ratio. The molar composition of the solutions was varied by changing the amount of alloying metal added to the Pt in the reaction, Pt-Ni-(1:1), Pt-Ni-(1:2), Pt-Ni-(1:3). The solutions all contained 500 mg PVP and 1.0 M NaOH.

6.2.3. Characterization

Transmission electron microscopy (TEM) images were acquired using a JEOL JEM-2100 microscope installed with a Gatan CCD camera device. The powder X-ray diffraction (XRD) diffractograms were generated from the PANalytical X'Pert Pro X-ray diffraction system. A BET Micrometrics TriStar II 3020 Surface area porosity system was used to determine the surface area of the catalysts, with degassing overnight at 90 °C overnight before measurement. X-ray photoelectron spectra (XPS) of the catalysts were recorded on a PHI 5000 Versaprobe – Scanning ESCA microprobe. The system uses an Al monochromator X-ray beam at 25 W and 15 kV, with pass energy of 11.8 eV for individual elements. Peak correction was done using the carbon peak shift before curve fitting by use of Multipak^(R) software.

6.2.4. Cyclic voltammetry

Electrocatalytic measurements were performed on a Metrohm Autolab single electrochemical cell system with scanning potentials from 0 – 1.2 V at a scan rate of 10 mV/s. The catalyst ink was prepared from the nanoparticle powder (2.0 mg), Nafion (80 μ l), and isopropanol (60 μ l) and the mixture was sonicated for 2 hours. Then 2.0 μ l of the catalyst ink was deposited onto a polished glassy carbon electrode (0.0314 cm²). The electrolyte solutions were purged with N₂ for 30 minutes. The voltammograms recorder resulted from the 10th cyclic scan.

6.3. Optimization of microwave-irradiation synthesis parameters

In order to understand the microwave-irradiation synthesis procedure, optimization of the reaction parameters was performed. The variable studied were the amount of surfactant or capping agent and the pH of the starting solution. This is because it was discovered that these two parameters affected the size and morphologies of the nanoparticles and as well as their electrocatalytic activity.

6.3.1. Change in the Pt/PVP molar ratio

The amount of the capping agent, in this case polyvinyl pyrrolidone (PVP), was varied to determine the optimum amount to be used in the microwave-irradiation

synthesis of bimetallic Pt-Ni nanoparticles. The reason is that the capping agent can control the particle size and the morphologies of the nanoparticles [18-20]. As catalysis is a surface process, it is therefore important to get an optimum particle size and controlled particle porosity or agglomeration. The amount of capping agent was varied from 0 mg – 1000 mg and their resulting TEM images are presented in Fig 6.1 and 6.2 (note that these images were taken at low and high magnification). The particle size distribution is presented in Fig. 6.3.

A directly proportional link was determined between the amount of PVP used and the particles size. The particle size increased with an increase in the PVP/Pt ratio, resulting in more agglomerated structures when PVP was not added into the solution (i.e. 0 mg PVP, Fig 6.1 a). Thus it is clear that the size of the nanoparticles can be controlled by varying the PVP ratio. It was also noted that contaminant-free nanoparticles were obtained which removed the need for any further calcination of the materials compared to the conventionally synthesized nanoparticles (see Chapter 4). Long et al. [17], determined that at high PVP concentrations PVP monolayers form on the surface of the nanoparticles due to the presence of their PVP chains. This means that the nanoparticles can be used as electrocatalysts as-is, without any surfactant blocking the catalytically active sites.

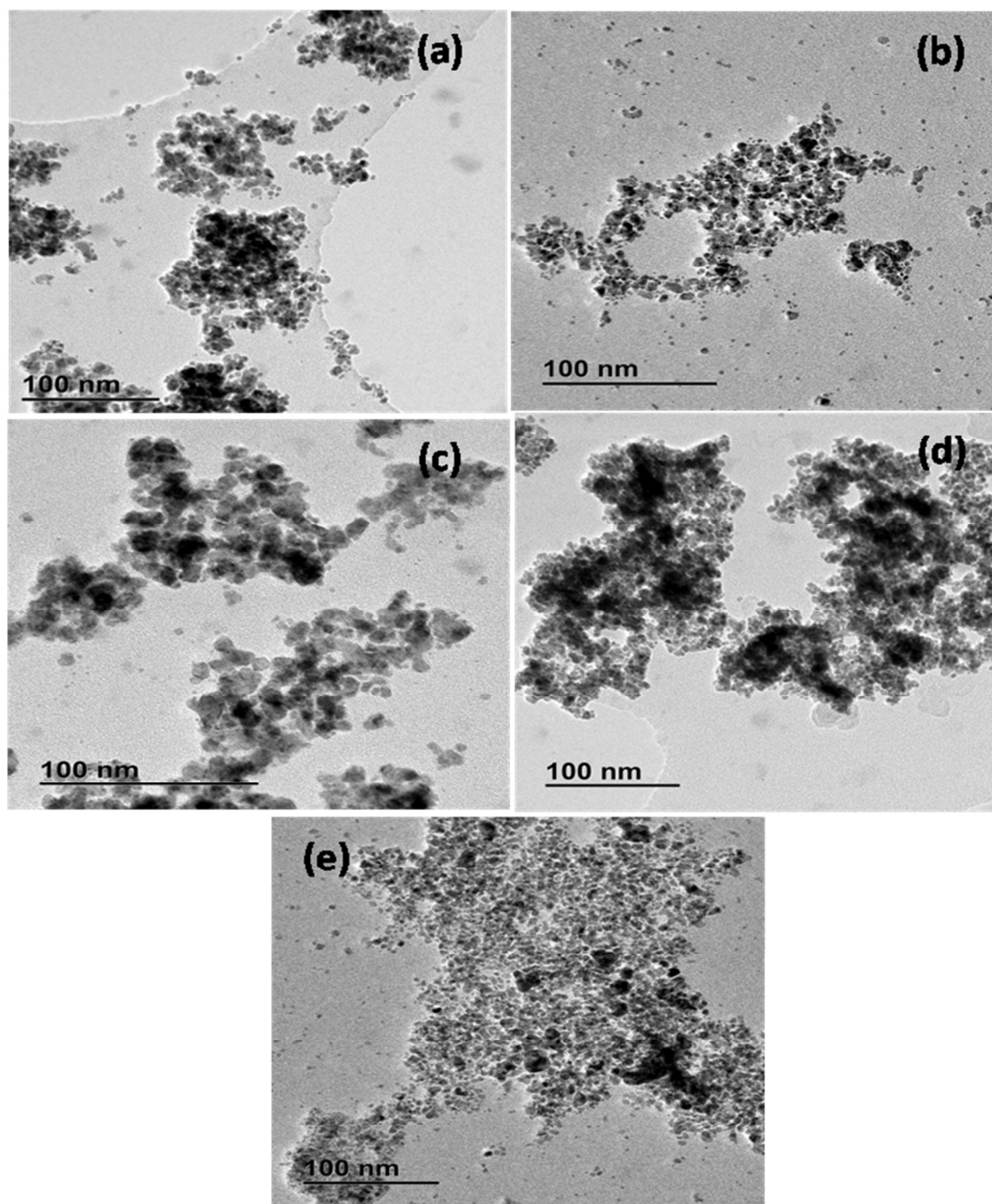


Figure 6.1. TEM images of Pt-Ni nanoparticles with different amounts of PVP; (a) 0 mg, (b) 250 mg, (c) 500 mg, (d) 750 and (e) 1 000 mg. The images were taken at low magnification (X60 – 100 K).

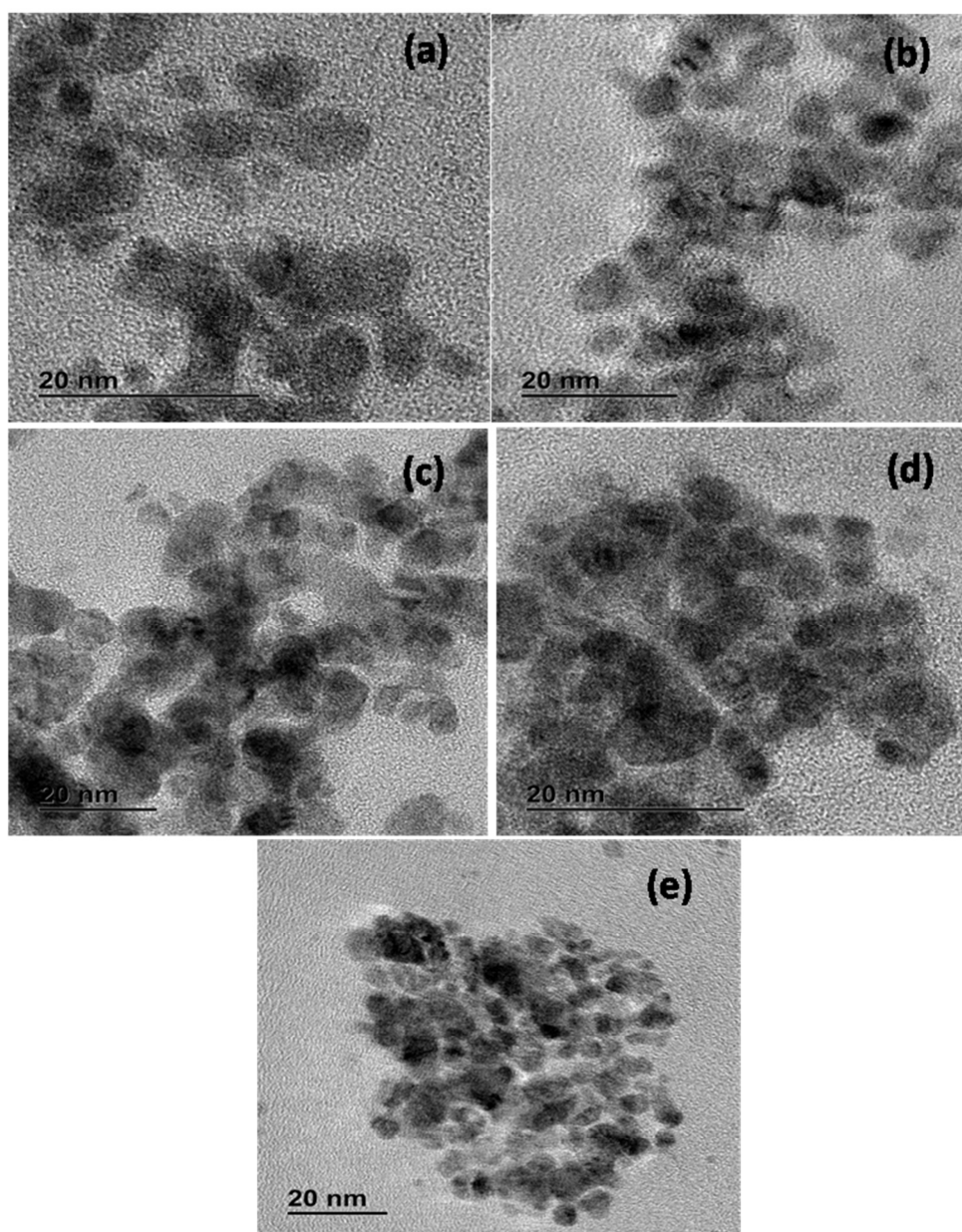


Figure 6.2. TEM images of Pt-Ni nanoparticles with different amounts of PVP; (a) 0 mg, (b) 250 mg, (c) 500 mg, (d) 750 and (e) 1 000 mg. The images were taken at high magnification (X150 – 250 K).

In other work done for microwave irradiation, Xu et al. [19] discovered that the PVP concentration affected the morphology (nanoflower structures) more than the particle size due to the rapid and homogenous heating of the microwave. They showed that there needs to be an appropriate PVP/NiCl₂ molar ratio in order to obtain the desired properties. On the other hand, Bensebaa et al. [20] determined that there was a

slight particle size decrease with an increase in the amount of PVP in at Pt-Ru alloy system, which they ascribed to the rapid formation of alloy clusters in microwave. We determined that there was only a slight increase in the particle size with an increase in the PVP/Pt ratio, shown in Fig 6.3 (a) – (e) for the particle size distribution.

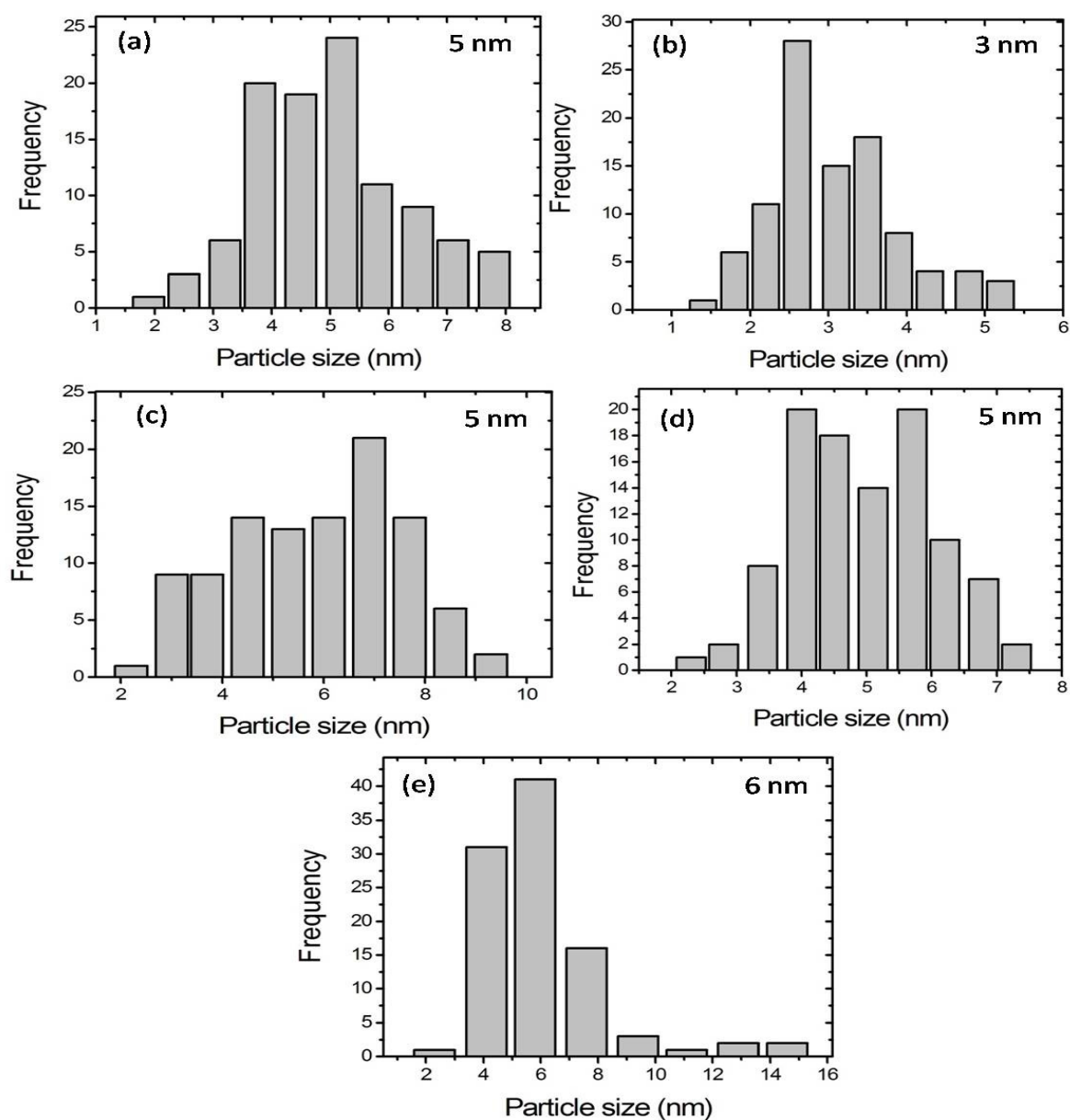


Figure 6.3. The particles size-distribution measurements of PVP/Pt nanoparticles, (a) 0 mg, (b) 250 mg, (c) 500 mg, (d) 750 mg and (e) 1 000 mg.

6.3.2. Change in the pH of the reaction solution

To further understand the microwave-irradiation procedure, the pH of the solution was varied by the addition of NaOH of different concentrations (0.5 M, 1.0 M and 2.0 M NaOH). The TEM images and accompanying particle size distribution are presented in Fig. 6.4 (a) – (h). Small, spherical and randomly dispersed nanoparticles were obtained at low pH (0.5 M NaOH, Fig. 6.4 (a) & (d)). The structures of the nanoparticles then changed as the concentration of NaOH was increased forming more agglomerated structures at 1.0 M NaOH (Fig. 6.4 (b) & (e)) and 2.0 M NaOH (Fig. 6.4 (c) & (f)). Thus increasing the NaOH concentration resulted in the formation of agglomerated or hierarchical network structures made up of smaller nanoparticles.

This formation of large structures with the addition of an excess amount of NaOH was also observed by Xu et al. [19]. They also observed little or no formation of colloids when NaOH was not used. This phenomenon was also observed in this study. It is because NaOH is said to increase the reduction rate of ethylene glycol during the microwave-irradiation process [11, 21]. Deivaraj et al. [21] also determined that NaOH has a dual role; to adjust the pH of the solution and to control the size of the nanoparticles.

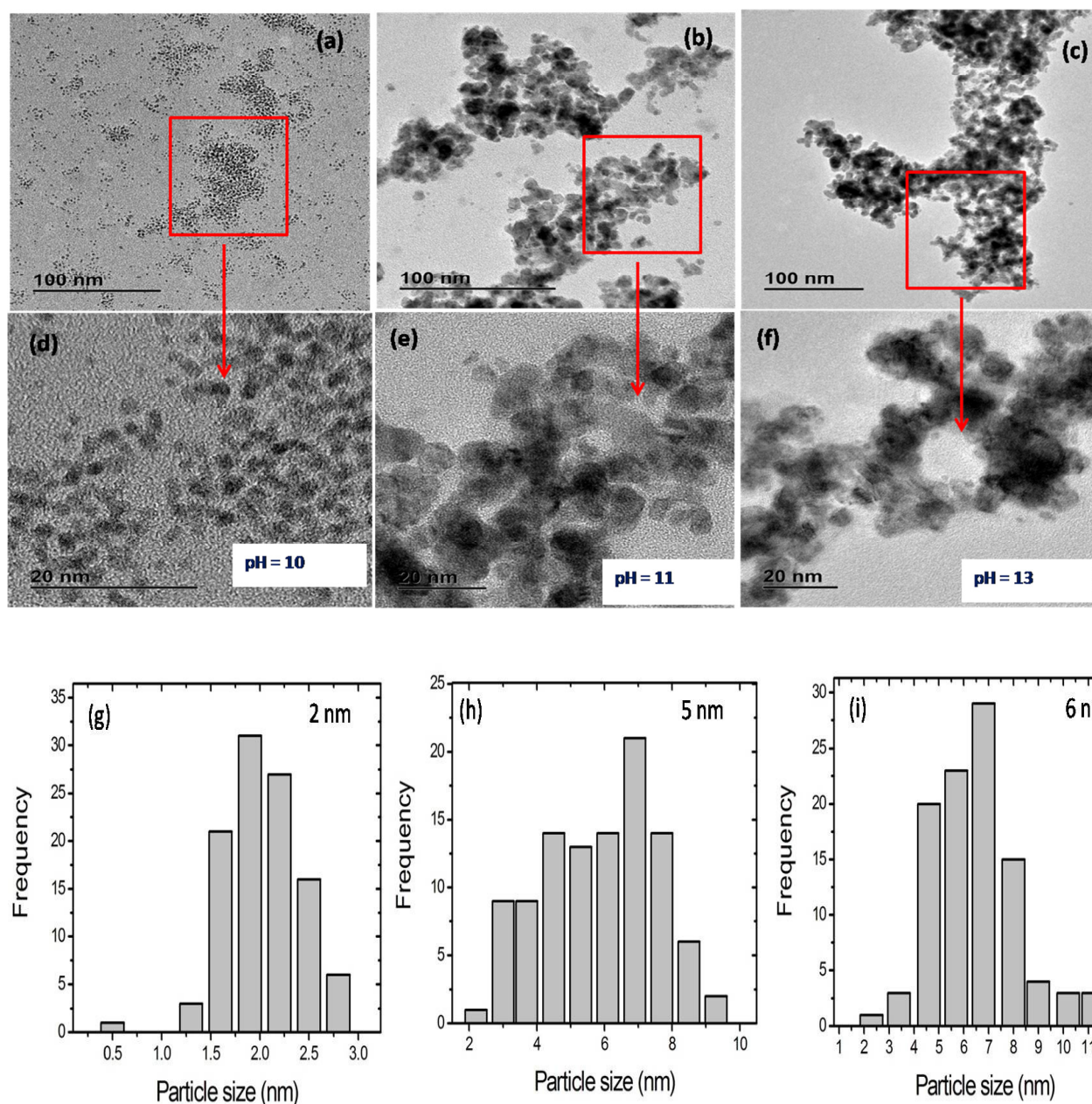


Figure 6.4. TEM images and particles size distribution measurements for Pt-Ni nanoparticles synthesized with (a,d,g) 0.5 M NaOH, (b,d,h) 1.0 M NaOH and (c,e,i) 2.0 M NaOH.

The particle size increased with an increase in the concentration of NaOH, from 2 – 6 nm (Fig. 6.4). Further, the size distribution at low pH (0.5 M, Fig 6.4 (g)) was relatively narrower than that at higher NaOH concentrations (1.0 M and 2.0 M).

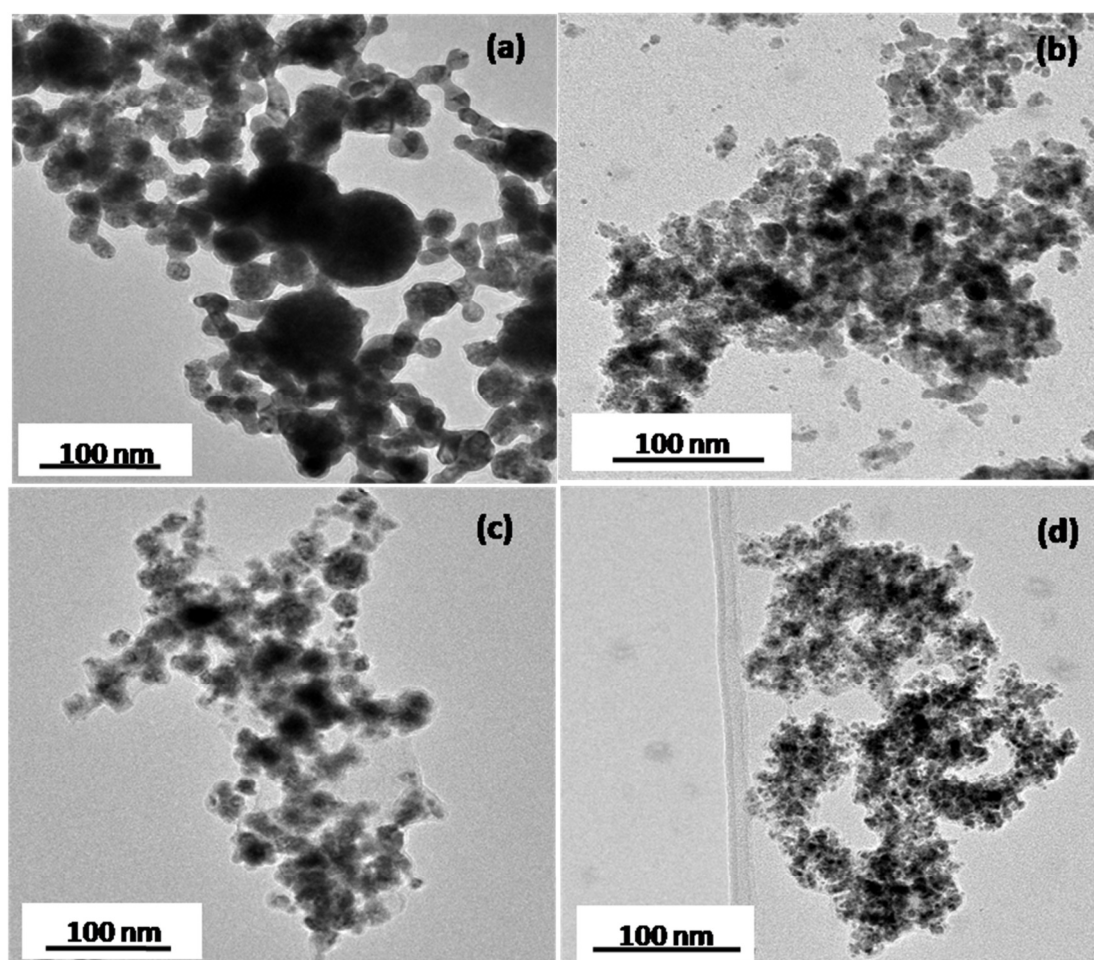
Therefore it is possible to control the size of the nanoparticle and since the structure relates to the shape this should allow a study of this property as a function of shape. Due to the high cost of platinum, it is ideal to alloy it with transition metals and the next section will elaborate on the effect that the addition as well as the amount of the alloying metal has on the properties of the nanoparticles. The alloying metal studied in this chapter is nickel (Ni).

6.4. Change in the Pt-Ni molar ratio

6.4.1. Microscopic analysis

TEM analysis was used to determine the size and morphology of the obtained nanoparticles. Figure 6.5 (a) depicts a TEM image of monometallic Pt. Bulb-like interconnected structures were observed with varying sizes. The morphology did not exhibit individual nanoparticles instead an agglomerate network of nanostructure was observed. Upon the addition of Ni, i.e. for the Pt-Ni-(1:1) sample (Fig. 6.5 (b)), a hierarchical-network structure was also observed, with a narrower size distribution. However, an increase in the amount of Ni in the nanoparticles a large size distribution of nanoparticles was seen for the Pt-Ni-(1:2) sample (Fig. 6.5 (c)). A less agglomerated structure with clustered nanoparticles was obtained for Pt-Ni-(1:3) sample (Fig. 6.5 (d)). This sample also showed small individual nanoparticles forming porous clustered structures.

The finding is in contrast to work by Ahernstorf et al. [22], who determined that the particle size increased with an increase in the amount of Ni. There was a decrease in the particle size with an increase in the Ni molar content from 32 – 5 nm with the Pt-Ni-(1:2) samples exhibiting a higher particle size at 12 nm.



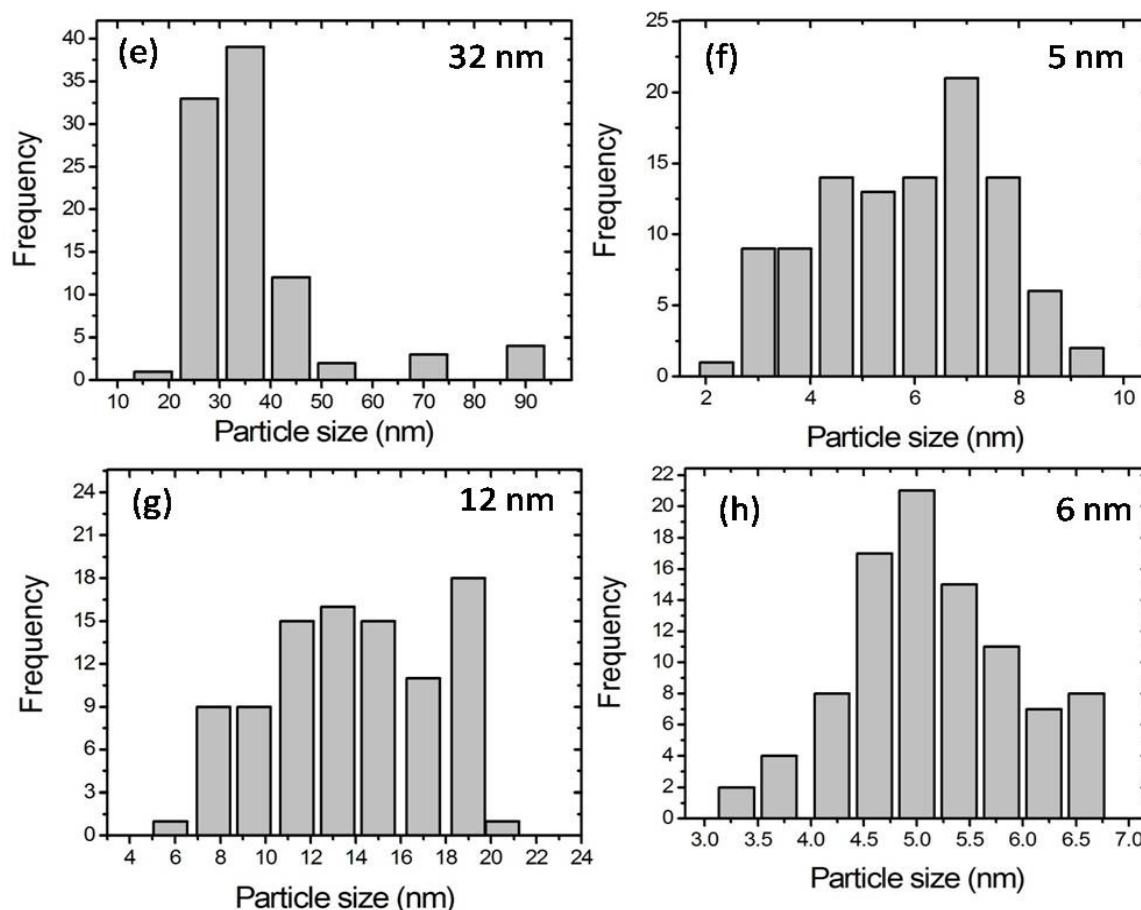


Figure 6.5. TEM images and particle size distribution of Pt-Ni nanoparticles, (a,e) 1:0, (b,f) 1:1, (c,g) 1:2 and (d,h) 1:3 molar ratio.

Therefore it can be seen that using microwave-irradiation to synthesize Pt-Ni nanoparticles, a network of nanostructured material was seen, rather than individual randomly distributed nanoparticles, (see Chapter 5) [8], as observed conventional synthesis procedures done by this group (see Chapter 4) [23].

6.3.3. Structural analysis: X-ray diffraction measurement

X-ray diffraction was used to determine the crystalline properties of the Pt-Ni catalysts (Fig. 6.6 and Table 6.1). The Pt-Ni samples showed a shift in the peak

positions after the addition of Ni as the alloying metal with the Pt-Ni-(1:3) sample exhibiting a $\sim 3.5^\circ$ 2θ -value shift. This is due to the incorporation of the Ni atoms into the crystal lattice of Pt. Therefore this means that there is a possible high degree of alloying of Pt with Ni, which is said to be in agreement with Vegard's law of mixing [22].

The (111) peaks for Pt were present in all the samples, regardless of the amount of Ni. However, a substantial peak broadening of diffraction peaks was observed as the amount of Ni was increased. Pt and Ni have been shown to alloy by Park et.al [24], which would result in lattice contractions and give a shift in the Pt peak positions. The variation of the Pt and Ni molar ratio is said to lead to changes in the compositions of the nanoparticles [22]. The peak positions of the samples are presented in Table 6.1, with the change in d-spacing shown in Fig. 6.7. The XRD crystalline sizes were calculated using the Scherrer equation (see section 3.2.3).

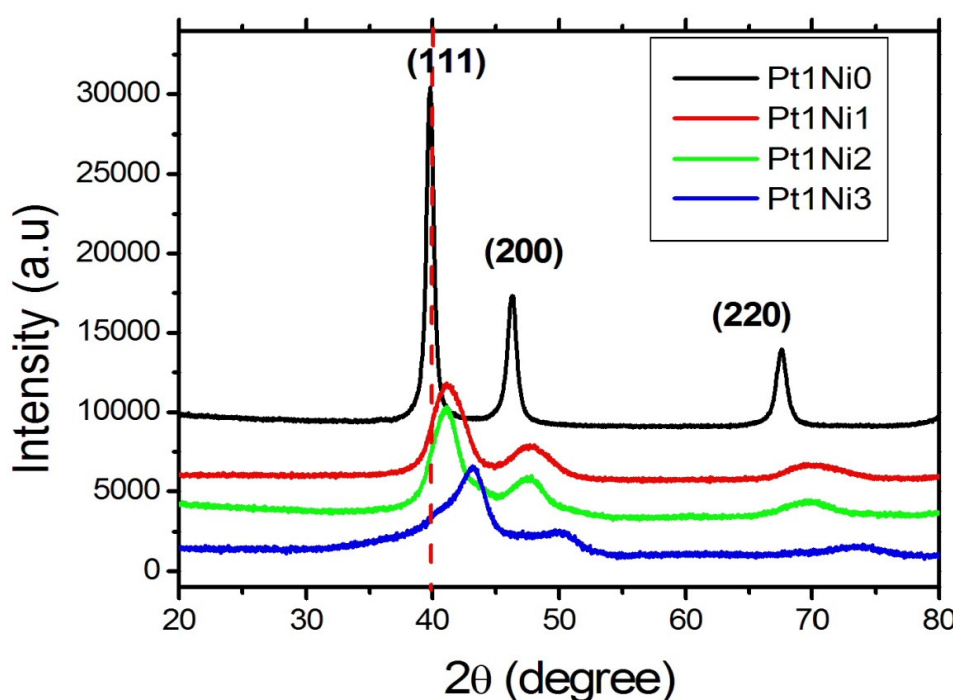


Figure 6.6. XRD diffractograms of Pt-Ni nanoparticles with different molar ratios in 500 mg PVP and 1.0 M NaOH.

Table 6.1. XRD peak position of the bimetallic platinum nanoparticles.

Sample	Molar ratio	(111)	Size (XRD, nm)	Size (TEM, nm)
Pt	1:0	39.8	13	32
Pt-Ni	1:1	41.3	4	5
	1:2	41.1	4	12
	1:3	42.7	4	6

As expected, the d-spacing of the alloy systems decreased with an increase in the amount of Ni (Fig. 6.7). This indicates that there is a crystallite size decrease which was also observed by Yang et al. [25] ascribed to the system preventing Pt-Ni alloy particle agglomeration at high Ni concentrations.

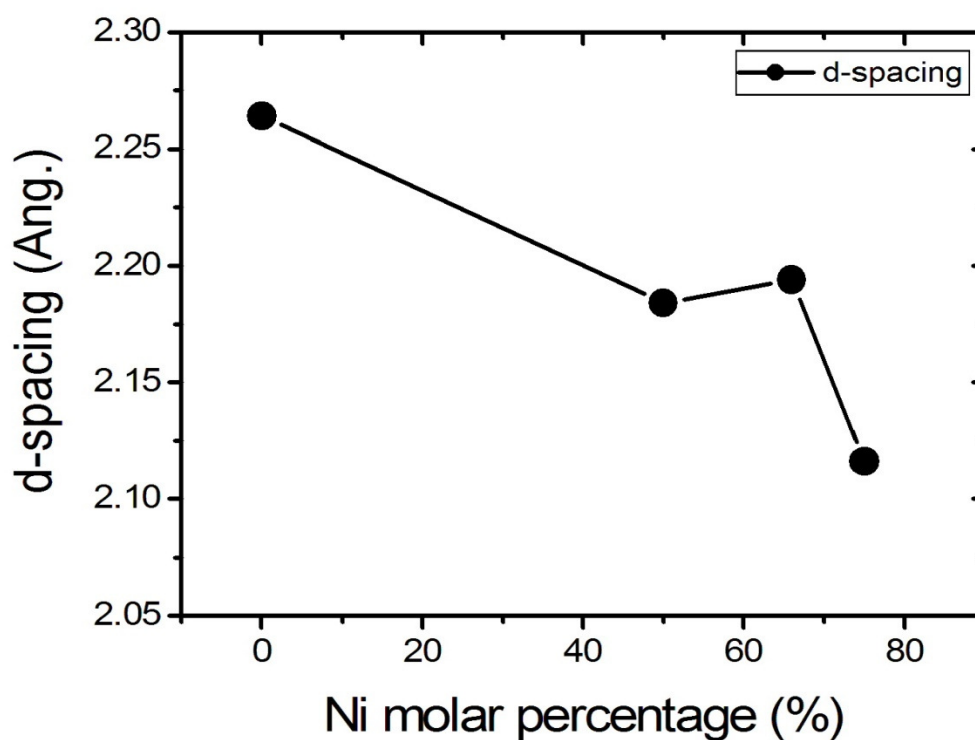


Figure 6.7. d-spacing calculation vs. molar percentage of Ni in the samples.

6.4.2. BET surface area measurements

The BET surface areas for the nanoparticles were determined and compared with the calculated crystallite sizes from XRD (Fig. 6.8). It was observed that the surface areas generally increased with an increase in the amount of Ni added into the nanoparticles. The surface area systematically increased with the amount of Ni to a maximum at 75%Ni25%Pt, i.e. Pt-Ni-(1:3). As expected, the crystalline size showed the opposite effect where the same sample with the highest surface area, possessed the smallest crystallite size.

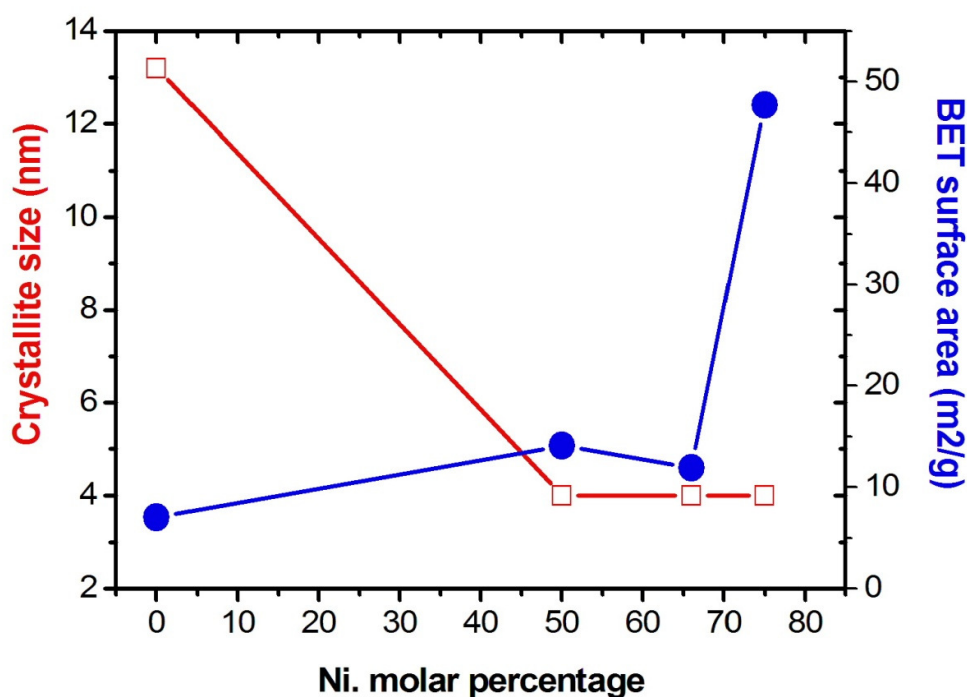


Figure 6.8. BET surface area vs. XRD crystallite of the Pt-Ni nanoparticles with increasing molar ratio.

These increased surface areas can be related to the morphology of the nanoparticles where the Pt-Ni-(1:3) sample was made up of small nanoparticles which lead to a generally higher relative surface area. Therefore, the BET surface area relationship with particle / crystallite size was realised.

6.5. Surface characterization by XPS

The surface oxidation and electronic states of the metals were determined for the nanoparticles using X-ray photoelectron spectroscopy (XPS). The samples containing different Pt-Ni molar ratios were studied.

6.5.1. Full XPS scans

The full XPS spectra were recorded on the samples to determine the elements present on the surface (Fig. 6.9) as well as their atomic concentrations (Table 6.2). It was noted that the Pt-Ni-(1:0) sample did not possess the Ni-2p peak but these peaks were present for all the other Ni-containing samples. This was to be expected as this sample did not contain any Ni precursor. The atomic concentrations of the materials revealed that the Pt-Ni-(1:0) sample contained the highest amount of Pt (68 at.%) and that this content decreased as the Ni content was increased, though the Pt-Ni-(1:2) (0.1 at.%), contained the lowest amount of Pt. The opposite trend was noted for the surface oxygen concentration (O) where the O atomic concentrations increased with nominal Ni concentrations. This is due to the formation of Ni-oxide or hydroxide species which increase as the amount of Ni is increased (see Table 6.2). Narrow scan XPS analysis was performed for the Pt-4f, O-1s and Ni-2p signals.

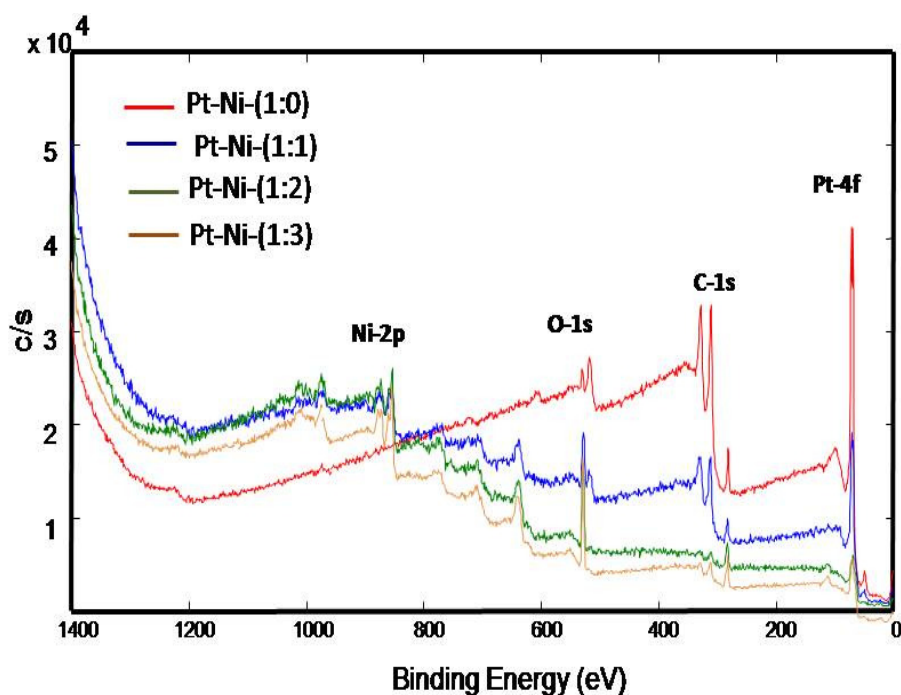


Figure 6.9. Full XPS scans of the Pt-Ni nanoparticles at different molar ratios.

Table 6.2. Atomic ratio of Pt-M species present on the nanoparticles surface from XPS. (The presence of carbon is attributed to residues from the synthesis process and the XPS carbon substrate)

Sample	Pt (at.%)	Ni (at.%)	Pt:Ni ratio	C (at.%)	O (at.%)
Pt-Ni-(1:0)	69.8	0	1:0	24.4	5.8
Pt-Ni-(1:1)	6.2	11.0	1:1.8	40.7	42.1
Pt-Ni-(1:2)	0.1	5.2	1:52	46.3	48.5
Pt-Ni-(1:3)	0.9	5.6	1:6.2	42.4	51.2

Pt-4f spectra

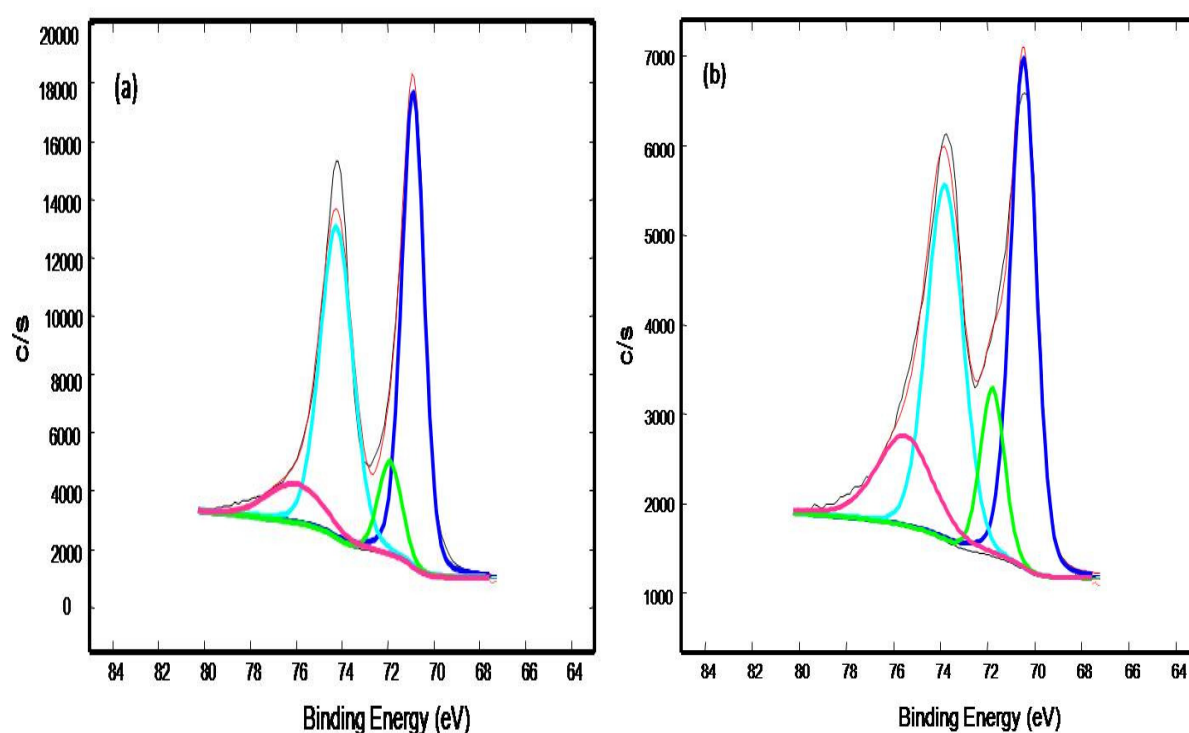
The Pt-4f peaks for the Pt-Ni nanoparticles containing different amount of Ni were analyzed. This data gave information on the oxidation states of the Pt species

present on the surface of the materials. In literature, the Pt-4f peak occurs as a doublet appearing at 71.2 and 74.5 eV with a 3.3 eV difference between the 2 peaks. The typical Pt species that can be obtained for Pt are Pt⁰ (71.2 eV and 74.5 eV), PtO (72.4 and 75.7 eV) and Pt(OH)₂ (72.6 and 75.9 eV) [26, 27]. In assigning the peaks shown in Fig. 6.10 (a) – (d), these literature peak positions were used. The peaks obtained were assigned as such: Pt⁰ (70.9, 70.4, 70.4 and 70.8 eV) and PtO (72.0, 71.8, 71.4 and 71.7 eV) for the Pt-Ni-(1:0), Pt-Ni-(1:1), Pt-Ni-(1:2) and Pt-Ni-(1:3), respectively.

Table 6.3. The binding energies and relative intensities of Pt species observed from Pt-4f_{7/2}, O-1s and Ni-2p_{3/2} XPS spectra for Pt-Ni nanoparticles.

Sample	Pt-4f_{7/2} BE (eV)	O-1s BE (eV)	Ni-2p_{3/2} BE (eV)
Pt-Ni-(1:0)	70.9 (83.6)	531.1 (23.6)	-----
	72.0 (16.4)	532.0 (57.1)	
		533.1 (19.3)	
Pt-Ni-(1:1)	70.4 (77.2)	528.5 (6.7)	851.8 (15.3)
	71.8 (22.8)	530.8 (78.9)	854.1 (9.8)
		532.7 (14.3)	855.2 (74.9)
Pt-Ni-(1:2)	70.4 (78.8)	528.8 (10.7)	851.5 (18.2)
	71.4 (21.2)	531.1 (76.5)	854.7 (15.6)
		532.6 (12.8)	855.6 (66.2)
Pt-Ni-(1:3)	70.8 (59.7)	529.7 (8.9)	853.2 (11.0)
	71.7 (40.2)	531.0 (75.8)	855.5 (14.6)
		532.2 (15.3)	856.0 (74.4)
() peak relative intensities percentages			

It was noticed that the peak positions were shifted to lower binding energies compared to the traditional literature peaks. This effect has been seen in bimetallic samples where the Ni incorporated into the lattice of Pt [28], resulting in some lattice contractions (also seen in XRD) and thus affecting the electronic structure (i.e the 5-d band vacancy) of the Pt. The interesting observation was that the shift was also noticed for the monometallic Pt samples (Pt-Ni-(1:0)), where Ni was not added into solution.



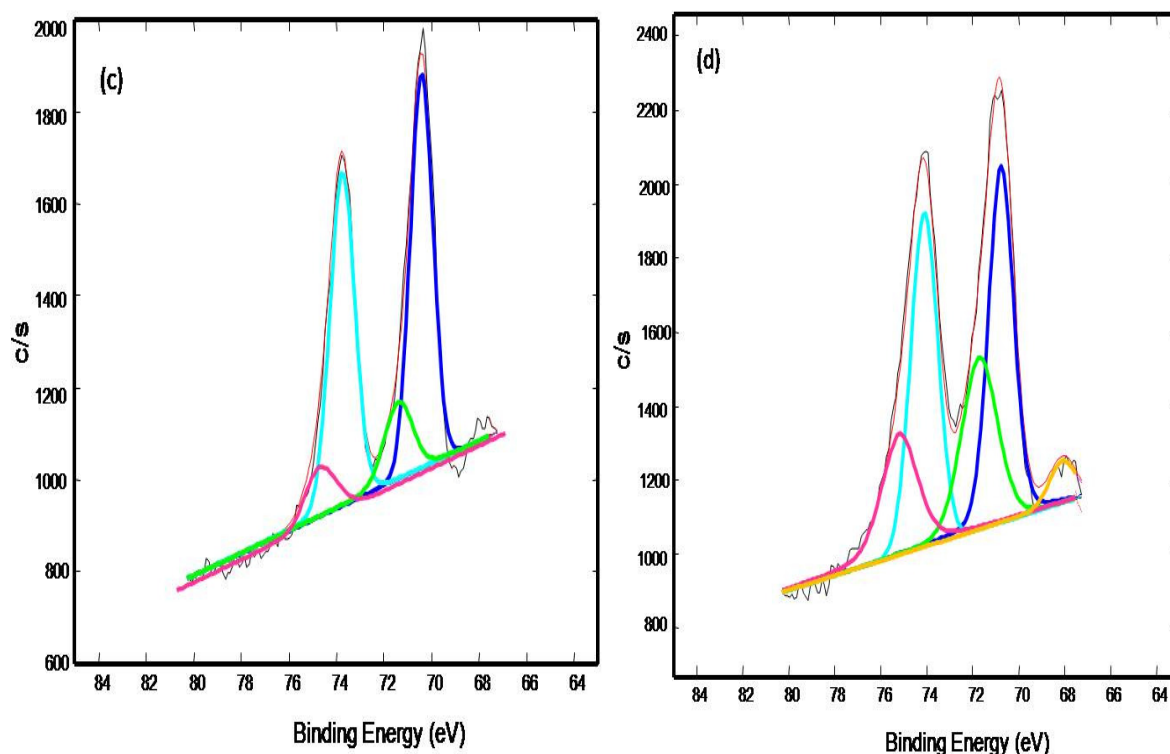
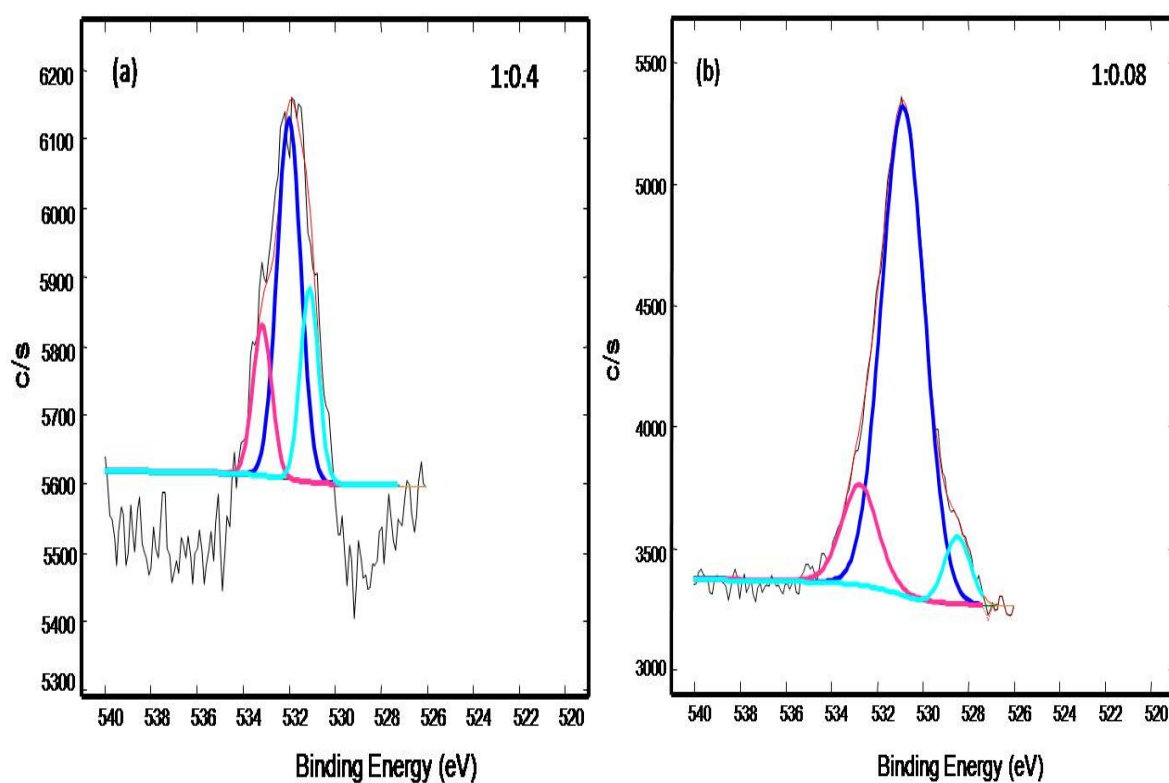


Figure 6.10. Pt-4f spectra of Pt-Ni nanoparticles, (a) Pt-Ni-(1:0), (b) Pt-Ni-(1:1), (c) Pt-Ni-(1:2) and (d) Pt-Ni-(1:3).

O-1s spectra

The oxygen species on the surface of the nanoparticles were also explored by analyzing the accompanying O-1s spectra (Fig. 6.11 a-d). The peaks were assigned using known peak positions for O-1s species such as M-O (529.79 eV), M-(OH) (531.07 eV) and M-(H₂O) (533.5 eV) [29, 30]. For the nanoparticles in this work, it is worthy to note that the XPS data showed 3 O peaks assigned to M-O, M-OH and M-(H₂O) species (see table 6.3), with the main O peak observed at ~ 532.0 eV. Though the Pt-Ni-(1:0) nanoparticle contained a relatively smaller amount of O, (see Table 6.2), it did possess clearly defined O-1s peak which were assigned to Pt-OH (531.1 eV) and Pt-(H₂O) (532.0 eV). In contrast, the Pt-Ni samples contained M-O species (528.5, 528.8 and 529.7 eV) for the Pt-Ni-(1:1), Pt-Ni-(1:2) and Pt-Ni-(1:3),

respectively. The reason is due to the fact that Pt on its own does not oxidize easily and thus when Ni is added into the solution, more Ni-oxides or hydroxide species will be observed. The M-O/M-OH ratio was similar for all the samples, i.e. 1:0.4 ~1:0.1 with the M-OH species dominating the surfaces of the nanoparticles.



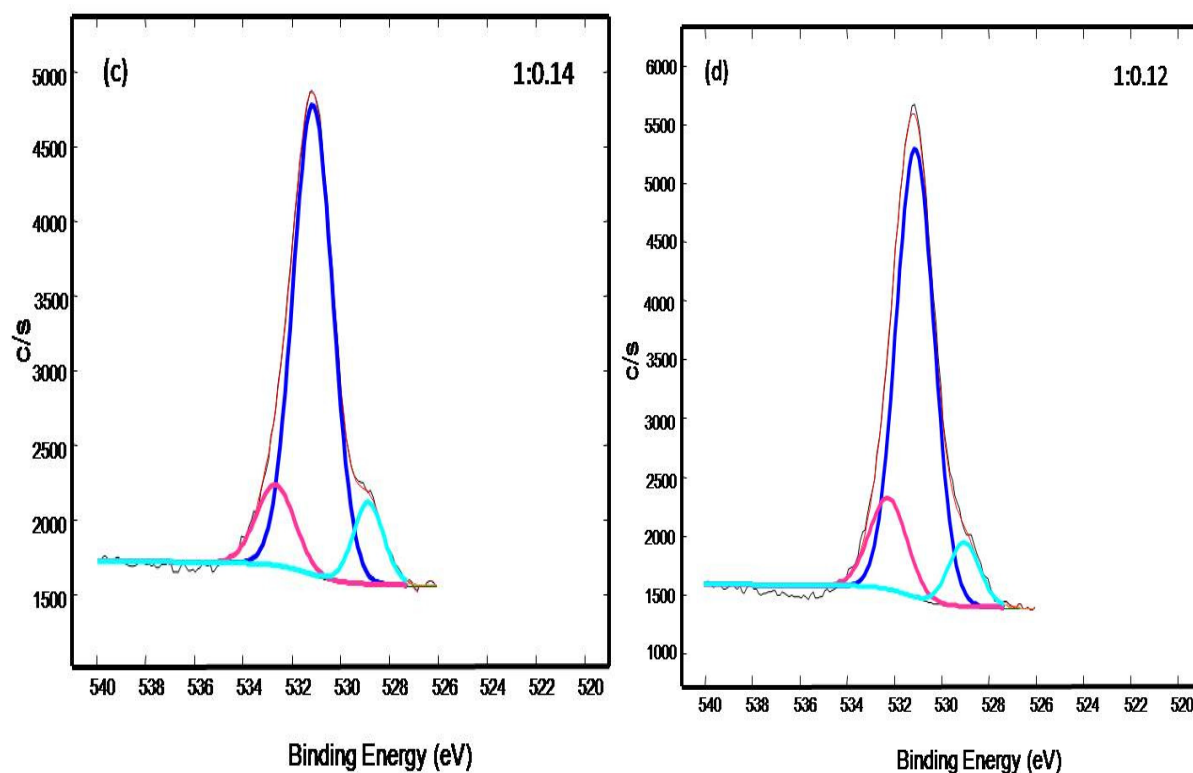
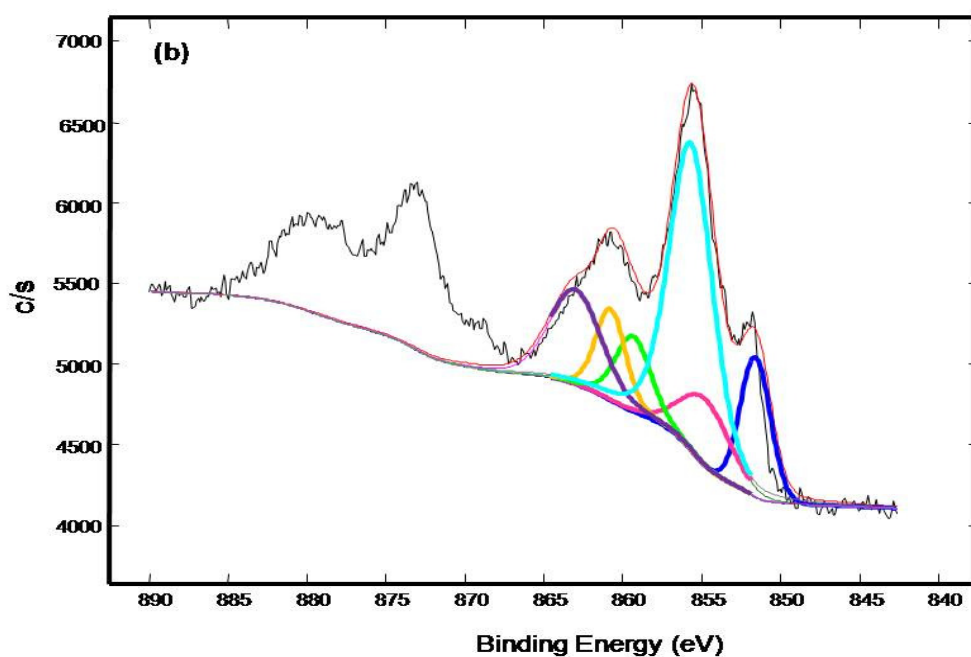
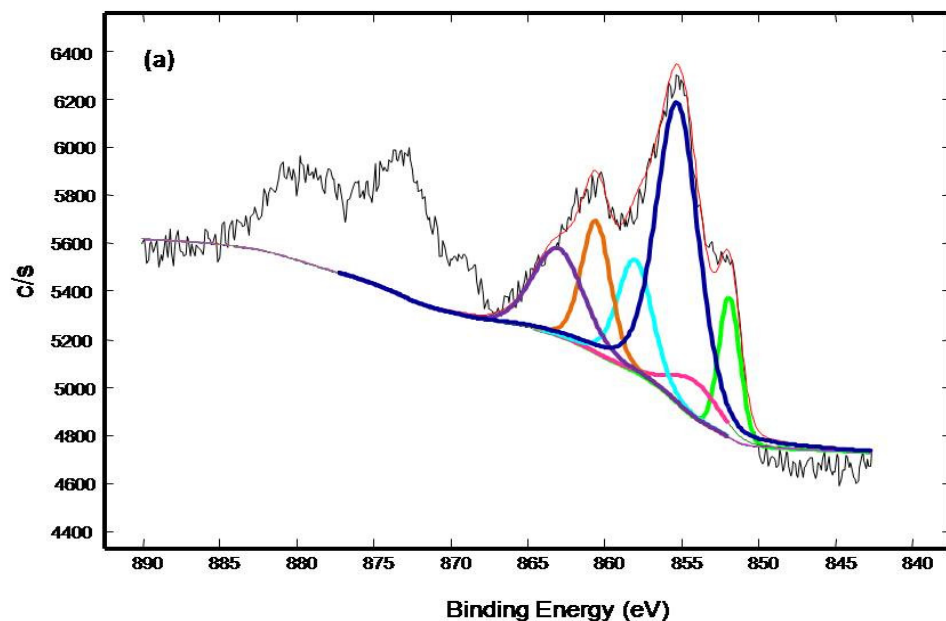


Figure 6.11. O-1s spectra of Pt-Ni nanoparticles, (a) Pt-Ni-(1:0), (b) Pt-Ni-(1:1), (c) Pt-Ni-(1:2) and (d) Pt-Ni-(1:3).

Ni-2p spectra

Analysis of the Ni-2p spectra was performed to determine the different oxidation states of the Ni species obtained on the surfaces of the nanoparticles. The Ni-2p peaks were deconvoluted according to the method of Biesinger [29] and Grosvenor [31], where only the Ni-2p_{3/2} peaks were fitted. Traditional Ni-2p peak positions have been assigned to Ni⁰ (852.6 and 869.8 eV), Ni(OH)₂ (853.7 and 870.9 eV) and NiO (854.9 and 872.1 eV) [32], as well as satellites peaks present on the higher binding energy shoulders of the main peaks [33]. It was observed that the samples containing lower amounts of Ni (Pt-Ni-(1:1) (Fig. 6.12 (a)) and Pt-Ni-(1:2) (Fig. 6.12 (b)) both possessed the Ni⁰ peaks at 851.8 and 851.5 eV respectively, while at the higher Ni content, no metallic Ni observed, only the NiO (853.2 eV) and Ni(OH)₂

(855.5 eV) species were observed (see Table 6.3 and Fig. 6.12). There was an observed shift in the Ni-2p BE values for the Pt-Ni-(1:3) (Fig. 6.12 (c)) sample, which was also seen with the Pt-4f peaks. This shift can be attributed to the addition of the Ni atoms into the fcc lattice of Pt causing lattice contractions and a decrease in the Pt-Pt interatomic distance.



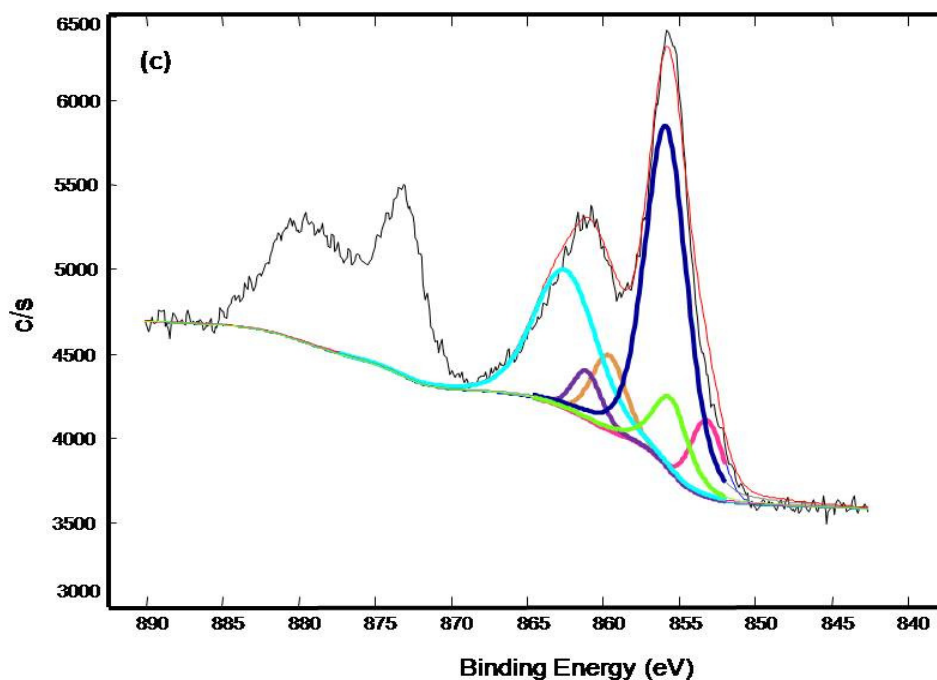


Figure 6.12. Ni-2p spectra of Pt-Ni nanoparticles, (a) Pt-Ni-(1:1), (b) Pt-Ni-(1:2) and (c) Pt-Ni-(1:3).

As with the O-1s spectra, there was an observed shift in the Ni-2p binding energies for the Pt-Ni-(1:3) samples to higher BE values. The shift has been attributed to factors such as the difference in the valence electron densities of the metals by Kim et al. [34]. The observed peaks for this samples were assigned to NiO (853.5 eV) and NiOOH (855.5 eV). In contrast, the Pt-Ni-(1:1) and Pt-Ni-(1:2) peaks were assigned to Ni(OH)₂ at 854.1 and 854.7 eV respectively.

Due to the importance of the Ni-oxide and hydroxide species in the assisting the enhancement of MOR, the amount of Ni species on the surface of the nanoparticles are summarized in Fig. 6.13. It should be noted that the Pt-Ni-(1:0) sample did not contain any Ni from the synthesis process, thus the 0% relative amounts seen in Fig. 6.13.

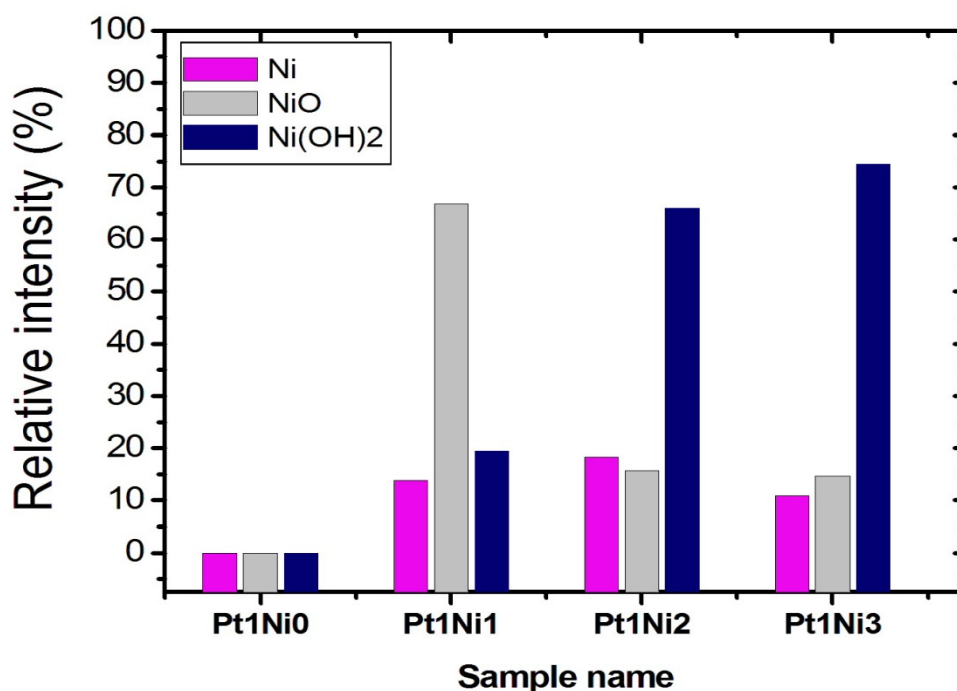


Figure 6.13. Ni-2p oxides and hydroxides species with their relative intensity.

Summary of XPS studies

Pt metal surface segregation was observed with decreasing Pt surface content and with an increasing amount of Ni. The opposite effect was seen for oxygen (O) concentration which increased with the Ni concentration. This was expected due to the ability of Ni to form oxide and hydroxide species compared to Pt. It was also realized that the peak obtained for microwave-irradiation were well-defined compared to the conventional synthesis (see Chapter 4). For all the samples, the amount of metallic Ni detected was less than the amount of Ni²⁺ (NiO and Ni(OH)₂) found on the surface, but his ratio (Ni/Ni²⁺) could be affected by oxidation of Ni metal on standing in air. Further, an increase in the Ni molar content gave a larger amount of Ni(OH)₂ species, possibly indicating a preference of Ni to form hydroxides when in larger amounts.

6.6. Electrochemical characterization

The effect of the change in MW parameters on the catalytic activity of the catalysts will be explored in 0.5 M H_2SO_4 electrolyte solution with Ag/AgCl acting as the reference electrode.

6.6.1. Change in amount of capping agent

Differing catalytic activities were observed as the amount of capping agent (PVP) was varied (Fig. 6.14). The activity increased by a factor of approximately 10 on addition of more PVP (250 mg to 500 mg). As the amount of PVP was doubled (1000 mg), the activity decreased substantially. This indicates there is capping agent saturation, where the capping agent eventually blocks the active sites in the catalysts. The Pt-oxidation onset potential was determined as: 250 mg (0.44 V) < 500 mg (0.49 V) < 1000 mg (0.52 V) < 0 mg (0.56) < 750 mg (0.59). The peak current density was determined for Pt-reduction peaks and appeared at 9.45 mA/cm² (0 mg), 2.26 mA/cm² (250 mg), 22.6 mA/cm² (500 mg), 6.69 mA/cm² (750 mg) and 6.83 mA/cm² (1000 mg), seen in Fig. 6.14 and Table 6.4.

In determining the electrochemical active surface area (ECSA), there was a difference in the ECSA when the amounts of PVP in the solutions were increased. The trend was as follows: 0.15 m²/g Pt (250 mg) < 0.22 m²/g Pt (750 mg) < 0.60 m²/g Pt (500 mg) < 0.73 m²/g Pt (1000 mg) < 1.04 m²/g Pt (0 mg). This is in contrast to the peak current densities observed for the Pt-oxidation in the materials where the

500 mg sample showed the highest H_2 desorption area. The samples contained the same amount of Pt thus the area was normalized using the Pt loading.

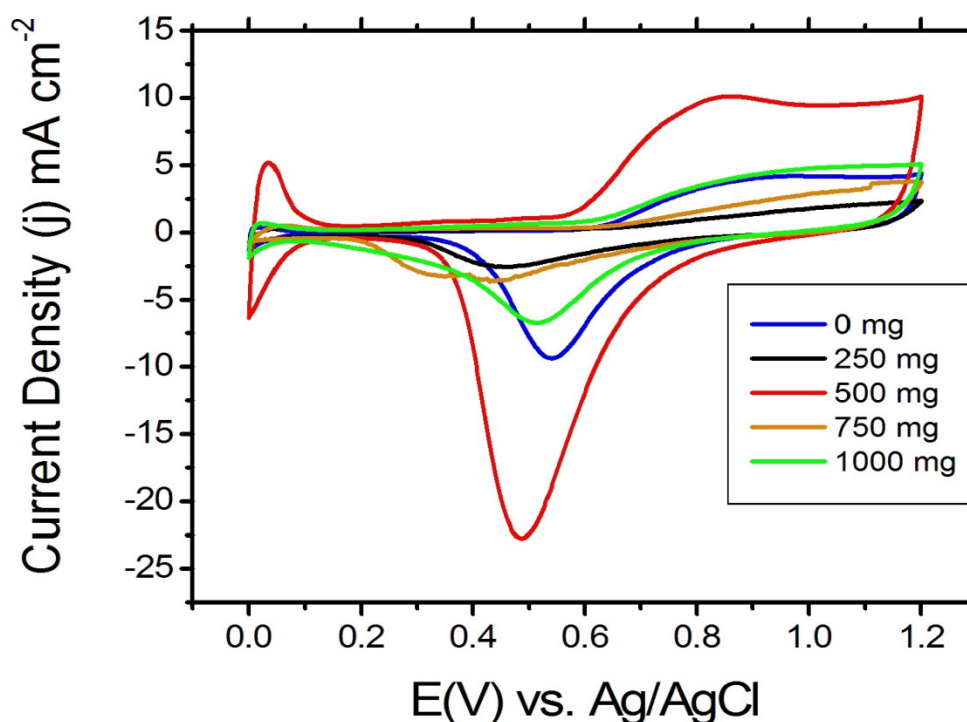


Figure 6.14. Cyclic voltammograms of Pt-Ni-(1:1) nanoparticles in 1.0M NaOH and with varying amounts of PVP.

Therefore it is evident that the amount of capping agent plays an important role in determining the current output obtained from the catalysts. The effect of PVP on the MW-irradiation synthesis of monometallic Pt was studied by Tu et al. [11] who determined that the particle size changed with the amount of PVP added into the solution. This in turn resulted in different electrocatalytic activities based on the PVP content, which is what was observed in this work.

Table 6.4. Cyclic voltammetry peak parameters of the Pt-Ni-(1:1) samples.

Sample name	0.5M	1.0M	2.0M	0mg	250mg	500mg	750mg	1000mg
Pt_{oxidation} (E_{onset}, V)	-----	0.49	0.58	0.56	0.44	0.49	0.49	0.55
Pt_{reduction} (I, mA/cm²)	-----	22.6	42.5	9.45	2.26	22.6	3.45	6.83
ECSA (m²/g Pt)	-----	0.60	1.20	1.04	0.15	0.60	0.22	0.73

6.6.2. Change in concentration of NaOH.

The pH of the reaction solution assists in the nucleation, growth and precipitation of the metal nanoparticles especially in MW synthesis [19]. The voltammograms of Pt-Ni-(1:1) in Fig. 6.15 and Table 6.4, showed the effect of pH on the electrocatalytic activity of the nanoparticles. The sample prepared with 2.0 M (pH = 12.0) possessed the highest Pt-O oxidation current followed by the 1.0 M (pH = 11.0) sample, and the 0.5 M (pH = 9.0) samples showed no activity in the forward and reverse scans. The Pt-oxidation onset peaks of Pt-oxidation (forward) were observed at 0.49 V (2.0 M) and 0.55 V (1.0 M). The peak current densities for Pt-reduction (reverse) were also observed at 42.5 and 22.6 mA/cm² for the 2.0 and 1.0 M samples respectively.

The calculated ECSAs were 0.60 and 1.20 m²/g Pt for the 1.0 M and 2.0 M NaOH, respectively.

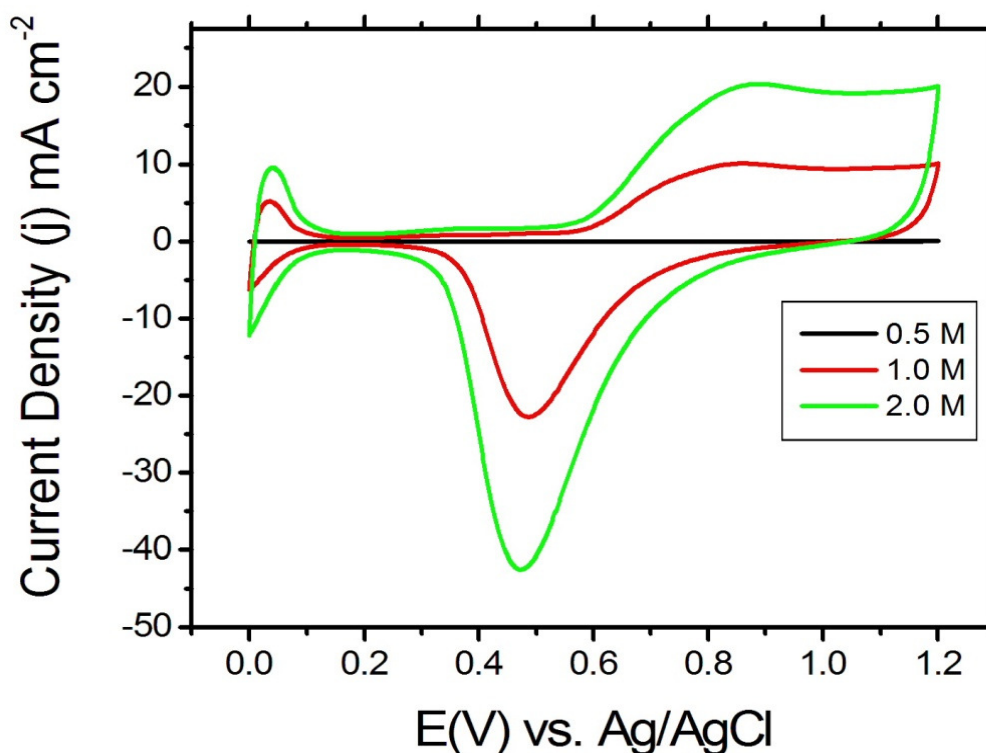


Figure 6.15. The cyclic voltammograms of Pt-Ni-(1:1) nanoparticles synthesized using 500 mg PVP and different concentrations of NaOH.

The effect of pH of the solution on the electrocatalytic activity of MW-irradiation was also determined by Zhao et al. [35] for Pt/C catalysts. They determined that when the pH of the solution was increased there was an increase in the peak current density due to the smaller particle sizes obtained for these materials. The stabilization of the nanoparticles by acetate, resulting from the ethylene glycol reduction process, is also said to occur at pH = 7.4 – 9.5, whereas at low pH acetate is a poor stabilizer [11, 35, 36].

6.6.3. Change in molar ratio

Cyclic voltammograms of the Pt-Ni samples prepared with different molar ratios are shown Fig. 6.16 and Table 6.5. Traditional Pt oxidation/reduction peaks were observed for all the samples including monometallic Pt. Typical Pt-oxidation (forward) and Pt-reduction (reverse) peaks were observed as well as the H₂ desorption/adsorption area (0 – 0.05 V) followed by the presence of a strong double-layer. There was also a shift in the Pt-reduction peak potentials where; Pt-Ni-(1:2) (0.57 V) > Pt (0.55 V) > Pt-Ni-(1:3) (0.52) > Pt-Ni-(1:1) (0.49 V). The Pt-Ni-(1:2) sample had the lowest current output (0.034 mA/cm²) in the same range under the same reaction conditions; in contrast the Pt-Ni-(1:1) sample possessed current values higher than the other samples (22.6 mA/cm²).

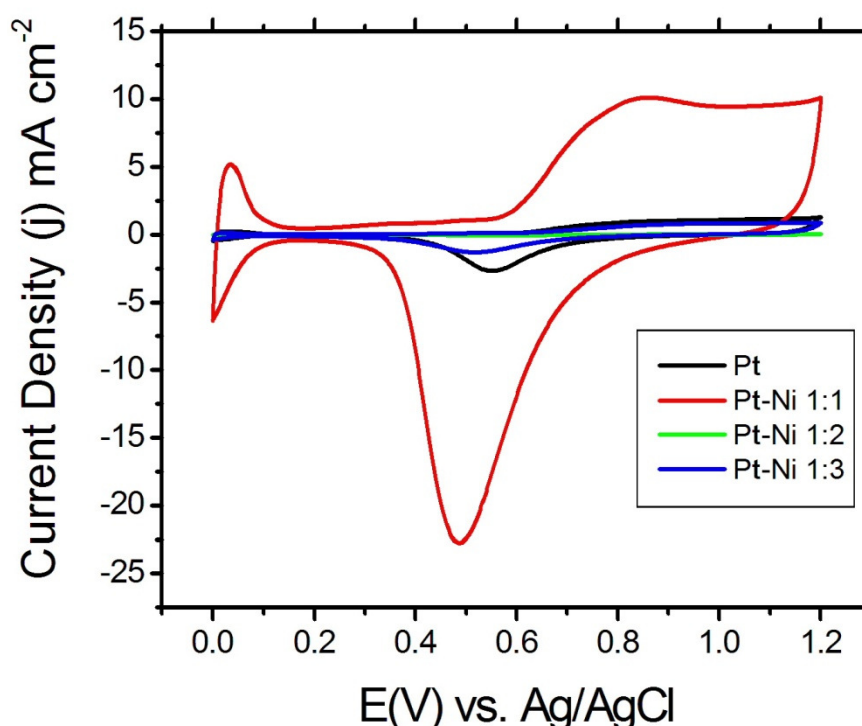


Figure 6.16. Cyclic voltammograms of different molar ratio Pt-Ni in 500 mg PVP and 1.0 M NaOH.

Table 6.5. Pt-peak parameters from acid electrolyte cyclic voltammograms (Pt-Ni).

Sample	Pt-Ni-(1:0)	Pt-Ni-(1:1)	Pt-Ni-(1:2)	Pt-Ni-(1:3)
Pt_{oxidation} (E_{onset}, V)	0.60	0.56	0.75	0.63
Pt_{reduction} (I, mA/cm²)	2.64	22.6	0.034	1.27
ECSA (m²/g Pt)	0.006	0.60	0.01	0.17

Coupled with the low onset potential of this sample, the Pt-Ni-(1:1) catalysts can be deemed as superior catalyst. Based on this analysis, the Ni% saturation in this case was determined as 50%, i.e. Pt50%-Ni50% will give the best performing catalyst. This was also seen in the electrochemical active surface area (ECSA) of the nanoparticles calculated as follows: Pt (0.006 m²/g Pt), Pt-Ni-(1:1) (0.60 m²/g Pt), Pt-Ni-(1:2) (0.01 m²/g Pt) and Pt-Ni-(1:3) (0.17 m²/g Pt). Further addition of Ni into the solution resulted in a drop in the electrocatalytic activity of the nanoparticles in the acid electrolyte.

6.7. Methanol Oxidation Reaction (MOR) analysis

Methanol oxidation studies were performed on the samples in 0.5 M H₂SO₄ + 1.0 M CH₃OH electrolyte with the current normalized by the glassy carbon area (0.0314 cm²). The solutions were purged with N₂ for 30 minutes before each measurement.

6.7.1. Change in amount of surfactant

In increasing the amount of capping agent there was a general increase in the activity of the samples (Fig. 6.17). The onset potentials of the catalysts were; 0.21 V (500 mg) < 0.23 V (250 mg) > 0.24 V (750 mg) < 0.25 V (0 and 1000 mg). A low onset potential indicates the catalysts ability to adsorb methanol, therefore the lower the value the better the catalyst [16]. For these catalyst, the onset potential was relatively low ~ 0.20 V, which is in the same range as that found by Frelink et al. [37], for polycrystalline Pt electrodes. The peak current density at 500 mg was observed to be the highest (271.1 mA/cm^2), followed by 0 mg (219.2 mA/cm^2), 750 mg (162.4 mA/cm^2), 1000 mg (137.3 mA/cm^2) with the 250 mg (73.9 mA/cm^2) presenting the lowest current (see Table 6.6). This also indicated the sample containing 500 mg of PVP showed good electrocatalytic activity revealing that there is a saturation point in the amount of capping agent that can be added in the solution.

In terms of the shape of the shapes and sizes of the nanoparticle determined from TEM (Fig. 6.1), the most active catalyst (500 mg PVP) exhibited a network of nanostructures compared to the less active 250 mg (6 nm) and 1000 mg (9 nm) catalysts, which comprised of randomly dispersed nanoparticle. Thus it is apparent that the more dispersed the nanoparticles, the less the MOR electrocatalytic activity of the material. This is in agreement with Gasteiger et al. [38], who stated that an ideal unsupported electrocatalyst for methanol oxidation should have a porous network of nanostructures for methanol adsorption. The current response with applied voltage is thus dependent on the morphology of the catalyst.

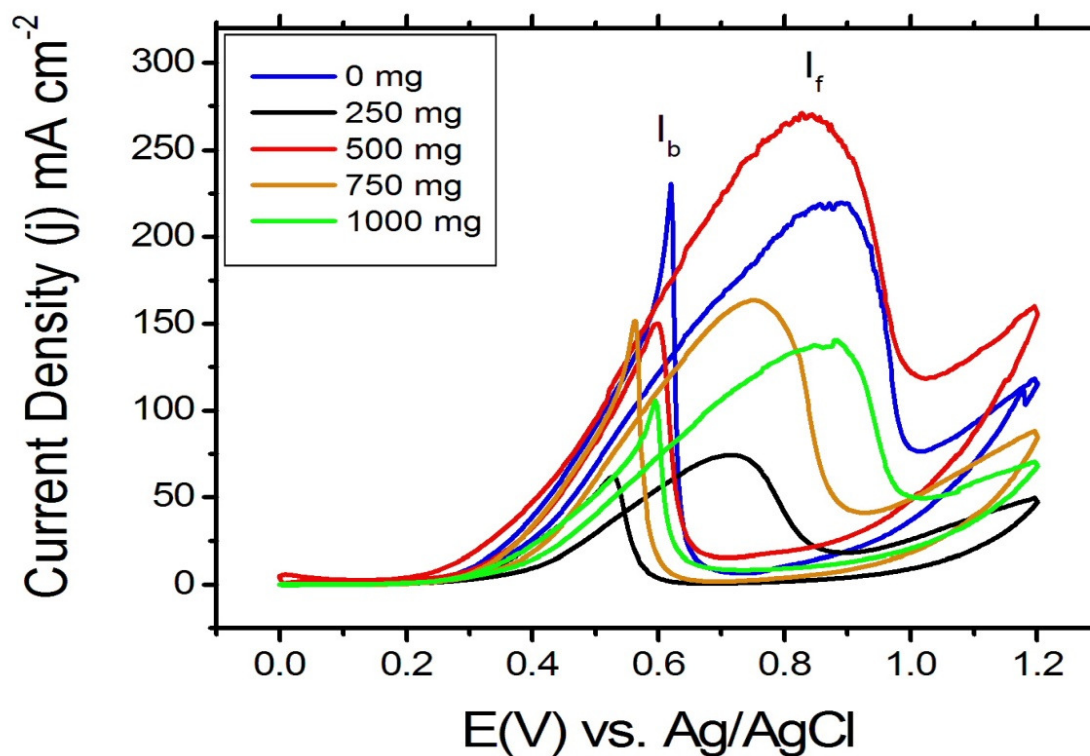


Figure 6.17. MOR voltammograms of different amounts of PVP as the capping agent in 0.5 M H_2SO_4 + 1.0 M CH_3OH electrolyte at 10 mV/s.

Table 6.6. MOR peak parameters of the Pt-Ni-(1:1) electrocatalysts with varied PVP ratio.

Sample	E_{onset}	E_f (V)	I_f (mA/cm ²)	E_b (V)	I_b (mA/cm ²)	I_f/I_b	I (mA/mgPt)
0 mg	0.25	0.86	219.2	0.62	228.0	0.96	163.4
250 mg	0.23	0.70	73.9	0.52	61.7	1.20	55.1
500 mg	0.21	0.84	271.1	0.60	152.3	1.78	202.3
750 mg	0.24	0.74	162.4	0.56	151.1	1.07	121.2
1000 mg	0.25	0.86	137.3	0.58	101.7	1.35	102.5

This was further determined by the I_f/I_b ratios of the catalysts. This is an important parameter used to show the catalysts ability to remove the carbonaceous species formed in the methanol dissociation process. The values were 1.78 (500mg) > 1.35 (1000 mg) > 1.20 (250 mg) > 1.07 (750 mg) > 0.96 (0 mg) (presented in Table 6.6), revealing the same trend observed for the onset potential and peak current density. It was thus determined that the amount of surfactant has an effect on the electrocatalytic activity of the nanoparticles.

In summary, the catalyst containing 500 mg PVP exhibited the lowest onset potential as well as the highest peak current density (I_f) value. It can thus be concluded that the optimum amount of surfactant for this microwave-irradiation synthesis procedure is 500 mg. The particle size was related to the MOR activity of the particles, where the highest activity was observed at 5 nm, below and above which the activity drastically dropped.

6.7.2. Change in concentration of NaOH

There was an observed change in the electrocatalytic activity of the materials with a change in pH achieved by using different concentrations of NaOH in the synthesis process (Fig. 6.18 and Table 6.7). It was observed there was no activity towards MOR for the sample prepared with 0.5 M NaOH (pH = 10). By increasing the concentration of NaOH and thus the pH to more basic solution, the current output peaked at 1.0 M NaOH (pH = 11) and decreased again at 2.0 M NaOH (pH = 12). The onset potentials for the active samples were 0.21 V (1.0 M) and 0.33 V (2.0 M) where the ideal onset potential is low in order to aid in methanol adsorption.

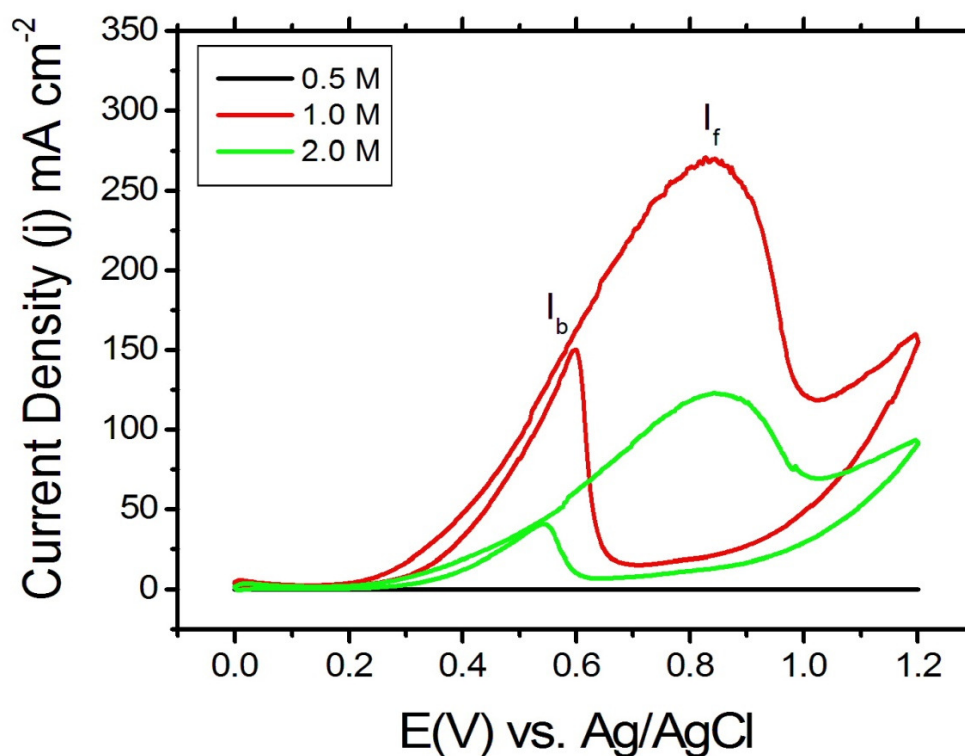


Figure 6.18. Voltammograms from Pt-Ni-(1:1) nanoparticles synthesized using 500 mg PVP and varying concentrations of NaOH.

The corresponding TEM images of the catalysts were shown in Fig. 6.3. As with the PVP samples, the more agglomerated the structures (1.0 M NaOH), the more active the catalyst mainly due to the number of available Pt sites available for methanol adsorption. The measured particle sizes for the less active materials were 3 nm and 6 nm for the 0.5 M and 2.0 M samples respectively. It should be noted that the 0.5 M NaOH sample had small particle sizes and showed no activity. This was also observed by Park et al. [39], for Pt/C nanoparticles where the methanol oxidation activity diminished as the particle size decreased. Zhao et al. [35], also studied the effect of pH (3.4 – 9.5) on the electrocatalytic activity of Pt/C and determined that the peak current densities increased with an increase with pH.

Table 6.7. The MOR peak parameters of Pt-Ni-(1:1) nanoparticles at different pH values.

Sample	E_{onset}	E_f (V)	I_f (mA/cm²)	E_b (V)	I_b (mA/cm²)	I_f/I_b	I (mA/mgPt)
0.5 M	----	----	----	----	----	----	----
1.0 M	0.21	0.84	271.1	0.60	152.3	1.78	202.3
2.0 M	0.20	0.84	122.7	0.54	41.5	2.95	91.5

The peak current density showed that the catalyst activity observed at 271.1 mA/cm² (1.0 M) and 122.8 mA/cm² (2.0 M) (see Table 6.7). This indicates that the sample made with 1.0 M NaOH (pH = 11.0), is ideal in preparing the bimetallic Pt catalysts using microwave-irradiation. The ratios of the forward scan (I_f) and reverse (I_b) scan was calculated as 2.95 and 1.78 for the 2.0 M and 1.0 M samples, respectively. The I_f/I_b ratio values indicate the materials ability to effectively remove poisonous species formed in the forward methanol dissociation scan [40]. The increase in peak current density with pH is said to indicate the improved methanol electrooxidation activity of the samples [35]. This is because at high pH the acetate from ethylene glycol breakdown is better at stabilising the metal colloids compared to in more acidic medium.

In general from the NaOH and PVP studies, the use of 1.0 M NaOH and 500 mg PVP (5 nm) was determined to be the most superior catalyst. Therefore in studies in which the molar ratio of the solution we changed, these two values were used.

6.7.3. Change in the Pt-Ni molar ratio

Full scan voltammograms of the Pt-Ni nanoparticles showed varying degrees of activity with an increase in the Ni amount (Fig. 6.19 and Table 6.8). The lower Ni content sample, Pt-Ni-(1:1) (271.1 mA/cm^2) exhibited the highest current output followed by monometallic Pt-Ni-(1:0) (101.4 mA/cm^2), Pt-Ni-(1:3) (36.5 mA/cm^2) and the poorest performing Pt-Ni-(1:2) (1.38 mA/cm^2). It should also be noted that the Pt-Ni-(1:1) sample had the highest peak current compared to commercial Pt/C ETEK (2.41 mA/cm^2) [41].

The ratio of the forward (I_f) and reverse (I_b) methanol peaks for the Pt-Ni samples was: Pt-Ni-(1:0) (0.92) < Pt-Ni-(1:2) (1.15) < Pt-Ni-(1:3) (1.31) < Pt-Ni-(1:1) (1.78) (see Table 6.8). This trend indicates that the Pt-Ni-(1:1) catalyst is the superior catalyst. It possess a good ability to remove carbonaceous species such as CO and formaldehyde, [16, 41], formed in the forward methanol dissociation reaction of MOR. The high I_f/I_b ratio also would suggest that the catalyst has long-term stability in fuel cell applications [42].

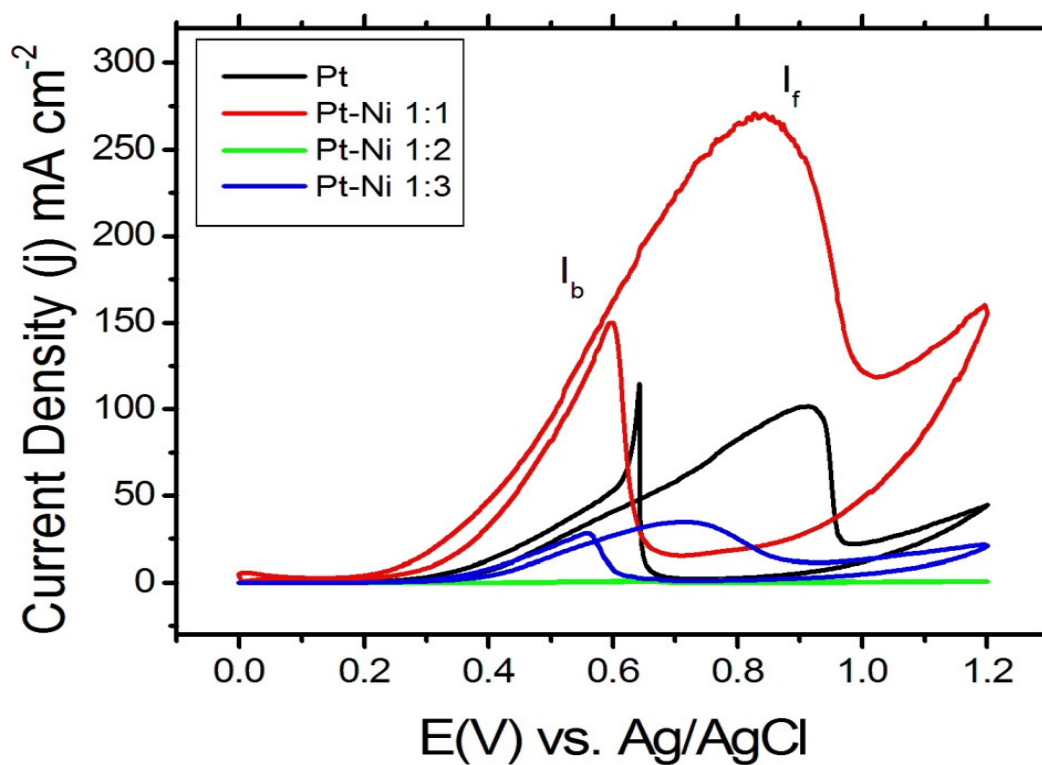


Figure 6.19. MOR voltammograms of Pt-Ni at different molar ratios in 0.5 M H_2SO_4 + 1 M CH_3OH . The amount of PVP was 500 mg in 1.0 M NaOH solution.

Table 6.8. Peak parameters of MOR voltammograms for the microwave-synthesized bimetallic nanoparticles.

Sample	Molar ratio	E_{onset}	E_f (V)	I_f (mA/cm ²)	E_b (V)	I_b (mA/cm ²)	I_f/I_b	I (mA/mgPt)
Pt	1:0	0.38	0.91	101.4	0.63	110.8	0.92	0.55
Pt-Ni	1:1	0.21	0.84	271	0.60	152.2	1.78	202
	1:2	0.31	0.81	1.38	0.65	1.20	1.15	1.21
	1:3	0.35	0.71	36.5	0.55	27.8	1.31	130
Pt-Ni	1:1	0.20	0.65	0.8	0.45	0.55	1.45	

[21]^{*}

^{*} Pt-Ni nanoparticles synthesized by Deivaraj et al. using microwave-irradiation [21].

The high onset potential in Pt compared to Pt-Ni-(1:1) could be ascribed to the fact that Pt does not have the ability to produce OH species in contrast to Co and Ni which have been shown to possess surface oxides and hydroxides. This was determined from our previous XPS studies on microwave-synthesized Pt-Co and Pt-Ni nanoparticles [8]. The peak height of the forward anodic reaction, with the highest I_f samples, represents the CO tolerance of the materials [42]. Thus the Pt-Ni-(1:1) shows the best tolerance compared to monometallic Pt and the rest of the samples prepared with different Pt-Ni molar ratios. Overall this catalyst also showed good and improved catalytic activity due to its low onset potential, high peak current density, [41], and subsequently mass current density as well as its I_f/I_b value.

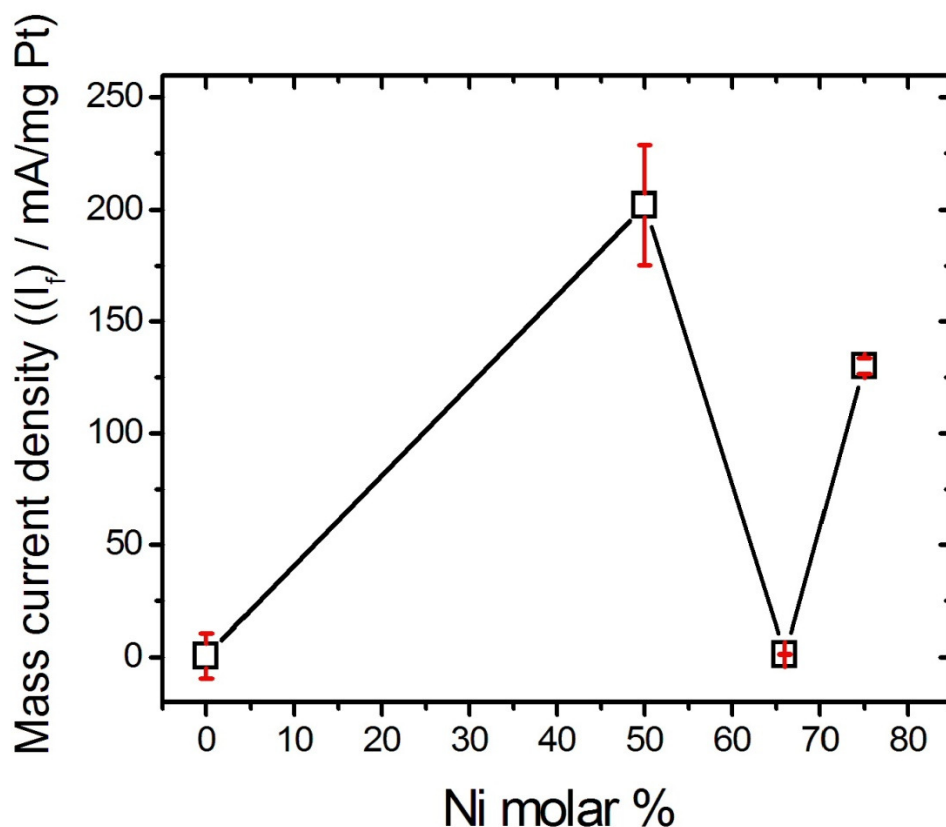


Figure 6.20. Relationship of the mass current density of the Pt-Ni nanoparticles and Ni molar percentage.

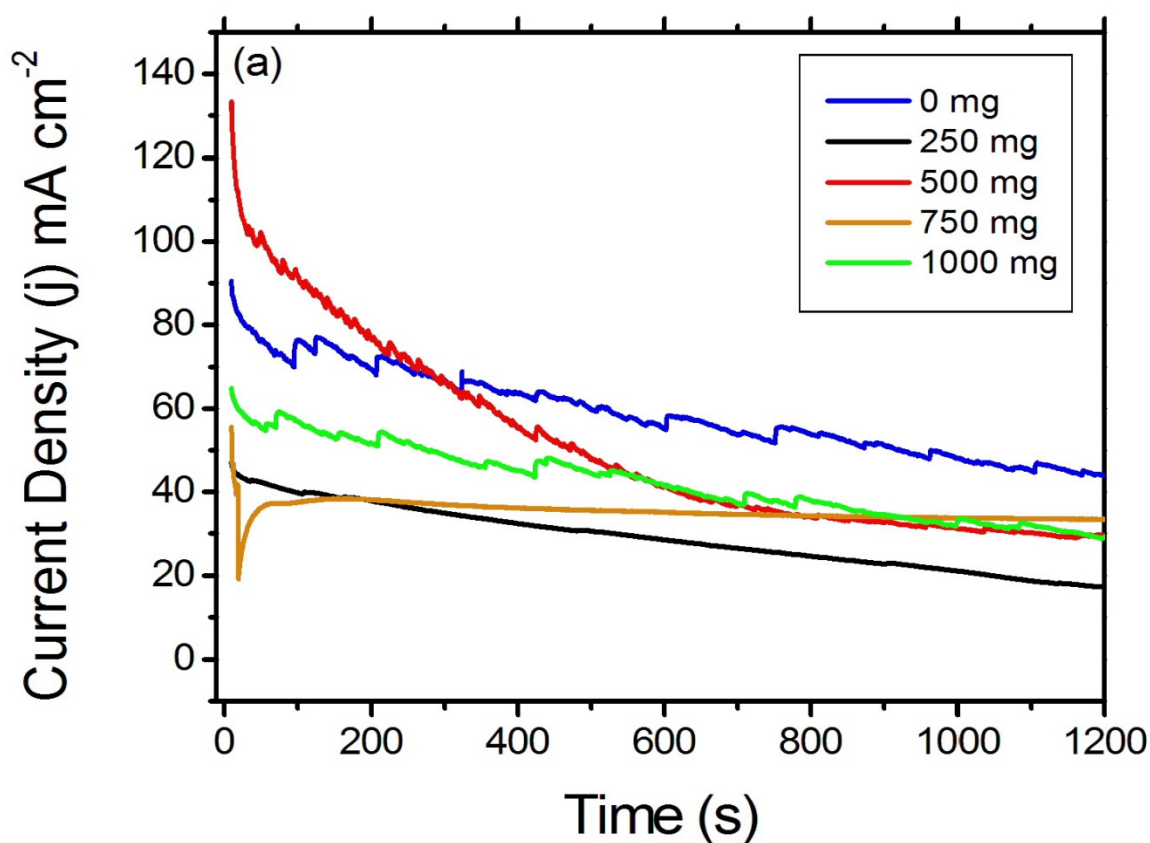
The structure of the nanoparticles also play a role in determining the catalytic activity where aggregation might lead to a reduction in the number of active sites and therefore the overall electrocatalytic activity [42]. The high peak potentials signals to a parallel mechanism for methanol oxidation, as determined by Okamoto et al. [43]. For their studies they varied the voltammetry scan rate, sweep potential and methanol concentrations. The same result was also observed by Murthy et al. [44] for MOR using a derivative of the linear scan voltammograms to determine peak positions for PtSn and PtRu nanoparticles. They discovered that at high peak potentials the forward scan peak determined a parallel reaction pathway where methanol dissociation resulted in the formation of CO_{ad} and CO_2 , this being the rate determining step of the reaction.

An important consideration in alloying Pt with Ni is finding the optimum Ni percentage that will give the highest current density. In this work we determined that the 50% Ni, i.e. Pt-Ni-(1:1), gives a superior catalyst. In work performed by Antolini et al. [45] they determined that the $\text{Pt}_{75}\text{Ni}_{25}/\text{C}$ (i.e. 25% Ni) catalyst gave the best activity, and Yang et al. [25] showed that 30-40% Ni can be added to the Pt solution and this will result in superior catalysts.

6.8. Chronoamperometry measurements

Chronoamperometric, i.e current vs. time, measurements were performed to determine the current decay of the catalysts over time at a constant polarization potential of 0.5 V in 0.5 M H_2SO_4 + 1.0 M CH_3OH electrolyte. The resulting current-

time curves are presented in Fig. 6.21(a) (variation of PVP), Fig. 6.21(b) (variation of NaOH concentration) and Fig. 6.21(c) (variation of molar ratio). As expected the 500 mg / 1.0 M NaOH sample exhibited the highest current density as well as current decay over 1200 s. The percentage of current left after 1200 s was as follows: 53.8% (1000 mg) > 44.4% (250 mg) > 48.8% (0 mg) > 38.7 (750 mg) > 28.5% (500 mg) and for the NaOH concentration it was 21.4% for the 2.0 M sample (see Table 6.9).



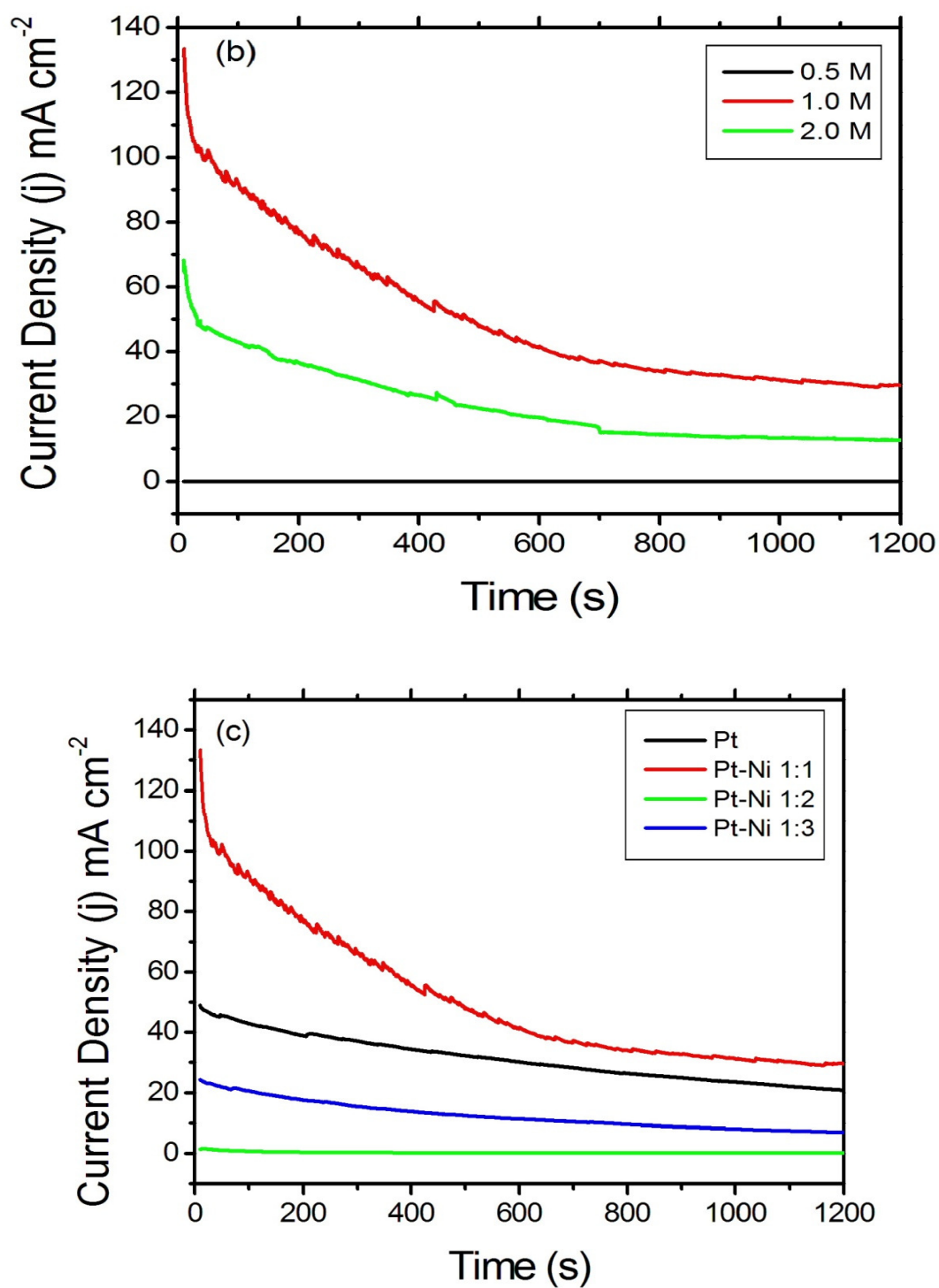


Figure 6.21. Chronoamperometry curves for Pt-Ni nanoparticles with changes in (a) capping agent PVP, (b) NaOH concentration and (c) Ni content molar ratio.

The chronoamperometry results for the Pt-Ni with different molar ratio are presented in Fig. 6.21 (c). The current decay was also observed with time at a polarization potential of 0.5 V where the rate of decay for Pt-Ni-(1:1) was faster than for the rest of the Pt-Ni samples as well as monometallic Pt. The current decay can be related to the catalysts tolerance to intermediate species such as CO, with a faster decay showing less tolerance than a slower rate of decay [17]. The percentage of current after a 1200s time interval was 28.5% (Pt-Ni-(1:1)), 31.2% (Pt-Ni-(1:3)), 31.6% (Pt-Ni-(1:2)) and 42.9% for monometallic Pt.

Table 6.9. Chronoamperometry data for the Pt-Ni nanoparticles.

Sample name	Particle size (nm)	I_0 (mA/cm²)	I_{1200} (mA/cm²)	ΔI (mA/cm²)	Current decay (%)
Pt-Ni-0.5M	2	-----	-----	-----	-----
Pt-Ni-1.0M	5	134	30.3	104	28.5
Pt-Ni-2.0M	6	67.6	12.6	55.0	21.4
Pt-Ni-0mg	5	90.2	45.1	45.1	48.8
Pt-Ni-250mg	3	48.3	17.0	31.3	44.4
Pt-Ni-500mg	5	134	30.3	104	28.5
Pt-Ni-750mg	5	54.7	33.5	21.2	38.7
Pt-Ni-1000mg	6	66.3	29.0	37.3	53.8
Pt-Ni-(1:0)	32	50.7	21.3	29.4	42.9
Pt-Ni-(1:1)	5	134	30.3	104	28.5
Pt-Ni-(1:2)	12	2.60	0.70	1.90	31.6
Pt-Ni-(1:3)	6	24.5	7.10	17.4	31.2

Although the Pt-Ni-(1:1) sample showed the highest current density of all the samples, its high decay rate suggest that this catalyst does not possess a good

ability in relation to the intermediate species formed during the reaction. The current decay is dictated by a number of factors among them the surface blockage by organic residues formed at high anodic potentials [46].

6.9. Conclusions

Bimetallic platinum nanoparticles were successfully prepared using microwave-irradiation as a synthesis procedure. Reaction parameters were varied to determine the optimum synthesis conditions as well as the effect that changing the surfactant and pH of the solution had on the size and ultimately the electrocatalytic activity of the nanoparticles. An increase in the activity of the catalyst towards MOR was noticed when PVP was increased, peaking at 500 mg and decreasing again. This indicated that there is an optimum PVP/Pt ratio which gives the best catalysts. When the pH of the solution was changed it was observed that the higher the pH, the higher the catalytic activity of the nanoparticles. Therefore it was shown that the optimum synthesis parameters in our work were 500 mg PVP and 1.0 M NaOH. The addition of Ni into the Pt lattice, gave a shift in the XRD peaks of the Pt fcc which was attributed to lattice contractions. This indicated that the Ni atoms are incorporated into the lattice of Pt which in turn results in favourable and much smaller Pt-Pt interatomic distances. The optimum Ni percentage that gave the catalyst with the highest activity was 50% which is higher than noted for Pt-Ni and Pt-Ru alloy systems. An optimum particle size was observed in the optimization process at 5 nm where the highest electrocatalytic activity was observed for the methanol oxidation reaction.

References

1. Peng, Z. and H. Yang, *Designer platinum : control of shape, composition in alloy, nanostructure and electrocatalytic properties*. Nano Today, 2009. **4**: p. 143 - 169.
2. Wang, D., T. Xie, and Y. Li, *Nanocrystals: Solution-based synthesis and applications as nanocatalysts*. Nano Research, 2009. **2**(1): p. 30-46.
3. Antolini, E. and J. Perez, *The renaissance of unsupported nanostructured catalysts for low-temperature fuel cells: from the size to the shape of metal nanostructures*. Journal of Materials Science, 2011. **46**: p. 4435 - 4457.
4. Tu, W. and H. Liu, *Continuous synthesis of colloidal metal nanoclusters by microwave irradiation*. Chemistry of Materials, 2000. **12**: p. 564 - 567.
5. Gao, Y., et al., *Evidence of monolayer assembly of poly(vinylpyrrolidone) on the surface of silver nanowires*. Journal of Physical Chemistry B, 2004. **108**: p. 12877 - 12881s.
6. Yee, C.K., et al., *Novel one-phase synthesis of thiol-functionalized gold, palladium, and iridium nanoparticles using superhydride*. Langmuir, 1999. **15**: p. 3486 - 3491.
7. Yee, C., et al., *One-phase synthesis of thiol-functionalized platinum nanoparticles*. Langmuir, 1999. **15**: p. 4314 - 4316.
8. Mathe, N.R., M.R. Scriba, and N.J. Coville, *Methanol oxidation reaction activity of microwave-irradiated and heat-treated Pt/Co and Pt/Ni electrocatalysts*. International Journal of Hydrogen Energy, 2014. **39**: p. 18871 - 18881.
9. Zhu, Y.-J., et al., *Microwave-assisted synthesis of single-crystalline Tellurium nanorods and nanowires in ionic liquids*. Angewandte Chemie, 2004. **116**: p. 1434 - 1438.
10. Komarneni, S., et al., *Microwave-polyol process for Pt and Ag nanoparticles*. Langmuir, 2002. **18**: p. 5959 - 5962.
11. Yu, W., W. Tu, and H. Liu, *Synthesis of nanoscale platinum colloids by microwave dielectric heating*. Langmuir, 1999. **15**: p. 6 - 9.
12. Vollath, D. and D.V. Szabó, *The microwave plasma process - a versatile process to synthesize nanoparticulate materials*. Journal of Nanoparticle Research, 2006. **8**: p. 417 - 428.
13. Grace, A.N. and K. Pandian, *One pot synthesis of polymer protected Pt, Pd, Ag and Ru nanoparticles and nanoprisms under reflux and microwave mode of heating in glycerol - A comparative study*. Materials Chemistry and Physics, 2007. **104**: p. 191 - 198.
14. Bensebaa, F., et al., *Microwave synthesis of polymer-embedded Pt-Ru catalyst for direct methanol fuel cell*. Journal of Physical Chemistry, 2005. **109**: p. 15339 - 15344.
15. Mathe, N.R., et al., *TEM and EELS studies of microwave-irradiation synthesis of bimetallic platinum nanocatalysts*. Journal of Physics: Conference Series, 2014. **522**: p. 012066.
16. Ramulifho, T., et al., *Fast microwave-assisted solvothermal synthesis of metal nanoparticles (Pd, Ni, Sn) supported on sulfonated MWCNTs: Pd-based bimetallic catalysts for ethanol oxidation in alkaline medium*. Electrochimica Acta, 2012. **59**: p. 310 - 320.
17. Long, N.V., et al., *Effects of heat treatment and poly(vinylpyrrolidone) (PVP) polymer on electrocatalytic activity of polyhedral Pt nanoparticles towards methanol oxidation*. Coll. Poly. Sci., 2011. **289**: p. 1373 - 1386.
18. Wang, D. and Y. Li, *Bimetallic nanocrystals: liquid-phase synthesis and catalytic applications*. Advanced Materials, 2011. **23**: p. 1044 - 1060.

19. Xu, W., et al., *Microwave-assisted synthesis of nickel nanoparticles*. Materials Letters, 2008. **62**: p. 2571 - 2573.
20. Bensebaa, F., et al., *Tunable platinum-ruthenium nanoparticle properties using microwave synthesis*. Journal of Materials Chemistry, 2004. **14**: p. 3378 - 3384.
21. Deivaraj, T.C., W. Chena, and J.Y. Lee, *Preparation of PtNi nanoparticles for the electrocatalytic oxidation of methanol*. Journal of Materials Chemistry, 2003. **13**: p. 2555 - 2560.
22. Ahrenstorf, K., et al., *Colloidal synthesis of Ni_xPt_{1-x} nanoparticles with tuneable composition and size*. Small, 2007. **3**(2): p. 271 – 274.
23. Mathe, N.R., et al., *The effect of reducing agents on the electronic, magnetic and electrocatalytic properties of thiol-capped Pt/Co and Pt/Ni nanoparticles*. Electrocatalysis, 2014. doi:10.1007/s12678-014-0241-y.
24. Park, K.-W., et al., *Chemical and electronic effects of Ni in Pt/Ni and Pt/Ru/Ni Alloy nanoparticles in methanol electrooxidation*. Journal of Physical Chemistry B, 2002. **106**: p. 1869 - 1877.
25. Yang, H., et al., *Structure and electrocatalytic activity of carbon-supported Pt-Ni alloy nanoparticles towards oxygen reduction reaction*. Journal of Physical Chemistry B, 2004. **108**: p. 11024 - 11034.
26. Arico, A.S., et al., *An XPS study on oxidation states of Pt and its alloys with Co and Cr and its relevance to electroreduction of oxygen*. Applied Surface Science, 2001. **172**: p. 33 - 40.
27. Guo, J.W., et al., *Preparation and characterization of a PtRu/C nanocatalyst for direct methanol fuel cells*. Electrochimica Acta, 2005. **51**: p. 754 - 763.
28. Park, K.-W., et al., *Chemical and electronic effects of Ni in Pt/Ni and Pt/Ru/Ni alloy nanoparticles in methanol electrooxidation*. Journal of Physical Chemistry B, 2002. **106**: p. 1869-1877.
29. Biesinger, M.C., et al., *Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni*. App. Surf. Sci., 2011. **257**: p. 2717 - 2730.
30. Casella, I.G., M.R. Guascito, and M.G. Sannazzaro, *Voltammetric and XPS investigations of nickel hydroxide electrochemically dispersed on gold surface electrodes*. Journal of Electroanalytical Chemistry, 1999. **462**: p. 202 - 210.
31. Grosvenor, A.P., et al., *New interpretations of XPS spectra of nickel and oxides*. Surface Science, 2006. **600**: p. 1771 - 1779.
32. Biesinger, M.C., et al., *X-ray photoelectron spectroscopic chemical state quantification of mixed nickel metal, oxide and hydroxide systems*. Surface and Interface Analysis, 2009. **41**: p. 324 - 332.
33. Castle, J.E., *Use of "shake-up" satellites in photoelectron spectra for analysis of oxide layers on metals*. Nature Physical Science, 1971. **234**: p. 93 - 95.
34. Kim, K.S. and N. Winograd, *X-ray photoelectron spectroscopic binding energy shifts due to matrix in alloys and small supported metal nanoparticles*. Chemical Physics Letters, 1975. **30**: p. 91-95.
35. Zhao, J., et al., *Microwave polyol synthesis of Pt/C catalysts with size-controlled Pt particles for methanol electrocatalytic oxidation*. Journal of Materials Science, 2006. **41**: p. 5514 - 5518.
36. Mabena, L.F., et al., *Ruthenium supported on nitrogen-doped carbon nanotubes for the oxygen reduction reaction in alkaline media*. Fuel Cells, 2012. **12**: p. 862 – 868.
37. Frelink, T., W. Visscher, and J.A.R.v. Veen, *Particle size effect of carbon-supported platinum catalysts for the electrooxidation of methanol*. Journal of Electroanalytical Chemistry, 1995. **382**: p. 65 - 72.
38. Gasteiger, H.A. and M.M. Markovic, *Just a dream - or future reality*. Science, 2009. **324**: p. 48 - 49.
39. Park, S., Y. Xie, and M.J. Weaver, *Electrocatalytic pathways on carbon-supported platinum nanoparticles: comparison of particle-size-dependent rates of methanol, formic acid, and formaldehyde electrooxidation*. Langmuir, 2002. **18**: p. 5792 - 5798.

40. Mu, Y., et al., *Controllable Pt nanoparticle deposition on carbon nanotubes as an anodic catalyst for direct methanol fuel cells*. Journal of Physical Chemistry B, 2005. **109**: p. 22212 - 22216.
41. Sun, S., et al., *Single-atom catalysis using Pt/graphene achieved through atomic layer deposition*. Scientific Reports, 2013. **3**: p. 1775.
42. Yung, T.-Y., J.-Y. Lee, and L.-K. Liu, *Nanocomposite for methanol oxidation: synthesis and characterization of cubic Pt nanoparticles on graphene sheets*. Science and Technology of Advanced Materials, 2013. **14**: p. 035001.
43. Okamoto, H., W. Kon, and Y. Mukouyama, *Five current peaks in voltammograms for oxidation of formic acid, formaldehyde and methanol on platinum*. Journal of Physical Chemistry B, 2005. **109**: p. 15659 - 15666.
44. Murthy, A. and A. Manthiram, *Application of derivative voltammetry in the analysis of methanol oxidation reaction*. The Journal of Physical Chemistry C, 2012. **116**: p. 3827 - 3832.
45. Antolini, E., J.R.C. Salgado, and E.R. Gonzalez, *The methanol oxidation reaction on platinum alloys within the first row transition metals. The case of Pt-Co and Pt-Ni alloy electrocatalysts for DMFCs : A short review*. Applied Catalysis B: Environmental, 2006. **63**: p. 137 - 149.
46. Iwasita, T., *Methanol and CO Electrooxidation*, in *Handbook of Fuel Cells - Fundamentals, Technology and Applications*, W. Vielstich, H.A. Gasteiger, and A. Lamm, Editors. 2003, John Wiley & Sons. p. 603 - 624.

CHAPTER 7: CARBON MONOXIDE (CO) ELECTRO-OXIDATION OF THE Pt-Ni NANO ELECTROCATALYSTS

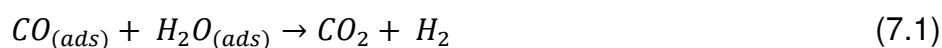
Carbon monoxide (CO) stripping measurements were performed in an electrochemical cell with the acid electrolyte saturated with carbon monoxide (CO). This procedure was performed to determine the resistance of the catalysts to CO poisoning. The resulting voltammograms before and after CO saturation are discussed in this chapter.

7.1. Introduction

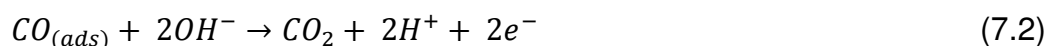
Due to the poisoning effect that carbon monoxide (CO) has on the catalytic activity of electrocatalysts during the methanol oxidation reaction (MOR), various studies have been undertaken to understand the CO electrooxidation of Pt nanoparticles [1-4]. CO as well as other carbonaceous species such as formaldehyde are the intermediate species formed during MOR and have a tendency to poison the electrodes [5, 6]. Because the focus of this study was to improve the quality of anode catalysts for direct methanol fuel cells, it is important to understand the mechanism of poisoning. This will ultimately allow for the synthesis of catalysts that are more resistant to CO poisoning. Of the various ways that have been explored to enhance the resistance of Pt catalysts to CO, one procedure centres around the addition of a second alloying

metal to platinum since Pt on its own is easily poisoned by adsorbed CO molecules. The choice of the alloying metal is influenced by the ability of the metal to form surface oxides which donates O to CO to form CO₂.

A mechanism that rationalizes the CO tolerance for Pt-M alloys is the bifunctional mechanism; and another is a mechanism involving ligand effects [7] (see Chapter 2, section 2.3.2). In terms of the CO electrooxidation mechanism, it is generally accepted that the reaction can be obtained by the Langmuir-Hinshelwood mechanism [8-10] (Eq. 7.1). In this mechanism, the adsorbed CO reacts with an adsorbed oxygen-containing species on the metal surface, either OH_{ads} or H₂O_{ads}.



An alternative mechanism, the Eley-Rideal mechanism, [11], (Eq. 7.2) can also explain CO to CO₂ oxidation but this involves the attack by solution-phase OH_{ads} on the adsorbed CO, not via the metal surface:



The work in this chapter was performed to evaluate CO poisoning of Pt-metal alloys as this reaction is an important limitation in the development of commercial applications of DMFCs and thus to the contribution of these types of fuel cells in alternative energy industries. In Chapter 6, it was shown that the microwave-irradiated electrocatalysts gave the best results in terms of Pt-Ni electrocatalysts. This chapter will thus focus on the CO stripping studies of these catalysts and describe the effect of the amount of surfactant, alloying metal and the pH of the starting solutions on the CO stripping reactions.

7.2. Experimental Procedure

The synthesis of the catalysts studied here was discussed in Chapter 6. For the CO stripping studies, an electrochemical cell contained 40 ml of 0.5 M H₂SO₄ electrolyte with the catalyst deposited on a polished glassy carbon electrode (working electrode); an Ag/AgCl (reference electrode) and Pt rod (counter electrode), made up the electrochemical cell. The CO stripping procedure was performed at a scanning range of 0 – 1.2 V and a scan rate of 10 mV/s for all the experiments, with further procedures being:

- The solution was purged for 30 min with N₂, and then scanned for 20 cycles. **(Called: N₂-before)**
- The electrolyte was saturated with CO for 30 min while it was scanned and then the electrode was scanned for a further 20 cycles. **(Called: CO)**
- The solution was purged again for 1 hour with N₂ to remove residual CO, and then scanned again for 20 cycles. **(Called: N₂-after)**

7.3. CO electro-oxidation

The effect of CO on the electrocatalysts as described above was studied. This was so as to determine the behaviour and the overall tolerance of the catalyst to CO poisoning in an acid electrolyte. The reactions were performed in an acid electrolyte so as to eliminate the effect of the CO from methanol dissociation.

7.3.1. Effect of the surfactant (PVP) and pH (NaOH)

The effect of the surfactant or capping agent (PVP) and the pH of the solution in optimizing the microwave-irradiation synthesis of bimetallic Pt-Ni in the presence and absence of CO were explored. In Fig. 7.1a, the Pt-Ni-(1:1) catalyst with no surfactant added (i.e. 0 mg PVP) is presented. The CO stripping voltammogram did not exhibit a typical CO oxidation peak in the Pt-oxide oxidation region (forward scan) after CO exposure and saturation. After the removal of CO from the electrolyte there was a noticeable decrease in the H₂ adsorption/desorption area (0 – 0.1 V) as well as the Pt-reduction peak (see Fig 7.1a and Table 7.1). The H₂-area indicates a loss in the Pt catalytically active sites due to the CO_{ads} saturation blocking the current [12, 13].

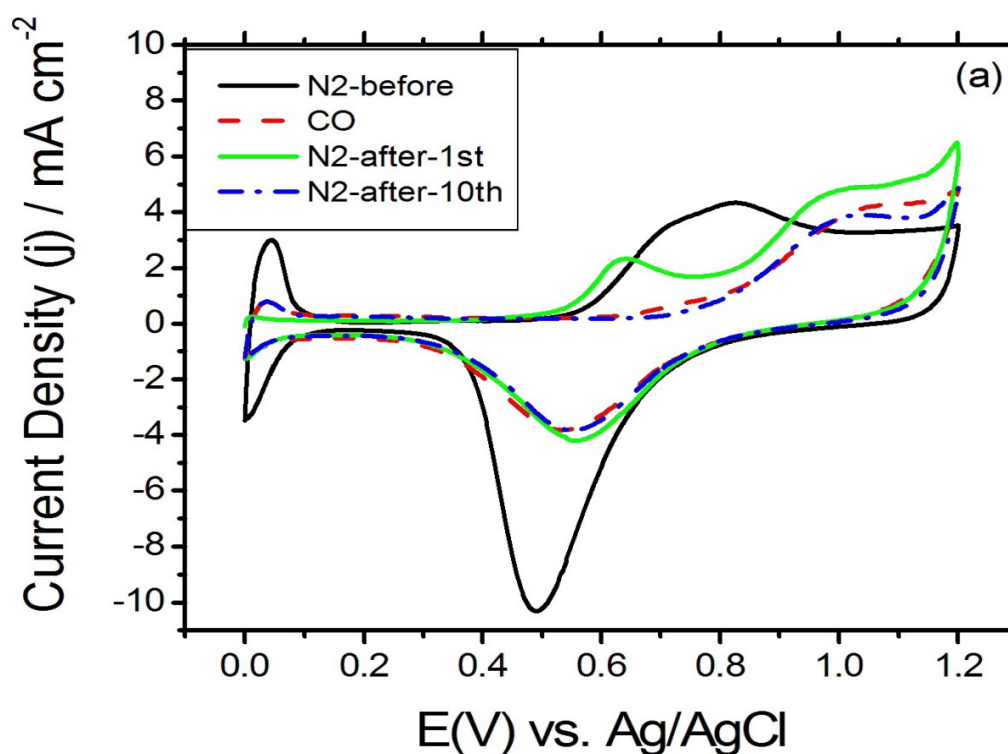
Table 7.1. CO oxidation peak parameters of the Pt-Ni-(1:1) catalysts prepared with varied NaOH and PVP.

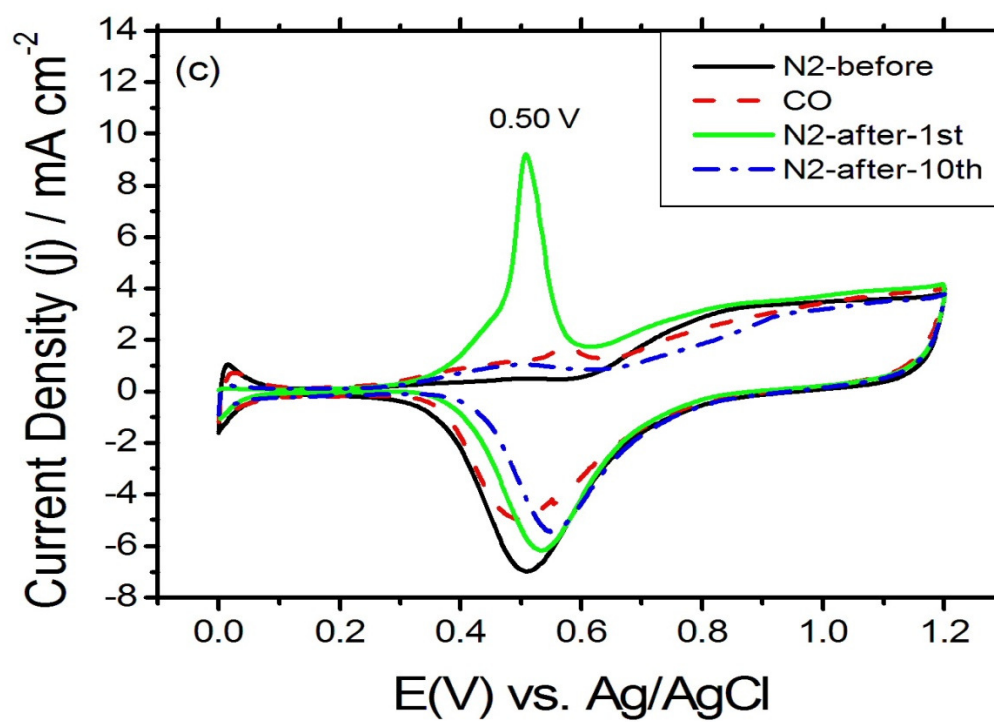
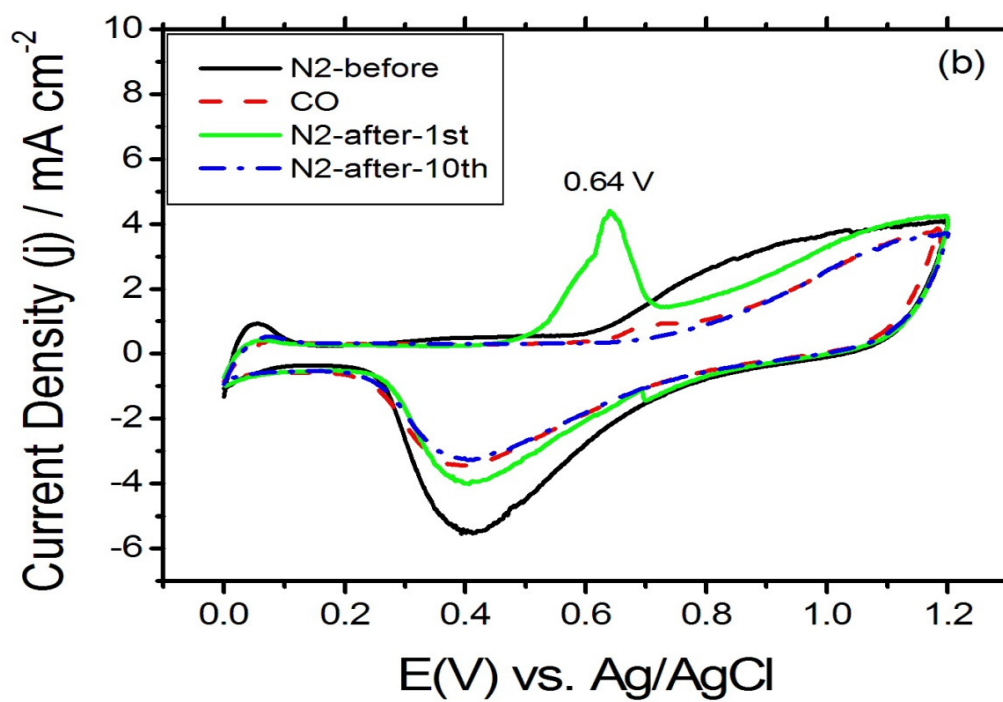
Sample name	Particle size (nm)	CO onset (V)	CO peak (V)	$\Delta I(\text{CO peaks})$	ΔE (Pt-oxide)	$\Delta I(\text{Pt-oxide})$
0 mg	5	-----	-----	-----	0.043	6.4
500 mg	5	0.50	0.64	3.5	0.020	2.1
750 mg	5	0.33	0.51	7.5	0.030	2.4
2.0 NaOH	6	-----	-----	-----	0.20	5.0

When 500 mg of the capping agent, PVP was added into the solution, a CO oxidation peak was seen to 0.64 V (Fig. 7.1b). As the amount of PVP was further increased to 750 mg (Fig. 7.1c), the CO peak shifted to even lower potentials (0.5 V), with less loss in the H₂-area and the Pt reduction/oxidation peaks. The shift in peak

potentials is said to arise from the Pt particle affinity for OH, which in turn increases the rate of CO oxidation, consistent with the bifunctional model [13]. This is positively shifted from the 0.583 V value reported for a bulk Pt electrode by Gasteiger et al. [14]. Studies by Ochal et al. [7], and Spendelow et al. [8] have revealed a CO oxidation peak at 0.8 V in 0.5 M H₂SO₄ for Pt-Ru/C nanoparticles.

The CO oxidation onset potentials occurred at 0.50 V and 0.33 V for the 500 mg and 750 mg samples respectively, showing a negative shift with an increase in the amount of the capping agent. This indicates the higher the PVP ratio, the more CO resistant the material (i.e. a lower or negatively shifted CO onset potential) when compared to literature Pt-Ru/C studies [7, 8].





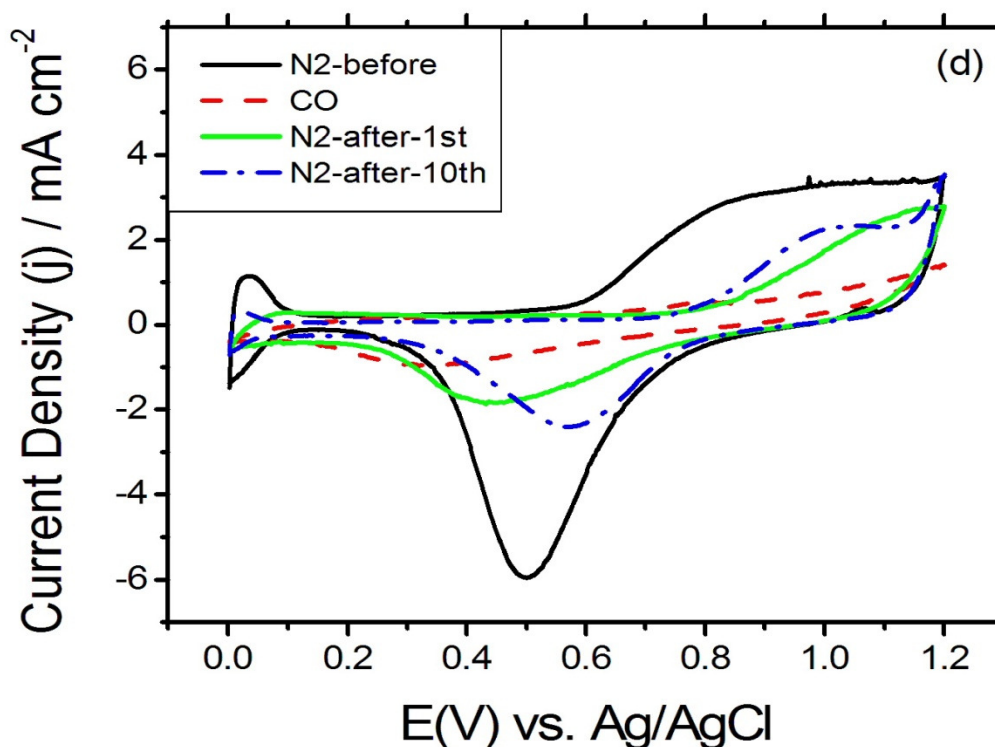


Figure 7.1. CO stripping voltammograms of Pt-Ni-(1:1) nanoparticles for (a) 0 mg PVP, (b) 500 mg PVP, 1.0 M NaOH, (c) 750 mg PVP and (d) 2.0 M NaOH.

The pH of the solution was increased using 2.0 M NaOH. No CO oxidation peak was observed, although there were substantial losses in the peak current densities after CO saturation. The loss in the H₂ adsorption/desorption peaks after CO stripping determined the ability of the catalysts to overcome CO poisoning during MOR. Therefore the trend obtained in this study was that the higher the pH of the solution, the more CO tolerant the catalyst.

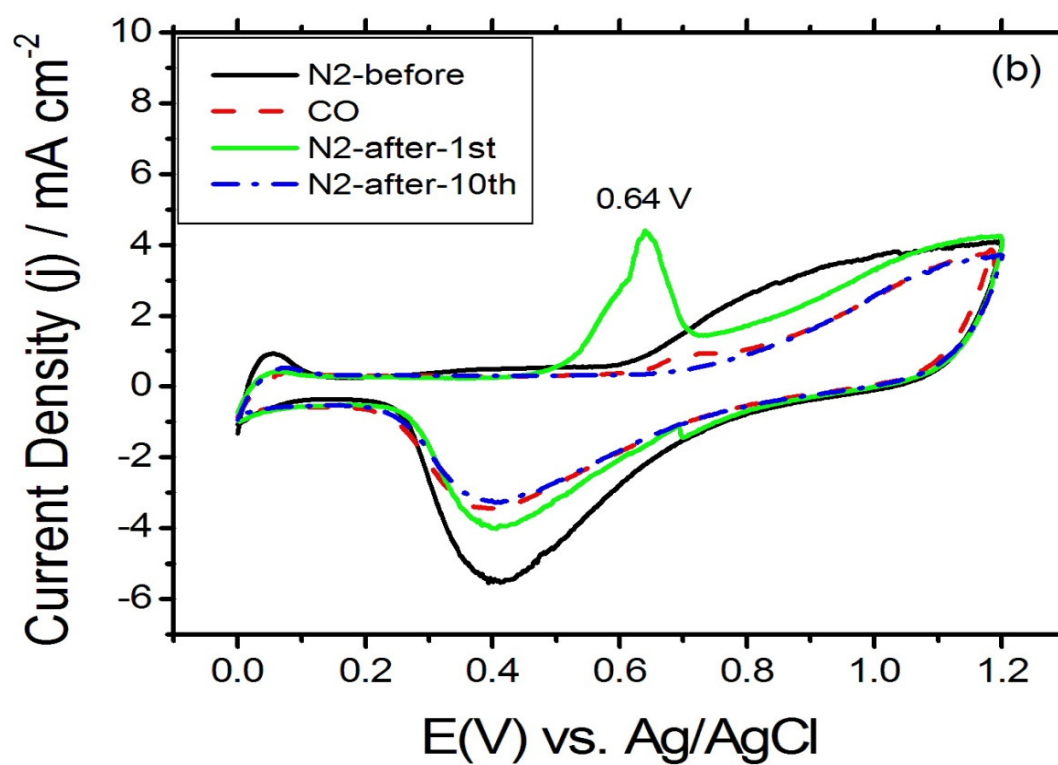
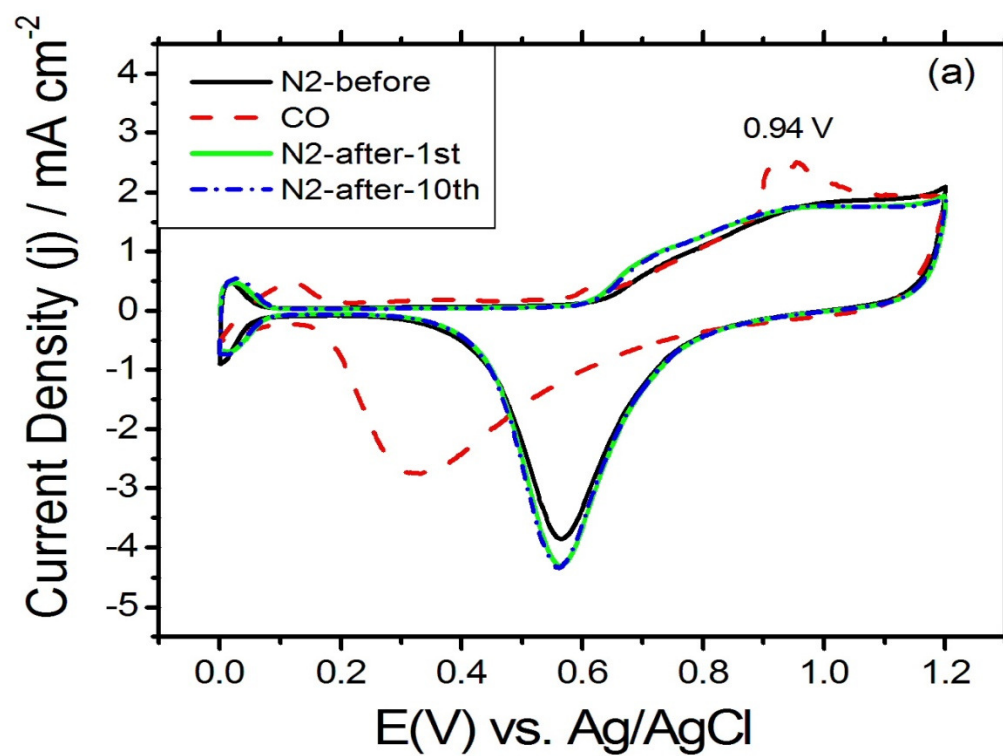
The particle sizes used in the study were similar (5nm, Table 7.1). No particle size effect was observed contrary to what was reported by Maillard et al. [15] for Pt-Ru/C catalysts. Therefore the CO oxidation process will not be influenced by particle size effects. The CO stripping peaks shifted to lower potentials with an increase in the amount of PVP. Due to the similarity in the Pt:Ni molar content for these samples,

the mechanism of oxidation is then more likely to be the bifunctional process rather than the ligand or electronic process [11, 16].

7.3.2. Effect of the Ni molar ratio

The composition-dependence of the CO electrooxidation was also determined by varying the amount of the alloying metal (Ni) in the Pt-Ni alloy. For the monometallic Pt catalyst (Fig. 7.2a), there was an observed peak at 0.94 V after the introduction of CO as well as a negative shift in the Pt-oxide reduction peak. After removal of CO, there was complete recovery of the current in the H₂ adsorption/desorption area and the Pt-reduction/oxidation peaks.

Addition of Ni into the system gave a CO oxidation peak at 0.64 V for Pt-Ni-(1:1) and 0.59 V for Pt-Ni-(1:3). However, no peak was observed for Pt-Ni-(1:2). The negative shift in the peak potential upon the addition of Ni can be attributed to the presence of Ni-oxide and hydroxide species (see from XPS) and the OH group assists with the oxidation of CO [13]. The lower onset potential is indicative of the catalyst's superiority in facilitating the removal of adsorbed surface CO [17].



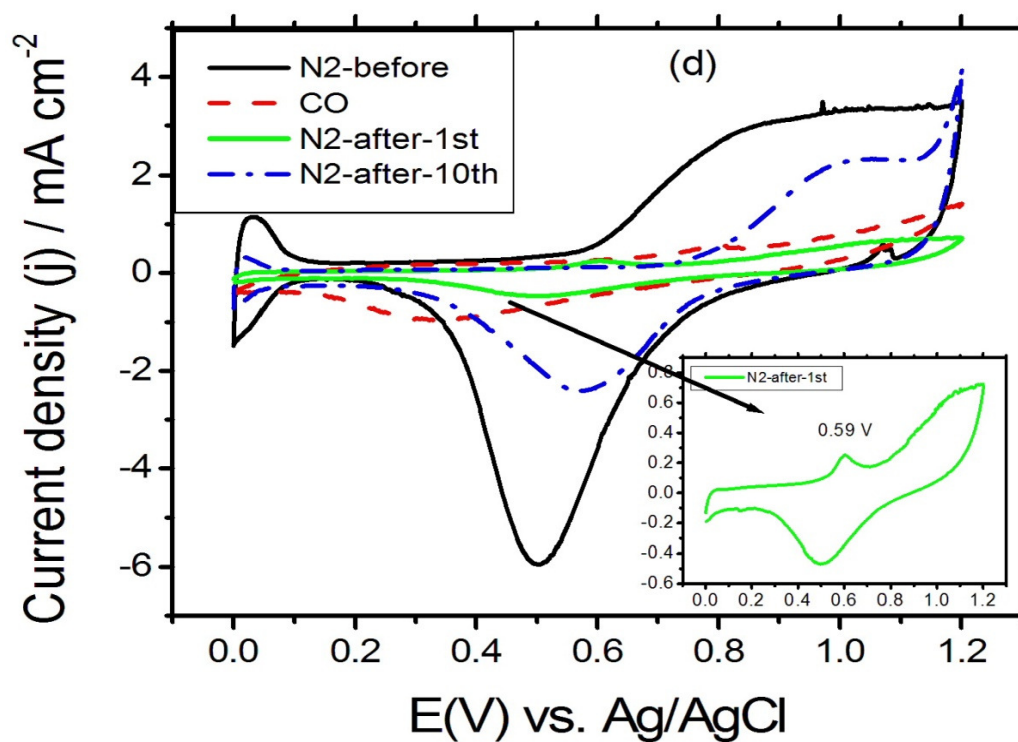
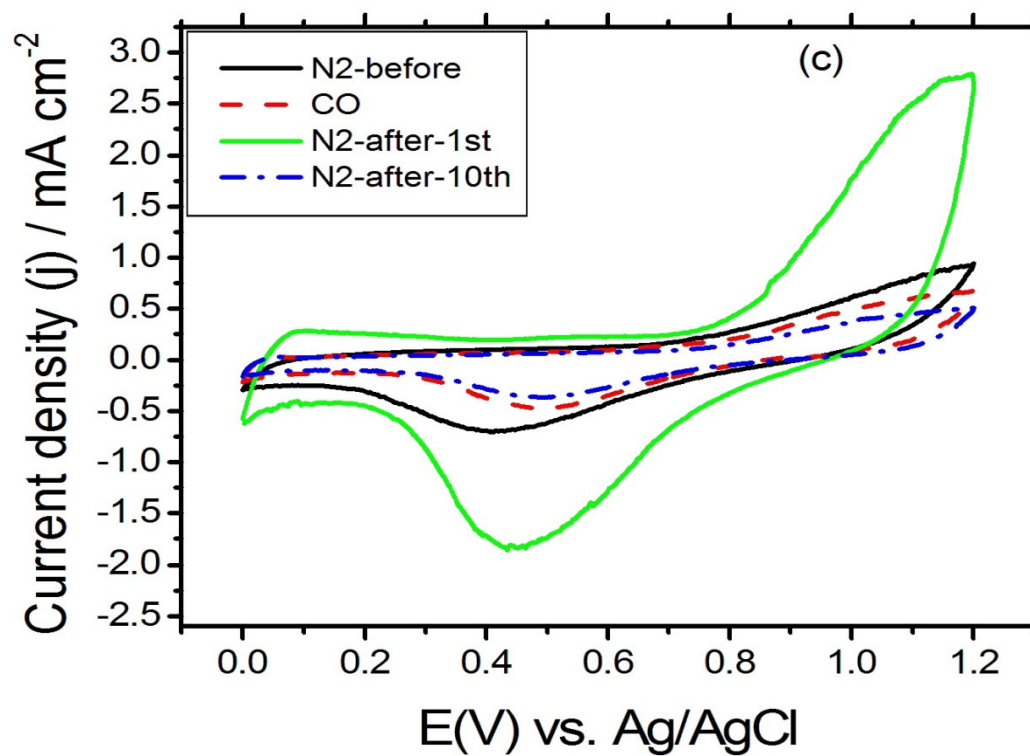


Figure 7.2. CO electrooxidation voltammograms of; (a) Pt-Ni-(1:0) (b) Pt-Ni-(1:1), (c) Pt-Ni-(1:2) and (d) Pt-Ni-(1:3) nanoparticles in 0.5 M H_2SO_4 .

The CO onset potential in these bimetallic alloys shifted to lower potentials (0.6 V) as the Ni was added into solution when compared to monometallic Pt which showed a CO onset potential at 0.88 V (see table 7.2). In comparison to Pt-Ru systems, which show an onset potential at 0.425 V, as seen by Vidaković [13], the potential obtained for Pt-Ni in this work were also lower than smooth Pt bulk electrode (0.80 V) [14].

Table 7.2. CO stripping peak information of Pt-Ni nanoparticles at different compositions.

Sample name	Particle size (nm)	CO onset (V)	CO peak (V)	$\Delta I(\text{CO peaks})$	ΔE (Pt-oxide)	$\Delta I(\text{Pt-oxide})$
Pt-Ni-(1:0)	32	0.88	0.94	0.88	0.24	1.6
Pt-Ni-(1:1)	5	0.50	0.64	3.5	0.02	2.1
Pt-Ni-(1:2)	13	-----	-----	-----	0.07	0.24
Pt-Ni-(1:3)	6	0.49	0.59	0.12	0.015	5.5

The absence or decrease of H₂ adsorption/desorption peaks after CO saturation and subsequent removal, may be related to the formation of the M-OH species and therefore the bifunctional mechanism [11, 18]. Therefore, in this case there was a drastic decrease in the adsorption peaks after CO saturation, seen more for the higher molar ratio sample, Pt-Ni-(1:3). This trend was also observed by Xu et al [19], for Pt-Co systems, where there was a decrease in the peaks with an increase in the Co content.

The addition of Ni into the solution thus contributes towards the electro-oxidation of CO through the negative shift of the onset as well as the CO oxidation peak potentials. In Pt-Ru systems, this shift has been attributed to the presence of Ru-rich domains present on the surface of the materials. Also Maillard et al. [12], have

determined that the modification of shape, size and lattice parameter of Pt through the addition of Ni leads to increased CO tolerance. The lower the potential, the more superior and CO tolerant the catalyst [8].

7.4. Conclusion

The study of CO electrooxidation provides information for the use of bimetallic nanoparticles as fuel cell anode catalysts. The poisoning effect that CO has on the catalysts during methanol oxidation was studied. In this work, CO stripping measurements were performed on the microwave-irradiated Pt-Ni samples to determine their tolerance to CO poisoning. Analysis of the results revealed that the CO tolerance of the materials was improved at the higher molar content (Pt-Ni-(1:3)) as well as when the highest amount of surfactant was used (750 mg). From the above analysis it can be seen that the addition of the second alloying metal (Ni) leads to an increase in the CO tolerance abilities of the catalysts. The shift of the onset potentials to lower values and the absence of the H₂ adsorption/desorption peaks after CO saturation following the addition of Ni is attributed to a bifunctional mechanism where the formation of OH_{ads} on the Ni site occurs at lower potentials than on Pt sites.

References

1. Iwasita, T., *Methanol and CO Electrooxidation*, in *Handbook of Fuel Cells - Fundamentals, Technology and Applications*, W. Vielstich, H.A. Gasteiger, and A. Lamm, Editors. 2003, John Wiley & Sons. p. 603 - 624.
2. Gasteiger, H.A., N.M. Markovic, and P.N. Ross, *H₂ and CO Electrooxidation on Well-Characterized Pt, Ru, and Pt-Ru. 1. Rotating Disk Electrode Studies of the Pure Gases Including Temperature Effects*. Journal of Physical Chemistry, 1995. **99**: p. 8290 - 8301.
3. Markovic, N.M., et al., *Electro-Oxidation Mechanisms of Methanol and Formic Acid on Pt-Ru alloy surfaces* Electrochimica Acta, 1995. **40**: p. 91 - 98.
4. Mayrhofer, K.J.J., et al., *CO surface electrochemistry on Pt-nanoparticles: A selective review*. Electrochimica Acta, 2005. **50**: p. 5144 - 5154.
5. Ramulifho, T., et al., *Fast microwave-assisted solvothermal synthesis of metal nanoparticles (Pd, Ni, Sn) supported on sulfonated MWCNTs: Pd-based bimetallic catalysts for ethanol oxidation in alkaline medium*. Electrochimica Acta, 2012. **59**: p. 310 - 320.
6. Sun, S., et al., *Single-atom catalysis using Pt/graphene achieved through atomic layer deposition*. Nature Scientific Reports, 2013. **3**: p. DOI:10.1038/srep01775.
7. Ochal, P., et al., *CO stripping as an electrochemical tool for characterization of Ru@Pt core-shell catalysts*. Journal of Electroanalytical Chemistry, 2011. **655**: p. 140 - 146.
8. Spendelov, J.S., et al., *Electrooxidation of adsorbed CO on Pt(111) and Pt(111)/Ru in alkaline media and comparison with results from acidic media*. Journal of Electroanalytical Chemistry, 2004. **568**: p. 215 - 224.
9. Mayrhofer, K.J.J., et al., *CO surface electrochemistry on Pt-nanoparticles: a selective review*. Electrochimica Acta, 2005. **50**: p. 5144 - 5154.
10. Micoud, F., et al., *Unique CO-tolerance of Pt-WO_x materials*. Electrochemistry Communications, 2009. **11**: p. 651 - 654.
11. Pereira, L.G.S., V.A. Paganin, and E.A. Ticianelli, *Investigation of the CO tolerance mechanism at several Pt-based bimetallic anode electrocatalysts in a PEM fuel cell*. Electrochimica Acta, 2009. **54**: p. 1992 - 1998.
12. Maillard, F., et al., *Effect of the structure of Pt-Ru/C particles on CO_{ad} monolayer vibrational properties and electrooxidation kinetics*. Electrochimica Acta, 2007. **53**: p. 811 - 822.
13. Vidakovic, T., M. Christov, and K. Sundmacher, *The use of CO stripping for in situ fuel cell catalyst characterization*. Electrochimica Acta, 2007. **52** p. 5606 - 5613.
14. Gasteiger, H.A., et al., *CO electrooxidation on well-characterized Pt-Ru alloys*. Journal of Physical Chemistry, 1994. **98**: p. 617 - 625.
15. Maillard, F., E.R. Savinova, and U. Stimming, *CO monolayer oxidation on Pt nanoparticles: Further insight into particle size effect*. Journal of Electroanalytical Chemistry, 2007. **599**: p. 221 - 232.
16. Kuk, S.T. and A. Wieckowski, *Methanol electrooxidation on platinum spontaneously deposited on unsupported and supported ruthenium nanoparticles*. Journal of Power Sources, 2005. **141**: p. 1 - 7.

17. Ding, L.-X., et al., *Hierarchical Pd-Sn alloy nanosheet dendrites: an economical and highly active catalyst for ethanol electrooxidation*. Nature Scientific Reports, 2013. **3**: p. 1 - 7.
18. Jiang, Q., et al., *Promoting effect of Ni in PtNi bimetallic electrocatalysts for the methanol oxidation reaction in alkaline medium: experimental and density functional theory studies*. Journal of Physical Chemistry C, 2010. **114**: p. 19714 - 19722.
19. Xu, Y., et al., *Composition-tunable Pt-Co alloy nanoparticle networks: facile room-temperature synthesis and supportless electrocatalytic applications*. Chem. Phys. Chem., 2012. **13**: p. 2601 - 2609.

CHAPTER 8: CONCLUSION

The main objective of this work was to synthesize bimetallic platinum nanoparticles to be used as anode catalysts for direct methanol fuel cells (DMFCs). This was achieved by alloying Pt with two transition metals; Co and Ni, in order to reduce the overall costs of the catalyst, enhance the electrocatalytic activity of the catalyst and increase the CO poisoning resistance of the materials. The objectives were achieved to varying degrees in this project.

Chapter 4 deals with the conventional thermal synthesis of bimetallic Pt-Co and Pt-Ni nanoparticles using the known reducing agents, NaBH_4 and N_2H_4 , at room temperature with octadecanethiol (ODT) acting as the capping agent. In using the different strength reducing agents, differences in the properties of the produced nanoparticles were observed. For the strong reducing agent, NaBH_4 , the nanoparticles obtained were larger in size and also had a wider size distribution in comparison with the particles produced by N_2H_4 . Also there were more oxide and hydroxide groups observed on the surfaces of these nanoparticles (from XPS analysis).

When the alloying metal was added, there was a decrease in the Pt-Pt interatomic distance as calculated from the XRD lattice parameters. This effect was larger for the NaBH_4 reduced metal than for N_2H_4 reduced metal. This is related to the electrocatalytic activities of the materials. In conclusion, changing the reducing agent (as well as the molar ratio and type of alloying metal) resulted in differences in the

activities of the nanoparticles. It was also determined that the NaBH_4 -reduced Pt-Ni samples exhibited the highest activity. The current output using this synthesis procedure was still very low. The low current output were attributed to the presence of the thiol-ligand from the capping agent (octadecanethiol) blocking the catalytically active Pt sites. Therefore a new synthesis procedure was explored in later studies. This involved the use of microwaves to make mixed metal catalysts.

Conventional and heat-treated (HT) Pt-Ni and Pt-Co nanoparticles were compared with the microwave-irradiation (MW) synthesized nanoparticles in **Chapter 5**. Microwave-irradiation was used because it is regarded as an environmentally safe synthesis procedure that provides a more uniform heat distribution in the synthesis process. Using the same amount of precursor metals, there was an observed increase in the electrocatalytic activity of the MW synthesized nanoparticles when compared to the HT samples. This was attributed to the decrease in the XRD lattice parameters of the microwave-irradiated Pt-Co and Pt-Ni samples brought about by a favourable Pt-Pt interatomic distance indicating better alloying compared to conventionally synthesized Pt-Co and Pt-Ni samples. The higher relative amounts of hydroxide species observed for the MW samples compared to HT also resulted in the higher MOR activities of the MW catalysts.

As the microwave-irradiation synthesized samples in Chapter 5 showed higher electrocatalytic activity, **Chapter 6** contains details on further experiments performed using the microwave-irradiation synthesis procedure. The focus was on varying the reaction parameters in order to determine the optimum microwave synthesis

parameters to make Pt-Ni nanoparticles. The pH of the precursor solutions, the amount of capping agent and the Ni molar content were the parameters that were varied in the optimization process. In changing the above parameters, it was determined that an optimum concentration was required to give a maximum current output above which the electrocatalytic activity dropped drastically. The best performing catalyst in this work was found to contain 500 mg PVP, 1.0 M NaOH and had a 1:1 Pt:Ni ratio. Furthermore, as with the previous work, a decrease in XRD lattice parameters on addition of Ni into the solution resulted in a more favourable Pt-Pt distance and thus increased electrocatalytic activity.

Chapter 7 focused on the carbon monoxide (CO) electro-oxidation of the Pt-Ni nanoparticles. Carbon monoxide poisoning is one of the drawbacks in the application of direct methanol fuel cells as alternative energy devices when Pt is used as the anode catalyst. This is because CO is an intermediate product of the methanol oxidation reaction and it blocks the electrocatalytic active sites of Pt during the reaction. The data obtained for the CO electro-oxidation study was found to be consistent with the bifunctional mechanism. In this mechanism the donation of O to CO by the alloying metals oxide and hydroxide species explains the increased CO tolerance of the materials.

The main aim of this work was to determine the effect of the second metal (Co and Ni) on the Pt and to possibly provide a mechanism of enhancement for the Ni and Co metals in the electrocatalytic activity of Pt. In all the different synthesis procedures generated the presence of the M-oxide and M-hydroxide species in particular by

XPS analysis and these were determined to be the source of the enhancement in the electrocatalytic activity on addition of Co and Ni to Pt. This is because these species donate O to CO thus leading to increased Pt CO tolerance as well as the general enhancement of the MOR that can be explained by a the bifunctional model.