Microwave Assisted Synthesis of Graphene Supported PtCo Alloys as Efficient Cathode Electrocatalysts for PEM Fuel Cells

Çiğdem İyigün Karadağ[1]
[1]TÜBİTAK Marmara Research Center Hydrogen and Fuel Cell Technologies Research Group,
Barış Mah. Dr. Zeki Acar Cad. No:1, P.O Box 21, 41470 Gebze, Kocaeli/TÜRKİYE

Abstract

In this study, graphene supported PtCo electrocatalysts were synthesized via microwave assisted polyol reduction method with varying irradiation temperatures and their performance were evaluated as cathode electrodes in polymer electrolyte membrane fuel cells (PEMFCs). The impact of microwave irradiation temperature on the structural, morphological, and electrochemical properties of the catalysts was systematically investigated. Among the synthesized catalysts, the sample prepared at 170 °C (PtCo/G-170) exhibited the highest performance, acheiving a peak power density of approximately 520 mW/cm² and an ECSA value of 87.3 cm²/g. These results demonstrate that the microwave-assisted synthesis method yields a more effective nanoparticle dispersion compared to conventional heating method, significantly enhancing the electrocatalyst's efficiency.

1.Introduction

The important characteristics of polymer electrolyte membrane fuel cells (PEMFC) like high energy efficiency, low temperature operation and zero emission make them promising clean energy devices [1–3]. The problems that are encountered in their widespread commercialization is the high cost due to the use of precious metal electrocatalysts and limited durability, due to sluggish kinetics of oxygen reduction reaction (ORR) [4,5]. There are tremendous research on overcoming these limitations, i.e. alloying Pt with transition metals (Co, Ni, etc.) for enhancement of ORR characteristics and decreasing the cost with the reduction of noble metal amount [6–8]. PtCo alloys exhibit high catalytic activity and stability under acidic PEMFC conditions [9], where the activity and durability are affected not only by the morphology of the catalyst but also the nature of the support material.

Graphene is denoted as an ideal support for noble metal electrocatalysts with its large specific surface area, excellent electrical conductivity, mechanical strength, and chemical stability [10–12]. Due to increased metal-support interaction and uniform distribution, there is an enhancement in the catalytic activity where graphene is used as a support. Moreover, the catalyst preparation method has a significant impact on morphology and catalytic activity. Conventional synthesis methods, such as chemical reduction under reflux, often lead to particle aggregation, broad size distribution, and incomplete alloy formation, limiting the catalyst's efficiency. Microwave-assisted synthesis has recently gained attention as an efficient and sustainable alternative due to its rapid volumetric heating, reduced reaction times, and improved control over nanoparticle growth [13–15]. By providing homogeneous thermal energy, microwave irradiation promotes uniform nucleation and prevents excessive particle growth, enabling the formation of finely dispersed and well-alloyed nanoparticles on graphene supports.

In this study, we report the synthesis of PtCo/graphene composite electrocatalysts via a microwave-assisted polyol method and evaluate their performance as cathode catalysts in PEMFCs. The effects of synthesis temperature on the structural, morphological, and electrochemical properties of the catalysts are systematically investigated. The results demonstrate that the microwave-assisted approach not only enhances nanoparticle dispersion and alloy formation but also significantly improves fuel cell performance compared to conventional methods. This work highlights the potential of microwave-assisted synthesis in designing high-performance, graphene-supported electrocatalysts for next-generation PEMFC applications.

2.Experimental

Graphene samples were obtained from CealTech (Norway). Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, ≥99.9%), cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, ≥98%), ethylene glycol (EG, ≥99%), Nafion® solution (5 wt%), and isopropanol (≥99.5%) were purchased from Sigma-Aldrich and used without further purification. Ultrapure water (resistivity 18.2 MΩ·cm) was used throughout all experiments.

Dr. Çiğdem İyigün Karadağ received her Ph.D degree from Middle East Technical University Department of Chemistry. She has been working as a Senior Chief Researcher at TÜBİTAK Marmara Research Center (MAM) Hydrogen and Fuel Cell Technologies Research Group since 2007. Her research focuses on proton exchange membrane fuel cells, electrocatalyst development, and hydrogen production technologies. She has led and contributed to numerous national and international projects on hydrogen technology and has authored multiple peer-reviewed publications and conference papers in the field of clean energy technologies.

Corresponding author: Çiğdem İyigün Karadağ, e-mail: cigdem.karadag@tubitak.gov.tr tel:+902626772721

2.1 Synthesis of PtCo/Graphene Catalysts

PtCo/graphene catalysts were synthesized using a microwave-assisted polyol reduction method. First, 160 mg of graphene was dispersed in 10 mL of ethylene glycol (EG) via ultrasonication for 1 h to ensure homogeneous suspension. In a separate container, 79 mg of $H_2PtCl_6 \cdot 6H_2O$ and 20 mg of $CoCl_2 \cdot 6H_2O$ were dissolved in 1 mL of EG under ultrasonication for 10 min. The metal precursor solution was then added dropwise to the graphene suspension under magnetic stirring. The resulting mixture was transferred into Monowave 400 microwave reactor (Anton Paar) and heated to 90 °C under continuous stirring. After the reaction, the product was cooled to room temperature, filtered, and washed thoroughly with ethanol and deionized water. The obtained black powder was dried under vacuum at 80 °C overnight. For comparison, additional samples were synthesized at 110 °C and 170 °C, and a control sample was prepared using a conventional reflux method at 170 °C for 8 hours.

The morphology and particle size of the catalysts were analyzed using transmission electron microscopy (TEM, JEOL JEM-2100F). X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex 600 diffractometer using Cu Kα radiation (λ = 1.5406 Å) to confirm alloy formation. Elemental mapping and compositional analysis were performed using energy-dispersive X-ray spectroscopy (EDS) coupled with scanning electron microscopy (SEM, Phenom XL).

The electrochemical analysis was performed on the Fuel Cell Test Station (Scribner Associates). Cathode electrodes were prepared by spraying the catalyst ink onto the gas diffusion layer (GDL, Sigracet 29 BC) till 0,2 mg/cm^2 loading was achieved (Fig. 1). For the anode side, 0,6 mg/cm^2 of %20 Pt/C was coated on the gas diffusion layer (Sigracet 29 BC). The membrane electrode assembly was prepaed by hot pressing the anode and cathode electrodes with the membrane (Nafion XL).

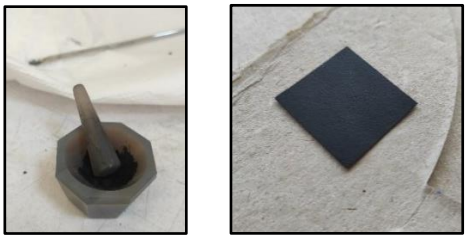

Fig 1. The prepared electrocatalyst and coated gas diffusion layer

3. Results and Discussion

The SEM and TEM images of the graphene support before catalyts preparation step is shown in Fig 2.

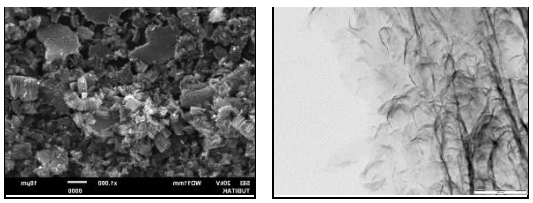

Fig 2. The SEM and TEM images of graphene support

Graphene-supported PtCo catalysts were synthesized via microwave-assisted processing at sequential temperatures of 90 °C, 110 °C, and 170 °C to investigate the effect of synthesis temperature on catalyst properties. Moreover, the polyol reduction with conventional reflux method was applied, to investigate the effect of microwave heating. The EDS analysis of the graphene-supported PtCo catalyst is presented in Fig. 3. The EDS spectrum confirms a Pt:Co atomic ratio of approximately 1:1 and a homogeneous distribution of both elements on the graphene support

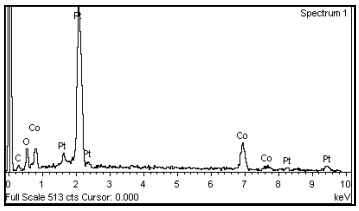

Fig 3. EDS sprectrum of graphene supported PtCo catalysts

The XRD patterns of the catalysts synthesized via conventional reflux and microwave-assisted polyol methods at different temperatures (90 °C, 110 °C, and 170 °C) shows that all samples exhibit diffraction peaks characteristic of face-centered cubic (fcc) Pt, indicating the formation of Pt-based alloy structures. Notably, samples synthesized at higher microwave irradiation temperatures (170 °C) demonstrate slight peak shifts compared to those produced under reflux conditions, suggesting lattice contraction due to cobalt incorporation into the Pt lattice. This structural modification, typically associated with PtCo alloy formation, was further supported by the calculated lattice parameters, which were lower than that of pure Pt (3.92 Å) and consistent with reported values for PtCo alloys (3.85–3.89 Å). These findings confirm that microwave-assisted synthesis at elevated temperatures promotes alloying and produces well-dispersed nanoparticles on the graphene support.

The TEM images of graphene supported catalysts prepared by microwave sysnthesis at 90, 110 and 170 °C and conventional reflux method are shown in Figure 5.

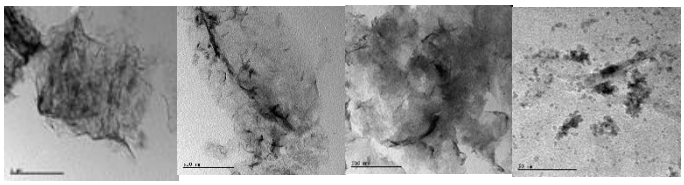

Fig 5. TEM images of the catalysts prepared at 90, 110. 170°C by microwave irradiation and conventional reflux, respectively.

The microstructural evidence indicates that microwave irradiation facilitates uniform nucleation and controlled growth kinetics, resulting in a homogeneous dispersion of catalyst nanoparticles on the support, whereas conventional reflux heating leads to non-uniform thermal gradients and pronounced particle agglomeration.

The electrochemical specific surface area (ESCA) of the prepared electrocatalysts by conventional reflux method and microwave assisted synthesis at 90, 110 and 170 °C are calculated from the cyclic voltammograms reported at 60 and 80 °C are listed in Table 1.

Table 1. The electrochemical specific surface area (ESCA) values of the electrocatalysts.

	ESCA (cm^2/g)	
Temperature	60 °C	80 °C
PtCo/G-Reflux	51,59	62,70
PtCo/G-90	49,20	42,85
PtCo/G-110	67,46	69,04
PtCo/G-170	80,95	87,30

Fuel cell performance tests of the prepared electrocatalysts were performed under H_2/O_2 gases with 1.2:2.0 stoichiometric ratio, under humidified conditions at 80 °C. Fig 6, represents the polarization curves of the catalyts prepared by microwave assisted synthesis at 90, 110, 170 °C and conventional reflux method.

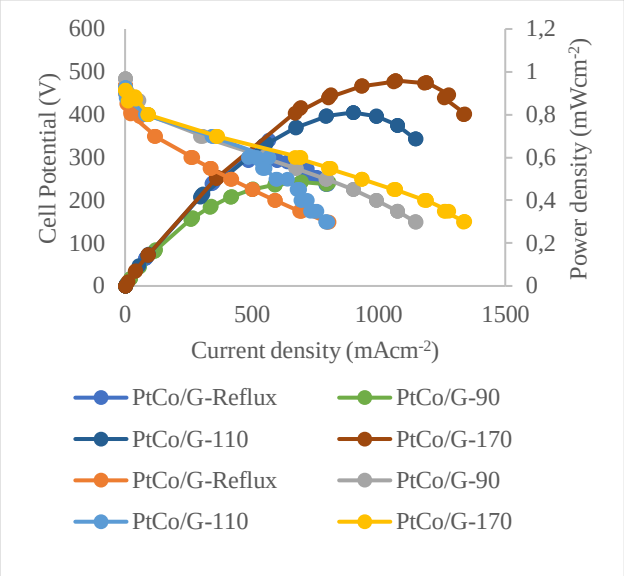

Fig 6. Polarization curves of graphene supported PtCo electrocatalysts

According to the polarization and power density curves, the **PtCo/G-170** catalyst exhibited the highest cell performance, delivering a peak power density of 520 mW cm^{-2}, while **PtCo/G-110** reached 410 mW cm^{-2}. In contrast, the **PtCo/G-90** and conventionally synthesized **PtCo/G-Reflux** catalysts exhibited significantly lower power densities of approximately 330 mW cm^{-2} and 230 mW cm^{-2}, respectively. A direct comparison between the Reflux-derived catalyst and the microwave-synthesized **PtCo/G-170** clearly indicates a substantial improvement (>500 mW cm^{-2}) in the latter, particularly in the mid-to-high current density region of the polarization curve. This demonstrates the superior catalytic activity and enhanced efficiency of the microwave-assisted PtCo/Graphene catalyst relative to its conventionally prepared counterpart.

In terms of high-current-density operation, PtCo/G-170 maintained a power density of approximately 520 mW cm^{-2} even at 1.3 A cm^{-2}, confirming its excellent electrochemical stability under heavy load conditions.

From an electrochemical perspective, the improved performance is attributed to the synergistic effects of the PtCo alloy and the graphene support. The incorporation of Co enhances oxygen reduction reaction (ORR) kinetics by modifying the Pt electronic structure, while the graphene support improves electron conductivity, suppresses nanoparticle agglomeration, and mitigates corrosion-related degradation. Consequently, the catalyst exhibits stable performance at high current densities, indicating homogeneous nanoparticle dispersion, strong structural integrity, and sustained catalytic activity over extended operation. These findings demonstrate that the microwave-assisted synthesis route yields a high-performance and durable PtCo/Graphene catalyst, outperforming conventionally synthesized materials in terms of power density, stability, and ORR activity.

4- Conclusions

This study has demonstrated that the production of PtCo/graphene-based cathode catalysts via a microwave-assisted synthesis method offers significant technical and economic advantages over conventional methods. Microwave irradiation enables rapid and uniform heating without the need for high temperatures or prolonged processing, thereby substantially reducing synthesis time, lowering energy consumption, and minimizing production costs. Furthermore, the catalysts produced using this method exhibit enhanced electrochemical performance due to characteristics such as smaller particle size, uniform metal dispersion, and well-defined crystal structure. However, for the widespread commercialization of such high-performance systems, cost-effective production processes must be scalable and applicable at the industrial level.

Acknowledgement

The work was supported by TÜBİTAK under Grant No. 122N064 which the author gratefully acknowledges. CealTech (Norway) and Fan Huang are kindly acknowledged for the graphene samples. The study is part of a collaborative project (LOCOMOTION) under MARTERA programme, where SINTEF is the coordinator. The project partners are kindly acknowledged.

References

[1] A. EG&G Technical Services, Inc., “Fuel Cell Handbook,” 7th ed., U.S. Department of Energy, Office of Fossil Energy, Morgantown, WV, 2004.
[2] B. C. H. Steele and A. Heinzel, “Materials for fuel-cell technologies,” Nature, vol. 414, no. 6861, pp. 345–352, Nov. 2001.
[3] O. Z. Sharaf and M. F. Orhan, “An overview of fuel cell technology: Fundamentals and applications,” Renewable and Sustainable Energy Reviews, vol. 32, pp. 810–853, Apr. 2014.

[4] J. Larminie and A. Dicks, Fuel Cell Systems Explained, 2nd ed. Chichester, U.K.: Wiley, 2003.
[5] M. H. Rashid, *Hydrogen Production, Storage and Applications*, 1st ed., Academic Press, 2015.
[6] N. Z. Muradov and T. N. Veziroglu, “Hydrogen energy

problems and perspectives," *International Journal of Hydrogen Energy*, vol. 33, no. 23, pp. 6804–6839, Dec. 2008.

[7] Z. Wang, G. Yin, and S. Zhang, "Pt-based electrocatalysts with high performance towards oxygen reduction reaction," *Journal of Power Sources*, vol. 171, no. 2, pp. 331–339, Oct. 2007.

[8] H. A. Gasteiger et al., "Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs," *Applied Catalysis B: Environmental*, vol. 56, no. 1–2, pp. 9–35, Mar. 2005.

[9] S. Gottesfeld and T. A. Zawodzinski, "Polymer electrolyte fuel cells," in *Advances in Electrochemical Science and Engineering*, vol. 5, Wiley-VCH, 1997, pp. 195–301.
2, pp. 9–35, Mar. 2005.

[10] V. R. Stamenkovic et al., "Improved oxygen reduction activity on Pt3Ni (111) via increased surface site availability," *Science*, vol. 315, no. 5811, pp. 493–497, Jan. 2007.

[11] M. Shao, "Electrocatalysis in fuel cells: A non- and low-Pt perspective," *ACS Catalysis*, vol. 1, no. 4, pp. 402–416, Apr. 2011.

[12]Jamil E, YararKaplan B, Sadhu V, AlkanGürsel S. "Argi nine-glycine-aspartate (RGD) peptide-modified graphene as efficient support material for Pt electrocatalyst in proton exchange membrane fuel cells". *Int J Energy Res*. 2022; 46(4): 4712-4725. doi: 10.1002/er.7467

[13] S. M. Haile, "Fuel cell materials and components," *Acta Materialia*, vol. 51, no. 19, pp. 5981–6000, Nov. 2003.

[14] R. Borup et al., "Scientific aspects of polymer electrolyte fuel cell durability and degradation," *Chemical Reviews*, vol. 107, no. 10, pp. 3904–3951, Oct. 2007.

[15] V. Mehta and J. S. Cooper, "Review and analysis of PEM fuel cell design and manufacturing," *Journal of Power Sources*, vol. 114, no. 1, pp. 32–53, Jan. 2003.