

Solution route synthesis of PtCuNi nano-particles supported on treated carbon, electrocatalysts for ORR

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Pt-based ternary compounds supported on carbon have been proposed as a catalyst for oxygen reduction reaction (ORR), with relatively low over-potential, leading to high reaction rates compared to Pt/C catalysts. In this research, samples of 20% wt platinum-copper-nickel (at 2 : 1 : 1 and 6 : 1 : 1 ratios) supported on treated carbon (N115 and Vulcan XC-72) were prepared by solution route method, using NaBH₄ as a reducing agent. The XRD patterns of the product samples match well with the simulated PtCuNi alloy cubic structure and carbon phases. The SEM and TEM images show well-dispersed metal particles on the treated carbon supports. Metal particle sizes, measured from TEM micrographs, were 2.50-3.00 nm. The electrochemical performance of the PtCuNi alloy at the ratio of 6 : 1 : 1 on carbon Vulcan XC-72 delivered the highest current of 278.70 A/cm² · g_{Pt} at 600 mV.

Key words: Platinum-based catalysts, PEMFC, Solution method and oxygen reduction reaction.

Introduction

With finite fossil fuel resources, and the environmental costs of burning fossil fuels and nuclear waste, development of alternative energy sources are of considerable research and commercial interest. One attractive option is energy from electrochemical reactions, or fuel cells- in particular, proton exchange membrane fuel cells (PEMFC) [1-3]. While the efficiency of fuel cells depends on several factors, the catalyst used is a primary factor. The catalysts at the anode and cathode activate hydrogen oxidation and oxygen reduction, respectively. Precious metals, such as platinum, have long been preferred catalysts on both electrodes [4]. Supporting Pt nanoparticles on a high surface area carbon supporter contributes to the high surface area of catalysts, minimizing the amount of Pt required [5]. However, to activate the oxygen reduction reaction, the cathode requires 10 times more catalyst than the anode [6]. Moreover, a hydrogen peroxide intermediate phase forms, and with its high oxidizing power, the catalyst active site on the electrode surface is destroyed.

To address these problems, catalysts using Pt alloys and non-precious metals have been investigated [7-10].

PtCuNi alloy supported on carbon is an effective catalyst for ORR. It catalyzes the reaction without H₂O₂ formation at a 2-3 fold reaction rate compared with Pt catalyst, with a low degree of particle agglomeration after long-term operation. Metal leaching during cell operation is also lower than with Pt/C catalysts [9]. Generally, PtCuNi alloy can be prepared thermodynamically at 1500-1700 °C in an inert atmosphere [11-12].

This research will prepare a PtCuNi alloy supported on carbon using a simple chemical reduction method at room temperature. This method has been used previously to prepare Lithium-ion anode material, SnSb/C composite [13], and thermoelectric material, Cu(In,Ga)Se₂ [14]. It is a simple and economical method for preparing nanoparticle metals and alloys at ambient temperature. Two types of carbon, commercial carbon Vulcan XC-72 and Thai carbon black N115, were investigated for their effect as carbon supporters on cell efficiency.

Experimental Procedure

Carbon Vulcan XC-72 (Fuel Cell Scientific) and Thai carbon black N115 (Thai Carbon Black Public Co. LTD.) were treated as described in Thungprasert *et al.* [15]. The treated carbons (Vulcan XC-72 and N115) were added to ethylene glycol (99.9%, J.T. Baker), and the pH adjusted to 9 by adding potassium hydroxide (30%wt, NCG). Then, stoichiometric amounts of metal precursors (H₂PtCl₆·xH₂O (37.50% Pt, Sigma), Cu(NO₃)₂ · 3H₂O

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(99.5%, Caelo Erba), and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.0%, BDH) were added in Pt : Cu : Ni ratios of 2 : 1 : 1 and 6 : 1 : 1. For the reduction reaction to occur, the stoichiometric amount of NaBH_4 powder (96%, Merck) was added and the solution stirred overnight. The final powders were filtered and washed with methanol and dried overnight in an oven. The catalysts properties were characterized using X-ray diffractometry, XRD (D500/D501, Siemen); scanning electron microscopy, SEM (JSM-5910LV, JEOL) equipped with energy dispersive spectroscopy, EDS (INCA, The Microanalysis Suite Issue-16); and transmission electron microscopy, TEM (JEM-2010, JEOL).

The electrochemical properties of the prepared catalysts were examined using an in-house test station (single cell testing at Thep Center Building, Department of Physics, Faculty of Science, Chiang Mai University, Thailand). The membrane electrode assembly (MEA) consisted of a catalyst on membrane electrodes and a micro-porous layer on the gas diffusion layer (GDL), with both prepared by spraying technique. The standard cell was prepared using commercial 20% Pt/C for both anode and cathode. The test cell was fabricated using commercial catalysts on the anode side and the prepared catalysts on the cathode side. The anode and cathode were exposed to flows of hydrogen and oxygen gas, respectively, at 50 sccm of pressure. The single cell was operated at a current density from 0 to 1.0 A at room temperature for four rounds.

For cell preparation, the micro-porous layer was prepared by spraying a suspension of mixed 0.05 g of carbon black, 8 ml of propyl alcohol and 0.6 ml of 5% Nafion solution on GDL. The GDL was then dried at 70 °C for 1 hour in an oven.

For membrane treatment, the membrane (Nafion NR-212) was cleaned with hydrogen peroxide at 70 °C for 2 hours. Then, it was washed with deionized water at 70 °C for 2 hours. Next, the membrane was treated with 1 M sulfuric acid at 70 °C for 2 hours. Finally, it was washed with deionized water at 70 °C for 2 hours. It was stored in deionized water before use.

For the catalyst ink preparation, the catalyst ink was prepared by mixing 0.05 g of catalyst, 8 ml of propyl alcohol and 0.6 ml of 5% Nafion solution. The mixture was sonicated for 30 minutes. Then, the catalyst ink was sprayed using nitrogen as the driving gas, on the membrane while placing on a hotplate at 70 °C. The catalyst (0.4 mg/cm²) was sprayed on one side of the membrane, in an area of about 1 cm². After one side was finished, the membrane was dried at 70 °C for 5 minutes. The other side of the membrane was sprayed with catalyst ink using the same method and dried at 70 °C for 5 minutes. Finally, the electrode was ready to be tested with the single-cell test station.

Results and Discussion

The prepared catalysts were coded according to

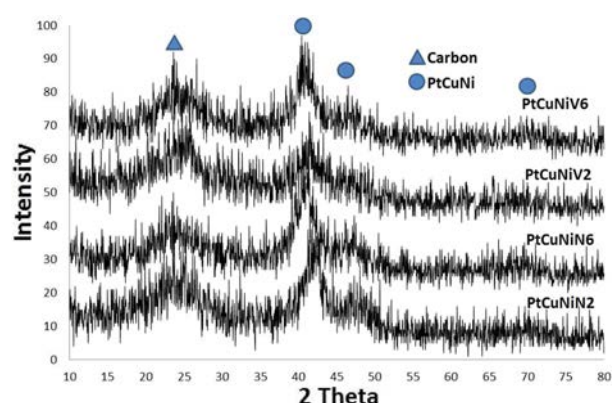


Fig. 1. XRD patterns of catalyst samples prepared in all synthesis conditions.

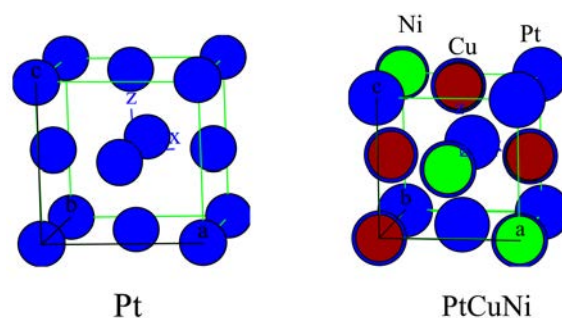


Fig. 2. Unit cell structure of Pt metal and PtCuNi alloy.

carbon type (V = Vulcan XC-72 and N = N115) and the weight ratio of Pt in the alloy (6 and 2 for 6 : 1 : 1 and 2 : 1 : 1 ratios of Pt in PtCuNi, respectively). Powder XRD patterns of the products from all synthesis conditions are illustrated in Fig 1. The XRD patterns show no differences among the four samples, with the first diffracted peak corresponding to the carbon (002) supporter (JCPDS file no. 41-1487). The remaining three broad peaks were identified as the PtCuNi alloy by the approximation that these peaks appeared at 2θ , but shifted slightly to higher angles than the Pt metal standard (JCPDS no 4-802). This peak shift is possibly due to the decrease in lattice parameters originating from the atomic size difference between Pt (177 pm), Cu (145 pm) and Ni (149 pm). Replacing the Pt position with Cu and Ni atoms can reduce the unit cell volume, resulting in a lattice parameters reduction. There is no standard JCPDS file for the PtCuNi alloy. Therefore, to confirm the occurrence of the PtCuNi alloy, a computer program (CaRine 3.1) was used to view the PtCuNi alloy structure based on the cubic structure of Pt; in which Pt, Cu and Ni atoms randomly and partly (according to its ratio) occupied all face-centered cubic coordinates. The lattice parameter (a) obtained from T. Itoh *et al.* [12] was adopted for the calculation.

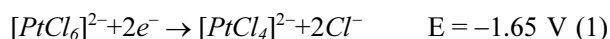
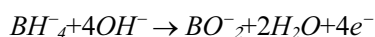
Fig 2 displays a simulated PtCuNi unit cell in comparison with the pristine structure of Pt. Diffracted data was obtained with calculated degree 2θ and

Table 1. Comparison of calculated and experimental degree 2q for all samples. The numbers in parenthesis are the relative intensities.

hkl	Pt	PtCuNi (6 : 1 : 1)cal	PtCuNiV6	PtCuNiN6	PtCuNi (2 : 1 : 1)cal	PtCuNiV2	PtCuNiN2
111	39.76(100)	41.12(100)	40.88	41.24	41.12(100)	41.40	41.64
200	46.24(53)	47.85(47.1)	47.68	47.88	47.85(46.8)	48.16	48.04
220	67.45(31)	69.99(26.6)	69.84	70.00	69.99(26.0)	71.08	71.16

relative intensities for (111), (200) and (220) planes of PtCuNi alloys with 6 : 1 : 1 and 2 : 1 : 1 ratio and tabulated in Table 1 in comparison with the experimental data. The 2θ values from the experimental data are close to PtCuNi alloys in both catalyst ratios, confirming the alloy formation. The calculated relative intensities of the (200) and (220) peaks differ between the 6 : 1 : 1 and 2 : 1 : 1 ratio samples as a result of the lower value of the atomic scattering factor (f_p) of Cu and Ni compared to Pt. However, this observation cannot apply to the experimental data due to the broadening of these two peaks. The broad peaks may come from the small particles size effect.

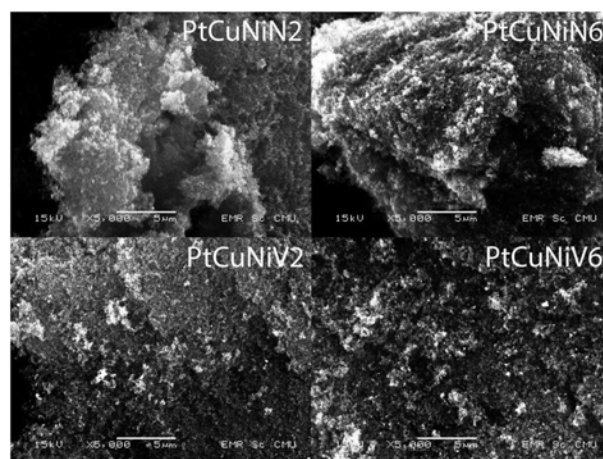
Theoretically, the formation of PtCuNi alloy at room temperature is not favored thermodynamically. However, by applying the NaBH_4 reduction method, the PtCuNi alloy forms within a short period. The reduction reaction in the solution favors the metal ions combining with the electrons to kinetically form the alloy over solid-state formation. The standard reduction potential of NaBH_4 in basic solution equals 1.65 V (Equation 1 [16]), which is low enough to reduce all metal ions into metals (Equations 2-4 [17, 18]) at a relatively high reaction rate. Conducting carbon draws electrons to its surface, where the metal reduction reaction then occurs. Moreover, introducing functional groups on the carbon surface by H_2O_2 treatment provides sites for the metal or alloy to deposit, with a resulting high particle distribution on the carbon surface [15, 19]. Additionally, alloy formation from Pt, Cu and Ni metals is feasible because the pristine structure of Pt, Cu and Ni are all in face center cubic system.



Back-scattered electron images (Fig 2) display the overall morphology of the prepared catalysts. The PtCuNi alloy particles appeared bright, while carbon appeared dark. EDS analysis identified the type and approximate amounts of the elements (Table 2). Pt, Cu and Ni were all detected, but in different amounts.

Table 2. EDS analysis of catalyst samples prepared in all synthesis conditions.

Sample	Elements (Wt %)			
	C	Pt	Cu	Ni
PtCuNiN2	75.07	5.32	4.46	2.16
PtCuNiN6	74.65	10.17	1.55	0.27
PtCuNiV2	80.11	7.39	5.05	0.56
PtCuNiV6	81.35	9.37	2.72	1.02

**Fig. 3.** SEM images of catalyst samples prepared in all synthesis conditions.

However, the amount of metal obtained from the EDS signals does not equal the actual amounts, due to the limitations of this technique.

TEM analysis allowed the alloy particles distributed on the carbon to be observed and the particle size determined. TEM images taken from each sample are presented in Fig 4, including the corresponding ring patterns, in which all of the patterns were indexed to the PtCuNi alloy phase. Particles size was measured from several TEM images using the Image J program. Histograms were obtained and the average particle sizes are presented in Table 3. The average particle size of all samples was in the same range, 2-3 nm. This result confirms the small particles size effect, which caused the broad peaks in the XRD patterns.

Samples prepared from different types of carbon and different metal ratios showed no differences in chemical and physical properties as examined by XRD, SEM and TEM techniques. The electrochemical properties of the standard and sample cells were then identified using single cell testing. Fig 5 presents the polarization curves

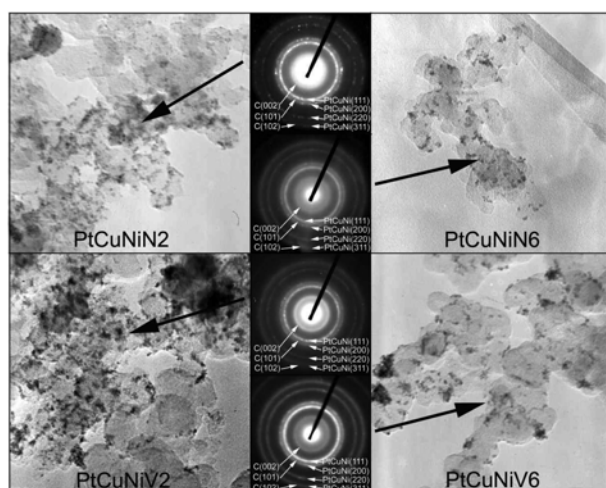


Fig. 4. TEM images of catalyst samples prepared in all synthesis conditions and its corresponding ring patterns.

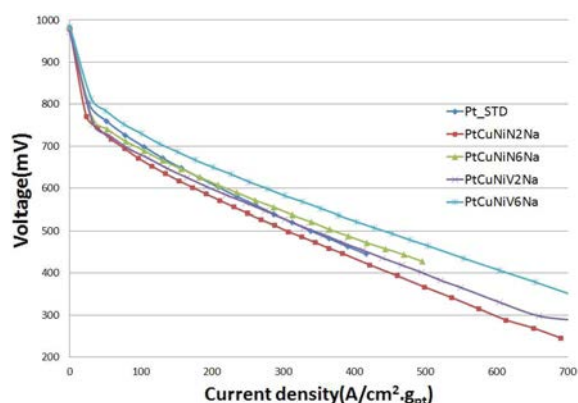


Fig. 5. Polarization curves of catalyst samples prepared in all synthesis conditions in comparison with standard cell.

Table 3. Particle size measurement from TEM images.

Sample	Particle size (nm)
PtCuNiN2	2.81 ± 0.52
PtCuNiN6	2.75 ± 0.56
PtCuNiV2	2.78 ± 0.70
PtCuNiV6	2.73 ± 0.55

of the standard and four samples cells, normalized by mole of alloy (from EDS). Table 3 shows the current density measured from the curves at 0.6 V for each sample. The catalytic activity of the 6 : 1 : 1 ratio samples was greater than standard Pt. The sample prepared using carbon Vulcan XC-72R generated the highest activity. Using the Pt alloy supported on carbon catalysts reduced the catalyst cost. Finally, comparing the carbon types, carbon Vulcan-with its high conductivity, high surface area and low size distribution [20, 21]-delivered higher current than carbon N115, which has lower conductivity and surface area, but high size distribution [22].

Table 4. The measurement of current density at 0.6 V from polarization curves compared with commercial Pt standard catalyst.

Sample	Current density ($\text{A}/\text{cm}^2 \cdot \text{g}_{\text{Pt}}$)
Pt/C (Fuel Cell)	211.30
PtCuNiN2	174.35
PtCuNiN6	218.70
PtCuNiV2	198.52
PtCuNiV6	278.70

Conclusions

Nanoparticles of PtCuNi alloy supported on treated carbon Vulcan XC-72R and carbon N115 were successfully synthesized by NaBH_4 reduction method at room temperature. The size of the alloy particles measured from TEM images was 2.50-3.00 nm. Single cell testing of the electrochemical property found high catalyst activity of the prepared catalysts compared to the standard catalyst. The high-content Pt alloy catalyst (6 : 1 : 1) delivered better cell performance than the low-content Pt alloy catalyst (2 : 1 : 1). The sample using the carbon Vulcan supporter delivered better cell performance than the sample using carbon N115.

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References

1. X. Yu, S. Ye, *Journal of Power Sources*, 172 (2007) 145-154.
2. M.A. J. Cropper *et al.*, *Journal of Power Sources*, 131 (2004) 57-61.
3. S. Lertviriyapaian, N. Tantavichet, *Int. J. Hydrogen. Energ.*, 35 (2010) 10464-10471.
4. E. Antolini, *Mater. Chem. Phys.* 78 (2003) 563-573.
5. R. Hector Col'on-Mercado, B. N. Popov, *Journal of Power Sources*, 155 (2006) 253-263.
6. W. Vielstic, A. Lamm, H.A. Gasteiger (2003) "Handbook of Fuel Cell Fundamentals Technology and Application" Vol.3, Wiley, pp. 468-487.
7. N. P. Subramanian, S. P. Kumaraguru, H. Colon-Mercado, H. Kim, B. N. Popov, T. Black, D. A. Chen., *J. Power Sources*, 157 (2006) 56-634.
8. N.P. Subramanian, X. Li, V. Nallathambi, P. Swaminatha, H. Kumaraguru, Colon-Mercado, G. Wu, J.-W. Lee, B. N. Popov, *J. Power Sources*, 188 (2009) 38-44.
9. A. Seo, J. Lee, K. Han, H. Kim, *Electrochim. Acta.*, 52

- (2006) 1603-1611.
10. J. Luo, N. Kariuki, L. Han, L. Wang, C.-J. Zhong, T. He, *Electrochimica Acta*, 51 (2006) 4821-4827.
 11. P. Mani, R. Srivastava, P. Strasser, *J. Power Sources*, 196 (2011) 666-673.
 12. T. Itoh *et al.*, United states Patent number 5,178,971.
 13. K. Adpakpang, T. Sarakonsri, K. E. Aifantis, and S. A. Hackney, *Reviews on Advance Materials Science Journal*, 32(2012) 12-18.
 14. T. Siritanon, T. Sarakonsri, C. Thanachayanont, *J. Ceram Process Res*, 10 (2009) 437-442.
 15. S. Thungprasert, T. Sarakonsri, W. Klysubun, T. Vilaithong, *J. Alloy Comp.*, 509 (2011) 6812-6815.
 16. A. Züttel, A. Borgschulte, L. Schlapbach (2008) "Hydrogen as a Future Energy Carrier", Wiley, pp. 370.
 17. L. S. Sarma, C.-H. Chen, S. M. S. Kumar, G.-R. Wang, S.-C. Yen, D.-G. Liu, H.-S. Sheu, K.-L. Yu, M.-T. Tang, J.-F. Lee, C. Bock, K.-H. Chen, B.-J. Hwang, *Langmuir* 23 (2007) 5802-5809.
 18. <http://www.webelements.com>, Accessed 26 August 2012.
 19. C. Moreno-Castilla, M.V López-Ramón, F Carrasco-Marín., *Carbon*, 38 (2000) 1995-2001.
 20. E. Antolini, *Appl Catal B-Environ*, 88 (2009) 1-24.
 21. G. Wang, G. Sun, Z. Zhou, J. Liu, Q. Wang, S. Wang, J. Guo, S. Yang, Q. Xin, B. Yia, *Electrochem Solid St*, 8 (2005) A12-A16.
 22. G.A. Schwartz, S. Cervenya, A. J. Marzoccaa, M. Gerspacher, L. Nikiel, *Polymer*, 44 (2003) 7229-7240.