

Preparation of PtNi Nanoparticles for the Electrocatalytic Oxidation of Methanol

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Abstract — Carbon supported PtNi nanoparticles were prepared by hydrazine reduction of Pt and Ni precursor salts under different conditions, namely by conventional heating (PtNi-1), by prolonged reaction at room temperature (PtNi-2) and by microwave assisted reduction (PtNi-3). The nanocomposites were characterized by XRD, EDX, XPS and TEM and used as electrocatalysts in direct methanol fuel cell (DMFC) reactions. Investigations into the mechanism of PtNi nanoparticle formation revealed that platinum nanoparticle seeding was essential for the formation of the bimetallic nanoparticles. The average particle size of PtNi prepared by microwave irradiation was the lowest, in the range of 2.9 – 5.8 nm. The relative rates of electrooxidation of methanol at room temperature as measured by cyclic voltammetry showed an inverse relationship between catalytic activity and particle size in the following order PtNi-1 < PtNi-2 < PtNi-3.

Index Terms—Direct methanol fuel Cells, platinum nickel alloy nanoparticles, microwave assisted synthesis, electrooxidation of methanol.

I. INTRODUCTION

A variety of methods are available for the preparation of nanoparticles [1]: chemical reduction[2]-[4], sonication [5], [6], γ -ray radiolysis [7], UV irradiation [8], [9], thermal decomposition [10], [11], vapor deposition [12] and electrochemical synthesis [13]; just to name a few. Recently microwave assisted synthesis has been increasingly used to replace conventional heating in synthesis because it offers more efficient and uniform

heating which are conducive to homogenous nucleation and a shorter crystallization time [14]-[16]; factors which are generally believed to be the prerequisite to the formation of monodisperse nanoparticles. Furthermore, microwave heating has also been found to increase reaction kinetics by one to two orders of magnitude [16]-[18]. Thus microwave assisted synthesis could pave way for the preparation of highly effective catalytic nanoparticles where the high surface-to-volume ratio of the particles can substantially reduce the loading of the cost-bearing active components.

On the other hand, there is increasing interest to develop direct methanol fuel cells (DMFC) as a future power source for small portable electronic devices [19]-[21]. While platinum has traditionally been the electrocatalyst for most fuel cell anodes, platinum is highly susceptible to carbon monoxide poisoning particularly for room temperature operations. The use of alloys of platinum and other less noble and oxophilic metals has been proposed as a solution [22]-[26]. A reaction mechanism based on bifunctional catalysis has been proposed to explain the increased CO resistance of platinum alloy DMFC anodes. In brief, platinum activates the C-H bond cleavage in the surface adsorbed methanol. The Pt_x-CO species that is formed in the process is strongly held by the Pt surface. When a neighboring oxophilic metal is present the adsorbed CO could be oxidized to CO₂ through a reaction involving surface adsorbed water on the oxophilic metal [22]-[26]. Among the Pt alloys the PtRu system is the most extensively investigated for DMFC applications. However, there is increasing interest to explore other Pt alloy systems involving metals such as Ni, Fe, Sn, Mo, Os and W [26]-[31]. Theoretical calculations have shown that the segregation processes that generally lead to Pt surface enrichment are unlikely to occur in the Pt-Ni system [32]. Furthermore, in the potential range useful for methanol oxidation, Ni from the PtNi alloy would not dissolve in the electrolyte the way Ru would be for the PtRu alloys. The resistance to electrolyte dissolution has been attributed to a

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nickel hydroxide passivated surface and by the enhanced stability of Ni in the Pt lattice [27]. Despite these apparent advantages, the use of carbon supported Pt-Ni system as a DMFC anode remains relatively unexplored.

Based on these literature findings we deem it meaningful to explore the use of microwave synthesis to prepare carbon-supported PtNi catalysts effective for DMFC applications. In the process we have discovered the importance of Pt nanoparticle seeding in the preparation, and a probable mechanism for the formation of the PtNi nanoparticles was proposed accordingly.

II. EXPERIMENTAL SECTION

A. Materials and Methods

K_2PtCl_4 , hydrazine hydrate and poly (*N*-vinyl-2-pyrrolidone) (PVP, mol.wt. 10,000) were purchased from Aldrich Chemicals, while $NiCl_2 \cdot 6H_2O$ was purchased from Merck. Carbon black (Vulcan XC 72) with surface area $250 \text{ m}^2/\text{g}$, obtained from Cabot Corporation, was used as the support for the catalysts. All chemicals were used as received without any further purification. Distilled water was used throughout the study and all glasswares were washed with chromic acid and distilled water in succession and dried in an oven before usage. X-ray photoelectron spectroscopic analysis of the samples was carried out on a VG ESCALAB MKII spectrometer and the XPSPEAK (version 4.1) software was used to deconvolute the narrow scan XPS spectra of Pt and Ni. A JEOL JEM2010 microscope was used to obtain all TEM images of the nanoparticles, while a JEOL MP5600LV was used for SEM examination and EDX analysis of the catalyst samples. X-ray diffraction was recorded on a Rigaku D/Max-3B diffractometer using $CuK\alpha$ radiation. A CEM Discover microwave reactor was used for the microwave preparation of carbon supported PtNi catalyst material.

Electroactivities of the catalysts were measured by cyclic voltammetry using a EG&G 273 potentiostat/galvanostat and a standard three electrode test cell at a scan rate of 50 mV sec^{-1} . A Pt gauze and standard calomel electrode were used as the counter and the reference electrodes while a thin film of nafion impregnated PtNi/C composite cast on a vitreous carbon disk electrode was used as the working electrode. $2M \text{ CH}_3\text{OH}$ in $1M \text{ H}_2\text{SO}_4$ was used as the electrolyte for all cyclic voltammetry experiments. The cyclic voltammograms were recorded after twenty activation cycles for all samples.

B. Preparation of PtNi-1

To a well-stirred suspension of Vulcan Carbon XC 72 (0.1 g) in 30 mL of water, 10 mL each of 5 mM solutions of K_2PtCl_4 and $NiCl_2 \cdot 6H_2O$ were added followed by 0.2 g of poly (*N*-vinyl-2-pyrrolidone) (PVP, mol.wt. 10,000). The resulting mixture was placed in a constant temperature water bath at 60°C . Hydrazine (40 μL) and 400 μL of 1 M

NaOH were added in succession to the reaction mixture. The pH of the reaction mixture was found to be 10.5. The reaction mixture was stirred for about two hours before the carbon supported PtNi nanoparticles were filtered, washed copiously with water and dried in a vacuum oven at 120°C .

C. Preparation of PtNi-2

The preparation and the post-processing of PtNi-2 followed essentially the same procedures as those of PtNi-1 with the exception that the reduction reaction took place at room temperature for 12 hrs.

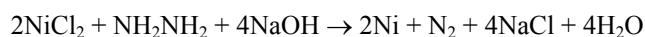
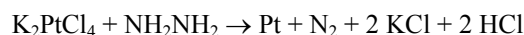
D. Preparation of PtNi-3

PtNi-3 was synthesized using the same amounts of reactants as in the preparation of PtNi-1, but the reaction mixture was exposed to microwave irradiation. Basically, the reaction vessel was placed in a CEM microwave reactor and subjected to a 100W radiation for 10 minutes. The reaction mixture was stirred during the microwave heating. The reaction mixture was then allowed to cool to room temperature and the suspension was filtered to recover the solid product, which was subsequently washed with water and dried in a vacuum oven.

III. RESULTS AND DISCUSSION

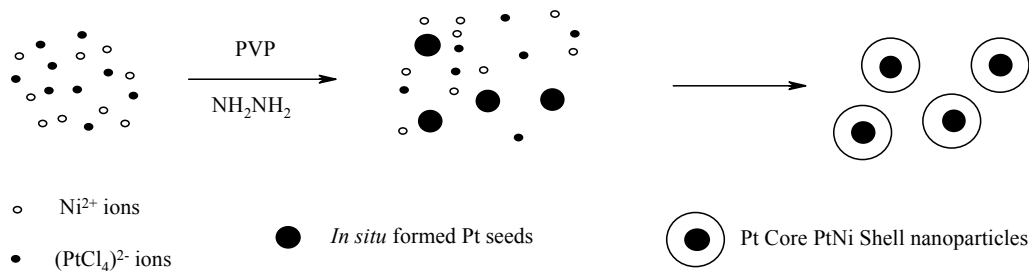
A. Synthesis of carbon supported Pt-Ni particles

The carbon/Pt-Ni alloy composites were prepared by chemical reduction using hydrazine in the presence of PVP, a proven and versatile stabilizing agent. The co-reduction reactions could be summarized as follows:



In the absence of NaOH, the catalytic materials prepared as such contained a lower Ni content, where the stoichiometric ratios between Pt and Ni were not 1:1 as would be expected from a starting equimolar mixture of Ni^{2+} and $(PtCl_4)^{2-}$. In their attempt to prepare Ni nanoparticles by hydrazine reduction, Chen and Hsieh³³⁻³⁴ noted that Ni nanoparticles could only be obtained under alkaline pH conditions [33], [34]. Furthermore the addition of NaOH during the reduction of H_2PtCl_6 by ethylene glycol also favored the formation of smaller particles possibly through an enhancement effect on the rate of reduction [15]. Thus the addition of NaOH serves a dualistic advantageous role: NaOH maintains the pH of the reaction environment for the facile reduction of Ni^{2+} ions; and NaOH can also be used to control the size of the bimetallic nanoparticles formed.

Chen and Hsieh stated that the reduction of Ni ions to Ni nanoparticles was not feasible at room temperature even after stirring for 24 hrs. However, under the experimental conditions employed in the current study, the co-reduction



Scheme 1. Proposed mechanism for the formation of PtNi nanoparticles (Schematic diagram is not to scale)

of Ni^{2+} and PtCl_4^{2-} ions using hydrazine was able to proceed at room temperature to result in the deposition of PtNi nanoparticles. The apparent contradiction prompted us to search for a probable mechanism for the formation of PtNi nanoparticles to account for the different experimental observations

B. Mechanism of PtNi nanoparticle formation:

Two anomalies were noted during the preparation of the PtNi nanoparticles. They were (1) the formation of PtNi nanoparticles could proceed at room temperature contrary to other reports in the literature [33], [34] and (2) pristine Ni nanoparticles could not be produced by the same technique. These observations indicated that the presence of a platinum salt was instrumental to the formation of the bimetallic nanoparticles. Hence it is hypothesized that platinum nanoparticles were initially formed and seeded the growth of the PtNi nanoparticles. In order to confirm the same, attempts were made to prepare Ni nanoparticles by a similar route with the intentional addition of Pt nanoparticle seeds prepared elsewhere. In brief, a 10 mL solution of 5mM NiCl_2 solution was added to a 10 mL aqueous solution containing 0.1 g of PVP. 1 mL solution containing 2-3 nm PVP protected Pt nanoparticles^ψ was then introduced followed by the addition of hydrazine (40 μL) and NaOH (1 M, 400 μL). A brownish solution along with some precipitate was obtained after the reaction mixture was stirred at room temperature for 12 hours. The solution was centrifuged and the supernatant was analyzed by UV-visible spectroscopy. Comparison of the UV-visible spectra of the supernatant solution and of NiCl_2 in a solution of PVP clearly showed the absence of Ni^{2+} ions

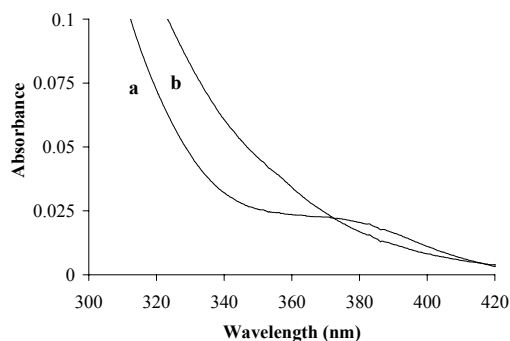


Fig. 1. UV-vis spectra of (a) NiCl_2 in the presence of PVP and (b) after reduction of NiCl_2 by hydrazine in the presence of Pt seeds

(Fig 1). The experiment demonstrated the beneficial effects of Pt nanoparticle seeds in the formation of Ni nanoparticles at low temperatures. Similar results were obtained when the experiment was carried out by conventional heating at 60°C for 2 hrs or by microwave irradiation for 10 minutes. Based on the indirect evidence it is postulated that the formation of PtNi nanoparticles went through the following steps: (1) The formation of Pt nanoparticle seeds and (2) the simultaneous reduction of $(\text{PtCl}_4)^{2-}$ and Ni^{2+} ions to result in bimetallic PtNi nanoparticles. The possibility of forming Pt-core-Ni-shell nanoparticles could be ruled out since the carbon supported bimetallic particles were able to electrooxidize methanol, a property which Ni nanoparticles alone would not exhibit (see below). The proposed mechanism is graphically presented in Scheme 1. Since part of Pt went into seeding, it was expected that the surface of the bimetallic nanoparticles would be enriched with Ni, and this was corroborated experimentally by XPS measurements (see below).

C. XRD, EDX, XPS and TEM characterizations of carbon supported Pt-Ni nanoparticles

Figure 2 shows the X-ray diffraction patterns of the carbon supported PtNi nanoparticles. *fcc* Pt and *fcc* Ni have distinctive diffractions and hence can be differentiated as such. The XRD of nickel is characterized by three peaks at $2\theta = 44.5$ (111), 51.8 (200) and 76.4° (222), while that of *fcc* Pt by peaks at $2\theta = 39.9$ (111), 46.2 (200), 67.9 (220), 81.0 (311) and 86.1 (222). The XRD patterns of PtNi-1, PtNi-2 and PtNi-3 in Figure 2 therefore display primarily the characteristics of *fcc* Pt without any trace of *fcc* Ni [27], [33], [34]. This could be the result of alloy formation between Pt and Ni since platinum is known to alloy well

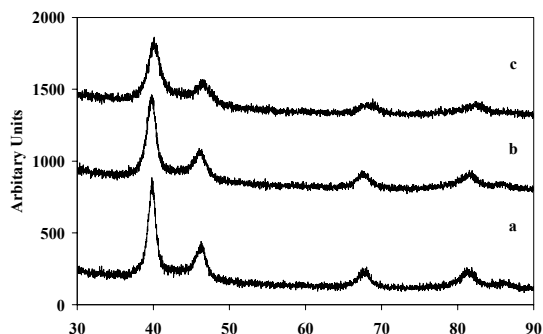


Fig. 2. X-ray diffraction pattern of (a) PtNi-1, (b) PtNi-2 and (c) PtNi-3.

with Ni. Peaks due to the hydroxides or oxides of Ni were not observed possibly because of their amorphous nature; although the presence of oxidized Ni was confirmed by XPS measurements (see below). In addition to the peaks

TABLE I
XPS DATA AND POSSIBLE CHEMICAL STATES OF PLATINUM AND NICKEL

Sample	XPS of Pt4f (B.E. in eV)	XPS of Ni2p (B.E. in eV)
PtNi-1	71.3 (Pt ⁰)	852.7 (Ni ⁰)
	72.6 (PtO)	855.7 (Ni(OH) ₂)
	74.6 (Pt ⁰)	857.3 (NiOOH)
	75.80 (Pt(OH) ₂)	
PtNi-2	71.1 (Pt ⁰)	852.6 (Ni ⁰)
	72.5 (PtO)	855.6 (Ni(OH) ₂)
	74.5 (Pt ⁰)	857.2 (NiOOH)
	75.70 (Pt(OH) ₂)	
PtNi-3	71.25 (Pt ⁰)	852.7 (Ni ⁰)
	72.65 (PtO)	855.7 (Ni(OH) ₂)
	74.45 (Pt ⁰)	857.3 (NiOOH)
	75.75 (Pt(OH) ₂)	

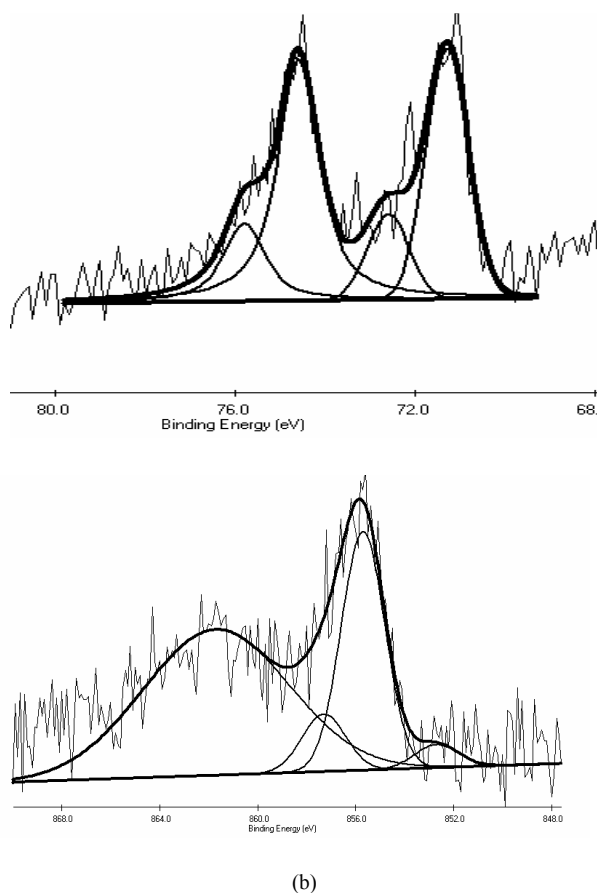


Fig. 3. XPS spectra of (a) Pt and (b) Ni region of PtNi-1.

due to Pt, a weak broad peak was also observed at ~26°, corresponding well with the diffraction of Vulcan Carbon XC-72 [28]. EDX analyses of all the samples revealed an approximate 1:1 stoichiometric ratio between Pt and Ni. EDX analyses also showed that these bimetallic samples were free from impurities such as potassium and chlorine.

XPS measurements based on the Pt4f and Ni2p regions, on the other hand, showed that platinum was predominantly metallic in PtNi-1, PtNi-2 and PtNi-3. A

typical XPS spectra is shown in Figure 3 and the results have been tabulated in Table 1. For PtNi-1, the Pt4f spectrum consisted of two peaks for metallic platinum at 71.25 (Pt4f_{7/2}) and 74.45 eV (Pt4f_{5/2}); with two more peaks at 72.65 and 75.75 eV which could be assigned to Pt²⁺ species as in PtO and Pt(OH)₂ [35],[36]. A comparison of the relative intensities of the peaks due to Pt(0) and those of PtO and Pt(OH)₂ showed that Pt in the PtNi nanoparticles was predominately metallic.

The Ni2p spectrum was made complicated by the presence of a high binding energy satellite peak (~861.7 eV) adjacent to the main peaks [27], [37]. Taking the satellite peak into account, the Ni2p_{3/2} peak could be deconvoluted into three peaks at 852.7, 855.7 and 857.3 eV associated well with the Ni⁰, Ni(OH)₂ and NiOOH species respectively [27], [37],[38]. From the intensities of the deconvoluted XPS signal of Ni, it is obvious that the proportion of Ni⁰ on the surface of the nanoparticles was quite low irrespective of the methods of preparation. These observations concurred well with each other and appeared to be a characteristic of Pt based bimetallics [27]. The XPS spectra of PtNi-2 and PtNi-3 also exhibited similar features and thus do not warrant any further discussion. The XPS data and their assignments are summarized in Table 1. Quantification using XPS data revealed that the surface of the bimetallic nanoparticles were Ni rich as some Pt was used for seeding the particle growth. The ratios between Pt and Ni for PtNi-1, PtNi-2 and PtNi-3 were found to be 1:8.63, 1: 8.60 and 1: 3.61 respectively. Microwave irradiation is expected to form smaller Pt seeds for the subsequent formation of bimetallic PtNi nanoparticles. Consequently the extent of Ni enrichment was considerably lower compared to the other two methods.

TEM images of the three samples showed interesting differences (Figures 4 – 6). PtNi-1, prepared by conventional heating, showed a high degree of agglomeration and very broad particle size distribution (12.5 - 50 nm), PtNi-2, prepared at room temperature in otherwise similar reactions, consisted of nanoparticles in the range of 13 – 25 nm. On the contrary, PtNi-3, prepared using the microwave irradiation method, showed well dispersed nanoparticles of size ranging from 2.9 - 5.6

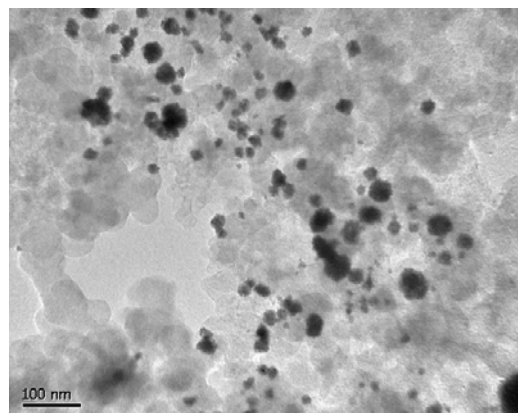


Fig. 4. TEM images of carbon supported PtNi-1.

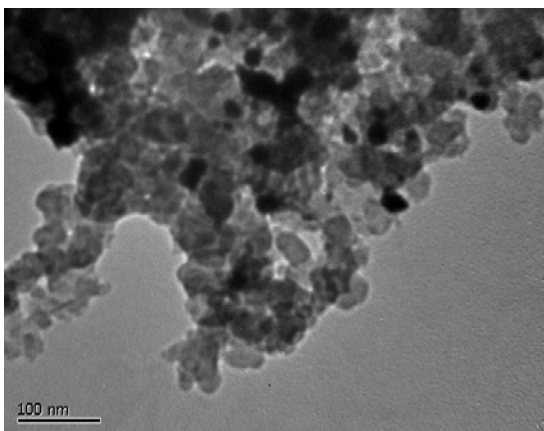


Fig. 5. TEM image of PtNi-2.

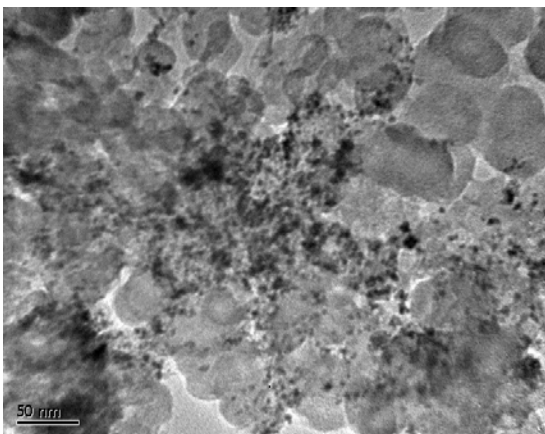


Fig. 6. TEM image of PtNi-3.

nm on the carbon support. The benefit of using microwave heating to obtain smaller and better-dispersed PtNi on carbon was thus confirmed by TEM examinations.

It is generally believed that the formation of uniform colloidal particles is assisted by the uniform growth of the nanoparticles. Presence of concentration and temperature gradients should be avoided in order to provide a conducive environment for uniform growth. In sharp contrast to conventional heating, microwave assisted heating is able to reach the maximum reaction temperature within seconds [39]. In our experiments the color of the reaction mixture (in the absence of carbon) turned black after a few seconds of microwave irradiation, indicating the substantial increase in reaction rate in the microwave method. The ability to maintain a well-stirred environment in the microwave reactor during microwave heating was equally important to the formation of particles with more uniform size.

D. Cyclic voltammetric studies

Figure 9 shows the overlay of a few cyclic voltammograms for methanol oxidation over PtNi-1, PtNi-2 and PtNi-3 in a solution of 1M H₂SO₄ and 2 M CH₃OH. The potential was swept between 0 and 1.0 V at 50 mV/s during the experiments. In the forward scan the catalysts showed a methanol oxidation peak at 0.66 V (vs. SCE) for

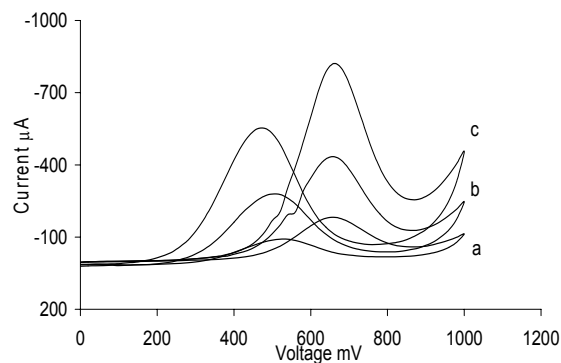


Fig. 7. Cyclic voltammograms of (a) PtNi-1, (b) PtNi-2 and (c) PtNi-3.

all three samples. However, the onset potential for methanol oxidation and the peak current densities showed interesting differences. The onset of methanol oxidation for PtNi-1 (0.42 V vs. SCE) occurred at a higher anodic potential than that for PtNi-2 and PtNi-3 (0.36 V vs. SCE). Another peak was detected in the reverse scan which is commonly attributed to the reactivation of oxidized platinum oxide. The peak current densities associated with methanol oxidation in the forward scan for PtNi-1, PtNi-2 and PtNi-3 were -0.18, -0.43 and -0.82 mA/cm² respectively. The electrocatalytic activities could therefore be ranked in the following order: PtNi-1 < PtNi-2 < PtNi-3. The order parallels that of the average particle size of the PtNi nanoparticles. The dependence of electroactivity on the particle size of the catalytically active component is a well-established finding [28], [40]. It should also be emphasized that PtNi-3 had the lowest extent of Ni enrichment than either PtNi-1 or PtNi-2 and this could also contribute to the observed improvement in the electrocatalytic activity.

It should be noted that although PVP was used as a stabilizing agent during the preparation of the PtNi nanoparticles and was not deliberately removed thereafter, there appeared to be no adverse effect of their presence in the electrocatalytic oxidation of methanol. The observation was consistent with the results of Li et al and Toshima et al, wherein they reported that the PVP protected Pd colloids were found to be an efficient catalyst for the Suzuki reactions [41], [42].

IV. CONCLUSIONS

Carbon supported PtNi nanoparticles were prepared by the reduction of K₂PtCl₄ and NiCl₂·6H₂O by hydrazine using PVP as a stabilizer and in the presence of carbon. Three reaction conditions were used: (a) conventional heating, (b) prolonged room temperature reactions and (c) microwave irradiation. The prepared PtNi/C composites were characterized by various techniques. A probable mechanism for the formation of the bimetallic nanoparticles was proposed, particularly on the role of Pt nanoparticle seeds in the Ni²⁺ reduction reaction. The PtNi

nanoparticles obtained by microwave heating had the smallest and the most uniform particle size, were well dispersed on the carbon support, and consequently showed the highest electrocatalytic activity in room temperature methanol oxidation reactions. This study clearly demonstrates microwave-assisted reactions as a method of choice in the preparation of functional nanomaterials: the microwave method (a) requires a shorter processing time and (b) produces smaller and more uniform particles which are often the attributes for desirable application properties.

V. ACKNOWLEDGEMENTS

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REFERENCES

- [1] Metal nanoparticles: Synthesis, Characterization and Applications. D.L. Feldheim and C.A. Foss, Eds., Marcel Dekker, Inc., New York, 2002.
- [2] J. Turkevich and G. Kim, "Palladium: preparation and catalytic properties of particles of uniform size," *Science*, vol. 169, 873-879, 1970.
- [3] T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein and M. A. El-Sayed, "Shape-controlled synthesis of colloidal platinum nanoparticles," *Science*, vol. 272, 1924-1926, 1996.
- [4] K. Esumi, A. Suzuki, A. Yamahira and K. Torigoe, "Role of poly(amidoamine) dendrimers for preparing nanoparticles of gold, platinum, and silver," *Langmuir*, vol. 16, 2604-2608, 2000.
- [5] W. Huang, X. Tang, Y. Wang, Y. Kolytyn and A. Gedanken, "Selective synthesis of anatase and rutile via ultrasound irradiation" *Chem. Commun.*, 1415-1416, 2000.
- [6] J. C. Yu, J. Yu, W. Ho and L. Zhang, "Preparation of highly photocatalytic active nano-sized TiO₂ particles via ultrasonic irradiation," *Chem. Commun.*, 1942-1943, 2001.
- [7] Y. Yin, X. Xu, X. Ge, C. Xia and Z. Zhang, "Synthesis of cadmium sulfide nanoparticles in situ using gamma-radiation," *Chem. Commun.*, 1641-1642, 1998.
- [8] K. Mallik, M. Mandal, N. Pradhan and T. Pal, "Seed Mediated Formation of Bimetallic Nanoparticles by UV Irradiation: A Photochemical Approach for the Preparation of "Core-Shell" Type Structures," *Nano Lett.*, vol. 1, pp. 319-322, 2001.
- [9] Y. Zhou, C. Y. Wang, Y.R. Zhu and Z.Y. Chen, "A Novel ultraviolet irradiation technique for shape-controlled synthesis of gold nanoparticles at room temperature," *Chem. Mater.*, vol. 11, pp. 2310-2312, 1999.
- [10] K. Soulantica, A. Maisonnat, M.-C. Fromen, M.-J. Casanove, P. Lecante and B. Chaudret, "Synthesis and self-assembly of monodisperse indium nanoparticles prepared from the organometallic precursor [In(\square -C₅H₅)]," *Angew. Chem. Int. Ed.*, vol. 40, pp. 448-451, 2001.
- [11] K. Esumi, T. Tano and K. Meguro, "Preparation of organo palladium particles from thermal decomposition of its organic complex in organic solvents," *Langmuir*, vol. 5, pp. 268-270, 1989.
- [12] K. J. Klabunde, Y.-X. Li and B.-J. Tan, "Solvated metal atom dispersed catalysts," *Chem. Mater.*, vol. 3, pp. 30-39, 1991.
- [13] M. T. Reetz and W. Helbig, "Size-Selective Synthesis of Nanostructured Transition Metal Clusters," *J. Am. Chem. Soc.*, vol. 116, pp. 7401-7402, 1994.
- [14] W. Tu and H. Liu, "Continuous synthesis of colloidal metal nanoclusters by microwave irradiation," *Chem. Mater.*, vol. 12, pp. 564-567, 2000.
- [15] W. Yu, W. Tu and H. Liu, "Synthesis of nanoscale platinum colloids by microwave dielectric heating," *Langmuir*, vol. 15, pp. 6-9, 1999.
- [16] S. Komarneni, D. Li, B. Newalker, H. Katsuki and A. S. Bhalla, "Microwave-polyol process for Pt and Ag nanoparticles," *Langmuir*, vol. 18, pp. 5959-5962, 2002.
- [17] S. Komarneni, R. Roy and Q.H. Li, "Microwave-hydrothermal synthesis of ceramic powders," *Mater. Res. Bull.*, vol. 27, pp. 1393-1405, 1992.
- [18] S. Komarneni, Q. H. Li and R. Roy, "Microwave-hydrothermal processing for synthesis of layered and network phosphates," *J. Mater. Chem.*, vol. 4, pp. 1903 - 1906, 1994.
- [19] M. P. Hogarth and G.A. Hards, "Direct methanol fuel cells. Technological advances and further requirements," *Platinum Met. Rev.*, vol. 40, pp. 150 - 159, 1996.
- [20] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangapani, E.S. Smotkin and T.E. Mallouk, "Combinatorial electrochemistry: A highly parallel, optical screening method for discovery of better electrocatalysts," *Science*, vol. 280, pp. 1735 - 1737, 1998.
- [21] P. N. Ross, In *Electrocatalysis*; J. Lipkowski, P.N. Ross, Eds.; Wiley-VCH: New York, 1998; Chapter 2.
- [22] W. Chrzanowski and A. Wieckowski, "Ultrathin films of ruthenium on low index platinum single crystal surfaces: An electrochemical study," *Langmuir*, vol. 13, pp. 5974-5978, 1997.
- [23] A. Hammett, "Mechanism and electrocatalysis in the direct methanol fuel cell," *Catal. Today*, vol. 38, 445-457, 1997.
- [24] G. K. Chandler, J. D. Genders and D. Pletcher, "Electrodes based on noble metals, essential components for electrochemical technology," *Platinum Met. Rev.*, vol. 41, pp. 54-63, 1997.
- [25] X. Ren, M. X. Wilson and S. Gottesfeld, "High performance direct methanol polymer electrolyte fuel cells," *J. Electrochem. Soc.*, vol. 143, pp. L12-L15, 1996.
- [26] J. T. Moore, D. Chu, R. Jinag, G. A. Deluga and C. M. Lukehart, "Synthesis and characterization of Os and Pt-Os/carbon nanocomposites and their relative performance as methanol electrooxidation catalysts," *Chem. Mater.*, vol. 15, pp. 1119-1124, 2003.
- [27] K.-W. Park, J.-H. Choi, B.-K. Kwon, S.-A. S.-A. Lee, Y.-E. Sung, H.-Y. Ha, S.-A. Hong, H. Kim and A. Wieckowski, "Chemical and electronic effects of Ni in Pt/Ni and Pt/Ru/Ni alloy nanoparticles in methanol electrooxidation," *J. Phys. Chem. B*, vol. 106, pp. 1869-1877, 2002.
- [28] Z. Liu, J. Y. Lee, M. Han, W. Chen and L. M. Gan, "Synthesis and characterization of PtRu/C catalysts from microemulsions and emulsions," *J. Mater. Chem.*, vol.12, pp. 2453-2458, 2002.
- [29] D. L. Boxall, E. A. Kenik and C. M. Lukehart, "Synthesis of PtSn/carbon nanocomposites using trans-PtCl(PEt₃)₂(SnCl₃) as the source of metal," *Chem. Mater.*, vol. 14, pp. 1715-1720, 2002.
- [30] E. S. Steigerwalt, G. A. Deluga and C. M. Lukehart, "Pt-Ru/carbon fiber nanocomposites: Synthesis, characterization, and performance as anode catalysts of direct methanol fuel cells. A search for exceptional performance," *J. Phys. Chem. B*, vol. 106, pp. 760-766, 2002.
- [31] S.-A. Lee, K.-W. Park, J.-H. Choi, B.-K. Kwon and Y.-E. Sung, "Nanoparticle synthesis and electrocatalytic activity of Pt alloys for direct methanol fuel cells," *J. Electrochem. Soc.*, vol. 149, pp. A1299-A1304, 2002.
- [32] F. F. Abraham, N.-H. Tsai and G. M. Pound, "Bond and strain energy effects in surface segregation: an atomic calculation," *Surf. Sci.*, vol. 83, pp. 406 -422, 1979.
- [33] D.-H.Chen and C.-H. Hsieh, "Synthesis of nickel nanoparticles in aqueous cationic surfactant solutions," *J. Mater. Chem.*, vol. 12, pp. 2412 - 2415, 2002.
- [34] D.-H. Chen and S.-H. Wu, "Synthesis of nickel nanoparticles in water-in-oil microemulsions," *Chem. Mater.*, vol. 12, pp. 1354-1360, 2000.
- [35] Y. Baer, P. F. Heden, J. Hederman, M. Klasson, C. Nording and K. Siegbahn, "Band structure of transition metals studied by ESCA [electron spectroscopy for chemical analysis]," *Phys. Scr.*, vol. 1, pp. 55-65, 1970.
- [36] X. Zhang and K.-Y. Chan, "Water-in-oil microemulsion synthesis of platinum-ruthenium nanoparticles, their characterization and electrocatalytic properties," *Chem. Mater.*, vol. 15, pp. 451-459, 2003.
- [37] I. G. Casella, M. R. Guascito and M. G. Sannazzaro, "Voltammetric and XPS investigations of nickel hydroxide electrochemically dispersed on gold surface electrodes," *J. Electroanal. Chem.*, vol. 462, pp. 202-210, 1999.
- [38] D.-J. Jeong, W.-S. Kim, Y.-K. Choi and Y.-E. Sung, "Intercalation/deintercalation characteristics of electrodeposited and anodized nickel thin film on ITO electrode in aqueous and nonaqueous electrolytes," *J. Electroanal. Chem.*, vol. 511, pp. 79-87, 2001.

- [39] W. Tu and H. Liu, "Rapid synthesis of nanoscale colloidal metal clusters by microwave irradiation," *J. Mater. Chem.*, vol. 10, pp. 2207-2211, 2000.
- [40] S. Mukerjee and J. McBreen, "Effect of particle size on the electrocatalysis by carbon-supported Pt electrocatalysts: an in situ XAS investigation," *J. Electroanal. Chem.*, vol. 448, pp. 163-171, 1998.
- [41] Y. Li and M. A. El-Sayed, "The effect of stabilizers on the catalytic activity and stability of Pd colloidal nanoparticles in the Suzuki reactions in aqueous solution," *J. Phys. Chem. B*, vol. 105, pp. 8938-8943, 2001.
- [42] N. Toshima, Y. Shiraishi, T. Teranishi, M. Miyake, T. Tominaga, H. Watanabe, W. Brijoux, H. Bönemann and G. Schmid, "Various ligand-stabilized metal nanoclusters as homogeneous and heterogeneous catalysts in the liquid phase," *Appl. Organometal. Chem.*, vol. 15, pp. 178-196, 2001.