



Oxygen reduction characteristics of several valve metal oxide electrodes in HClO_4 solution

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ABSTRACT

In the search for active cathode catalysts for polymer electrolyte fuel cells (PEFCs) using inexpensive materials, several valve metal oxide electrodes, TiO_x , ZrO_x , and TaO_x , with corresponding binary oxide electrodes were selected for the evaluation of catalytic activity for oxygen reduction reaction (ORR) by means of cyclic voltammetry in 0.1 M HClO_4 at 60 °C. These oxide electrodes were prepared mainly by the dip-coating method on a titanium plate substrate at a temperature between 400 °C and 500 °C and were characterized by scanning electron microscopy (SEM), X-ray diffractometry (XRD), and X-ray photoelectron spectroscopy (XPS). Among the oxide-coated electrodes investigated, $\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_x/\text{Ti}$ provided the highest ORR specific activity, with an onset potential, E_{ORR} , of 0.86 V vs. RHE during the cathodic potential sweep. Fine TaO_x particles prepared as an extension of the dip-coating method, showed very high catalytic activity determined by means of hydrodynamic voltammetry in 0.1 M HClO_4 at 30 °C with an E_{ORR} of 0.90 V vs. RHE.

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1. Introduction

Although fuel cells have attracted public attention in terms of both environment factors and convenience, the technology is not yet widely used mainly due to issues regarding cost and durability. The typical cathode catalysts presently used for polymer electrolyte fuel cells (PEFCs) are expensive Pt-based catalysts with high oxygen reduction activity [1–3]; however, practical use requires higher durability, and the dissolution and coagulation of the platinum must be minimized [4,5]. Various approaches have been taken to overcome these problems, with a particular focus on searching for suitable non-platinum elements, including oxides [6–9], carbides [10], nitrides, silicides, metal complexes [11,12], and other compounds [13–15]. Recently, some interesting studies were reported on the development of Pt-free oxide cathodes, such as Ta–O–N, Ta–C–N–O, and Nb–C–N–O [16–21]. In previous investigations [8,9], we reported the ORR activity of dip-coated IrO_2/Ti catalyst electrodes. An increase in catalytic activity was attained using lanthanum in the preparation of oxide-coated catalyst electrodes. We have tested valve metal oxides as candidate cathode catalysts for PEFCs because they are stable in acid. Although the cathodic properties of oxynitrides, oxycarbonitrides and oxides of several valve metals have already been reported, the preparation involves high temperatures or sputtering. All oxide catalysts in this investigation

were prepared at a temperature lower than 500 °C; therefore, the crystallite size was small and probably contained a large number of oxide ion lattice defects.

This study presents the basic physical properties and the ORR results for titanium oxide, zirconium oxide, tantalum oxide catalysts, and some of the corresponding binary oxides, using a Ti plate substrate prepared mainly by the dip-coating method at a temperature between 400 °C and 500 °C. The results may provide approaches for designing less expensive oxide cathode catalysts for ORR.

2. Experimental

2.1. Preparation of oxide-coated electrodes by the dip-coating method

The oxide-coating film of each valve metal was prepared on a Ti plate (10 mm × 10 mm × 1 mm) substrate by the conventional dip-coating method [22–25] using a 0.5 M butanolic solution of metal salt: titanium tetrabutoxide, zirconium tetrabutoxide or tantalum pentachloride. The titanium substrate was etched with 10% oxalic acid at 80 °C for 1 h and then rinsed with deionized water before the dipping procedure. Calcination of the dip-coated salts was conducted in air at various temperatures between 400 °C and 500 °C. The dip-drying/calcination (alternating 10 min each) procedure was typically repeated 5 times. In addition, TaO_x powder was prepared as follows. First, TaO_x oxide was formed on a porous titanium disk (Tiporous® purchased from Osaka Titanium Technologies Co.,

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Ltd.) by the dip-coating method with the same dip-coating solution used to prepare the TaO_x/Ti electrode. The calcination in air was carried out at 320°C for 10 min. The $\text{TaO}_x/\text{Tiporous}^\circledast$ was then ultra-sonicated in ethanol to remove the TaO_x particles from the Tiporous[®] disk. The TaO_x particles were separated from the ethanol at 60°C with a vacuum oven followed by calcination in air at 450°C for 30 min.

2.2. Characterization of the physical properties of the various oxide-coated electrodes and oxide powder

The structures of the oxide-coated electrodes and TaO_x powder were characterized using two different scanning electron microscopes (SEM, Hitachi S-3000N and HR-SEM, Hitachi S-5000) and X-ray diffraction (XRD, Rigaku RINT-2550 with monochromated $\text{CuK}\alpha$ radiation at 40 kV and 40 mA). The XRD profiles in the 2θ range of $15\text{--}90^\circ$ were scanned at a speed of 2° min^{-1} . The chemical species of the surfaces were characterized by X-ray photoelectron spectroscopy (XPS, Kratos Analytical, AXIS ULTRA) with $\text{MgK}\alpha$ radiation at 15 kV and 15 mA. The binding energy of the photoelectrons was calibrated with that of C1s (284.6 eV). The BET surface area of the TaO_x powder was determined with BELSORP-28 (BEL Japan Inc.) using nitrogen as an adsorbent.

2.3. Electrochemical measurements

The ORR activity of the oxide electrodes was evaluated by cyclic voltammetry (CV) in 0.1 M HClO_4 using a beaker-type electrolytic cell in a stationary state at 60°C . A hydrogen electrode was used as the reference electrode, and a bundle of carbon fibers, rather than Pt, was used as the counter electrode to avoid Pt deposition onto the test electrode through dissolution. A Luggin capillary was set facing the working electrode at a distance of 2 mm. All electrode potentials refer to the $\text{RHE}(t)$ scale, corrected for the temperature effect. For the ORR experiment, oxygen gas was bubbled into the 0.1 M HClO_4 solution at 60°C . In addition to the above method, the rotat-

ing disk electrode (RDE) was applied to the more precise evaluation of the ORR behavior of TaO_x powder. The working electrodes were prepared using the thin-film electrode method [26,27]. Briefly, a mixed powder of TaO_x and carbon black (CB, Vulcan XC-72R) was loaded on the glassy carbon surface of the RDE electrode and then was fixed with Nafion[®] ionomer. The loading amount of the TaO_x and the loading ratio of the TaO_x to CB in weight were 1.0 mg cm^{-2} and 95:5, respectively.

3. Results and discussion

3.1. Basic physical properties of TiO_x/Ti , ZrO_x/Ti , TaO_x/Ti , and binary oxide-coated electrodes

The surface morphology of the TiO_x/Ti , ZrO_x/Ti and TaO_x/Ti electrodes after the electrochemical measurement for the ORR in 0.1 M HClO_4 was observed by scanning electron microscopy. Typical micrographs at different magnifications are shown in Figs. 1 and 2. The TiO_x/Ti electrode had only a few isolated mud cracks on the surface and was composed of very fine particles that were connected to each other and formed meso-pores less than a few nanometers in width, as seen in (a-2) in Fig. 2. On the other hand, the ZrO_x/Ti electrode had no mud cracks and was composed of fine particles with $0.1\text{--}0.3\text{ }\mu\text{m}$ in diameter that were connected to each other and formed macro-pores. On the TaO_x/Ti electrode, many isolated cracks were observed; however, no oxide particles were observed even on the micrograph at the highest magnification (Fig. 2(c-2)) used in this study. No appreciable differences in the surface morphology were observed for these oxide-coated electrodes before and after the electrochemical measurement described in Section 2.3. Fig. 3 shows a comparison of the surface morphology of the pristine ZrO_x/Ti electrode and that of the electrode exposed to the electrochemical measurement described in Section 2.3.

The morphology of the Ti–Zr–O/Ti binary electrodes was affected by the characteristics of the TiO_x/Ti and ZrO_x/Ti electrodes.

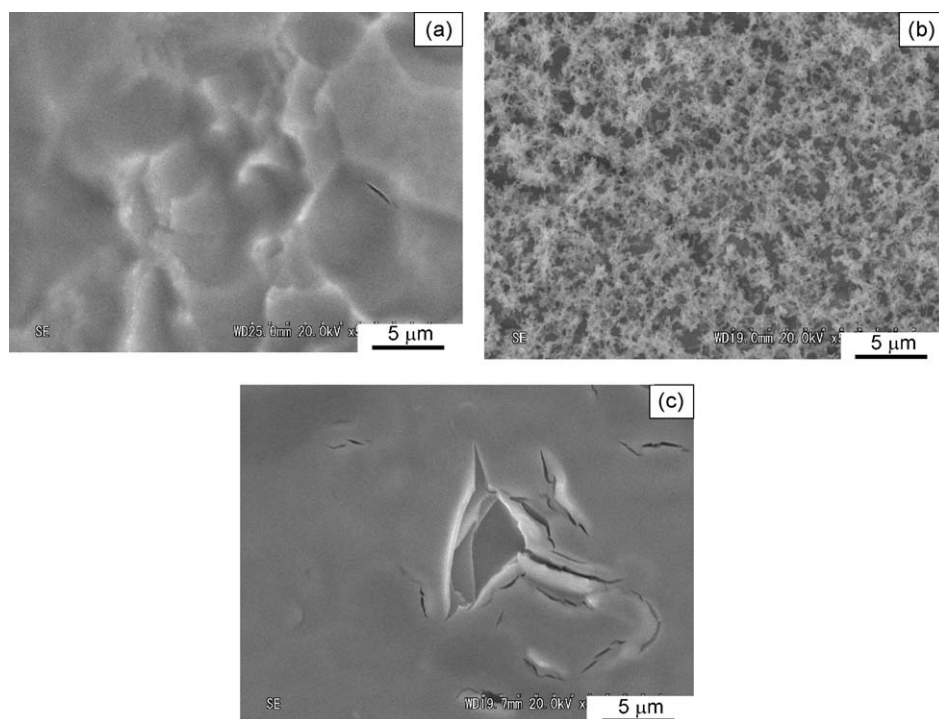


Fig. 1. SEM micrographs of the TiO_x/Ti , ZrO_x/Ti , and TaO_x/Ti electrodes prepared by dip-coating method at 450°C (at low magnification). Electrode: (a) TiO_x/Ti , (b) ZrO_x/Ti , and (c) TaO_x/Ti .

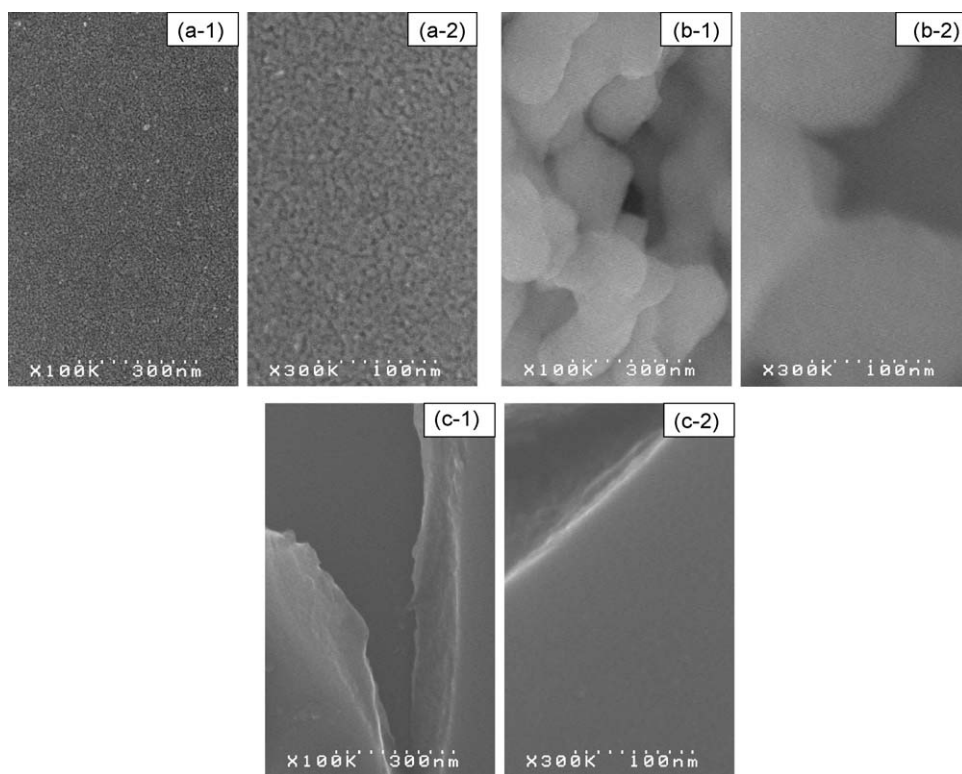


Fig. 2. SEM micrographs of the TiO_x/Ti , ZrO_x/Ti , and TaO_x/Ti electrodes prepared by dip-coating method at 450°C (at higher magnifications). Electrode: (a-1 and a-2) TiO_x/Ti , (b-1 and b-2) ZrO_x/Ti , and (c-1 and c-2) TaO_x/Ti .

As shown in Fig. 4, the $\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_x/\text{Ti}$ electrode had isolated cracks on the surface; however, the $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_x/\text{Ti}$ and $\text{Ti}_{0.3}\text{Zr}_{0.7}\text{O}_x/\text{Ti}$ electrodes had no cracks and, like the ZrO_x/Ti electrode, were composed of small, connected oxide particles forming a macro-pore struc-

ture. For the Ti–Ta–O/Ti binary electrodes (Fig. 5), typical connected mud cracks were observed on the $\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_x/\text{Ti}$ and $\text{Ti}_{0.3}\text{Ta}_{0.7}\text{O}_x/\text{Ti}$ electrodes, except that a few isolated cracks were observed on the $\text{Ti}_{0.7}\text{Ta}_{0.3}\text{O}_x/\text{Ti}$ electrode.

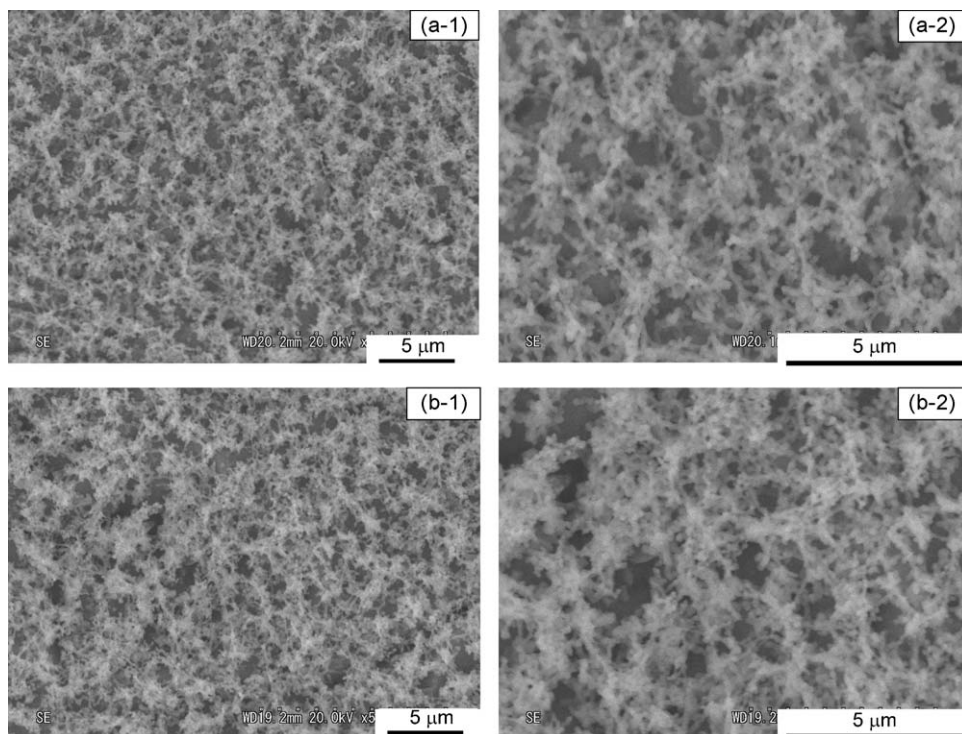


Fig. 3. A comparison of the surface morphology of the pristine ZrO_x/Ti electrode and that of after the polarization. Treatment: (a-1 and a-2), pristine; (b-1 and b-2), after the electrochemical measurement as described in Section 2.3.

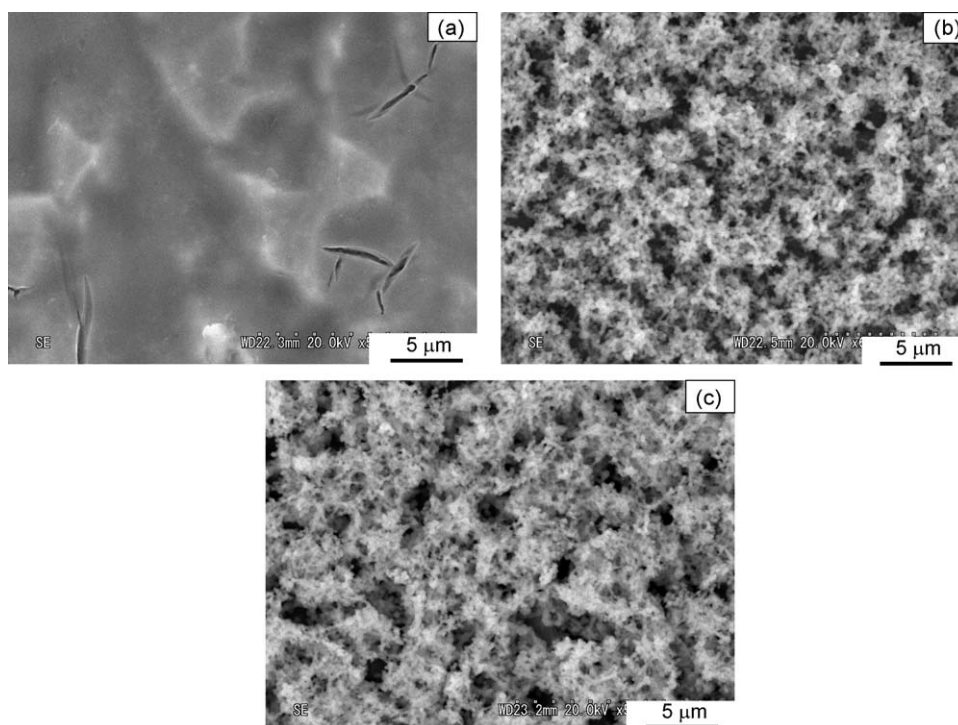


Fig. 4. SEM micrographs of the Ti–Zr–O/Ti binary electrodes prepared by dip-coating method at 450 °C. Electrode: (a) $\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_x/\text{Ti}$, (b) $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_x/\text{Ti}$, and (c) $\text{Ti}_{0.3}\text{Zr}_{0.7}\text{O}_x/\text{Ti}$.

Fig. 6 shows the XRD patterns of the various oxide-coated electrodes prepared by the dip-coating method at 450 °C. Since the oxide-coated layers were thin, many diffraction peaks from metallic titanium were observed. For the TiO_x/Ti , ZrO_x/Ti and TaO_x/Ti electrodes, weak anatase TiO_2 peaks, weak ZrO_2 peaks and broad peaks from TaO_x , respectively, were observed. These broad peaks from TaO_x might be assigned as TaO_2 , because the main three diffraction peaks from tetragonal TaO_2 appear at $2\theta = 26.749$,

34.939 and 52.718. The Ti–Zr–O/Ti binary electrodes, (d)–(f) in Fig. 6, gave no appreciable diffraction peak except the peaks from the Ti substrate; however, a broad peak around 30° (2θ) increased with an increase in the zirconium content. A similar phenomenon was observed for the Ti–Ta–O/Ti binary electrodes, shown in (g)–(i) in Fig. 6, where no appreciable diffraction peak except the peaks from the Ti substrate was observed; however, broad peaks around 27° , 35° and 53° (2θ) increased with an increase in the tantalum

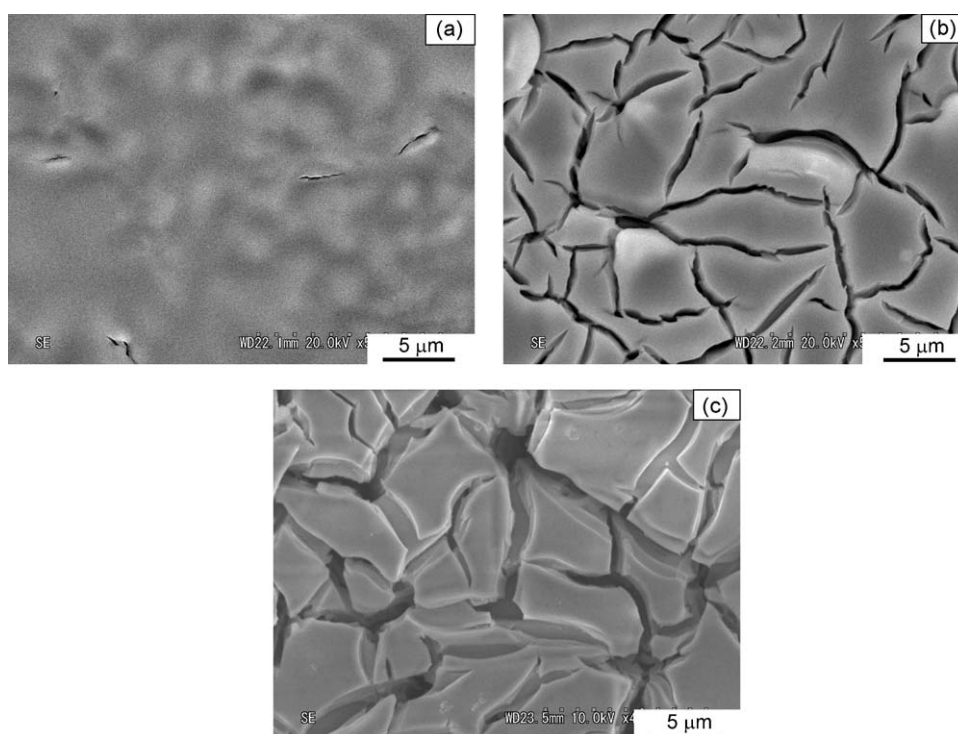


Fig. 5. SEM micrographs of the Ti–Ta–O/Ti binary electrodes prepared by dip-coating method at 450 °C. Electrode: (a) $\text{Ti}_{0.7}\text{Ta}_{0.3}\text{O}_x/\text{Ti}$, (b) $\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_x/\text{Ti}$, and (c) $\text{Ti}_{0.3}\text{Ta}_{0.7}\text{O}_x/\text{Ti}$.

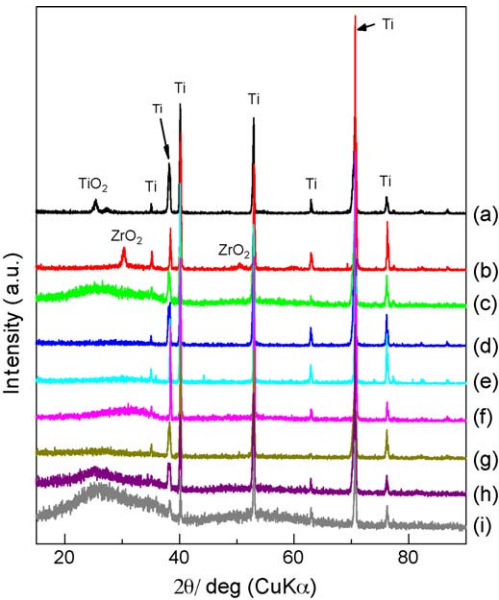


Fig. 6. XRD patterns for the various oxide-coated electrodes prepared by dip-coating method at 450 °C. Electrode: (a) TiO_x/Ti , (b) ZrO_x/Ti , (c) TaO_x/Ti , (d) $\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_x/\text{Ti}$, (e) $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_x/\text{Ti}$, (f) $\text{Ti}_{0.3}\text{Zr}_{0.7}\text{O}_x/\text{Ti}$, (g) $\text{Ti}_{0.7}\text{Ta}_{0.3}\text{O}_x/\text{Ti}$, (h) $\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_x/\text{Ti}$, and (i) $\text{Ti}_{0.3}\text{Ta}_{0.7}\text{O}_x/\text{Ti}$.

content, suggesting the formation of ultra-fine TaO_2 particles or something like that.

The $\text{Ti}2p$, $\text{Zr}3d$ and $\text{Ta}4f$ XPS spectra of the Ti-Zr-O/Ti and Ti-Ta-O/Ti binary electrodes exposed to electrochemical measurement are presented in Figs. 7 and 8, and the values of the binding

Table 1
Binding energy and content ratios of metal species of various oxide-coated electrodes determined by XPS (after the electrochemical measurement).

Electrode	Binding energy (eV)			Content ratios	
	$\text{Ti}2p_{3/2}$	$\text{Zr}3d_{5/2}$	$\text{Ta}4f_{7/2}$	Ti:Zr	Ti:Ta
TiO_x/Ti	458.0				
ZrO_x/Ti		181.7			
TaO_x/Ti			25.8		
$\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_x/\text{Ti}$	458.3	182.2		39:61	
$\text{Ti}_{0.3}\text{Zr}_{0.7}\text{O}_x/\text{Ti}$	457.7	181.5		23:77	
$\text{Ti}_{0.7}\text{Ta}_{0.3}\text{O}_x/\text{Ti}$	458.0		25.7		50:50
$\text{Ti}_{0.3}\text{Ta}_{0.7}\text{O}_x/\text{Ti}$	458.0		25.5		13:87

The binding energy of metal species: $(\text{Ti}^{4+})2p_{3/2} = 458.7 \text{ eV}$, $(\text{Zr}^{4+})3d_{5/2} = 182.2 \text{ eV}$, $(\text{Ta}^{4+})4f_{7/2} = 25.1 \text{ eV}$, and $(\text{Ta}^{5+})4f_{7/2} = 26.5 \text{ eV}$.

energy of these elements are listed in Table 1. Although no evident difference was observed in the binding energy for these single and binary oxide-coated electrodes, all of the values were lower than those of Ti^{4+} (458.7 eV), Zr^{4+} (182.2 eV), and Ta^{5+} (26.5 eV), respectively. This fact strongly suggests that the oxides prepared by the dip-coating method at 450 °C were formed at a somewhat lower oxidation state than the TiO_2 , ZrO_2 and Ta_2O_5 . As presented in Table 1, the surface content of titanium on these Ti-Zr-O/Ti and Ti-Ta-O/Ti electrodes was considerably decreased by the electrochemical measurement described in Section 2.3.

3.2. ORR catalytic activity of TiO_x/Ti , ZrO_x/Ti , and TaO_x/Ti electrodes

To determine the appropriate number of dip-coating repetitions for the preparation of these oxide electrodes, three TiO_2/Ti electrodes were prepared at 450 °C with 2, 5 and 10 dipping repetitions.

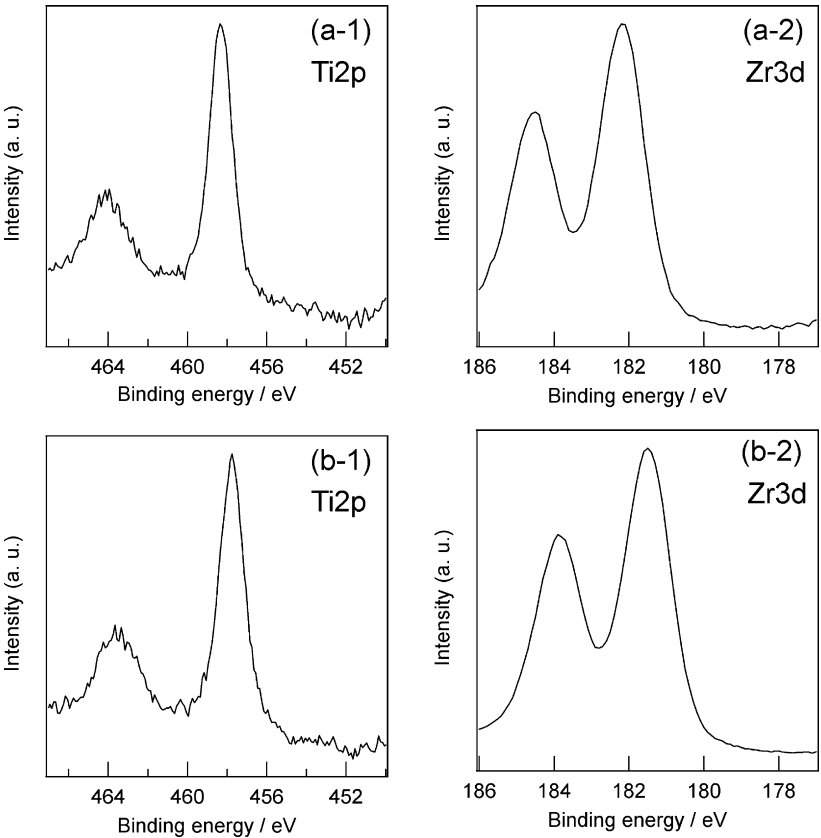


Fig. 7. XPS spectra of $\text{Ti}2p$ and $\text{Zr}3d$ from the Ti-Zr-O/Ti binary electrodes prepared by dip-coating method at 450 °C. Electrode: (a-1 and a-2) $\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_x/\text{Ti}$ and (b-1 and b-2) $\text{Ti}_{0.3}\text{Zr}_{0.7}\text{O}_x/\text{Ti}$.

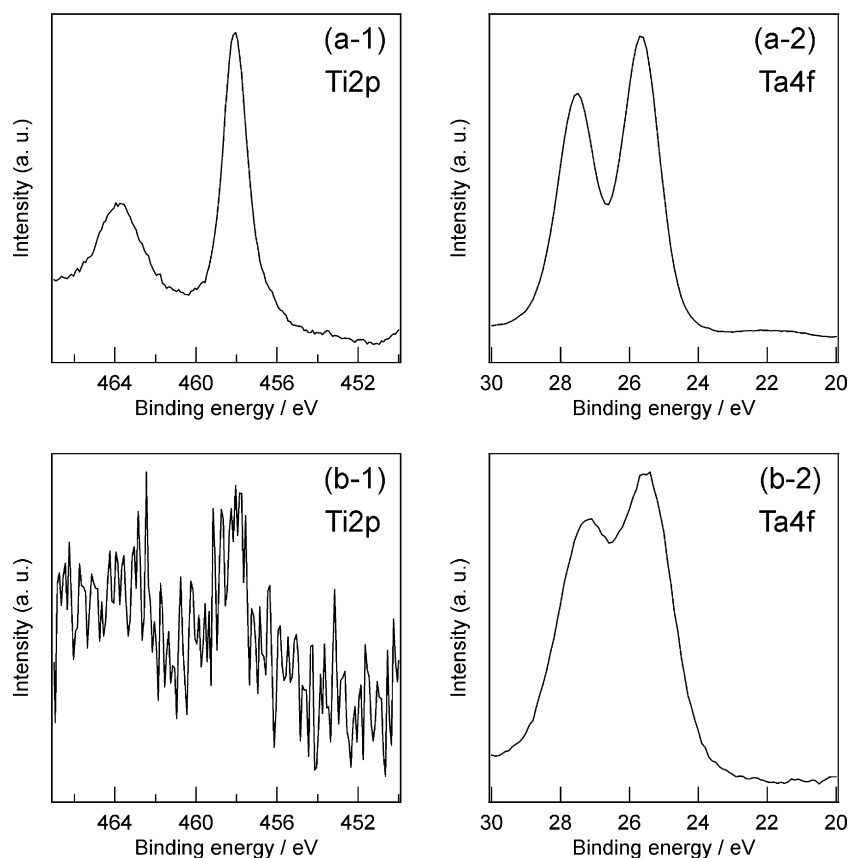


Fig. 8. XPS spectra of Ti2p and Ta4f from the Ti–Ta–O/Ti binary electrodes prepared by dip-coating method at 450 °C. Electrode: (a-1 and a-2) $\text{Ti}_{0.7}\text{Ta}_{0.3}\text{O}_x/\text{Ti}$ and (b-1 and b-2) $\text{Ti}_{0.3}\text{Ta}_{0.7}\text{O}_x/\text{Ti}$.

Since the electrode prepared with 5 repetitions provided the highest ORR activity per geometric surface area of the electrode, the dip-coating procedure was fixed to 5 repetitions throughout this investigation. The ORR onset potentials, E_{ORR} , during the cathodic potential sweep of the TiO_x/Ti electrodes prepared at 400 °C, 450 °C, and 500 °C were 0.87, 0.91 and 0.88 V vs. RHE, respectively. Based on this result, the preparation temperature for the oxide electrodes in this investigation was fixed at 450 °C.

Fig. 9 shows cyclic voltammograms of the TiO_x/Ti , ZrO_x/Ti and TaO_x/Ti electrodes, which were prepared at 450 °C and measured in both deaerated 0.1 M HClO_4 (broken lines) and in O_2 -saturated 0.1 M HClO_4 (solid lines) at 60 °C. The additional cathodic current of each voltammogram measured in an O_2 -saturated solution compared to that in the deaerated electrolytic solution shows the reduction in oxygen. These voltammograms provide the following information: (1) the approximate pseudocapacitance value of each oxide catalyst electrode for the voltammograms in the deaerated solution; (2) the ORR onset potential, E_{ORR} , where the reduction in oxygen becomes apparent during the cathodic potential sweep of the test electrodes; and (3) the current density corresponding to the ORR, that is, the current density in the O_2 -saturated solution deducted from that in the deaerated solution at any potential measured.

Due to the difficulty in determining the surface area of the oxide catalyst layers of these oxide-coated electrodes by the BET method, for example, the pseudocapacitance of these oxide electrodes was evaluated with the anodic voltammetric charge measured in the deaerated 0.1 M HClO_4 between 0.4 and 1.0 V (vs. RHE); half the total charge (anodic charge + cathodic charge) was divided by 0.6 V. Despite a lack of information on the “effective surface area” that actually contributes to ORR in porous oxide electrodes, the current

density divided by the pseudocapacitance is used when discussing the specific activity of oxide electrodes. Since not every inner surface of the porous oxide catalysts contributes to ORR due to the restriction in the transport of oxygen through narrow pores, the comparison of specific activity among the oxide catalyst electrodes using the current density divided by the pseudocapacitance has limitations. The pseudocapacitance of these oxide electrodes is listed in Table 2 along with the respective specific activities, or the ORR current density at 0.7 V vs. RHE divided by the respective pseudocapacitance. Under the described conditions of electrode preparation and electrochemical measurement, the TiO_x/Ti electrode provided the highest ORR specific activity at 0.7 V vs. RHE. The considerable difference in the morphology of the oxide layer for these three oxide-coated electrodes, as shown in Figs. 1 and 2, must also affect the ORR activity due to the effect of the mass transport of the reactants. As shown in Fig. 2, the TaO_x/Ti electrode had a smooth surface. While isolated cracks were observed, the pseudocapacitance was almost same as that of the ZrO_x/Ti electrode and was about 60% of that of the TiO_x/Ti electrode. This result means that (1) the effective surface area towards the ORR should be determined for a reasonable comparison of the surface-specific activity of the oxide-coated catalyst electrodes and (2) the design of an oxide catalyst with a large surface area which can contribute to the ORR is important from a practical viewpoint. Moreover, the electric resistance of these oxide layers must be very low; therefore, the effective surface must be restricted by the region in which electric contact is guaranteed. The TiO_x/Ti electrode showed the highest activity among these three electrodes, perhaps because of the semi-conductive property of TiO_x prepared at low temperature. In addition to these factors affecting catalytic activity, residual chloride ions usually contained in the oxide layers pre-

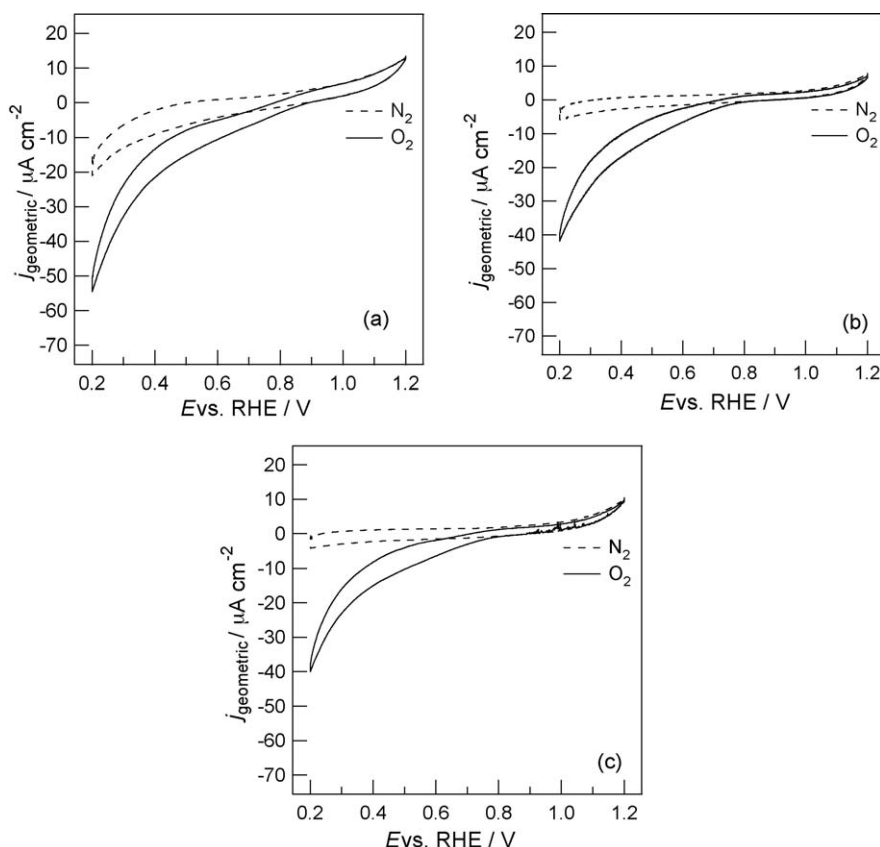


Fig. 9. Cyclic voltammograms of the TiO_x/Ti , ZrO_x/Ti , and TaO_x/Ti electrodes prepared by dip-coating method at 450°C . Electrode: (a) TiO_x/Ti , (b) ZrO_x/Ti , and (c) TaO_x/Ti . Electrolyte: broken lines, in deaerated 0.1 M HClO_4 with N_2 at 60°C ; solid lines, in O_2 -saturated 0.1 M HClO_4 at 60°C . Electrode potential sweep rate: 5 mV s^{-1} .

pared by the dip-coating method with chloride precursors must also be considered for the discussion of the catalytic activity of oxide catalysts. A precise investigation of both the effective surface area and the precise surface-specific catalytic activity for the ORR is needed in order to examine the morphology, electric conduction and probable effect of impurities such as residual chloride ions.

3.3. Enhancing the catalytic activity of TiO_x/Ti , ZrO_x/Ti , and TaO_x/Ti electrodes by the formation of binary oxides

The formation of binary oxides is sometimes useful in order to increase the surface area of the oxide due to the inhibition of oxide particle crystallization. In the case of the formation of binary oxides from elements with different valencies, the occurrence of O^{2-} vacancies and changes in valencies of the constituting metal elements is expected.

Figs. 10 and 11 show cyclic voltammograms of the binary oxide electrodes of $\text{Ti-Zr-O}/\text{Ti}$ and $\text{Ti-Ta-O}/\text{Ti}$ with different compositions, which were prepared at 450°C and measured in both deaerated 0.1 M HClO_4 (broken lines) and in O_2 -saturated 0.1 M HClO_4 (solid lines) at 60°C . The ORR behavior of some of these binary oxide-coated electrodes, along with those of the single oxide-coated electrodes, TiO_x/Ti , ZrO_x/Ti , and TaO_x/Ti , are shown in Fig. 12. The electrocatalytic activity is presented as mass-current density. Although the TiO_x/Ti electrode gave the highest mass activity among these oxide-coated electrodes, as shown in Fig. 12, the catalytic activity will be discussed with the surface-specific activity. As presented in Table 2, the addition of TiO_x to ZrO_x resulted in an increase in pseudocapacitance, while its addition to TaO_x resulted in a slight decrease in capacitance. The catalytic activity presented by $j_{\text{SA}, 0.7}$ of these binary oxide electrodes is shown in Figs. 13 and 14. An evident increase in both specific activity and E_{ORR} by the formation of binary oxide was observed at the $\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_x/\text{Ti}$ electrode.

Table 2
Electrochemical characteristics of various oxide-coated electrodes.

Electrode	E_{ORR} vs. RHE (V)	C_{pc} $\mu\text{F cm}^{-2}$ (geometric)	$j_{\text{geo}, 0.7}$ $\mu\text{A cm}^{-2}$ (geometric)	$j_{\text{SA}, 0.7}$ mA F^{-1} (oxide)	$j_{\text{m}, 0.7}$ mA g^{-1} (oxide)
TiO_x/Ti	0.91	478	3.9	8.2	24
ZrO_x/Ti	0.81	274	2.0	7.3	11
TaO_x/Ti	0.82	284	1.8	6.3	10
$\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_x/\text{Ti}$	0.86	287	3.6	12.5	21
$\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_x/\text{Ti}$	0.85	297	1.7	5.7	10
$\text{Ti}_{0.3}\text{Zr}_{0.7}\text{O}_x/\text{Ti}$	0.76	373	1.0	2.7	5.6
$\text{Ti}_{0.7}\text{Ta}_{0.3}\text{O}_x/\text{Ti}$	0.90	415	2.1	5.1	12
$\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_x/\text{Ti}$	0.81	196	2.3	11.7	13
$\text{Ti}_{0.3}\text{Ta}_{0.7}\text{O}_x/\text{Ti}$	0.84	279	2.7	9.7	17

E_{ORR} , onset potential for the ORR at the cathodic potential sweep; C_{pc} , pseudocapacitance; $j_{\text{geo}, 0.7}$, current density for the ORR at 0.7 V vs. RHE divided by the pseudocapacitance of the electrodes; $j_{\text{m}, 0.7}$, current density of the oxide-coated electrodes for the ORR at 0.7 V vs. RHE per mass of the oxide loaded on each Ti substrates.

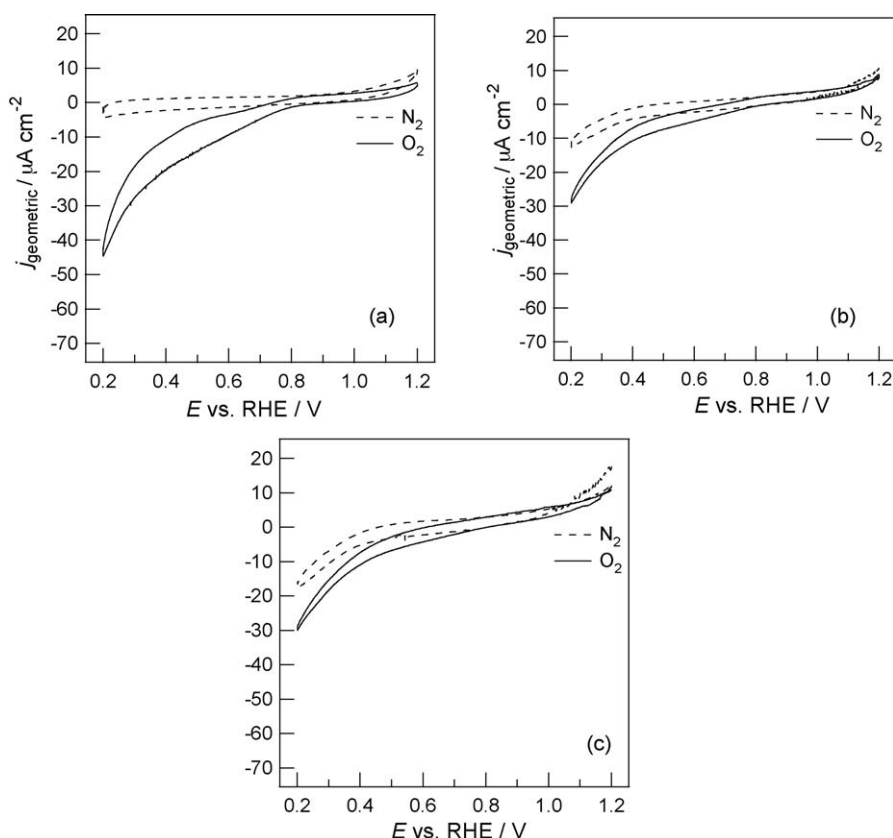


Fig. 10. Cyclic voltammograms of the Ti–Zr–O/Ti binary electrodes prepared by dip-coating method at 450 °C. Electrode: (a) $\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_x/\text{Ti}$, (b) $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_x/\text{Ti}$, and (c) $\text{Ti}_{0.3}\text{Zr}_{0.7}\text{O}_x/\text{Ti}$. Electrolyte: broken lines, in O_2 -purged 0.1 M HClO_4 with N_2 at 60 °C; solid lines, in O_2 -saturated 0.1 M HClO_4 at 60 °C. Electrode potential sweep rate: 5 mV s^{-1} .

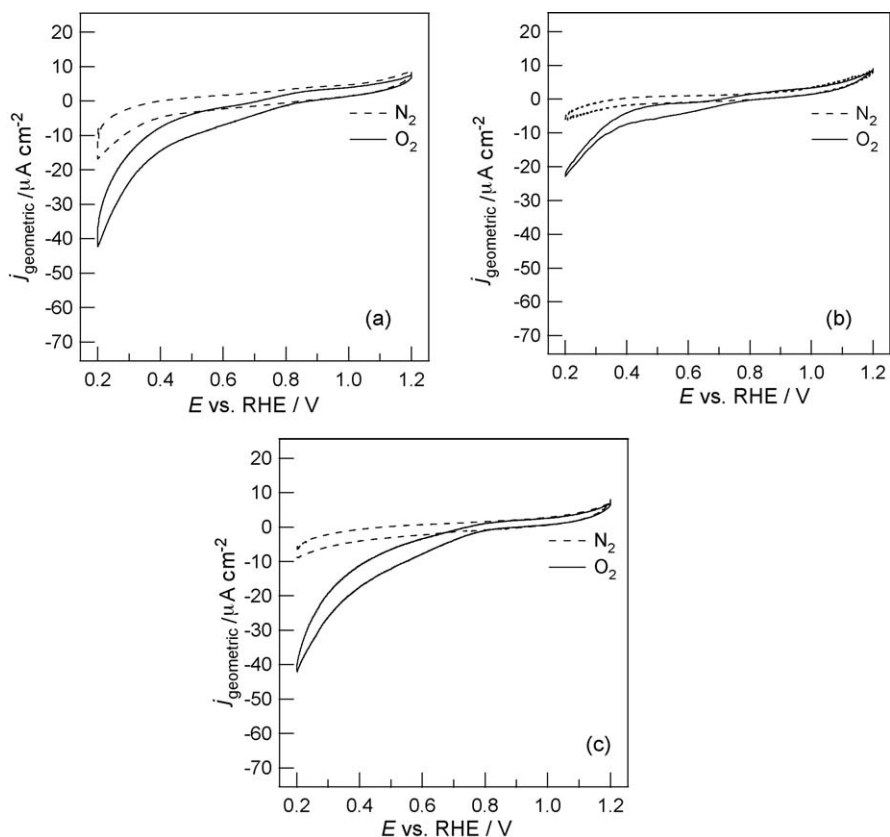


Fig. 11. Cyclic voltammograms of the Ti–Ta–O/Ti binary electrodes prepared by dip-coating method at 450 °C. Electrode: (a) $\text{Ti}_{0.7}\text{Ta}_{0.3}\text{O}_x/\text{Ti}$, (b) $\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_x/\text{Ti}$, and (c) $\text{Ti}_{0.3}\text{Ta}_{0.7}\text{O}_x/\text{Ti}$. Electrolyte: broken lines, in O_2 -purged 0.1 M HClO_4 with N_2 at 60 °C; solid lines, in O_2 -saturated 0.1 M HClO_4 at 60 °C. Electrode potential sweep rate: 5 mV s^{-1} .

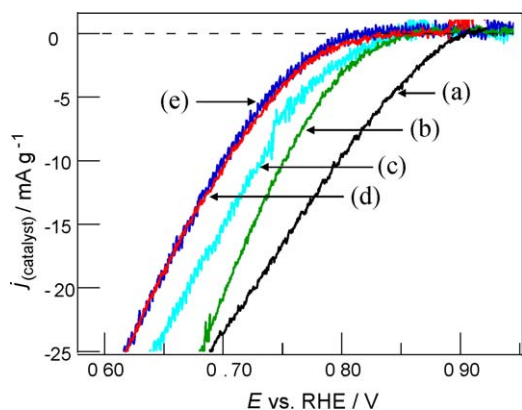


Fig. 12. ORR-current curves of the TiO_x/Ti , ZrO_x/Ti , TaO_x/Ti , $\text{Ti-Zr-O}/\text{Ti}$, and $\text{Ti-Ta-O}/\text{Ti}$ binary electrodes prepared by dip-coating method at 450°C . The ORR-current curves were drawn by deducting the voltammograms in the deaerated HClO_4 solution from those of the O_2 -saturated solution presented in Figs. 9–11. Electrode: (a) TiO_x/Ti (black), (b) $\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_x/\text{Ti}$ (green), (c) $\text{Ti}_{0.3}\text{Ta}_{0.7}\text{O}_x/\text{Ti}$ (light blue), (d) ZrO_x/Ti (red) and (e) TaO_x/Ti (dark blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

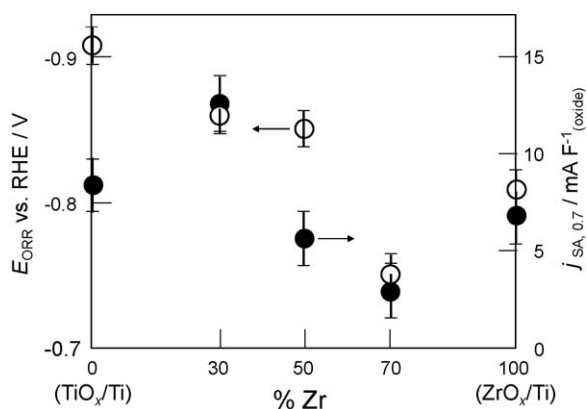


Fig. 13. ORR onset potential, E_{ORR} , and ORR current density at 0.7 V vs. RHE, j , of the $\text{Ti-Zr-O}/\text{Ti}$ electrodes. Open circles, E_{ORR} ; solid circles, j .

The $j_{\text{SA},0.7}$ of this electrode, $12.5 \text{ mA F}^{-1}(\text{oxide})$, gave values 2.0 and 1.7 times higher than those of TiO_x/Ti and ZrO_x/Ti , respectively.

$\text{TiO}_2\text{-ZrO}_2$ binary oxides, not only in mixed states but also as a solid solution such as TiZrO_2 , are well-known catalysts or catalyst support materials except in the research field of electrocatalysis [28]. Various preparation methods, characterizations and applications to catalysis processes, such as dehydrogenation, partial or

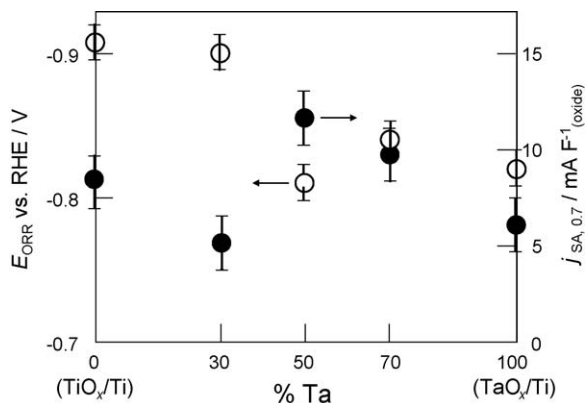


Fig. 14. ORR onset potential, E_{ORR} , and ORR current density at 0.7 V vs. RHE of the $\text{Ti-Ta-O}/\text{Ti}$ electrodes. Open circles, E_{ORR} ; solid circles, j .

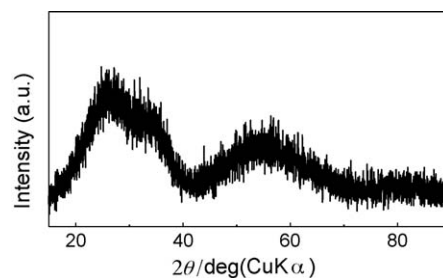


Fig. 15. The XRD pattern of the TaO_x powder calcined at 450°C for 30 min.

deep oxidation and hydrogenation, have thus far been reported. The control of acidity within the content is important in designing catalysts and catalyst support materials. The acidity of this binary oxide as a function of the content reported by Wang et al. [29] showed a volcano-type pattern with a maximum value at 50 mol% of TiO_2 . Although we had expected that some relationship existed between the acidity and the oxide content of this binary oxide, no clear relationship was found in the specific activity. In addition to the acidity, the specific activity of TiO_x/Ti was enhanced by the addition of 30 mol% of ZrO_x , while that of ZrO_x was reduced by the addition of 30 mol% of TiO_x . A detailed investigation into the effects of structure, morphology, and acidity on the catalytic behavior of this binary oxide is presently underway.

3.4. ORR activity of TaO_x powder prepared from the dip-coating solution

As an extension of the dip-coating method, tantalum oxide powder was prepared from the dip-coating solution of the butanolic solution of TaCl_5 . The specific surface area of the TaO_x powder calcined at 450°C was $4.2 \text{ m}^2 \text{ g}^{-1}$. The X-ray diffraction pattern of the powder, shown in Fig. 15, gave very broad diffraction peaks at the same diffraction angles from TaO_x/Ti electrode. As assigned for the oxide-coated electrode, this powder sample might be TaO_2 or something like that. The $\text{Ta}4f_{7/2}$ peak from this powder sample appeared at 26.0 eV, suggesting that the valency of the tantalum ions of this oxide was lower than that of Ta^{5+} (26.5 eV). The XPS analysis revealed that this TaO_x powder contained traces of titanium species less than 0.3%. As shown in the hydrodynamic voltammograms (Fig. 16), the TaO_x powder provided high ORR cur-

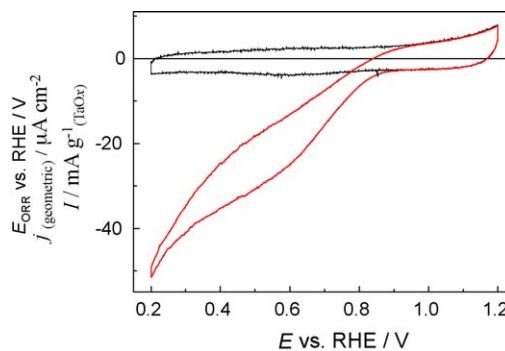


Fig. 16. Hydrodynamic voltammograms of the (TaO_x particles + carbon black) electrode rotated at 2000 rpm with the RDE equipment. Electrode: TaO_x (95 mass%) mixed with carbon black (Vulcan XC-72R; 5 mass%). TaO_x powder was prepared by calcination of the dried dip-coating solution at 450°C for 30 min. Loading amount of TaO_x on the GC (glassy carbon) surface of the working electrode of the RDE: 1 mg cm^{-2} . Electrolyte: black line, in deaerated 0.1 M HClO_4 with N_2 at 30°C ; red line, in O_2 -saturated 0.1 M HClO_4 at 30°C . Electrode potential sweep rate: 5 mV s^{-1} . Rotating speed of the test electrode in the RDE measurements: 2000 rpm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

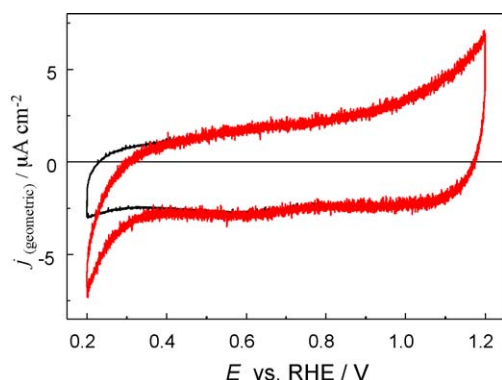


Fig. 17. Hydrodynamic voltammograms of the electrode loading carbon black rotated at 2000 rpm with the RDE equipment. Electrode: carbon black (Vulcan XC-72R). Loading amount of carbon black powder on the GC (glassy carbon) surface of the working electrode of the RDE: 0.05 mg cm^{-2} . Electrolyte: black line, in deaerated 0.1 M HClO_4 with N_2 at 30°C ; red line, in O_2 -saturated 0.1 M HClO_4 at 30°C . Electrode potential sweep rate: 5 mV s^{-1} . Rotating speed of the test electrode in the RDE measurements: 2000 rpm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

rent density; the ORR onset potential, E_{ORR} , and the ORR current density at 0.7 V vs. RHE , $j_{\text{m},0.7}$, were 0.90 V vs. RHE and 12 mA g^{-1} at 60°C , respectively. The 12 mA g^{-1} for the ORR mass-current density of the powder catalyst at 0.7 V vs. RHE was similar in value, 10 mA g^{-1} , as determined for the TaO_x/Ti electrode prepared by the dip-coating method at the same calcination temperature, 450°C (Table 2). Fig. 17 shows that the ORR current density of the carbon black added to the TaO_x powder was very low compared to the electrode of ($\text{TaO}_x + \text{carbon black}$).

Although the high ORR catalytic activity of tantalum oxynitrides and related compounds has already been reported by other research groups [16–20], significantly high activity of TaO_x containing no nitrogen or carbon for the reaction has not yet been reported. The E_{ORR} of the Ta_2O_5 powder prepared at 1000°C by Ota's research group was about 0.5 V vs. RHE . The large difference in value between the E_{ORR} of tantalum oxide prepared by Ota's group and that in this work was likely due to the differences in preparation methods and temperatures. Since the oxide ion vacancies may contribute to ORR, a detailed examination on the characteristics of tantalum oxide is necessary to clarify the active site and its stability.

4. Conclusions

In our search for inexpensive candidate oxide cathode catalysts for PEFCs, we investigated the electrocatalytic oxygen reduction reaction (ORR) of several valve metal (Ti, Zr, and Ta) oxide coatings prepared on a titanium substrate by the dip-coating method between 400°C and 500°C (typically 450°C). The ORR onset potentials, E_{ORR} , of TiO_x , ZrO_x and TaO_x prepared at 450°C were 0.91 , 0.81 , and 0.82 V vs. RHE at 60°C , respectively. The catalytic activity of TaO_x/Ti evaluated by ORR current density at 0.7 V vs. RHE , $j_{\text{geo},0.7}$, was $1.8 \mu\text{A cm}^{-2}(\text{geometric})$. To enhance the catalytic activity of TiO_x , ZrO_x , and TaO_x electrodes, Ti–Zr–O/Ti and Ti–Ta–O/Ti binary oxide electrodes were investigated, and an enhancement of the catalytic

activity was found at the $\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_x/\text{Ti}$ and $\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_x/\text{Ti}$ electrodes, although the extent was not highly significant. Finally, TaO_x powder prepared from the dip-coating solution at 450°C showed ORR catalytic activity, $j_{\text{m},0.7}$, similar to that of the TaO_x/Ti electrode. The E_{ORR} and the ORR current density at 0.7 V vs. RHE , $j_{\text{m},0.7}$, of the TaO_x powder were 0.90 V vs. RHE and 12 mA g^{-1} at 30°C , respectively. However, the TiO_x powder was prepared at a temperature considerably lower than those for TaNO_x and related powder catalysts reported to date. A detailed examination on the characteristics of tantalum oxide is necessary to clarify the active site and its stability.

Acknowledgments

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