Conducting Polymer-Mixed Oxide Composite Electrocatalyst for Enhanced Urea Oxidation

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Abstract

Considerable interest in urea electrooxidation reaction has developed recently because of possible generation of hydrogen and in direct urea fuel cell applications. Nickel and nickel-containing catalysts are the preferred electrode materials because of their efficient activity for this reaction. This work investigates a novel platform composed of a conducting poly(aniline) modified with lanthanum-nickel-based oxides/reduced graphene oxide as an electrocatalyst for urea electrooxidation in alkaline medium. The catalyst was prepared using a one-step and energy-saving procedure with graphene oxide as a substrate. The glassy carbon electrode modified with this catalyst exhibits an exceptional high specific current activity of 342 mA mg⁻¹ with onset potential 0.25 V (vs. Ag/AgCl) and current density of 160 mA cm⁻², which is four times the value obtained using Ni-catalyst. Among other catalysts with different morphologies, design and substrate are: nickel nanowire arrays electrode with onset potential 0.25 V (vs. Ag/AgCl) and current density of 160 mA cm⁻², nanocluster of Ni-W-carbide/carbon with onset potential of 0.42 V (vs. Hg/HgO) and current density of 700 mA cm⁻², Rh-Ni electrodes with onset potential of 0.38 V (vs. Hg/HgO) and current density of 180 mA cm⁻², cup-like pore arrays nickel hydroxide arrays electrode with onset potential of 0.31 V (vs. SCE) and current density of 32 mA cm⁻², one-dimensional nickel hydroxide nanoribbons with onset potential of 0.42 V (vs. SCE) and current density ten times higher than Ni(OH)₂, 0.24 V (vs. Ag/AgCl) and current density of 290 mA cm⁻², graphene-nickel nanocomposites with onset potential of 0.45 V (vs. Hg/HgO) and current density two times higher than Ni₂.

Poly(aniline) (PANi) is an intrinsic conducting polymer with catalytic properties. Hydroquinone was oxidized at PANi electrode anticipating its catalytic property. Pt/three dimensional graphene (PANI) catalyst was synthesized hydrothermally with superior electrocatalytic activity for methanol oxidation. In another study, reduced graphene oxide-PANI/TiO₂ in three-dimensional network was constructed with excellent mineralization ability and removal rates of total organic carbon. Perovskites oxides have the formula ABO₃, where A is a transition metal with small radius cation, and B is an alkaline earth or rare earth metal with larger radius cation. Perovskites are used in several applications including electrocatalytic oxidation of urea, biosensors, solar cells, supercapacitor, and water splitting.

Urea, a nitrogen-rich compound is extensively used in fertilizers and constitutes main component of human and livestock urine. The release of urea through industrial production and extensive application of urea-rich fertilizers has adverse environmental effects. Urea is naturally converted to ammonia and other toxic species such as nitrates, nitrites, and NOx that release to air, groundwater and sewage systems. Several methods were introduced for urea decomposition including thermal, chemical oxidation, enzymatic, and catalytic. Besides its abundance, urea is considered a good energy carrier because of its relatively high energy density.

The resulting urea-rich wastewater triggered the development of direct urea fuel cell (DUCF). An early study reported the use of Pt-black surfaces as electrodes in an electrochemical method for de-ureation. Urea electrochemical oxidation reaction (UEOR) is generally sluggish and increased the current density two folds compared to Ni catalyst. NiMoO₄.xH₂O nanosheet arrays were grown over Ni-foam using a hydrothermal process. The prepared catalyst displayed a specific current density of 830 mA cm⁻² which is four times the value obtained using Ni-catalyst. Among other catalysts with different morphologies, design and substrate are: nickel nanowire arrays electrode with onset potential 0.25 V (vs. Ag/AgCl) and current density of 160 mA cm⁻², nanocluster of Ni-W-carbide/carbon with onset potential of 0.42 V (vs. Hg/HgO) and current density of 700 mA cm⁻², Rh-Ni electrodes with onset potential of 0.38 V (vs. Hg/HgO) and current density of 180 mA cm⁻², cup-like pore arrays nickel hydroxide arrays electrode with onset potential of 0.31 V (vs. SCE) and current density of 32 mA cm⁻², one-dimensional nickel hydroxide nanoribbons with onset potential of 0.42 V (vs. SCE) and current density ten times higher than Ni(OH)₂, 0.24 V (vs. Ag/AgCl) and current density of 290 mA cm⁻², graphene-nickel nanocomposites with onset potential of 0.45 V (vs. Hg/HgO) and current density two times higher than Ni₂.

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The choice of good substrate and efficient catalyst results in lowering of oxidation potential and increase of specific current density for UEOR. In this study, we prepared a LaNiO$_3$/reduced graphene oxide (RGO) composite using microwave-assisted method. The composite was used to modify an electropolymerized PANi film deposited over glassy carbon substrate. No previous reports mentioned the use of PANi/LaNiO$_3$/RGO composite (PANI/LNOG) as a catalyst for UEOR. The proposed catalyst proved highly efficient with exceptional stability in alkaline electrolyte.

**Experimental**

**Materials.**—All chemicals are analytical grades and were used as received without further purification. Graphite, P$_2$O$_5$, K$_2$SO$_4$, H$_2$SO$_4$, KMnO$_4$, KOH, H$_2$O$_2$, Ni(NO$_3$)$_2$·6H$_2$O, La(NO$_3$)$_3$·xH$_2$O, NH$_4$OH, and urea (CO(NH$_2$)$_2$) were purchased from Sigma-Aldrich (USA) and all solutions were prepared using double distilled water.

**Synthesis of graphene oxide (GO) and reduced graphene oxide (RGO).**—Graphene oxide was prepared by modified Hummer’s method as mentioned elsewhere. Briefly, 5 g of highly pure graphite was cured with H$_2$SO$_4$, P$_2$O$_5$, K$_2$SO$_4$ in order to prepare pre-oxidized graphite. 5 g of dried pre-oxidized graphite was stirred with 115 mL of 98% H$_2$SO$_4$ in an ice bath for 10 min followed by the gradual addition of 15 g of KMnO$_4$ and stirring was continued for two more hours. The mixture acquired a bright yellow color after dilution by water and addition of H$_2$O$_2$. The bright yellow suspension was filtered and washed with 1:10 HCl-solution, afterwards it was dried overnight at 80°C in an oven. For comparison, graphene was prepared by the chemical reduction of GO using microwave method in presence of hydrazine hydrate (HH) as a reducing agent as mentioned elsewhere. Briefly, 0.1 g of GO was sonicated with 20 mL of deionized water until a homogeneous dispersion was obtained. GO dispersion was subjected to centrifugation powered at 4000 rpm to get rid of the incompletely oxidized GO. After adding 150 μL of HH, the solution was placed in a conventional microwave oven (MC-9283 JLR, 900W) and operated at full power 900 W in 30 s cycles (on for 10 s, and off for 20 s) for total reaction time of 120 s. After microwave irradiation the yellowish brown solution was converted into black which indicates the complete reduction of GO into graphene. The graphene flakes were separated by Mark centrifuge operated at 4000 rpm for 15 min and dried overnight.

**Synthesis of LaNiO$_3$-Graphene (LNOG).**—LaNiO$_3$-graphene (LNOG) was prepared using the same procedure mentioned previously with some modification. In the modified procedure, 0.333 mole of Ni(NO$_3$)$_2$·6H$_2$O and 0.333 Mole of La(NO$_3$)$_3$·xH$_2$O were mixed with 0.2 g of GO in 20 mL of distilled H$_2$O. Then the brownish suspension was sonicated for 2h until it became completely homogeneous. After that, the pH of the solution was adjusted to 8.0 by NH$_4$OH solution. Then it was subjected to microwave irradiation operated at 720 W for 30 min (20 sec on and 10 sec off). During the operation, the suspension was dehydrated and a strong ignition took place resulting in a fluffy black powder. The resulting material containing reduced graphene was used as prepared for further structural, morphological and electrochemical experiments. For comparison LNOG was calcinated at 650°C for three hours to form LaNiO$_3$ (LNO).

**Structural and surface analysis.**—The structure of the prepared LNOG samples was characterized using X-ray diffraction (XRD) by Panalytical X’Pert using Cu-Kα radiation ($\lambda = 1.540\AA$). The microstructure of the samples was investigated using Quanta FEG 250 (USA) instrument and an EDAX coupled to SEM was used to analyze the composition of the prepared samples. For the purpose of surface analysis, a GC sheet was used for electrode preparation.

**Electrode preparation and electrochemical cells.**—LNOG suspension was prepared by sonication of 10 mg LNOG in 1 mL dimethylformamide (DMF) for 1h. For comparison, a physical mixture was prepared from graphene and LNO suspension.

**Results and Discussion**

**Structural and surface characterization.—**XRD.—LaNiO$_3$-graphene oxide (LNOG) was prepared using graphene oxide as the substrate. The first sample was used without further calcination (LNOG) and the second was calcinated at 650°C for three hours (LNO). Figure 1 shows X-ray diffraction patterns of the as-prepared LNOG and calcinated catalyst LNO powders. It can be observed that the composition of the prepared samples. For the purpose of surface characterization, a GC sheet was used for electrode preparation.

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LNOG sample contained trace of the LaNiO$_3$ perovskite-type structure. The intensity and sharpness of the diffraction peaks increased in the case of calcinated LNOG. The data of Figure 1, for non-calcinated LNOG, reveals that three crystalline phases can be identified: the primary phase is La$_2$NiO$_4$ with a tetragonal structure (JCPDS card number 11-0557), two secondary phases, LaNiO$_3$ and NiO, are also identified (JCPDS card number 33-0711 and JCPDS card number 47-1049). For calcinated LNOG, the major crystalline phase is LaNiO$_3$, and two secondary phases, La$_2$NiO$_4$ and NiO are identified. The formation of the mixed oxides La$_2$NiO$_4$ and NiO are attributed to the limited availability of oxygen from the reactants.35,36

SEM and EDAX.—The surface morphology of the catalyst affects the catalytic performance of the electrode toward UEOR. Figure 2a shows the SEM of non-calcinated LNOG and the inset is a higher magnification of the surface. The SEM reveals the presence of catalyst particles over the surface with different size ranging between 1 μm and 50 nm. The larger size particles are formed from aggregated smaller size structures. The EDAX measurement of Figure 2b shows the presence of La, Ni and O with the expected ratio of 2:1:4 which in agreement with the XRD analysis data confirming the presence of La$_2$NiO$_4$ as the main phase in the catalyst structure. The elemental surface mapping of the catalyst shows the distribution of the La and Ni homogeneously over the surface of the electrode.

Electrochemical activity toward urea electrooxidation.—The activation of nickel-based electrodes is a crucial step in the electrochemical urea oxidation. It results in the formation of highly electrocatalytic active Ni-form, NiOOH.8 The activation step was performed by cyclic voltammetry (CV) at scan rate 200 mV s$^{-1}$ for 50 cycles in a solution of 1.0 M KOH and 0.33 M urea (Figure not shown). It is observed that, the current increases with the successive repeated cycling due to the formation of NiOOH. As the number of the potential sweeps increases, the thickness of NiOOH layer increases due to the presence of OH$^-$ ions that enhanced the rate of Ni(OH)$_2$/NiOOH conversion. Earlier studies on the electrochemical behavior of Ni-electrode suggested that hydroxide formation from Ni(OH)$_2$ enhanced its rate of conversion to NiOOH.37 The catalyst prepared using the microwave-assisted method using graphene oxide as the substrate, without further calcination at relatively high temperature, results in the formation of La-Ni-based/graphene catalyst that will be represented as LNOG.

The electrochemistry of urea electrooxidation on the surface of different GC-modified electrodes was studied in a solution contain 0.33 M urea and 1.0 M KOH at the ambient air. Cyclic voltammograms (CVs) of glassy carbon modified with poly(aniline) (GC/PANI), catalyst (La-Ni-based) (GC/LNOG), and poly(aniline)/La-Ni-based catalyst (GC/PANI/LNOG) in 0.33 M urea/1.0 M KOH are shown in Figure 3a. It is shown that LNOG nanocomposite has high electrocatalytic activity towards urea electrooxidation. Although, PANI alone

Figure 2. a) SEM image of GC/PANI/LNOG, b) the corresponding EDAX analysis; c), d), e), and f) are the corresponding elemental surface mapping.
has no electrocatalytic activity towards urea electrooxidation (Figure 3b), GC/PANI/LNOG shows a noticeable increase in the peak current density compared to GC/LNOG. PANI furnishes a suitable surface that enforces the adsorption of LNOG to the electrode surface. Also, the porous nature of the PANI structure, high conductivity and relatively higher surface area increased the current response and efficiency of LNOG towards UEOR.

Two redox peaks are observed at 354 mV and 278 mV related to Ni(OH)\textsubscript{2}/NiOOH transformation. The other redox peaks at 480 mV and 370 mV are related to urea electrooxidation and CO oxidation to CO\textsubscript{2}, respectively. The CV of GC/PANI/LNOG (0.05 mg LNOG) in 0.33 M urea/1.0 M KOH; scan rate 100 mV s\textsuperscript{−1}. It is shown that, graphene has no electrocatalytic activity toward UEOR. To the best of our knowledge, no previous work reported the use of conducting polymers with Ni-based oxides or perovskites for UEOR. The data of Figure 3a report the electrochemical specific current activity for urea oxidation at PANI/LNOG as 342 mA mg\textsuperscript{−1} cm\textsuperscript{−2} (0.05 mg LNOG); this value is higher than those reported earlier using LaNiO\textsubscript{3}. Poly(aniline) film did not display appreciable electrochemical activity toward UEOR (Figure 3b). It was reported that, the calcination step at elevated temperature that reached 900°C is crucial to reorder the crystal structure and to form fine perovskite crystals. In this study the LNOG nanocomposite is synthesized by microwave-assisted method using GO as a substrate without further calculations step that represents an energy efficient method for perovskite preparation.

In order to investigate the effect of calcination step on the electrocatalytic activity of the catalyst toward urea electrooxidation, the as-prepared LNOG is calcinated at 650°C for three hours. The electrocatalytic activity of the as-prepared LNOG nanocomposite is compared to that of the calcinated catalyst. Also, physical mixtures of the calcinated catalyst LNO and graphene in various ratios were also tested. Figure 4 displays the CVs of glassy carbon modified with poly(aniline) and graphene (GC/PANI/graphene) and glassy carbon modified with poly(aniline) and calcinated catalyst (0.05 mg LNO) with different amounts of physically mixed graphene (GC/PANI/LNO-graphene) (0.05 mg LNO-graphene). The data also compares the response of glassy carbon modified with poly(aniline) and “non-calcinated” catalyst (GC/PANI/LNOG) (0.05 mg LNOG) in 0.33 M urea/1.0 M KOH at scan rate 100 mV s\textsuperscript{−1}. It is shown that, graphene has no electrocatalytic activity towards urea electrooxidation. Additionally, the calcination step leads to decreasing the electrocatalytic activity of the catalyst towards urea electrooxidation compared to the non-calcinated catalyst. However, mixing 20% graphene with 80% calcinated LNO leads to an enhancement in the electrocatalytic activity of LNO. However, the specific current responses of the physically mixed composites reveal lower values compared to LNOG. The presence of graphene sheets increases the conductivity of the perovskitic material and the surface area of the whole electrode. Therefore, this resulted in efficient electrochemical performance towards urea electrooxidation. For comparison, Table I displays a comparison between the current densities obtained at different catalysts and the current work. It can be noticed that the composite surface of GC/PANI/LNOG displayed higher current density compared to other surfaces cited in the literature. This set of experiments was repeated three times each; the relative standard deviations are: 1.67, 0.878 and 0.680 for 20%, 50% and 80% graphene loadings, respectively.
Table I. Comparison of the oxidation peak current densities for urea electrooxidation obtained at different catalysts. (Data obtained from cyclic voltammetric measurements using a scan rate of 10 mV s$^{-1}$).

| Electrode                                      | $I_p$ (mA cm$^{-2}$) | [Urea] M | [KOH] M | Reference |
|------------------------------------------------|----------------------|----------|---------|-----------|
| $\beta$Ni(OH)$_2$                             | 2.6                  | 0.33     | 1.0     | 9         |
| Nickel hydroxide/monolayer of nanocup arrays  | 6.4                  | 0.33     | 1.0     | 19        |
| Ni(OH)$_2$/nano-ribbons                       | 7.67                 | 0.33     | 5.0     | 20        |
| Ni/RGO                                        | 2.21                 | 0.33     | 0.5     | 22        |
| Ni/C Ni/MWCNTs Ni-WC/MWCNT                    | 3.1                  | 8.73     | 46.6    | 43        |
| RGO-LaNiO                                     | 11.98                | 0.33     | 1.0     | This work |

Effect of PANI thickness and LNOG loading.—Conducting polymer thickness is controlled by the time employed for polymerization. In this study, the effect of PANI thickness on the electrochemical performance of GC/PANI/LNOG electrode is investigated. In order to maintain the same thickness for all measurements, the same polymerization charge instead of polymerization time was kept the same. The data showed that the effect of polymerization charge (from 1500 to 3000 μC) on the specific current of UEOR increased with polymer film thickness (Figure 5a). The activity of GC/PANI/LNOG increased as PANI polymerization charge increases up to 2500 μC (electropolymerization charge), then the catalyst activity started to decrease. This result indicated that using 2500 μC was sufficient to optimize PANI thickness. PANI thickness affects the film morphology, porosity and conductivity. This will in turn affect the PANI electrochemical performance. The cost of the electrocatalysts has a dramatic impact in the energy related applications. So, it is significant to optimize the catalyst loading to achieve the best efficiency with the lowest amount of catalyst. Thus, the mass of LNOG was varied by casting different amounts of LNOG suspension (1-10 μL from a sonicated suspension containing 10 mg mL$^{-1}$) to the surface of GC/PANI. The results revealed that, as the amount of LNOG increased up to 0.05 mg, the anodic specific current increased. When using 10 μL (0.1 mg) of the catalyst suspension, the catalyst was not stable at the surface and part of the LNOG layer peeled off the electrode surface during the potential sweep. We observed a decrease in specific current of UEOR as the amount of catalyst decreased as shown in Figure 5b.

Effect of KOH and urea concentrations.—The concentration of supporting electrolyte has a significant effect on urea electrooxidation. This effect was studied by varying the KOH concentration. Figure 6a shows the CVs of GC/PANI/LNOG in 0.33 M urea and various KOH concentrations (0.1, 0.5, 1.0, 2.0, and 3.0 M) at scan rate 50 mV s$^{-1}$. The specific currents of urea electrooxidation increase as the KOH concentration increases (Figure 6b). This is attributed to the decrease in the diffusion resistance. Additionally, increasing OH$^-$ concentration leads to increasing the formation of NiOOH and consequently, higher electrocatalytic activity is observed. Moreover, as KOH concentration increases, the oxidation peak potential shifts to less positive value indicating that high KOH concentration is favored for urea electrooxidation. Additionally, Urea electrooxidation was studied at different urea concentrations ranged from (0.1 M to 1.0 M). As shown in Figures 6c and 6d, no surface saturation is observed in the studied concentration range. Anodic specific peak current of urea electrooxidation increases as the urea concentration increases. This finding indicates that the studied electrode could be used in relatively high urea concentrations applications such as waste water treatment and in DUCFs.

Effect of scan rate.—The effect of scan rate of urea electrooxidation was investigated by CV using GC/PANI/LNOG-electrode (0.05 mg LNOG) in 0.33 M urea/1.0 M KOH at various scan rates ranged from 10 to 400 mV s$^{-1}$ as shown in inset of Figure 7. It is observed that as the scan rate increases, the specific anodic peak current density for urea oxidation increased linearly indicating that urea electrooxidation on GC/PANI/LNOG electrode is a diffusion controlled process. Apparent diffusion coefficient ($D$) can be calculated from the relation between anodic peak current density and the square root of the scan rate ($\nu^{1/2}$) (see Figure 7) using Randles Sevcik equation:40

$$I_p = (2.687 \times 10^3) n^{3/2} \nu^{1/2} D^{1/2} A C_o$$

Where, $I_p$ is the peak current (A), $n$ is the number of electrons exchanged in electrochemical urea oxidation ($n = 6$), $\nu$ is the scan rate (V s$^{-1}$), $C_o$ is the concentration of urea (mol cm$^{-3}$), $A$ is the geometrical electrode area = 0.0707 cm$^2$, and $D$ is the diffusion coefficient (cm$^2$ s$^{-1}$).

Figure 5. a) Effect of polymerization charge of aniline on the electrocatalytic activity of GC/PANI/LNOG toward urea electrooxidation in 0.33 M urea/1.0 M KOH (scan rate 50 mV s$^{-1}$). b) Effect of LNOG loading on the electrocatalytic activity of GC/PANI/LNOG toward urea electrooxidation in 0.33 M urea/1.0 M KOH (scan rate 50 mV s$^{-1}$).
Figure 6. a) CVs of GC/PANI/LNOG in 0.33 M urea/different KOH concentrations at scan rate 50 mV s\(^{-1}\), b) Relation between anodic peak currents and KOH concentration, c) CVs of GC/PANI/LNOG in different urea concentration/1.0 M KOH (scan rate 50 mV s\(^{-1}\)); d) Relation between anodic peak currents and urea concentration.

The apparent diffusion coefficient (D) of urea in 0.33 M solution towards GC/PANI/LNOG was calculated as 3.4 \(\times\) 10\(^{-6}\) cm\(^2\) s\(^{-1}\).

Stability of the catalyst.—The durability is an important factor for electrocatalyst performance when used as anode material in fuel cells applications. The electrochemical stability of GC/PANI/LNOG was characterized by CV and chronoamperometry (CA) experiments in solution containing 0.33 M urea and 1.0 M KOH (Figure 8a). In one set of experiments, the electrode was cycled in KOH solution prior to the CA measurement to generate and stabilize NiOOH formation. Catalyst stability was then measured for 2 hours at constant potential 500 mV (vs. Ag/AgCl) in presence of 0.33 M urea. The catalyst shows decreasing in its activity that could be attributed to the partial surface poisoning from CO adsorption to the surface (Figure 8a). The durability of catalyst was also examined by repeated CVs up to 50 cycles. Figure 8b displays the 1\(^{st}\) and the 50\(^{th}\) cycles for comparison in solution containing 1 M KOH and 0.33 M urea. In general, the catalyst is stable with a decrease of about 23% of the specific anodic current density. We also tested the possibility of regeneration of the catalyst by re-activating the electrode by cycling in KOH solution (urea-free). The electrode restored 95% from its original specific current density values.

Effect of temperature.—The effect of temperature change on the catalyst performance in 0.33 M urea and 1 M KOH was studied. Figure 9 represents the Arrhenius plot of urea oxidation in the temperature range from 10 to 55° C. The linear relation between ln oxidation current and 1/T indicates that the mechanism of urea oxidation at GC/PANI/LNOG (0.05 mg LNOG) surface is partially activation controlled. By plotting log I_p versus reciprocal of temperature, the value of activation energy, E_a, is calculated. The calculated E_a is 43.1 kJ mol\(^{-1}\), suggesting a physical model of adsorption during UEOR.
Figure 8. a) Chronoamperometry of GC/PANI/LNOG in 0.33 M urea/1.0 M KOH for 2.0 hours at 500 mV for the freshly prepared electrode (non-activated) and after 75 CV cycles (activated electrode) in 1.0 M KOH; b) 1st vs. 50th CVs of GC/PANI/LNOG in 0.33 M urea/1.0 M KOH at scan rate 50 mV s$^{-1}$ (Inset: The relation between the recorded anodic peak current and cycle number).

Figure 9. Relation between Ln (anodic peak currents) and the reciprocal of temperature of GC/PANI/LNOG in 0.33 M urea/1.0 M KOH (data from CVs at scan rate 50 mV s$^{-1}$).

Table II. Electrochemical impedance parameters, obtained from the fitting the data of Figure 10 using the equivalent circuit of Figure 10c.

| Elements/[urea] | 0.10 M | 0.33 M | 0.50 M |
|----------------|--------|--------|--------|
| $R_s$ (Ω cm$^2$) | 20.1   | 24.7   | 26.5   |
| $Y_0$ (S cm$^{2}$) | $1.31 \times 10^{-3}$ | $1.00 \times 10^{-3}$ | 7.58 $\times 10^{-4}$ |
| $n$ | 0.889 | 0.913 | 0.867 |
| $R_{cl}$ (Ω cm$^2$) | 404    | 303    | 245    |
| $R_1$ (Ω cm$^2$) | 47.5   | 41.5   | 39.2   |
| $Y_0$ (S cm$^{2}$) | $7.51 \times 10^{-5}$ | 8.67 $\times 10^{-5}$ | 2.53 $\times 10^{-5}$ |
| $m$ | 0.942 | 0.941 | 0.984 |
| $\chi^2$ Weighed | 0.00268 | 0.631 | 0.00415 | 0.538 | 0.00157 | 0.368 |

Electrochemical impedance spectroscopy (EIS).—Interfacial interactions such as charge transfer and diffusion, and capacitive nature of film-modified electrodes can be evaluated using EIS technique. The electrochemical processes for the oxidation of urea at the GC/PANI/LNOG electrode were characterized using EIS. Figure 10 shows the Bode- and Nyquist complex-plane impedance spectra of GC/PANI/LNOG electrode in 1.0 M KOH and different urea concentrations (0.1, 0.33 and 0.5 M). In the studied potential, $E = 0.55$ V; the dc-potential was selected based on the data obtained from CV measurements in order to ensure maximum rate for the UEO. The Nyquist plots (Figure 10b) showed semi-circles with increasing diameter as the concentration of urea decreases. The experimental results were fitted to an equivalent circuit shown in Figure 10c. In the circuit, $R_s$ represented the solution resistance, $R_{cl}$ is the charge transfer resistance, $Y_0$ represented the double layer capacitance (taking into consideration the interfacial non-homogeneity), $R_1$ is the resistance of the inner layer at the electrode and $Y_0$ was the surface roughness associated with inner layer capacitance. The values of the elements present in the circuit are given in Table II. The value of charge transfer resistance, $R_{cl}$ which is estimated from the radii of the semicircles of Figure 10b, decreased as the concentration of urea increases. This was due to the increase in the rate of reaction at the electrode interface. This result was in good agreement with the data presented in the CVs of Figure 6c, in which the oxidation peak currents increased with the concentration of urea. The result indicates that the surface is not affect by CO production or its conversion to CO$_2$. The double layer capacitance which is represented by the constant phase element, $Y_0$, decreases slightly with increasing concentration. This can be explained by the partial adsorption of oxidation products at the surface of the electrode. EIS data are in good agreement with the CV results. In this potential, ca. 550 mV, the impedance spectra is displayed in the second quadrant. Similar results were observed for the electrooxidation of methanol and formic acid. In most cases, this suggests the presence of an inductive component which involves adsorbed intermediates. In the case of UEO, the adsorption arises from CO intermediate. In the Bode plots of Figure 10a, there was noticeable decrease in the low-frequency region from which the $R_{cl}$ value is estimated. The change in the phase angle with frequency displayed similar behavior indicating no appreciable change in the mechanism of charge transfer kinetics for the three concentrations studied. The values of $R_1$ and $Y_0$, on the other hand, did not appreciably change reflecting the stability of the film characteristics during the UEO.

Conclusions

Lanthanum-nickel-based nanoparticles were synthesized using a one-step and energy-saving method with microwave-assisted method. The substrate used during the reaction between lanthanum and nickel precursors was reduced graphene oxide. This replaced the conventionally used “fuel” component in thermal preparation of perovskites. The resulting material was used to modify a thin film of poly(aniline) electrodedeposited over glassy carbon substrate. The electrocatalyst showed high catalytic efficiency for urea electrooxidation reaction.
The catalyst prepared showed to be a mixture of a main phase, namely La$_2$NiO$_4$, two secondary phases: LaNiO$_3$ and NiO, and reduced graphene oxide. Repeated cycling of the electrode showed some reduction in the electroactivity of the surface. However, no complete poisoning was observed with the possibility of regenerating the surface by electrochemical activation in urea-free KOH solution. Chronoamperometry experiments were extended for two hours under relatively low potentials showing a stable current that introduce the use of the electrocatalyst for long term production of hydrogen gas, de-ureation in direct urea fuel cells applications. The morphology of the prepared catalyst showed the variation of the size of the particles obtained from nano- to few micro-meters.

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