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Research Paper

Palladium-Cobalt on Reduced Graphene Oxide as an Electro-catalyst for Ethylene Glycol Oxidation in Alkaline Medium: Synthesis and Electrochemical Performance

Hamid Reza Asgari[1], Somayeh Majidi[2*]
1. Department of Chemical Engineering, Health, Safety and Environment, Najafabad Branch, Islamic Azad University, Najafabad, Iran.
2. Department of Chemistry, Najafabad Branch, Islamic Azad University, Najafabad, Iran.

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ABSTRACT

In this study, Pd-Co alloying nanoparticles supported on reduced graphene oxide (rGO) were synthesized and characterized by various techniques such as field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray (EDX), X-ray diffraction (XRD), and Raman spectra. The prepared Pd-Co/rGO nanoparticle was used as the electro-catalyst for the ethylene glycol (EG) oxidation reaction in the alkaline medium. The activity of Pd-Co/rGO was evaluated in the half-cell by cyclic voltammetry (CV) technique. Results demonstrate that Pd-Co/rGO electro-catalyst has higher performance compared to simple alloyed-based Pd electro-catalysts for EG electro-oxidation in alkaline media. Pd-Co/rGO catalyst showed well-defined peaks for the EG oxidation reaction after 150 CV cycle. This result indicated that Pd-Co/rGO electro-catalyst is still active in EG oxidation reaction even after 150 CV cycles, suggesting high poisoning toleration of Pd-Co/rGO electro-catalyst in the EG oxidation reaction. The results of electrochemical experiments indicated that Pd-Co/rGO could be practically used as the high-efficiency anode electro-catalyst for the EG oxidation reaction in alkaline media.

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[*] **Corresponding Author**
E-mail address: s.majidi@pmt.iaun.ac.ir

1. Introduction

Direct alcohol fuel cells (DAFCs) represent one of the most promising renewable and clean energy devices found in portable, stationary, and mobile applications. DAFCs employ a wide range of liquid fuels such as mono-valent alcohols and aliphatic diols. Ethylene glycol (EG) as an alcoholic fuel has the following advantages: 1) renewable bio-fuel from the biomass fermentation, 2) low toxicity compared to methanol, 3) high theoretical mass-energy density (EG: 5.2 kWh kg^{-1}), 4) high-efficiency energy conversion, 5) easy to store and carry and 6) cheap and wide sources [1-3]. Therefore, developing such green, low-cost, and high-efficiency anodic fuel is desirable for direct EG fuel cells (DEGFCs).

The development of catalysts with high electro-catalytic activity for DEGFCs application is a central issue to accelerate the clean energy technology in an affordable manner [4, 5]. Due to the unique chemical, physical and electronic properties of Pt, it is one of the most common catalysts used for alcohol oxidation in DEGFCs. However, Pt and Pt-based catalysts easily adsorb intermediates of alcohols oxidation (e.g., CO), and their electro-catalytic activity is reduced rapidly [6]. Moreover, Pt is a precious metal with limited global reserves, resulting in considerable efforts to lower the Pt loading or even replace it with less expensive materials [7].

In general, three kinds of electro-catalyst (i.e., Pt-based, Pd-based and Au-based catalysts) have been regarded as electro-catalysts for the electro-oxidation of EG in alkaline media as follow: (i) Pt-based catalysts such as Pt-Ag nanotubes [8], Pt-CeO_2/C [9, 10], Pt-Co/rGO [11], Pt-Pd/rGO [12], Au-Pt deposited on Ni nano-particles [13], (ii) Pd-based catalysts such as Pd-M bimetallic electro-catalysts (M: Ni or Sn) supported on sulfonated multi-walled carbon nanotubes [14], Pd-In [15], Pd-Ni decorated manganite [16], Pd-(Ni-Zn)/C [17], FeCo-Fe-Pd/C [18], oxide (CeO_2, NiO, Co_3O_4 and Mn_3O_4)-promoted Pd/C [19, 20], (iii) Au-based catalysts such as oxide (CeO_2, Fe_2O_3 and RuO_2)-promoted Au/C [21], Pt-Au [22], Au-Bi/C, Pd-Au/C and Pd-Au-Bi/C [23]. The past studies on the electro-catalysts for EG electro-oxidation indicated that the electro-catalytic activity, stability, and durability of electro-catalysts could be further improved with binary alloy catalysts. The addition of the second transition non-precious metals, such as Co, forms a binary alloy with Pd, resulting in altering the electronic structures of the two metals (by shifts in the binding energy in X-ray photoelectron spectroscopy (XPS)). Furthermore, the surface segregation phenomenon of alloying leads to the suitable arrangement of the Co next to the Pd surface atoms [24, 25]. Apart from electro-catalyst alloying, the employment of reduced graphene oxide (rGO) as electro-catalyst support helps the effective dispersion of nano-catalyst and reduction in CO poisoning, this activates the functional sites of the catalyst due to its hydrophilic nature. In addition, rGO has many merits of a large theoretical specific surface area, high intrinsic mobility, and high thermal and electrical conductivity [26, 27].

To the best of our knowledge, Pd-Co/rGO electro-catalyst applied for EG oxidation reaction has not been reported so far. However, it is presented in the following articles that Pd-Co/rGO exhibits higher electro-catalytic activity in the oxidation of ethanol, formic acid, and methanol compared with the Pd electrocatalyst. Rostami et al. [28] synthesized the Pd-Co/rGO electrocatalyst, which had electrochemical catalytic ability toward the ethanol electro-oxidation in the alkaline medium. For Pd-Co/rGO, it was evidenced that the onset potential (E_s) and the peak current density (j_P) are 160 mV lower and 2.5 times higher than that of the Pd/C electrocatalyst, respectively. Results determined that the anti-poisoning ability of Pd-Co is improved by rGO as a catalyst support.

Duck et al. [29] prepared Pd-Co nano-structures decorated on graphene (Gr) as an electrocatalyst toward the formic acid electro-oxidation. The Pd-Co/Gr increased j_P to 7 times more than Pd/C. In addition, the E_s and peak potential (E_P) for Pd-Co/Gr electrocatalyst indicated a negative shift in comparison to Pd/C. The chronoamperometry (CA) experiment showed that the stability of the Pd-Co/Gr catalyst was significantly upgraded. Wang et al. [30] described a method for synthesizing carbon-supported Pd–Co core-shell nano-particles. PdxCo@Pd/C had a high activity comparable to Pt/C, exhibiting a high tolerance of PdxCo@Pd/C toward methanol in the oxygen reduction reaction. Wang et al. [30] also described a method for synthesizing carbon-supported Pd–Co core-shell nanoparticles. PdxCo@Pd/C had a high activity comparable to Pt/C, exhibiting a high tolerance of PdxCo@Pd/C toward methanol in the oxygen reduction reaction. Wang et al. [31] provided Pd-Co nano-particles supported on rGO sheets. Electrochemical measurements confirmed that the Pd-Co/rGO exhibits excellent performance for ethanol and methanol electro-oxidation in the alkaline medium with slightly decreased activity but significantly improved stability compared to Pd/rGO.

In this paper, Pd-Co alloy nanoparticles based on rGO were synthesized and employed as a promising candidate for the electrocatalyst toward EG oxidation in the alkaline medium. This electrocatalyst was prepared through a simple co-reduction process and characterized using field emission scanning electron microscope (FE-SEM), energy-dispersive X-ray (EDX), X-ray diffraction (XRD) technique, and Raman spectra. Then, Pd-Co/rGO nanoparticles were employed as the electrocatalyst for EG electro-oxidation in the alkaline electrolyte. The electrochemical performance of the Pd-Co/rGO electrocatalyst was evaluated by CV and CA techniques. Since the Pd-Co/rGO electrocatalyst showed high electro-catalytic activity in EG electro-oxidation, it would have more promising applications in DEGFCs.

2. Experimental

2.1. Materials Required

To synthesized the Pd-Co/rGO electrocatalyst, the used chemicals were powdered graphite, $PdCl_4$ (99.9%, Merck), $NaNO_3$ (Indian), H_2O_2 (30 wt.%, Merck), $Co(CH_3COO).5H_2O$ (98%, Alfa Aesar,), H_2SO_4 (98%, Merck), HCl (98%, Merck) $KMnO_4$ (98%, Merck), NaOH (Indian, ~98%), N_2H_4 (5 wt.%, Merck), ethanol (98%, Merck) and EG (98%, Merck). To prepare the catalyst ink, nafion 117 (10 wt.%, Aldrich) and isopropyl alcohol (20 v.%, Merck) were used. All the experiments were performed using de-ionized (DI) water.

2.2. Graphene Oxide (GO) and Pd-Co/rGO Synthesis

GO was synthesized through modified Hummer's method [32]. In summary, 1g of graphite powder, 1 g $NaNO_3$ was added in 40 mL H_2SO_4 while stirring. After 2 h, the mixture was placed into ice bath and 6 g of $KMnO_4$ was gradually added to it. Then, the mixture was kept at 35ºC under stirring for 24 h. 10 mL of H_2O_2 was added instantly to terminate the reaction. Finally, the suspension was filtered and washed with HCl (5 v.%) followed by washing with DI water for several times until reaching the neutral pH.

Pd-Co/rGO nano-particles with 1:1 Pd to Co metal ratio were synthesized using an in situ procedure as follows: 25 mg of synthesized GO was mixed in 25 mL of EG and ultra-sonicated for 30 min to obtain highly exfoliated GO homogenous dispersion. The calculated amount of $PdCl_4$ and $Co(CH_3COO)_2.5H_2O$ were dissolved in a few amount of ethanol and EG solvents, respectively. After that the metal salts were gradually added into the GO solution followed by stirring for 12 h. 0.25 g of NaOH was dissolved in 5 mL of N_2H_4 and added drop wise to the mixture followed by stirring for 1 h under N_2 atmosphere. Then the mixture was put in an oven at 200 ºC for 3 h. After self-cooling to the room temperature, the resulting sample was collected by super magnet and washed several times with DI water and ethanol until reaching the neutral pH. Then, the synthesized catalyst was dried in an oven at 45 ºC.

2.3. Morphological and Electrochemical Characterization

The surface morphology of GO and Pd-Co/rGO was investigated by FE-SEM (Mira III, TE-Scan, Czech Republic) in EDX mode. Raman spectrum was recorded between 500 and 3000 cm^{-1} on a Raman spectrometer (Takram P50C0R10, Teksan, Iran), using a 532 nm Nd: YAG laser at 10 mW power. XRD analysis was done to record the structural information by calculating crystallite size and lattice parameters in the range of 20 to 80 at the rate of 3 per minute. A diffractometer (PW3040, Philips, Netherlands) with a Cu K_α X-ray source was used for XRD. The electrochemical performance of the synthesized electrocatalyst was investigated through a conventional three-electrode electrochemical cell with a potentiostat–galvanostat workstation (SAMA, Iran) at room temperature. A glassy carbon (GC), platinum foil and Ag/AgCl in saturated KCl were used as the working electrode, counter electrode and reference electrode, respectively.

In order to prepare the working electrode, the GC electrode surface (area: 0.0314 cm^2) was carefully polished with the alumina powder on a polishing cloth, cleaned by sonication in ethanol and DI water, and allowed to dry at room condition. The catalyst ink was prepared by well-dispersing 1 mg of powdered catalyst in a solution of 0.05 mL of nafion solution in isopropyl alcohol (5 wt.%), 0.5 mL of DI water and 0.5 mL of ethanol. The required amount of the catalyst ink was pipetted on the pre-polished GC electrode surface and dried at room temperature. The catalyst loading on the pre-polished GC electrode was 0.033 mg cm^{-2}. All electrochemical measurements were carried out in the basic solution containing 1M KOH and 1M EG. For the electrochemical measurements, CV and CA were performed. CV test was carried out by scanning the potential between -0.7 and 0.4 V *vs.* Ag/AgCl electrode with the scan rate of 50 mV s^{-1}. CA test was also carried out at the potential of -0.1 V. All potential values in this article have been reported *vs.* Ag/AgCl potential.

3. Results and Discussions

3.1. Morphological Investigation of Synthesized GO

The prepared GO was characterized by the Raman spectrum (Fig. 1) and FE-SEM images (Fig. 2). The Raman Spectrum of GO is determined by a G band at ca. 1605 cm^{-1} and a D band at 1353 cm^{-1} which correspond to the E_{2g} phonon mode of the sp^2 C atoms and breathing mode of κ point phonons of A_{1g} symmetry, respectively [33]. In other words, the D band is an indication of disorder, resulting from certain defects such as vacancies, grain boundaries and amorphous carbon species [34]. As shown in Fig. 1, D and G bands of GO were observed at 1371 cm^{-1} and 1597 cm^{-1}, respectively. The I_D/I_G ratio of the Raman spectrum of GO indicates the degree of structural defects. This ratio of synthesized GO was 0.85 indicating that synthesized GO contains little defects. The band was observed in the range of 2500 cm^{-1} to 3000 cm^{-1} is known as the 2D band, which is an indicator of the number of GO layers [34]. As shown in Fig. 1, the 2D band is observed to be broadened, attributed to the fact that the prepared GO contains few layers.

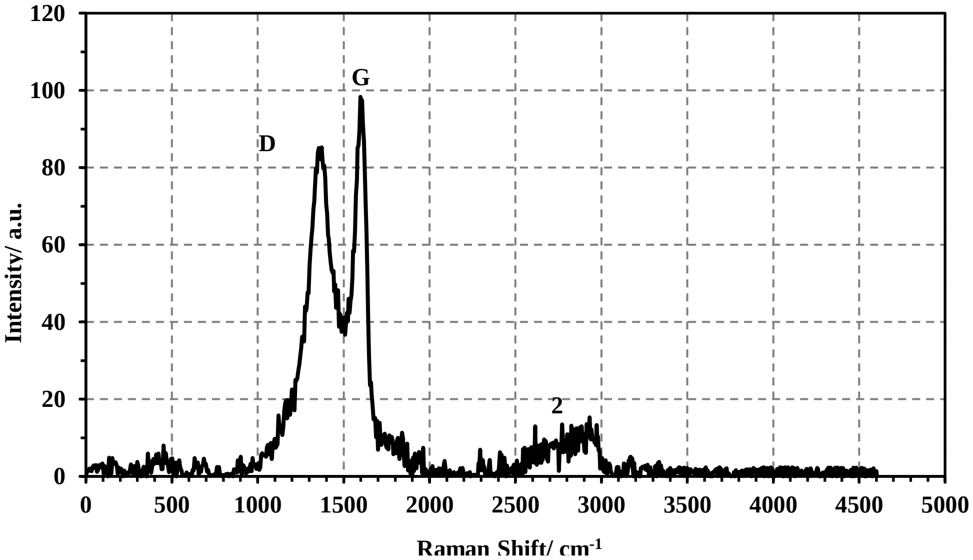

Fig. 1. Raman spectrum of GO (Graphene oxide)

Fig. 2 shows FE-SEM images of GO with different scales. These images have well defined three-dimensional GO sheets, forming a network that resembles a loose sponge-like structure.

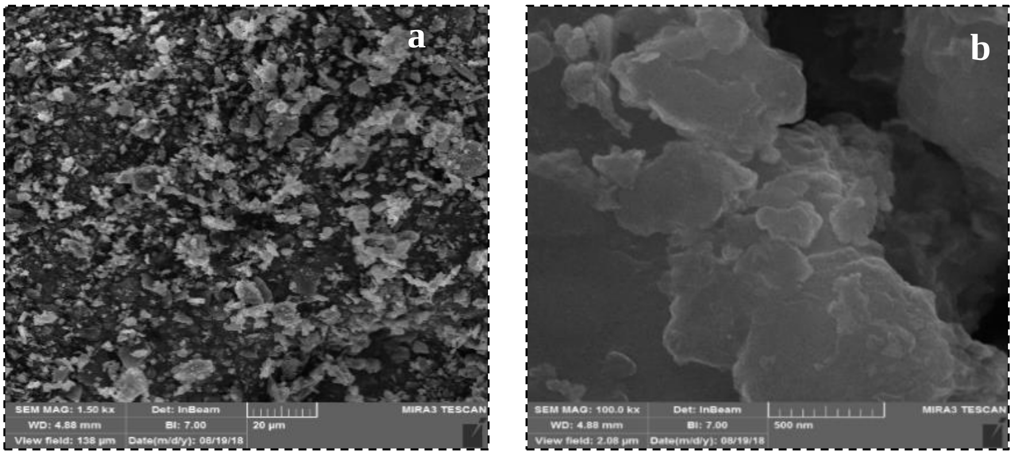

Fig. 2. FE-SEM images of GO with different scales a (20 μm and b) 500 nm

3.2. Structural Investigation of Synthesized Pd-Co/rGO Electrocatalyst

The XRD pattern of Pd-Co/rGO is shown in Fig. 3. The XRD pattern shows the peaks at 2θ of 40°, 46.86°, 67.73°, 82.36° and 86.4° are associated with the (111), (200), (220), (311) and (222) crystal planes of Pd, respectively, featuring a cubic phase with a= 0.39 nm). Compared to the cubic phase of pure Pd (JCPDS 01-087-0643), each peak of the XRD pattern (Fig. 3) are shifted to higher angles, suggesting the alloying of Pd and Co in the bimetallic Pd-Co/rGO electrocatalyst, and indicating a lattice contraction, which is caused by the incorporation of the small Co into the Pd structure [35].

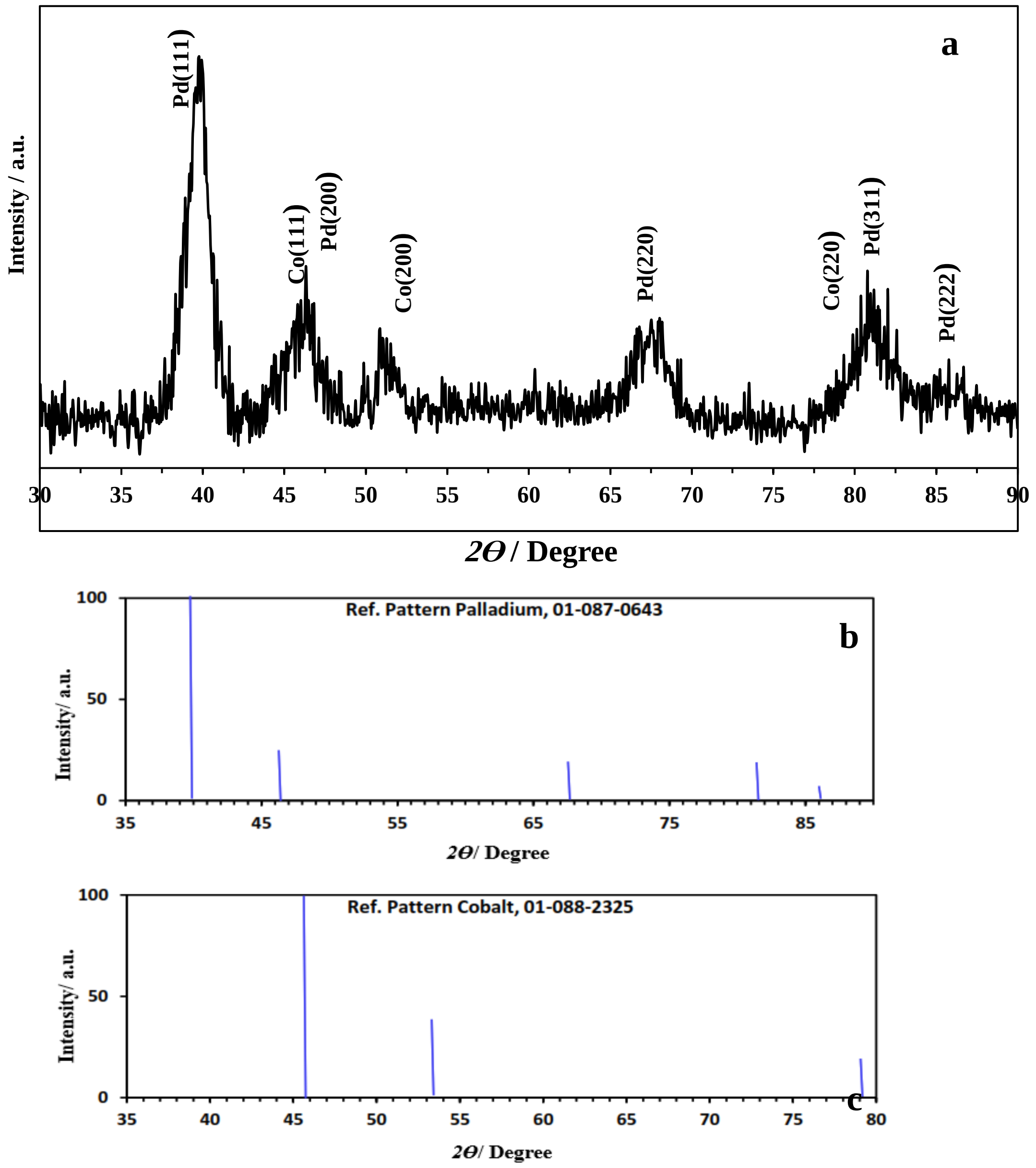

Fig. 3. XRD pattern of (a) Pd-CO/rGO, (b) Pd and (c) Co

As shown in Fig. 3, the characteristic peak was observed at 2θ of 51.18°, which is related to (200) crystal plane of Co cubic phase (JCPDS 01-087-0641, a=0.34 nm). It is expected that there are the Co (111) and Co (220) peaks at the range of 44°-48° and 79°-83°. According to the XRD pattern, the average nanoparticle crystallite size (*D*) was calculated by the Scherrer Eq. (1):

$$D = \frac{0.9\,\lambda}{\beta}\cos\theta \qquad (1)$$

where λ, β and θ are the wavelength of X-ray (λ for Cu Kα=0.154 nm), additional broadening and diffraction angle, respectively. β can be obtained by Eq. (2):

$$\beta = \mathrm{FWHM} \times \frac{3.1416}{180} \qquad (2)$$

where, FWHM is full width at half maximum reflection. By using Eq. (1) and Eq. (2), the average size of nano-particles was approximately 30 nm. Because of weak intensity belonging to carbon diffraction peaks, they were not observable in the XRD pattern of Pd-Co/rGO. The chemical composition of the synthesized electro-catalyst is determined by EDX analysis (Fig.4).

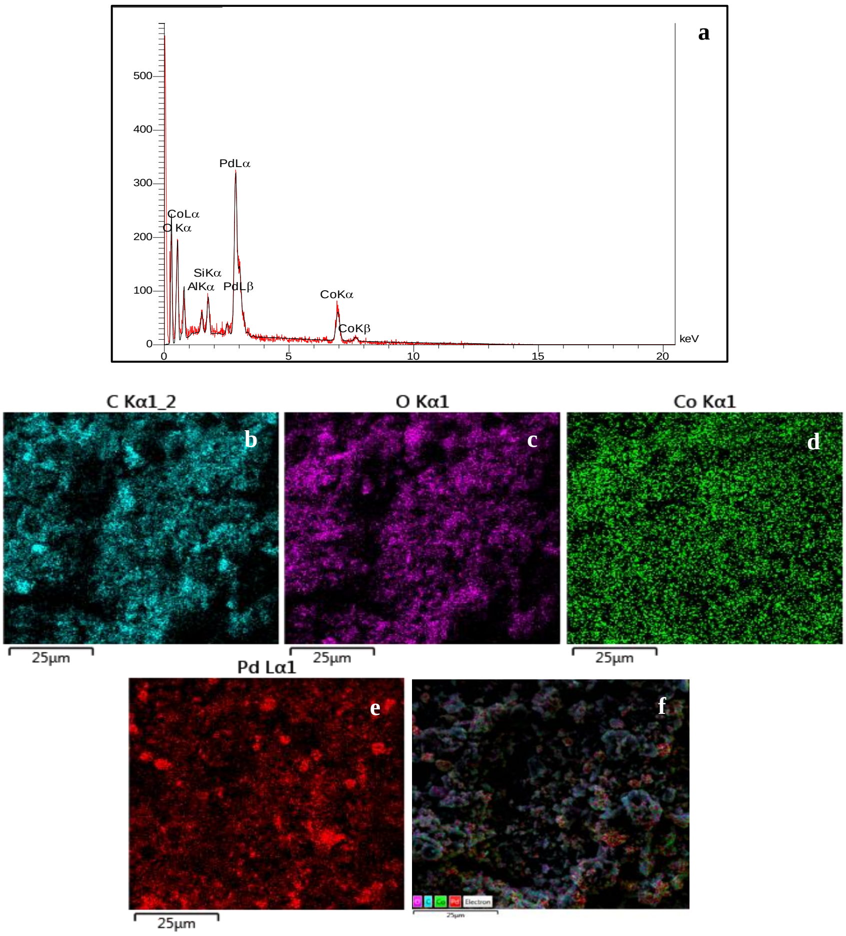

Fig. 4. a) EDX analysis, elemental mapping images of b) C, c) O, d) Co, e) Pd and f) all elements

Fig. 4(a) indicates the EDX spectrum of Pd-Co/rGO. Results indicate that the synthesized catalyst contains Pd, Co, O, and C elements. As shown in the inset of Fig. 4(a), C and Co have the most and less weight or atomic percentage compared to other elements, respectively. According to the weight percentage of Pd and Co, it is concluded that the molar ratio of Pd to Co is equal to 1.3. Fig. 4(b)-(d) shows the EDX mapping images of C, O, Pd, Co, and all these elements. The images confirmed the mentioned elements and showed their homogenous distribution. Fig. 5 shows FE-SEM images of synthesized catalysts in different scales. FE-SEM images indicate the 3D structure morphology of the electrocatalyst. Homogenous dispersion of electrocatalyst on rGO occurred without significant agglomeration. The average particle size was 30 nm, close to that estimated by XRD.

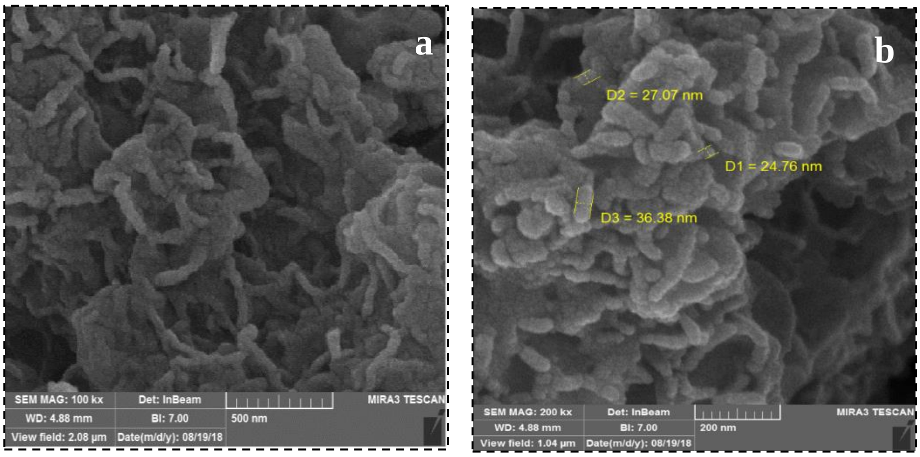

Fig. 5. FE-SEM images of Pd-CO/rGO electrocatalyst with different scales a) 500 nm and b) 200 nm

3.3. Electrochemical Characterization of Synthesized Pd-Co/rGO Electrocatalyst

The EG electro-oxidation reaction on the Pd-Co/rGO surface was investigated by the CV experiment. Fig. 6 shows the cyclic voltammogram of Pd-Co/rGO in the solution containing 1M KOH and 1M EG at room temperature. The EG oxidation peak can be clearly observed in Fig. 6. It can be concluded that EG oxidation on the Pd-Co/rGO surface is performed in the forward scan at -0.09V and reduction of not-oxidized carbonaceous species can be obviously observed with a peak position at around -0.35V in the reverse scan. Table 1 indicates the electrochemical parameters such as E_s, forward anodic peak potential (E_p), j_p and specific peak current density (Sa_p) of the EG oxidation reaction on the Pd-Co/rGo electrocatalyst compared to Pd-based and Pt-based electrocatalysts as reported in the literature, previously [12, 14, 20].

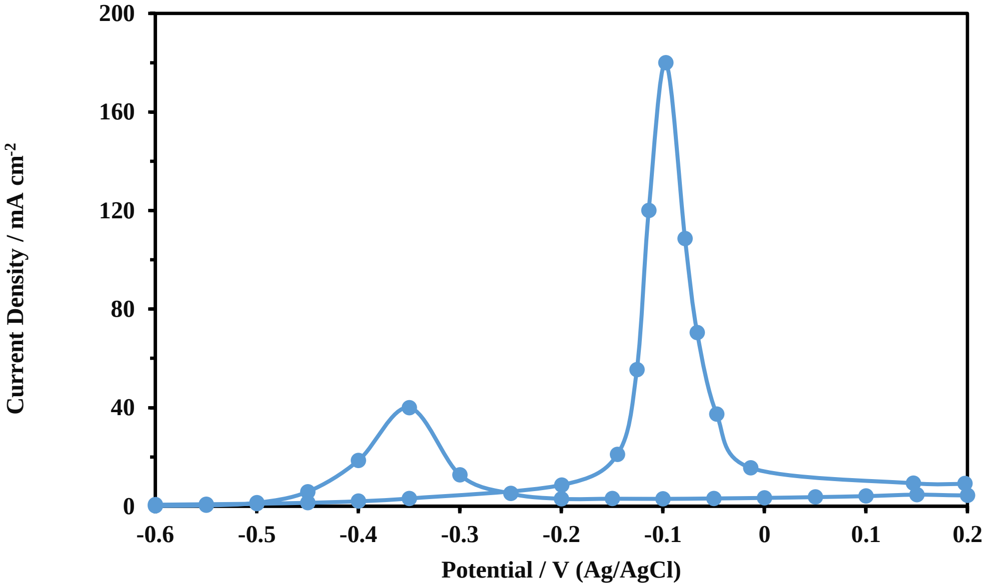

Fig. 6. Cyclic voltammogram of Pd-Co/rGO electrocatalyst in the solution containing 1M KOH and 1M EG at room temperature with the scan rate of 50 mV s^{-1}.

Results demonstrate that Pd-Co/rGO electrocatalyst has higher and lower performance compared to alloyed-based Pd and Pt electrocatalysts, respectively. High activity of Pd-Co/rGO toward EG oxidation reaction results from the strategic co-operation of Pd and Co by alloying. Pd is predicted to migrate from the core of the particle to the surface layer on Co. In other words, Pd and Co were found to occupy shell and core positions in a Pd-Co nano-alloy catalyst, respectively. The reason of this fact can be generally described by two independent factors: i) cohesive energy and ii) atomic size (quantified by Wigner-Seitz radius). A positive cohesive energy value ($\Delta E_{Pd(Co)}$ = 0.75 eV) means that the core-shell structure prefers Co in the core and Pd in the shell [36]. On the other hand, an element with a small atomic radius (1.39 Å of Co vs. 1.52 Å of Pd) tend to occupy the core to relieve the compressive strain [37].

The ratio of the forward peak current density (j_f) to the reverse peak current density (j_r), j_f/j_r, is employed to determine the tolerance of Pd-Co/rGO against poisoning intermediate carbonaceous species accumulated on the electrode surface. A higher ratio than one is related to the efficient oxidation of alcohol during the forward scan and less accumulation of carbonaceous residues on the electrode surface [31]. According to Fig. 6, j_f/j_r of EG oxidation is 4.5, indicating that the tolerance of Pd-Co/rGO toward poisoning is high in the EG oxidation reaction.

Table 1, Comparative electro-catalytic properties of the Pd-based and Pt-based nano-catalysts toward EG oxidation reaction in the alkaline medium

Catalyst	**Catalyst loading (mg$_{Pd}$ cm^{-2})**	**KOH (M)**	**EG (M)**	E_s **(V)**	E_P **(V)**	j_P **(mA cm^{-2})**	Sa_p **(mA mg$^{-1}_{Pd}$)**	**Ref.**
Pd-Sn/MWCNT	0.21	0.5	0.5	-0.44	0.23	51.9	247	[14]
Pd-Ni/MWCNT	0.21	0.5	0.5	-0.39	0.25	35.3	168	[14]
Pd-NiO/C	0.3	1	1	-0.48		104	347	[20]
Pd-Co_3O_4/C	0.3	1	1	-0.55		98	327	[20]
Pd/C	0.25	0.1	0.5	-0.45	0.08	88	352	[20]
Pd-CeO_2/C	0.3	1	1	-0.46		68	227	[20]
Pd-Mn_3O_4/C	0.3	1	1	-0.5		72	240	[20]
Pt-Pd/rGO	0.085	1	0.5	-0.46	-0.16	134.5	1582	[12]
Pt-Pd/C	0.085	1	0.5	-0.56	-0.11	59.8	703	[12]
Pt/C	0.085	1	0.5	-0.54	-0.01	60.3	709	[12]
Pt/rGO	0.085	1	0.5	-0.48	-0.16	53.2	623	[12]
Pd/rGO	0.085	1	0.5	-0.3	-0.16	10.7	125	[12]
Pd-Co/rGO	0.4	1	1	-0.3	-0.1	180	450	Current

Fig. 7 shows products obtained for electro-oxidation of EG in the alkaline medium [38, 39]. Results indicate that the oxidation of EG is mechanistically complicated and most EG oxidation intermediates can be produced and accumulated on the electrocatalyst surface, resulting in blocking the active sites and reducing the electrocatalyst stability.

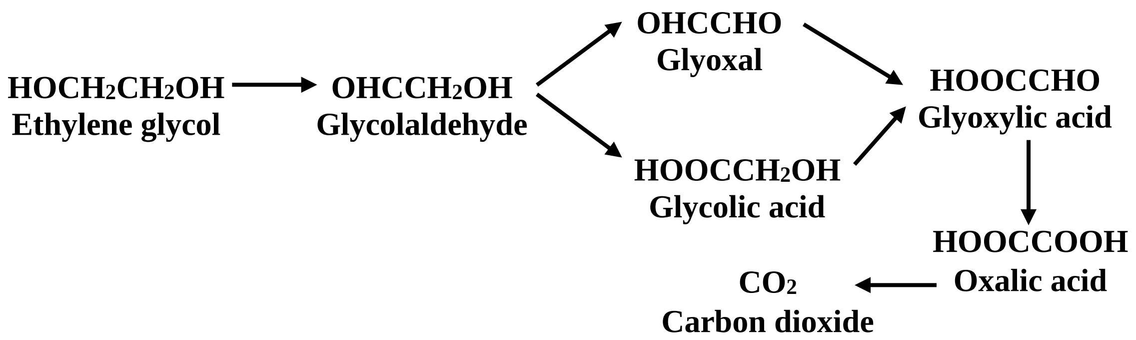

Fig. 7. Products obtained by electro-oxidation of EG [38, 39].

The stability of current density and electro-catalytic activity of the Pd-Co/rGO electrocatalyst was also investigated by CV experiment during 150 CV cycles. Fig. 8 shows consecutive CV patterns for EG electro-oxidation on the Pd-Co/rGO.

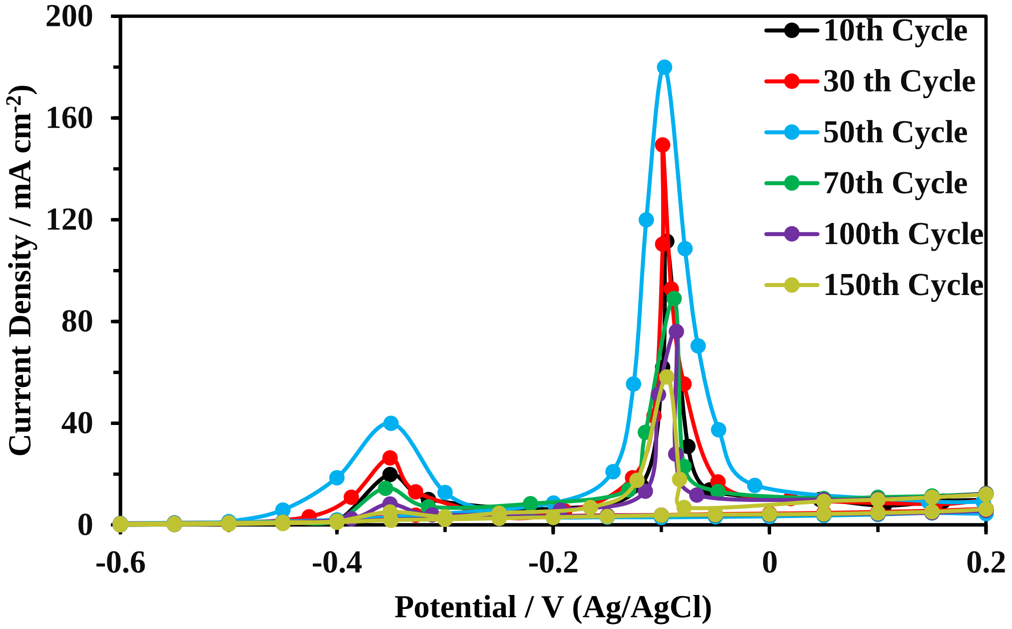

Fig. 8. Consecutive CVs of Pd-Co/rGO electrocatalyst in the solution containing 1M KOH and 1M EG at room temperature with the scan rate of 50 mV s^{-1}.

It can be seen in Fig. 8 that j_P value was increased during the time up to 50th CV cycle, exhibiting the Pd-Co/rGO activation period. After 50th CV cycle, as shown in Fig. 8, j_p value was decreased with increasing of the CV cycle number because EG was consumed and the electrocatalyst surface was poisoned by the produced intermediates. The j_p value of EG oxidation on the Pd-Co/rGO declined 68% under 150 CV cycle. However, Pd-Co/rGO catalyst still exhibits well-defined peaks for the EG oxidation reaction after 150 CV cycle. This result demonstrates that Pd-Co/rGO electrocatalyst is still active in EG oxidation reaction even after 150 CV cycles. It can be concluded that the poisoning toleration and stability of Pd-Co/rGO electrocatalyst is high in the EG oxidation reaction.

The long-term electro-catalytic activity of Pd-Co/rGO in the EG oxidation reaction has also been investigated by CA experiment in the solution containing 1M KOH and 1M EG, with an applied potential of -0.1V. The time period of CA testing was set 1000 s. Fig. 9 shows the chronoamperogram of Pd-Co/rGO in the EG oxidation reaction. CA curve displays the decay of current during the time, which would be related to the remaining of the adsorbed intermediate products of EG oxidation on the surface of the electrocatalyst.

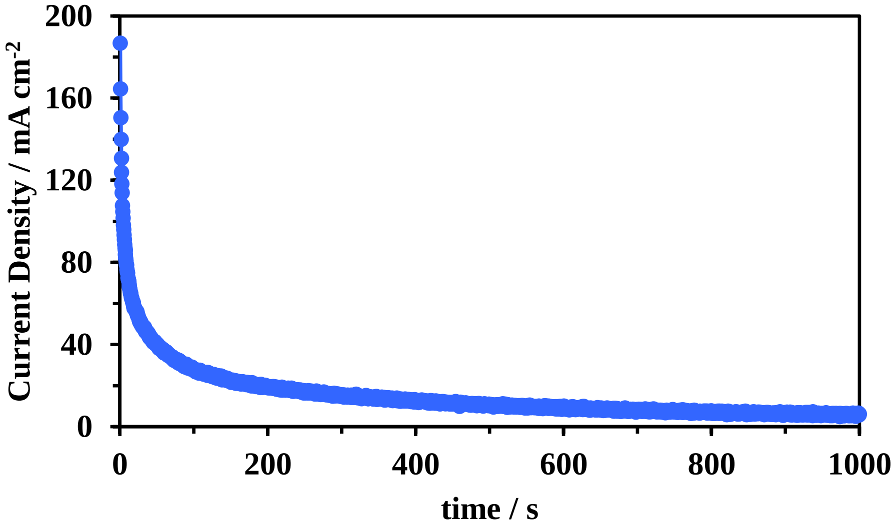

Fig. 9. Chronoamperometric curve for Pd-Co/rGO electrocatalyst in the solution containing 1 M KOH and 1M of EG with an applied potential of -0.1V.

4. Conclusions

In this work, Pd-Co/rGO nano-particles were synthesized with the simple one-step method. During the catalyst synthesis process, GO was reduced to rGO. Pd-Co/rGO electrocatalyst were characterized by XRD, EDX and FE-SEM and Raman spectra techniques. The electrochemical performance of the Pd-Co/rGO was investigated by CV technique. Pd-Co/rGO exhibited high j_p (180 mA cm^{-2}) and low E_s (-0.3V) in EG oxidation reaction. Results showed an excellent catalytic activity of Pd-Co/rGO in terms of Sa_p compared to the reported results in the literature for EG electro-oxidation in alkaline media. The j_p value of EG oxidation on the Pd-Co/rGO declined 68% under 150 CV cycle, suggesting that synthesized Pd-Co/rGO nanoparticles were durable for EG electro-oxidation.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. Also, there are not any conflicts of interest.

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