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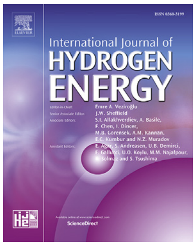

Micro and nano-architectures of Co_3O_4 on Ni foam for electro-oxidation of methanol

G. Rajeshkhanna, G. Ranga Rao[*]

Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600036, India

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ABSTRACT

Spinel Co_3O_4 material with different morphologies is directly grown on Ni foam by simple hydrothermal method and subsequent calcination processes. The direct growth of binder free active phase of Co_3O_4 on Ni foam is an effective approach to enhance the electrocatalytic activity of the material. The morphologies of Co_3O_4 strongly depend on the anion of the precursor salt used. Microflowers, microspheres and nanograss morphologies of Co_3O_4 are obtained using chloride, sulfate and acetate salts of cobalt, respectively. The BET surface areas of these cobalt oxide materials are found to increase in the order of microflower-Co_3O_4 (53 $m^2\ g^{-1}$) < nanograss-Co_3O_4 (65 $m^2\ g^{-1}$) < microsphere-Co_3O_4 (100 $m^2\ g^{-1}$). The electrocatalytic activity of these Co_3O_4 materials has been tested for methanol oxidation by cyclic voltammetry and chronoamperometry. All three samples show low onset potentials (0.32–0.34 V) for methanol oxidation. The vanodic peak current of methanol oxidation is found to increase in the order of microflower-Co_3O_4 (28 A g^{-1}) < nanograss-Co_3O_4 (34.9 A g^{-1}) < microsphere-Co_3O_4 (36.2 A g^{-1}) at 0.6 V. This study highlights the significance of the morphology of cobalt oxide in the development of oxide based non-precious electrocatalysts for methanol oxidation.

Introduction

In order to reduce the usage of fossil fuels, current research is intensively focused on developing of environmental friendly energy conversion devices such as fuel cells. In this perspective, direct methanol fuel cells (DMFC) are considered as promising power sources due to advantages of high efficiency, low operating temperature, and low pollutant emission [1–3]. Besides, methanol fuel is readily available, economical and easy to transport. However, successful commercialization of DMFCs is still a challenge due to cost issues and life cycles of the electrode materials. At present, Pt and Pt-based catalyst are extensively studied and they are the major anode electrocatalysts for DMFCs due to their faster electrochemical kinetics [1–9]. However, their high cost and electrode inactivity caused by the intermediate species generated during the oxidation of methanol are the roadblocks for commercialization of DMFCs. This has triggered the search for an alternate and efficient low cost materials such as $(NiOH)_2$ [10], $Co(OH)_2$ [11], NiO [12–16], Co_3O_4 [17], $NiCo_2O_4$ [18–25], $CuCo_2O_4$ [26], Ni–Cu–P alloy [27] and NiSe [28]. Significant efforts are devoted in developing $NiCo_2O_4$ electrode material for electro-oxidation of methanol [18–25]. However, the development of efficient non-precious electrode material is still unsatisfactory. Therefore exploring metal oxides as anode catalysts with higher electrochemical kinetics and rich electroactive sites is still a key challenge.

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[*] *Corresponding author.*
E-mail address: grrao@iitm.ac.in (G. Ranga Rao).

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It is known that transition metal oxides are versatile materials for energy related applications because of availability of multiple oxidation states, controllable morphological, chemical, and textural properties [12–26,29–35]. Generally, the essential properties of electrode materials for electrochemical applications include high surface area, suitable porosity, tiny particle size and favourable morphology. In particular, electrode material with these essential properties is directly grown on conductive substrate offers short transport pathways for electrons as well as ions/molecules [26,29,36–38]. In this context, nanostructured Co_3O_4 grown on Ni foam is widely studied as an electrode for supercapacitor and battery applications, by exploiting its redox behaviour [37,38]. Though there are many reports available on the synthesis and application of Co_3O_4 on Ni foam for various purposes, to the best of our knowledge reports on the application of Co_3O_4 grown on Ni foam as an electrode for electrochemical oxidation of methanol are very limited. Recently Cheng et al. reported the electrocatalytic behaviour of $CuCo_2O_4$ nanograsses on Cu foam for electro-oxidation of methanol [26]. Gu et al. synthesized nanosphere-like $NiCo_2O_4$ and then coated on Ni foam and demonstrated that it shows better electrocatalytic activity [21].

The main purpose of the present work is to study the electro-oxidation of methanol on a Co_3O_4 material grown on Ni foam. The direct growth of binder free active phase on Ni foam is proven to be effective approach to enhance the electrochemical properties of the electrode material [30]. In oxide materials the electrocatalytic activity strongly depends on surface area, morphology and porosity. These parameters can be controlled by various synthetic strategies, especially by using different surfactants in hydrothermal method [17]. However, the role of metal salt precursor on the morphology, surface area and porosity of Co_3O_4 has not been explored in detail. In this perspective, the size and overall charge of the anions are expected to affect the above parameters during the synthesis. In this report we demonstrate cost effective synthesis procedure to grow the binder free Co_3O_4 on Ni foam for widespread utilization of the material. The morphological properties are tuned by changing the parent metal salt precursor during synthesis of Co_3O_4. We have exploited the morphological dependent electrocatalytic properties of Co_3O_4 on Ni foam for electro-oxidation of methanol. The comparison of electrocatalytic activity in alkaline medium of different morphologies of Co_3O_4 has been discussed. The Co_3O_4 samples with intercalated sulfate and acetate anions have microsphere-like and nanograss-like structures, respectively, with large surface areas. These two samples exhibit higher electrocatalytic activity compared to microflower-like structure of Co_3O_4 with intercalated chloride ion.

Experimental

Synthesis of Co_3O_4

In a typical batch experiment, 1.2 mmol of $CoCl_2\cdot6H_2O$, 2.4 mmol of NH_4F and 0.6 mmol of CTAB were dissolved in 30 mL of triple distilled water stirred for 1 h to form a homogeneous pink solution. To this solution 2.4 mmol of solid urea was added and continued stirring further for 2 h to attain a complete homogeneity. Nickel foam (approximately 1 cm × 1 cm) was carefully cleaned with 3 M HCl solution in an ultrasonic bath for 10 min in order to remove the surface NiO layer, and then deionized water and acetone were used for 5 min each two times to ensure the surface of the Ni foam was well cleaned. The aqueous solution and the Ni foam were transferred to a Teflon lined autoclave of 50 mL capacity and subjected to heating at a temperature of 120 °C for 12 h. The uniformly grown solid material on Ni foam was observed after auto-cooling the autoclave to room temperature. The material deposited on Ni foam was washed several times with distilled water and ethanol after that dried in a conventional oven at 60 °C for 12 h. This sample is labelled as flower-Co_3O_4-uc. It was further heated slowly at the rate of 1 °C min^{-1} from room temperature to 350 °C and kept for 2 h in air atmosphere in order to get the oxide phase. The calcined sample is labelled as microflower-Co_3O_4. In order to study the effect of metal salts on physicochemical and electrochemical properties, we also prepared cobalt oxide using two different parent precursor solutions, one with $CoSO_4\cdot6H_2O$ and the other with $Co(CH_3COO_2)\cdot4H_2O$, following the same procedure as described above. The uncalcined cobalt oxide precursor samples prepared, using cobalt sulfate and cobalt acetate salts, by hydrothermal method are denoted as microsphere-Co_3O_4-uc and nanograss-Co_3O_4-uc, respectively. The precursor samples are calcined at 350 °C in air and denoted as microsphere-Co_3O_4 and nanograss-Co_3O_4, respectively.

Characterization

The powder X-ray diffraction (PXRD) patterns recorded from 10° to 80° using a Bruker AXS D8 Advance diffractometer at room temperature employing Cu Kα ($\lambda = 0.154$ nm) radiation generated at 40 kV and 30 mA. The XPS analysis was carried out on SPECS X-ray photoelectron spectrometer with Mg Kα radiation (1253.6 eV). The PHOBIOS 100 MCD analyzer was used at 40 eV pass energy and the binding energies are reported with respect to C 1s line at 284.5 eV. Multipoint N_2 adsorption-desorption experiment was carried out on Micromeritics ASAP 2020 analyzer and the surface area was determined using the Brunauer-Emmett-Teller (BET) gas adsorption method, at 77 K. The sample is outgassed at 150 °C for 12 h in a dynamic vacuum before physisorption measurements. The pore size distribution plots were generated from desorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) method. The pore volume was obtained from the pore size distribution data. Surface morphologies of the calcined samples were obtained using an FEI Quanta FEG 400 high-resolution scanning electron microscope (HRSEM). The powder samples were deposited on a conducting carbon tape before being mounted on the microscope sample holder for analysis. The high resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL 3010 HRTE microscope operated at 300 kV.

Fabrication of electrode and electrochemical measurements

For evaluation of electrocatalytic properties of Co_3O_4 samples, cyclic voltammetry (CV), chronoamperometry (CA) and linear

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