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A Spin-coated Si/TiO$_x$/Pt/TaO$_x$ Electrode for Electrochemical Ozone Generation

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A novel electrode, with the composition Si/TiO$_x$/Pt/TaO$_x$ (TiO$_x$: titanium oxide, TaO$_x$: tantalum oxide), was fabricated by spin-coating, and its effectiveness at electrochemical ozone generation was compared with that of a traditional Pt plate electrode. The electrode achieved a high current efficiency (1.3%) at a low current density (30 mA·cm^{-2}). The results confirm that TaO$_x$ is effective for the ozone generation in electrochemical ozone generation.

Ozone is a powerful oxidizing agent with a broad range of applications such as the oxidation of organic and inorganic compounds, sterilization,[1–3] deodorization, and decolorization.[4] The use of ozone in aqueous solutions is of particular importance as it represents a safe alternative to chlorine, decomposing via a free radical chain mechanism[5] to yield O_2. The electrochemical generation of ozone in the aqueous phase has several advantages over current corona discharge systems; these include the miniaturization of the ozonizer apparatus, reduction of power demands, ease of production, and as such low costs.

β-PbO_2 electrodes have long been used for ozone production by the semiconductor industry, as they possess a high current efficiency (7%) at a current density of 600 mA·cm^{-2} in 5 M H_2SO_4 solution at 0 °C.[6] However, the dissolution of poisonous lead ions into the solution has restricted their implementation in other fields. Pt has the highest oxygen overpotential of any noble metal; however, it does not have a high ozone production efficiency (<2% at a current density of 400 mA·cm^{-2}).[6] Our group is currently concerned with the development of a new class of dimensionally stable anodes for ozone production. These electrodes have the structure Ti/Pt/Pt–TaO$_x$ and are prepared by thermal decomposition.[7–9] Their current efficiency for ozone generation is among the highest values at room temperature. However, preparation via thermal decomposition is a lengthy process, requiring several days to complete and also results in undesirable features, such as a concave–convex surface and a variation in the film thickness.

In this study, spin coating was used to adhere a TaO$_x$ film onto the surface of a Si/TiO$_x$/Pt substrate, which had itself been fabricated by RF sputtering. Spin coating and RF sputtering are significantly faster than thermal decomposition and also yield a more uniform surface. The performance of the novel Si/TiO$_x$/Pt/TaO$_x$ electrode for ozone generation in imitating tap water was examined, using a Pt electrode for comparison.

The Si/TiO$_x$/Pt/TaO$_x$ electrode was prepared according to the procedure described below. A Si substrate was washed with distilled water and placed inside the chamber of the RF sputtering unit (ULVAC). A TiO$_x$ film was deposited onto the Si substrate for 500 s at room temperature (rt) under a total gas pressure of 0.6 Pa (Ar/O_2 ratio $= 0.71/0.29$) and an RF power density of 6.2 W·cm^{-2}. The TiO$_x$ layer acted as a binding agent between the Si substrate[7,8] and the subsequent Pt layer, increasing the durability of the electrode. It also suppresses the mutual diffusion of the Si and Pt layers. The Pt film was deposited onto the TiO$_x$ film, hitherto deposited on the Si substrate, by sputtering for 200 s at rt under an Ar gas pressure of 0.4 Pa and RF power density of 3.1 W·cm^{-2}.

Finally, the precursor of TaO$_x$ was deposited on the Pt film by spin coating (KYOWA RIKEN) at 1000 rpm for 5 s, then at 3000 rpm for 15 s. After spin coating, the electrode was dried at rt (10 min), 200 °C (10 min) and then calcined at 600 °C (10 min). The thickness of TaO$_x$ was determined by X-ray fluorescence spectrometric analysis (JEOL) and was found to be approximately 25 nm.

The cyclic voltammograms shown in Figure 1 were obtained from a Pt electrode with geometric area of 0.36 cm^2 and the Si/TiO$_x$/Pt/TaO$_x$ electrode with geometric area of 2.25 cm^2. Cyclic voltammetry was performed in the potential range between oxygen and hydrogen generation. In curve (a), the characteristic behavior of the Pt electrode is shown; the formation of adsorbed oxygen or platinum oxide layer over a wide potential range and

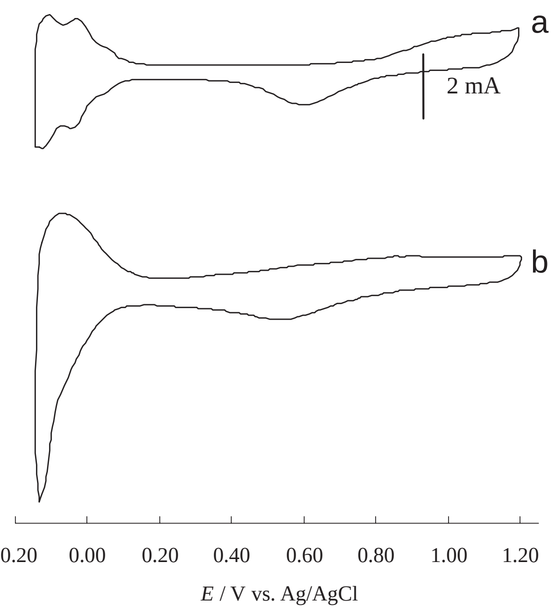

Figure 1. Cyclic voltammograms obtained at (a) Pt and (b) Si/TiO$_x$/Pt/TaO$_x$ electrode in 0.5 M H_2SO_4 solution at 22 °C under N_2 atmosphere. Potential scan rate: 100 mV·s^{-1}.

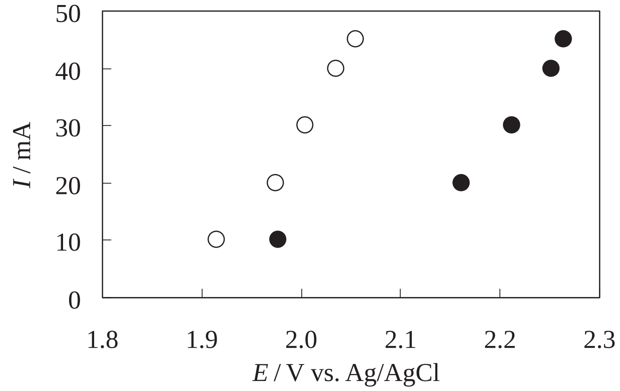

Figure 2. Steady-state polarization curves obtained at (○) Pt and (●) Si/TiO_x/Pt/TaO_x electrodes measured in 0.5 M H_2SO_4 solution at 22 °C.

the reduction of the oxide layer peak at 0.6 (V vs Ag/AgCl). In addition, the hydrogen adsorption/desorption is shown in the potential range 0.1 to −0.14 (V vs Ag/AgCl). In curve (b) at the Si/TiO_x/Pt/TaO_x electrode, the peaks are also visible. As TaO_x is electrochemically inert in this potential range,[10] the observed redox response is considered to be due to the presence of Pt at the electrode surface. The real surface (i.e., electrochemically active) area of the electrode was, therefore, estimated from the amount of charge corresponding to the hydrogen desorption using a reported value of 210 μC cm^{-2}.[11] From the observed value of 210 μC cm^{-2} the surface area of Pt on the Si/TiO_x/Pt/TaO_x electrode was estimated to be 1.14 cm^2, very similar to that of the bare Pt electrode, with a surface area of 1.12 cm^2. Therefore, if only Pt at the surface of the Si/TiO_x/Pt/TaO_x electrode is involved in the electrogeneration of ozone, then the amounts of ozone obtained by Si/TiO_x/Pt/TaO_x and the bare Pt electrodes would be similar.

Figure 2 shows the steady-state polarization curves at both electrodes for the electrolytic oxidation of H_2O in 0.5 M H_2SO_4 solution at 22 °C. At 45 mA of current and with a minimal ohmic drop in the solution, the potential at 45 mA of the Si/TiO_x/Pt/TaO_x electrode was approximately 210 mV more positive than that of the bare Pt electrode. As the two electrodes have nearly identical active surface areas this result means that the Si/TiO_x/Pt/TaO_x electrode operates with a higher potential than that on the bare Pt electrode. A high potential such as this is a requirement for an electrode to generate O_3 efficiently.

Figure 3 illustrates the dependency between the amount of electrogenerated ozone and the applied current for both the Si/TiO_x/Pt/TaO_x and Pt electrodes. A cell separated by a cation-exchange membrane (Nafion®) was used to perform the electrolysis. A Pt plate was used as the cathode and the distance between the anode and cathode was 10 mm. Model tap water, prepared in the laboratory, having the following composition (0.25 mM $NaHCO_3$ + 0.25 mM $CaCl_2$ + 0.25 mM $MgSO_4$ + 0.025 mM $KHCO_3$) was used as the electrolyte in both the anode and cathode compartments (150 mL per compartment). The solution temperature was maintained at 15 °C and the electrolysis time was 1 min. The amount of ozone generated was determined by colorimetry (HACH).

As shown in Figure 3, when the electrolysis was performed at 45 mA, ozone was only generated at the Si/TiO_x/Pt/TaO_x electrode but not at the bare Pt electrode. Furthermore, at higher electrolysis currents, the Si/TiO_x/Pt/TaO_x electrode consistently generated more ozone than the bare Pt electrode.

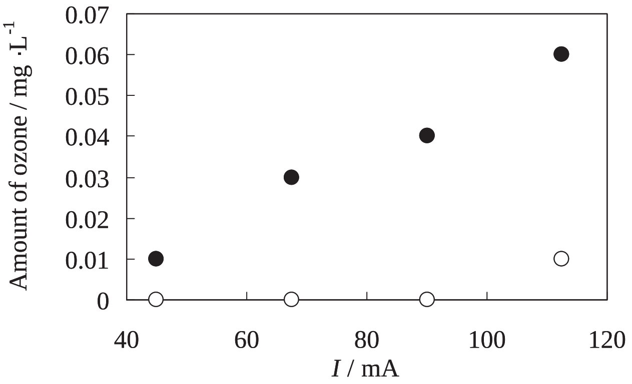

Figure 3. The variation in the amount of generated ozone under the constant current electrolysis. (●) Si/TiO_x/Pt/TaO_x electrode; (○) Pt electrode.

The current efficiency is ca. 1.3% at 68 mA and ca. 1.6% at 113 mA, with the assumption that the reaction consumes six electrons per ozone molecule (eq 1).

$$O_3 + 6H^+ + 6e^- = 3H_2O \quad E^0 = 1.51\,V \qquad (1)$$

The real surface areas of both the Si/TiO_x/Pt/TaO_x and the bare Pt electrodes are almost identical. Therefore, the electrogeneration of ozone at the Si/TiO_x/Pt/TaO_x electrode does not depend only on the electrochemically active Pt. In other words, TaO_x is also effective for ozone generation even together with the exposed Pt area. Further studies are currently running to understand the mechanism and to clear the effects of other parameters.

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