Perovskite-Type LaFeO_3 and LaFeO_3 -CNTs Nanocrystals as Active Anode for Methanol Oxidation in Alkaline Solutions

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Abstract: In the current study, perovskite type LaFNPs (LaFeO_3 nanoparticles) were prepared by a rapid microwave-assisted co-precipitation method and their presence was confirmed by XRD, EDX and SEM techniques. LaFNPs and LaFNPs-CNTs (LaFeO_3 NPs-carbon nanotubes) nanocomposites were successfully prepared. GC (glassy carbon) electrode was modified with LaFNPs and LaFNPs-CNTs for methanol electrooxidation. The electrocatalytic activity of LaFNPs and LaFNPs-CNTs nanocatalysts toward methanol electrooxidation was examined through cyclic voltammetry and chronoamperometry methods. The effect of some experimental factors such as methanol, LaFNPs amounts, electrolyte concentrations and scan rate was studied. The catalytic activity of LaFNPs-CNTs and LaFNPs nanocatalysts was compared with each other. According to the electrochemical investigations, LaFNPs nanocatalyst had a considerable activity for methanol electrooxidation in comparison to LaFNPs nanocatalyst.

Key words: Nanocomposite, nanocatalyst, methanol electrooxidation.

1. Introduction

Direct methanol fuel cells are attracting more and more attention as renewable and clean power sources for electric vehicles and portable electronic devices. Methanol as a liquid fuel has unique advantages in comparison to hydrogen, such as easy producing, storage and transportation, simple structure and high energy density. Also, methanol has good kinetics of oxidation at low temperatures compared to other alcohols. It can be oxidized completely to CO_2 with maximum transfer of electrons. Thus, methanol oxidation has been investigated extensively over the past several decades. Noble metals, especially Pt-based [1] and Pt Ru bimetallic systems [2] show excellent activities toward methanol electrooxidation,

but the price of pure platinum is relatively high. Furthermore, the intermediates produced during the methanol oxidation such as CO (carbon monoxide) would poison the noble metal sites [1] and this cause the deterioration in the performance of noble metal-based fuel cell electrodes. Such poisoning phenomenon can be also avoided by using electronically conducting mixed oxides as anode materials. Though the oxides of V, Fe, Ni, In, Sn, La and Pb were earlier used as anode materials [3]. In recent years, studies on various transition metal mixed oxides have shown that the perovskite oxides can be used as fuel cell electrodes at high temperatures instead of noble metals [4-7]. Perovskite-type solids especially with general formula, ABO_3 with different combinations of A and B cations (A = rare earth metals, B = transition metals) have been considered promising catalytic materials for increasing anodic reaction kinetic in direct alcohol fuel cells. They can

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be used in important processes [8-10] such as, electrochemical evolution/reduction of oxygen, oxidation of alcohols [11, 12], reduction of nitrogen oxides and chemical oxidation of CO and hydrocarbons [13, 14] etc. Recently, several studies on perovskite oxides with a large amount of oxygen vacancies and excellent electrical conductivities have shown that these compounds can be used as electrodes in direct alcohol fuel cells [15-18].

CNTs (carbon nanotubes) are considered an attractive supporting material due to nanometer size, large surface to volume ratio, high electronic and thermal conductivity, in addition to good mechanical and chemical stability [19-21].

In this work, we have prepared perovskite-type LaFeO_3 and LaFeO_3 -CNTs nanocatalysts and used them for electrocatalysis of methanol oxidation in alkaline media. Alkaline medium was chosen since these materials are unstable in acid medium. The electrochemical characterization of LaFNPs and LaFNPs -CNTs nanocatalysts toward methanol oxidation was investigated by cyclic voltammetry and chronoamperometry techniques. The effect of some experimental factors on the anodic current density and potential of methanol electrooxidation was investigated and the optimum conditions were determined.

2. Experimental

2.1 Materials

Nafion@117 solution was purchased from Merck and used as received. $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NaOH, methanol and octanoic acid were purchased from Merck, and used without further purification. MWCNTs (multiwall carbon nanotubes), with nanotube diameters, OD = 20-30 nm, wall thickness = 1-2 nm, length = 0.5-2 μm and purity > 95% was purchased from Aldrich. All solutions were prepared using doubly distilled water. Purified N_2 (99.9%) was used without further treatment.

2.2 Instrumentation

EDX and SEM images were got by Philips XL30 apparatus. The ultrasonic apparatus with Eurosonic 4D model was used for synthesis of the nanocomposites. The XRD spectra were obtained by Philips analytical PC-APD apparatus with graphite monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The centrifuge apparatus with Sigma 101 model was used for separation of the precipitate. Electrochemical investigations were done by POTENTIOSTAT GALVANOSTAT AUTOLAB controlled by a personal computer.

2.3 Preparation of LaFeO_3 Nanocatalysts

Perovskite oxide nanoparticles with the molecular formula of LaFeO_3 were synthesized by a microwave-assisted co-precipitation method using octanoic acid as surfactant. Preparation of LaFeO_3 nanocatalyst was as follows, at first, 20 mL of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 0.2 M and 20 mL of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ 0.2 M aqueous solutions were mixed in a beaker and stirred until the complete solving. And 2 mL of octanoic acid was added as surfactant to the resulted orange solution. Then, 25 mL of NaOH solution was added very slowly and drops wise to the mixture until the pH of 7-8 and preparation of the brown precipitate. After complete precipitation, the liquid precipitate was transferred to the microwave infrared irradiation (900 W/180 $^\circ\text{C}$) for 6 min. After cooling, the mixture was centrifuged with 3,000 rpm for 15 min and washed by ethanol and water for several times. The product was calcinated at 800 $^\circ\text{C}$ in the furnace for 4 h to lose all its residual organic materials. The prepared LaFeO_3 nanocatalysts were kept for characterization.

2.4 Electrochemical Investigations

Electrochemical measurements have been done with a POTENTIOSTAT GALVANOSTAT AUTOLAB controlled by a personal computer. A conventional three-electrode cell with platinum and a

SCE (saturated calomel electrode) as the counter and reference electrodes, respectively was used for electrochemical investigation at room temperature. All potentials were reported with respect to the reference electrode. The GC (glassy carbon) electrode with 2 mm of diameter was used as the working electrode. The working solution was N₂-saturated 1.75 M of methanol and 1.5 M NaOH. All experiments were performed under nitrogen atmosphere at room temperature. All glassware was thoroughly cleaned with freshly prepared aqua regain (3:1; HCl/HNO₃) and rinsed comprehensively with double distilled water prior to use. Scan rate for all the experiments was 100 mV s⁻¹.

2.5 Preparation of the Electrode

To prepare GC/LaFNPs electrode, 2 mg of LaFeO₃ nano-powder and 5 µL Nafion were dispersed in 0.5 ml of double distilled water by sonication for 120 min to obtain a suspension. Then 5 µL of the prepared suspension was spread by pipette onto the glassy carbon substrate. The subsequent evaporation of the solvent led to the formation of the deposited catalyst layer. In order to prepare GC/LaFNPs-CNTs electrode, 2 mg of LaFeO₃ nanocatalyst, 5 µL Nafion and 1 mg MWCNTs were dispersed in 0.5 mL of double distilled water and ultrasonicated for 120 min to obtain a suspension. 5 µL of the prepared suspension was spread by pipette onto the glassy carbon substrate. The subsequent evaporation of the solvent led to the formation of LaFeO₃-CNTs layer.

3. Results and Discussion

3.1 Characterization of LaFeO₃ Nanocatalyst

SEM image of LaFeO₃ nanoparticles was shown in Fig. 1A. As seen in Fig. 1A, LaFNPs were very homogenate and sphere like with the particle size of about 71.96 nm. The XRD analysis showed clearly the pattern corresponding to perovskite-type LaFeO₃ (JCPDS File No. 37-1493), which crystallizes in the orthorhombic system with a main diffraction peak at d

= 2.77 Å ((1 2 1) plane) (Fig. 1B). The following Eq. (1) [22] was used for determining the lattice parameters:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (1)$$

where d was the distance between crystalline planes with Miller indices (hkl), also a , b and c were the lattice parameters. The lattice parameters of LaFeO₃ nanocrystals were $a = 5.58$, $b = 7.84$ and $c = 5.53$ Å. The particle size of LaFeO₃ nanocrystals was calculated with Debye-Scherrer equation [23]:

$$D_c = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

D_c is the particle size of LaFeO₃ nanocrystals, K is the shape factor which usually takes a value about 0.9, λ is the wavelength of the X-ray source used in XRD, β is the breadth of the observed diffraction line at its half-intensity maximum in radian and θ is the Bragg peak angle. The particle size of LaFeO₃ nanocrystals was 73.55 nm. The EDX spectrum of LaFNPs shown at Fig. 1C clearly revealed the presence of La and Fe elements. The element percent obtained from the EDX spectrum of LaFNPs was shown in the inset of Fig. 1C.

3.2 Methanol Oxidation on LaFNPs and LaFNPs-CNTs Nanocatalysts

Electrocatalytic property of LaFNPs and LaFNPs-CNTs nanocatalysts toward methanol electrooxidation was determined by cyclic voltammetry in 1.5 M NaOH and 1.75 M CH₃OH aqueous solution. The typical cyclic voltammograms for GC/LaFNPs and GC/LaFNPs-CNTs were shown in Fig. 2 and their catalytic activity toward methanol electrooxidation was compared with each other. The typical cyclic voltammograms for GC/Nafion and GC/LaFNPs in 1.5 M NaOH and 1.75 M CH₃OH were shown in Fig. 2A. As seen in Fig. 2A (a), GC/Nafion electrode did not show any catalytic activity toward methanol oxidation. Fig. 2A (b) showed the cyclic voltammogram of GC/LaFNPs in 1.5 M NaOH. The anodic current obtained at potential greater than 0.7 V

Fig. 1 (A) SEM image; (B) XRD spectrum; (C) EDX with elemental composition of LaFNPs.

is due to the oxygen evolution reaction [24]. Cyclic voltammogram of GC/LaFNPs in 1.5 M NaOH and 1.75 M CH_3OH was shown in Fig. 2A (c). As seen in

Fig. 2A (c), there was a large increase in current during the forward scan ($E_p = 1.3$ V) showing the high catalytic activity of LaFNPs nanocomposite for

methanol oxidation. The onset potential of methanol oxidation on GC/LaFNPs electrode was observed at 0.8 V. The characteristics of the CV curves are in agreement with other works [24-27]. This indicates that LaFeO₃ is a good catalyst for methanol oxidation in alkaline solution. Similar to the mechanisms of methanol oxidation on Pt surface [28, 29] and on the perovskite ARuO₃ surface [30], it seems that the possible reaction pathway on the perovskite (LaFeO₃) surface is as follows:

The cyclic voltammograms of GC/CNTs-Nafion and GC/LaFNPs-CNTs electrodes were shown in Fig. 2B. The typical cyclic voltammograms for GC/CNTs-Nafion in 1.5 M NaOH and 1.75 M CH₃OH was shown in Fig 2B (a). As seen in Fig. 2B (a), GC/CNTs-Nafion electrode did not show any catalytic activity toward methanol oxidation. Fig. 2B (b) showed the cyclic voltammogram of GC/LaFNPs-CNTs in 1.5 M NaOH. Cyclic voltammogram of GC/LaFNPs-CNTs electrode in 1.5 M NaOH and 1.75 M CH₃OH was shown in Fig. 2B (c). As observed in Fig. 2B (c), there was a large increase in the current density of the forward scan ($E_p = 1.267$ V). The onset potential of methanol oxidation on GC/LaFNPs-CNTs electrode was 0.565 V. Also the catalytic activities of GC/LaFNPs and GC/LaFNPs-CNTs electrodes toward methanol oxidation were compared with each other in Fig. 2C. As can be clearly seen, using CNT decreased the onset potential from 0.8 to 0.565 V. Thus, LaFNPs-CNTs nanocomposite has better catalytic activity for methanol oxidation than LaFNPs nanocomposite.

Fig. 2 Cyclic voltammograms of (A) LaFeO₃ nanocatalyst in 1.5 M NaOH and 1.75 M CH₃OH with a: GC/Nafion, b: GC/LaFNPs (in NaOH 1.5 M) and c: GC/LaFNPs electrodes; (B) Cyclic voltammograms of LaFNPs-CNTs nanocatalyst in 1.5 M NaOH and 1.75 M CH₃OH with a: GC/CNTs-Nafion, b: GC/LaFNPs-CNTs (in NaOH 1.5 M) and c: GC/LaFNPs-CNTs electrodes; (C) Cyclic voltammograms of a: GC/LaFNPs and b: GC/LaFNPs-CNTs electrodes in 1.5 M NaOH and 1.75 M CH₃OH.

3.3 Determination of Surface Acid-Base Property (PZC)

The electrocatalytic activity depends on the electronic and geometric factors [31, 32]. The nature of the active sites and also the electronic structure of the catalyst can control the electronic factor, but the geometric factor depends on the real surface area and the number of the active sites. To determine the origin of the electrocatalytic activity and to optimize the electrode selection, separation of these two factors is essential. Separation can be obtained by evaluation of surface acid-base properties of the oxides in the aqueous solution and measurement of the actual surface area. The former is an intensive property that only depends on the nature of the active sites and does not depend on the surface area of the oxides. The surface acid-base property of the oxides is determined by measuring the pH of zero charge (PZC), the pH at which the oxide surface is electrically and chemically neutral. PZC is a measure of Lewis acidity [32]. The PZC value of LaFNPs was determined by acid-base potentiometric titrations [31]. A specific amount of LaFNPs was suspended in 10 mL of KNO_3 0.005 M during 1 h of nitrogen bubbling to prevent any contamination from the CO_2 present in the atmosphere. At first, the pH of the solution was 6.7 and it reached to 12 with addition of known amount of 0.1 M NaOH. Then, the suspension was titrated with 0.1 M HNO_3 . The readings were recorded at each point after the pH became stable. The PZC of the oxide particles was obtained by determination of the intersection point of the titration curve in the presence and absent (blank solution) of LaFNPs. The titration curve to determine the PZC value for LaFNPs was shown in Fig. 3 and was found to be 11.25 that is much more than those reported for La_2NiO_4 , $\text{La}_{1.75}\text{Sr}_{0.25}\text{NiO}_4$, $\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$, LaSrNiO_4 and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0.0 \leq x \leq 0.4$) [25]. It seems that, the PZC value of the oxide has influence on the electrocatalytic activity of the catalyst. In fact, the acidity of the surface OH group and also its bond strength to the active metal sites (M-OH) in the oxide

decreases with increasing of the PZC value [33]. Thus, the higher values of PZC will show the higher reactivity of OH_{ads} because of the weakening of its bond strength. So, according to the PZC values, the rate of the methanol electro-oxidation at LaFeO_3 nanoparticles would be greater than those reported before [25].

3.4 Parameters Affecting on the Electrooxidation of Methanol on LaFNPs and LaFNPs-CNTs Nanocomposites

3.4.1 Effect of Methanol Concentration

Fig. 4A and 4B showed the effect of methanol concentration on the anodic current density of methanol oxidation on GC/LaFNPs electrode. It can be clearly observed that increasing the methanol concentration up to 1.75 M increased the anodic current density and, there was not any significant increase in the current density of methanol oxidation in methanol concentrations higher than 1.75 M. This effect was probably observed because of the saturation of active sites on the surface of the electrode. Also, this indicated further that the electrooxidation of methanol at modified electrode is controlled by diffusion process. Thus, to get a higher current density, this concentration of the methanol (1.75 M) was selected

Fig. 3 The titration curve for determination of the PZC value of LaFNPs.

Fig. 4 Cyclic voltammograms for methanol oxidation on (A, B) GC-LaFNPs and (C, D) GC-LaFNPs-CNTs in 1.5 M NaOH in different concentrations of methanol: a) 0.08, b) 0.16, c) 0.24, d) 0.31, e) 0.39, f) 0.47, g) 0.55, h) 0.62, i) 0.70, j) 0.77, k) 0.85, l) 0.92, m) 0.99, n) 1.07, o) 1.14, p) 1.21, q) 1.29, r) 1.36, s) 1.43, t) 1.50, u) 1.57, v) 1.64, w) 1.70, x) 1.75 M.

as the optimum concentration. When the methanol concentration increased from 0.08 to 1.75 M, E_f shifted toward positive direction from 1.17 to 1.3 V. It seemed that the shift of potential to more positive ones was due to the increase in the poisoning rate of the catalyst with increasing the methanol concentration [34]. The effect of methanol concentration on the anodic current density of methanol oxidation on GC/LaFNPs-CNTs electrode was shown in Fig. 4C and 4D. As seen in Fig. 4 C and 4D, when the

methanol concentration increased from 0.08 to 1.75 M, the current density of methanol oxidation increased from 32.93 to 133.87 mA cm^{-2} and E_f shifted toward positive direction from 1.16 to 1.269 V. The shift of the anodic peak potential toward the positive potentials was due to the increasing of the methanol concentration and thus increasing of the poisoning rate of the catalyst.

3.4.2 Effect of LaFNPs Amounts

The effect of LaFNPs amounts on the anodic

current of methanol oxidation at GC-LaFNPs electrode was investigated by cyclic voltammetry and chronoamperometry in 1.75 M of methanol and 1.5 M NaOH (Fig. 5). Different concentrations of LaFNPs (8, 16 and 32 mM) were used. The anodic peak potentials were observed at 1.36, 1.3, 1.39 V respectively and the current densities of methanol oxidation peaks for 8, 16 and 32 mM of LaFNPs nanocatalyst were 162.39, 149.99, 108.56 mA cm^{-2} respectively (Fig. 5A). The best catalytic activity of LaFeO_3 nanocatalyst toward methanol oxidation was obtained in LaFeO_3 16 mM. This concentration of LaFNPs nanocomposite was selected as the optimum concentration with respect to the anodic peak potential and the current density of methanol oxidation peak. The effect of LaFNPs amount was also determined by chronoamperometry at Fig. 5B. The curve of current density vs. time was obtained at constant methanol oxidation potential (1.1 V) and constant concentration of methanol (1.75 M). As seen in Fig. 5B, there was an initial decay in the current density, and then it became stable. GC/LaFNPs electrode with 2 mg of LaFeO_3 had the best catalytic activity toward methanol oxidation in comparison to 1 and 4 mg of the catalyst. Also the catalytic activity of LaFeO_3 and LaFeO_3 -CNTs nanocatalysts toward methanol oxidation were compared with each other by chronoamperometry at Fig. 5C. As seen, LaFNPs-CNTs (2 mg LaFNPs and 1 mg CNT) nanocatalyst had better catalytic activity for methanol oxidation than LaFeO_3 nanocatalyst. As observed, GC/LaFNPs-CNTs electrode had lower initial decay than GC/LaFNPs electrode showing the lower rate of deactivation of GC/LaFNPs-CNT electrode. Lower rate of deactivation of GC/LaFNPs-CNTs electrode showed that this electrode can probably remove the poisoning intermediates on its surface.

3.4.3 Effect of Sodium Hydroxide Concentration

In order to investigate the effect of NaOH concentration on the anodic current density (j_r) and potential (E_f) of the methanol electrooxidation at

Fig. 5 (A) Cyclic voltammograms; (B) chronoamperograms of methanol oxidation at GC-LaFNPs electrode with different amounts of LaFNPs: a) 1, b) 2, c) 4 mg; (C) chronoamperograms of a) LaFNPs and b) LaFNPs-CNTs nanocatalysts with 2 mg of LaFNPs and 1 mg CNTs in 1.5 M NaOH and 1.75 M methanol.

Perovskite-Type LaFeO_3 and LaFeO_3 -CNTs Nanocrystals as Active Anode for Methanol Oxidation in Alkaline Solutions

Fig. 6 Effect of NaOH concentration on the anodic peak current density and potential of methanol electrooxidation at GC/LaFNPs and GC/LaFNPs-CNTs electrodes.

Fig. 7 Anodic current density (j) vs. square root of scan rate ($v^{0.5}$) and the plot showing peak potential (E) vs. $\ln v$ for (A) GC/LaFNPs and (B) GC/LaFNPs-CNTs electrodes in 1.5 M NaOH and 1.75 M CH_3OH at the scan rates of 30, 50, 70, 100, 120, 140 and 180 mV s⁻¹.

GC/LaFNPs (Fig. 6A) and GC/LaFNPs-CNTs (Fig. 6B) electrodes, the experiments have been done in different concentrations of NaOH (0.5, 0.75, 1 and 1.5 M). As seen in Fig. 6A and 6B, the best catalytic activity of as prepared electrodes toward methanol oxidation was obtained in NaOH 1.5 M., so the experiments were done in this concentration of sodium hydroxide.

3.4.4 Effect of Scan Rate

Cyclic voltammograms of methanol oxidation on GC/LaFNPs and GC/LaFNPs-CNTs electrodes at different scan rates (ν) in the range of 30 to 180 mVs⁻¹ were studied in Fig. 7A and Fig. 7B, respectively. As observed in Fig. 7A and 7B, the anodic current density of methanol oxidation on GC/LaFNPs and GC/LaFNPs-CNTs electrodes increases with increasing of the scan rates. It can be also seen that there was a linear correlation ($R^2 = 0.98$) between the anodic current density and $\nu^{1/2}$, indicating that the kinetics of the overall process is controlled by mass-transport. The peak potential of methanol oxidation (E_p) amplifies with increasing the scan rate and a linear relationship ($R^2 = 0.95-0.99$) has been obtained between E_p and $\ln(\nu)$. This shows that the methanol oxidation is an irreversible charge transfer process. The plot of E_p and $\ln(\nu)$ was a straight line with a slope [35]:

$$\frac{\delta E_p}{\delta(\ln \nu)} = \frac{RT}{(1 - \alpha) \times nF} \quad (7)$$

In this formula, α is the electron transfer coefficient. It characterizes the effect of electrochemical potential on the activation energy of an electrochemical reaction. The slope of E_p vs. $\ln(\nu)$ plot was 0.13 and 0.09 V for GC/LaFNPs and GC/LaFNPs-CNTs electrodes, respectively. α value was calculated as 0.97 and 0.95 ($n = 6$ and $T = 20$ °C) for GC/LaFeO₃NPs and GC/LaFeO₃NPs-CNTs electrodes, respectively which is close to 1. This indicates that the methanol oxidation has super kinetics.

4. Conclusions

The study has shown that LaFNPs and

LaFNPs-CNTs electrodes are quite active anodes for methanol electrooxidation in alkaline medium. It has also demonstrated that the electrocatalytic activities of LaFNPs electrodes for methanol oxidation in alkaline solutions are greatly enhanced in the presence of carbon nanotubes. This result was obtained due to the lower onset potential and lower anodic peak potential of LaFNPs-CNTs nanocatalyst than LaFNPs nanocatalyst for methanol oxidation.

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