



Cobalt-incorporated, nitrogen-doped carbon nanofibers as effective non-precious catalyst for methanol electrooxidation in alkaline medium

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ABSTRACT

Among the nanosupports, carbon nanofibers distinctly enhance the performance of the functional electrocatalysts because the adsorption capacity and low resistance electron transfer due to the large axial ratio. Moreover, nitrogen doping shows positive influence toward electrooxidation ability. In this study, Co-incorporated and nitrogen-doped carbon nanofibers are introduced as effective non-precious electrocatalyst for methanol oxidation in the alkaline medium. The introduced NFs have been prepared using facile, simple, high yield, low cost, and effective technique; electrospinning. Typically, calcination of cobalt acetate/urea/poly(vinyl alcohol) electrospun mats at 850 °C in argon atmosphere leads to produce the introduced nanofibers. The structure, composition and morphology were characterized by FT-IR, XRD, EDX, FE-SEM and TEM techniques. The electrocatalytic activity of the introduced nanofibers toward methanol oxidation was evaluated by cyclic voltammetry (CV). Study the influence of the nitrogen content could be investigated by adjusting the urea content in the original electrospun nanofiber mats. The results indicated that the activity of the catalyst increases with increasing urea content in the electrospun solution up to 4%. A maximum current density was 100.84 mA cm⁻² for Co/N(4%)-CNFs that was higher than the undoped ones (63.56 mA cm⁻²). Moreover, good chemical stability was observed due to covering the metals NPs by carbon shells. Overall, nitrogen doping enhances electrocatalytic activity of Co/CNFs toward methanol oxidation in alkaline media.

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1. Introduction

Development a future energy system from sustainable energy sources as an alternative for fossil fuels is considered a key objective of modern research. Direct methanol fuel cells (DMFCs) are the most promising sustainable energy devices because methanol is an inexpensive, readily available, and easily stored and transported liquid fuel [1,2]. Unfortunately, high production cost due to

utilizing precious metals electrodes (e.g. Pt) is facing wide commercial application for not only DMFCs but also all the other fuel cells. Accordingly, more efforts are being done to develop low cost materials having good chemical stability and high catalytic activity to replace platinum [3–5]. In the DMFCs, methanol is oxidized to carbon dioxide at the anode according to the reaction: CH₃OH + H₂O = CO₂ + 6H⁺ + 6e. The reaction is considered to be a combination of adsorption and electrochemical reaction on the anode surface [6,7]. Accordingly, because of the adsorption capacity of carbon, the later has been incorporated in many recently reported electrocatalytic materials, not only for the DMFCs but also other kinds of fuel cells [8–12]. Among the utilized carbon nanostructural supports, the large axial ratio provides the carbon nanofibers additional feature due to the low electron transfer compared to other structures [13,14].

Transition metals nanostructures and their alloys have been studied as an electroactive material for methanol oxidation and

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potentially cheaper than platinum [15–18]. However, the high chemical activity is a forcible constraint facing wide utilizing of this new class of materials. Among the utilized transition metals, cobalt gained the lowest attention due to the low electrocatalytic activity of the pristine cobalt. Instead, it is used as a co-catalyst to annihilate the Pt poisoning. Pt–Co alloys have been found to be excellent CO-tolerant catalysts [19]. However, some recent reports have introduced cobalt as a main catalyst [13,20,21]. Compared to nanoparticulate morphology, nanofibers do have low specific surface area which can be considered as negative characteristic in catalytic applications however the large axial ratio proved that it has distinct positive impact in the electrocatalytic oxidation of methanol [22,23]. Currently, many studies are focusing on improving the catalytic activity and stability through incorporation of heteroatoms such as nitrogen into the carbon nanostructure supports. Nitrogen-doped carbon nanostructure owns high surface nucleation sites which allows the anchorage and high dispersion of the catalyst nanoparticles on the support surface material that results in high interaction between nitrogen-doped carbonaceous support and the catalytic metals [24–26]. On the other hand, nitrogen doping improves the durability of the resultant carbon-support catalysts because of the enhanced π bonding [27,28], and the basic property [29] due to the strong electron donor behavior of nitrogen. Nitrogen-doped carbon nanotubes/nanofibers (N-CNT/N-CNF) showed enhanced catalytic activity toward oxygen reduction reaction (ORR) [30–32]. Most of the previous studies were used nitrogen doped carbon nanostructure with noble metals or their alloys as catalysts (e.g. Pt, Ru, etc.) for methanol oxidation [33]. Recently, the same authors studied the influence of nitrogen doping on the electrocatalytic activity of nickel-doped carbon nanofibers; the results indicated that nitrogen doping has featured influence [34]. In literature, there are several methods have been introduced to synthesis the nanofibers, however among these reported techniques, electrospinning have drawn the most attention due to several advantages including simplicity, high yield, low cost and easy morphology control [35–38].

In this work, cobalt-decorated and nitrogen-doped carbon nanofibers (Co/N-CNFs) are introduced as anode for methanol oxidation. The introduced catalysts was fabricated by using electrospinning technique and followed by carbonization process at 850 °C. The experimental results revealed good electrocatalytic activity and non-observable influence on the good stability of Co/N-CNFs toward methanol oxidation in alkaline medium especially at high nitrogen content.

2. Experimental

2.1. Materials

Cobalt(II) acetate tetrahydrate (CoAc·H₂O, 98%), poly(vinyl alcohol) (PVA, MW = 88 Kg mol⁻¹), urea (99%), methanol, potassium hydroxide, isopropyl alcohol, Nafion 117 (10 wt%), diamond suspension and acetone were purchased from Sigma–Aldrich Co. Those materials were utilized without any further purification. Distilled water was used as solvent.

2.2. Preparation of N-CoCNFs catalysts

PVA (10%, w/w) solution was prepared at 70 °C with a mechanical stirring for 2 h to obtain clear solution. Cobalt acetate tetrahydrate Co(Ac·4H₂O) aqueous solution (20%, w/w) was prepared by sonication for 15 min at room temperature using ultrasonication. The sol–gel was prepared through mixing PVA and CoAc·4H₂O solutions in a weight ratio of 4:1 and then different concentrations of urea (0, 1, 2, 3, 4, 5%, w/w) were added and

stirred for 5 h at 50 °C. The viscous gels were electrospun to produce nanofibers mats. The procedure can be summarized as following; the sol–gel of PVA/CoAc or PVA/CoAc/urea was placed in 20 mL plastic syringe attached to the digital hypodermic syringe and fed into the stainless steel needle at a flow rate of 0.9 mL/h, which was maintained by the digital hypodermic syringe pump. A collecting drum was covered with a polyethylene sheet. The applied voltage was 17–20 kV and TCD was 15 cm. The electrospinning process was carried out at room temperature and humidity was $\geq 35\%$. The collected NFs mats were peeled from surface of polyethylene sheet. The NFs mats were dried for 24 h at 80 °C under vacuum. Later on, the collected nanofibers mats were calcined in an argon atmosphere at 850 °C with a heating rate of 2.83 °C min⁻¹ for 5 h. Nanofiber mats were left inside the furnace until cooled to room temperature and evolved argon gas in the reaction medium to prevent oxidation.

2.3. Preparation of working electrode for methanol oxidation

It was carried out by mixing 2 mg of the functional material, 20 μ L Nafion 117 (5 wt%) and 420 μ L isopropanol. The slurry was sonicated for 30 min at room temperature. A 15 μ L from the prepared slurry was poured on the active area of the glassy carbon electrode (0.07 cm² area) which was then subjected to drying process at 80 °C for 20 min. Before poured the slurry solution on the glassy carbon electrode, it should be cleaned by acetone and distilled water then polished by adding one drop of diamond suspension to smooth emery paper and moved the glassy carbon electrode on it until became like mirror and then cleaned by acetone and distilled water and again cleaned by acetone and distilled water.

2.4. Characterization

The surface morphology of samples was studied by FESEM (JEOL-JSM-2100F, Japan) equipped. Thermogravimetric analyses (TGA) for the prepared electrospun mats were performed on TA Instruments (Q500 TGA) to study thermal properties of nanofibers mats. The crystallinity and structure of the as-prepared catalyst was studied by X-ray diffractometer (XRD, Bruker D8 DISCOVER), FT-IR (Bruker Optic Tensor 27, Germany), respectively. Normal and high resolution images of prepared catalysts were observed by transmission electron microscope (TEM, JEOL-JEM-2100, Japan). The electrocatalytic activities of prepared catalysts as anode (working electrode) for methanol electro-oxidation were performed by Versa STAT 4 (USA) electrochemical analyzer and a conventional three electrodes electrochemical cell. An Ag/AgCl electrode and Pt wire were used as the reference and auxiliary (counter) electrode, respectively.

3. Results and discussion

3.1. Characterization of Co/N-CNFs catalyst

FESEM instrument was used to study the changes in morphology of fibers caused by addition of urea with different concentration before and after calcination and determine the average diameters of nanofibers. Fig. 1 shows FE-SEM images of the electrospun PVA/CoAc nanofiber mats without and with different concentration of urea before calcination. As shown in this figure, the obtained nanofibers are relatively smooth and the diameter of nanofibers increase with increase the concentration of urea. This may be attributed to the increasing of viscosity of the precursor solution due to the urea interaction with PVA polymer which demonstrated by FT-IR in Fig. 5. Moreover, as shown in Fig. 1, NFs have a random orientation because of the bending instability associated with the

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