



# Preparation of Ni-metal oxide nanocomposites and their role in enhancing the electro-catalytic activity towards methanol and ethanol



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## ABSTRACT

Ni-metal oxide ( $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{Co}_3\text{O}_4$  and  $\text{MnO}_2$ ) nanocomposites were synthesized on carbon substrates by electrodeposition technique. These catalysts were tested as anodes for electrooxidation of both methanol and ethanol. To study the chemical composition of the deposits, energy dispersive X-ray spectroscopy (EDX) was used and the maximum wt% of metal oxides in the prepared composites was found to be 11.4, 11.7, 9.3 and 3.8 for  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{MnO}_2$  and  $\text{Co}_3\text{O}_4$ , respectively. The morphology of the catalysts surface is significantly affected by the existence of metal oxides as confirmed by scanning electron microscope (SEM) images. The phase structure and the particle size of the catalysts were recognized from X-ray diffraction (XRD). A reduction in the Ni grains was seen in the matrix of the composites compared with that of Ni/C. Cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) were employed to study the electrocatalytic activity of the prepared nanocomposites. All the results displayed a satisfactory electrocatalytic activity, better stability, lower charge transfer resistance, and stronger resistance to the poisoning of the nanocomposites compared with that of Ni/C. A synergistic effect among multiple active sites due to the presence of mixed oxides for the nanocomposites could enhance their electrocatalytic activity. The performance of the different prepared catalysts towards the electrooxidation process was established in the order of: Ni- $\text{Fe}_2\text{O}_3$ /C > Ni- $\text{ZnO}$ /C > Ni- $\text{Co}_3\text{O}_4$ /C > Ni- $\text{MnO}_2$ /C > Ni/C. Ni-metal oxide nanocomposites appeared to be promising and less expensive anode catalysts for fuel cell applications.

## 1. Introduction

The lack of natural energy resources is a real challenge for the modern life. Efforts are being made to find new energy resources that can supply human needs. Nowadays, other alternative fuels such as non-fossil Syngas ( $\text{H}_2/\text{CO}$ ) is used, it is a very valuable and versatile energy carrier because it can be converted into liquid fuels. It is considered a renewable source of energy and it can be produced by electrochemical  $\text{CO}_2$  reduction in an ionic liquid [1]. In addition, some alcohols like methanol and ethanol are being used as renewable fuels. It is known that the electrochemical power sources, for instance, fuel cells have been developed and used in a variety of life applications such as domestic and public transportation. Direct methanol or ethanol fuel cells are promising systems. Chemical energy of methanol or ethanol fuel is converted to electricity efficiently without combustion [2]. However, there are some limitations restrict the use of fuel cells at a commercial level. This is attributed to the high-cost materials used to design the fuel cell, particularly Pt catalyst that used as anodes especially in acid media [3–8]. Attempts have been employed to change Pt

by some cheap materials as electrocatalysts for methanol and ethanol electrooxidation particularly in alkaline media [9–12].

For many years, nanocomposite electrodes have attracted interest because they are feasible to be prepared by properly incorporating nano-particulate to be co-deposited in the metal matrix through chemical or electrochemical methods. Moreover, they exhibited remarkable and technologically attractive properties due to their extremely fine microstructure and higher surface area. They exhibited higher catalytic activity towards the electrooxidation processes. Meanwhile, nanocomposites appeared to be promising and less expensive anode catalysts for fuel cell applications [13]. Some composites containing metal oxides ( $\text{CeO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{MoO}_2$ ) were used as anodes as they were more useful than Pt and less expensive. It was mentioned that metal oxides can supply  $\text{OH}^-$  species which induce oxidation/reduction process between different oxidation states of nanocomposite metal oxides to improve the catalytic efficiency [14]. Furthermore,  $\text{CeO}_2$ - $\text{ZrO}_2$  mixed oxides have been extensively used as oxygen storage components. It is noteworthy that cerium oxide may make CO-like species oxidated to prevent the catalyst deactivation [15]. Also, a

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platinum catalyst supported on a double oxide nanocomposite of tin oxide clusters and carbon-doped titanium dioxide nanocoatings on carbon nanotubes is used for electrooxidation of methanol. It leads to a much lower onset potential for the adsorbed CO oxidation with a much enhanced bifunctional effect in tin oxide [16]. Moreover, various metal oxides, for example,  $\text{CeO}_2$ ,  $\text{MnO}_x$ ,  $\text{NiO}$ ,  $\text{Co}_3\text{O}_4$  and their hydroxide analogues were found to be active materials for the electrocatalytic applications [17–22]. It was observed that inclusion of small amounts of metal oxides in addition to the active redox properties can help for developing the Pt electrocatalysts for fuel cells [23–26]. Also, cobaltous oxide deposited on a Pt electrode, shows prominent electrocatalytic activity towards the mediated electrooxidation of glucose and methanol [27]. The electrocatalytic activity of nano- $\text{CoO}_x$  and MWNT composite modified GCE ( $\text{CoO}_x$ -MWNT/GCE) has been examined towards the oxygen evolution reaction (OER) by linear sweep voltammetry [28]. The addition of nickel oxide into both Pt/C and Pd/C catalysts could improve the methanol oxidation performance in terms of poisoning resistance and the reaction activity [10]. Moreover,  $\text{SnO}_2$  promotes PtRu catalyst towards ethanol oxidation and it shows a lower onset potential and larger current density. Also, it could activate ethanol chemisorptions and increase the electroactive surface area, together with a faster intrinsic activity at lower overpotential [29]. It was previously seen that Pd/ $\text{Cu}_2\text{O}$ /MWCNT catalyst can be used as an excellent anode catalyst for ethanol electrooxidation in alkaline solution. The occurrence of  $\text{Cu}_2\text{O}$  increases the stability and CO poisoning tolerance of the Pd towards electrooxidation of ethanol [30]. Among various different metal oxides are MgO [31], NiO [32,33],  $\text{MnO}_2$  [34],  $\text{SnO}_2$  [35,36],  $\text{CeO}_2$  [37],  $\text{Mn}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4$  were used with Pd as a catalyst for fuel cells.

Ni-based catalysts like Ni–metal oxide nanocomposites have attracted importance in a wide range of fundamental researches and technological applications, for example; electrocatalysis and fuel cells [33,38–43]. This is due to the good distribution of the Ni particles and the high active surface area which lead to enhancement of the catalytic activity towards the electrooxidation processes. Ni–metal oxide nanocomposites are synthesized by co-depositing metal oxides like ZnO,  $\text{Cr}_2\text{O}_3$ , MgO or  $\text{TiO}_2$  in the Ni-plated layer under the electric field [38,39,44–47]. Moreover, the rate of oxide particle co-deposition depends on many factors such as size, shape, charge, current density, temperature, pH and time. Their applications as anode catalysts were estimated towards electrooxidation of relatively low molecular mass alcohols in alkaline fuel cells [48,49]. Their catalytic activity is attributed to the formation of a higher valence Ni oxide which acts as chemical oxidizing agent [50]. An enhancement of the durability and catalytic activity is achieved when using these composite materials as electrocatalysts [51,52]. It was seen that Ni–MgO composite exhibits low overvoltage for alcohol oxidation, acts as effective anode materials with higher efficiency, increases the anti-poisoning ability of the Ni catalysts and improves the kinetic processes [40,53–55]. Also, the existence of  $\text{TiO}_2$  co-deposited within the Ni matrix as a nanocomposite increases its electrocatalytic activity [38,39]. Moreover, nickel modified with  $\text{MnO}_x$  is significantly active for the methanol electrooxidation [54]. Effective electrocatalysts for oxygen reduction reaction (ORR) was carried by using transition metal oxides [56–58]. This is due to the multiplicity of the active sites which may be responsible for the improvement of ORR activities. Additionally, Ni–NiO@C nanocomposites showed a high electrocatalytic activity for methanol oxidation [59].

Accordingly, the main goal of this work is to develop Ni-based nanocomposites for methanol and ethanol electrooxidation. Ni–metal oxides ( $\text{Fe}_2\text{O}_3$ , ZnO,  $\text{Co}_3\text{O}_4$  and  $\text{MnO}_2$ ) nanocomposites were synthesized on carbon electrodes using a simple electrodeposition technique. The prepared electrodes will be used as anodes for alcohols electrooxidation. It is anticipated to improve the catalytic activity of the Ni and find reasonable explanations for the effect of metal oxides in enhancing the electrooxidation process.

## 2. Experimental techniques

### 2.1. Synthesis of Ni–metal oxide nanocomposites

For the synthesis of the Ni–metal oxide nanocomposite working electrodes, carbon substrates were used for the electrodeposition process, each of a geometrical electrode area of  $0.125\text{ cm}^2$ . The carbon electrodes were cleaned mechanically using metallurgical papers of various grades, then they were soaked in acetone, rinsed with double distilled water and finally dried. The electrode surface area was calculated from the geometrical area and the current density value was referred to it. Ni Watts' bath was utilized for the deposition of Ni and Ni–metal oxide nanocomposites, it has the composition of:  $240\text{ g l}^{-1}$  nickel sulphate,  $45\text{ g l}^{-1}$  nickel chloride and  $30\text{ g l}^{-1}$  boric acid, operated at pH 5,  $55\text{ }^\circ\text{C}$ , 150 rpm and  $40\text{ mA cm}^{-2}$  for 30 min in the absence and presence of different concentrations  $(1\text{--}12)\text{ g l}^{-1}$  of each metal oxide. Before the electrodeposition of composites, the oxide particles were stirred in the electrolyte solution by using a magnetic stirrer to achieve a uniform suspension of particles and break down the agglomeration. Ethanol and methanol were used without purification. Triple distilled water was used for the solutions preparation. Chemicals used were Sigma-Aldrich products of analytical grade and used without any further purification.

### 2.2. Electrochemical measurements

The electrochemical techniques were done in a conventional three-electrode system. The working electrode was Ni/C or Ni–metal oxide nanocomposites, the reference electrode to which all potentials were referred is the Hg/HgO/1.0 M NaOH (MMO), and a Pt sheet was used as a counter electrode. Measurements were done in an aerated 1.0 M NaOH at room temperature of  $25 \pm 0.2\text{ }^\circ\text{C}$ . The electrochemical measurements were performed by cyclic voltammetric and chronoamperometric techniques using Amel 5000 (supplied by Amel Instrument, Italy) driven by an IBM PC for data processing. The PC was interfaced with the instrument through a serial RS–232 card. To control the Amel 5000 system, Amel easyscan software was used and connected to PC. The electrochemical impedance spectroscopy (EIS) data was measured at frequencies ranging from 100 kHz to 10 MHz at 10 mV amplitude. Zahner Elektrik Meßtechnik, IM6, Germany, was used to perform the EIS and the experimental impedance spectra were fitted with the equivalent circuits included with the IM6 package using the "SIM" program. The suitability of the elements in the proposed equivalent circuits to fit the experimental data was judged by the error 1.5% of the fitting and by comparing the calculated and the experimental impedance plots.

### 2.3. Surface analysis techniques

Scanning electron microscopy Model Quanta 250 FEG (Field Emission Gun) attached with EDX unit (Energy dispersive X-ray analyses), with accelerating voltage 30 KV (FEI Company, The Netherlands) was applied to investigate both the chemical composition and the surface morphology of the prepared nanocomposites. X-ray diffractometer (XRD, Rigaku, Japan) with  $\text{CuK}\alpha$  ( $\lambda = 1.540\text{ \AA}$ ) was used to study the crystal structure and particle size of the prepared catalysts. It is operated at 45 kV and 40 mA. The step scanning size, range and rate were  $0.02^\circ$ ,  $10^\circ\text{--}100^\circ$ , and  $0.05^\circ/\text{s}$ , respectively.

The values of zeta potential for each metal oxide particles ( $\text{Fe}_2\text{O}_3$ , ZnO,  $\text{Co}_3\text{O}_4$  and  $\text{MnO}_2$ ) was measured using a laser zeta meter (Zetasizer 2000, Malvern Instruments, UK). A sample powder of every metal oxide (about 0.02 g) was placed into  $\approx 50\text{ ml}$  of Ni Watts' solution and the sample was stirred for 50 min at pH 5, after that the measurement of zeta potential was done. Actual surface areas of the prepared catalysts were measured using Nova 2000 series based on the well-known Brunauer, Emmett and Teller (B.E.T.) theory.

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