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Manganese Dioxide/Reduced Graphene Oxide with Poly(3,4-ethylenedioxythiophene) for Improved Electrocatalytic Oxygen Reduction Reaction

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Poly(3,4-ethylenedioxythiophene)-(PEDOT)-functionalized reduced graphene oxide (rGO) with MnO_2 nanoparticles ($MnO_2/PEDOT/rGO$) was prepared using electrochemical methods. The $MnO_2/PEDOT/rGO$ was obtained through the electrochemical reduction of PEDOT/GO and under electrochemical treatment in KMnO₄. The PEDOT/rGO and $MnO_2/PEDOT/rGO$ were characterized by several instrumental and electrochemical methods. The electrocatalytic O_2 reduction for both electrodes was investigated via cyclic and hydrodynamic voltammetry in 0.1 M KOH aqueous solutions. The kinetic analysis in comparison to PEDOT/rGO a significant enhancement was found for the $MnO_2/PEDOT/rGO$. The proposed main path in the oxygen reduction reaction (ORR) mechanism on the $MnO_2/PEDOT/rGO$ was the direct four-electron transfer process with faster transfer kinetic rate. The better ORR kinetics were obtained due to the excellent composite formation and well attachment of MnO_2 NPs within oxide form. The PEDOT/rGO was less stable for long term use than $MnO_2/PEDOT/rGO$.

Keywords: Electrocatalyst, Functionalized Reduced Graphene Oxide, Oxygen Reduction Reaction, Poly(3,4-ethylenedioxythiophene).

1. INTRODUCTION

The oxygen reduction reaction (ORR) plays an important role in the field of electrochemical energy conversion in fuel cells.¹ Pt-based materials are used as the efficient electrocatalysts for the reaction.^{2, 3} Due to the high cost and limited supply of this precious metal, the commercialization of fuel cells has been hindered. Hence, the development of non-precious metal, like manganese (Mn) or metal-free ORR electrocatalysts has attracted a lot of interest to reduce the usage of precious metal electrocatalysts.^{4–8} Among the many research reports on non-platinum catalysts, Mn-oxides have received a lot of interests because of its low cost, natural abundance and environment-friendliness.^{9–13}

Graphene sheets consist of a monolayer of sp²hybridized carbon atoms in two-dimensional flat lattices.¹⁴ Its excellent physical and chemical properties, such as high electrical conductivity and high surface area,¹⁵ have been studied for various electrochemical applications. This material has been used in various fields, especially in sensors^{16,17} and ORR catalysts.^{18,19} After oxidation of graphene, graphene oxide (GO) still keeps a layered structure with some distortions due to oxygen functional groups such as hydroxyl, carbonyl, carboxyl and epoxy. Such oxygen functional groups ensure excellent chemical modification and functionality.²⁰ The most attractive property of GO is that it can be reduced to graphene-like sheets by reducing the oxygen functional groups present on the surface of GO. Chemical reduction of GO is an efficient approach to large scale production at low cost, which includes noncovalent and covalent functionalization of rGO.²¹

The poly 3,4-ethylenedioxythiophene (PEDOT) is widely in various chemistry fields including sensors, polymers and catalysis chemistry^{22–27} due to its' unique chemical properties such as, excellent conductivity, high

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stability, good capacitive behavior and mechanical flexibility. PEDOT is a low band gap polymer with high stability and good conductivity. EDOT as monomer has strong electron donating ability and small steric interaction between repeating units in polymers.^{23, 24} However, GO can be functionalized by PEDOT, one of the most promising conducting polymers with high electrical conductivity and stability. It has been studied widely and has been shown to have a superior electrochemical catalytic property in fuel cells.^{25–27}

In this work, PEDOT/rGO was synthesized using chemical methods. MnO₂/PEDOT/rGO was prepared using electrochemical methods from PEDOT/rGO. However, the PEDOT/rGO and MnO₂/PEDOT/rGO were characterized via several instrumental and electrochemical methods. The electrochemical behavior and of their electrocatalytic O₂ reduction were investigated via CV, RDE and RRDE in 0.1 M KOH aqueous solutions.

2. EXPERIMENTAL DETAILS

2.1. Instruments

TEM and EDX were carried out in a JEM-2100F microscope at 200 kV. XPS measurements were performed on a MultiLab 2000 (Thermo Electron Corporation, England) with a 14.9 keV Al Ka X-ray source. XRD spectra were carried out on a Rigaku D/max-2500, using filtered Cu K α radiation. Raman spectra were obtained with LabRam HR800 UV Raman microscope (Horiba Jobin-Yvon, France), with an excitation of 514 nm Ar⁺ laser. EIS was performed using Versa STAT3 electrochemical analysis. All the Voltammetric measurements were taken using a three-electrode potentiostat (CHI 700C Electrochemical Workstation, USA) in a grounded Faraday cage. A Pt wire electrode was used as the auxiliary electrode. A calibrated Ag/AgCl electrode from Bioanalytical Systems Inc. (BAS) in 3 M NaCl solution was used as a reference electrode. A rotating electrode (glassy carbon electrode, GCE-disk area: 0.196 cm²; Pt ring area: 0.041 cm²) was employed as a working electrode. An EG and G Model 636 RRDE system and a CHI 700C electrochemical workstation were used for hydrodynamic voltammetry.

2.2. Chemicals

The graphite powder (325-mesh) and EDOT were from Aldrich. The H_2SO_4 was from DC Chemical Co. Ltd. All the other reagents were of analytical grade and were used without further purification. Double-distilled water (DW) was used in the preparation of the aqueous electrolyte solutions.

2.3. Preparation of Catalyst and Electrode

GO was prepared by oxidizing graphite according to the improved Hummers method.^{28, 29} Briefly, the mixture of concentrated H_2SO_4/H_3PO_4 (9:1) was added to a mixture

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of graphite/KMnO₄ (1:6) at 50 °C and stirred for 12 h. The reaction was cooled to RT and transferred onto ice with 30% H₂O₂. The obtained solution was centrifuged, and then filtered. The solid material was then washed with water, and finally washed with 30% HCl. Then, 20 mg GO powder was dispersed in 30 mL acetonitrile (MeCN) with 10 min ultrasound, then 20 μ L EDOT was added to the solution under stirring for 15 h. After that, it was centrifuged and washed with DW and ethanol for several times. Finally, the resulting product was dried at 50 °C in a vacuum oven for 24 h.

For the electrode preparation, EDOT/GO suspension in DW (1 mg/mL) was prepared by introducing a predetermined amount of the corresponding sample under sonication. 10 μ L portions of the PEDOT/GO suspension was then dropped onto the surface of a GCE that was prepolished with a 0.05 μ m alumina suspension on a polishing cloth (BAS, USA). The PEDOT/GO-coated GCE was electrochemically polymerized by five successive scan by cyclic voltammetry (CV) in an electrochemical cell containing 1 M KCl solution over a potential range of ± 1.5 V at a 100 mV/s scan rate. Then it was electrochemically reduced by two successive cycles using CV in same solution over a potential range of 0 to -1.5 V at a 10 mV/s scan rate. To make MnO₂/PEDOT/rGO, the MnO₂ NPs were added to the PEDOT/rGO coated GCE using electrochemical method. Only five successive cycles were performed by CVs in 0.05 M H₂SO₄ containing 10 mM KMnO₄ solution over a potential range of 0.3 to -0.5 V at a 10 mV/s scan rate.²⁹ The experiments were carried out under Ar atmosphere at room temperature. The resulting MnO₂/PEDOT/rGO-coated GCE was washed with distilled water before and after each experiment. Electrochemical measurements of the electrocatalytic reduction of O_2 using the MnO₂/PEDOT/rGO modified electrodes were conducted in Ar and O₂-saturated 0.1 M KOH. For comparison, the rGO, PEDOT/rGO, MnO₂/rGO, are prepared in the same procedure without EDOT and KMnO₄, KMnO₄, EDOT, respectively. The 205 Pt/C was prepared in ethanol (1 mg/ml) and casted 10 μ l each separately.

3. RESULTS AND DISCUSSION

3.1. Instrumental Characterizations

Figures 1(a) and (b) show the TEM images of PEDOT/ rGO and MnO₂/PEDOT/rGO. PEDOT was attached tightly onto the rGO surface in 3D structure; also PEDOT was polymerized into the rGO plan can be seen. The TEM image of MnO₂/PEDOT/rGO shows black spherical spots representing MnO₂ nanoparticles (NPs) on the rGO demonstrating that MnO₂ NPs were set successfully onto the rGO. The average particle size range was estimated to be $5\sim10$ nm. The high resolution TEM (HRTEM) in Figure 1(c) represents the MnO₂ lattice lines clearly and the *d*-spacing between two lines was estimated as 0.302 nm.^{30,31}



Figure 1. TEM images of PEDOT/rGO (a) and MnO₂/PEDOT/rGO (b). HRTEM image of MnO₂/PEDOT/rGO (c) and the corresponding EDS spectra are shown below (d).



Figure 2. The XPS survey spectra (a), the core level of C 1s spectra (b) of PEDOT/rGO and MnO₂/PEDOT/rGO and the core level of Mn 2p spectra of MnO₂/PEDOT/rGO (c).

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Figure 3. The XRD spectra (a) and EIS in a 0.1 M KCl solution containing 5 mM 1:1 [Fe(CN)₆]^{3-/4-} (b) of PEDOT/rGO and MnO₂/PEDOT/rGO.

The presence of the elements of PEDOT/rGO and $MnO_2/PEDOT/rGO$ were also confirmed by the EDX spectrum (Fig. 1(d)). The EDX spectrum of PEDOT/rGO shows signals from C, O, S and Cu. However, the Mn peaks are shown only in the $MnO_2/PEDOT/rGO$ spectrum with increased O peak. Indicating the Mn is in the oxide form in the $MnO_2/PEDOT/rGO$ catalyst. The peaks of elemental Cu attributed to the TEM grid. It clearly demonstrated that the presence of Mn in oxidized form with 17.35 wt% as the component element in $MnO_2/PEDOT/rGO$.

The XPS spectra of as prepared PEDOT/rGO and MnO₂/PEDOT/rGO are shown in Figure 2. The XPS data showed distinct C 1s O 1s and S 2p peaks at around 286 eV, 534 eV, and 163.1 eV, respectively (Fig. 2(a)).^{18,28} For MnO₂/PEDOT/rGO, the XPS data confirmed the presence of Mn once again upon K₂MnO₄ treatment via electrochemical process. The high-resolution C 1s XPS spectra for PEDOT/rGO and MnO₂/PEDOT/rGO are shown in Figure 2(b). The spectrum of PEDOT/rGO shows three peaks of the C=C, C-O and O=C-O groups with about 284.9, 286.3 and 289.6 eV, respectively, while oxygenated carbon peaks are reduced upon electrochemical reduction at MnO₂/PEDOT/rGO. Very importantly, the O 1s peak was much higher in MnO₂/PEDOT/rGO than that of PEDOT/rGO due to Mn was in the oxide form in the MnO₂/PEDOT/rGO (the oxygen containing carbon bands are reduced as shown in Fig. 2(b)). The Mn 2p peaks were centered at 642.7 eV (Mn 2p1/2) and 654.3 eV (Mn $2p_{3/2}$), with a 11.6 eV spin energy separation (Fig. 2(c)), which is in good agreement with the reported data.^{4, 10, 32, 33} The numerical results of XPS are as below.

Elements wt%	PEDOT/rGO	MnO ₂ /PEDOT/rGO
С	86.71	64.12
0	9.58	14.63
S	3.71	3.33
Mn	-	17.91

The structure of the PEDOT/rGO and $MnO_2/PEDOT/$ rGO were investigated by XRD and the pattern is shown in Figure 3(a). The peak at the 2θ value of about 26.33° is

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ascribed to the crystal plane of graphite (C111) plan. The other characteristic reflections of the sample are shown at $2\theta = 37.44^{\circ}$, 41.44° , 49.83° , 56.39° , 60.27° , 65.69° , 80.42° corresponding to the lattice planes of (211), (301), (411), (600), (521), (541), (311) respectively, that proves the MnO₂ is in crystalline form.

3.2. Electrochemical Characterization

Nyquist plots were obtained at 10⁵-10⁻² Hz using a 5.0 mM $[Fe(CN)_6]^{3-/4-}$ (1:1) redox couple as an electrochemical probe (Fig. 3(b)). The measured electricalresistance values of the two modified electrodes were as follows: MnO₂/PEDOT/rGO < PEDOT/rGO. It was concluded that the electrical conductivity of MnO2/PEDOT/ SrGO was enhanced due to Mn loading via electrochemical method and the well attachment of MnO₂ NPs onto the PEDOT/rGO smooth sheets. The GO on the GCE surface greatly increased the electrical resistance, suggesting that GO acted as an insulating layer that hindered interfacial electron transfer due to the disrupted sp² bonding networks.34,35 The increasing conductivity of PEDOT/rGO over GO is attributed to the recovery of the disrupted sp² bonding in the synthetic process of PEDOT/rGO. MnO₂/PEDOT/rGO showed almost linear plot at all frequencies, suggesting that the electrode reaction was



Figure 4. The CVs of ORR on rGO, MnO₂/rGO, PEDOT/rGO and MnO₂/PEDOT/rGO at 50 mV/s in O₂-saturated 0.1 M KOH.



Figure 5. RDE voltammograms for ORR on PEDOT/rGO and MnO_2 /PEDOT/rGO at 10 mV/s in O_2 -saturated 0.1 M KOH at various rpm, the corresponding Koutecky–Levich plots for PEDOT/rGO and MnO_2 /PEDOT/rGO at different electrode potentials.

controlled by diffusion. The MnO₂/PEDOT/rGO was at various rotation rates and a scan rate of 10 mV/s. highly conductive, and allowed electron transfer with Figure 5 shows the LSV curves at various different rotagreater ease than the other modified electrodes. American Stion rates for PEDOT/rGO and MnO₂/PEDOT/rGO mod-

3.3. ORR on Several Modified Electrodes 3.3.1. CV Study

The catalytic performance of rGO, MnO₂/rGO, PEDOT/ rGO and MnO₂/PEDOT/rGO for ORR were tested using CVs in O₂-saturated 0.1 M KOH solution at a 50 mV/s scan rate. As can be seen in Figure 4, the rGO modified GCE electrode has low response to the ORR. When MnO₂ was incorporated on the rGO sheets, the ORR onset potential was shifted back with better current density than that of only rGO. It is, however, the PEDOT/rGO composite has much better response (in onset and current density) towards ORR due to high conductivity. The onset potential for ORR of the MnO₂/PEDOT/rGO electrode shifted maximum compared to the other electrodes with highest current density. The MnO₂/PEDOT/rGO electrode had better ORR catalysis due to probably two reasons; first, the well composite formation that have the PEDOT as conductive and low band gap polymer, and second, well attachment of MnO₂ NPs and acts as a reaction face in the oxide form.

3.3.2. Hydrodynamic Voltammetry Study

To further investigate the ORR performance, we carried out the linear sweep voltammetry (LSV) measurements on a rotating disk electrode (RDE) for PEDOT/rGO and MnO₂/PEDOT/rGO in O₂-saturated 0.1 M KOH at various rotation rates and a scan rate of 10 mV/s. Figure 5 shows the LSV curves at various different rotation rates for PEDOT/rGO and $MnO_2/PEDOT/rGO$ modified electrodes, respectively. The ORR limiting current density of the $MnO_2/PEDOT/rGO$ modified electrode was always larger than that of the PEDOT/rGO electrode at any constant rotation rate. In addition, RRDE was used to evaluate the ORR performance of the PEDOT/rGO and $MnO_2/PEDOT/rGO$ electrodes (Fig. 6). The ORR at the $MnO_2/PEDOT/rGO$ electrode commenced at around -0.05 V (onset potential). The onset potential of the $MnO_2/PEDOT/rGO$ electrode for the ORR was higher than



Figure 6. RRDE voltammograms for ORR on the Pt/C, PEDOT/rGO and MnO₂/PEDOT/rGO modified electrodes at 900 rpm rotation speed and at 10 mV/s scan rate in the same solution.

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Figure 7. The plot of transferred electron number (a) and the Tafel plots (b) for Pt/C, PEDOT/rGO and MnO₂/PEDOT/rGO.

that of the PEDOT/rGO electrode at about -0.12 V. The ring currents detected the amount of generated H₂O₂. The MnO₂/PEDOT/rGO modified electrode showed a lower ring current density than the PEDOT/rGO electrode. This indicates that the ORR has less peroxide production in solution throughout the potential region for O₂ reduction with MnO₂/PEDOT/rGO.

Although the ORR electrocatalytic activity of the asprepared MnO₂/PEDOT/rGO electrode is lower than that of a commercial Pt/C electrode, the ease with which conventional graphene materials can be converted into non-precious metal ORR electrocatalysts simply by the electrochemical method suggests considerable room for cost-effective preparation of various non-precious metal catalysts for ORR.

3.3.3. Kinetic Study

The transferred electron numbers (n) per O₂ involved in the oxygen reduction at the Pt/C, PEDOT/rGO and MnO₂/PEDOT/rGO electrodes were determined using the slopes from Koutecky–Levich equation given below.^{36, 37}

$$1/i = 1/i_{\nu} + 1/i_{\nu} \tag{1}$$

$$i_l = 0.62nFACD^{2/3}\nu^{-1/6}\omega^{1/2}$$
(2)

Here, *i* is the measured current density, i_k is the kinetic current density of the ORR, i_l is the limiting current density, *n* is the overall number of electrons transferred during the oxygen reduction, *F* is the Faraday constant (96,485 Cmol⁻¹), *C* is the bulk concentration of O₂ (1.2 × 10⁻³ M), *D* is the diffusion coefficient of O₂ in the 0.1 M KOH solution (1.9×10^{-5} cm² s⁻¹), ν is the kinetic viscosity of the electrolyte (1×10^{-2} cm² s⁻¹) and ω is the rotating rate (rpm).¹⁸

The Koutecky–Levich plots of -0.3, -0.4, -0.5, -0.6, -0.7, -0.8 and -0.9 V are show a linear dependence at all the potentials in Figure 5. The solid lines are plotted from the plateau current. The *n* value per O₂ molecule was calculated using Eq. (2), the Koutecky– Levich equation. The *n* values per O₂ molecule are shown in Figure 7(a), in which the *n* values were found to be dependent on the potential for the Pt/C, PEDOT/rGO and MnO₂/PEDOT/rGO electrodes. The *n* value is increased

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gradually, and Pt/C and $MnO_2/PEDOT/rGO$ electrodes are maintaining four electron transfer (>3.5) in the cited potentials while the PEDOT/rGO electrode is around only two. Indicating within the range of the ORR proceeded via a four-electron pathway.

The Tafel behavior in the mixed kinetic-diffusion control region was examined using Tafel plots for Pt/C, PEDOT/rGO and MnO₂/PEDOT/rGO electrodes at i_k region (Fig. 7(b)). Generally, the slope of 118 mV observed for bulk Pt, indicates the first electron transfer rate-determining step. The Tafel slopes were 126 mV and 124 mV at MnO₂/PEDOT/rGO and Pt/C, respectively. Although the PEDOT/rGO has 251 mV as Tafel slope. The slope values are different due to the reaction kinetic difference such as, *n* values and Koutecky– Levich slopes.³⁸ Therefore, the rate-determining step for O₂ reduction was identical and the first electron exchange is the rate-determining step on MnO₂/PEDOT/rGO has demonstrated.

The long-term CVs of ORR on MnO₂/PEDOT/rGO and PEDOT/rGO have carried out in 0.1 M KOH to investigate their stability. The plot of peak current density (electrode area normalized, mA cm⁻²) versus cycle number has shown in Figure 8. Therefore, the MnO₂/PEDOT/rGO was much stable than that of PEDOT/rGO for long term application.



Figure 8. The plot of peak current density versus cycle number on PEDOT/rGO and MnO_2 /PEDOT/rGO for long tern stability investigation in O_2 -saturated 0.1 M KOH at a scan rate of 100 mV/s.

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4. CONCLUSION

In this study, we synthesized PEDOT/rGO subsequently was prepared $MnO_2/PEDOT/rGO$ by adding MnO_2 NPs on PEDOT/rGO using an electrochemical method. $MnO_2/PEDOT/rGO$ showed enhanced catalytic activity for ORR. $MnO_2/PEDOT/rGO$ had higher ORR activity than PEDOT/rGO in a 0.1 M KOH solution. The electrocatalytic reduction of O_2 at the $MnO_2/PEDOT/rGO$ electrode established a pathway of four-electron transfer reduction. This type of material will provide an opportunity to develop various low-cost and environment-friendly efficient ORR catalysts, which are essential for practical applications in fuel cells.

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