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Synthesis and characterization of $Co/SrCO_3$ nanorods-decorated carbon nanofibers as novel electrocatalyst for methanol oxidation in alkaline medium

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Abstract

In this study, $Co/SrCO_3$ nanorods-decorated carbon nanofibers are introduced as novel and effective electrocatalyst for alkaline methanol fuel cells. Synthesis of the presented nanostructure could be achieved by calcination of electrospun mat composed of strontium acetate (SrAc), cobalt acetate (CoAc) and poly(vinyl alcohol) in nitrogen environment at 600 °C. The crystal structure was verified by X-ray diffraction (XRD) while the morphology was observed using FESEM and high resolution transmission electron microscopy (HR-TEM). In addition, further evidence for the chemical composition of the product was obtained by energy dispersive analysis of X-ray (EDX). The invoked characterization technique indicated that the obtained material is composed of $Co/SrCO_3$ nanorods-decorated carbon nanofibers. The electrochemical oxidation of methanol was investigated in the alkaline medium using cyclic voltammetry (CV) analysis. The introduced modified carbon nanofibers exhibited distinct electrocatalytic activity toward methanol electro-oxidation as the corresponding onset potential was very small (~ 0.08 V vs. Ag/AgCl) compared to the reported non-precious electro-catalysts. Moreover, the corresponding current density increased with increasing methanol concentration in the alkaline medium.

Keywords: Non-precious catalyst; Electrospinning; Strontium carbonate; Decorated carbon nanofibers; Methanol onset potential

1. Introduction

From an environmental concern over the increasing greenhouse gas concentration, the renewed interest in finding sustainable energy resource for lowering our dependence on fossil fuels and mitigating global warming is an urgent demand. Among the various contestants, fuel cell is a good technological option for resolving energy and pollution problems; it offers many advantages such as simple design, low environmental pollution, high energy conversion efficiency, and convenient fuel transportation, storage and supply [1–5]. Among the various types of fuel cells, considerable attention has been attracted by direct methanol fuel cells (DMFCs) due to easier supply of methanol to the community using existing infrastructure, and methanol can be produced from biomass so it can be considered a renewable energy source [6,7].

The effectiveness of the fuel cells depends on the catalytic activity of the corresponding catalysts. Due to outstanding catalytic activity, platinum (Pt) is a universal choice as an electrocatalyst in DMFCs electrodes [8]. However, commercialization of these fuel cells is facing serious difficulties due to the high cost [9]. Nonetheless, it is well known that Pt-based catalysts lose their activity due to formation of intermediate products which blocks the active sites of Pt [10,11].

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Thus, the development of new cheap and effective anodic catalysts is an urgent need. In the short-term, the electrocatalyts containing low amount of Pt received a considerable interest; however in the long term, non-noble metal catalysts could become low-cost substitutes. Numerous types of non-noble catalysts have been explored in recent years including transition metal alloys, metal nitrides, and chalcogenides [12–14].

Among the investigated transition metals, cobalt is the most popular electro-co-catalyst in fuel cell application [15–18]. In the recent years, considerable attention has been attracted by strontium carbonate, as an inorganic compound in materials chemistry, due to its various applications [19,20]. Based on their various applications, variety of processes for the preparation of $SrCO_3$ including catalytic decomposition, refluxing process, ion entrapment method and biological synthesis have been reported [21–24].

On the other hand carbon nanostructures are most widely studied as an electrocatalyst, not only for the DMFCs but also other kinds of fuel cells due to their adsorption capacity [25–30]. Specially, nanofibers possess the most attentions of the researchers due to the good performance in many applications [31–33]. The large axial ratio of the nanofibers results in decreasing the total surface area compared to the nanoparticulate morphology; this might be considered a negative influence upon utilizing the nanofibers as catalysts. However, recently it was reported that the large axial ratio provides priority for the nanofibers over the nanoparticles in the electrons transfer-based processes as the nanofibers reveal better performances [34,35]. Accordingly, carbon nanofibers (CNFs) can be considered the best support for the functional materials. Poly(vinyl alcohol) (PVA) is a semi-crystalline polymer with comparatively high carbon content (ca. 54.5%) and low cost compared to the wisely used polyacylonitrile (PAN) precursor. It was reported that the easy splits hydroxyl groups in the polymer chain make PVA favorable for use as a precursor for the production of the carbonaceous materials; however low yield is the main constraint. The decomposition of PVA at temperatures slightly higher than its melting point is the main reason for the low carbonization yield. To overcome this problem, some strategies have been introduced including dehydration under tension in a mixed gas atmosphere [36], pre-oxidation or subsequent dehydration [37], and dehydrogenative polymerization during carbonization [38]. Recently, the same authors reported that cobalt distinctly enhances the graphitization of PVA [39,40].

In this research, $Co/SrCO_3$ NRs-decorated CNFs have been synthesized by using a low cost and high yield technique; electrospinning. To the best of our knowledge, $Co/SrCO_3$ NRs-doped CNFs have not yet been reported. $Co/SrCO_3$ NRs-decorated CNFs are prepared by electrospinning of an aqueous solution consisting of strontium acetate (SrAc), cobalt acetate CoAc and polyvinyl alcohol (PVA), followed by drying and calcination of the obtained electrospun NFs mat under an inert atmosphere. The introduced $Co/SrCO_3$ NRs-decorated CNFs have been investigated as an electrocatalyst for methanol oxidation; the results were promising as the synthesized nanofibers could strongly enhance the onset potential.

2. Experimental

2.1. Procedure

2.1.1. Materials

Strontium acetate (SrAc, 99.9%) and Cobalt (II) acetate tetra hydrate (CoAc, 98%) were bought from Sigma-Aldrich Corporation, St. Louis, MO, USA and Junsei chemicals Corporation Ltd. Japan, respectively. Poly (Vinyl alcohol) (PVA) with a molecular weight 65,000 g/mol was obtained from Sigma-Aldrich Corporation, St. Louis, MO, USA. Distilled water was used as solvent.

2.1.2. Preparation of Co/CeO_2 NRs-doped CNFs

SrAc and CoAc aqueous solutions were firstly prepared by dissolving 0.3 g of SrAc and 0.7 g of CoAc in 3 ml of distilled water with 6 h stirring at room temperature and then mixed with 15 g PVA aqueous solution (10 wt%). Finally the mixture was stirred at 50° C for 6 h to get see-through, clear and consistent mixture. The achieved sol–gel was electrospun at a high voltage of 22 kV using DC power supply at room temperature with 65% relative humidity. The distance between needle tip (positive electrode) and rotating cylinder (negative electrode) was kept constant at 22 cm. The ready nanofibers (NFs) mat were normally dried at room temperature for 12 h and then under vacuum for 24 h at 70° C and finally calcined at 600° C for 6 h in nitrogen atmosphere with a heating rate of 2.0° C/min.

2.2. Electrode preparation and electrochemical measurement

2.2.1. Preparation of working electrode

Preparation of the working electrode was carried out by mixing 2 mg of the electro-catalyst, 20 μL of Nafion solution (5 wt%) and 400 μL of isopropanol. The slurry was sonicated for 30 min at room temperature. The ultrasonically dispersed nanocatalyst (15 μL) was spread by micropipette on to the active area of the glassy carbon electrode which was then subjected to drying process at 80 °C for 20 min. The glassy carbon working electrode with 3 mm of diameter and 0.0706 cm^2 of the apparent electrode area was polished with diamond suspension to a mirror finish before being used.

2.2.2. Electrochemical measurement

The electrochemical measurements were carried out in a conventional three electrode electrochemical cell (VersaSTAT 4, USA) at room temperature in a 1 M KOH solution. A glassy carbon electrode made by the above mentioned procedure was used as a working electrode while Pt wire and an Ag/AgCl electrode were used as the auxiliary and reference electrodes, respectively. All the potentials were quoted with regard to the Ag/AgCl electrode. Normalization of the current density was achieved based on the surface area of the utilized glassy carbon electrode (0.0706 cm^2).