

Available online at www.sciencedirect.com



ELECTROCHIMICA

Electrochimica Acta 52 (2007) 6304-6309

www.elsevier.com/locate/electacta

# Electrochemical generation of hydrogen peroxide using surface area-enhanced Ti-mesh electrodes

Kyung Shik Yang, Guido Mul\*, Jacob A. Moulijn

Reactor and Catalysis Engineering, DelftChemTech, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Received 17 November 2006; received in revised form 8 March 2007; accepted 3 April 2007 Available online 7 April 2007

## Abstract

Ti-mesh electrodes coated with Ti were obtained by using an electrophoretic deposition (EPD) method. The Ti coating was porous and showed a good adherence to the Ti-mesh surface, due to sintering of Ti particles during thermal treatment at 900 °C. The Ti-coated mesh electrode has a BET surface area of  $3.5 \text{ m}^2/\text{g}$ , about four times larger than that of the bare electrode. The surface area-enhanced Ti-mesh electrode was applied in electrical generation of hydrogen peroxide. It was shown that the rate of hydrogen peroxide generation increased drastically compared to the fresh electrode, since the larger electrode surface area enhanced not only current density, but also the oxygen mass transfer rate. © 2007 Published by Elsevier Ltd.

Keywords: Ti-mesh; Electrode; Electrophoretic deposition; Hydrogen peroxide; Oxygen reduction

# 1. Introduction

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is widely applied as a bleaching agent and disinfectant in the paper and textile industry. It is considered an environmentally friendly chemical since it leaves no hazardous residues. It is industrially produced by the oxidation of alkylhydroanthraquinones and by the electrolysis of ammonium bisulphate [1]. On-site production of H<sub>2</sub>O<sub>2</sub> has become of great interest because of the cost and hazards associated with the transport and handling of concentrated-H<sub>2</sub>O<sub>2</sub>. The industrial process is not an option for the in situ production of  $H_2O_2$ , because of the need of quinones, organic solvents and multiple reaction steps. Different alternatives for the bulk process, such as direct synthesis from oxygen and hydrogen [2,3], enzymatic [4,5], electrocatalytic [6] and electrochemical processes [7,8], have therefore recently been investigated. Electrochemical synthesis is the most popular alternative among them for the production of  $H_2O_2$  on a small scale by the oxygen reduction reaction. On the electron level two different pathways can be distinguished: (i) the four electron pathway, forming water or hydroxyl groups, and (ii) the two electron pathway, forming per-

0013-4686/\$ – see front matter © 2007 Published by Elsevier Ltd. doi:10.1016/j.electacta.2007.04.021

oxide. The pathway of oxygen reduction is strongly determined by the electrode materials [9].

Carbon is a well-known cathode for two-electron reduction of oxygen to hydrogen peroxide in alkaline solution [7]. Graphite has been widely used for the reaction but a gas diffusion electrode (GDE) is more common, to overcome the problem of the low solubility of oxygen, causing mass transfer limitations at the cathode surface. However, several problems such as electrode stability, and the cost, are still associated with using a GDE.

Recently several techniques were investigated to enhance the  $O_2$  electroreduction to  $H_2O_2$ . Gyenge and Oloman [10,11] tried to investigate electrochemical reactors with three-dimensional cathodes, consisting of graphite felt (GF) or reticulated vitreous carbon (RVC). The influences of surfactants and pH were examined for enhancing electroactivity and stability.

Applying an anthraquinone coating to carbon electrodes by novel approaches has also been suggested. Anthraquinone can chemically bind to the surface of the carbon electrode, and function as an organic catalyst [12]. The advantage of the quinone modified electrodes is that a high peroxide selectivity can be obtained.

Titanium has long been used as an electrode material in the production of  $H_2O_2$  from dissolved oxygen, since it is electrochemically stable. To obtain a satisfactory  $H_2O_2$  yield, noble

<sup>\*</sup> Corresponding author. Tel.: +31 15 278 4381; fax: +31 15 278 5006. *E-mail address:* G.Mul@tudelft.nl (G. Mul).

metals were doped on titanium. For example, Baez and Pletcher [13] tried to develop gold coatings on titanium as alternative cathodes to replace carbon.

In this work, we investigated surface areas-enhanced Timesh electrodes instead of Au/Ti electrode, employing an electrophoretic deposition (EPD) method. Titanium powder was selected as deposition material to increase the surface area of the Ti-mesh. It will be reported herein that Ti-coated wire-mesh has a highly porous layer with a large surface area. An increase of the production rate of  $H_2O_2$  is reported. The data will be discussed based on calculations of the oxygen mass transfer rate.

# 2. Experimental

#### 2.1. Preparation of Ti-coated wire-mesh electrodes

In previous work, we investigated the EPD method to deposit aluminum as catalyst support material on stainless steel wire-mesh [14,15]. Similar experiments were performed with suspensions of Ti metal powder in ethanol. We used Ti wiremesh as a substrate instead of stainless steel in this case, since we would apply this as electrode. Since the density of titanium is higher than that of aluminum, more ultrasonification and mechanical stirring is required for suspension of Ti particles. There are several other EPD variables, such as the Ti amount, additive concentration, applied voltage and deposition time. The concentration of additive is in particular critical for EPD, since it creates particle charges and stabilizes the suspensions. Therefore, we first fixed the Ti concentration to 0.5 wt.%, the DC voltage to 50 V and the deposition time to 5 min, referring to the previous result [14]. Then we changed the amount of Ti-isopropoxide to determine the optimal amount for the EPD procedure of Ti.

Titanium powder (99.5%, 325 mesh, Alfa Aesar) was used as a deposition material, with a specific BET surface area of  $0.92 \text{ m}^2/\text{g}$ . Titanium isopropoxide (Aldrich) was used as additive, which was expected to control the suspension conductivity and enhance the dispersion.

Commercial wire mesh, made of titanium grade 1 (Cleveland Wire Cloth and Manufacturing Co., 24 Taylor mesh screen) was used as a substrate. It has an open pore size of around 0.8 mm and a wire diameter ( $d_w$ ) of 0.25 mm. The mesh weighs about 0.055 g/cm<sup>2</sup>, on average. The surface of the substrate was treated with acetone to remove dirt and grease.

First, a suitable amount of additive  $(1.0 \times 10^{-2} \text{ to} 5.0 \times 10^{-3} \text{ M})$  was added to ethanol (99.9%, Aldrich), under stirring, and then titanium powder (0.5 wt.%) was added to the suspension. The slurry solution was well mixed, using an ultrasonic bath for 5 min. The apparatus used for the electrophoretic deposition is described elsewhere [14]. For particle deposition at the cathode, the wire mesh was cut into pieces (1.2 cm × 7 cm). A titanium plate was used as an anode and the size was the same as that of the cathode. The distance between the two electrodes was kept at 10 mm and the DC voltage was changed from 50 to 300 V. The titanium-coated samples were dried at room temperature for 12 h, sintered at 900 °C (heating rate was 5 °C/min), under 10% H<sub>2</sub> in N<sub>2</sub> flow for 3 h.



Fig. 1. A schematic diagram of the electrochemical cell, including representation of the applied mesh electrodes.

# 2.2. Electrode characterization

Polarization curves were obtained by cyclic voltammetry using a three-electrode potentiostat (Hokuto Denkdo HSV-100). A saturated Ag/AgCl (HS-205C, TOA Electronics) electrode was used as the reference electrode. A platinum wire was employed as the counter electrode. All potentials are quoted versus the saturated Ag/AgCl reference electrode. The cathodic potential was swept from 0 to -1.0 V at a linear scan rate of 10 mV/s. The specific surface area of the various samples was determined by nitrogen adsorption in a constant volume adsorption apparatus (Micrometrics, ASAP 2021C). X-ray diffraction (XRD, Mac Science Co., M18XHF) was employed to identify the phase of the coated-samples. The surface structure and the cross section of the coated wire were studied by means of scanning electron microscopy (SEM, Hitachi, S-2460N), equipped with an EDX system.

#### 2.3. Electrochemical cell for hydrogen peroxide generation

Fig. 1 shows the schematic diagram of the reaction system. The cathodic and anodic compartments had a volume of 300 and 900 ml, respectively. During the experiments, 200 ml of catholyte and 300 ml of anolyte were used, and the catholyte was thoroughly mixed by a magnetic stirrer. The distance between the cathode and anode was kept at 2 cm. A nafion membrane was used to separate the two compartments. This membrane prohibits the diffusion of anions and H<sub>2</sub>O<sub>2</sub> molecules, but allows cations to freely penetrate. As a result,  $H_2O_2$  generated at the cathode will be confined in the catholyte, avoiding its decomposition at the anode. Moreover, protons generated at the anode will be electrically driven to the catholyte, partially supplementing the protons consumed for H<sub>2</sub>O<sub>2</sub> synthesis. 0.1 M of sodium perchlorate (NaClO<sub>4</sub>) was used as the inert supporting electrolyte. The developed Ti-mesh with enhanced surface area and Ti-mesh were used as cathode and anode, respectively. Compressed air was used to dissolved oxygen (DO). A flow of 150 ml/min was sparged into the catholyte through a porous pipe-diffuser. The catholyte was pre-saturated with DO by purging air for 30 min before electrolysis was initiated. The electro-generation of  $H_2O_2$  was carried out under a constant potential mode.

The concentration of  $H_2O_2$  was determined by the indometric titration method [16] with subsequent UV absorbance measurement. The iodide solution was prepared by mixing 2.5 ml of solution A (potassium iodide 66 g/l, ammonium heptamolybdate 0.2 g/l, sodium hydroxide 2 g/l), and 2.5 ml solution B (potassium hydrogenphtalate 20 g/l). When a sample containing  $H_2O_2$  is added, the iodide reacts with  $H_2O_2$  and forms a triiodide solution that has a yellow color at low concentrations to dark red at high concentrations. Triiodide can be analysed in low concentrations using the UV absorption at 350 nm. For the UV measurement a Thermo Spectronics Unicam UV Series 5000 spectrometer was used. Measurements were done using the deuterium arc lamp of the spectrometer. The absorbance of light at 350 nm has a linear dependence on the concentration of triiodide and thus on the concentration of  $H_2O_2$  in the sample.

# 3. Results and discussion

### 3.1. Electrophoretic deposition of Ti particles

Fig. 2 shows the deposition weight of Ti particles versus Ti isopropoxide additive concentration at constant time (5 min) and voltage (50 V). No noticeable deposition took place without any additives. When titanium isopropoxide is added to the suspension, the following reaction might occur:

 $Ti(OC_3H_7)_4 \leftrightarrow [Ti(OC_3H_7)_3]^+ + OC_3H_7^-$ 

The positively charged titanium alkoxides are adsorbed on the surface of Ti particles (Fig. 3). As a result, titanium particles become positively charged, and move towards the cathode under the applied field.



Fig. 2. Effect of additive concentration on the weight of Ti particles deposited (closed circle). The effect of additive concentration on pH is indicated by the open triangles. Solvent: ethanol; additive: Ti-isopropoxide; deposition time: 5 min.



Fig. 3. A schematic diagram of electrophoretic deposition of Ti particles.

For the Ti suspensions, the deposited weight increased sharply with increasing additive concentration in the range up to  $1.0 \times 10^{-3}$  M. The deposited weight decreased when the concentration of the additive was higher than  $1.0 \times 10^{-3}$  M. This can be explained as follows. When the concentration of Ti isopropoxide was over  $1.0 \times 10^{-3}$  M, the adherence of the deposit became poor and the deposition layer on the wire surface became non-uniform. Since for the Ti particles at the point, where full adsorption was reached, extra ions, that were not adsorbed, move also towards the cathode, competing with the charged titanium particles under the electrical field. This phenomena is exactly corresponding to the result of Al deposition previously reported [15]. Therefore there exists an optimal concentration of Ti isopropoxide, which is in the range from  $1.0 \times 10^{-3}$  to  $5.0 \times 10^{-3}$  M for good adherence.

After deposition of Ti particles, the Ti-coated wire-meshes were thermally treated with a  $H_2$  gas purge for particle sintering. The adherence of the metal-coatings has been evaluated according to the ultrasound method described in the literature [17]. Ti coatings were easily detached from the metallic substrate when the temperatures were less than 700 °C, since titanium particles do not sinter at those temperatures. It was shown that the detached amount of the Ti coatings was below 1 wt.% at sintering temperature over 850 °C. The coating were hardly detached from the metallic substrate at 1000 °C. However, the Ti coating layer was highly sintered at that temperature, so it had a non-porous surface structure with a low surface area. The optimal temperature range, therefore, is around 900 °C for thermal treatment.

#### 3.2. Physical and electrochemical properties

The surface areas of fresh Ti wire-mesh, Ti powder and Ticoated samples were measured by the BET method (Table 1). The surface areas of Ti wire-mesh and Ti powder were found to be very small, 0.01 and  $0.9 \text{ m}^2/\text{g}$ , respectively. The titaniumcoated wire-mesh has a surface area of  $3.5 \text{ m}^2/\text{g}$ , about four

Table 1 BET surface areas

Material	Thermal treatment	BET surface area (m <sup>2</sup> /g)
Titanium wire-mesh	×	0.01
Fresh titanium powder	х	0.92
Ti-coated wire mesh (average thickness of coating layer)	900 $^{\circ}\text{C},$ 3 h with 10% H_2 in N_2	3.5 (70 µm)

times larger than that of the fresh electrode. The result must be caused by formation of micro-pores in the deposition layer as Ti particles experience a certain extent of sintering during the thermal treatment, as shown in the SEM images (Fig. 4). We could estimate the thickness of the Ti coating being around 70  $\mu$ m from the cross-section view of the SEM image.

Cathodic polarization of the surface area-enhanced Ti-mesh and bare Ti-mesh electrodes are shown in Fig. 5. The *I–E* curves were obtained by linear sweep voltammetry from 0 to -1.0 V at 10 mV/s in a saturated oxygen solution at pH 12. The highly exposed surface area of the Ti-coated wire-mesh electrode resulted in a much higher current density in this potential range than observed for the fresh Ti-mesh electrode. There exists a plateau that represents the limiting current region for



Fig. 4. SEM pictures of the surface of Ti-coated wire-meshes after thermal sintering at 900  $^\circ C$  with H\_2 gas purge: (a) low magnification and (b) high magnification.



Fig. 5. Polarization curves of the surface area-enhanced Ti-mesh and fresh Ti-mesh. Sweeping rate = 10 mV/s, pH 12, air feed rate = 150 ml/min, 0.1 M NaClO<sub>4</sub>.

 $H_2O_2$  generation in the range from -0.35 to -0.55 V. The current increases sharply above -0.55 V, since side reactions, for example  $H_2O_2$  decomposition or  $H_2$  evolution, start to occur.

In the limiting current region,  $H_2O_2$  generation is controlled by mass transfer of dissolved oxygen (DO) through the cathodesolution diffusion layer, rather than by the electron transfer between DO and the cathode. Since the DO concentration at the cathode surface rapidly approaches zero after electrolysis starts, the limiting current under a steady-state condition can be expressed by the following Eq. (1) for macroscopic electrodes [18].

$$I_{\rm L} = k_{\rm m} n F A_{\rm e} C^* \tag{1}$$

where  $I_L$  represents the limiting current (A),  $k_m$  the mass transfer coefficient (m/s), *n* the stoichiometric number (=2) of electrons transferred, F the Faraday's constant (96,485 C/mol), Ae the effective cathode surface area  $(m^2)$  and  $C^*$  is the DO concentration in bulk solution  $(mol/m^3)$ . We could estimate the limiting current density from Fig. 5, and a  $C^*$  value of 0.55 mol/m<sup>3</sup> at 20 °C, therefore, the oxygen mass transfer coefficients of surface area-enhanced Ti-mesh and bare Ti-mesh could be obtained by substituting DO and cathode surface area in Eq. (1). The results are listed in Table 2. The oxygen mass transfer coefficient is  $9.2 \pm 1.0 \times 10^{-5}$  m/s for surface area-enhanced Ti-mesh. It is more than twice that of bare Ti-mesh. Therefore, we could expect that the surface area-enhanced Ti-mesh electrode would be more effective than bare Ti-mesh for H2O2 generation since it enhanced not only current density but also oxygen mass transfer rate in this range. These are the result of an enlarged specific electrode surface area and a reduced size of the stagnant layer,

Table 2				
Calculated	mass	transfer	coeffic	ients

Materials	Limiting current density (A/m <sup>2</sup> )	Mass transfer coefficient (m/s)
Titanium wire-mesh	$4.0 \pm 0.6$	$3.8 \pm 0.6  imes 10^{-5}$
Surface area-enhanced	$9.8 \pm 1.0$	$9.2\pm1.0\times10^{-5}$
Ti-mesh		



Fig. 6. Hydrogen peroxide generation at the potentials of -1.05 and -0.55 V over the surface area-enhanced Ti-mesh and fresh Ti-mesh. pH 12, air feed rate = 150 ml/min, 0.1 M NaClO<sub>4</sub>.

induced by the 3-D shape of the electrode structure and the irregular shape of the electrode surface, respectively.

# 3.3. Electrochemical generation of $H_2O_2$

Electrochemical generation of  $H_2O_2$  was performed to evaluate the surface area-enhanced Ti-mesh electrode in a saturated oxygen solution at pH 12 and 0.1 M NaClO<sub>4</sub> at two different applied potentials of -0.55 and -1.05 V. A concentration of  $H_2O_2$  was obtained as shown in Fig. 6. Regardless of the applied potential, the amount of  $H_2O_2$  produced increased more than 70%, as a result of the electroplating procedure. The reason was that the developed-electrode enhances current intensity and oxygen mass transfer as described in Section 3.2.

The H<sub>2</sub>O<sub>2</sub> production rate gradually decreased at higher potential of -1.05 V, since side reactions such as H<sub>2</sub>O<sub>2</sub> reduction or hydrogen evolution occur at these potentials. Indeed the current density increased at a potential of -1.05 V as time goes on, but at a potential of -0.55 V it was constant (Fig. 7). The selectivity of the cell for a certain reaction is given by the current efficiency ( $\eta$ ). This is the percentage of the total cell current that is used for the desired reaction. It can be calculated by dividing the amount of charge in Coulomb for a specific reaction by the total charge that has passed the electrode (Eq. (2)):

$$\eta(\%) = \frac{nFC^*V}{\int_{t_0}^t I\,\mathrm{d}t} \times 100$$
(2)

where *n* is the stoichiometric coefficient of electrons (=2), *F* the Faraday's constant (96,485 C/mol),  $C^*$  the concentration of reactant in the bulk, *V* the electrolyte volume and *I* is the cell current intensity. Current efficiency is higher at a cathode potential of -0.55 V. Fig. 7 shows that current efficiency of the surface area-enhanced Ti-mesh was almost constant around 60% at -0.55 V.

The effect of the cathode geometrical surface area was investigated with increasing the number of cathodes, standing in a



Fig. 7. (a) Current intensity and (b) current efficiency at the potentials of -1.05 and -0.55 V over surface area-enhanced Ti-mesh and fresh Ti-mesh. pH 12, air feed rate = 150 ml/min, 0.1 M NaClO<sub>4</sub>.

row, and shown in Fig. 8. The applied potential was kept at -0.55 V in a saturated oxygen solution. It is obvious that the amount of H<sub>2</sub>O<sub>2</sub> generated increased with increasing number of cathode electrodes, due to a higher overall current intensity. The H<sub>2</sub>O<sub>2</sub> production rate gradually decreased, especially for large geometrical surface areas, since there is more chance for side reactions to happen, due to the higher current intensity, and H<sub>2</sub>O<sub>2</sub> concentration. However, the initial production rate of H<sub>2</sub>O<sub>2</sub> showed a linear relationship as a function of geometrical surface area of the cathodes as shown in Fig. 9. This means that the main side reaction might be H2O2 reduction under these conditions. We can maintain the initial H<sub>2</sub>O<sub>2</sub> production rate if we use a continuous reaction system, in order to keep the H<sub>2</sub>O<sub>2</sub> concentration below a certain level. The surface area-enhanced Ti-mesh electrode showed an optimized H2O2 production rate of  $0.3 \text{ mol/l h m}^2$ . Future work will focus on the deposition of active metals such as gold and palladium on the developed-Ti-mesh,



Fig. 8. Effect of cathode geometrical surface area on hydrogen peroxide generation. pH 12, air feed rate = 150 ml/min, 0.1 M NaClO<sub>4</sub>.



Fig. 9. Effect of cathode geometrical surface area on the initial hydrogen peroxide rate in the surface area-enhanced Ti-mesh electrode.

to increase electrocatalytic activity and current efficiency. The feasibility of a continuous reactor system will also be evaluated.

# 4. Conclusions

The present study shows that  $H_2O_2$  generation benefits from enhancement of the surface area of Ti-mesh electrodes. We successfully prepared Ti-mesh coated with Ti particles employing an electrophoretic deposition method, and determined the effect of parameters such as concentration of additive, applied voltage and time. The highly exposed surface area of Ti-coated mesh enhanced not only the current density, but also the oxygen mass transfer rate.

### References

- G. Goor, J. Glenneberg, S. Jacobi, Hydrogen Peroxide, Ullman's Encyclopedia of Industrial Chemistry, 2000.
- [2] P. Landon, P.J. Collier, A.F. Carley, D. Chadwick, A.J. Papworth, A. Burrows, C.J. Kiely, G.J. Hutchings, Phys. Chem. Chem. Phys. 5 (2003) 1917.
- [3] R. Burch, P.R. Ellis, Appl. Catal. B 42 (2003) 203.
- [4] J. Bao, K. Furumoto, K. Fukunaga, K. Nakao, Biochem. Eng. J. 8 (2001) 91.
- [5] T. Tzanov, S.A. Costa, G.M. Gubitz, A. Cavaco-Paulo, J. Biotechnol. 93 (2002) 87.
- [6] H. Nguyen-Cong, V. de la Garza Guadarrama, J.L. Gautier, P. Chartier, Electrochim. Acta 48 (2003) 2389.
- [7] Z. Qiang, J.H. Chang, C.P. Huang, Water Res. 36 (2002) 85.
- [8] A.D. Pozzo, L.D. Palma, C. Merli, E. Petrucci, J. Appl. Electrochem. 35 (2005) 413.
- [9] E. Yeager, Electrochim. Acta 29 (1984) 1527.
- [10] E.L. Gyenge, C.W. Oloman, J. Appl. Electrochem. 31 (2001) 233.
- [11] E.L. Gyenge, C.W. Oloman, J. Electrochem. Soc. 152 (2005) D42.
- [12] A. Sarapuu, K. Vaik, D.J. Schiffrin, K. Tammeveski, J. Electroanal. Chem. 541 (2003) 23.
- [13] V.B. Baez, D. Pletcher, J. Electroanal. Chem. 377 (1994) 231.
- [14] K.S. Yang, Z. Jiang, J.S. Chung, Surf. Coat. Technol. 168 (2003) 103.
- [15] K.S. Yang, J.S. Choi, J.S. Chung, Catal. Today 97 (2004) 159.
- [16] J.E. Frew, P. Jones, G. Scholes, Anal. Chim. Acta 155 (1983) 139.
- [17] M. Valentini, G. Groppi, C. Cristiani, M. Levi, E. Tronconi, P. Forzatti, Catal. Today 69 (2001) 307.
- [18] H. Wendt, G. Kreysa, Electrochemical Engineering: Science and Technology in Chemical and other Industries, Springer, Berlin, Germany, 1999, p. 53.