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# Electrodeposited nanocomposite coatings for fuel cell application

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#### 1. Introduction

Surface modification by coatings has become an essential step to improve the surface properties of materials. Coatings can protect a substrate by providing a barrier between the metal and its environment [1]. The nanostructured coatings have long been recognized to exhibit remarkable and technologically attractive properties due to their extremely fine microstructure [2]. Highly sophisticated surface-related properties such as optical, magnetic, electronic, catalytic, mechanical, chemical and tribological properties can be obtained by advanced nanostructured coatings, making them attractive for industrial application [3,4].

Composite electroplating is a method that involves codepositing fine particles of metallic, non-metallic compounds or polymers in the plated layer under the effect of electric field. Previously, the co-deposition of various metallic matrices as Ni, Ni–P, and Zn with a great variety of powders from hard carbides as SiC, oxides as ZnO and nitrides as AlN has been extensively studied by Abdel Aal et al. [3–7]. During this process, the powder particles are suspended in a conventional plating electrolyte and are captured in the growing metal film. Moreover, the rate of particle incorporation depends on the nature of particles (size, shape and charge) and the operating conditions (current density, temperature, pH and time) [3–7].

#### ABSTRACT

Ni–TiO<sub>2</sub> nanocomposite coatings were prepared by the co-deposition of Ni and nanoparticles of TiO<sub>2</sub> powder onto the surface of commercial carbon for fuel cell application, in particular the electro-oxidation of methanol. The influences of the TiO<sub>2</sub> powder concentration and applied current density on the composition of nanocomposite coatings were investigated. The chemical composition and phase structure of coatings were studied by X-ray diffractometer (XRD) and energy dispersive X-ray spectroscopy (EDX), respectively. The surface morphology of deposited Ni and Ni–TiO<sub>2</sub> coatings was studied using scanning electron microscope. The performance of the prepared electrodes towards electro-oxidation of methanol as a function of co-deposited TiO<sub>2</sub> content was studied. The catalytic activity was found to increase with increasing TiO<sub>2</sub> content up to 9 wt.%. The chronoamperometric data showed that the stability of the fabricated electrodes towards the electro-oxidation process was improved with the content of co-deposited TiO<sub>2</sub>. © 2008 Elsevier B.V. All rights reserved.

> Small organic molecule's fuel cells are regarded as promising electrochemical systems for directly converting the chemical energy of a fuel and an oxidant into electric energy in a wide range of the portable and transportation applications. A short list of their advantages may include, interalia, their suitability for applications where mass and volume constraints are stringent, the compatibility of liquid methanol for handling and storage in the existed gasoline infrastructure, and their ability for quick start-up and immediate response to consumer needs [8].

> The activity of electrocatalysts is one of the main factors affecting the cell performance. The procedure and method for the preparation of the electrocatalysts play an important role in their particle size, surface morphology, composition and electrocatalytic activity with direct consequences to the fuel cell performance [9–12]. Song et al. [8] have reported that the electrode fabrication process, especially for the decal transfer fabrication technology, which involves several intermediate processing steps, should also have an obvious effect on the physical characteristics of electrocatalysts, and accordingly on their electrochemical activity.

During the past decade, the electrochemical oxidation of small organic molecules on nickel-based electrodes attracted considerable attention and impact [13,14]. TiO<sub>2</sub> and Ti coated with oxides of several other metals; Pt, Au, Fe, Co, Ni, Mo, Mn, Cr, Cu and Hg or their combinations Sb–Sn, Co–Mn, Ni–Si, Ni–Cr–Mo and Fe–Cr are used for methanol electro-oxidation [15]. The introduction of TiO<sub>2</sub> into Ni matrix is expected to improve the catalytic activity of Ni-based electrodes. Hence, the present article reports on the preparation of nanocomposite coatings of Ni–TiO<sub>2</sub>





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onto the commercial carbon electrodes and their application for the electro-oxidation of methanol.

#### 2. Experimental procedures

Ni-TiO<sub>2</sub> nanocomposite layers were deposited on commercial carbon substrates by conventional direct current electrodeposition process. Electroplating was performed using a plating cell consisting of carbon rod and nickel plate as cathode and anode, respectively, and vertically maintained at 5 cm. The basic compositions of the electrolyte are as follows: 240 g/l nickel sulfate, 30 g/l nickel chloride, 30 g/l boric acid. The plating bath is heated to 55 °C and pH 5 value was adjusted by ammonia water or dilute sulfuric-acid. The titanium dioxide, TiO<sub>2</sub>, used in this work (Degussa P-25 anatase) with 25 nm was obtained from Degussa Company, Ridgefield Park, NJ. Different concentrations were added to plating solution in order to form Ni-TiO<sub>2</sub> nanocomposite coatings. During the co-deposition process, the bath was stirred by a magnetic stirrer (150 rpm) in order to keep the particles dispersed and prevent sedimentation in the electrolyte suspension. For comparison, pure Ni coatings were also prepared in almost the same solution mentioned above except TiO<sub>2</sub> particles were introduced under the same electrodeposition conditions. In order to standardize the comparison, the thickness of all coatings was controlled to be approximately 20 µm by the plating time for a specific current density.

The phase structure of the composite coatings was studied by X-ray diffractometry (BRUKER axc-D8) using Cu K $\alpha$  radiation with  $\lambda$  = 0.1542 nm. The surface morphology of the coatings was observed using a scanning electron microscopy (JEOL-JSM-5410) and the weight percentage (wt.%) of co-deposited TiO<sub>2</sub> particles was evaluated by using energy dispersive X-ray spectroscopy (EDX-Oxford) analysis tool. In each measurement an area of 10  $\mu$ m in diameter was examined to a depth of about 2  $\mu$ m. From EDX analysis, wt.% of Ti metal can be determined and accordingly the TiO<sub>2</sub> percentage.

Electrochemical measurements were performed on the above-prepared electrodes of a disc-shaped each of apparent surface area of  $0.125 \text{ cm}^2$ . The surface area was calculated from the apparent area and the current density was referred to it. A conventional three-electrode glass cell with a Pt sheet as a counter electrode and Hg/HgO/1.0 M NaOH (MMO,  $E^0 = 140 \text{ mV vs. NHE}$ ) as a reference electrode were used. All experiments were carried out at room temperature of  $30 \pm 2$  °C. The electrochemical measurements were performed using an Amel 5000 system (supplied by Amel instrument, Italy) driven by a PC for data processing. The PC was interfaced with the instrument through a serial RS-232C card. Amel Easy Scan software was used in connection with the PC to control the Amel 5000 system.

#### 3. Results and discussion

#### 3.1. Electrodeposition and characterization

The effect of bath loads (0.5-5 g/l) was studied at various current densities of 1, 2, and 3 A/dm<sup>2</sup>, maintaining all other deposition parameters constant as pH 5 and temperature 55 °C (Fig. 1). The composition of composite layer was determined by EDX as shown in Fig. 2. The embedded weight percentage (wt.%) of TiO<sub>2</sub> in the composite was found to increase with increase in bath loads, reaching a



Fig. 1. Dependence of TiO<sub>2</sub> content in deposit on the bath load and current density at constant pH 5.5 and 55 °C.



Fig. 2. EDX of samples coated with (a) Ni and (b) Ni-9% TiO<sub>2</sub>.

maximum of 9 wt.% for a bath load at 1 g/l. The embedding of  $TiO_2$  can be attributed to the adsorption of suspended particles on the cathode surface, as suggested by Guglielmi's two-step adsorption model [16]. Once the particle is adsorbed, the metal begins building around the cathode slowly, encapsulating and incorporating the particles. Further increase of bath load up to 5 g/l resulted in a slight decrease in the weight of the  $TiO_2$  in the deposited composite and indicated that the adsorption of  $TiO_2$  particles in the coating has reached the saturated state [17].

Fig. 1 shows also the correlation between the  $TiO_2$  content in the deposit and the current density at various  $TiO_2$  concentrations in the electroplating bath. The wt.% of co-deposited  $TiO_2$  increases with current density. According to the Stokes model, assuming the shape of the colloidal particle is sphere, the electrophoretic velocity  $(V_E)$  in an electric field (*E*) can be expressed as:

$$V_{\rm E} = \mu_{\rm E} E = \frac{q}{6\pi\eta r} E \tag{1}$$

where  $\mu_{\rm E}$  is the electrophoretic mobility, q is the charge of the particle, r is the radius of the particle, and  $\eta$  is the viscosity of the suspension [18]. The Stoke's model indicates that increasing the current density accelerates the electrophoretic velocity of TiO<sub>2</sub> particles and increases the Coulombic force between Ni<sup>+2</sup> adsorbed on particles and the cathode which in accordance increases the TiO<sub>2</sub> content in the Ni deposit.

Besides the Guglielmi's model for the co-depositing process, several mechanisms have been proposed describing the co-deposition process, such as absorbing theory in which the codeposition of particles and metal depends on van der Waal's force on the cathode surface. Once the particles are absorbed on the cathode surface, they will be imbedded into the composite coatings [19-22]. On the other hand, the particles in the mechanical mechanism are deposited into the matrix through the simple mechanical course. In this model, the particles are transmitted to the cathode surface by the flowing fluids to contact the cathode. Then, they will stay on the cathode surface by the external force and be captured by the deposited metal. In the electrochemical mechanism, the field intensity between the interface of electrodes and solution and electric charges of the particle surface plays a significant role in the co-deposition process [16-22]. In general, the co-deposition mechanism is still not clear and further studies will have to address the details of the process.



Fig. 3. SEM images of (a) pure Ni, (b) Ni-4 wt.% TiO<sub>2</sub>, (c) Ni-8 wt.% TiO<sub>2</sub> and (d) Ni-9 wt.% TiO<sub>2</sub> deposited at different current densities and constant pH 5.5 and 55 °C, 3 A/dm<sup>2</sup> and 1 g/l TiO<sub>2</sub> powder.

The scanning electron micrographs (SEM) of the Ni and Ni–TiO<sub>2</sub> coatings are presented in Fig. 3a–d. A regular pyramidal structure as shown in Fig. 3a is observed at the surface of the nickel film. The obtained composite layers have a mat-gray metallic surface with white Ni spots visible to the naked eye. Therefore, with the additions of TiO<sub>2</sub> nanoparticles, the morphology of coatings is changed to spherical particle, as shown in Fig. 3b–d.

The phase structure of Ni–TiO<sub>2</sub> coating is represented in Fig. 4. The XRD pattern of the Ni–TiO<sub>2</sub> layer showed that the structure of



Fig. 4. XRD patterns of Ni–9 wt.% TiO\_ nanocomposite coating deposited at pH 5.5 and 55  $^\circ$ C, 3 A/dm² and 1 g/l TiO\_ powder.

this type of coatings exhibits a nickel matrix at different  $2\theta$  angles corresponding to the crystalline matrix of the Ni layer. The pattern of such a composite layer additionally contains two small peaks characterized for crystalline TiO<sub>2</sub> (anatase) indicating the embedding of the TiO<sub>2</sub> particles into the nickel matrix.

The grain size of Ni and Ni–TiO $_2$  coatings can be estimated by the Scherrer equation:

$$t = \frac{0.9\lambda}{B\cos(\theta_B)} \tag{2}$$

where  $\lambda$  is the Cu K $\alpha$  wavelength, *B* is the broadening of the full width at half maximum (F.W.H.M.) and  $\theta_B$  is the Bragg's angle. The grain sizes of the pure Ni and Ni-TiO<sub>2</sub> nanocomposite coatings were calculated from the diffraction peak widths (with the instrumental width eliminated) by the Scherrer formula. The results are listed in Table 1. It is clear that increasing of TiO<sub>2</sub> content (0–9 wt.%) into deposit reduces the size of Ni grains (from 108 to 37 nm), due to the distribution of TiO<sub>2</sub> nanoparticles on the boundaries of Ni grains, which restricts the growth of Ni grains in the deposition process and results in the fine and smooth surface [23].

#### 3.2. Electro-oxidation of methanol

The performance of  $Ni-TiO_2/C$  catalysts towards methanol electro-oxidation was studied in 2 M NaOH and compared with the

#### Table 1

The applied electrodes and grain size of Ni coating as a function of content of TiO<sub>2</sub>.

Electrode	TiO <sub>2</sub> content, wt.%	Ni grain size, nm
Pure Ni	0	108
(I)	4 wt.% TiO <sub>2</sub>	57
(II)	8 wt.% TiO <sub>2</sub>	42
(III)	9 wt.% TiO <sub>2</sub>	37
(II) (III)	8 wt.% TiO <sub>2</sub> 9 wt.% TiO <sub>2</sub>	42 37



Fig. 5. Cyclic voltammograms of Ni/C electrode in 2 M NaOH solution in the absence (the dashed line) and in the presence of 2 M methanol (the solid line).

performance of Ni/C electrodeposited electrode. Fig. 5 shows the cyclic voltammograms of Ni/C electrode in 2 M NaOH solution in the absence (the dashed line) and in the presence of methanol (the solid line). Polarization was started from -1200 to +1500 mV (MMO) at a scan rate of 50 mV/s in the anodic direction and then the scan was reversed in the cathodic direction back to -1200 mV (see the inset figure). In addition to the hydrogen evolution taking place at the starting potential characterized by a high cathodic current and the oxygen evolution takes place at relatively high positive potential, two small peaks are observed in the blank voltammogram, one in the anodic direction at about +380 mV due to the formation of NiOOH and the other in the cathodic direction at about +480 mV due to the reduction of NiOOH to Ni(OH)<sub>2</sub> [24]:

$$Ni(OH)_2 + OH^- = NiOOH + H_2O + e^-$$
 (1)

In the presence of 2.0 M methanol, the oxidation process starts at +400 mV (MMO) with gradual increase in the oxidation current density and reaches its maximum value of 259 mA cm<sup>-2</sup> at about +1079 mV in the anodic direction. Then, the scan was reversed and another reoxidation peak appeared in the reverse scan at a potential of about +950 mV probably due to the reoxidation of methanol or the intermediate products generating during methanol oxidation. Adsorbed CO is one of the most known intermediate products of methanol oxidation which causes deactivation and blocking of the active sites of the electrode surface during the oxidation process with the time [25]. On the other hand, formate and CO<sub>2</sub> were identified as the main solution reaction products in NaOH solution [26]. It was found that the electro-oxidation of organic compound requires the presence of oxide, hydroxide and/or oxyhydroxide groups [27]. On the Ni-P/C electrode, the oxidation process of methanol starts at a potential value corresponds to the formation of NiOOH species and the oxidation process starts as Ni(III) species is formed as shown in Fig. 5 (the solid voltammogram). It was suggested that, methanol is oxidized on the Ni/C electrode through the reaction with NiOOH to form Ni(OH)<sub>2</sub>, i.e. NiOOH acts as electron transfer mediator for the oxidation process [28]:

$$NiOOH + methanol \leftrightarrow Ni(OH)_2 + products$$
 (II)

The same experiments were repeated on Ni–TiO<sub>2</sub>/C electrodes with different amounts of TiO<sub>2</sub> as shown in Table 1. Three different ratios of TiO<sub>2</sub> were found in the prepared electrodes which are Ni–4 wt.% TiO<sub>2</sub>(I), Ni–8 wt.% TiO<sub>2</sub>(II) and Ni–9 wt.% TiO<sub>2</sub>(III) and the three electrodes named as (I, II and III). The electro-oxidation of methanol on the three Ni–TiO<sub>2</sub>/C electrodes in 2 M NaOH solution was examined.

Fig. 6a illustrates cyclic voltammograms of the three electrodes (I, II and III) in 2 M NaOH as a blank solution at a scan rate of 50 mV/s from -1200 to 1500 mV (MMO) and the represented part is from 0 to +1000 mV (MMO). The shape of these cyclic voltammograms in



**Fig. 6.** (a) Cyclic voltammograms of Ni–TiO<sub>2</sub>/C electrodes (I, II and III) in 2 M NaOH solution at 50 mV/s (MMO). (b) Cyclic voltammograms of Ni–TiO<sub>2</sub>/C electrodes (I, II and III) in 2 M NaOH solution in the presence of 2 M methanol at a scan rate of 50 mV/s (MMO).

2 M NaOH is almost the same as the cyclic voltammogram pattern of Ni/C electrode (Fig. 6) in the same electrolyte with a few differences. It was found that, H<sub>2</sub> evolution peak appeared at the starting negative potential while the O<sub>2</sub> evolution peak appeared at more positive potential. The two peaks of Ni redox couples, i.e. (Ni<sup>3+</sup>/Ni<sup>2+</sup>) are formed in the potential range from +350 to +650 mV (MMO), depending on the amount of Ni as well as the amount of TiO<sub>2</sub> in the prepared electrode. The higher amount of TiO<sub>2</sub> in the prepared electrode, the higher height of the peak current densities of the redox couples. On the other hand, the potential of the cathodic peak shifted towards the less positive one. It can be observed that the presence of TiO<sub>2</sub> in the prepared electrode enhances the formation of Ni redox couple (Ni<sup>3+</sup>/Ni<sup>2+</sup>).

Fig. 6b represents cyclic voltammograms of these electrodes in 2 M NaOH in the presence of 2.0 M MeOH at a scan rate of 50 mV/s. It was found that, the oxidation process starts at +400 mV as NiOOH species is formed and the oxidation current density of methanol increases in the anodic direction up to +1500 mV. With reversing the scan down to +200 mV, another reoxidation process of the adsorbed methanol and/or its intermediate products generating during its oxidation taking place in the reverse scan. Oxidation of methanol at these electrodes is characterized by very broad peaks over wide range of potentials, so one must measure and compare values of oxidation current density at a constant selected potential value of about 1000 mV (MMO) (Table 2). It was found that, the oxidation current density of methanol measured at constant potential of +1000 mV (MMO) for all electrodes increases as the amounts of TiO<sub>2</sub> increase in the prepared electrodes. Compared to the Ni/C electrode, the oxidation current density of methanol at these electrodes is much higher. Notably, as the amount of TiO<sub>2</sub> increases in the prepared electrodes, the oxidation process occurs at less positive potential as shown from Fig. 6b and Table 2. For all the three electrodes, the oxidation process starts as the NiOOH is formed which acts as an electron transfer mediator for the oxidation process.

#### Table 2

Oxidation peak current densities and potentials for electro-oxidation of methanol at different electrodes.

Electrode	I/mA cm <sup>-2</sup> at +1000 mV (MMO)	$I_{\rm p}/{ m mAcm^{-2}}$	$E_{\rm p}/{\rm mV}~({\rm MMO})$
Pure Ni	247	259	1079
(I)	214	248	1151
(II)	329	341	1090
(III)	395	400	1043



Fig. 7. Steady state oxidation current density of methanol oxidation at Ni/C and Ni–TiO<sub>2</sub>/C (I, II, and III) electrodes at constant potential of +1000 mV (MMO) and the time in minutes.

From the above results, a conclusion can be drawn that the performance of Ni–TiO<sub>2</sub>/C electrodes is superior to Ni/C electrode towards the electro-oxidation of methanol. The enhancement of the catalytic activity of Ni–TiO<sub>2</sub>/C electrodes probably was attributed to the presence of the mixed oxides (i.e. the nickel oxides and titanium oxides) which may serve as good electron transfer mediators for the oxidation process [29].

In addition, the presence of TiO<sub>2</sub> reduces the particle size of Ni and increases the actual surface area, which improves the catalytic activity towards electro-oxidation of small organic molecules by increasing the number of active sites [30]. Hence, the electrodes of Ni–TiO<sub>2</sub>/C exhibited higher stability with time in comparison with Ni/C electrode, as shown from the chronoamperometric experiment in Fig. 7. This experiment represents the relation between the steady state current of methanol oxidation at the peak potential of about 1000 mV (MMO) and the time in minutes for Ni/C and Ni-TiO<sub>2</sub>/C electrodes. It is clear that Ni-TiO<sub>2</sub>/C (II and III) electrodes gave the highest stability with time than the Ni/C. Since TiO<sub>2</sub> suppresses the deactivation of the electrode surface and improves the stability of these electrodes through complete oxidation of intermediate product of the oxidation process such as CO. Moreno et al. [31,32] found that TiO<sub>2</sub> acts as a Pt protecting matrix in the hydrogen oxidation reaction which increases CO oxidation. Additionally,

Mehandru et al. [33] have proved that CO dissociates on Pt–Ti alloys much easier than on pure Pt.

#### 4. Conclusions

Nanocomposite coatings consisting of nickel matrix and  $TiO_2$  nanoparticles can be successfully synthesized by means of electrodeposition onto commercial carbon substrate. The content of  $TiO_2$  particles in the coatings increases with increasing  $TiO_2$  concentration in the electrolyte. The nanocomposite Ni– $TiO_2$  coatings showed a smaller grain size and higher catalytic activity towards the electrochemical oxidation of methanol compared with pure Ni coating.

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