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Electrochemical deposition of silver on manganese dioxide coated reduced graphene oxide for enhanced oxygen reduction reaction

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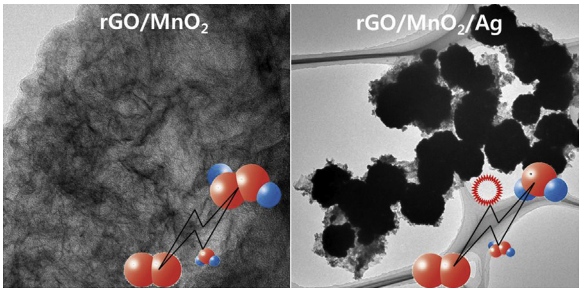
HIGHLIGHTS

- Electrochemical deposition of MnO_2 and Ag, subsequently, onto rGO at rGO/MnO_2/Ag.
- 1.2 folds higher current density on rGO/MnO_2/Ag than Pt/C at 0.3 V during ORR.
- Higher electron transfer rate, better stability & anodic fuel tolerance.
- ORR possess 4-electron pathway with lower H_2O_2 & faster electron transfer kinetic.

GRAPHICAL ABSTRACT



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ABSTRACT

We have prepared a reduced graphene oxide (rGO)-supported silver (Ag) and manganese dioxide (MnO_2) deposited porous-like catalyst (denoted as rGO/MnO_2/Ag) through a facile electrochemical deposition route and have been used as a cathode catalyst for oxygen reduction reaction (ORR) in alkaline fuel cells. The physical properties of rGO/MnO_2/Ag have been investigated *via* several instrumental methods. This material exhibits a polycrystalline structure characterized by Ag/MnO_2 microsphere formation as a result of Ostwald ripening. The X-ray diffraction and X-ray photoelectron spectroscopy data reveal that the MnO_2 and Ag have been slightly alloyed and Mn presents with the dioxide form on rGO. The electrochemical properties of the electrocatalyst have been studied *via* several voltammetric methods. The results demonstrated that the rGO/MnO_2/Ag has an excellent catalytic activity for ORR in alkaline media compared to the other tested electrodes. Particularly, it shows 1.2 times higher current density and better electron transfer rate at 0.3 V per O_2 than that of 20 wt% Pt/C. The other kinetic analysis reveals that the O_2 has reduced directly to H_2O through a nearly four-electron pathway with better anodic fuel tolerance and duration performance than that of 20% Pt/C.

1. Introduction

Graphene is a 2D honeycomb-like structure consisting of sp^2-carbon atoms. The sp^2 π-conjugative structure of graphene that allows to interact with various compounds and metal nanoparticles (NPs) through $\pi-\pi$ electronic interaction [1,2]. The electrochemistry of graphene has gained great interest owing to its unique role in energy conversion and storage devices including fuel cells (FCs) and supercapacitors [1,3–8]. One of the most extensively studied electrocatalytic applications of graphene is the oxygen reduction reaction (ORR) occurring at the cathode of FCs and metal-air batteries due to its unique properties, such as, excellent thermal, mechanical, optical, and electrical characteristics [9–11].

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Typically, the Pt-based materials are usually used as the electrocatalysts in FCs, which are limited by cost, durability issues and CO poisoning [1,3] because of the slow reaction kinetics of ORR on the cathode [12]. Nevertheless, the uses of Pt and Pt based catalysts have been hindered large-scale commercialization and application of FCs [13,14]. Therefore, it is still important to develop a low cost and efficient electrocatalysts for ORR at the cathode in FCs and even metal-air batteries. The recent efforts have been focused on the discovery of electrocatalysts with non-precious metal [15–17] as a replacement of Pt for reducing cost of FCs. Among the various candidates of non-Pt metal catalysts, silver (Ag) is an attractive catalyst to replace Pt. It has already been established that the Ag is a promising electrocatalyst and an attractive alternative of Pt because it's abundantly available in nature and used, much cheaper and higher electrical and thermal conductivity than Pt [18,19]. Previous research has revealed that the Ag is not only less expensive than other noble metals but also has higher catalytic activity. For example, 20% Ag/C shifts 50 mV toward a negative potential when compared to the onset potential of 20% Pt/C with higher methanol tolerance [20]. In addition, Ag cathodes show superior long term stability in alkaline media [21]. Unfortunately, Ag tends to favor H_2O_2 production through the 2-step mechanism [22]. But manganese dioxide (MnO_2) has therefore been combined with Ag, as it capably affects peroxide decomposition [23-26].

It is, however, among all kinds of FCs, alkaline fuel cells (AFCs) are the most attractive due to their superior kinetic activity for the ORR than that of FCs which utilizing acidic media. In addition, AFCs do not require precious metals for stable activity [27]. The ORR takes place in the cathode electrode and could be followed by two main pathways as below:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \tag{1}$$

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \tag{2}$$

In equation (1), O_2 undergoes a single-step four-electron reduction, directly forming H_2O; meanwhile, in equation (2), O_2 first undergoes a two-electron reduction to H_2O_2, followed by an additional two-electron reduction to H_2O [28]. Therefore, because H_2O_2 production inhibits the efficiency of FC, the development of a system that favors the four-electron reduction pathway is crucially needed.

On the basis of the above considerations, we have synthesized rGO/MnO_2/Ag *via* a facile electrochemical deposition route, which has the following merits: First, the porous-like rGO/MnO_2/Ag catalyst is easily synthesized and Mn can be found as a dioxide form. Second, the Mn is slightly alloyed with Ag which may enhance the ORR activity in alkaline media. Third, the as-prepared rGO/MnO_2/Ag exhibits higher tolerance to anodic fuels (i.e. methanol, ethanol) and long term durability during ORR than that of Pt/C. Particularly, the results prove that the rGO/MnO_2/Ag promotes outstanding electrocatalysis for ORR and possess a four electron transfer pathway.

2. Experimental

2.1. rGO synthesis

First, graphene oxide (GO) was prepared by oxidizing graphite (graphite powder (~325 mesh, 99.999%) was obtained from Sigma–Aldrich.) using the modified Hummers method [1,29]. The rGO synthesis was started by mixing 125 mg GO into 250 mL of deionized H_2O for 30 min sonication. Then, deionized H_2O (250 mL), 35% aqueous hydrazine solution (0.5 mL), and 28% aqueous ammonia solution were added subsequently and stirred for 11 h at 100 °C. The black solid product, rGO, was obtained *via* filtration, washed with deionized H_2O, and dried under vacuum for 24 h at 50 °C.

2.2. Electrode preparation by electrochemical deposition

The rGO/MnO_2/Ag was prepared through an electrochemical deposition process, as illustrated in Scheme 1. First, rGO was suspended in H_2O (1 mg mL^{-1}) by introducing a predetermined amount of the rGO under sonication. Then, 16 μL of the solution was dropped on the surface of a glassy carbon electrode (GCE) with a diameter of 0.5 cm that had been polished with a 0.05 μm alumina suspension and a polishing cloth (Bioanalytical Systems). After coating, rGO/MnO_2 was synthesized by sweeping through potentials from 1.3 to 0.5 V at 10 mV s^{-1} for 10 cycles in a 10 mM $KMnO_4$ containing 0.01 M H_2SO_4 aqueous solution [30]. Subsequently, the rGO/MnO_2/Ag was then synthesized by sweeping through potentials from 0.3 to −0.6 V at 100 mV s^{-1} for 30 cycles in a 0.1 M NaCN, 0.1 M $NaNO_3$, and 0.01 M $AgNO_3$ aqueous solution system [31,32]. For comparison, the rGO, and rGO/MnO_2 (as mentioned above) modified GCE have also been employed for ORR. Also, The 20 wt% Pt/C suspension was prepared by dispersing 1 mg mL^{-1} in ethanol in the presence of 5 μL of 5% Nafion solution in aliphatic alcohol and used 16 μL from the suspension onto GCE.

All electrochemical experiments were taken using a three-electrode potentiostat [CHI 700C electrochemical workstation (U.S.A.)]. A Pt wire and Ag/AgCl electrodes were used as auxiliary electrode and reference electrode, respectively. The potential of the Ag/AgCl reference electrode is corrected with the reversible hydrogen electrode (RHE), in 0.1 M KOH, $E_{(RHE)} = E_{(Ag/AgCl)} + 0.982$ V. All electrochemical experiments were performed in a high purity O_2 purged (for at least 30 min) 0.1 M KOH solutions at room temperature (RT, ~25 °C).

2.3. Physical characterization

X-ray photoelectron spectroscopy (XPS) was performed using a VG multilab 2000 spectrometer (ThermoVG Scientific, Southend-on-Sea, Essex, UK) in an ultrahigh vacuum using an unmonochromatized Mg Kα (1253.6 eV) radiation source and a spherical section analyzer. Avantage 4.54 (Thermo Electron, UK) was used for XPS data analysis. Data were collected using a pass energy of 50 eV. Scanning electron microscopy (SEM) images of the modified electrode were obtained on a JSM-7500F microanalyzer (JEOL). The high resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS) were carried out using a Tecnai 20 microscope at 200 kV. XRD spectra were carried out on a Rigaku D/max-2500, using filtered Cu Kα radiation.

3. Results and discussion

3.1. Physical properties analysis of catalysts

Fig. 1(a) shows the entire XPS spectra for rGO, rGO/MnO_2, and rGO/MnO_2/Ag. All spectra have shown signals for C1s, and O1s at around 285 and 531 eV, respectively. The rGO/MnO_2 and rGO/MnO_2/Ag are also showing Mn2p signal at around 654 eV and Ag3d signal shown by rGO/MnO_2/Ag at 368 eV. The C/O ratios (wt%) are significantly decreased from 4.0 to 2.0 and 2.3 (for rGO, rGO/MnO_2, and rGO/MnO_2/Ag, respectively). These values are indicating much higher oxygen in rGO/MnO_2 and rGO/MnO_2/Ag than that of rGO, confirming Mn being in oxidized form [1]. Furthermore, the C/O ratio is higher for rGO/MnO_2/Ag compared to rGO/MnO_2, indicating the degree of Mn oxidation is higher in rGO/MnO_2/Ag [33]. Fig. 1(b)