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Preparation and characterization of ZrO_2/Ti electrode for waste water purification system

Han-Joo Kim[a], Won-Keun Son[b], Tae-Il Kim[c], Kyung-Suk Kang[c],
Tetsuya Osaka[d], Soo-Gil Park[a,*]

[a] *Department of Industrial Chemical Engineering, Chungbuk National University, 12, Kaeshin, Heungduk, Cheongju, Chungbuk 361-763, Republic of Korea*
[b] *Research Center of Advanced Material, Chungnam National University, 220 Gungdong, Yuseong, Daejeon 305-764, Republic of Korea*
[c] *Siontech. Co. Ltd., 530 Yongsan, Yuseong, Daejeon, Republic of Korea*
[d] *Graduate School of Science and Engineering, Waseda University, Tokyo 169-8555, Japan*

Abstract

We have investigated the effects of the etching method of a Ti substrate for a metal oxide electrode on the electrochemical characteristics of the electrode. The preparation method and electrochemical characterization of zirconium oxide films on etched Ti substrate has been also studied. The HCl etching was developed a fine and homogeneous roughness on the Ti substrate. Fabrication and material properties of the metal oxide electrode, which is known to be so effective to generate ozone and sodium hypochlorite (NaOCl) as power oxidant, were studied. A proper metal oxide material focus zirconium oxide through reference paper. A coating method to enhance the fabrication reproducibility of the zirconium oxide electrode was used dip-coating method by zirconium oxychloride. Zirconium oxide films on the Ti substrate were analyzed by SEM, XPS and cyclic voltammetry.

Keywords: Sol-gel; Dip coating; Overpotential electrode; Ozone; Sodium Hypochlorite

1. Introduction

The electrochemical method for generation on ozone and sodium hypochlorite by using waste water treatment and semiconductor washing has attracted a great deal of recent attention because of the ease of control and increased efficiency provided from the use of new electrode for overpotential use.[1] Such electrode is prepared using a coating with a precursor solution, where chloride salts of one or two metals are dissolved with/without auxiliary metal chlorides as characteristic modifiers of the catalytic oxide, on a substrate metal, usually Ti.[3] The surface of the substrate for the catalytic oxide must be etched to an appropriate degree of roughness in order to achieve good adhesion of the oxide on the substrate. The surface condition of the substrate can affect several properties of the oxide electrode such as morphology, roughness, cohesion of the oxide coating, and so on, which subsequently result on an effect on the electrode activity, electrode lifetime, etc. The literature related to the effect of etching method of Ti substrate on the oxide electrode is scant when compared to the amount of literature[4] on the electrochemical property of the electrode itself. Most of the papers use oxalic acid solution of 10–15 wt% at 70–80 °C for etching the Ti substrates. Zirconium oxide is very interesting material mainly due to its thermal stability and mechanical properties. On the other hand, it is claimed to be the only oxide catalyst that has acid, basic, reducing and oxidizing surface properties. Zirconia is used in a number of applications, such as structural ceramics, solid electrolytes, etc. The protection of metal in corrosive environments is one of promising applications of sol–gel coatings technique. Zirconia, borosilicate, aluminosilicate and ceria coating have been extensively studied as barriers against oxidation on metal substrates. Among these coating, zirconia has the advantage of a high mechanical toughness and a thermal expansion coefficient closed to that of many metals, and can act as a reactive element. Some reports have been dedicated to the study of corrosion protection of titanium by zirconia sol–gel coatings, but few of them involved the use of zirconia coatings on titanium.[2]

In this paper, we report that preparation, physical and electrochemical characterization of zirconium oxide coated on the titanium substrate.

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* Corresponding author. Tel.: +82 43 261 2492; fax: +82 43 273 8221.
E-mail address: sgpark@cbnu.ac.kr (S.-G. Park).

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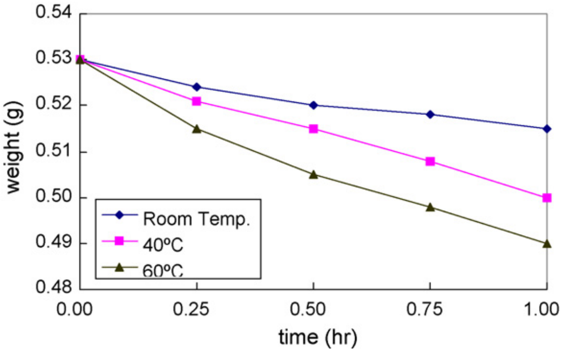

Fig. 1. Weight loss of Ti substrate by etching temperature.

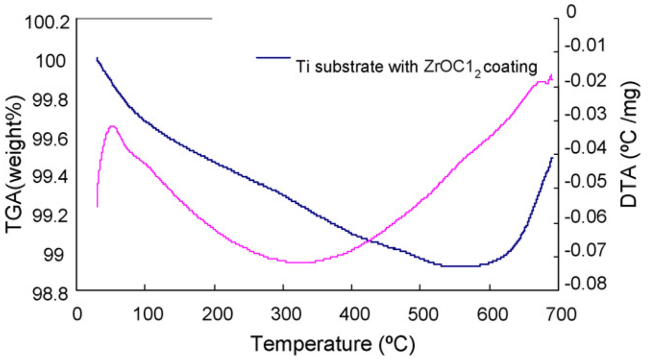

Fig. 3. TGA and DTA spectra of $ZrOCl_2$ coating on the Ti substrate with sintering temperature.

2. Experimental

All reagents for the precursor solutions used on this work were chemical reagent grade and used as received. $ZrOCl_2$ (Aldrich) was dissolved in anhydrous ethanol to precursor stock solutions of 1 M. The stock solution was painted on the Ti substrate, demineralized water of 18.2 MΩ prepared by distilling twice, and an ion-exchanger (Mill-Q plus) was used for the preparation of the precursor solution and washing the Ti substrate. The Ti mesh for the coating oxide was 99.4% and 2 cm × 2 cm × 0.1 cm. The Ti substrate was first washed with acetone and degreased in tri-chloroethylene for one night. It was then etched in 35 wt% HCl at 61 ± 1 °C for 1 h. The etched Ti thoroughly rinsed with water and a sonicator because even a tiny amount of residual impurity on the Ti substrate after etching causes poor reproducibility of the surface color of the electrode after sintering. The zirconium oxide sols are transparent and no precipitate is formed at room temperature even after half a year. The films were deposited by dip-coating in air art a relatively humidity of 45–55% and withdraw speed of 42.4 cm/min obtaining monolayer films.

The weight changes of the Ti substrate and oxidized electrode after etching and sintering were two of them were used for ex situ analyses of scanning electron microscopy (SEM) and an adhesion test of the oxide.

The thermal behavior of the dried gel was investigated by thermo gravimetric analysis (TGA) in air atmosphere at a scanning rate of 10 °C/min. The chemical binding states of the films were identified using X-ray photoelectron spectroscopy (XPS) performed with a pass energy of 29.35 eV and a Mg Kα line excitation source ($h\nu = 1253.6$ eV). The binding energy of contaminated carbon (C 1s: 284.6 eV) was used as the reference.

3. Results and discussion

3.1. Etching effect

Fig. 1 shows the weight loss of the Ti substrates after etching HCl with etching temperature. Weight loss is increased along with etching time and temperature. The average weight losses of Ti substrate by HCl etching for 1 h after 10 measurements are 2.83 wt% at room temperature, 5.66 wt% at 40 °C, and 7.55 wt% at 60 °C, respectively. The rates of etching by HCl at 60 °C are about 2.67 times higher than that at room temperature.

The surface of the Ti substrate after etching in HCl at low temperature was metallic color, the same color as before etching. However, the surface color after etching in HCl at high temperature was dark gray due to titanium hydride (TiH_2). Fig. 2 shows the SEM images of Ti substrates (a) before and (b) after HCl etching at 60 °C for 1 h. The Ti substrate etched in HCl at high temperature has a sharp rippled surface with fine roughness without the initial grain boundary shape present before etching.

3.2. Sintering temperature

Fig. 3 shows that TGA and DTA of Ti substrates coated with a $ZrOCl_2$ solution. The weight of the $ZrOCl_2$ coating on the

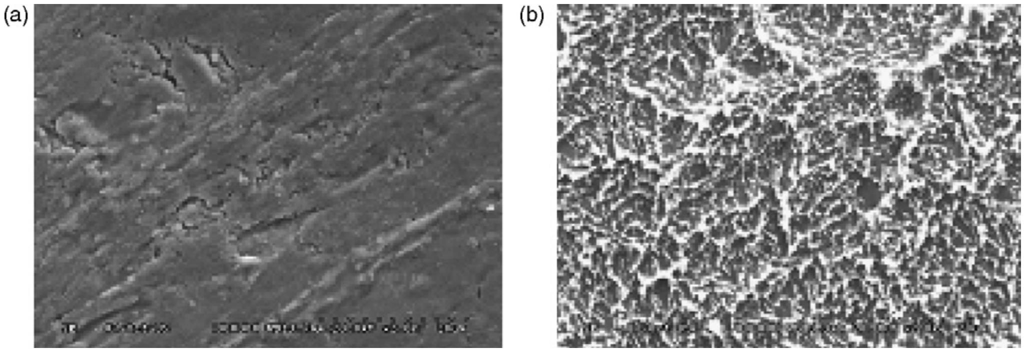

Fig. 2. SEM images of titanium substrates (a) before and (b) after HCl etching at 60 °C for 1 h.

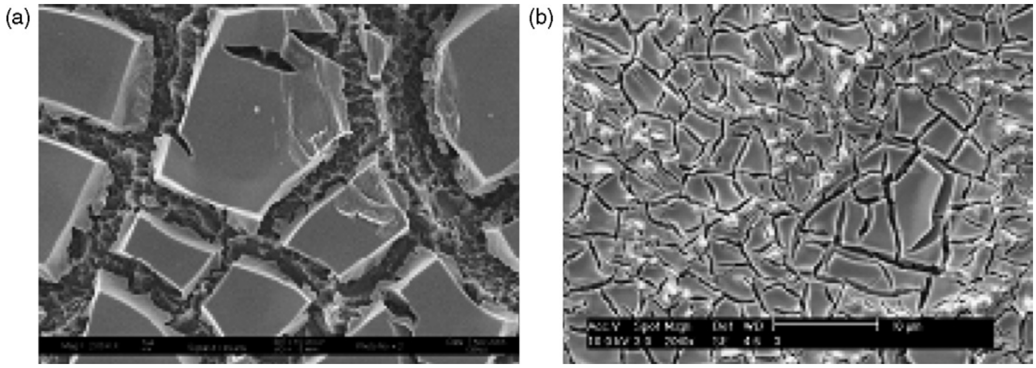

Fig. 4. SEM images of ZrO_2/Ti by dip-coating with coated layers: (a) one layer and (b) two layers.

Ti substrate is observed to decrease steadily as low as 500 °C and rapidly increase after 600 °C. This is possibly due to two reasons. The first one is the loss of Cl_2 by evaporation during sintering. The second one is a suppression of the oxidation of the Ti substrate itself by the metal oxide coating on the Ti substrate. These results mean that when the oxide weight on the Ti substrate just attributed to the $ZrOCl_2$ solution is evaluated, a portion of the weight increase due to the Ti substrate in the total oxide weight has to be taken into account.

3.3. Physical characterization

Representative SEM images of zirconium oxide coated titanium substrates by dip-coating with coated layers ((a) one layer and (b) two layers) are presented in Fig. 4. All coatings present the "cracked mud" morphology, characteristic of zirconium oxide electrode (one layer) presents larger cracks than two layers. The two layers electrode presents a morphology showing more homogeneously distributed cracks. Large islands were obtained in the first layer after annealing. This phenomenon was clearly seen at which the gel coatings were completely transformed to ceramic oxide structures. That is to say, the size of the coating islands was decreased. Depending on the coating thickness or number of dipping, the canals were removed owing to layer-on-layer. Notably, the substrate was completely coated after second layers.

The Ti oxide generated from the Ti substrate may present a solid diffusion through the oxide cracks at the Ti substrate generated during sintering. In order to check this, wide-scanned XPS spectra near the surfaces of the Zr oxide on the Ti substrate sintered at 600 °C was measured and this is shown in Fig. 5. The Ti 2p peak (451.4 eV) was not observed for the Zr oxide sintered 600 because the Ti oxide of the substrate was not developed enough to diffuse to the surface. The resistivity of the Ti substrate goes up tremendously like an insulating material at high temperature.

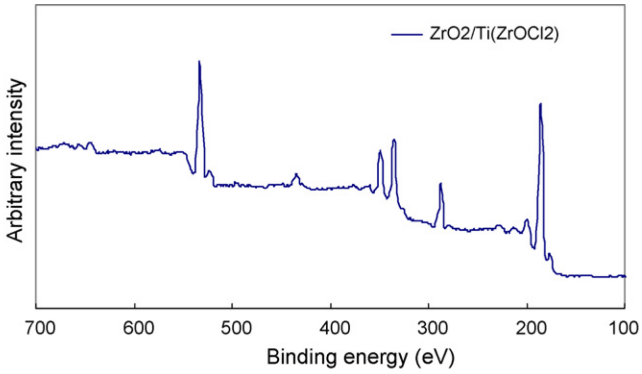

Fig. 5. Wide-scanned XPS spectra of Zr oxide/Ti by dip-coating method.

XPS spectra of Zr 3d, O 1s in Zr oxide films are shown in Fig. 6(a) and (b). The binding energy of Zr 3d $_{5/2}$ is measured at 185 eV and O 1s at 532.3 eV, both illustrating the presence of tetragonal Zr oxide.

3.4. Electrochemical characterization

Fig. 7 shows that cyclic voltammetry of zirconium oxide coated on the titanium substrate with electrolytes (1 M H_2SO_4, 1 M NaCl). The electrochemical property of the Zr oxide/Ti electrode was measured with a counter electrode of Pt wire and

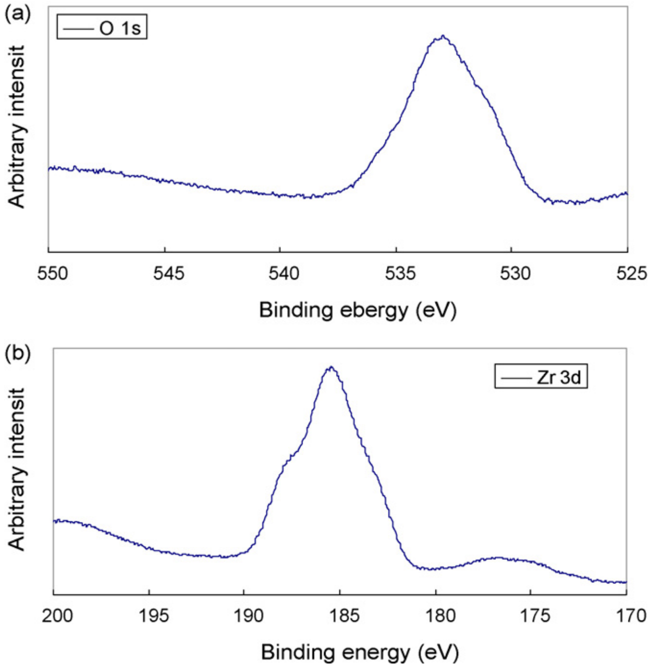

Fig. 6. XPS spectra of (a) Zr 3d and (b) O 1s.

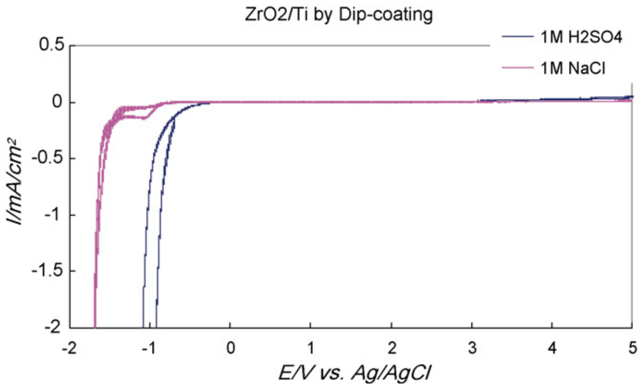

Fig. 7. Cyclic voltammetry of Zr oxide/Ti electrode.

with a reference electrode Ag/AgCl (1 M KCl) and scan rate is 50 mV/s. Zr oxide/Ti electrode is endured −0.2 to 3.8 V (4.0 V) in 1 M H_2SO_4 electrolyte and −0.8 to 3.9 V (4.7 V) in 1 M NaCl electrolyte. Wide potential window of Zr oxide/Ti electrode is applied to generate ozone and sodium hypochlorite as power oxidant.

4. Conclusion

This study has investigated the effects of the etching method of a Ti substrate for a zirconium oxide electrode on the physical properties and electrochemical characteristics of the electrode.

The rate of etching by HCl at 60 °C is about 2.67 times higher than that at room temperature. The Ti substrate etched in HCl at high temperature has a sharp rippled surface with fine roughness without the initial grain boundary shape present before etching. The weight of the $ZrOCl_2$ coating on the Ti substrate (TGA) is observed to decrease steadily as low as and rapidly increase as high as 600 °C. Depending on the coating thickness or number of dipping, the canals were removed owing to layer-on-layer. Notably, the substrate was completely coated second layers. XPS is shown that the Ti 2p peak (451.4 eV) was not observed for the Zr oxide sintered 600 °C because the Ti oxide of the substrate was not developed enough to diffuse to the surface. Cyclic voltammtery is shown that Zr oxide/Ti electrode is used wide potential application because Zr oxide/Ti electrode is endured −0.2 to 3.8 V (4.0 V) in 1 M H_2SO_4 electrolyte and −0.8 to 3.9 V (4.7 V) in 1 M NaCl electrolyte. Wide potential window of Zr oxide/Ti electrode is applied to generate ozone and sodium hypochlorite as power oxidant.

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