



Research Article

Electrosynthesized Ni-Al Layered Double Hydroxide-Pt Nanoparticles as an Inorganic Nanocomposite and Potent Anodic Material for Methanol Electrooxidation in Alkaline Media

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Abstract

In this study, Ni-Al layered double hydroxide (LDH)-Pt nanoparticles (PtNPs) as an inorganic nanocomposite was electrosynthesized on the glassy carbon electrode (GCE) by a facile and fast two-step electrochemical process. Structure and physicochemical properties of PtNPs/Ni-Al LDH/GCE were characterized by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectrometry and electrochemical methods. Then, electrocatalytic and stability characterizations of the PtNPs/Ni-Al LDH/GCE for methanol oxidation in alkaline media were investigated in detail by cyclic voltammetry, chronoamperometry, and chronopotentiometry measurements. PtNPs/Ni-Al LDH/GCE exhibited higher electrocatalytic activity than PtNPs/GCE and Ni-Al LDH/GCE. Also, the resulted chronoamperograms indicated that the PtNPs/Ni-Al LDH/GCE has a better stability. Copyright © 2017 BCREC GROUP. All rights reserved

Keywords: Ni-Al layered double hydroxide; Pt nanoparticles; inorganic nanocomposite; electrodeposition; electrooxidation; methanol; fuel cell

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1. Introduction

Fuel cells (FCs) as the electrocatalytic energy conversion devices are expected to play a main role in the development of sustainable technologies that mitigate the global warming and the pollution of fossil fuels [1,2]. Due to the increasing energy demand from modern manufacture industry, all intermediate processes required for production and integration of a prod-

uct's components, FCs have become the promising energy conversion apparatus for powering portable electronics and vehicles [3,4]. FCs powered vehicles are currently under development world-wide in an attempt to diminish the emissions of green-house gas (CO₂) as well as other noxious gases, such as NO_x, SO_x, CO, and hydrocarbons from the transport area [5,6]. The direct alcohol fuel cells (DAFCs), belong to the family of fuel cells that where the fuel, alcohol, is fed directly to the FCs, are favorable power devices due to their low operating temperature, simple transportation and fuel storage, high energy efficiency, low exhaustion and

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fast start-up [7,8]. On the other hand, alkaline fuel cells (AFCs) with electrolytes, such as KOH and NaOH aqueous solution, show a higher performance in popular low temperature FCs such as polymer electrolyte membrane fuel cells (PEMFCs) and DAFCs [9,10]. It was reported that alcohol oxidation kinetics was improved by using alkaline medium [11]. Research and development activities on the DAFCs in alkaline media have increased extremely in recent years [11-15]. Alkaline DAFCs have drawn specific attention in this area for the advantage of high alcohol oxidation kinetics and of the potential use of cheaper non-Pt electrocatalysts [16]. Among various alcohols used for FCs, methanol is considered one of the most promising alternative fuels from a non-petroleum source. The electrochemical process of direct methanol fuel cells (DMFCs) is a coupled process of electrochemical reactions and transport phenomena of ions and methanol occurring simultaneously in a complex procedure [17-19].

In the recent years, inorganic layered materials have attracted growing interest for use in various fields owing to their favorable properties, including low cost, high thermal stability and suitable catalytic activity [20-22]. Layered double hydroxides (LDH) belong to a class of anionic clay or hydrotalcite-like clays consist of stacked brucite-type octahedral layers with anions and water molecules occupying the interlayer spaces, family providing numerous applications due to their unique physicochemical properties [23-25]. The $[M^{II}_{1-x}M^{III}_x(OH)_2]([A^{n-})_{x/n}.mH_2O]$, where M^{II} is a divalent cation, such as Ni^{2+} , Mg^{2+} , etc., and M^{III} is a trivalent cation, such as Al^{3+} , Fe^{3+} , etc., and A^{n-} is an anion, such as CO_3^{2-} , Cl^- , etc., is a general formula for LDH [26,27]. In particular, the LDH containing transition metal ions in the lattice of their octahedral layer with redox properties, such as Cu, Ni and Fe, have been widely synthesized and exploited in many practical catalytic applications [19,28]. Ni-Al LDH not only possess all the advantages of common LDH but also have the electrochemical activity because of the presence of a reversible one-electron redox couple, Ni(III)/Ni(II), which allows their application in electrochemistry area [29-31]. Electrochemical applications of LDH to electrochemical sensors, electrocatalysts, dye-sensitized solar cells and super capacitors were presented [32-37]. In the fuel cell applications, recently Ni-Al LDH has been reported to catalyze the electrooxidation of primary alcohols and sugars [38-41].

Different approaches were used to synthesis of LDH and different methods have been pro-

posed to modify electrode surfaces with LDH films; the most common one consists of depositing a fixed amount of a colloidal solution of the LDH, previously synthesized in bulk size [36,37], onto the electrodes [38-41]. A drawback of this method is the poor adhesion of the LDH films to the electrode surfaces. To overcome the above problem and to broaden the application of the LDH film modified electrodes recently the electrochemical deposition of LDH films was carried out to electrosynthesized well-adhered thin films of LDH on electrode materials [41-44]. The great advantages of the electrochemical methods are the short time needed to modify the electrodes surface and excellent application in electrochemistry; whereas a drawback is that the electrodeposited materials have a poor crystallinity [44-47].

In the present investigation, we have prepared the Ni-Al LDH-Pt nanoparticles (PtNPs) as an inorganic nanocomposite on the glassy carbon electrode (GCE) by a two-step electrodeposition process: (i) Ni-Al LDH film was fabricated by an electrodeposition in the first step, and (ii) the PtNPs were precipitated electrochemically on/in the Ni-Al LDH film on the GCE from $H_2PtCl_6.5H_2O$ solution in the second step. Then, the structure and physicochemical properties of the PtNPs/Ni-Al LDH/GCE were attentively characterized and the electroactivity and stability of the PtNPs/Ni-Al LDH/GCE toward methanol oxidation in NaOH solution was investigated by cyclic voltammetry, chronoamperometry, and chronopotentiometry methods. The electrochemical measurements show that the PtNPs/Ni-Al LDH/GCE has superior catalytic activity for methanol electrooxidation compared to the PtNPs/GCE and Ni-Al LDH/GCE. Also, the chronoamperometric result indicates that the PtNPs/Ni-Al LDH/GCE has a better stability.

2. Materials and Method

2.1. Reagents and apparatus

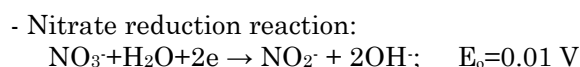
$H_2PtCl_6.5H_2O$, KNO_3 , $Al(NO_3)_3.9H_2O$, $Ni(NO_3)_2.6H_2O$, methanol and NaOH with pure analytical grade were purchased from Merck and used as received. All solutions were prepared with doubled distilled water.

X-ray powder diffraction (XRD) patterns were recorded by a Bruker AXS model D8 Advance (Karlsruhe, Germany) instrument, using Cu-K α radiation source (1.54 Å) at 40 kV and 35 mA at room temperature. The 2θ angle of the diffractometer was stepped from 10° to 90° at a scan rate of 5 min^{-1} . The morphology of electrodes surface was investigated using scan-

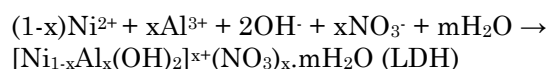
ning electron microscopy (SEM) on A LEO1430 vp (Carl Zeiss, Germany) instrument equipped with an energy dispersion X-ray spectroscopy (EDX) device. The electrochemical measurements were carried out with an AUTOLAB PGSTAT-100 (potentiostat / galvanostat) equipped with a USB electrochemical interface and controlled by GEPS software. A conventional three-electrode system was employed comprising a modified GCE as working electrode, a platinum wire as counter electrode and an aqueous saturated calomel electrode (SCE) as reference electrode.

2.2. Preparation of electrocatalyst

Electrodeposition is an efficient method for the preparation of nanoparticles, has been used to fabricate LDH films on the metal or other substrates [42-44,48,50-52]. It is widely used with different procedures, such as potential step deposition, cyclic voltammetry, double-pulse, and galvanostatic methods [49]. Among these, potential step deposition provides a tool to fine-tune the amount of the deposited materials, the number of active sites and their size. In this work, prior to the electrodeposition and the modification process, the bare GCE was carefully polished with alumina slurry on fine abrasive paper and then entirely cleaned ultrasonically in solution of containing ethanol and doubled distilled water. The electrodeposition processes were performed by using the potentiostatic deposition. Firstly, the Ni-Al LDH film on the GCE was constructed by cathodic reduction in a solution containing 22.5 mM Ni(NO₃)₂, 7.5 mM Al(NO₃)₃ and 0.3 M KNO₃ at the applied potential of -0.9 V vs. SCE [50]. The reactions are shown as follows [51].

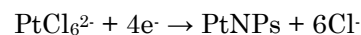


Both reactions can potentially lead to the deposition of LDH by causing a steep local increase in the pH close to the cathode (GCE) as [52]:



The obtained Ni-Al LDH/GCE was rinsed with double distilled water. Then, the PtNPs were electrodeposited on/in the Ni-Al LDH/GCE by cathodic reduction of an aqueous solution of 0.1 M H₂SO₄ containing 1 mM

H₂PtCl₆·5H₂O at the applied potential of -0.2 V vs. SCE [49,53]. The reaction is shown as:



3. Results and Discussion

3.1. Physicochemical characterization

XRD technique is a very strong instrumental method for characterizing the structure and crystallinity of materials. XRD analysis was used to characterize the structure and phase of the PtNPs/Ni-Al LDH/GCE and other materials, and the corresponding resulted patterns were shown in Figure 1. Figure 1 shows XRD patterns of bare GCE (A), PtNPs/GCE (B), Ni-Al LDH/GCE (C) and PtNPs/Ni-Al LDH/GCE (D), respectively. As can be seen at the bare GCE, only an intense reflection peak located on the 2θ angle of 26.4° was observed, indicating a basic (002) reflection of GCE [53]. While after coating the GCE surface with PtNPs, the XRD pattern of the PtNPs/GCE (Figure 1B) presents the main characteristic peaks of the face-centered cubic (fcc) crystalline Pt at 2θ = 39.9°, 46.4°, 67.6° and 81.7°, corresponding to the (111), (200), (220) and (311) planes of a face centered cubic (fcc) lattice of Pt nanoparticles,

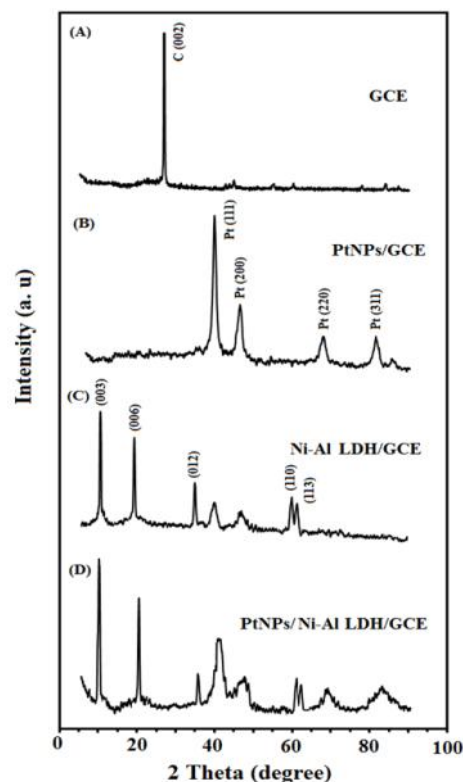


Figure 1. XRD patterns of the GCE (A), PtNPs/GCE (B), Ni-Al LDH/GCE (C) and PtNPs/Ni-Al LDH/GCE (D)

respectively [54]. Figure 1C presents the XRD pattern and the characteristic reflections of the Ni-Al LDH/GCE structure with a series of sharp and intense lines corresponding to structure of Ni-Al LDH, four peaks appeared at $2\theta = 10.02^\circ$, 19.86° , 34.52° and 60.73° , corresponding to the (003), (006), (012), and (110) diffraction planes [53,55,56]. The series of intense basal reflections for the Ni-Al LDH/GCE indicate that LDH film was successfully electrodeposited on GCE surface. All reflections can be indexed as those typical of a hydrotalcite-like LDH family (JCPDS: 38-0487), which also establishes the purity of the Ni-Al LDH obtained from the electrodeposition procedure [44]. The XRD pattern of PtNPs/Ni-Al LDH/GCE (Figure 1D) shows reflections due to both the Ni-Al LDH and PtNPs. After electrodeposition of the PtNPs on/in the Ni-Al LDH film at the surface of GCE and construction of PtNPs/Ni-Al LDH/GCE, the new series of basic reflections

indicate that the PtNPs were successfully electrodeposited on/in the Ni-Al LDH film.

The surface morphology of the Ni-Al LDH/GCE, PtNPs/GCE and PtNPs/Ni-Al LDH/GCE was examined by SEM. SEM images of these materials are shown in Figure 2 (A-C). SEM image of Ni-Al LDH/GCE (Figure 2A) shows an aggregate that consists of crystallites were collected as small spherical particles, and the surface coverage is almost uniform without any holes and deficiencies. Figure 2B revealed that the PtNPs are homogeneously distributed on the GCE. While after electrodeposition of the PtNPs on the surface of Ni-Al LDH/GCE, the underlying Ni-Al LDH film was coated by cauliflower-like PtNPs (Figure 2C) which could greatly increase the surface area and improve the catalytic performance. The EDX measurements were used to analysis the surface composition of the electrosynthesized composite and other materials. The EDX spectrums of these

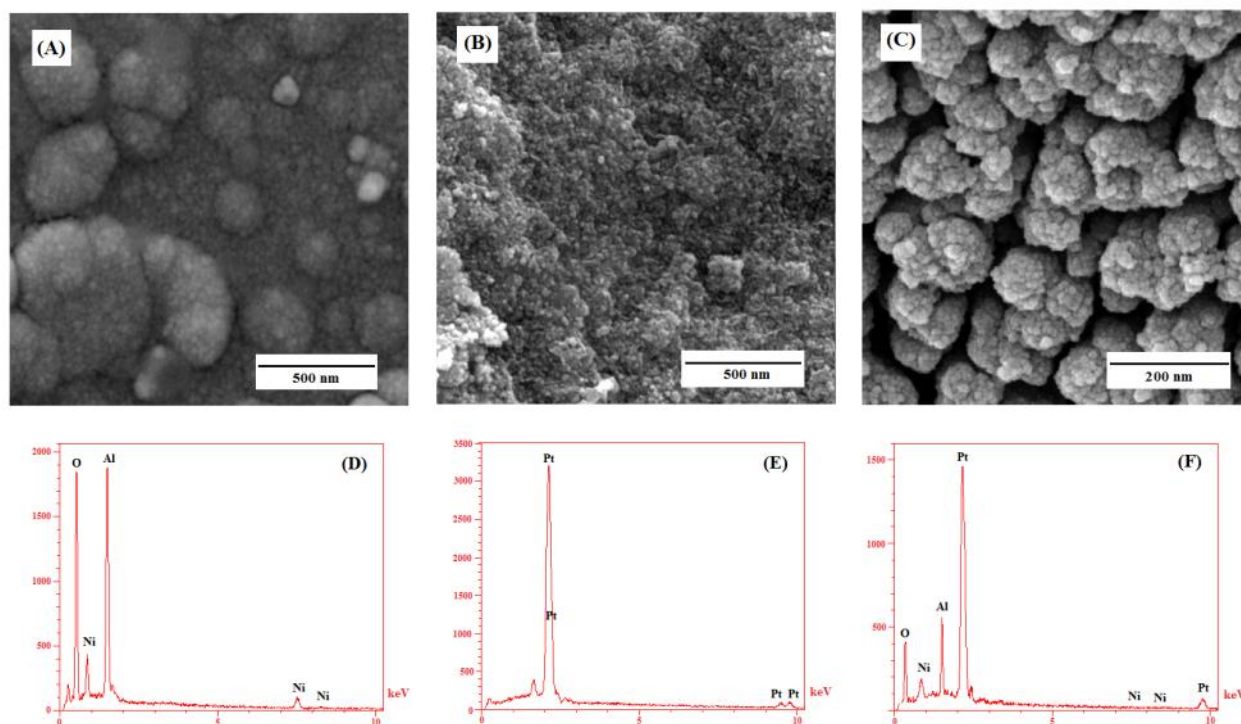


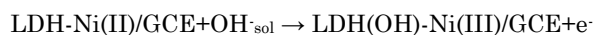
Figure 2. SEM images of the Ni-Al LDH/GCE (Electro deposition Time: 300 s) (A), PtNPs/GCE (Electro deposition Time: 660 s) (B) and PtNPs/Ni-Al LDH/GCE (C). EDX spectrums of the Ni-Al LDH/GCE (D), PtNPs/GCE (E) and PtNPs/Ni-Al LDH/GCE (F)

Table 1. Surface chemical composition of modifiers in the present work

Modifier	Atoms	Mass content (%)	Atomic content (%)
PtNPs/Ni-Al LDH	Pt: Ni: Al	15.07: 11.32: 73.61	2.58: 6.43: 90.99
Ni-Al LDH	Ni: Al	10.46: 89.54	5.10: 94.90

materials are shown in Figure 2 (D-F). The presence of Ni, Al and O elements was verified in the EDX spectra of Ni-Al LDH/GCE (Figure 2D), also the presence of only Pt element (Figure 2E) and Ni, Al, O and Pt elements (Figure 2F) was verified in the EDX spectrums of PtNPs/GCE and PtNPs/Ni-Al LDH/GCE, respectively. Therefore, the presence of PtNPs in the Ni-Al LDH film is further confirmed from the EDX spectrum. The atomic compositions obtained from EDX analysis for the decorated PtNPs/Ni-Al LDH and Ni-Al LDH/GCE catalysts are shown in Table 1 confirming the presence of Pt, Ni and Al on the GCE surface.

For electrochemical characterization of the PtNPs/Ni-Al LDH/GCE and Ni-Al LDH/GCE, their electrochemical behaviors were investigated by cyclic voltammetry. Figure 3 shows the cyclic voltammograms (CVs) of the PtNPs/Ni-Al LDH and Ni-Al LDH/GCE in 0.5 M NaOH solution. Both electrodes show the CVs with a pair of redox peaks between 0.2 V to 0.5 V, which can be attributed to the quasi-reversible one electron transfer of Ni(III)/Ni(II) in this condition, suggesting that the Ni-Al LDH was successfully electrofabricated on the surface of GCE [55]. As reported in the literatures [52] for a Ni-Al LDH, the redox process in basic medium can be represented by the following reaction:



The charge transport inside the electrode material, Ni-Al LDH film, is due to a mixed mechanism involving an "electron hopping" along the Ni-Al LDH layers, and migration of

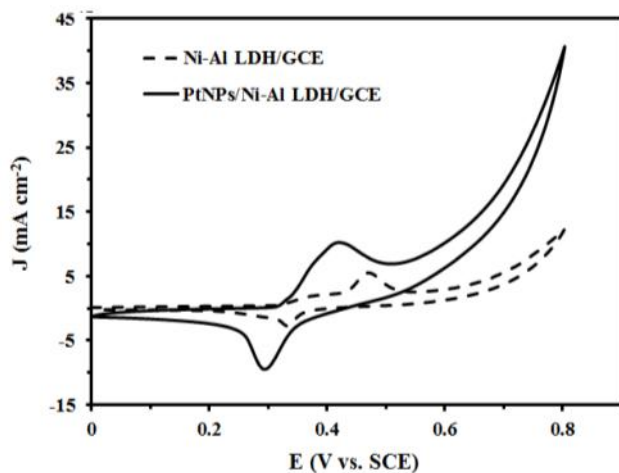


Figure 3. CVs of the Ni-Al LDH/GCE and PtNPs/Ni-Al LDH/GCE in 0.5 M NaOH electrolyte at room temperature and at scan rate of 50 mV s^{-1}

OH^- ions from the solution into the interlayers to compensate the positive extra-charge in the applied anodic potential [52].

On the other hand, a 2-fold enhancement in the anodic peak current density of Ni(III)/Ni(II) and about 55 mV diminution in the anodic and cathodic peak potentials were achieved by coating and doping the PtNPs on/in Ni-Al LDH film at the surface of GCE. The enhancement in the anodic peak current density of Ni(III)/Ni(II) couple and diminution of the anodic and cathodic peak potentials in the PtNPs/Ni-Al LDH/GCE can be attributed to increasing the conductivity of the PtNPs/Ni-Al LDH composite with respect to undoped Ni-Al LDH and also catalysis effects of the doped PtNPs in the vicinity Ni(III)/Ni(II) couples.

3.2. Electrocatalytic characterization

The purpose of the present study was to fabricate a catalyst for the electrocatalytic oxidation of methanol in alkaline media. Therefore, we have prepared the PtNPs/Ni-Al LDH/GCE and Ni-Al LDH/GCE where the both of them have almost the same number of electroactive Ni centers, which have electrocatalytic activity toward methanol oxidation, by controlling the deposition time in the first step of catalyst preparation. On the other hand, in the PtNPs/Ni-Al LDH/GCE in addition to Ni centers, the PtNPs with special electrocatalytic properties toward this fuel, methanol, were electrodeposited in the second step in order to achieve better results. Therefore, in the following, electrocatalytic characterizations of these

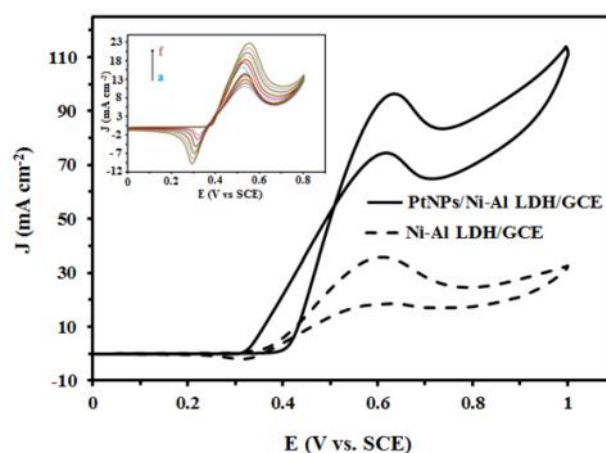


Figure 4. CVs of the Ni-Al LDH/GCE and PtNPs/Ni-Al LDH/GCE in 0.5 M NaOH + 0.25 M methanol at scan rate of 50 mV s^{-1} . Inset is CVs of PtNPs/Ni-Al LDH/GCE in 0.5 M NaOH + 0.1 M methanol at different scan rates (30, 50, 90, 130, 150, 200 and 250 mV s^{-1})

catalysts were tested as the anodic catalysts for methanol oxidation in alkaline media. The electrocatalytic characterizations of the PtNPs/Ni/Al-LDH/GCE and Ni/Al-LDH/GCE toward methanol oxidation were evaluated in details by cyclic voltammetry, chronoamperometry, and chronopotentiometry methods and the obtained CVs in alkaline media were shown in Figure 4. As can be seen, both CV curves show a similar methanol oxidation current peak in the forward scan and an oxidation peak in the backward scan corresponding to the removal of the residual carbonaceous species formed during methanol oxidation in the forward scan [8,53]. Meanwhile, the anodic peak appeared during the forward scan reappeared almost at the same potential during the backward scan [55]. As we know, the magnitude of the peak current density in the forward scan indicates the electrocatalytic activity of the electrocatalyst for methanol oxidation. From Figure 4, can see that the methanol oxidation current in the forward scan is significantly higher on the PtNPs/Ni/Al-LDH/GCE (97 mA/cm²) than on the Ni-Al LDH/GCE (37 mA/cm²) and also on the PtNPs/GCE (50.5 mA/cm²), indicating that there is a contributory effect between PtNPs and Ni-Al LDH in the obtained nanocomposite and enhances their performance in methanol electrooxidation [43,49]. This result approves that the PtNPs/Ni-Al LDH/GCE has a better electrocatalytic activity for methanol oxidation in alkaline media. The possible reason for this trend can be summarized as follows: (1) synergistic effect between PtNPs and Ni-Al LDH and its promoting properties; (2) content increase of metallic state of the PtNPs in the PtNPs/Ni-Al LDH/GCE nanocomposite, which is well known that the more

content of metallic state in catalysts, the better catalytic performance; (3) increasing the conductivity of the PtNPs/Ni-Al LDH nanocomposite with respect to undoped Ni-Al LDH; and finally (4) as a hydroxide ion conductor, Ni-Al LDH could deliver OH⁻ and increase the concentration of OH⁻ around the PtNPs and bifunctional effect between the OH⁻ and PtNPs similar with the commonly accepted bifunctional effect between Pt and Ru [57,58] in the case of Pt-Ru electrocatalyst [59] to remove the intermediate carbonaceous species and contribute to the low poisoning.

It should be noted that, under a low concentration of methanol (0.1 M), the anodic peak current in the forward scan for methanol oxidation and cathodic peak current of Ni(III)/Ni(II) couple in the backward scan presented in the CV gram (inset of Figure 4) due to unmasking the cathodic current of Ni(III)/Ni(II) couple by the methanol oxidation peak [55].

In this section, the effects of some parameters on the electrocatalytic activity of the PtNPs/Ni-Al LDH/GCE and Ni-Al LDH/GCE were studied. Firstly, the effect of electrodeposition times in the both steps of electrocatalyst preparation; Ni-Al LDH deposition on the GCE for preparation of Ni-Al LDH/GCE and PtNPs deposition on/in the Ni-Al LDH film for the preparation of PtNPs/Ni-Al LDH/GCE, on the anodic current density of methanol oxidation reaction in the forward scan was studied. Figure 5 shows the value of the anodic current density for methanol oxidation on the PtNPs/Ni-Al LDH/GCE (A) and Ni-Al LDH/GCE (B) after 60, 180, 300, 420, 540, 660, 780 and 900 s for the Ni-Al LDH electrodeposition and 300, 420, 540, 660, 780 and 900 s for the PtNPs electrodeposition, respectively.

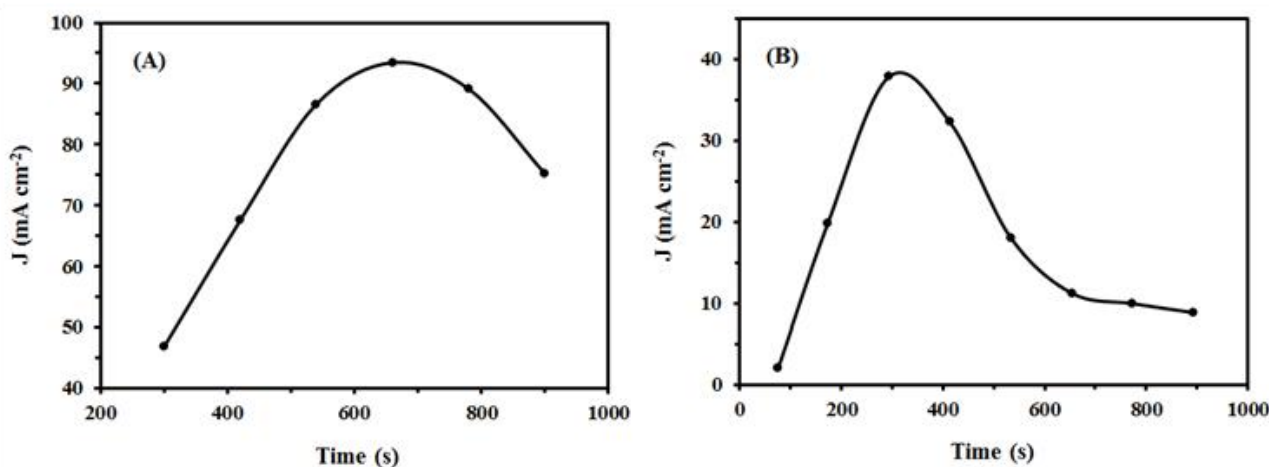


Figure 5. The plots of the anodic peak current density in the forward scan versus time (s) for electro deposition of PtNPs (A) and electro deposition of Ni-Al LDH (B)

These experiments were repeated for 3 times and the same results were obtained (mean of data were shown). The anodic current density for methanol oxidation increased with increasing the electrodeposition time up to 300 s and 660 s respectively for Ni/Al-LDH and PtNPs electrodeposition. Increasing of anodic current density is due to increase in the real surface area of the electrocatalyst. With further increase in the electrodeposition times, the methanol oxidation current density started to decrease [41]. Possible explanation could be that the decreasing the real surface area of the electrocatalyst due to the agglomeration of PtNPs or decreasing the conductivity of the Ni-Al LDH film by increasing the thickness [41,55].

In order to investigate the kinetic charac-

terization of methanol oxidation on the PtNPs/Ni-Al LDH/GCE electrocatalyst, we looked into the effect of scan rate on the anodic current density of methanol oxidation in the forward scan. The effect of scan rate on the electrooxidation of 0.25 M methanol in 0.5 M NaOH solution is shown in Figure 6 (A). The results clearly exhibit that the anodic peak current density associated to methanol electrooxidation increases linearly with the increase of the scan rate. The relation between the peak current density obtained from forward scan and $v^{1/2}$ is shown in Figure 6 (B). There is a linear relationship with a high correlation coefficient ($R^2 > 0.97$) between peak current density and square root of scan rate, implying that the methanol oxidation is typically under diffusion control [57-60]. Moreover,

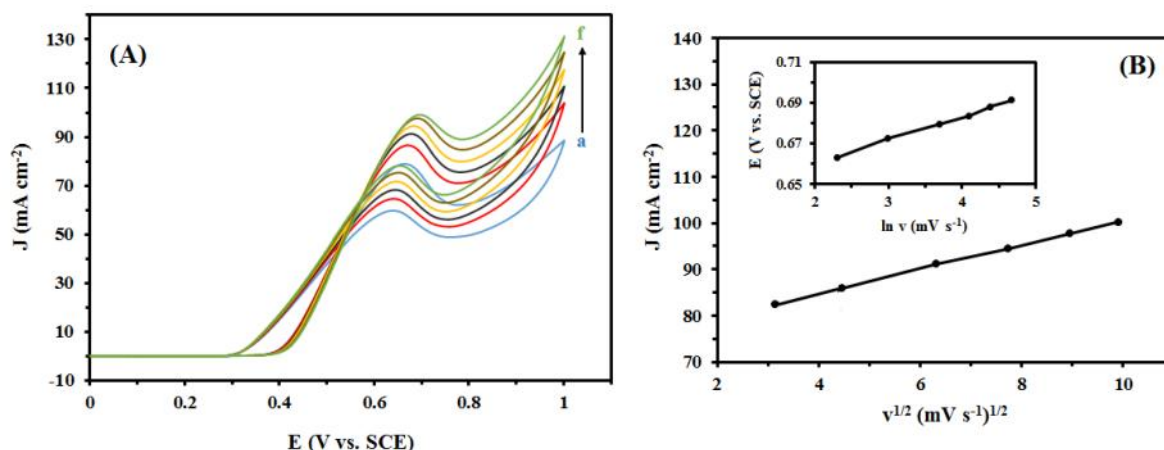


Figure 6. (A) CVs of the PtNPs/Ni-Al LDH/GCE in 0.5 M NaOH + 0.25 M methanol at different scan rates (10, 20, 40, 60, 80 and 100 mV s^{-1}). (B) Plot of the anodic peak current density versus the square root of scan rates. The inset is E (V vs. SCE) versus the $\ln v$ (mV s^{-1})

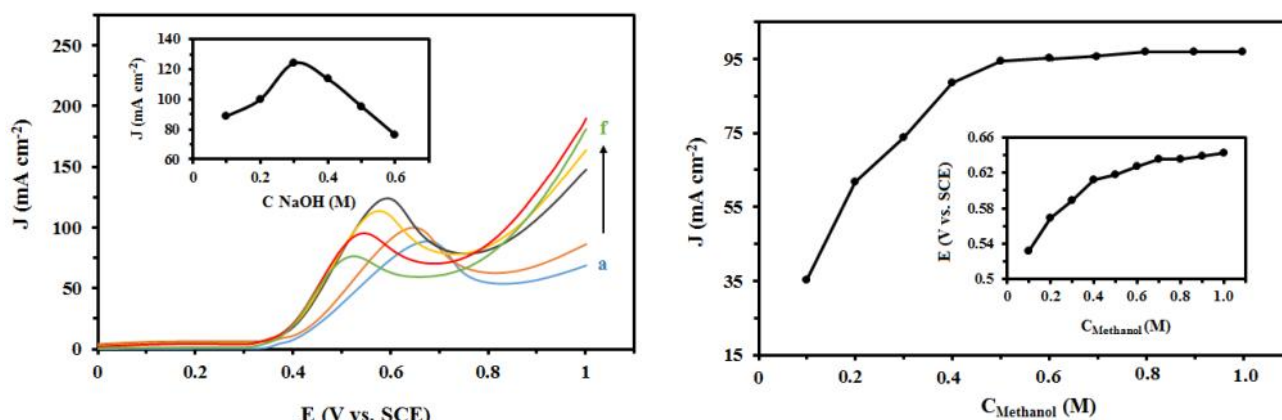


Figure 7. CVs of the PtNPs/Ni-Al LDH/GCE for 0.25 M methanol at a scan rate of 50 mV s^{-1} at various NaOH concentrations (0.1 to 0.6 M from a to f). The inset is the anodic peak current density at various electrolyte concentrations

Figure 8. The plot of the anodic peak current density on the PtNPs/Ni-Al LDH/GCE at various methanol concentrations. The inset is E of the anodic peak in the forward scan versus fuel concentration

the oxidation peak potential in the forward scan (E_f) shifts positively with increasing scan rate (v). A linear relationship can be obtained between E_f and $\ln(v)$, as shown in the inset of Figure 6 (B). This indicates that the oxidation of methanol on the PtNPs/Ni-Al LDH/GCE electrocatalyst is completely an irreversible process [8,58].

The role of OH^- ion in the oxidation of methanol has been discussed at various Ni containing species modified electrodes [38-41,53,55,60-62]. The effect of NaOH concentration on the methanol oxidation at the PtNPs/Ni-Al LDH/GCE was investigated. The CVs of PtNPs/Ni-Al LDH/GCE were recorded in 0.25 M methanol solution in the presence of various concentrations of NaOH ranging from 0.1 to 0.6 M at a scan rate of 50 mV s^{-1} . Figure 7 shows the effect of NaOH concentration on the oxidation of methanol (only forward scans were shown). It can be seen that with an increase in OH^- concentration the peak potential shifts toward more negative values and the anodic peak current density of methanol oxidation increase by increasing the NaOH concentration up to 0.3 M and then decrease at concentration higher than 0.3 M. These results indicate that the OH^- ion participates in the oxidation of methanol and may be adverse to the oxidation of methanol for the competitive adsorption on the active sites to methanol. At low OH^- concentration ($<0.3 \text{ M}$), the peak potential shifts toward more negative values with an increase in OH^- concentration, because as mentioned already the anodic current density in forward scan mainly comes from the oxidation of methanol and increasing the concentration of OH^- around the PtNPs increase the bifunctional effect between the OH^- and PtNPs [57-59] to remove the intermediate carbonaceous species and contribute to the low poisoning. On the other hand, in more alkaline electrolytes ($>>0.3 \text{ M}$) the adsorption of OH^- prevents the methanol adsorption on the electrocatalyst sites and so the reaction rate of methanol oxidation decreases [63].

Figure 8 shows the effect of methanol concentrations on the electrooxidation current density of this fuel at the PtNPs/Ni-Al LDH/GCE in 0.5 M NaOH solution. It can be clearly observed that increasing the methanol concentration up to 0.6 M increases the anodic current density and, there is not any significant increase in the current density of methanol oxidation in methanol concentrations higher than 0.6 M. This effect might be due to the saturation of active sites on the surface of the electrode by methanol molecules and also contami-

nation of the electrocatalyst surface which is mainly arisen from the CO_{ads} intermediate during the methanol oxidation [64-66]. When the fuel concentration increases, the peak potential of the anodic peak in the forward and backward scan (inset of Figure 8 for forward scan) were shifted to high positive values. These may be occur because of this probably reason: the poisoning rate of the PtNPs sites increases with increasing the fuel concentration and the oxidative removal of the strongly adsorbed intermediates would shift to a more positive potential [67]. In accordance with this result, it displays that the concentration value of 0.6 M indicates a critical concentration after which the adsorption of the oxidation products at the PtNPs/Ni-Al LDH/GCE catalyst surface causes the hindrance of further methanol oxidation.

3.3. Stability characterization

Long-term structural durability is one of the most essential characteristics for FCs to be accepted as a viable product. Poisoning of the electrocatalysts with intermediate species produced during alcohol oxidation reaction influences their long-term performance. The resistance of the electrocatalysts to CO_{ad} -poisoning has been evaluated by various stability and durability tests such as repetitive potential cycling, change in the CV profile after many cycles [66-68], potential holding method [69] and potential step method [70]. In this work, to evaluate the long-term stability of PtNPs/Ni-Al LDH/GCE for methanol oxidation, the forward anodic peak current density was followed over 200 successive cycles at a scan rate of 50 mV s^{-1} in NaOH solution containing 0.25 M methanol (1st, 25th and 50th cycles was shown in inset of

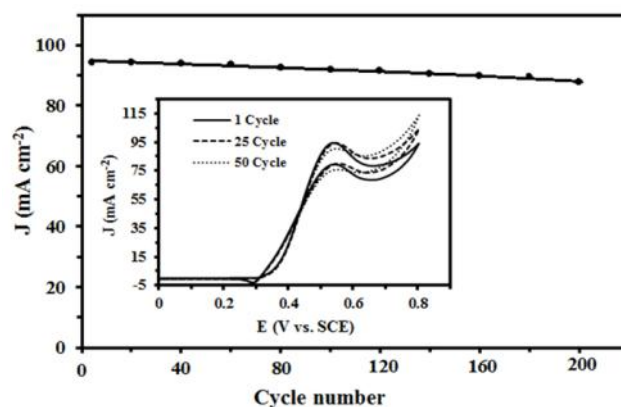


Figure 9. Plot of the anodic peak current density in the forward scan at the PtNPs/Ni-Al LDH/GCE in 0.5 M NaOH + 0.25 M methanol solution at scan rate of 50 mV s^{-1} in different scans (Long-term stability). Inset is the CVs of 1, 25 and 50th cycles

Figure 9). The current density of anodic peak in the forward scan versus number of cycles is shown in Figure 9. It can be observed that the peak current density decreases very slowly with the consecutive scans. After 200 cycles, the anodic peak current density remains at 95.41% of the 1st cycle (the good performing cycle). Ni-Al LDH particles, with the presence of sites and functional groups, may lead to a strong LDH-Pt interaction and resultant resistance of Pt to poisoning, and therefore enhanced durability [38-41,71]. The loss of the electrocatalytic activity may be related to Pt nanoparticles aggregation/degradation.

The stability of current generated by the electrocatalysts can be tested by further experiments; chronoamperometric method. Thus, in our following experiments, the stability of the PtNPs/Ni-Al LDH/GCE and Ni-Al LDH/GCE was tested by chronoamperometry. Figure 10 shows the typical chronoamperograms of the PtNPs/Ni-Al LDH/GCE and Ni-Al LDH/GCE in 0.5 M NaOH and 0.25 M methanol aqueous solution at a fixed potential of 0.65 V for 2000 s. The superior performance of the PtNPs/Ni-Al LDH/GCE with respect to the Ni-Al LDH/GCE is also reflected in the chronoamperometry measurements. The initial sharp rapid decrease at the initial stage in the polarization current density for the Ni-Al LDH/GCE is attributed to the poisoning effect of the intermediate species during the methanol electrooxidation reaction in alkaline medium. However, rapidly decreasing in the current density for PtNPs/Ni-Al LDH/GCE occurs in the first milliseconds but is very much slower than compared with Ni-Al LDH/GCE and subsequently the current density reaches a pseudo steady state [72]. The approximate steady current values af-

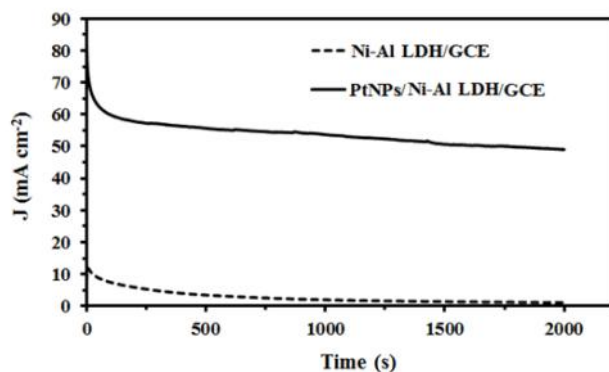


Figure 10. Chronoamperometric curves for the PtNPs/Ni-Al LDH/GCE and Ni-Al LDH/GCE in 0.5 M NaOH + 0.25 M methanol solution (polarization potential: 0.65 V) for 2000 s

ter 10 s methanol oxidation period were found to be 60.1 and 9.7 mA cm⁻², respectively on the PtNPs/Ni-Al LDH/GCE and Ni-Al LDH/GCE. The quasi-stable current densities at the end of the test after 2000 s were 49.7 and 1.6 mA cm⁻² respectively on the PtNPs/Ni-Al LDH/GCE and Ni-Al LDH/GCE. It can be seen from chronoamperometry test that the methanol oxidation on the PtNPs/Ni-Al-LDH/GCE possesses higher initial and limiting current density and this electrocatalyst gave the very higher stable current response, which displays better catalytic activity and stability. These results corroborate our observation from the cyclic voltammetry.

Further performance evaluation test of the PtNPs/Ni-Al LDH/GCE was carried out by chronopotentiometry. Chronopotentiometry is a powerful method to study the poisoning-resistance abilities of electrocatalysts for alcohol oxidation. Figure 11 shows the chronopotentiometric curves, measured in 0.5 M NaOH solution that contains 0.25 M methanol at a current of 95 mA cm⁻² and 35 mA cm⁻², respectively for PtNPs/Ni-Al LDH/GCE, and Ni-Al LDH/GCE. Theoretically, the electrode potential will increase to a higher value when charged by a positive current based on the electrochemical principle [73]. The markedly different shape of the V-t curve strongly indicates that these different electrocatalysts exhibited various electrochemical responses when being charged. It is obvious that the electrode potential of PtNPs/Ni-Al LDH/GCE remains the lower value than Ni-Al LDH/GCE. Also, it can be clearly seen from Figure 11 that the potential increased rapidly in the first seconds and the polarization potential gradually increases

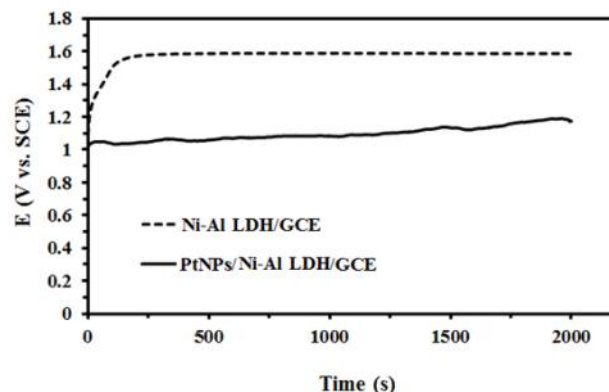


Figure 11. Chronopotentiometric curves for the PtNPs/Ni-Al LDH/GCE and Ni-Al LDH/GCE in 0.5 M NaOH + 0.25 M methanol solution (polarization current: 95 mA cm⁻² for PtNPs/Ni-Al-LDH/GCE and 35 mA cm⁻² for Ni-Al-LDH/GCE) for 2000 s

with time. The over potential of Ni-Al LDH/GCE is higher than PtNPs/Ni-Al LDH/GCE electrocatalyst; therefore, PtNPs/Ni-Al LDH/GCE is conducive to lower overpotential of Ni-Al LDH/GCE. A lower overpotential is an indication of better electroactivity, thus PtNPs/Ni-Al LDH/GCE represents the better electroactivity than Ni-Al LDH/GCE [74]. Some reported results confirm that LDH films have anti-poisoning property, which turns easier any oxidation reaction [41,55,72], and this is more efficient in fuel cells.

4. Conclusions

In this study, Ni-Al layered double hydroxides (Ni-Al LDH)-Pt nanoparticles (PtNPs) composite by a facile two-step electrochemical method is electrodeposited on the GCE. After physicochemical characterizations of PtNPs/Ni-Al LDH/GCE, its electrocatalytic and stability characterizations toward methanol oxidation in alkaline media were investigated in detail by cyclic voltammetry, chronoamperometry and chronopotentiometry measurements. PtNPs/Ni-Al LDH/GCE exhibited higher electrocatalytic activity than PtNPs/GCE and Ni-Al LDH/GCE and also the obtained chronoamperograms indicated that the PtNPs/Ni-Al LDH/GCE has a better stability. Therefore, this work provides an effective method to electrodepositing the PtNPs/Ni-Al LDH on the GCE surfaces to prepare a relatively low-cost nanocomposite that may be used as potential anode material for DMFCs in alkaline media.

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