# Superior Electrocatalysis of Spin-coated Titanium Oxide Electrodes for the Electrochemical Ozone Production

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A cheap spin-coated $Si/TiO_x/Pt/TiO_x$ electrode is fabricated and proved to possess an excellent catalysis for ozone electrogeneration. A high current efficiency of 2.5% was obtained at 33 mA cm$^{-2}$ in 10 mM $HClO_4$ at room temperature.

Over the past few years, an intensive effort was dedicated to produce ozone for several green applications in chemical, water treatment, pulp, food, and recently in medical industries.[1] Unlike chlorine, ozone does not generate harmful residues and is about six times as strong as chlorine in terms of oxidizing power. The use of the classical UV-light and corona-discharge approaches, which have been widely used to generate ozone, is currently limited due to their high cost and/or low efficiency.[2] The electrochemical ozone production, EOP, from water electrolysis has then become of interest because of its simplicity, high efficiency, and low cost.[3] In this reaction, ozone is produced at the anode and hydrogen is produced at the cathode of an electrolytic cell. The electrode material and electrolyte composition are critical to identify the ozone production efficiency.

Lead dioxide electrodes were the best candidates for EOP, and a current efficiency of more than 7% was reported at a current density of 600 mA cm$^{-2}$ in 5 M $H_2SO_4$.[4] However, the use of lead-containing materials is unsafe and currently not recommended. Platinum, although being the best among the noble metals, exhibited a much lower efficiency towards EOP (less than 2% at a current density of 400 mA cm$^{-2}$ at 0 °C).[4] Tantalum-based composites have recently proven efficient for EOP,[5,6] with a current efficiency of 6% at 20 mA cm$^{-2}$. This efficiency is remarkable in EOP; nevertheless, the electrode material is highly expensive and the preparation by thermal decomposition is time-consuming and complicated. Titanium oxide electrodes have recently proposed as a cheap material for oxygen reduction.[7,8]

Herein, we report on the catalytic activity of a spin-coated $Si/TiO_x/Pt/TiO_x$ electrode towards EOP. This electrode appeared economic and powerful at low current density and room temperature (rt).

This novel electrode has the structure of $Si/TiO_x/Pt/TiO_x$. A spin-coater (Kyowariken, K-359 S-1, Japan) was used to deposit the titanium precursors (alcohol-dissolved Ti (3%) precursors, Koujundo Kagaku. Co., Ltd., Japan) on the $Si/TiO_x/Pt$ substrate. The substrate itself was prepared by RF sputter-depositing (ULVAC, Inc): a titanium oxide ($TiO_x$) film on a Si substrate for 10 min at rt under a total gas pressure of 0.6 Pa ($Ar/O_2$ ratio = 0.48/0.52) and an RF power density of 6.4 W cm$^{-2}$. Next, the Pt film was deposited on the $TiO_x$ film for 1 min at rt under an Ar gas pressure of 0.7 Pa and RF power density of 4.8 W cm$^{-2}$. The intermediate $TiO_x$ layer was deposited to strengthen the adhesion of the Pt film to the Si substrate and to suppress the mutual diffusion of Si and Pt. Spin-coating of the $TiO_x$ precursors on the $Si/TiO_x/Pt$ substrate was done in two consecutive steps: a spinning at 1000 rpm for 10 s followed by another one at 3000 rpm for 30 s. After that, the electrode was dried in air at rt for 10 min and next at 200 °C for another 10 min. The average thickness of the Ti layer was ca. ≈60 nm. Finally, the electrode was annealed at 600 °C for 10 min in air.

Figure 1 displays the relevant range ($20° \leq 2\theta \leq 80°$) of the XRD pattern of the $Si/TiO_x/Pt/TiO_x$ electrode. As the thickness of the titanium oxide film was very thin, the major intensive peak appeared for the platinum layer at $2\theta = 40.0°$ (assigned for Pt(111)).[9] The diffraction characteristic peaks of anatase (tetragonal) $TiO_2$ appeared at $2\theta = 25.3°$ ((101) facet), and 37.8° ((004) facet).[10,11] The peaks at $2\theta =$ ca. 36.0, 70.0, and 76.0° likely belong to the bare titanium metal.[12] The XRD investigation revealed that metallic titanium is converted partially to the anatase phase upon annealing and that both ingredients constituted the surface layer of the electrode.

Figure 2 shows the cyclic voltammograms (CVs) obtained at the bare $Si/TiO_x/Pt$ substrate (curve a), and the $Si/TiO_x/Pt/TiO_x$ electrode (curve b) in deoxygenated ($N_2$-saturated) 0.5 M $H_2SO_4$ solution. The characteristic behavior of polycrystalline Pt electrode is clearly shown at both of the substrate and the electrode; the oxidation of Pt, which extends over a wide range of potential, is coupled with the reduction peak at ca. 0.5 V vs. Ag/AgCl. In addition, well-defined peaks for the hydrogen

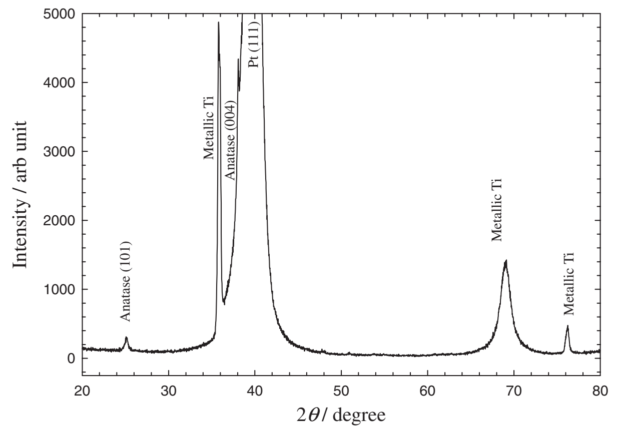


**Figure 1.** X-ray diffraction pattern of the $Si/TiO_x/Pt/TiO_x$ after annealing at 600 °C.

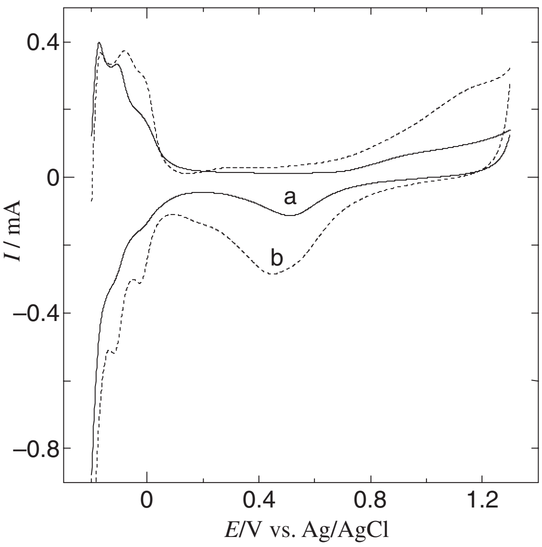


**Figure 2.** Cyclic voltammograms obtained at (a) the $Si/TiO_x/$Pt substrate, and (b) the $Si/TiO_x/Pt/TiO_x$ electrode in $N_2$-saturated 0.5 M $H_2SO_4$ at a scan rate of $100\,mV\,s^{-1}$.

adsorption/desorption are shown in the potential range from ca. 0.0 to −0.2 V vs. Ag/AgCl. Curve b in Figure 2 infers that the platinum layer beneath the spin-coated titanium oxide layer is exposed to the electrolyte, i.e., the oxide film is porous. More careful inspection of Figure 2 reveals increases in the real surface area and the charging current of the $Si/TiO_x/Pt/TiO_x$ electrode than those of the bare $Si/TiO_x/Pt$ substrate. The real surface areas of the electrode and the substrate were 1.81 and $0.53\,cm^2$, respectively, based on the charge associated with the reduction of the Pt oxide layer ($420\,\mu C\,cm^{-2}$). Annealing the substrate is expected to change the electrode roughness, which, in turns, affects the surface area. The deposition of the insulator $TiO_x$ film is likely behind the increase of the charging current and the film capacitance.

Ozone was next generated galvanostatically at rt in 10 mM $HClO_4$ solution for 5 min in a two-compartment Nafion membrane cell. Ag/AgCl (KCl sat.) was used as a reference electrode and the ohmic drop was minimized using a Luggin capillary approaching the working electrode. The counter electrode was Pt electrode of a large surface area. A simple and rapid potentiometric method was used to measure the concentrations of both the gaseous and soluble (dissolved in the electrolyte solution) ozone.[13] The current efficiency was determined according to Faraday's law based on eq 1 using the total concentration of $O_3$.

$$3H_2O = O_3 + 6H^+ + 6e^-, E^\circ = 1.52\,V \text{ vs. NHE}, \quad (1)$$

Figure 3 depicts the effect of the electrolysis current density on the amount and the efficiency of ozone generated. The amount of ozone increased with the current density, and a maximum was observed in the current efficiency at about $33\,mA\,cm^{-2}$. The increase in the current density was always accompanied by an increase in the cell voltage and the electrolyte temperature. Increasing the local heating at the vicinity of the electrode with increasing the current density will definitely increase the rate of ozone decomposition and consequently the efficiency decreases. A maximum current efficiency of 2.5% is obtained at $33\,mA\,cm^{-2}$ for the $Si/TiO_x/Pt/TiO_x$ electrode in

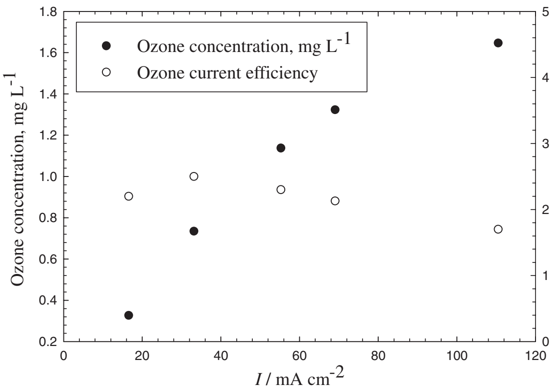


**Figure 3.** The effect of current density on the ozone concentration and efficiency. Electrolysis was performed on the $Si/TiO_x/Pt/TiO_x$ electrode for 5 min at rt in 10 mM $HClO_4$. The current is normalized to the real surface area.

10 mM $HClO_4$ at rt. This efficiency is almost comparable to that obtained previously on $\beta$-$PbO_2$ in 6 M $HClO_4$ solution (3.5% at 0 °C and $0.90\,A\,cm^{-2}$).[14] Considering the previous values reported for ozone electrogeneration on Pt,[4] it seems that the titanium oxide (anatase structure) is influencing much the ozone generation. The effect of other parameters such as the annealing temperature of the electrode, the electrolyte composition and temperature on the ozone concentration and efficiency is currently under investigation. Our results introduced a novel low-priced material for the ozone generation technology.

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