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Investigation of methanol electrooxidation at Ir-modified C/Ni electrode in alkaline solution

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Abstract

This study presents electrochemical preparation of Ir loaded Ni-modified C felt electrode (C/Ni-Ir) and its characterization with the help of cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), chronoamperometry (CA), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) techniques. The experimental results show that, the modification of C felt by Ni increases the rate of methanol electrooxidation reaction. Moreover, the catalytic efficiency more and more enhances when a low amount of Ir is loaded over the surface. The Ir-modified catalyst has good time stability.

Keywords: Electrodeposition, Irridium-modified carbon felt electrode, electrooxidation.

1. Introduction

Direct methanol fuel cells (DMFCs) have recently received increasing interest as one of the most important power sources for both mobile and stationary electronic devices and vehicles by converting chemical energy directly into electrical energy in an environmentally friendly manner [1-3]. However, commercialization of DMFCs has been facing serious difficulties due to (*i*) the poor kinetics of anode reaction and deactivation/poisoning, (*ii*) the crossover of methanol from the anode to the cathode side through the proton-exchange membrane, (*iii*) limited abundance and high cost of noble metal electrocatalysts for the methanol electrooxidation reaction (MOR) [3-5].

The electrode materials and the supporting materials are clearly important factors for the enhancement of the methanol electrooxidation performance. The current research efforts have particularly focused upon the development of highly efficient electrocatalysts by increasing catalytic activity and reducing noble metal loadings. In order to overcoming the poisoning effects and limitation of using a higher amount of precious metals as catalyst, several non-noble metal electrodes have been investigated as anode materials for the MOR in an alkaline media [2,6]. Among those metals, nickel and its alloys are versatile catalytic materials due to their unique surface oxidation properties.

As catalysis is a surface effect, the supporting materials with high surface area are vital to disperse noble metal particles and to reduce the catalyst loading under the condition of keeping high catalytic activity [7]. Carbon black has been used as catalyst support broadly and commercially. However, this catalyst support has several disadvantages according to published reports [8,9]. In the current study, a Ni-modified C, which has low-cost, good conductivity and high surface area, is being alternatively reporting as a potential supporting material. It was reported that the Ni-Ir modified C electrode is a good electrocatalyst as cathode material for the hydrogen evolution reaction [10]. However, the C/Ni-Ir electrocatalyst has not been studied for the methanol electrooxidation reaction, and will be first time published. In this study, the electrode was tested as anode for methanol electrooxidation in 0.1 M KOH solution. For this aim, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA) techniques were used.

2. Experimental

The catalyst support was C substrate with 10x10x5 mm dimensions and the average weight of 0.05 g with the specific electrical resistance of 0.35 Ω cm^{-1}. The preparation of the C/Ni-Ir catalyst was achieved by two consecutive steps [10]; the modification of C support by electrodeposition of a thin Ni film and then, the loading a low amount of Ir over the formerly modified surface.

i) Preparation of C/Ni support: The bath composition for Ni was the same as reported previously [11,12]. 164.4 C per 0.05 g C charge was passed through the electrolysis system at a 50 mA constant current. In this way, 1g Ni/1g C was theoretically deposited over the C samples according to Faraday's laws taking into account the current efficiency is 100%, and the quantity of the charge is mainly due to faradic reaction;

$$Ni_{(aq)}^{2+} + 2e^- \rightarrow Ni_{(s)} \qquad (1)$$

i) Ir loading over the C/Ni support (C/Ni-Ir): The following two stock solutions were prepared:

A) Stock A solution: 7.46 g KCl + 6.1832 g H_3BO_3 + 2.7810 g $Na_3C_6H_5O_7.2H_2O$ (Total volume was 1000 mL) [13].

B) Ir Stock solution: 0.0164 g $IrCl_3.xH_2O$ was dissolved in 100 mL Stock A (This solution contains 10 mg Ir/100mL).

50 mL Stock A solution was added to a beaker. The C/Ni and a Pt electrode were immersed in this solution as the cathode and the anode, respectively. Then, 10 mL Ir stock solution was added to a burette. After starting the electrolysis at a 5 mA constant current, this solution was dropped to the beaker (~1 drop per 5 seconds). After all the solution was dropped to the beaker, the same current was applied for additional 10 minutes. Then, a 50 mA constant current was applied for 30 minutes. After completion of the electrolysis, it was assumed that, all the Ir^{3+} ions were completely reduced to their metallic form according to the equation (2). In this way, 20 mg Ir/1g C was theoretically loaded over the C/Ni surface.

$$Ir_{(aq)}^{3+} + 3e^- \rightarrow Ir_{(s)} \qquad (2)$$

The electrodeposition was carried out under galvanostatic conditions at room temperature using a DC supply. After the deposition, the working electrodes were carefully rinsed with distilled water to remove residues of bath chemicals and unattached particles, dried in an oven and kept in a desiccator before the measurements.

The electrochemical measurements were performed using a CHI 660D electrochemical analyzer under computer control. A double-wall one-compartment cell with a three-electrode configuration was used. The reference electrode to which all potentials are referred is the Ag/AgCl (3 M KCl) and a platinum sheet with 2 cm^2 total surface area was used as the counter electrode. The cyclic voltammograms were recorded starting from the negative direction with a scan rate of 10 mV s^{-1}. The EIS experiments were conducted at +0.80 V in the frequency range from 100 kHz to 0.01 Hz. The amplitude was 5 mV. The MOR stability of the catalyst was investigated by the CA technique at +0.80 V constant potential for 7200 s. The measurements were carried out at room temperature in 0.1 M KOH solution in the absence and presence of 1.0 M CH_3OH. All the test solutions were prepared from analytical-grade chemical reagents in distilled water without further purification. For each experiment, freshly prepared test solutions as well as electrodes were used.

The surface morphologies were examined with a JEOL SEM instrument (JSM-6510) at high vacuum and 20 kV. The atomic ratios of the catalysts were determined by EDX coupled to the same SEM instrument.

3. Results and discussion

In Figure 1, the SEM and the EDX mapping images of the catalysts are presented [10]. As it is shown in Figure 1a (inset), non-modified C sample contains fibers and have spacious space, which is an advantage for diffusion of ions and gas bubbles through inner zones and reduction of diffusion resistance. Figures 1a and b show that a porous Ni/Ir film forms over the C surface, after the modification. The EDX dot mapping of Ni (green zones on Figure 1c) and Ir (purple zones on Figure 1d) clearly show that, both Ni and Ir evenly distribute throughout the substrate, and not preferentially localize on specific sites. The average percentage metal ratios of Ni and Ir are 87.2 % and 12.8 %, respectively. The relatively low percentage of Ir makes cheaper the fabrication cost of the electrode.

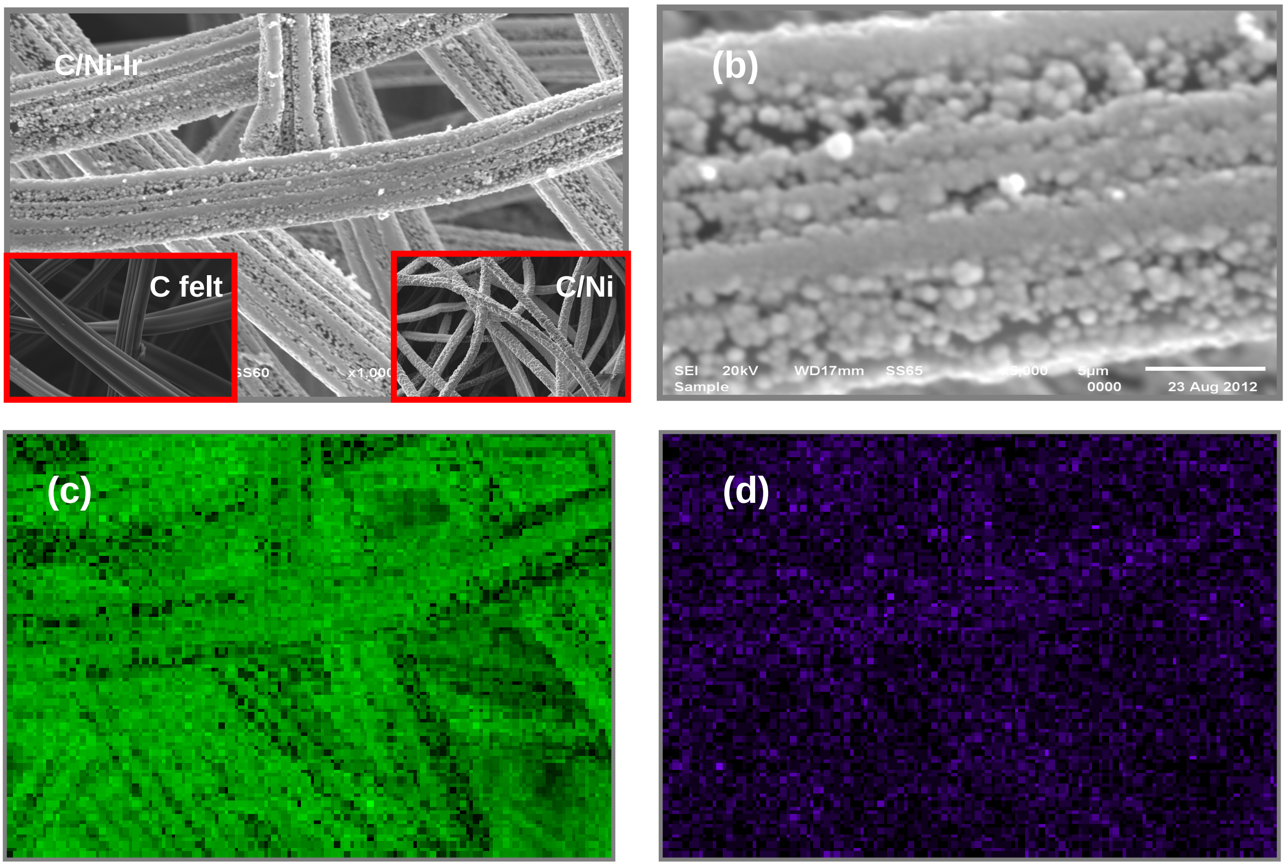

Figure 1. SEM images of C (inset in Fig. 1a), C/Ni (inset in Fig. 1a), C/Ni-Ir (a) and (b) [10], the distribution of Ni (green zones on Fig. 1c) and Ir (purple zones on Fig. 1d) over the support (EDX mapping).

The cyclic voltammograms of C, C/Ni and C/Ni-Ir electrodes recorded in 0.1 M KOH solution in the presence of 1.0 M CH_3OH are given in Figure 2. As it can be seen from Figure 2, the modification of the C substrate by Ni (C/Ni) enhances the MOR; the peak current density increases and the onset potential for the methanol oxidation shifts to a more negative potential. The increased efficiency can be related to better electrocatalytic activity of Ni [14,15] whose kinetics reported in detail [2] and higher porous surface. The observed results clearly suggest that the Ni-modified C could be a good substrate for the preparation of electrocatalysts. Moreover, the MOR activity at the electrode more and more enhances after the loading low amount of Ir through the Ni-modified substrate; the onset potential shifts to a more negative potential and the current density further increases. The current densities observed for C, C/Ni and C/Ni-Ir electrodes at +0.70 V are 43.04, 511.0 and 578.8 mA/g C, respectively.

Figure 3 shows the representative Nyquist plots of working electrodes obtained in 0.1 M KOH solution with the addition of 1.0 M CH_3OH. The results of EIS measurements are quite good in agreement with the CV results. As it can be seen from Figure 3, all the Nyquist diagrams contain a capacitive loop at high frequencies and followed a second slightly depressed capacitive semi-circular shape at lower frequencies. The representative Nyquist plots of the C sample were obtained at three different potentials, where MOR takes place and the data obtained are added to Figure 3b as the inset. As it is seen from Figure 3b, although the diameter of the high-frequency loop nearly remains the same, the diameter of the low capacitive one reduces with increasing the applied potential. Therefore, the potential dependent low-frequency loop could be attributed to the kinetic of the MOR. The EIS data were fitted to the electrical equivalent circuit diagram suggested in literature [16,17]. According to the fitted results, charge transfer resistances (R_{ct}) are 20.6, 6.5 and 5.8 Ω for C, C/Ni and C/Ni-Ir electrodes, respectively. The reduction in the R_{ct} indicates the higher MOR activity at the modified electrodes. The constant phase elements (CPE) correspond to the low frequency loops are 0.0020, 0.0085 and 0.061 F for C, C/Ni and C/Ni-Ir electrodes, respectively. The increase in the CPE at the same potential at C/Ni-Ir catalyst can be explained by the onset of the Faradic reaction of the MOR, which indicates the increasing electrocatalytic activity [14].

The current-time curves of C (a) and C/Ni-Ir (b) catalysts at +0.80 V are given in Figure 4. It is clear from Figure 4 that, after an initial decrease, the current densities are nearly remained the constant, which shows that the Ir-modified electrocatalyst has good time stability and tolerant to CO poisoning.

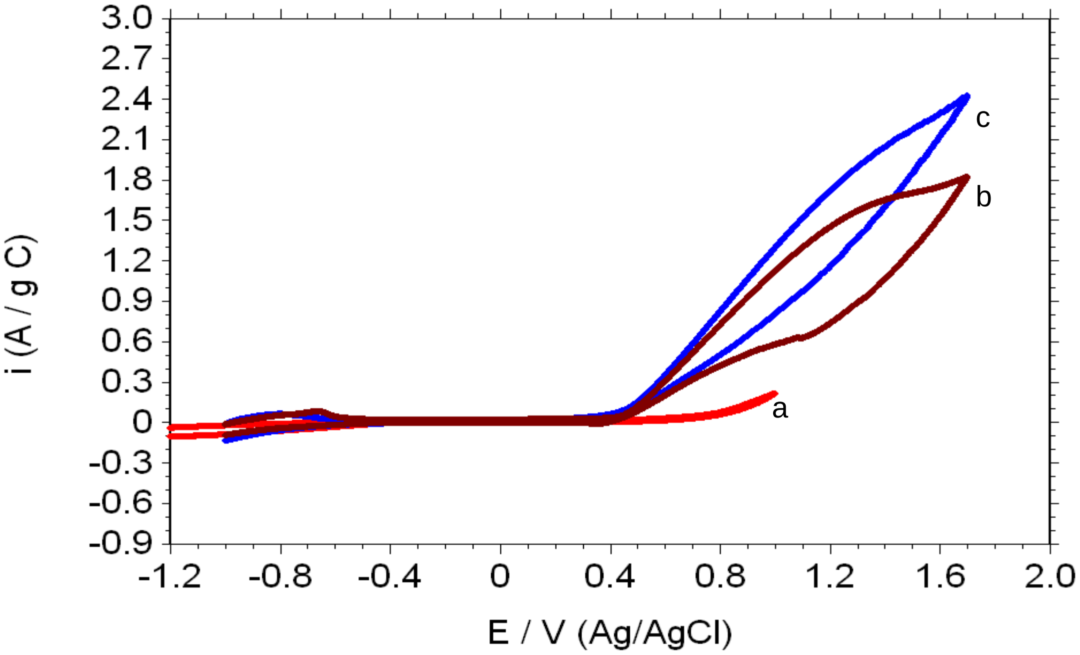

Figure 2. Cyclic voltammograms of C (a), C/Ni (b) and C/Ni-Ir (c) electrodes in 0.1 M KOH solution in the presence of 1.0 M CH_3OH.

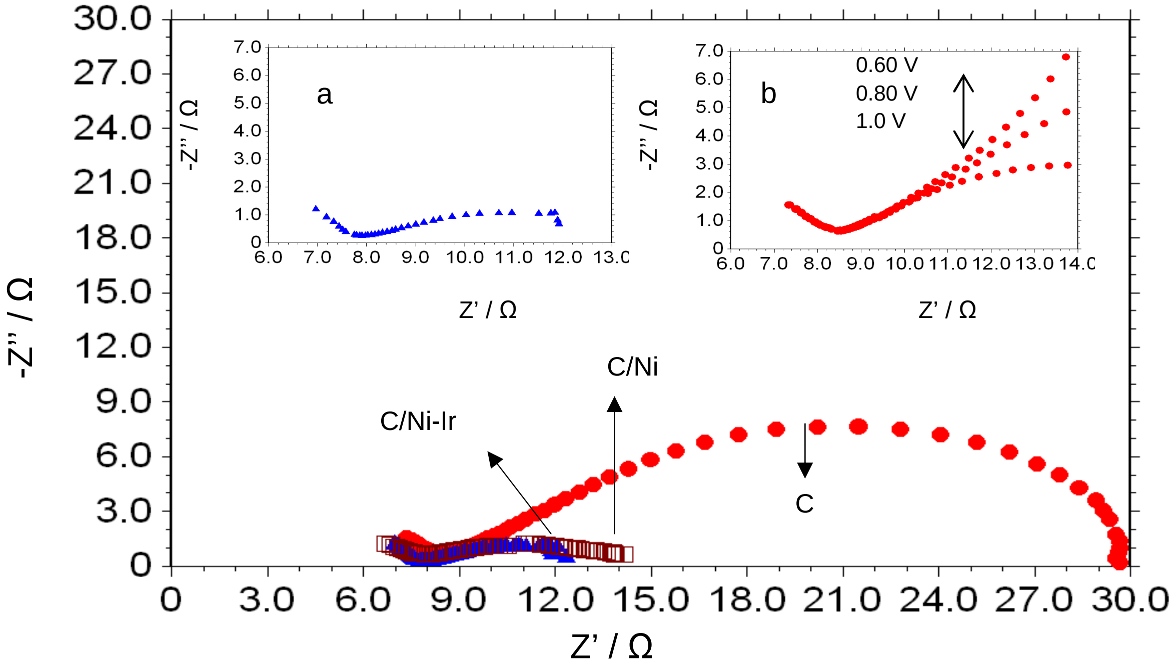

Figure 3. Nyquist plots of C, C/Ni and C/Ni-Ir electrodes in 0.1 M KOH solution in the presence of 1.0 M CH_3OH at 0.80 V (The inset in Fig. 3a shows magnified Nyquist plot of the C/Ni-Ir, the inset in Fig. 3b shows the magnified high-frequency range of Nyquist plots of the C electrode obtained at three different potential).

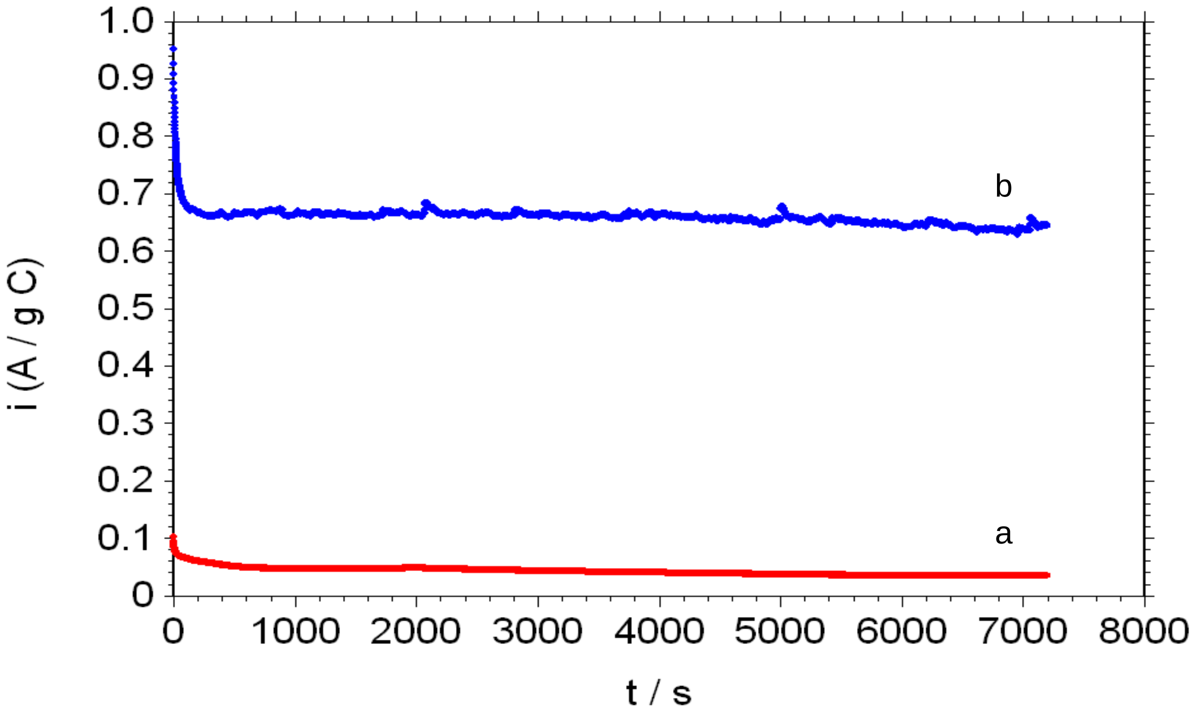

Figure 4. The current-time curves of C (a) and C/Ni-Ir (b) catalysts in 0.1 M KOH solution in the presence of 1.0 M CH_3OH at +0.80 V.

Conclusion

The data obtained indicate that:

1) The modification of C substrate by the electrodeposition of Ni enhances the MOR activity of the substrate.
2) The further modification of previously Ni-modified C substrate by the low amount of Ir further enhances the rate of methanol electrooxidation.
3) The Ir-modified catalyst has good time stability.
4) C and Ni are cheaper material in comparison to Ir. So, the deposition of a low amount of Ir through the Ni-modified substrate reduces the cost of catalyst when compared to bulk Ir usage.

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