Analysis of the effect of formation potential on the electrochemical response of doped titanium oxides

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Abstract

The electrochemical and semiconductor behavior of oxides of pure Ti and two Ti-based binary alloys, $\text{Ti}_{99}\text{Sn}_1$ and $\text{Ti}_{99}\text{Cr}_1$, were investigated using electrochemical impedance spectroscopy (EIS), Mott-Schottky analysis, intensity modulated photocurrent spectroscopy (IMPS), and potentiodynamic polarization in order to understand differences in measured oxygen reduction catalytic activity with the goal of suppressing the capability of titanium to drive galvanic corrosion. The combination of EIS techniques with IMPS was used to determine such semiconductor properties as the band gaps, flat band potentials, dielectric constants, defect concentrations, and catalytic properties, *i.e.*, the reaction rate constants, of the oxides. The semiconductor properties of the oxides were observed to change as a function of oxide formation potential but the greatest changes in oxygen reduction rates in an alkaline solution were only found to occur with alloying, with the greatest decrease seen for the $\text{Ti}_{99}\text{Sn}_1$ alloy.

Keywords

Titanium oxide; oxygen reduction reaction; intensity modulated photocurrent spectroscopy; galvanic corrosion

1. Introduction

In galvanic corrosion, unlike in other forms of corrosion, the electrochemical properties of the cathodic material are almost as important as the properties of the anodic material in determining the rate of corrosion. While the potential difference between the two materials gives an indication of the thermodynamic driving force for galvanic corrosion, it is, of course, the magnitude of the corrosion current that determines the amount of anode dissolution [1]. The sites for metal oxidation and oxygen reduction are located on the different materials of the galvanic couple; thereby requiring the establishment of an electron transport path between the materials of the galvanic couple. The corrosion rate of the more active material in the galvanic couple is strongly influenced by such environmental conditions as the presence of aggressive anions, which impact anodic reaction kinetics, but also, in many instances, by the amount of exposed surface area of the cathode and by the ability of the cathode to support a suitable reduction reaction [2-4]. Of particular interest to this work is the oxygen reduction reaction (ORR), with the overall reaction given in equation (1)[5].

The ORR on transition metal oxides, as on platinum, can proceed via either the 2-electron or 4-electron pathway. However, unlike platinum, the surface cations of a transition metal oxide do not have their full complement of oxygen anions and so they coordinate with the oxygen atoms in water molecules that become adsorbed onto the oxide surface [6]. To create OH^- ions, the reduction of the surface metal cation must compensate the protonation of the surface oxygen atoms. The new $M-OH^-$ species interact with dissolved O_2 molecules which adsorb on the oxide surface in either the end-on or side-on configurations. The direct pathway on TiO_2 in alkaline solutions is suggested to proceed in the following manner [7]:

where $Ti^{3+}-OH^-$, for example, indicates a coordination complex. Competition from the indirect pathway can replace equation (5):

The reaction in equation (5) is thought to be the rate-determining step (RDS) for the direct pathway and the step in equation (7) is considered the RDS for the indirect pathway.

The ORR rate on TiO_2 can be expressed using a Butler-Volmer formulation[6]:

$$j = j_0(1 - \theta_B)e^{\left[-\frac{\alpha F(E-E_0)}{RT}\right]}e^{\left[\frac{-\alpha \Delta G_B^0}{RT}\right]} \quad (8)$$

where j_0 is the exchange current density, θ_B is the surface coverage of OOH^- provided by a Langmuir adsorption isotherm, E is the constant potential, E_0 is the standard state reversible potential, α is the charge transfer coefficient, and ΔG_B^0 is the free energy difference between adsorbed and non-adsorbed OOH^- from equation (5). Then, for a constant potential, the reaction rate:

(a) Increases as the adsorption energy of the intermediate product increases from weaker to stronger, and

(b) Decreases as the availability of surface sites to form the intermediate product becomes limited with increasing adsorption strength.

These opposing influences give rise to a “volcano” curve when plotting reaction rate versus adsorption energy.

Computer simulations of oxygen reduction reactions on various transition metal oxides that predicted ORR “volcano” curves[8], suggested that tin and chromium would be potentially disruptive elements to consider as alloying elements in titanium. Electrochemical measurements of natively formed oxides on titanium with these alloying elements, in prior work [9], indicated

that ORR kinetics could be decreased. These prior results suggested that, in order to investigate the underlying mechanisms, the following courses of action needed to be pursued:

- (1) Use available electrochemical measurement techniques to confirm the effect of alloying on the reaction shown in equations (2) – (6).
- (2) Evolve the native oxides under potentiostatic control to determine if oxide thickness and/or composition could impact catalysis

2. Experimental Details

2.1 Alloy formation

Titanium (99.995% purity) and Ti-based minor solute alloy ingots were produced at solute concentration of 1 at% using the arc-melting technique using high purity metals (Sn 99.999% and Cr 99.996%). Ingots were suction cast into a custom copper mold consisting of two cylindrical regions of 1 cm and 0.6 cm diameter, the latter for RDE test specimens, which were then annealed for four hours at 827°C, within the single phase HCP region, followed by a water quench. The casts were then machined and ground to 4 mm diameter discs. X-ray diffraction (XRD), using Cu k- α x-rays, was used to verify single phase structure and determine the lattice coefficients using whole pattern fits. Prior to electrochemical testing, samples were abraded using successively finer grits to 1200 grit SiC paper, then polished using 1 micron alumina. For baseline electrochemical testing, samples were mounted in insulating epoxy.

2.2 Chemical property characterization

X-ray photoelectron spectroscopy (XPS) scans were performed on each of the oxides to determine oxide composition using a k- α XPS system. An Al k- α x-ray source was used for monochromatic radiation that was focused to a 400 μ m diameter spot size. Twenty high-resolution scans of the pure Ti were examined to provide baseline oxide information on the native Ti oxide while 50 high-resolution scans of each alloying element were performed to maximize signal capture to aid in determining values of the dopant concentrations. Data analysis was performed using the CasaXPS software system.

2.3 Semiconductor property characterization

Electrochemical impedance spectroscopy (EIS) characterization of the various titanium alloys was performed in 0.6 M NaCl + 0.01 M NaOH (pH 12) solution using a platinum wire counter electrode and a saturated calomel (SCE) reference electrode. The titanium alloy oxides were stabilized at room temperature and ambient aeration for 1 hour. The EIS scans were performed at the oxides' open-circuit potentials with a 5 mV_{RMS} perturbation at frequencies from 100 kHz to 0.1 Hz.

Mott-Schottky (MS) analysis of the various oxides was performed in 0.6 M NaCl + 0.01 M NaOH (pH 12) solution using a platinum wire counter electrode and a saturated calomel

reference electrode. The titanium alloy oxides were stabilized at room temperature and ambient aeration for 1 hour. The applied DC potentials were stepped in 100 mV increments from -0.3 V vs. SCE to -1.9 V vs. SCE. The oscillating potential was applied at 100 Hz at ± 5 mV_{RMS}.

2.4 Photoelectrochemical property characterization

Intensity modulated photocurrent spectroscopy (IMPS) characterization[10] of the various oxides was also performed in 0.6 M NaCl + 0.01 M NaOH (pH 12) solution using a platinum wire counter electrode and a silver-oxide pseudo-reference cell[11]. The titanium alloy oxides were stabilized at room temperature and ambient aeration for 1 hour. Two potentiostats were used for these characterizations. The primary potentiostat applied the baseline DC current and AC modulation to the LED while the secondary potentiostat received the clock signal from the primary potentiostat and measured the response of the sample. The AC current supplied to the LED varied in frequency from 5000 Hz to 0.1 Hz while the magnitude of the oscillation was varied to account for the maximum current permitted through the LED. Fifteen LEDs were used that spanned the spectrum from infrared to ultraviolet light: 1450 nm, 1200 nm, 850 nm, 660 nm, 617 nm, 590 nm, 530 nm, 505 nm, 470 nm, 420 nm, 405 nm, 385 nm, 375 nm, 365 nm, and 310 nm, identified by the emitted wavelength with the highest intensity.

2.5 Electrochemical property characterization

Potentiodynamic polarization characterization of the various titanium alloys was performed in 0.6 M NaCl + 0.01 M NaOH (pH 12) electrolyte with a platinum wire counter electrode and a saturated calomel reference cell. The titanium alloy oxides were stabilized at room temperature and ambient aeration for 1 hour. The potentiodynamic polarizations were performed over a range of potentials starting from +0.02 V above the open circuit potential to -1.5 V vs. SCE. The potentials were stepped at a rate of -0.167 mV/sec.

3. Results

3.1 Alloy and oxide characterization

XRD results reported previously[9] indicate that the annealing process for both Ti99Cr1 and Ti99Sn1 resulted in solid solution alloying and the minor alloying elements were incorporated into the single HCP phase. For both Cr and Sn the HCP lattice contracted, likely due to substitutional alloying of the smaller atomic radii.

3.1.1 XPS measurements

The results of the XPS measurements of the oxide composition and thickness are shown in Table 1. These values indicate that anodic polarization led to thicker oxides and increased the fraction of TiO₂ vs Ti₂O₃ as compared to the ratio in a natively formed oxide while cathodic polarization led to reduced oxide thickness and reduced the fraction of TiO₂ vs Ti₂O₃ as compared to the anodically polarized oxide. Note that the similar ratio of concentrations of TiO₂ to Ti₂O₃ for the two cathodic potentials most likely arise because there is little TiO₂ formation at these potentials at the expense of the natively formed oxide composition.

Table 1. Comparison of oxide thickness and composition as a function of formation potential.

Oxide	Formation potential vs. SCE/V	Thickness/nm	TiO ₂ /Ti ₂ O ₃ ratio
Pure Ti	0.1	8.6	91%/9%
	-0.4	5.6	80%/20%
	-1.7	5.2	82%/18%
Ti99Sn1	0.1	8.7	91%/9%
	-0.4	5.9	83%/17%
	-1.7	5.4	80%/20%
Ti99Cr1	0.1	8.5	90%/10%
	-0.4	5.7	81%/19%
	-1.7	5.9	80%/20%

3.1.2 EIS and Mott-Schottky measurements

Example Bode plots of the oxide responses to three repetitions of EIS scans for pure titanium at +0.1, -0.4, and -1.7 V vs. SCE are shown in Figure 1. The modulus of the impedance and phase

responses have been plotted as functions of frequency. Solution resistances, averaging $10\ \Omega$, was determined from the measured response at high frequencies and capacitance and polarization resistance changes in the oxide response can be determined from the oscillating applied potential at lower frequencies. Similar sets of experiments were performed for each alloy. A three element constant phase element (CPE) equivalent circuit model, similar to a Randle's circuit, was fit to the impedance measurements to obtain solution resistance, polarization resistance, and equivalent capacitance values.

The inverse square of the capacitance as a function of potential for each of the oxides is shown in Figure 2. Each curve represents the average response obtained from three iterations of the experiment. In general, between $-0.3\ \text{V vs. SCE}$ and $-1.0\ \text{V vs. SCE}$ there was a linear relationship between potential and $1/C^2$, which indicated the oxide was acting as a Schottky barrier and the Mott-Schottky relationship was expected to hold [12]. The positive slope of the response curves between $-0.3\ \text{V vs. SCE}$ and $-1.0\ \text{V vs. SCE}$ was indicative of an n-type semiconductor [13]. The increase in $1/C^2$ from $-1.4\ \text{V vs. SCE}$ to $-1.6\ \text{V vs. SCE}$ indicated changes in the majority charge carrier type in the semiconductor oxide, *i.e.* from n-type to p-type. However, because this transition occurred close to the potential at which Ti_2O_3 became thermodynamically stable with respect to TiO_2 , the n-type to p-type transition and the increase in the fraction of Ti_2O_3 present in the oxide appeared to be related [14].

7a.

b.

c.

Figure 1. Plots of Z_{mod} vs. frequency (line+symbol) overlaid on plots of phase angle vs. frequency (symbols only) for pure titanium oxide in 0.6 M NaCl + 0.01 M NaOH at potentials: (a) 0.1 V vs. SCE, (b) -0.4 V vs. SCE, and (c) -1.7 V vs. SCE. The single time

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180 constant response to the voltage perturbation suggested that a constant-phase element equivalent
181 circuit was sufficient for capturing the oxide behavior.

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Figure 2. Plots of $1/C^2$ vs. applied potential at 100 Hz for (a) Ti and the binary alloys: (b) $Ti_{99}Sn_1$ and (c) $Ti_{99}Cr_1$ in 0.6 M NaCl + 0.01 M NaOH solution at oxide formation potentials of 0.1 V vs. SCE, -0.4 V vs. SCE, and -1.7 V vs. SCE.

3.1.3 IMPS measurements

Examples of the photoelectrochemical response of the titanium oxide, evolved at different potentials, to a range of photon energies and light modulation frequencies is shown in Figure 3. The incident photon energies are shown in ascending order of energy, on the right side: 1450 nm to 310 nm; spanning the infrared, visible light, and ultraviolet regions. Similar response curves were obtained for all of the doped oxides. Incident photons with energies greater than the oxide band gap were expected to induce photocurrents arising from either photo-generated holes or excited conduction band electrons while incident photons with energies less than the band gap were not expected to induce photocurrents. This trend held for the UV incident photons, which had energies exceeding the band gaps of the various oxides and induced high photocurrents, and the IR incident photons, which had energies far below the band gaps of the various oxides. However, within the visible light region, in which the incident photons had less energy than the nominal band gaps, the photocurrent response was mixed. Below ~1 kHz light modulation frequency, the magnitude of the photocurrents generally decreased as the photon energies decreased. Current spikes near 60 Hz correspond to interference from oscillations at the power supply frequency. The response of the oxides to light modulation above 1 kHz did not follow any identifiable trends.

Figure 3. Plots of the photocurrent response, I_{IMPS}^{mod} , vs. light modulation frequency for each wavelength LED for the oxide on pure Ti at formation potentials of (a) 0.1 V vs. SCE, (b) -0.4 V vs. SCE, and (c) -1.7 V vs. SCE.

3.2 Electrochemical characterization

Cathodic polarization curves for each of the oxides are shown in Figure 4. Various regions of the current response of each oxide to the applied potential are indicated on the plot, including the most likely dominant reduction reaction and the most likely controlling mechanism. Each alloy shows clear mixed activation and diffusion control regimes for oxygen reduction at potentials above -1 V vs. SCE and a clearly defined mass transport limited current density at potentials between -1 V vs. SCE and -1.4 V vs. SCE. At potentials below -1.4 V vs. SCE, hydrogen reduction provides the dominant contribution to the cathodic current. **Note that the oxide formed on the Ti₉₉Cr₁ alloy shows a slightly suppressed average hydrogen evolution current density in relation to the other two materials.**

Figure 4. Plots of the cathodic polarization curves for Ti and the two binary alloys: Ti₉₉Sn₁, and Ti₉₉Cr₁, in 0.6 M NaCl + 0.01 M NaOH solution, with regions of the current response to the applied potential highlighted where different reaction mechanisms were dominant.

4. Discussion

The oxide on titanium is generally considered to behave as a semiconductor with an approximate 3.1 eV band-gap[15, 16]. The interface between the oxide and the electrolyte can be envisioned in the semiconductor energy level diagram in Figure 5[17, 18] and semiconductor properties of the oxides, such as the band gap, the flat band potential, and the dielectric constant, can be obtained from the EIS and Mott-Schottky experimental results.

Figure 5. The band energy diagram for TiO_2 shows the valence and conduction bands and the band gap in the oxide, the interface with the electrolyte, and approximate density of states at the interface for selected redox reactions. The shaded regions represent occupied density of states.

Because only single time constants are present in the EIS responses in Figure 1, the CPE equivalent circuit model was used to capture the behavior of the oxide. From the equivalent circuit models, values for the charge-transfer resistance, R_p , and the constant-phase-element parameters, Y_0 and α , were obtained for the oxides on pure Ti, $\text{Ti}_{99}\text{Sn}_1$, and $\text{Ti}_{99}\text{Cr}_1$, and are shown in Table 2, Table 3, and Table 4, respectively. Values for solution resistance, R_U , were also obtained but they only varied by approximately $1/\Omega$ from 9-10 $/\Omega$ and are not shown in the table.

Table 2. Values determined from a CPE equivalent circuit model fit to EIS data obtained from pure titanium oxide along with the calculated oxide film capacitance.

Formation potential vs. SCE/V	Fit Parameter			Capacitance/($\mu\text{F}/\text{cm}^2$)
	α	$Y_0/(\text{S}^*\text{s}^\alpha)$	$R_p/\text{k}\Omega*\text{cm}^2$	
0.1	0.824	34.4×10^{-6}	881	111
-0.4	0.822	40.0×10^{-6}	438	116
-1.7	0.897	3880×10^{-6}	0.042	4790

Table 3. Values determined from a CPE equivalent circuit model fit to EIS data obtained from the oxide on $\text{Ti}_{99}\text{Sn}_1$ along with the calculated oxide film capacitance.

Formation potential vs. SCE/V	Fit Parameter			Capacitance/($\mu\text{F}/\text{cm}^2$)
	α	$Y_0/(\text{S}^*\text{s}^\alpha)$	$R_p/\text{k}\Omega*\text{cm}^2$	
0.1	0.857	24.5×10^{-6}	575	62
-0.4	0.847	29.6×10^{-6}	413	76
-1.7	0.855	2820×10^{-6}	0.180	4100

Table 4. Values determined from a CPE equivalent circuit model fit to EIS data obtained from the oxide on $\text{Ti}_{99}\text{Cr}_1$ along with the calculated oxide film capacitance.

Formation potential vs. SCE/V	Fit Parameter			Capacitance/($\mu\text{F}/\text{cm}^2$)
	α	$Y_0/(\text{S}^*\text{s}^\alpha)$	$R_p/\text{k}\Omega*\text{cm}^2$	
0.1	0.814	31.3×10^{-6}	919	101
-0.4	0.800	38.6×10^{-6}	662	130
-1.7	0.894	2670×10^{-6}	0.130	3380

In addition, using equation (9), values for double-layer capacitance were calculated and are listed in the final column of each of the tables [19].

$$C = \frac{(Y_0 R_p)^{\frac{1}{\alpha}}}{R_p} \quad (9)$$

C represented the double-layer capacitance, R_p the charge transfer resistance, Y_0 was the magnitude of the CPE[20], and α represented an empirical constant to capture the deviation of the CPE from an ideal capacitor. Note that the capacitance increased for each of the oxides when the formation potential changed from 0.1 V vs. SCE to -0.4 V vs. SCE, but that there was a two-orders of magnitude increase after the oxide was exposed to a potential of -1.7 V vs. SCE; a potential at which Ti_2O_3 was thermodynamically favored to form at the expense of TiO_2 and which was detected in the XPS results. **These values suggest that the oxides were becoming more defective at the more cathodic potentials.**

The Mott-Schottky relationship [21, 22], equation (10), was employed to determine the flat band potential and defect concentrations of the oxides.

$$\frac{1}{C^2} = \frac{2 * \left(V_{app} - E_{FB} - \frac{k_B T}{e} \right)}{\epsilon \epsilon_0 e N_D A^2} \quad (10)$$

where E_{FB} is the flat band potential, C is the interfacial capacitance, e is the charge on the electron, A is the interfacial contact area, ϵ is the dielectric constant of the oxide, ϵ_0 is vacuum permittivity, and V_{app} is the externally applied potential. The Mott-Schottky equation proposes an inverse relationship between capacitance and applied potential with the slope related to the defect concentration, N_D .

The dielectric constants, ϵ , for the oxides were obtained from equation (11).

$$C = \frac{\epsilon \epsilon_0 A}{D} \quad (11)$$

where C is the resistance-corrected capacitance [23], ϵ is the dielectric constant of the oxide, ϵ_0 is vacuum permittivity, and A is the exposed area, and D is the oxide thickness[24]. The exposed areas were approximately $0.69/\text{cm}^2$, $0.66/\text{cm}^2$, and $0.72/\text{cm}^2$ for the pure Ti, $\text{Ti}_{99}\text{Sn}_1$, and $\text{Ti}_{99}\text{Cr}_1$ oxides, respectively. The oxide thicknesses were estimated by XPS sputtering. Using the capacitance values estimated from plots of C_{real} vs. frequency calculated from the EIS data, the dielectric constants in Table 5 were obtained:

Table 5. Oxide thicknesses obtained from XPS analysis and calculated dielectric constants for the metal oxides as a function of the oxide formation potential.

Metal Oxide	Formation potential vs. SCE/V	Corrected capacitance/nF	Oxide thickness /nm	Dielectric Constant
Pure Ti	0.1	750	8.6	106
	-0.4	820	5.6	74
	-1.7	12	5.2	0.11
$\text{Ti}_{99}\text{Sn}_1$	0.1	620	8.7	92
	-0.4	760	5.9	77
	-1.7	2	5.4	0.02
$\text{Ti}_{99}\text{Cr}_1$	0.1	531	8.5	71
	-0.4	540	5.7	48
	-1.7	4	5.9	0.03

The donor concentration was determined by manipulating (10) to obtain:

$$\text{Slope} = \frac{2}{\epsilon\epsilon_0 e A^2 N_D} \quad (12)$$

where the slope is from the linear best-fit line to the $1/C^2$ vs. potential plot for each oxide from the Mott-Schottky measurements. The flat band potential were also obtained by manipulating equation (10) to arrive at:

$$V_{app} = E_{FB} + \frac{k_B T}{e} \quad (13)$$

The flat band potentials, shown in Table 6, are consistent with TiO_2 values published in the literature and with each other. The defect concentrations, N_D , of the oxides formed at 0.1 V vs. SCE and -0.4 V vs. SCE are approximately equal to the published values of defect concentrations in TiO_2 of $N_D \approx 3 \times 10^{20}/\text{cm}^{-3}$ [25]. There was a clear trend, however, that, as the formation potential was decreased, the defect concentration also increased until, for the oxides exposed to the -1.7 V vs. SCE potential, the defect concentrations were two orders of magnitude higher than the expected value. The defect concentrations were likely increasing because the -0.4 V vs. SCE potentials drove changes in the TiO_2 structure and at -1.7 V vs. SCE, the applied potential was driving the formation of a highly defective Ti_2O_3 oxide.

Table 6. Values for E_{FB} , the flat band potential, and the defect concentration, N_D , determined from analysis of the Mott-Schottky tests performed on the pure titanium oxide and oxides of titanium alloys, as a function of the oxide formation potential.

Metal Oxide	Formation potential vs. SCE/V	E_{FB} vs. SCE/V	N_D/cm^{-3}
Pure Ti	0.1	-1.2	6.2×10^{20}
	-0.4	-1.2	8.7×10^{20}
	-1.7	-1.2	3.5×10^{23}
$\text{Ti}_{99}\text{Sn}_1$	0.1	-1.3	5.4×10^{20}
	-0.4	-1.3	5.7×10^{20}
	-1.7	-1.2	14×10^{23}
$\text{Ti}_{99}\text{Cr}_1$	0.1	-1.2	4.5×10^{20}
	-0.4	-1.2	6.5×10^{20}
	-1.7	-1.1	5.1×10^{23}

The flat band potentials fix the lower bound of the conduction band in the n-type semiconductor oxides but the band gaps are also needed to determine the top edge of the valence bands. The response of the oxide films to the IMPS experiments, as shown in Figure 3, was used to determine the band gaps. As the incident photon energies transitioned from the UV-portion of the spectrum into the visible light region, the photocurrents dropped rapidly to negligible values. Linear fits to the photocurrents normalized to account for variation in photon irradiance at the sample, shown in Figure 6, provided the estimates of the band gap energies[26].

Figure 6. Normalized photocurrent response as a function of photon energy for oxides formed at 0.1 V vs. SCE, -0.4 V vs. SCE, and -1.7 V vs. SCE for (a) Ti, (b) Ti₉₉Sn₁, and (c) Ti₉₉Cr₁.

The band gaps obtained from this approach [27] were in keeping with the accepted band gap of 3.1 eV for rutile TiO₂. The tops of the valence band energies were then obtained by subtracting the band gap energy from the base of the conduction band energies, with those results shown in Table 7. The cathodic polarizations did not appreciably alter the band gaps; with the exception of the polarization at -1.7 V vs. SCE for the Ti₉₉Cr₁ oxide. The apparent narrowing of the band gap occurs from the response seen in Figure 6c, which may arise from the development of surface states in the oxides resulting from the formation of Ti₂O₃ [28] and which could account for the slight suppression in the hydrogen evolution reaction on the Ti₉₉Cr₁ oxide.

Table 7. Values for the band gap energies and valence band energies for titanium oxide and the oxides of the titanium alloys.

Metal Oxide	Formation potential vs. SCE/V	E _g /eV	E _{VB} vs. SCE /V
Pure Ti	0.1	3.2	2.0
	-0.4	3.1	1.9
	-1.7	3.1	1.9
Ti ₉₉ Sn ₁	0.1	3.1	1.9
	-0.4	3.1	1.9
	-1.7	3.1	2.0
Ti ₉₉ Cr ₁	0.1	3.1	1.9
	-0.4	3.1	1.9
	-1.7	2.9	1.8

The above analysis indicated that the addition of the dopant atoms and the application of different formation potentials induced only minor shifts in the band structure and band gaps and that, as shown in Figure 5, both the hydrogen evolution reaction and the oxygen reduction reaction from equation (1) were thermodynamically allowed on these oxides at this pH [29]. Thus, the variance in the semiconductor properties of the different oxides appears to be insufficient to account for the catalytic differences in the oxide behaviors observed in the potentiodynamic polarization experiments.

The photoelectrochemical responses of the oxides, on the other hand, demonstrated a greater range of variability. Nyquist representations of the photoelectrochemical responses are shown in Figure 7. The imaginary component of the photocurrent arises from a phase shift in the photocurrent offset from the incident light modulation frequency. Figure 7 shows I_{imag} vs. I_{real} for responses of the oxides for each alloy formed at 0.1 V vs. SCE, -0.4 V vs. SCE, and -1.7 V vs. SCE to 365 nm wavelength UV light with modulation frequencies from 5000 Hz to 10 Hz. For the majority of the light modulation frequencies, the imaginary component of the photocurrent response was negative, which was attributed to the space-charge capacitance of the oxide [30]. Note that the overall magnitudes of the photocurrents were smaller for the alloy oxides than for the pure titanium oxide, which suggested that the oxides on the alloys have slower reaction kinetics than for the oxide on pure Ti. Note, as well, that for the oxides of pure Ti and $\text{Ti}_{99}\text{Sn}_1$ exposed to the -1.7 V vs. SCE potential, the photocurrents responses were higher in magnitude than for the oxides exposed to the -0.4 V vs. SCE potential and for the oxide on $\text{Ti}_{99}\text{Cr}_1$, the photocurrent responses were nearly identical. This suggests that once the formation of Ti_2O_3 was thermodynamically favored, the oxides became more active with respect to catalyzing the ORR.

Figure 7. Nyquist plot of I_{imag} vs. I_{real} for oxides formed at 0.1 V vs. SCE, -0.4 V vs. SCE, and -1.7 V vs. SCE in pure Ti, $\text{Ti}_{99}\text{Sn}_1$, and $\text{Ti}_{99}\text{Cr}_1$.

A kinetic model of the oxide behavior in response to photo-excitation was developed following the Ponomarev-Peter approach [31-33] and was used to predict charge transport in the oxide band structure. From the band diagram in Figure 5, it can be supposed that incident photons, with energy greater than the band gap, will excite electrons from the valence band into the conduction band, leaving positively charged holes behind, shown as equations (17) and (18). Once in the conduction band, some of the electrons recombine with the holes [34], at a rate k_2 , and are lost while the majority will be transported through the external circuit to the counter electrode [35]. Only a few will be able to travel to the interface to participate in a reduction reaction. The valence band holes, on the other hand, have much lower mobility than the electrons and, those that are not extinguished due to recombination, will reach the oxide-electrolyte interface and help drive water oxidation or other available reactions [36] at a rate, k_1 . The governing equations are written as the following:

$$\frac{q_S}{C_S} + \frac{q_H}{C_H} = I_{\text{ext}}R \quad (14)$$

$$\frac{dq_S}{dt} = A_0(1 + e^{i\omega t}) - I_{\text{ext}} - k_2(q_S - q_H) \quad (15)$$

$$\frac{dq_H}{dt} = k_1(q_S - q_H) - I_{ext} \quad (16)$$

where q_S is the charge transported across the space-charge region of the oxide, C_S is the capacitance of the space charge region, q_H is the charge transported across the Helmholtz region of the electrolyte, and C_H is the capacitance of that region. I_{ext} is the current through the external circuit, R is the total series resistance in the electrolyte, oxide, and electrical contacts, A_0 is the magnitude of the photo-generated hole current – determined by photon irradiance on the sample and the ability of the oxide to absorb photons, ω is the light modulation frequency, k_2 is the recombination rate constant, and k_1 is the rate constant for photo-generated hole transfer across the interface from the valence band. The flux of holes into the interface region in response to the modulated light is given by[37]:

$$A = A_0(1 + e^{i\omega t}) \quad (17)$$

where

$$A_0 = I_0 \left(1 - \frac{e^{-\frac{\alpha}{W}}}{1 + \alpha L_p} \right) \quad (18)$$

where I_0 is the incident photon flux, α is the absorption coefficient, L_p is the diffusion length for holes, and W is the width of the space-charge region.

Taking the Laplace transform of the equations in (14) - (16) gives:

$$(s + k_2)Q_1 - k_2Q_2 + I_S = \frac{A_0}{s} + \frac{A_0}{s - i\omega} \quad (19)$$

$$-k_1Q_1 + (s + k_1)Q_2 + I_S = 0 \quad (20)$$

$$\frac{1}{C_1}Q_1 + \frac{1}{C_2}Q_2 - I_S R = 0 \quad (21)$$

The expression for the external current, obtained from solving (19)–(21) and simplifying, is:

$$I_{ext}(t) = \left[\frac{A_0 k_1}{k_1 + k_2} \right] \quad (22)$$

$$\begin{aligned}
& + \left[\frac{A_0}{(k_1 + k_2 + i\omega)} \right] \left\{ \frac{2 \left(k_1 + \frac{i\omega C}{C_S} \right)}{1 + i\omega\tau} \right\} e^{i\omega t} \\
& - \left[\frac{1}{(k_1 + k_2 + i\omega)} \right] \left\{ \frac{\left(\frac{C}{C_H} k_1 - \frac{C}{C_S} k_2 \right) (k_1 + k_2 + A_0(k_1 + k_2 + i\omega))}{(1 + \tau(k_1 + k_2))(k_1 + k_2)} e^{(k_1 + k_2)t} \right\} \\
& + \left[\frac{2(C_S R k_1 + 1)(i(1 + A_0) + A_0 \tau \omega)}{(i\omega\tau - 1)(1 + \tau(k_1 + k_2))} \right] C_H e^{\frac{t}{\tau}}
\end{aligned}$$

where

$$C = \frac{C_S C_H}{C_S + C_H} \quad (23)$$

and

$$\tau = RC \quad (24)$$

The oscillating component of the photocurrent is obtained from the second term in (22):

$$I_{ext}(\omega) = \left[\frac{A_0}{(k_1 + k_2 + i\omega)} \right] \left\{ \frac{2 \left(k_1 + \frac{i\omega C}{C_S} \right)}{1 + i\omega\tau} \right\} \quad (25)$$

The plots in Figure 8 overlay the predicted response, $I_{ext}(\omega)$, obtained from parameters inserted into equation (25), with the measured I_{mod} response for each of the alloys when exposed to UV light at 365 nm and light modulations from 5000 Hz to 10 Hz. The parameters for each predicted response are found in Table 8 with the values for the capacitance of the space charge region and the Helmholtz capacitance obtained from the area-corrected impedance results found in Table 2 - Table 5. The total series resistance, R , is an estimate of the resistance of the electrolyte, hole conduction resistance in the oxide valence band, and electrical contacts. The parameters k_1 and k_2 are adjusted to fit the predicted response with the measured response.

For light modulation frequencies above 1 kHz, the model overestimates the measured response; likely because there are fast reactions occurring at the actual interface that were not included in the reaction constants in the model. However, the predicted responses and the measured

photocurrent responses are in good agreement for light modulation frequencies below 1 kHz. In this regime, a comparison of the k_1 reaction rates for the oxides formed at 0.1 V vs. SCE and -0.4 V vs. SCE – assuming the electron-hole recombination rates, k_2 , are constant at 2000 s^{-1} across the oxides – shows that the reaction kinetics on the oxides on the alloys are approximately 70-80% slower than on the oxide on pure Ti.

The theoretical model for the oxygen reduction reaction on titanium oxide, given in (2)-(6), with the transition from surface peroxide formation to surface oxide formation, (5), generally held to be the rate-determining step [38]. The experimental results and IMPS model presented here support the original theoretical models of the “volcano” curve that suggested that Cr and Sn-containing oxides, having higher adsorption energies for intermediate reaction products of the ORR, will suppress ORR kinetics on these oxides [8, 39]. For the oxides polarized at -1.7 V vs. SCE, the reaction rates for electron-hole recombination and interfacial reactions increased for all the oxides. However, the interfacial reaction rates for the oxides on the alloys were still lower than for the oxide on pure Ti.

Figure 8. Bode plots of I_{mod} vs. light modulation frequency for oxides of (a) Ti, (b) $\text{Ti}_{99}\text{Sn}_1$, and (c) $\text{Ti}_{99}\text{Cr}_1$ formed at potentials of 0.1 V vs. SCE, -0.4 V vs. SCE, and -1.7 V vs. SCE, overlaid with model predictions obtained from the model expressed in equation (24).

Table 8. Fit parameters for model predictions of the photocurrent response for each of the oxides in Figure 8.

Parameter	Oxide								
	Pure Ti			Ti ₉₉ Sn ₁			Ti ₉₉ Cr ₁		
	Formation potential vs. SCE/V								
	0.1	-0.4	-1.7	0.1	-0.4	-1.7	0.1	-0.4	-1.7
k ₁ /s ⁻¹	3500	4000	4000	550	700	1500	750	1000	900
k ₂ /s ⁻¹	2000	2000	3000	2000	2000	3000	2000	2000	3000
R/KΩ	0.22	0.13	12	1.4	1.3	270	1.3	1.1	220
C _S /μF	0.75	0.82	0.012	0.62	0.76	0.002	0.53	0.54	0.004
C _H /μF	77	80	3310	41	50	2710	73	94	2430

Measurements of the oxygen reduction reaction kinetics on each of the oxide surfaces using potentiodynamic polarization, as shown in Figure 4, indicate that the addition of these alloying elements suppressed the ORR. For example, at -0.8 V vs. SCE, a potential at which the oxygen reduction reaction would occur on these oxides, the currents obtained from the cathodic polarization experiments, summarized in Table 9, show that the cathodic current can be suppressed approximately 30-60% in a high pH environment.

Table 9. Comparison of reduction currents on the oxides of pure Ti, Ti₉₉Sn₁, and Ti₉₉Cr₁ at -0.8 V vs. SCE in 0.6 M NaCl + 0.01 M NaOH taken from the polarization curves.

Oxide	Reduction current/(A/cm ²)
Pure Ti	4.1×10 ⁻⁶
Ti ₉₉ Cr ₁	2.8×10 ⁻⁶
Ti ₉₉ Sn ₁	1.7×10 ⁻⁶

5. Summary and Conclusions

The oxide that forms on titanium is generally cathodic to the majority of steel and aluminum engineering alloys and so can contribute to galvanic corrosion under some environmental conditions. However, the experimental results presented above indicate that alloying titanium with low concentrations of certain other metals can reduce ORR kinetics on the oxide and thereby suppress galvanic corrosion. Previous work [9] examined the effect on cathodic kinetics of alloying low concentrations of several elements in titanium on natively formed oxides. This report focused on the effect of formation potential along with alloying on the ability of the oxide to catalyze reactions.

The results presented above support the hypothesis that the additions of the minor alloying elements to the alloy were incorporated into the oxide, as shown by the XPS measurements, and their presence altered the electrochemical behavior of the oxide without substantially changing its composition or semiconductor properties when the oxide was formed under potential control. However, an important caveat to this conclusion is that the oxide had to be exposed to a potential that remained in the potential-pH region in which TiO_2 was thermodynamically stable. Exposing the oxide to cathodic potentials at which Ti_2O_3 was favored to form introduced changes in the oxide capacitance and polarization resistance and shortened the band gap while increasing the ORR catalytic capability of the oxide.

However, because the physical and semiconductor properties of pure Ti were not significantly altered by low levels of alloying with Sn and Cr, only by using the IMPS technique – and employing a model with a sufficient number of parameters, including recombination rate, k_2 , reaction rate of interest, k_1 , and space-charge capacitance, C_S – was the mechanism for the catalytic behavior of the alloying elements adequately captured to permit comparison with theoretical predictions.

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