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Controlled Electrodeposited of Cobalt Oxide Nanoparticles on Graphenized Pencil Lead Electrode as Efficient Electrocatalyst for Oxygen Evolution Reaction in Alkaline Medium

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Abstract

In this study cobalt oxide nanoparticles were electrodeposited on the surface of graphenized pencil lead electrode (GPLE) as a low cost and efficient electrocatalyst for the OER in alkaline media. The prepared cobalt oxide modified GPLE (CoOx/GPLE) was carefully characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, electrochemical impedance spectroscopy and cyclic voltammetry techniques. The developed electrocatalyst represents remarkably low OER overpotential of 1.41V (vs. RHE) at the current density of 10 mA cm^{-2} and Tafel slope of 149 mV dec^{-1} in 0.1 M KOH solution. The CoOx/GPLE was highly stable and capable for maintaining catalytic activity for at least 5 h. Due to distinctive electrical conductivity, high mass transfer, and adequate active sites of GPLE, the electrocatalytic activity of the cobalt oxide nanoparticles were incredibly improved in CoOx/GPLE.

Keywords: Oxygen evolution reaction, Graphene, Cobalt oxide nanoparticles

Introduction

Abundance, ease of discovery, transportation and usability has made the fossil fuels such as natural gas, coal, oil and gasoline as the first source of energy for industrial and daily uses since 18th century. Massive consumption of these substances, can give off big amounts of carbon dioxide and sulfur dioxide leading to greenhouse effect and acid rains respectively. Due to global warming, oil leaks caused from transportations and oil rigs and non-renewable nature of these fuels, finding suitable alternatives energy source is necessary. In many studies hydrogen is proposed as a green, renewable and cheap candidate to fill the role. For this propose, researches are being conducted in different fields such as fuel cells [1], photocatalysis [2], electrolysis [3], biomass and CO_2 conversion technologies [4] to overcome the hydrogen evaluation challenge. Among these techniques, electrolysis and water splitting has various merits such as being pollution free process, high degree of purity, simplicity of the process and abundance of resource [5-8].

The process of electrochemical water splitting is a chemical reaction for splitting of water into its origin elements, which provides an efficient way for producing hydrogen. Water splitting consists of two half reactions of oxygen evaluation reaction (OER) and hydrogen evaluation reaction (HER). Kinetically, the OER is tardy and it necessitates over potential which are larger than the assessed theoretical over potential (1.23 V) [9]. For this reason, an efficient electrocatalysts needed to hasten reaction rate, reduce over potential, and improve the energy conversion efficiency. Noble metals and their oxides such as Ru, Pt and Pd have been used as the most efficient electrocatalysts for the task of water splitting [10]. Considering scarcity and high expenses of these elements, demand a suitable replacement which to be stable, cheap and active in various conditions is required. For this purpose, transition metal oxides/hydroxides, metal sulfides and metal phosphides has drawn lots of attentions.

New studies tend to employ cobalt based electrocatalysts since they fulfill mentioned conditions [11-13]. Abundance, low expense, and its worthy electrocatalytic behavior for water splitting reactions make the cobalt-based materials as suitable choice for present study.

According to previous studies, exfoliation of pencil lead electrode (PLE) is a newly emerged method for obtaining graphene in a simple and inexpensive manner [14]. By applying anodic and cathodic potentials and successively, PLE exfoliates into graphenized pencil lead electrode (GPLE). Owing to outstanding properties of GPLE such as high surface to volume ratio and excellent conductivity and electron transfer rate, electrodeposition of cobalt oxide on GPLE could result an efficient electrocatalyst for OER.

In this study, cobalt oxide nanoparticles were controllably electrodeposited on the surface of GPLE. The developed electrocatalyst was successfully used for OER in alkaline media. High electrical conductivity, fast mass transfer, adequate active sites and cheapness have made the developed electrocatalyst as stable and utilizable electrocatalyst for OER.

Experimental

Chemicals and Materials

The pencil lead graphite rod (HB grade) was purchased from Rotring Co. LTD, Germany (R 505210N) with a diameter of 2.0 mm. $CoCl_2 \cdot 6H_2O$ was provided by Sigma-Aldrich (St. Louis, MO, USA). Standard solution of 0.1 M Co (II) and 0.1 M KNO_3 were prepared and stored at 4 ˚C for further use and diluted as necessary. All other chemicals were of analytical grade and were used without further purification.

Apparatus

Cyclic voltammetry (CV) and amperometry studies were carried out using an AUTOLABPGSTAT-204 (Metrohm, Switzerland) equipped with an USB electrochemical interface and driven NOVA software in conjunction with a three-electrode system and a personal computer for data storage and processing. The utilized three electrode system was composed of a saturated (KCl) calomel electrode (SCE) as the reference electrode, a platinum wire as the auxiliary electrode and modified electrodes as the working electrodes. Scanning electron microscopy (SEM) images were obtained using a Phenom ProX scanning electron microscope (Hitachi, Tokyo, Japan). An AC/DC power supply was used for electrochemical exfoliation of pencil lead electrodes.

All the potentials recorded in this research work were converted to the reversible hydrogen electrode (RHE) values using the following equations:

$$E_{\mathrm{RHE}} = E_{\mathrm{Ag}/\mathrm{AgCl}} + 0.0591\,\mathrm{pH} + 0.197 \quad \text{(Eq. 1)}$$

and the overpotential (η) was acquired by the following equation:

$$\eta = E_{\mathrm{RHE}} - 1.23\ \mathrm{V} \quad \text{(Eq. 2)}$$

Preparation of graphenized pencil lead electrode

For preparation of GPLE, the obtained pencil lead electrodes (diameter of 2 mm) were polished using polishing papers (mesh of 800 and 1200), and after conjunction with a copper wire, the resulted electrode was wrapped in Teflon stripes to a point that only tip left exposed. Two of the resulting pencil lead electrodes as anode and cathode was rinsed with doubly distilled water and dipped upright in 1 M sulfuric acid solution for exfoliation process. The electrochemical exfoliation was carried out by applying an optimized potential (alternating bias between +8 V and −8 V for 5 cycles and each cycle consisting of 1 second). Through applying positive potentials to the PLE, positive charge at the electrode will be occurred, leading to attraction and intercalation of bulky negative ions such as sulfate anions. This process, in turn expands the interlayer spacing between graphene sheets and results in the subsequent exfoliation of the sheets. Similarly, in cathodic exfoliation by applying a negative bias to the PLE, positively charged ions in the solution enter in between graphene layers, spacing sheets and aiding the exfoliation further. The prepared electrodes were left to dry in room temperature and stored until further use and modifications.

Preparation of cobalt oxide modified graphenized pencil lead electrode (CoOx/GPLE)

For electrodepositing of the CoOx on the fabricated GPLE, cyclic voltammetry method was employed. Figure 1 illustrates the successive CVs of the GPLE in 0.01 M Co (II) and 0.01 KNO_3 at the scan rate of 50 mV s^{-1}.

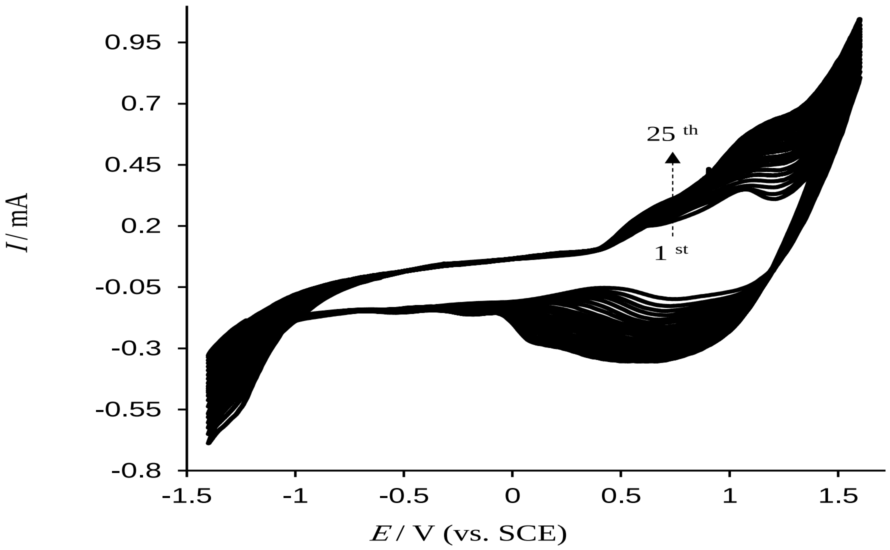

Figure 1. Cyclic voltammograms during the electrodeposition of cobalt oxide on GPLE in 0.01 M $Co(NO_3)^{2+}$ and 0.01 M KNO_3, scan rate of 50 mV s^{-1} for 25 cycles

At early cycles, two separate peaks appear at about 0.6 and 1.1 V, which gradually grows and merges into a single broad anodic peak in later cycles. Also, another cathodic peak was perceived at about 0.75 V which grows and broadens similarly. This uneven number of peaks and their location of occurrence indicates that this electrochemical process can be interpreted as quasi reversible [15]. Both of the oxidation and reduction peaks tend to intensify during increasing repetitive cycles indicating the deposition of CoOx on the

GPLE surface according to equations 3 and 4:

$$\mathrm{Co(OH)_2 + OH^- \longleftrightarrow CoOOH + H_2O + e^-} \quad \text{(Eq. 3)}$$

$$\mathrm{CoOOH + OH^- \longleftrightarrow CoO_2 + H_2O + e^-} \quad \text{(Eq. 4)}$$

Results and discussion

Characterization of CoOx/GPLE

For the purpose of studying characteristics of the CoOx/GPLE electrode, SEM images of the GPLE as well as fabricated CoOx/GPLE were acquired Fig. 2. As apparent in Figure 2A and 2B, exfoliation of graphite into a rough, jagged and three dimensional layered of graphene can be seen on the surface of GPLE. As these images show, a semi porous morphology was obtained by utilizing harsh exfoliation method. SEM Imaging of CoOx/GPLE electrode clearly depicts the fact that cobalt oxide nanoparticles are properly dispositioned and trapped in the spikey network of the graphene layers and has formed a granular nanocluster on porous exfoliated graphene layers (3C and 3D).

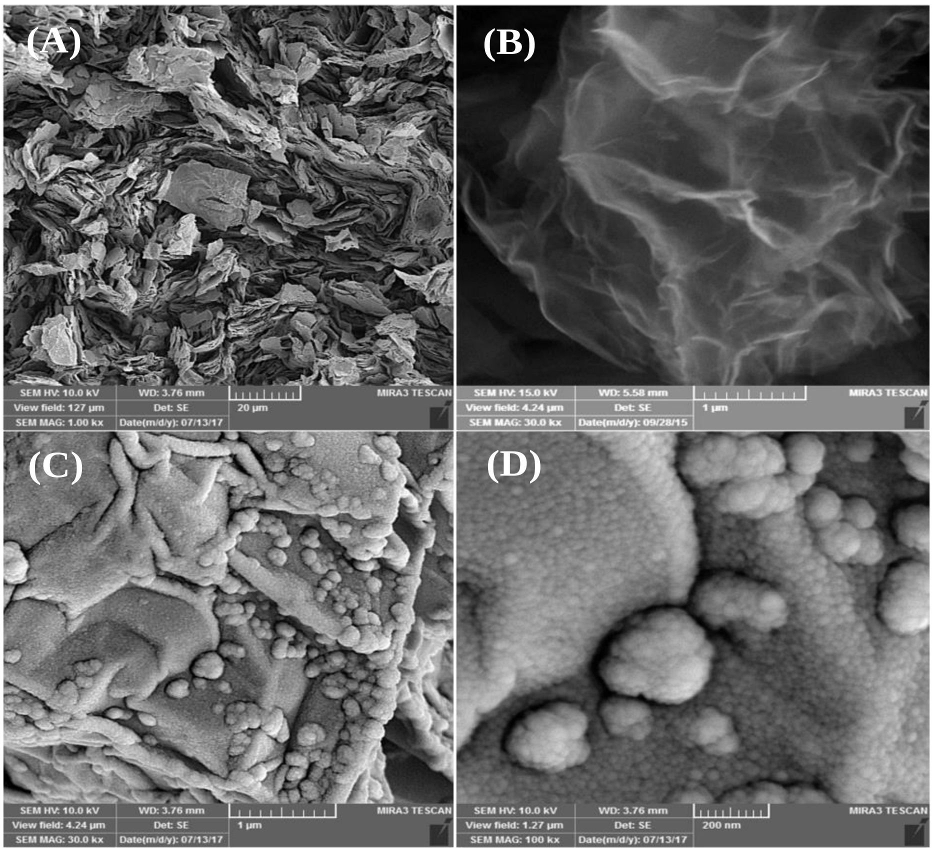

Figure 2. SEM images taken from surface of GPLE (A and B), and CoOx/GPLE at different magnifications (C and D)

Results from the acquired images supports the idea of suitability of the GPLE for the task of electrodeposition of solid-state transition metal oxides, and fabrications of desired electrochemical electrodes. Similarly, encrusted rough structure of GPLE could be supportive for mass transfer and stabilization of electroactive reagents in desired modified electrodes.

Electrochemical behavior of CoOx/GPLE

After completion of electrochemical deposition procedure of CoOx on GPLE, the fabricated electrodes were engaged in CV method for electrochemical characteristic assessment. Cyclic Voltammograms of CoOx/GPLE, GPLE, and PLE were assessed in 0.01 M solution of NaOH (pH=12) with potential window of -1 V to 0.9 V and scan rate of 0.05 mV s^{-1}. Comparison of the three obtained CVs are shown in Figure 3. As represented, there are no redox peaks for neither of PLE nor GPLE, albeit an amplified background current for GPLE is obvious. Attained electrochemical behavior of CoOx/GPLE is almost identical to its electrodeposition plot, but the redox peaks have occurred in different potential values.

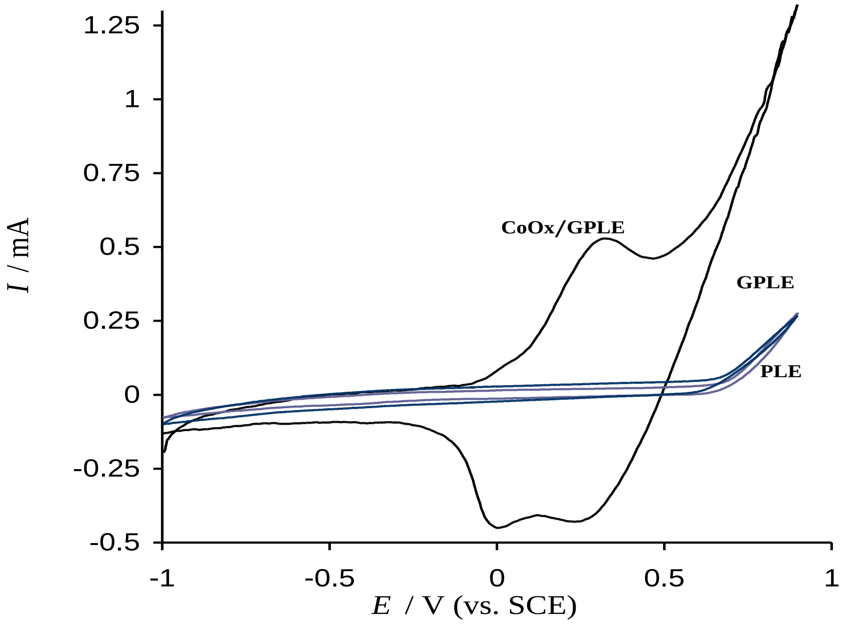

Figure 3. Cyclic voltammograms corresponding to electrochemical behavior of CoOx/GPLE in 0.1 M KOH, at the scan rate of 25 mVs^{-1}

In order to obtain more information about the nature of the electrode reaction, cyclic voltammograms of CoOx/GPLE were recorded in different scan rates (25 to 175 mV s^{-1}) in 0.01 NaOH (Figure 4). The well-ordered increase in all peaks current vs. scan rate express a linear behavior which anticipated for surface redox reactions.

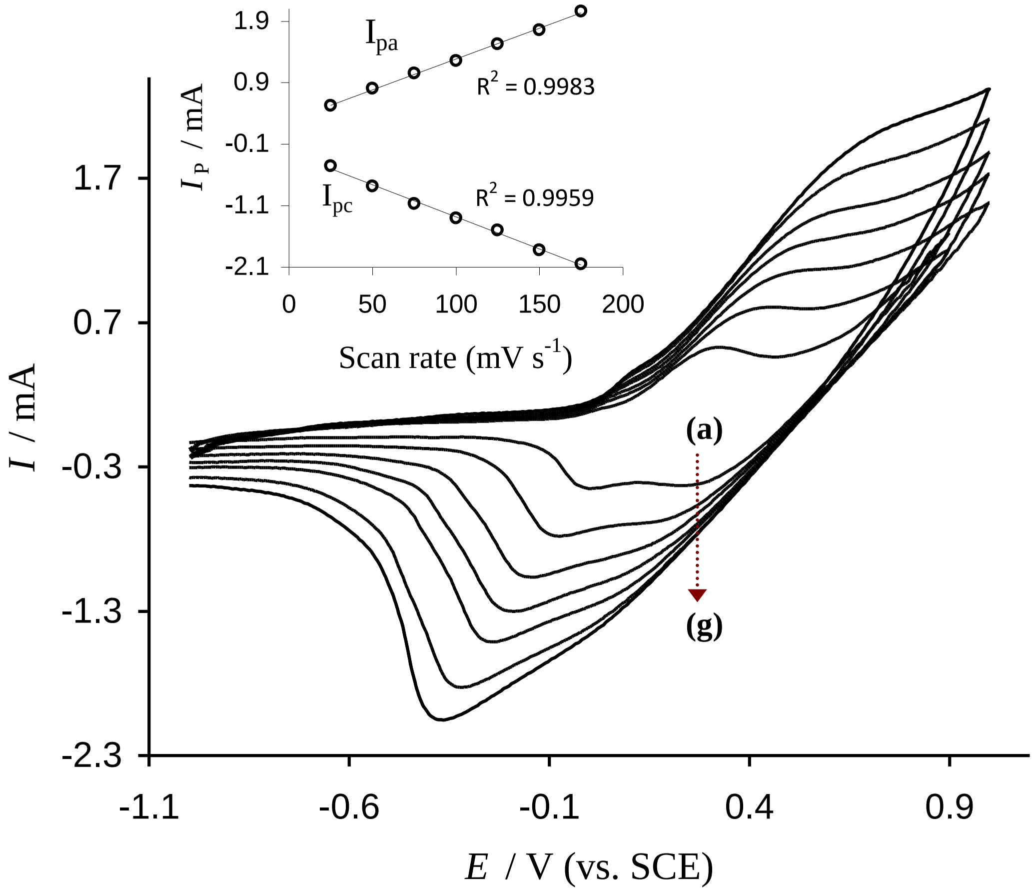

Figure 4. Cyclic voltammograms of the CoOx/GPLE in 0.1 M KOH solution (pH 12), at different scan rates; Inset shows the relation of anodic and cathodic peak currents vs. the scan rate

To compare the charge transfer rate of PLE, GPLE and CoOx/GPLE, Nyquist plots of the electrodes were recorded in the frequency of 0.1 to 10^5 HZ and the results was shown in Figure 5. As can be seen, the semi-circle radius of the Nyquist diagram for the CoOx/GPLE (c) in decreased in comparison with PLE (a) and GPLE (b) proving that charge transfer performance of CoOx/GPLE in intensified.

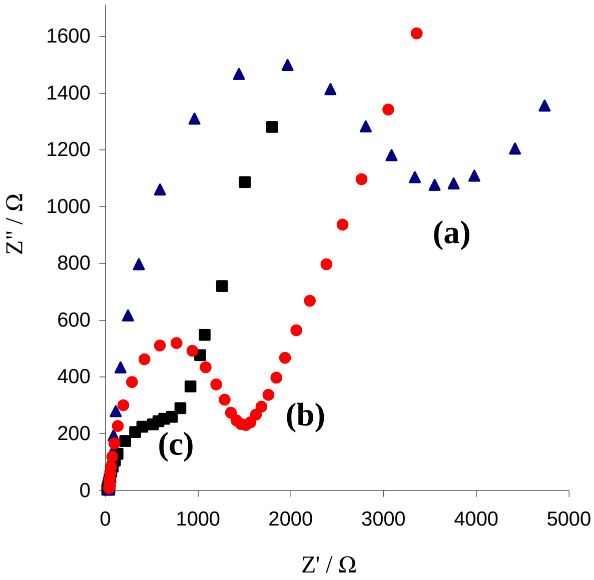

Figure 5. Nyquist plot of the PLE (a), GPLE (b) and CoOx/GPLE (c)

Oxygen evaluation reaction

For observing the electro-catalytic properties of prepared CoOx/GPLE, oxygen evaluation reaction has been conducted in 0.1 M KOH by employing linear sweep voltammetry method (LSV). The resulting LSVs of CoOx/GPLE, GPLE and PLE are represented in Figure 6A. By considering the current density of 10 mA cm^{-2}, the OER potential was shift to more negative value in the case of CoOx/GPLE proving its astonishing electrocatalytic performance in water oxidation. Also, the inset potential of CoOx/GPLE is more negative because of the high electrocatalytic ability of CoOx as well as elevated surface to volume ratio of the fabricated electrode.

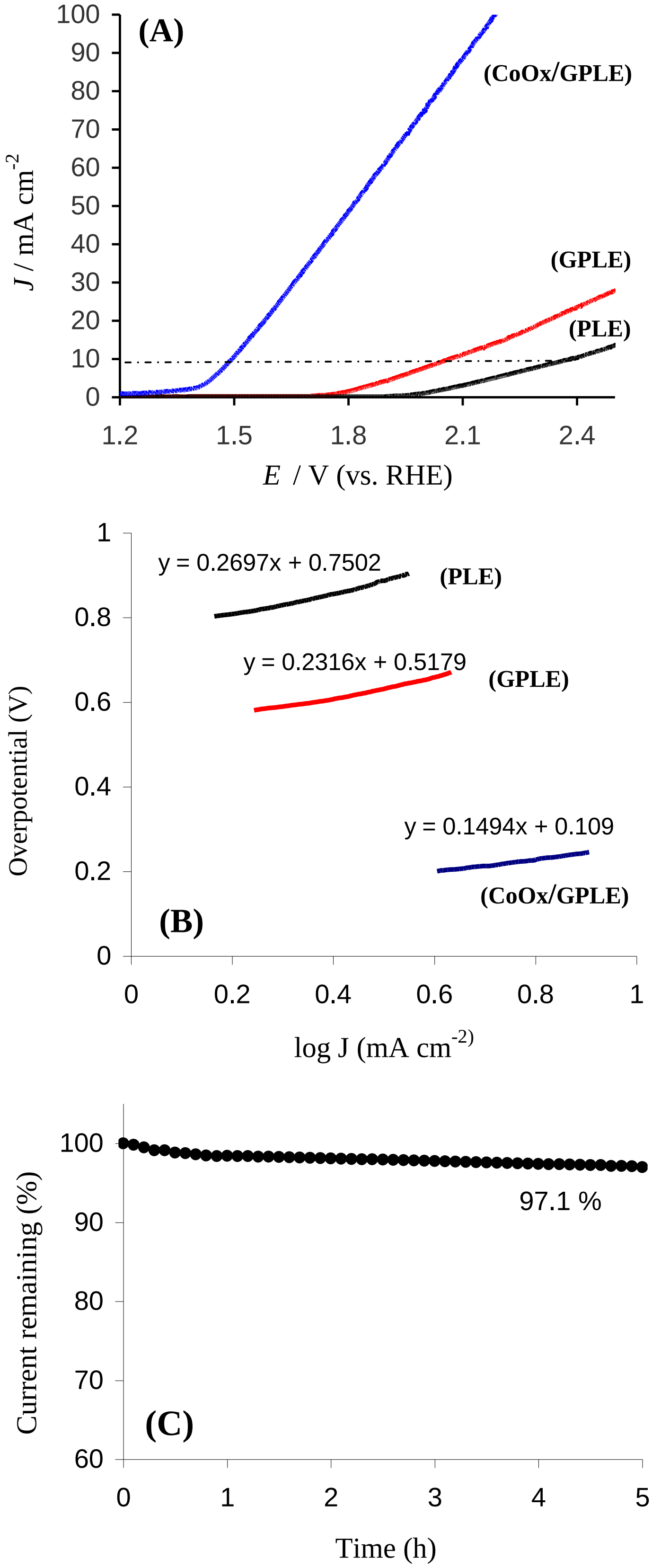

Figure 6. (A) OER curves and (B) Tafel plot of the CoOx/GPLE, GPLE and PLE; (C) OER I-t curve for stability assessment of CoOx/GPLE in a 0.1 M KOH solution

In order to evaluate the kinetic of OER on the electrode surfaces, the Tafel plot were recorded (Figure 6B) in 0.1 M KOH solution which are corresponding from Figure 6A. By comparing the results, it can be found that, CoOx/GPLE exhibits the highest slope in comparison with GPLE and PLE which reflect the suitable electrocatalysts behavior of CoOx/GPLE for the OER.

The matter of chemical and mechanical stability is vital for the developing of electro catalysts. The stability of fabricated Co-GPLE has been put to test for continues OER for 5 hours under the same conditions using E-t curve. As presented in Fig. 6C, after showing an initial drop, current density turns out to be rather stable and the values remain fairly fixated at this time period. Also, the OER test were conducted multiple times over a month using a single and same electrode. The recorded current densities did not show considerable changes proving high stability of the fabricated CoOx/GPLE.

Conclusions

In summary, a novel and efficient electrocatalyst for OER using graphenized pencil lead electrode modified cobalt oxide nanoparticles was reported. Controllable electrodeposition process improved the catalytic performance of the fabricated CoOx/GPLE. The superior properties of the prepared electrocatalyst originated from the 3D and porous structure of GPLE, and high catalytic properties and stability of CoOx/GPLE. Owing to the ease of the preparation method, inexpensive materials and highly effective OER catalytic activity, the developed electrocatalyst is a promising candidate for water splitting and energy conversion devices.

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