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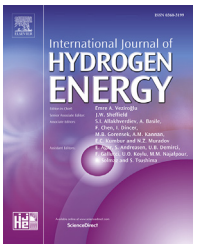

$CoCr_7C_3$-like nanorods embedded on carbon nanofibers as effective electrocatalyst for methanol electro-oxidation

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ABSTRACT

$CoCr_7C_3$-like nanorods encapsulated in carbon nanofibers shell [$CoCr_7C_3$-CNFs] were prepared using a simple electrospinning technique. The as-prepared nanocomposite was physically characterized using XRD, SEM, TEM and EDX analysis techniques. The electrocatalytic activity of $CoCr_7C_3$-CNFs was examined for methanol electro-oxidation in alkaline medium using cyclic voltammetry and chronoamperometry. The fabricated $CoCr_7C_3$-CNFs revealed good electroactivity towards methanol oxidation reaction. The measured low onset potential value [−80 mV (Ag/AgCl)] implied a marked enhancement in the oxidation kinetics at $CoCr_7C_3$-CNFs surface. Chronoamperometry test also displayed an increased steady state oxidation current density value of 18.42 mA cm^{-2} at 400 mV after 1800 s. This synthesized low cost, highly active and stable nanocomposite could be widely employed as a promising anode material in direct methanol fuel cells.

Introduction

Energy consumption is considered as one of the top 4th critical problems facing the growth of human society [1]. With continuous human population increase in the world, there is an increased demand of energy that is mainly produced from fossil fuels (e.g., coal, oil and gas). Furthermore, the combustion of these fuels would release not only carbon dioxide but

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also methane and nitrous oxide as the greenhouse gases [2]. This could provide a fresh impetus to develop high-performance renewable energy sources. Direct alcohol fuel cells have recently attracted much attention as a hopeful source of renewable energy for automobile industries and portable electronics [3–7]. Among the examined direct alcohol fuel cells (DAFCs), direct methanol fuel cells (DMFCs) appear to be one of the most promising renewable energy sources with high performance and power density. However, there are still some technical obstacles that affect the large-commercialization such as high cost and low abundance of the main catalytic materials (e.g., Pt, Ru and their alloys). Some limitations should be also considered regarding catalyst selection as: (1) the corrosion stability during the harsh chemical and electrochemical oxidation conditions, (2) the alcohol electro-oxidation kinetics, (3) the oxygen electro-reduction kinetics, (4) the electrocatalyst poisoning due to CO or CHO species adsorption and (5) the alcohol crossover current. Thus, exploration of new low cost catalytic materials with high efficiency and durability is desirable from commercialization viewpoint. Recently, transition metal carbides (TMCs) have been introduced as good catalytic materials for various applications (e.g., production of olefins, ammonia decomposition, carbon dioxide reduction, and hydrogen evolution) owing to their characteristic features such as low cost, high electronic conductivity, corrosion resistance, and chemical stability [8,9]. TMCs show Pt-like behavior in these catalytic processes due to their similarity in d-band electronic density to noble metals. In direct alcohol fuel cells, Co_2C, Fe_3C, Mo_2C, TiC, and WC have been used as efficient catalysts and alternatives to Pt-based materials [1]. X-ray absorption and X-ray photoelectron spectroscopic analysis techniques of Pt nanoparticles supported on MoC-reduced graphene oxide indicated a strong chemical coupling interaction between platinum nanoparticles and molybdenum carbide-reduced graphene oxide. An efficient improvement in this electro-catalyst activity towards methanol oxidation reaction was shown [10]. Yan et al. [11] have stated that the electron transfer between hollow molybdenum carbide sphere and platinum nanoparticles allowed for the formation of small-sized Pt nanoparticles and promoted the electrocatalytic action of formed electrocatalyst. Chronoamperometry, CO stripping and accelerated durability test indicated an enhanced resistance against CO-poisons accumulation during methanol oxidation at platinum nanoparticles deposited on tungsten carbide-reduced graphene oxide [12]. The specific current density of methanol oxidation at Pt–WC/MWCNTs electrocatalyst was 5.83 times higher than that at commercial Pt/C [13]. Fabricated Pd nanoparticles on mesoporous tungsten carbide exhibited an increased methanol oxidation current density by 1.55 folds when compared to that at Pd/C [14]. A higher I_f/I_b value during methanol oxidation reaction was measured at platinum nanoparticles supported on titanium carbide surface in relation to that achieved at Pt nanoparticles on Vulcan XC-72 carbon [15]. Although Chromium carbides have an excellent electrical conductivity, high corrosion resistance, and good stability, they have been rarely utilized in catalytic processes, and particularly for DAFCs. The fact that the catalytic performance of these materials is considerably lower than Pt-based materials, their catalytic activity should be improved to become appropriate electrocatalysts for various potential applications [16]. Gómez–Marín et al. [2] and Xiong et al. [17] have improved the electrocatalytic activity of Mo_2C towards hydrogen evolution reaction using transition metals and heteroatoms. This modification can effectively enhance the electronic and chemical properties of TMCs [9]. Cobalt metal or its composites (e.g., transition metals, noble metals, and metal carbides) has been employed as an efficient catalyst in wide range of chemical reactions [2,3,18–23]. The inclusion of cobalt into materials is expected to minimize the poisoning species accumulated at Pt surface in DAFCs. This is clearly evident by the work of Paulus et al. [24] who have demonstrated that using Co–Pt alloy dramatically enhanced CO tolerance behavior for hydrogen activation. Moreover, the high adsorption capacity of carbon makes it a good support for different metallic based nanocomposites [25]. Cd-doped cobalt nanoparticles encapsulated in graphite shell, prepared using sol-gel technique, have displayed increased electrocatalytic activity towards methanol oxidation reaction with a current density value of 70 mA cm^{-2} and onset potential value of 600 mV (NHE) [26]. Barakat and Motlak [27] have measured an increased electrocatalytic performance for $Co_{0.2}Ni_{0.2}$ alloy nanoparticles formed on graphene during methanol oxidation reaction compared to a worse behavior at $Co_{0.1}Ni_{0.3}$ alloy.

In this study, Co-doped Cr_7C_3-like nanorods embedded on carbon nanofibers were introduced as a novel low cost and efficient catalyst. They were fabricated by simple electrospinning technique using sol-gel method with polyvinyl alcohol, chromium acetate monohydrate and cobalt acetate tetrahydrate as precursor salts. This prepared nanocomposite was characterized using XRD, SEM, TEM and EDX analysis techniques. Its electrocatalytic activity towards methanol oxidation in alkaline solution was examined. $CoCr_7C_3$-CNFs nanocomposite demonstrated an improved electrocatalytic performance for methanol oxidation with reasonable stability.

Materials and methods

Preparation of $CoCr_7C_3$-CNFs nanocomposite

$CoCr_7C_3$-CNFs nanocomposite was prepared using a lab scale electrospinning setup. In a typical experiment, 1 g chromium (II) acetate dimer monohydrate (CrAc, Sigma-Aldrich) and 0.25 g cobalt acetate tetrahydrate (CoAc, Sigma-Aldrich) were dissolved in 5 ml deionized water. 15 g polyvinyl alcohol (PVA, Aldrich, 10 wt% with average Mw ~ 1300 kg/mol) was then added to the solution in glass bottle. The mixture was stirred at 70 °C for 5 h to ensure complete dissolution as transparent and polycondensated sol-gel. The formed sol-gel was electrospun (lab scale with single-nozzle basic-level electrospinning machine) at high voltage value of 18 kV between the needle and the rotating cylinder to charge the solution through the needle. The needle tip-to-collector distance was kept at 15 cm. The produced CNFs were collected on a polyethylene sheet and subjected to vacuum drier at 50 °C for 24 h, then heated at 850 °C for 6 h with a heating rate of 2.3 °C min^{-1}.

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