Synthesis and application of Co/TiO2 nanoparticles incorporated carbon nanofibers for direct fuel cell

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Abstract. Well decorated Co/TiO2 nanoparticles incorporated carbon nanofibers are presented as operative electrocatalyst in term of current density and onset potential for methanol oxidation. The presented electrocatalyst has been prepared by well-known technique; electrospinning. The physicochemical properties have been confirmed by FE-SEM, EDX, SEAD and TEM analyses while the electrocatalytic studies has been performed by cyclic voltammetry technique. Obtained results indicate that TiO2 content has strong influence for direct fuel cell. Co (99%)/TiO2 (1%) incorporated carbon nanofibers showed best performance in term of high current density at low onset potential. Overall, the introduced Co (99%)/TiO2 (1%) incorporated carbon nanofibers as an electrocatalyst can be considered a promise material for direct methanol fuel cells applications.

1. Introduction

From supporting our normal lives to encouraging leading-edge industrial and technological developments, conventional fuels have played a very essential role for our civilization[1]. As the limited amount of fossil reserves are being dwindling at a rate that will not sustain the continuing growing human population, the need for reasonable alternative energy sources has become more prominent[2]. Therefore, the contemporary world faces massive challenges linked with meeting its energy needs, at the same time; the world faces the threat of environmental issues linked to CO2 emissions. Actually, global energy utilization has risen significantly since the industrial and technological revolution and is estimated to twice again in the next few years[3].

Therefore, numerous well-known direct electrochemical conversion processes in various fuel cells (FCs) with high efficacy and low CO2 release have been studied. Among the various fuel cells, direct methanol fuel cells (DMFCs) have attracted considerable attention in the past decade due to their potential application, easy storage and transportation of fuels[4].

The operation of a DMFC primarily depends on the following chemical reactions.

\[
\text{Cathode: } \frac{3}{2}O_2+6H^++6e^- \rightarrow 3H_2O \quad (1)
\]
\[
\text{Anode: } H_2O + CH_3OH \quad 6e^- +6H^+ + CO_2 \quad (2)
\]
\[
\text{Overall reaction: } CH_3OH+3/2O_2 \quad \rightarrow CO_2 +2H_2O \quad (3)
\]

It is well known that, platinum is amazing metal and considered the standard anode material for direct methanol fuel cell; but unfortunately it is costly and rare metal; moreover, Pt-based metal catalysts are sensitive with CO poisoning and their intolerance of methanol are the main limitations to commercial implementation of the direct methanol fuel cells[5-8]. Among transition metals catalyst Ni and Co are the most popular electrocatalyst in fuel cell applications but unfortunately, in the pristine metallic state Co has very less activity toward electrooxidation of methanol/ethanol. However, the catalytic activity of Co could be exploited by using proper co-catalyst [9]. Therefore, extensive research has been done in finding the proper co-catalyst for the Co.

In recent years, considerable attention has been focused on TiO2 for energy and environmental applications due to its compatibility and stability with various chemical species, unique electrochemical properties and high surface area [10]. According to reaction (2), oxidation reaction of
methanol takes place at the anode. Thus, the reaction is considered to be a composition of electrochemical reaction and adsorption on the anode surface [11, 12]. Accordingly, due to the adsorption capability of carbon and the combination of cobalt and TiO2, nanoparticles could not only increase the electrocatalytic activities but also increase the surface area of the effective material; thus the final product will own exciting performance in DMFCs.

Herein, the main target of this research is to present a new non-precious electrocatalyst for DMFCs application. Co/TiO2 nanoparticles incorporated carbon nanofibers were prepared by high yield technique and low cost electrospinning. To the best of our knowledge, Co/TiO2 nanoparticles incorporated carbon nanofibers have not yet been reported. The electrochemical properties of Co/TiO2 nanoparticles incorporated carbon nanofibers have been studied for application as electrocatalyst for direct fuel cell of methanol.

2. Experimental

Catalyst synthesis, characterizations and electrochemical measurements

Titanium (III) chloride solution ((TiCl3) 12%), Cobalt acetate ((CH3COO)2.4H2O) 98%) were obtained from Showa and Junsei chemicals Japan. Poly vinyl alcohol (PVA, 65000 g/mol) was received from sigma.

Firstly, the aqueous solutions were prepared by different amounts of cobalt acetate and titanium chloride in 5 ml of distilled water. Sol gel was prepared by adding 15 g of PVA solution at 50 ºC while stirring. Thereafter, prepared sol-gel was electrospun at high voltage of 20 kV. Finally, the synthesized nanofiber sheet was calcined at 750 ºC for 3 h under argon atmosphere.

The morphology of Co/TiO2 nanoparticles incorporated carbon nanofibers were analyzed by FESEM, Htachi S-7400 Japan while the electrochemical properties were measured by using VersaSTAT4(USA) at temperature about 25 ºC. The energy dispersive X-ray (EDX) and transmission electron microscope (TEM), JEOL JEM-2200FS, Japan, were used to observe the distribution of elements and high resolution images Co/TiO2 nanoparticles incorporated carbon nanofibers while the procedure used for electrode preparation in this study have followed according to our previous studies[13].

3. Results and Discussion

Carbon nanomaterials are widely considered as an electro catalyst, because of their high adsorption range [14-16], particularly, nanofibers possess much attention of the research communities because of the outstanding efficiency, not only for the DMFCs but also for several types of fuel cells [17-19]. The morphology of the prepared Co/TiO2 nanoparticles incorporated carbon nanofibers after the proposed calcination was studied by FESEM technique (Fig.1). As shown in Fig. 1(a) the prepared nanomaterials exhibit nanofibers morphology and also image clearly shows the formation of metallic nanoparticles with irregular shapes. As shown in the high magnification image (Fig.1 (b)), the metallic nanoparticles are densely distributed all over the surface of the carbon nanofibers.

Chemical composition of prepared Co/TiO2 nanoparticles incorporated carbon nanofibers after the proposed calcination was studied by SEM- EDX technique, as shown in the EDX map (Fig.2) nanocomposite is purely made of C, O, Ti and Co.

Fig.3 shows the TEM results for the prepared Co/TiO2 nanoparticles incorporated carbon nanofibers. In the normal TEM images as shown (Fig.3 (a&b)), the synthesized nanostructure composed of amorphous carbon matrix incorporated by metallic nanoparticles. Moreover, HR-TEM images (Fig.3 (c&d)), show that the metallic counter parts are crystalline with amorphous carbon body. From Fig.3(c&d) it can be observed that there are two different crystal structures (marked by red and green circles) with a diameter around 10 nm can be interpreted as TiO2 and Co metals.
The investigated SEAD image (Fig.4) further suggesting the polycrystalline nature of the nanocomposite.

Fig.5. shows the cyclic voltammetric behaviors of the prepared Co/TiO2 nanoparticles incorporated carbon nanofibers with different concentrations of TiO2 and Co contents (in 0.1 Methanol+ 1.0 M KOH solutions) at a scan rate of 50 mVs−1. It can be revealed that TiO2 content has quite reasonable influence on the current densities and onset potential. The carbon nanofiber having 1% TiO2 shows higher current density (217mA/cm2) at low onset potential than the other compositions.

The optimization of methanol is considered as a key factor for electrocatalyst. Fig.6 (a-c) exhibits the effect of methanol concentration on the current density for the direct methanol fuel cell. As shown in the figure all compositions are sensitive with methanol concentration. It can be seen from Fig.6 (a-c) the optimum methanol concentration is 0.1 M. Moreover, the Co (99%)/TiO2 (1%) nanoparticles incorporated carbon nanofibers reveals higher activity in term of current density and onset potential compared to the other compositions. Table1. Summarized the information embedded in Fig.6 (a-c). Generally, the observed outstanding electrocatalytic performance of the best composition can be accredited to formation of (Co,99%/TiO2,1%@CNFs)OOH/( Co,99%/TiO2,1%@CNFs)(OH)2 layer on the surface of the Co,99%/TiO2,1% nanoparticles incorporated carbon nanofibers.

Catalyst stability is another key factor to validate the catalytic performance. Fig.7 exhibits the chronoamperogram of direct methanol fuel cell electrode for 10000 s at potential of 0.4 V in 2 M methanol + 1 M KOH. It can be seen from figure, there is a preliminary current density decreased, followed by a very slow decay even the same electrode is utilized in the whole experiment. This findings further endorse the performance and stability of Co (99%)/TiO2 (1%) nanoparticles incorporated carbon nanofibers which can be attributed to the unique structure of the composite.

Table 1. Influence of methanol concentration on Co(x)/TiO2 (1−x) nanoparticles incorporated carbon nanofibers.

| Conc. Of MeOH(M) | Co99.5%/TiO2(0.5%) CNFs | Co99%/TiO2(1%) CNFs | Co98%/TiO2(2%) CNFs |
|------------------|-------------------------|---------------------|---------------------|
| 0.0              | 30                      | 57                  | 9.8                 |
| 0.1              | 117                     | 217                 | 198                 |
| 0.5              | 98                      | 98                  | 145                 |
| 1.0              | 82                      | 82                  | 82                  |

4. Conclusions
In conclusion, we have successfully synthesized Co/TiO2 nanoparticles incorporated carbon nanofibers by a simple electrospinning technique followed by a heat treatment. The result at nanomaterials shows satisfactory performance toward methanol electroxidation. Moreover, Co (99%)/TiO2 (1%) nanoparticles incorporated carbon nanofibers revealed a high current density of (217 mA/cm2) with low onset potential at low concentration of methanol (0.1 M). Finally, it can be concluded that, Co (99%)/TiO2 (1%) nanoparticles incorporated carbon nanofibers might be a good addition as an electrocatalyst for direct methanol fuel cells applications.

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Figures captions

Figure.1.(a&b) FESEM images of Co(99%)/TiO2(1%) nanoparticles incorporated carbon nanofibers after calcination at 750°C for 3 h in argon atmosphere.

Figure.2. EDX for the obtained Co(99%)/TiO2(1%) nanoparticles incorporated carbon nanofibers after calcination at 750°C for 3 h in argon atmosphere.

Figure.3. (a-d) TEM images of Co(99%)/TiO2(1%) nanoparticles incorporated carbon nanofibers after calcination at 750°C for 3 h in argon atmosphere.

Figure.4. SEAD image for the obtained Co(99%)/TiO2(1%) nanoparticles incorporated carbon nanofibers after calcination at 750°C for 3 h in argon atmosphere.

Figure.5. Influence of TiO2 and Co percentage on electrocatalytic activity toward methanol oxidation.

Figure.6. (a-c) Typical Cyclic voltammograms for the carbon nanomaterials containing different composition of metallic counter parts in different concentrations of methanol.
Figure 7. Chronamperometry for the obtained Co$_{0.0915}$/TiO$_2$[111] nanoparticles incorporated carbon nanofibers after calcination at 750°C for 3 h in argon atmosphere.

Figure 1
Figure 6

Figure 7