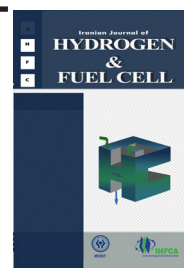


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Electro deposition of platinum nanoparticles on reduced graphene oxide as an efficient catalyst for oxygen reduction reaction

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Abstract

Reduced graphene oxide film was synthesized on a glassy carbon electrode by electro reduction of graphene oxide powders in aqueous solution. Then platinum Nano particles were deposited on reduced graphene oxide film that was deposited on the glassy carbon electrode via electro reduction of platinum salt. The Physical morphology of the platinum on reduced graphene oxide film was evaluated by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). The results showed that, Platinum particles were deposited on reduced graphene oxide film. The performance of Pt on reduced graphene oxide for oxygen reduction reaction was considered with linear sweep voltammetry and electrochemical impedance spectroscopy of catalyst in an acidic solution via three electrode configuration cell. The results showed the proper performance of this green synthesized catalyst for oxygen reduction reaction. So this method for catalyst fabrication is a good candidate for the cathode of proton exchange membrane fuel cells.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have long been thought of as a promising clean alternative energy electrochemical device. They have some advantages such as high power density, high efficiency, clean utilization and zero emission that makes them promising green power sources [1-3]. The oxygen reduction reaction (ORR) is one of the important electro catalytic reactions occurring in these particular fuel cells. It is well known that the

cell voltages of fuel cells are limited by the slow kinetics of ORR at the cathode. Oxygen is reduced by two different pathways: a single step four-electron pathway and consecutive steps that each involves two electrons [4, 5]. The oxygen reduction reaction determines the efficiency of these electrochemical systems because of its high over-voltage on different substrates, including Pt [4, 5]. Graphene, a new kind of two-dimensional carbon material with a single (or a few) atomic layer, has been found a promising

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candidate for catalyst support in fuel cells due to their unique properties such as high surface area, high conductivity and unique graphitized basal plane structure [6]. Graphene is a two dimensional sp^2 -hybridized carbon sheet [7]. Many methods have been proposed for graphene production, among which the chemical reduction of graphene oxide (RGO) obtained from ultrasonic exfoliation of oxidized graphite is the most convenient way to yield large quantities of graphene sheets [8]. Studies of electrochemically reduced graphene oxide have been reported by several authors [9]. Recently, an electrochemical RGO has been developed [6, 8, and 9]. It is attractive for graphene-film synthesis due to its simple, fast, and green nature. Typically, the electrochemical synthesis of graphene is carried out via two steps, namely, RGO being first assembled on the electrodes by dip-coating, drop-casting, or spray-coating methods and then being subjected to electrochemical reduction. Shortly after the development of electrochemical RGO an approach using GO-coated electrodes being immersed in a metallic precursor solution to perform one-step electrochemical reduction was proposed to fabricate graphene-metal nanocomposite films [9-11].

Platinum is widely used as the electrocatalyst for ORR due to its high activity and excellent chemical stability. However, Pt is expensive and the limited world supply of Platinum poses serious problems to widespread commercialization of fuel cell technology [6]. Thus, research efforts in the development of cathode electrocatalysts have been focused on decreasing the Pt content or replacing it with less expensive materials while maintaining high ORR activity. Direct electrochemical reduction of Platinum ions on a support is a relatively convenient way to fabricate nanoparticle based electrodes. There are some reports in the literature on the preparation of supported Platinum nanoparticles via the electro deposition method [12-14]. In this research, a RGO film was electrochemically synthesized on a glassy carbon electrode (GCE) by the cyclic voltammetry (CV) method. Subsequently, Platinum nanoparticles were electrodeposited on the RGO/GCE by the cyclic

voltammetry method. The catalytic properties of the electrodes in the oxygen reduction reaction were studied using cyclic voltammetry and electrochemical impedance spectroscopy (EIS).

2. Experimental

Sodium chloride (Merck, p.a.), sodium hydroxide (Merck, p.a.), hydrochloric acid (UNIVAR, analytical reagent), H_2PtCl_6 ($\geq 37.50\%$), Graphite (99.99%) and H_2SO_4 (Merck, 95% purity) were used as received. All other chemicals were of analytical grade and used without further purification. Distilled water was used throughout. The electrochemical experiments were performed in a three-electrode cell arrangement. The electrochemical impedance spectroscopy (EIS) measurements were done at the open circuit voltage (OCV). The root mean square (RMS) amplitude of modulation potential for the EIS measurements was 10 mV, and the frequency range was from 100 kHz to 50 MHz. Electrochemical experiments were carried out using EG&G PARSTAT 2273 advanced electrochemical systems.

A scanning electron microscope (Model VEGAII, TESCAN, Czech Republic) was employed with an accelerating voltage of 15 kV. To identify the element composition, an energy dispersive X-ray was employed with an accelerating voltage of 16 kV.

2.1. Reduced graphene oxide (RGO) film on a glassy carbon electrode

Graphite oxide was synthesized from natural graphite by a modified Hummers method as originally presented by Kovtyukhova and colleagues [17]. As-synthesized graphite oxide was then purified by dialysis and then subjected to ultra-sonication protocols which are described in detail elsewhere [8].

2.2. Electrochemical techniques

The cyclic voltammetry as well as the deposition

experiments were carried out using a three electrode setup including an Ag/AgCl reference electrode, a glassy carbon working electrode and a platinum sheet used as the auxiliary electrode. The chemical compositions for reduced graphene oxide film on a glassy carbon electrode were set as a GO suspension (0.5 mg mL^{-1}), NaCl (0.25 M), pH 7, Temperature ($27 \text{ }^\circ\text{C}$), and Reduction potential / V (0 to -2) using 25 Cycle.

2.3. Electro deposition of Pt particles on the RGO/ GCE electrode

The Pt particles were deposited on the RGO/GCE electrode by the cyclic voltammetry deposition method. The chemical compositions of the plating baths and the deposition conditions were set at H_2PtCl_6 (3 mM), H_2SO_4 (0.05 M), pH (4), temperature ($27 \text{ }^\circ\text{C}$), reduction potential / V (-0.5 to 1.5) using 25 cycle.

3. Results and discussion

3.1. Electrochemical characterisation of the reduced graphene oxide on the glassy carbon electrode

Successful electro-reduction of graphene oxide (GO) to reduce the graphene oxide was performed on GCE by CV. Figure 1 shows the cyclic voltammogram of the GO reduction in a GO suspension (0.5 mg mL^{-1}) which was mixed 1:1 with a sodium chloride solution ($\text{NaCl} = 0.25\text{M}$). The additional reduction current in the region of -1.0 V to -1.8 V indicated the reduction of GO.

Experiments showed that adding a supporting electrolyte to the GO suspension was essential for electro-deposition. An excess of reagent (acids, bases or salts), however, resulted in destabilization of the suspended GO particles. Graphene oxide contains anionic functional groups (e.g. phenolates and carboxylates); partial dissociation of these groups cause the negative charges to form an electrochemical double layer around of the GO particles

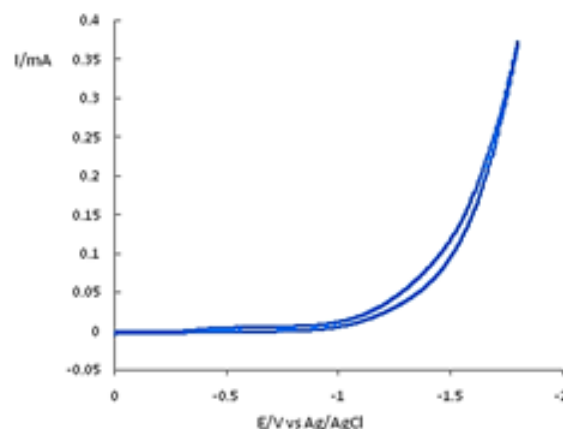


Fig. 1. Cyclic voltammogram of the GCE electrode in GO suspension (0.5 mg mL^{-1}) which was mixed 1: 1 with a sodium chloride solution ($\text{NaCl} = 0.25\text{M}$) Scan rate: 10 mV s^{-1} .

preventing them to agglomerate. The thickness of the double layer decreased when the electrolyte concentration increased; hence stabilization could only be achieved in very dilute systems.

3.2. Electrochemical studies of Pt electro-deposition on RGO/ GCE

The platinum electrochemical growth process on RGO/ GCE was investigated by CV. Figure 2 illustrates the first cyclovoltammetric scans for a solution of $3 \text{ mM H}_2\text{PtCl}_6$ and $0.05 \text{ M H}_2\text{SO}_4$ at RGO/ GCE. The first scan contains a characteristic “nucleation loop”, which arises from the greater over potential required for nucleation onto the electrode compared to deposition of metal onto metal. A reduction peak of Pt and the oxidation peak of deposited Pt can be seen [6, 15]. The typical peak at -0.26 V is related to the reduction of hydrogen ions to hydrogen atoms indicating the presence of platinum particles in an acidic media (Figure 3).

3.3. Characterization of the electrodes surface morphology

Figure 4 illustrates the SEM micrographs of RGO electrodeposited on GCE (a) and Pt on RGO/GCE (b).

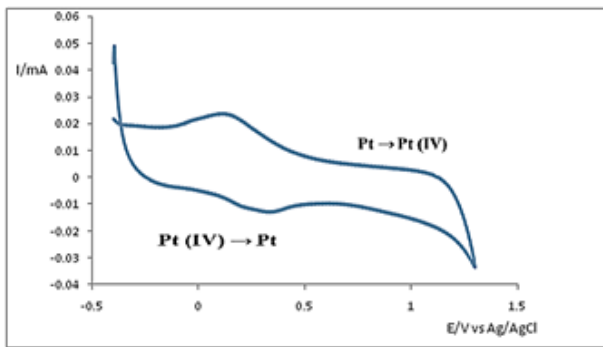


Fig. 2. Cyclic voltammograms for Pt electrodeposition on RGO/GCE in 0.05M H_2SO_4 solution containing 3mM H_2PtCl_6 at a scan rate of 20 mV s^{-1} .

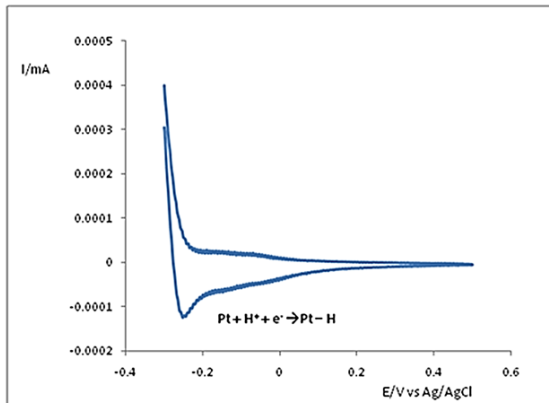


Fig. 3. Cyclic voltammograms for reduction of hydrogen ions to hydrogen atoms. In $1\text{M H}_2\text{SO}_4$ at 25°C . Scan rate: 20 mV s^{-1} .

It can be seen that the Pt particles with a high density are distributed in an almost homogeneous manner at the surface of the RGO/GCE. Figure 5 shows the EDX spectrum of the Pt/RGO/GCE electrode. The EDX results confirm the presence of the Pt particles on the RGO/GCE electrode surface. KOH and NaCl salt was used in electroplating presence. Therefore, K and Na were found in the EDX spectra. The presence of Si in the EDX spectra was related to the substance of the GCE electrode.

3.4. Electrochemical impedance spectroscopy (EIS) measurements

Impedance spectroscopy is an effective method for probing the features of a surface modified electrode.

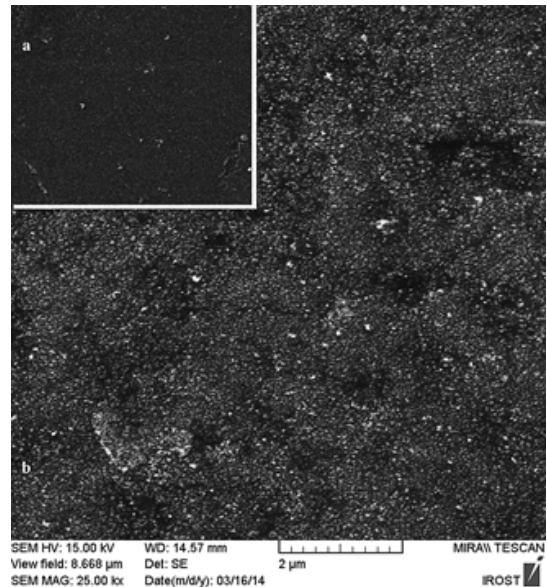


Fig. 4. SEM images of RGO/GCE (a) and Pt/RGO/GCE (b) with the same magnification.

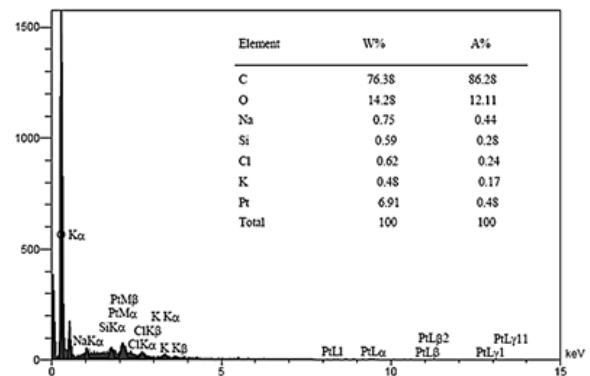


Fig. 5. EDX of the Pt/RGO/GCE electrode.

Figure 6 illustrates the results of impedance spectroscopy on GCE and RGO/GCE and Pt/RGO/GCE electrodes in a solution containing $1\text{M H}_2\text{SO}_4$. RGO accelerated the electron transfer between the probe and the electrode, which is attributed to the fact that RGO has a graphitic network of sp^2 bonds and thus the electrical conductivity of the RGO sheets is significantly improved [15, 16]. The electrochemical charge transfer resistances (R_{ct}) value for RGO/GCE decreased distinctively for RGO deposited on GCE, compared with bare GCE. Low electrochemical charge transfer resistances were

obtained on the Pt/ RGO/ GCE electrode compared with RGO/ GCE.

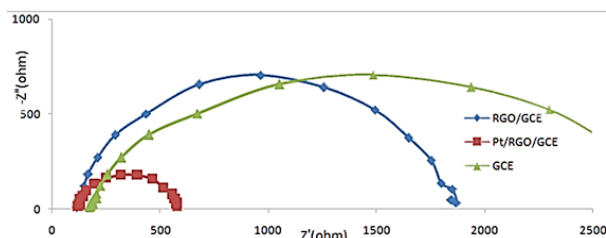


Fig. 6. Impedance responses presented in Nyquist form for the range 100 kHz–100 MHz, for the GCE, RGO/GCE and Pt/RGO/GCE electrodes.

3.5. Electro catalytic activity of Pt/RGO/GCE toward ORR

Figure 7 shows ORR voltammograms of oxygen reduction on the GCE, RGO/GCE and Pt/RGO/GCE in 1M H_2SO_4 at 27°C with a scan rate of 100 $mV s^{-1}$. There is a difference between current density for different electrodes at the same voltage. Also the LSV for Pt/RGO/GCE catalyst is presented the best performance for ORR [17].

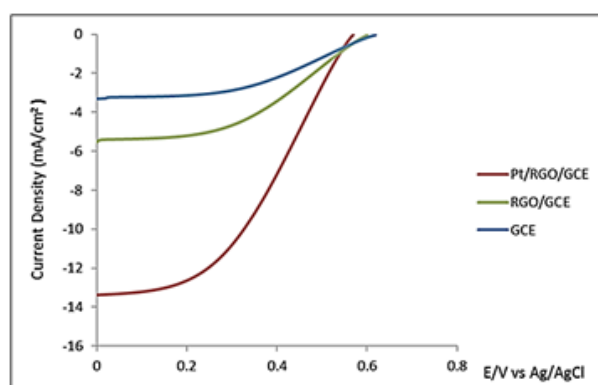


Fig. 7. ORR on Pt/GCE, RGO/GCE and Pt/RGO/GCE in O_2 saturated 1M H_2SO_4 solution.

4. Conclusions

RGO/GCE and Pt/RGO/GCE electrodes were successfully prepared by the electrodeposition method. Subsequently, the electro-catalytic activity of RGO/GCE and Pt/RGO/GCE electrodes for oxygen reduction

was evaluated using electrochemical voltammetric measurements and electrochemical impedance spectra. The Pt/RGO/GCE showed extremely higher currents of oxygen reduction than the GCE and RGO/GCE electrodes. In addition, a good activation range of oxygen reduction and low electrochemical charge transfer resistances (R_{ct}) was obtained on the Pt/RGO/GCE electrode. Finally, two advantages of the Pt/RGO/GCE electrode were the simultaneous presence of RGO and Pt in the electrode; this can improve the performance of PEMFCs for the reduction of oxygen.

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6. References

- [1] Zhu H., Luo M., Zhang S., Wei L., Wang F., Wang Z., Wei Y. and Han K., "Combined method to prepare core-shell structured catalyst for proton exchange membrane fuel cells", *Int. J. Hydrogen Energy*, 2013, 38: 3323.
- [2] Mehta V. and Cooper S.J., "Review and analysis of PEM fuel cell design and manufacturing", *J Power Sources*, 2003, 114: 32.
- [3] Cheng C.H., Malek K, Sui P.C. and Djilali N., "Effect of Pt nano-particle size on the microstructure of PEM fuel cell catalyst layers: Insights from molecular dynamics simulations", *Electrochim. Acta*, 2010, 55: 1588.
- [4] Termornvithit C., N. Chewasatn N. and Hunsom M., "Stability of Pt-Co/C and Pt-Pd/C based oxygen reduction reaction electrocatalysts prepared at a low temperature by a combined impregnation and seeding process in PEM fuel cells", *J Appl Electrochem*, 2012, 42: 69.
- [5] Oezaslan M., Hasche F. and Strasser P., "Oxygen

- electroreduction on PtCo₃, PtCo and Pt₃Co alloy nanoparticles for alkaline and acidic PEM fuel cells”, *J Electrochem Soc.*, 2012, 159 (B): 394.
- [6] Ye W., Zhang X., Chen Y., Du Y., Zhou F. and Wang C., “Pulsed Electrodeposition of Reduced Graphene Oxide on Glass Carbon Electrode as an Effective Support of Electrodeposited Pt Microspherical Particles: Nucleation Studies and the Application for Methanol Electro-Oxidation”, *J. Electrochem. Sci.*, 2013, 8: 2122.
- [7] Jafarian M., Gopal F., Mahjani M.G. and Hosseini Aliabadi M., “Multistep Reduction of Oxygen on Polycrystalline Silver in Alkaline Solution”, *Chin. J. Catalysis.*, 2010, 31: 541.
- [8] Hilder M., Winther-Jensen B., Li D., Forsyth M. and MacFarlane D.R., “Direct electro-deposition of graphene from aqueous suspensions”, *Phys. Chem. Chem. Phys.*, 2011, 13: 9187.
- [9] Liu C., Wang K., Luo S., Tang Y. and Chen L., “Direct Electrodeposition of Graphene Enabling the One-Step Synthesis of Graphene–Metal Nanocomposite Films”, *Small.*, 2011, 7: 1203.
- [10] Liu B., Liu L.R. and Liu X.J., “Effects of carbon nanotubes on crystallization in amorphous Ni–P electroplating coating”, *Surf. Eng.*, 2013, 29: 190.
- [11] Shamsolhodaei A., Rahmani H. and Rastegari S., “Effects of electrodeposition parameters on morphology and properties of Zn–TiO₂ composite coating”, *Surf. Eng.*, 2013, 29: 695.
- [12] Trojanec A., Langmaier J. and Samec Z., “Electrocatalysis of the Oxygen reduction at a polarised interface between two immiscible electrolyte solutions by electrochemically generated Pt particles”, *Electrochem. Comm.*, 2006, 8: 475.
- [13] Y. D. Yu Y.D., M. M. He M.M., M. G. Li M.G., H. F. Guo H.F., G. Y. Wei G.Y. and H. L. Ge H.L., “Effect of temperatures on electrodeposition of CoWP films”, *Surf. Eng.*, 2013, 29: 200.
- [14] Yu Y.D., Li M.G., Wei G.Y. and Ge H.L., “Effects of pH values on electroless deposition of CoP films”, *Surf. Eng.*, 2013, 29: 767.
- [15] Abdulah Mirzaie R. and Eshghi A., “Study of methanol electro-oxidation on Ni and Ni–Pt/carbon paper electrodes for direct methanol fuel cell applications”, *Surf. Eng.*, 2014, 30: 263.
- [16] Li B. and Chan S.H., “PtFeNi tri-metallic alloy nanoparticles as electrocatalyst for oxygen reduction reaction in proton exchange membrane fuel cells with ultra-low Pt loading”, *Int J Hydrogen Energy.*, 2013, 38: 3338.
- [17] N.I. Kovtyukhova, P.J. Ollivier, B.R. Martin, T.E. Mallouk, S.A. Chizhik, E.V. Buzaneva, A.D. Gorchinskiy, “Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations” *Chem. Mater.*, 1999, 11: 771.