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# Electrocatalytic activity of composite Fe/TiO<sub>2</sub> electrodeposits for hydrogen evolution reaction in alkaline solutions

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## ABSTRACT

Fe/TiO<sub>2</sub> composite coatings were obtained by electrodeposition using a methanesulfonate plating bath containing colloidal TiO<sub>2</sub> particles. Iron/titania electrodeposited composites exhibited enhanced electrocatalytic activity towards hydrogen and oxygen evolution reactions (HER and OER) in an alkaline solution. The electrocatalytic properties of Fe/TiO<sub>2</sub> composites towards the HER were studied by means of voltammetry, electrochemical impedance spectroscopy and chronoamperometry methods. An increase in TiO<sub>2</sub> content in iron matrix resulted in an increase in the electrocatalytic activity. The kinetic parameters were calculated on the basis of Tafel plots and EIS measurements and the possible mechanisms of the HER and OER were considered. The hydrogen evolution reaction on Fe/TiO<sub>2</sub> electrodes obeyed Volmer–Heyrovsky mechanism. It was concluded that the increase in the rate of the HER and OER on Fe/TiO<sub>2</sub> composite electrodes may be associated with the emergence of the redox couples on the electrode surface and the growth of the concentration of the surface active sites. The Fe/TiO<sub>2</sub> electrocatalysts showed a good catalytic stability in the HER and OER in 1 M NaOH solution.

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## Introduction

Searching for new and effective electrocatalysts for the hydrogen evolution reaction (HER) is very important in advanced industrial water electrolysis cells to produce hydrogen which is an environmentally clean and promising energy carrier. Various materials may be used as efficient and durable cathodic electrocatalysts for the HER [1]. Noble metals (Pt, Ru, etc.) seem to be the most active and stable materials, but their extremely high cost and limited natural abundance

impede their wide industrial applications. Thus, non-platinum active metals such as Fe, Ni or Co as well as their alloys and composites have received great attention as electrocatalysts for the HER because of their relatively low prices and accessibility [1–14]. For instance, different types of steel electrodes were reported to be suitable as electrocatalytic materials for the HER [15–18].

It should be observed that there are various available methods of electrocatalysts fabrication, electrodeposition being particularly attractive due to its simplicity, low cost and

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the possibility to influence easily on the structure, composition and properties of deposits obtained [1,7].

Although the most studied electrodeposited electrocatalysts for the HER in alkaline media are based on Ni and Co alloys and composites, electrocatalysts on the basis of electrodeposited iron also attract considerable attention, because Fe and its compounds are particularly cheap, available and low-toxic. Elezović N.R. et al. [9] studied the mechanism and kinetics of the HER in 1 M NaOH solution on Fe–Mo alloy prepared by electrodeposition. The real surface area of the electrodes was stated to increase with an increase in the molybdenum content. This factor was principally responsible for the increased electrocatalytic activity.

A suitable plating baths were developed to electroplate Fe–P, Fe–P–Pt and Fe–P–Ce amorphous alloys which act as electrocatalysts during alkaline water electrolysis [7]. Steady state polarization measurements and electrochemical impedance spectroscopy data showed that improved catalytic activity towards the HER was due to an increase in the effective surface area, a change in surface features upon heat treatment, the partial contribution of the Pt component, and the electrocatalytic synergism with Fe imposed by the Ce co-deposit.

It should be noted that the incorporation of colloidal particles into a metallic matrix (i.e. electrodeposition of composites) can enhance electrocatalytic activity towards the hydrogen evolution reaction. The incorporation of the Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> mixed oxide into Ni–P matrix substantially reduces overpotential during the HER in NaOH solution [3]. The Ni/TiO<sub>2</sub> [19] and Ni/Co<sub>3</sub>O<sub>4</sub> [20] composite layers electrodeposited from a conventional Watts' electrolyte containing TiO<sub>2</sub> or Co<sub>3</sub>O<sub>4</sub> powder, respectively, are characterized by enhanced electrochemical activity with respect to the HER in an alkaline electrolyte.

It is evident that the replacement of a nickel-containing matrix by an iron-containing one is very attractive from the economic and environmental viewpoints. It is known that the composites simultaneously containing iron and titanium have wide applications in catalysis, especially in photocatalytic degradation of organic pollutants [21–23], photo-electrochemical water splitting [24], and catalytic oxidation [25]. However, as far as we know, the electrodeposition of iron–titania composites with electrocatalytic activity towards hydrogen evolution reaction has not yet been described in the literature.

Therefore, the present study is aimed to obtain Fe/TiO<sub>2</sub> composite electrodeposits and investigate the effect of TiO<sub>2</sub> particles incorporation into a metallic matrix on the catalytic activity towards the HER in an alkaline solution. For iron matrix electrodeposition, we used methanesulfonate plating baths [26–28]. Methanesulfonate plating baths based on methanesulfonic acid CH<sub>3</sub>SO<sub>3</sub>H (MSA) are known to be an attractive alternative to common electroplating baths because MSA is considered as a “green acid” due to its environmental advantages [29]. MSA is far less corrosive and toxic than the usual mineral acids used in different branches of industry [30]. Methanesulfonates of various metals are highly soluble in water, the conductivity of the corresponding aqueous solutions is high. In addition, MSA is easily biodegradable [29]. Because of these advantages, electrochemical systems on the basis of MSA and its salts have been shown to be very

promising for electroplating of different metals, alloys and composites [31–35].

## Experimental

### Preparation of electrodeposits

A methanesulfonate iron plating bath developed in our previous studies [26–28] was used in this work. This plating bath allows obtaining nanocrystalline Fe coatings with a high current efficiency (ca. 95%) and a relatively high deposition rate (up to 2–4 μm min<sup>-1</sup>).

All solutions were prepared using double distilled water and reagent grade chemicals. Iron (II) methanesulfonate was synthesized by the procedure reported in detail elsewhere [29]. The pH value of the plating bath was controlled through a common potentiometric method and adjusted to the required value by adding either Na<sub>2</sub>CO<sub>3</sub> or MSA solutions. The concentration of Fe(II) ions in the electroplating bath was determined by the titrimetric analysis.

To obtain composite coatings, a weighed portion of TiO<sub>2</sub> nanopowder (Degussa P 25, Evonik; the average particle size 25 nm) was introduced directly into the electrodeposition bath. Before electrodeposition, the plating bath was stirred for 1 h by mechanical agitator and then ultrasonically treated with a UZDN-A ultrasonic disperser (1 h, 22.4 kHz, 340 W dm<sup>-3</sup>) to reach uniform distribution of colloidal particles in the bath. The electrodeposition of Fe/TiO<sub>2</sub> composite coatings was performed under the conditions of a continuous bath agitation with a magnetic stirrer (ca. 60 rev min<sup>-1</sup>).

Electrodeposition was performed at a steady current density in a usual thermostated glass cell (298 K) for 20 min. Iron and iron–titania films were deposited on the mild steel plates (S = 1 cm<sup>2</sup>) fixed in a plastic holder. Prior to each experiment, the sample surface was treated with magnesium oxide, etched for several minutes in 1:1 (vol.) HCl solution and then thoroughly rinsed with double distilled water. The electrolysis was carried out with anodes made from mild steel.

The composition and operating parameters of the plating bath used for deposition of Fe/TiO<sub>2</sub> composite coatings in the present study are summarized in Table 1.

### Physicochemical characterization of electrodeposits

The surface morphology of deposits was examined by the scanning electron microscopy (SEM) using scanning electron microscope REM 106 I. The composition of Fe/TiO<sub>2</sub> composite coatings was determined both by energy dispersive spectroscopy (EDS) and by chemical analysis [26].

Vickers microhardness (HV) test was carried out by means of a PMT-3 apparatus at a 100 g load, the coating thickness being not less than 20 μm. The average value of the deposits microhardness was calculated as a result of 5 separate measurements.

### Electrochemical characterization

The study of electrocatalytic activity was performed by means of voltammetry, chronoamperometry and electrochemical

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