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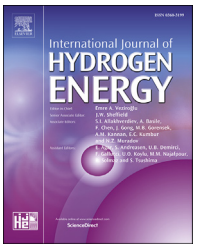

Thermodynamically controlled Pt deposition over graphene nanoplatelets: Effect of Pt loading on PEM fuel cell performance

Elif Daş [a], *Selmiye Alkan Gürsel* [b,c], *Lale Işıkel Şanlı* [b], *Ayşe Bayrakçeken Yurtcan* [a,d,*]

[a] *Department of Nanoscience and Nanoengineering, Atatürk University, Erzurum, 25240, Turkey*
[b] *Sabanci University Nanotechnology Research & Application Center (SUNUM), Istanbul, 34956, Turkey*
[c] *Faculty of Engineering &Natural Sciences, Sabanci University, Istanbul, 34956, Turkey*
[d] *Department of Chemical Engineering, Atatürk University, Erzurum, 25240, Turkey*

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ABSTRACT

Graphene is considered as a promising catalyst support for polymer electrolyte membrane (PEM) fuel cells because of its excellent properties. Recent studies showed that electrocatalytic activity, fuel cell performance, catalyst utilization efficiency and long term durability can be improved by using graphene as the catalyst support. In here, we report the synthesis of graphene nanoplatelets (GNPs) supported platinum catalysts using supercritical carbon dioxide ($scCO_2$) deposition technique. The prepared catalysts were characterized in terms of their structure, morphology and thermal behavior by using X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The electrocatalytic and half-cell performances of the as-prepared catalysts were investigated by cyclic voltammetry (CV) and PEM fuel cell performance testing. Small size and well distribution of Pt nanoparticles on GNPs surfaces were achieved by using $scCO_2$ deposition which improves the PEM fuel cell performance. To the best of our knowledge decoration of Pt nanoparticles on GNPs via $scCO_2$ deposition and their detailed fuel cell performances were presented for the first time in the literature.

Introduction

In the twenty-first century, special attention gained by fuel cells for being clean sources of energy [1,2]. Polymer Electrolyte Membrane (PEM) fuel cells gain more attention than other types of fuel cells because of their high efficiency, high power density, low cost, low weight and low working temperature [3,4]. In spite of remarkable progress in PEM fuel cells, both durability and stability of catalyst still need to be enhanced [5,6]. Up to now, there are various studies on development of alternative catalyst support materials for PEM fuel cells. In this regards, various carbon materials, including activated carbon, mesoporous carbon, carbon nanotubes, carbon fiber or carbon aerogel have been utilized as catalyst support materials due to

* *Corresponding author*. Department of Chemical Engineering, Atatürk University, Erzurum, 25240, Turkey.
E-mail address: ayse.bayrakceken@gmail.com (A. Bayrakçeken Yurtcan).
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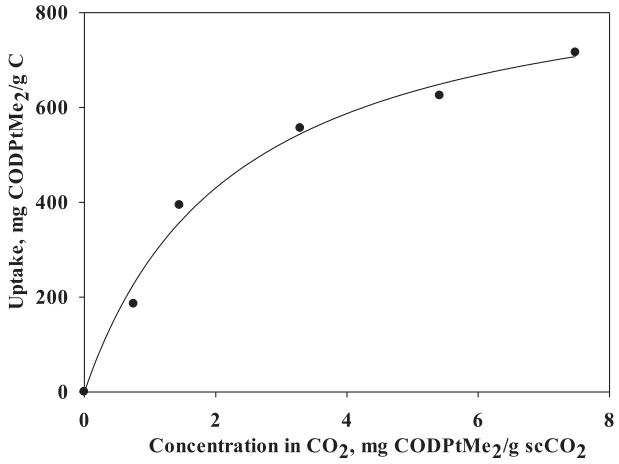

Fig. 1 – Adsorption isotherm of $CODPtMe_2$ on GNPs in $scCO_2$ (solid line represents Langmuir fit).

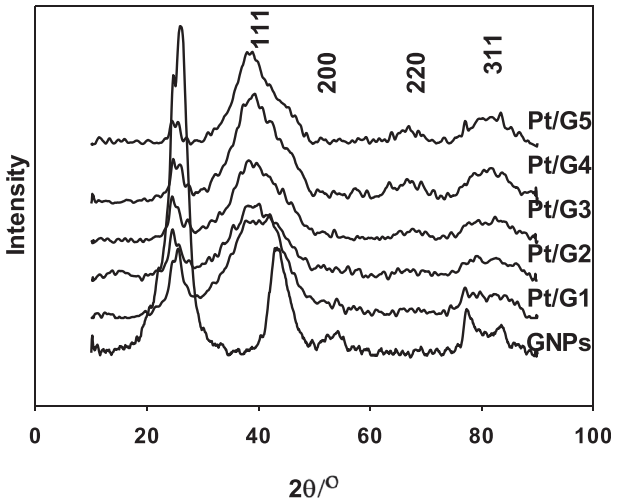

Fig. 2 – XRD patterns of plain GNPs and Pt/GNPs electrocatalysts.

their high surface area, low cost, high ORR activity and durability [7–10]. In addition to those carbon materials, graphene can serve as a promising catalyst support owing to its high surface area, excellent electrical conductivity, high surface area and strong affinity to metal particles [11,12].

Platinum (Pt)-based catalysts are significant in practical applications of PEM fuel cells because of their high efficiency stability and other factors affecting the catalytic activity of PEM fuel cells electrocatalyst, such as catalyst preparation conditions, the composition of the electrocatalyst and the metal loading over the support [13,14].

In the literature, various catalyst preparation methods, such as chemical reduction, impregnation, sputter deposition, electrochemical method and so on are used [15–20]. It is very critical to choose a proper method in order to achieve the targeted catalyst properties and also higher catalytic activities [21].

Supercritical carbon dioxide deposition ($scCO_2$) is also an alternative method for preparation of nanoparticles [13,22–24]. There has been a growing interest in exploiting advantages of $scCO_2$ as a "green" solvent with peculiar wetting abilities in the catalyst preparation for fuel cells applications [23]. $ScCO_2$ environment provides an excellent medium to decorate nanoparticles onto the porous support materials. Moreover, $scCO_2$ offers several advantages compared to conventional techniques. The high diffusivity, low viscosity and surface tension properties of $scCO_2$ allows it and its mixtures to penetrate into the nanostructures easily [24,25]. Furthermore, the support structure is preserved upon the CO_2 treatment. There are various studies about the deposition of Pt nanoparticles on carbon black, carbon nanotubes and carbon aerogels via $scCO_2$ [26–28]. However, there are only three studies in literature about the preparation of graphene supported Pt nanoparticles as the catalyst support for fuel cell reactions by $scCO_2$. In this regard, Zhao et al. showed enhanced stability and electrocatalytic activity of Pt nanoparticles on GO for methanol oxidation [24]. In their recent study, Zhao et al. compared Pt/graphene with Pt/carbon black and Pt/carbon nanotube prepared by sCO_2 deposition and reported better stability of Pt/graphene compared to other two supports [25]. In both studies authors employed GO prepared by Hummers method [29] and expanded thermally. In another recent study Pt nanoparticles on functionalized graphene were synthesized by $scCO_2$ [30]. In all these studies about graphene (GO or functionalized GO) supported Pt, authors investigated ex-situ electrocatalytic activity of catalysts yet fuel cell performances of these catalysts were not shown.

In this study, different Pt loadings over graphene nanoplatelets (GNPs) support were succesfully achieved with thermodynamic control via one-pot $scCO_2$ method using dimethyl (1,5-cyclooctadiene) platinum (II) ($PtMe_2COD$) as organometallic Pt precursor. The physical, structural and electrochemical properties of the catalysts were characterized using X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), cyclic voltammetry (CV) and fuel cell tests. To the best of our knowledge, decoration of Pt nanoparticles on GNPs and their detailed fuel cell performances were presented for the first time in the literature.

Table 1 – Langmuir equilibrium constants for $CODPtMe_2$, $scCO_2$ and GNPs compared with the literature.

Catalyst	Support surface area [m^2/g]	K_1	Q_o	$K_1 Q_o$	R^2	S_{Pt} [m^2/g]	Reference
Pt/GNPs	759	0.4357	924.34	403	0.99	329	In this study
Pt/BP2000	1450	0.54	1481	801	0.99	525	[32]
Pt/MWCNT	300	0.29	335	100	0.99	119	[32]
Pt/Vulcan	232	0.87	180	156	0.98	64	[28]

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