Cobalt oxide nanoparticle-modified carbon nanotubes as an electrocatalysts for electrocatalytic evolution of oxygen gas

JAHAN BAKHSH RAOOF^{1,*}, FERESHTEH CHEKIN² and VAHID EHSANI¹

¹Electroanalytical Chemistry Research Laboratory, Faculty of Chemistry, Department of Analytical Chemistry, Mazandaran University, Babolsar, Iran

²Ayatollah Amoli Branch, Department of Chemistry, Islamic Azad University, PO Box 678, Amol, Iran

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Abstract. A simple procedure was developed to prepare cobalt oxide nanoparticles (nano-CoO_x) on multiwall carbon nanotube-modified glassy carbon electrode (MWNT/GCE). Scanning electron microscopy revealed the electrodeposition of nano-CoO_x with an average particle size of 25 nm onto MWNT/GCE. Also, the presence of nano-CoO_x was revealed by energy dispersive X-ray spectra. The electrocatalytic activity of nano-CoO_x and MWNT composite-modified GCE (CoO_x-MWNT/GCE) has been examined towards the oxygen evolution reaction (OER) by linear sweep voltammetry. The OER is significantly enhanced at CoO_x-MWNT/GCE, as demonstrated by a negative shift in the polarization curves at the CoO_x-MWNT/GCE compared with that obtained at the CoO_x-GCE and GCE. Optimization of the operating experimental conditions (i.e., solution pH and loading level of nano-CoO_x) has been achieved to maximize the electrocatalytic activity of CoO_x-MWNT/GCE. The maximum electrocatalytic activity towards the OER was obtained in alkaline media (pH = 13). The electrocatalytic activity of CoO_x-MWNT/GCE increased with the number of potential cycles employed for the CoO_x deposition till a certain loading (20 cycles) beyond which an adverse effect is observed. The fabricated CoO_x-MWNT/GCE exhibited a good stability and durability. The value of energy saving per gram of oxygen gas at a current density of 10 mA cm⁻² is 19.3 kWh kg⁻¹.

Keywords. Cobalt oxide nanoparticles; oxygen evolution reaction; multiwall carbon nanotubes; electrolysis.

1. Introduction

Recently, mediator nanomaterials on an electrode as a catalyst to develop electrochemical sensor is a hot topic owing to their large specific surface area, excellent conductivity and catalytic activity.^{1–8} Nanomaterials can be directly used as electrode materials or as catalytic labels for the amplified electrochemical detection.⁹ Among numerous nanomaterials, cobalt (Co)-based nanomaterials have attracted a considerable interest because of its good electroactivity and low cost.^{10–13} For example, the Co hexacyanoferrate nanoparticles (NPs)-carbon nanotube-chitosan can be used to prepare a glucose sensor.¹⁴ Pt-Co NPs supported on single-walled carbon nanotubes (SWCNTs) have been applied in methanol sensing.¹⁵ Co NPs integrated with SWCNTs have been employed for sensitive detection of nitrite.¹⁶ Cobalt oxide-based nanomaterials, in particular, are used for the production of magneto-resistive devices,¹⁷ electrochromic thin films,¹⁸ energy storage systems,¹⁹ heterogeneous catalysts²⁰ and electrocatalysis.²¹ Electrochemical deposition is an economical and convenient choice for preparing uniform and size controllable nanomaterials,²² especially the preparation of metallic nanomaterials.^{23,24}

The oxygen evolution reaction (OER) attracts a reasonable deal of attention as a consequence of its importance

in a wide range of industrial applications, such as water electrolysis, energy conversion and storage devices.^{25–30} There is an extensive work in the literature addressing the development and characterization of suitable anodic materials for the applications in water electrolysis and batteries technology.^{31–33} As alternative to precious metals, metal oxide-based electrodes, particularly Ni and Co oxides, have long been used as electrocatalysts for the OER in alkaline electrolyzers due to their great stability and high activity.^{27,34–37}

In this study, the modification of glassy carbon (GC) and multiwall carbon nanotube-modified glassy carbon (MWNT/GC) electrodes with nano-structured Co oxide (nano-CoO_x) results in a significant enhancement in the electrocatalytic activity towards the OER. The effect of pH of the electrolyte and the effect of loading level of the electrocatalysts on the electrocatalytic activity have been investigated.

2. Experimental

2.1 Chemicals and apparatus

Cobalt nitrate and potassium hydroxide were purchased from Aldrich. Carbon nanotubes (outer diameter: 20–40 nm, length: 5–15 μm, purity > 97) were purchased from Shenzhen Nano-Technologies Port Co., Ltd (China) and were purified

*Author for correspondence (j.raoof@umz.ac.ir)

Figure 1. SEM image of (a) MWNT/GCE and (b) CoO_x -MWNT/GCE.

using a mixture of sulphuric acid and nitric acid in a composition of 3/2 by volume. Electrochemical measurements were performed with an Autolab Potentiostat/Galvanostat (The Netherlands). The three-electrode system consists of CoO_x -MWNT/GCE, CoO_x /GCE and GCE as working electrodes, $\text{Ag}/\text{AgCl}/\text{KCl}_{3\text{M}}$ as the reference electrode and a platinum wire as an auxiliary electrode (Metrohm) were used in all voltammetric experiments. Hitachi S-3500N scanning electron microscope (SEM) with energy dispersive X-ray (EDAX) spectroscopy was used for surface image measurements and chemical characterization of a specimen.

2.2 Preparation of CoO_x -MWNT/GCE

Appropriate amount of MWNTs were dispersed in 1 ml dimethyl formamide with the aid of ultrasonic agitation for 20 min. Prior to use, the GC electrode (diameter 1.8 mm) was first polished with alumina ($0.05\ \mu\text{m}$) slurry and ultrasonically cleaned with ethanol and double distilled water, then dried in room temperature. A quantity of $5\ \mu\text{l}$ of MWNT dispersed solution was coated on the GCE surface and dried in air. The fabrication of the nano- CoO_x on the MWNT/GCE surface was carried out by the cyclic voltammetry technique. Typically, the potential was scanned for 20 potential cycles with a scan rate of $100\ \text{mV s}^{-1}$ in the potential range between -0.7 and $0.8\ \text{V}$ vs. $\text{Ag}/\text{AgCl}/\text{KCl}_{3\text{M}}$ in phosphate buffer solution ($\text{pH} = 7$) containing $1\ \text{mM}$ cobalt nitrate.

3. Results and discussions

3.1 Characterization of CoO_x -MWNT/GCE

Figure 1 shows the SEM images of MWNT/GCE and CoO_x -MWNT/GCE. The SEM images reveal that cobalt oxide

Figure 2. EDAX pattern of CoO_x -MWNT/GCE.

particles with average size of about $25\ \text{nm}$ distributed on the surface of MWNT modified electrode. After the electrochemical modification step, EDAX spectra were carried out at nano- CoO_x -modified MWNT/GC electrode and the corresponding results are shown in figure 2. Inspection of this figure indicates the presence of C, Co and O elements at the electrode surface indicating formation of nano- CoO_x .

3.2 Electrochemical properties of nano- CoO_x deposited on MWNT/GC electrode

Figure 3 shows a cyclic voltammograms of the modified electrodes in $0.5\ \text{M}$ KOH solution in the potential window of -100 to $400\ \text{mV}$ with a potential sweep rate of $100\ \text{mV s}^{-1}$. As shown, at CoO_x -MWNT/GCE (curve b) in comparison to CoO_x -GCE (curve a), the anodic and cathodic peaks shift

Figure 3. Cyclic voltammograms of (a) CoO_x-GCE and (b) CoO_x-MWNT/GCE in 0.5 M KOH at potential scan rate of 100 mV s⁻¹.

Figure 4. (A) Cyclic voltammograms of CoO_x-MWNT/GCE in 0.5 M KOH solution at different scan rates. The scan rates are: (a) 5, (b) 10, (c) 25, (d) 50 and (e) 75 mV s⁻¹, respectively. (B) The plot of cathodic and anodic peak currents vs. scan rates.

towards less positive potentials with an increase in the oxidation and reduction peak current. The increase in peak current results from MWNT, due to high specific surface area, uniform-ordered porous structure and suitable pore size, played an important role in facilitating the electron transfer between the nano-CoO_x and GCE.

A couple of reversible and defined peaks with the apparent formal peak potential (E°) of 60 mV were observed at 100 mV s⁻¹ for CoO_x-MWNT/GCE. An anodic peak at 100 mV attributed to Co(II)/Co(III) redox transition associated with the electrode surface. The cathodic peak at 20 mV correspond to the reduction of various cobalt oxide species formed during the anodic sweep. The stability of the modified electrode was checked by consecutive cyclic voltammograms of CoO_x-MWNT/GCE electrode in 0.5 M KOH. For the CoO_x-MWNT composite almost no activity variation was observed even after 30 cycles, indicating its stability in KOH medium.

The redox potential of the CoO_x-MWNT/GCE is scan rate dependent. Figure 4a shows the cyclic voltammograms of the CoO_x-MWNT/GCE in 0.5 M KOH at various scan rates. It was observed that the values of E_{pa} and E_{pc} shift slightly to the positive and negative directions, respectively, and ΔE_p increases with increasing scan rate. The anodic and cathodic peak currents are linearly proportional to scan rate (figure 4b), suggesting that the reaction is not a diffusion-controlled process but a surface-controlled one.

A plot of E_p vs. $\log v$ yields straight line with slopes of $-2.3RT/anF$ and $2.3RT/(1-a)nF$ for the cathodic and anodic peak, respectively, so that a can be estimated as 0.51 from the slope of the straight lines. The surface concentration of the electroactive nano-CoO_x on CoO_x-MWNT/GCE, Γ (in mol cm⁻²), can be estimated by below equation:³⁸

$$\Gamma = Q/nFA, \quad (1)$$

where Q is the charge consumed in coulombs, obtained from integrating the anodic (or cathodic) peak area in cyclic voltammograms under the background correction, A is the electrode surface geometrical area (0.025 cm²), n represents the number of electrons involved in reaction ($n=1$) and F is Faraday constant ($F = 96493 \text{ C mol}^{-1}$). The average Γ value of $6.22 \times 10^{-10} \text{ mol cm}^{-2}$ was obtained.

3.3 Electrocatalytic behaviour of CoO_x-MWNT/GCE

Previous reports showed that nano-CoO_x-modified electrodes could display an electrochemical response towards the OER.^{36,37} Here, the electro-catalytic activity of CoO_x-MWNT/GCE in OER was also observed. As it is seen from figure 5, linear sweep voltammograms (LSVs) obtained for bare GCE, CoO_x-GCE and CoO_x-MWNT/GCE in 0.5 M KOH, the OER at bare GCE requires very high

positive potentials, leading to a poorly defined anodic wave involving very slow electrode kinetics. In contrast, OER at the CoO_x -GCE and CoO_x -MWNT/GCE in 0.5 M KOH occurred at much less positive potentials with an increase in current density. Also, a significant decrease of potential at a current density of 20 mA cm^{-2} (E_{20}) at the CoO_x -GCE (0.73 V) and CoO_x -MWNT/GCE (0.70 V) compared with GCE (>1.50) was observed. This indicates a significant enhancing role of the nano- CoO_x towards the OER. This corresponds to an equivalent decrease in the energy consumption accompanying the overall electrolysis process.

In order to express potential in terms of the oxygen overpotential, η (when the reference electrode is Ag/AgCl electrode) can be estimated using the equation:^{36,37}

$$\eta = E_{\text{meas}} - 0.207 \text{ V}, \quad (2)$$

where, E_{meas} is the measured electrode potential for the OER.

Table 1 lists the oxygen evolution of overpotentials (η) at the GCE, CoO_x -GCE and CoO_x -MWNT/GCE in 0.5 M KOH at various current densities. There is a variation of the values of η at the three substrates, at the same current density. What is also seen is that the overpotentials are lower on CoO_x -MWNT-modified GCE than on the CoO_x -MWNT-modified GCE. This might be attributed to great stability and high activity of nano- CoO_x electrocatalys at the surface MWNT/GCE for the OER.

Figure 5. LSV response for the OER in 0.5 M KOH at the (a) GCE, (b) CoO_x -GCE and (c) CoO_x -MWNT/GCE at potential scan rate of 100 mV s^{-1} .

Table 1. Oxygen evolution overpotential at modified electrodes in 0.5 M KOH at different current densities.

$I/\text{mA cm}^{-2}$	η/mV		
	GCE	CoO_x -GCE	CoO_x -MWNT/GCE
10	895	493	473
20	—	513	493
30	—	603	573
40	—	623	583
50	—	643	593
60	—	743	603

3.4 Effect of the nano- CoO_x loading level

The effect of loading of the nano- CoO_x on the electrocatalytic activity towards the OER is investigated to achieve the highest catalytic activity. As mentioned, CoO_x was electrodeposited by a potential cycling method, the number of potential cycles was varied to control the loading level of the nano- CoO_x on the MWNT/GCE. The corresponding LSVs of the OER at CoO_x -MWNT/GCE at different number of potential cycles were recorded in 0.5 M KOH and are shown in figure 6. The catalytic enhancement of the OER increases at the beginning with the increase in the number of potential cycles. The highest catalytic enhancement was obtained at the MWNT/GC electrode after depositing the nano- CoO_x for 20 potential cycles. When the number of potential cycles increased to 50, a significant reduction in the electrocatalytic activity was noticed.

3.5 Effect of pH

The effect of solution pH on the electrocatalytic activity of the CoO_x -MWNT/GCE towards the OER was examined by measuring the LSVs at the CoO_x -MWNT/GCE at various pH values (figure 7). As depicted from this LSVs, the maximum

Figure 6. LSV responses of CoO_x -MWNT/GCE at different number of potential cycles for the OER in 0.5 M KOH at potential scan rate of 100 mV s^{-1} .

Figure 7. LSV responses of CoO_x -MWNT/GCE for the OER in different pH of KOH solution at potential scan rate of 100 mV s^{-1} .

Table 2. The shift potential and the rate of energy saving at the anode obtained after the modification with CoO_x–MWNT at various current densities.

<i>I</i> /mA cm ⁻²	$\Delta E_{(a)}/\text{mV}$		$P_{(a)}/\text{kWh kg}^{-1}$	
	CoO _x –GCE	CoO _x –MWNT/GCE	CoO _x –GCE	CoO _x –MWNT/GCE
5	600	610	16.08	16.35
10	700	720	18.76	19.30
20	827	900	22.16	24.12

current densities of the OER was obtained in alkaline solution (pH = 13) at every current density. Stability of the active phase of CoO_x decreases in the electrocatalytic activity at neutral and acidic media. These results are similar to previous observation at the nano-NiO_x and nano-CoO_x modified electrodes.^{36,37} The OER proceeds, in alkaline medium, via the following steps sequentially:^{36,37}

3.6 Energy savings

The values of the rate of power savings of oxygen gas were calculated and are listed in table 2. The significant decrease in the potential obtained after the modification with nano-CoO_x corresponds to a reduction in the rate of energy consumption at the anode and consequently, decreases the energy consumption in the overall process. The energy saving at the anode is given by:^{36,37}

$$P_{(a)} = \Delta E_{(a)} F / 3600, \quad (7)$$

Where $\Delta E_{(a)}$ is anodic potential shift at a current density and $P_{(a)}$ is the KWh per kg of oxygen gas. The values of $P_{(a)}$ calculated at different current densities are listed in table 2. From the data in table 2, the best energy saving of oxygen gas is obtained at CoO_x–MWNT-modified GCE.

4. Conclusions

A cheap nano-sized electrocatalyst is introduced as an anode for water electrolysis. Nano-CoO_x electrocatalyst is fabricated in aqueous medium by a potential cycling method. SEM image shows the formation of nano-CoO_x with average particle size of 25 nm. The electrocatalysis of OER at modified electrodes with CoO_x–MWNT has been examined using LSV. The OER is significantly enhanced upon modification of the electrodes with CoO_x–MWNT, as demonstrated by a negative shift in the LSV curves at the

CoO_x–MWNT-modified electrodes compared to that obtained at the unmodified ones. The maximum electrocatalytic activity towards the OER is obtained in alkaline medium (pH = 13) after depositing the nano-CoO_x for 20 potential cycles to control the loading level of the nano-CoO_x on the MWNT/GCE. The fabricated CoO_x–MWNT-modified electrodes exhibited a good stability and durability as revealed from the experiments.

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