Oxygen Reduction at Palladium Decorated Copper-Molybdenum Oxide Modified Glassy Carbon Electrode

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Abstract

In this study, metal nanoparticles decorated metal oxide electrode was fabricated via electrochemical technique. Firstly, molybdenum/copper oxide was electrochemically deposited on the bare glassy carbon electrode surface. Then palladium nanoparticles were modified on this oxide functionalized surface by consecutive potential cycles. Resulting composite electrode was characterized with scanning electron microscopy. The proposed composite electrode was employed for electrocatalytic oxygen reduction in alkaline media. As compared to bare electrode, the resulting composite surface has tremendous effect on oxygen reduction in terms of accelerated peak current values.

Keywords: Oxygen reduction, Pd nanoparticles, Molybdenum and Copper oxide.

1. Introduction

Oxygen reduction reaction (ORR) is one of the most studied electrochemical reactions due to its importance in energy field, especially in fuel cells [1].The reduction of oxygen to water can occur via two parallel pathways that are highly influenced by the electrode material. In two step-two electron pathway that known as ''peroxide route'' occur with two electron reduction of oxygen to hydrogen peroxide. The other is reduction of molecular oxygen to water through a four-electron pathway [2]. The electrochemical behavior of oxygen reduction has been studied in alkaline, neutral, and acidic media [3-4].

Catalytic activity of the electrode mainly depends on its composition that is significant to design effective component for electrode modification. For this purpose various modifiers were employed such as carbon nanotubes [5], polymers [6], phthalocyanines [7], metal nanoparticles [8] and metal oxides [9]. In this study, we focus on the metal oxide and metal nanoparticles as electrode modifiers towards ORR.

Metal oxides comprised a significant group of versatile material for electrocatalysis with their high electronic conductivity and stability. Lower costs of metal oxides relative to platinum catalysts make them preferable for many applications. Several studies reported the use of metal oxides as sensitive electrodes for some analytes [10-11], and also oxygen reduction reaction [12].

Metal nanoparticles (MNPs) were also another group of modifier which facilitate electron transfer rate and increase the active surface area of electrode. Pd is one of the most widely used metals among all MNPs due to

its ability to promote electrode reaction [13] that is why it employed by various researchers [14-15].

In this paper, molybdenum/copper oxide (MoOx-CuOx) nanostructure supported on glassy carbon electrode surface (GCE/MoOx-CuOx) using a simple and practical method. And then Pd nanoparticles were modified on this surface by electrochemical technique (GCE/MoOx-CuOx). Electrocatalytic oxygen reduction reaction was investigated in alkaline media and satisfactory peak enhancement was obtained with the proposed electrode.

2. Materials and Methods
2.1. Reagents and Apparatus

Sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$), copper sulfate, sulfuric acid, acetic acid were purchased from Carlo Erba. NaOH was purchased from Riedel de Haen. Palladium acetate was purchased from Aldrich. All solutions were prepared using ultrapure water (Milli-Q 18.2 MΩ cm, Millipore System Inc.).

A GAMBRY 3000 was used for voltammetric studies. All measurements were carried out in a three-electrode system consisting of; a platinum wire as a counter electrode, Ag/AgCl/KCl as a reference electrode, and working electrode (bare GCE, GCE/MoOx-CuOx and GCE/MoOx-CuOx/Pd). Modified electrodes were characterized with scanning electron microscope (SEM; FEI QUANTA 450).

2.2. Preparation and Characterization of GCE/MoOx-CuOx/Pd

The bare GCE was initially freshly polished and the GCE/MoOx-CuOx/Pd was prepared in two steps; at

first, electrode was immersed into the cell containing 0.001 M $CuSO_4$ and 0.01 M Na_2MoO_4 in 0.01 M H_2SO_4 solution. The CV program was applied between the potential of −0.75 V to 0.8 V for 20 cycles (Fig.1a). The resulting electrode depicted as GCE/MoOx-CuOx. Then resulting electrode was immersed in 0.01 M Pd^{2+} containing 0.01 M HCl solution. A CV process was applied for 15 deposition cycles in the -0. 5 V to 0.7 V potential ranges (Fig.1b). Following electrode abbreviated as GCE/MoOx-CuOx/Pd. All modified electrodes were rinsed thoroughly with ultrapure water prior to use and voltammograms were measured at a scan rate of 50 mV s^{-1}.
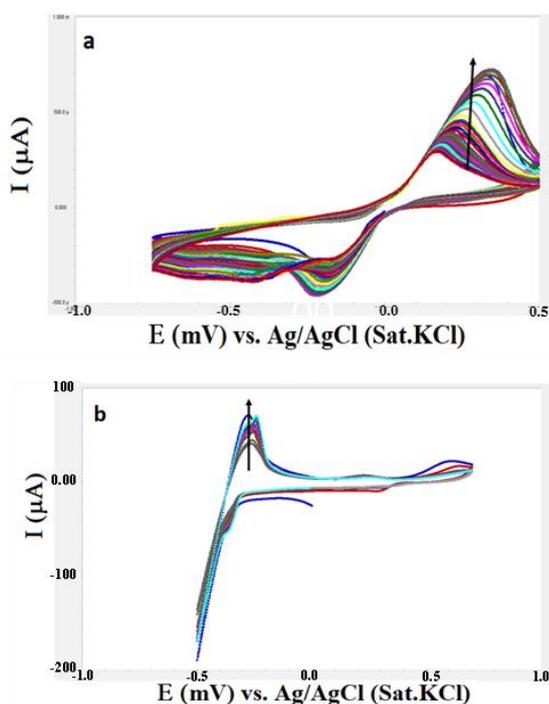

Figure 1. CVs of a) MoOx-CuOx and b) Pd nanoparticles deposition.

3. Results and Discussion

According to the Fig.1a two reduction peaks were occurred at -0.2 and -0.45 V. The peak currents were increased with increasing cycle number and cathodic peak potential shift was observed for these peaks. The peak at -0.2 V was associated with Cu^{2+} reduction [16] and the peak at -0.45 V can be attributed to MoO_4^{2-} reduction [17] at the electrode surface. The potential shift at both peaks indicating the deposition of the Cu and Mo. The peak at +0.25 V can be attributed oxidation of Cu. The deposition of Pd nanoparticles took place at 0.3 V [18] and increased with the increasing cycle number. The peak at -0.3 in anodic direction can be attributed to hydrogen adsorption/desorption peaks.

Characterization of the electrode surface utilized with scanning electron microscopy (SEM). Smooth surface was obtained for bare GCE (Fig.2a) while obviously different structure formed with presence of MoOx-

CuOx (Fig.2b). MoOx-CuOx particles were decorated on the GCE surface with grape-like structure. Moreover, Fig.2c represents the Pd nanoparticles on GCE in order to understand the exact difference between modified surfaces. And finally GCE/MoOx-CuOx/Pd surface was observed at Fig.2d with aggregate like structures. EDX result of GCE/MoOx-CuOx/Pd also confirms the presence of Mo, Cu and Pd content with a 5.4%, 5.3%, and 1.2% weight gain, respectively.
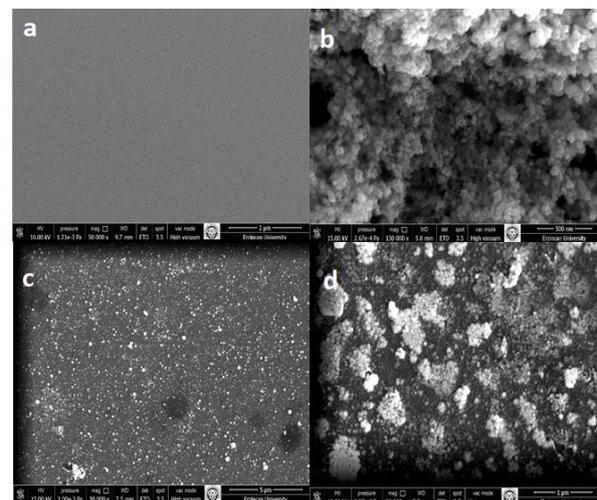

Figure 2. SEM images of a) Bare GCE, b) GCE/MoOx-CuOx c) GCE/Pd and d) GCE/MoOx-CuOx/Pd.

In order to calculate the electroactive surface area (ESA) of electrodes, CV with a ferrocyanide-ferricyanide redox couple is generally used. CVs were recorded at various scan rates in a ferro-ferricyanide redox couple-containing solution; the square root of the scan rate versus the peak current was then plotted. The ESA can be calculated based on the Randles-Sevcik equation as follow the previously published literature [19]. Scan rate studies were conducted for bare and modified electrode (10-350 mV s^{-1}). From the slope of the linear graph line, the electroactive areas of the GCE and GCE/MoOx-CuOx/Pd were calculated as 0.056, and 0.1 cm^2. These results confirm the improved activity of GCE/MoOx-CuOx/Pd towards ORR.

3.1. ORR Investigation with Voltammetry

In order to improve the activity of electrode, modifiers can be optimized. Therefore, cycle number of both Mo-Cu and Pd were studied with increasing values to obtained best results towards ORR. Cycle number of Mo-Cu was varied between 2 to 10 and electrode signal was exhibited in Fig. 3a. Fig 3c shows the effect of cycle number on the ORR peak currents with column graph. 5 number of cycles was chosen as an optimum due to the peak shape and improved current value. Moreover, cycle number of Pd deposition was varied between 5 to 20 (Fig. 3b). Dependence of cycle number on the ORR peak currents were presented with column graph in Fig. 3d. According to the graph, optimum value was chosen as 15 for further studies.
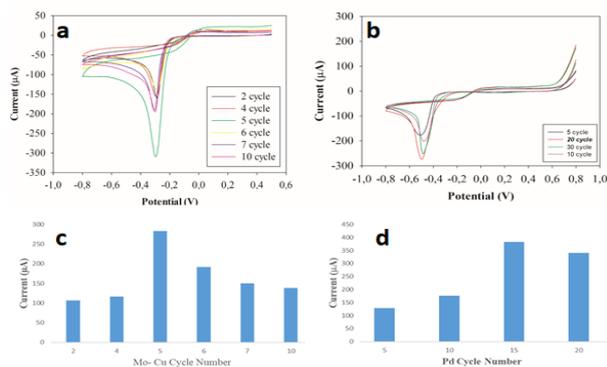
Figure 3. CVs of GCEs modified by electrodeposition of a) CuOx-MoOx and b) Pd nanoparticles with various cycle numbers in 0.1M NaOH at a scan rate of 50mVs⁻¹. Dependence of peak current for ORR on the cycle number used during electrodeposition of c) CuOx-MoOx and d) Pd nanoparticles onto GCE surface.

Comparative cyclic voltammograms of bare GCE, GCE/Pd, GCE/MoOx-CuOx and GCE/MoOx-CuOx/Pd were exhibited in Fig.4. Sluggish reduction peak at more negative potentials obtained for bare GCE and GCE/MoOx-CuOx. Individual presence of Pd nanoparticles improves the peak characteristics both for potential shift to positive values and current enhancement (200 µA). The best catalytic activity towards ORR was achieved with GCE/MoOx-CuOx/Pd in terms of both peak current (600 µA) and peak potential as compared to others.
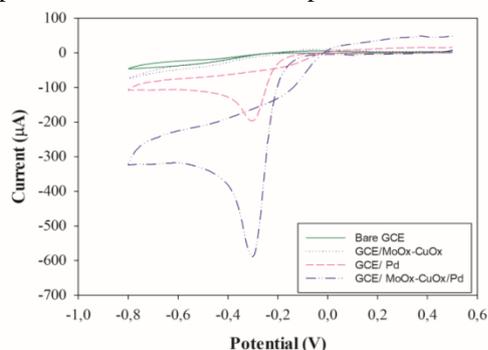

Figure 4. CVs of bare and various modified electrodes towards ORR in 0.1 M NaOH.

All over the results are indicating that the developed electrode is good candidate for fuel cell applications due to the lower ORR potential with high current enhancement. The synergistic effect of metal oxides and palladium nanoparticles not only provided higher peak current but also provide positive potential shift. Since the ORR potential is very important issue for electrocatalysis, the ORR potential is compared to the proper literatures. Xiao et al. used Ag nanoparticle decorated oxygen-doped carbonaceous polypyrrole nanotubes for ORR and the peak potential was found about -0.25 V [20], Pd nanoparticles supported on zeolite-templated mesocellular graphene was used as an electrocatlytic surface for ORR and reduction potential was found -0.2 V [21], and in another study spin coated

Pd nanoparticles was used for ORR and reduction potential was found as -0.3 V [22]. The ORR potential was found as -0.25 V for GCE/MoOx-CuOx/Pd electrode and this value is also compatible with literature values. The proposed electrode exhibited superior catalytic activity towards ORR since small amount of Pd loaded onto the electrode. In addition, electrochemical deposition provides a simple, low-cost and green methodology for the preparation of mixed oxide and Pd nanoparticles.

4. Conclusion

Here, GCE/MoOx-CuOx/Pd was fabricated with simple electrochemical technique with two steps that each step carry out with consecutive potential cycles. The resulting electrode characterized with SEM and existence of each component on the surface was proved with EDX results. The proposed composite GCE/MoOx-CuOx/Pd was used as an efficient surface for electrocatalytic oxygen reduction which significantly improves the peak current of ORR as compared to the other bare and modified electrodes.

Acknowledgement

Ethics

There are no ethical issues after the publication of this manuscript.

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