A mixture design approach to the service life and the oxygen evolving catalytic activity of Ru–Sn–Ti ternary oxide coated electrodes

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Ternary (Ru–Sn–Ti) oxide coatings on Ti substrates have been studied experimentally over their entire compositional range using the mixture design method. The results, involving the effects of calcination temperature and coating solution composition on service life and electrode oxygen evolving catalytic activity, are examined through regression models and response surface contour plots. The statistical equations effectively model the experimental results.

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1. Introduction

Over the past twenty years or so, there has been extensive interest in the electrochemical behaviour of a number of metallic-oxide coated electrodes consisting entirely of, or in proportions of, such compounds as RuO_2, IrO_2, SnO_2, Co_3O_4, etc. [1,2]. The most popular component of binary, ternary, etc., metallic-oxide electrodes is undoubtedly RuO_2, due to its high electrocatalytic activity in both chlorine and oxygen evolution [3]. Unfortunately, however, when a pure RuO_2 electrode is used under severe conditions, loss of active material, as a consequence of chemical and electrochemical corrosion, makes the process too expensive for technological applications. In order to overcome this problem, a binary $RuO_2 + TiO_2$ electrode, termed a dimensionally stable anode (DSA®) [4], was developed and successfully applied in the chlor-alkali industry. Although the $RuO_2 + TiO_2$ binary electrode, like the pure RuO_2 electrode, demonstrates good chlorine catalytic activity when used under acidic, anodic and oxygen evolving conditions, heavy corrosion (exemplified by RuO_2 to RuO_4 [5] oxidation and the formation of a nonconducting film of TiO_2 [6,7]) results. In yet another attempt at producing a long lasting chlorine/oxygen evolving electrode [8], additives, such as SnO_2 [9–11], ZrO_2 [12], IrO_2 [13–15], Ta_2O_5 [16,17] etc., were incorporated as a means of stabilizing RuO_2 during oxygen evolution. Of the additives, SnO_2 has proven cost effective and its presence has been claimed to improve selectivity for chlorine production [18–20].

Bandi *et al.* [21,22] compared the voltammetric properties of 20% Ru + 12% Sn + 68% Ti ternary, $RuO_2 + TiO_2$ binary, and pure RuO_2 coated electrodes. They found that the addition of SnO_2 to a RuO_2–TiO_2 electrode system makes it behave as if it had a higher RuO_2 content. Wagner *et al.* [23] studied, spectroscopically, the surface properties of an 15% Ru + 2% Sn + 83% Ti ternary electrode and reported that introduction of Sn (2%) to a RuO_2–TiO_2 anode enhances corrosion resistance of both the bulk ruthenium species and the Ti substrate interface. Recently, the effect of composition on the structural properties and the electrocatalytic activity of Ru–Sn–Ti ternary oxides were studied systematically as a function of the SnO_2 content [24–26]. Unfortunately, these experiments only focused on a constant value of Ru (30% Ru + x% Sn + (70 − x)% Ti), thereby severely limiting the scope of ternary system study. In order to gain the overall view, this paper statistically examines the stability as well as the catalytic oxygen evolving activity of various ternary oxide electrode systems by the mixture design method [27].

The strategy of the mixture design method is based on statistical theory, where a limited number of experiments are used in order to study the full range of the multicomponent system, the properties of which are then examined through polynomial regression models and contour plots. The composition against property contour plots shed an insight into the behaviour of these multicomponent systems. Although this approach is not new (see, for example, [28]), our study undertakes a systematic, statistically significant approach.

2. Statistical method

One of the principal problems to be solved in ternary metallic-oxide coated electrode systems is that of determining the optimal calcination temperature and composition of the coating solution, so that maximal electrochemical activity and stability is achieved. In most cases, a traditional approach is adopted, requiring a considerable expenditure of time and materials in the study of a number of test samples. Alternatively,

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a mixture design method can be used to study statistically, the properties of a multicomponent system. Such statistical methods have been used successfully in many industrial fields [29–33].

The mixture design method assumes that the properties of the electrode system are a function of its component (Ru, Sn, Ti) compositions. This relationship can be expressed as

$$\eta = f(y_1, y_2, \ldots, y_q),$$

where y_i ($i = 1, 2, \ldots, q$) is the molar proportion of these components. Since the sum of the proportions is unity, the experimental region can be represented by a regular simplex. For three components, this region is a triangle. The experimental region is explored at points of composition corresponding to an ordered arrangement known as a lattice. The lattice point results are represented by appropriate polynomials.

2.1. Mixture experiments with process variables

Process variables are factors in an experiment that do not form any portion of the mixture but whose levels, when changed, could affect the blending properties of the ingredients. In our case, the only process variable studied was the calcination temperature of the various sample systems.

As a means of determining the effects of this process variable on the mixture properties, a model combining compositions (y_i) and process variables (z_i) was subjected to regression analysis. A forward stepwise regression procedure was first used in order to choose an appropriate regression model with statistically significant parameters. A reparameterized model then enabled the effects of the process variables to be separated from the blending effects of the mixture components.

2.2. Pseudocomponents

Many experiments involving mixtures of components require at least a certain proportion of component i be present in all blends, i.e. $y_i \geqslant L_i \geqslant 0, i = 1, 2, \ldots, q$, so that the total range, $0 \leqslant y_i \leqslant 1$, of compositions is not explored. In these cases, the pseudocomponent, x_i, is often used as an alternative system of coordinates. It is defined as follows:

$$x_i = \frac{(y_i - L_i)}{(1 - L)}$$

where $L = \Sigma_{i=1}^{q} L_i$, and $\Sigma_{i=1}^{q} x_i = 1$.

In order to provide original component settings, the x_i design coordinates are then mapped back using the following relationship:

$$y_i = L_i + (1 - L)x_i$$

In this study, ruthenium pseudocomponent molar proportions that were $\geqslant 0.1$, were used because pure tin dioxide as well as titanium dioxide both possess low conductivities [34].

3. Experimental details

3.1. Preparation of electrodes

Oxide-coated electrodes of variable composition were prepared by the thermal decomposition of the following precursors: $RuCl_3 \cdot xH_2O$ (Johnson Matthey), $SnCl_2 \cdot 2H_2O$ (Wako Chemicals, Japan), and Ti-$(OC_4H_9)_4$ (Strem Chemicals, USA). The precursors, in the appropriate molar ratios (refer to Table 1), were dissolved in an isopropanol solution containing 10% by volume concentrated HCl, giving a 0.5 M total solution. The titanium supports were first degreased with soap and water, then etched for 1 h in a 3 M HCl solution at 80 to 90° C, followed by the formation of the desired layers of the mixed Ru, Sn and Ti oxides. These layers were formed by baking the etched plate at 85° C for several min. after it was dipped in its respective coating solution. After drying, the supports were heated under air flow at the chosen annealing temperature (either 400 or 500° C (Table 1)) for 10 min. This process was repeated five times and the final heating was carried out at the annealing temperature for 1 h. The amount of oxide (0.8–1.0 mg cm^{-2}) formed on the titanium supports was determined by weight.

3.2. Electrochemical characterization

The electrochemical characteristics of the prepared electrodes were investigated by cyclic voltammetry and potentiostatic techniques using a BAS-100B potentiostat/galvanostat system (Bioanalytic System, Inc., USA). An Ag/AgCl electrode (Argenthal, 3 M KCl, 0.207 V vs S.H.E. at 25° C) was used as the reference, while a platinum wire was employed as the counter electrode. A Luggin capillary, whose tip was set at a distance of about 1 mm from the surface of the working electrode, was used to minimize errors due to iR drop in the electrolytes. Voltammetry was carried out between 0.0 and 1.4 V vs R.H.E. at 100 mV s^{-1}. In the steady-state oxygen evolution experiments, the electrode current density was measured 10 min after the desired potential was reached. Note that these values are not iR corrected. Since it is important that a given catalyst demonstrate high activity under practical operating conditions, the oxygen evolving activity of the various electrodes were compared at high Tafel slope regions (1.6 V vs R.H.E.).

All solutions used in this work were prepared with doubly distilled water. In addition, the 0.5 M H_2SO_4 solution used for studying both the electrochemical behaviour and the electrocatalytic activities of oxygen evolution on the oxide-coated electrodes, was degassed before and during the experiments with purified nitrogen gas. Solution temperature was maintained at 25° C (with an accuracy of 0.05° C) by means of a water thermostat (HAAKE D8 and G).

3.3. Stability tests

The accelerated life tests of the electrodes were carried

Table 1. Design matrix and experimental results of Ru–Sn–Ti ternary electrodes.

Electrode	Solution composition			Pseudocomponent			x z^*	Current[†] $mA\,cm^{-2}$	Service[‡] life/h
	y_1 (Ru)	y_2 (Sn)	y_3 (Ti)	x_1	x_2	x_3			
1	1	0	0	1	0	0	−1	18.50	7.26
2	0.1	0.9	0	0	1	0	−1	1.20	2.37
3	0.1	0	0.9	0	0	1	−1	0.49	1.83
4	0.4	0.3	0.3	1/3	1/3	1/3	−1	5.60	7.13
5	0.55	0.45	0	1/2	1/2	0	−1	9.00	15.02
6	0.1	0.45	0.45	0	1/2	1/2	−1	0.70	1.05
7	0.55	0	0.45	1/2	0	1/2	−1	3.00	4.12
8	0.7	0.15	0.15	2/3	1/6	1/6	−1	9.40	7.50
9	0.25	0.6	0.15	1/6	2/3	1/6	−1	6.00	6.80
10	0.25	0.15	0.6	1/6	1/6	2/3	−1	3.20	3.05
11	0.775	0.225	0	3/4	1/4	0	−1	10.50	10.67
12	0.325	0.675	0	1/4	3/4	0	−1	5.00	9.37
13	0.775	0	0.225	3/4	0	1/4	−1	6.00	5.15
14	0.325	0	0.675	1/4	0	3/4	−1	1.90	4.20
15	0.1	0.675	0.225	0	3/4	1/4	−1	0.98	2.75
16	0.1	0.225	0.675	0	1/4	3/4	−1	0.63	1.60
17	1	0	0	1	0	0	1	7.30	4.00
18	0.1	0.9	0	0	1	0	1	0.62	2.17
19	0.1	0	0.9	0	0	1	1	0.10	2.01
20	0.4	0.3	0.3	1/3	1/3	1/3	1	3.20	13.83
21	0.55	0.45	0	1/2	1/2	0	1	4.60	34.50
22	0.1	0.45	0.45	0	1/2	1/2	1	0.24	1.01
23	0.55	0	0.45	1/2	0	1/2	1	2.30	7.67
24	0.7	0.15	0.15	2/3	1/6	1/6	1	5.75	12.75
25	0.25	0.6	0.15	1/6	2/3	1/6	1	2.50	11.95
26	0.25	0.15	0.6	1/6	1/6	2/3	1	1.22	9.02
27	0.775	0.225	0	3/4	1/4	0	1	6.20	15.50
28	0.325	0.675	0	1/4	3/4	0	1	2.30	37.80
29	0.775	0	0.225	3/4	0	1/4	1	3.60	4.50
30	0.325	0	0.675	1/4	0	3/4	1	1.02	4.90
31	0.1	0.675	0.225	0	3/4	1/4	1	0.39	1.50
32	0.1	0.225	0.675	0	1/4	3/4	1	0.35	1.15

[*] Calcination temperature ($z = -1 = 400°C$; $z = 1 = 500°C$)
[†] Current density at $1.6\,V/RHE$ in $1\,N\,H_2SO_4$ at $25°C$
[‡] Under anodization at $500\,mA\,cm^{-2}$ in $2\,N\,H_2SO_4$ at $30°C$

out in $1\,M\,H_2SO_4$ in simple undivided glass cells at $30°C$, under an anodic current density of $500\,mA\,cm^{-2}$, with two titanium cathodes as counter electrodes. Normally, cell voltage was approximately $3.7\,V$ under these conditions. The end of electrode service life was taken to be the time at which the cell voltage had tripled. In order to improve the reproducibility of the results, three separate tests were run and the results averaged for statistical analysis.

4. Results and discussion

4.1. Electrocatalytic activity

The electrocatalytic activities of the prepared electrodes were evaluated on the basis of their relative current densities at a constant electrode potential ($1.6\,V/RHE$) and are listed together with the design matrix (electrode configuration) in Table 1. Coefficients of the regression equations for the fourth degree approximation model were calculated from current densities (i) in Table 1 with the aid of the appropriate formulae [27]. The regression equations for the current densities of the electrodes (calcined at 400 and

$500°C$) are of the following form:

$$i_{400} = 17.64x_1 - 24.43x_1x_3 + 3.87x_2x_3$$
$$(0.66) \quad\quad (2.83) \quad\quad\quad (2.36)$$

$$- 17.71x_1x_2(x_1 - x_2) - 24.60x_1x_3(x_1 - x_3)$$
$$(6.86) \quad\quad\quad\quad\quad\quad (6.26)$$

$$+ 133.03x_1^2x_2x_3 + 103.61x_1x_2^2x_3 \quad\quad (1)$$
$$(88.18) \quad\quad\quad (86.78)$$

$$i_{500} = 7.24x_1 + 0.60x_2 + 2.32x_1x_2$$
$$(0.23) \quad\quad (0.17) \quad\quad (0.94)$$

$$- 5.98x_1x_3 + 3.95x_1x_2(x_1 - x_2)$$
$$(0.85) \quad\quad\quad (1.75)$$

$$- 5.12x_1x_3(x_1 - x_3) + 68.22x_1x_2x_3$$
$$(1.84) \quad\quad\quad\quad\quad (13.61)$$

$$- 99.83x_1x_2x_3^2 \quad\quad (2)$$
$$(35.94)$$

The numbers in parentheses below the coefficients are their standard errors based on error variance estimates (s^2 = mean square of error = 0.77 and 0.06 for i_{400} and i_{500}, respectively). The analysis of variance for i_{400} and i_{500} are shown in Tables 2 and 3, respectively. The test statistics, F and R^2_{adj}, are defined as

Table 2. The analysis of variance for the fit of current densities for electrodes that had been calcined at 400° C ($z = -1$).

Source	d.f.	Sum of squares	Mean square	F value
Model	7	769.64	109.95	142.25
Error	9	6.96	0.77	
Total	16	776.60		

$R^2 = 0.9910$; $R^2_{adj} = 0.9841$

$F = MSR/MSE$ and $R^2_{adj} = 1 - (SSE/(N - P)/SST/(N - 1))$, where MSR is the mean square of regression, obtained by dividing the sum of squares of regression with the degrees of freedom (d.f. $= P =$ number of parameters). MSE represents the mean square error from the analysis of variance. If the calculated value of F is greater than that of the table $F(P - 1, v, 1 - \alpha)$ value, then a 'statistically significant' regression model is obtained, where $v = N - P$ is the degrees of freedom of error and N is the number of experiments. $F(P - 1, v, 1 - \alpha)$ is the F value at the α probability level. R^2_{adj} is a measure of the reduction in the estimate of the error variance due to the fitting of the model, $SSE/(N - P)$, relative to the estimate of the error variance based on fitting the simple model $y = \beta_0 + \varepsilon$ [27]. A R^2_{adj} value close to 1 means a perfect fit to the experimental data.

The regression Equations 1 and 2, were used in constructing composition against property diagrams (Figs 1 and 2), which facilitate straightforward interpretations of the properties of both two and three-component systems. An examination of Figs 1 and 2 reveals a decrease in current density with increasing Ti and Sn content in an RuO_2 coated electrode, and that the activities of Ru–Sn binary electrodes are higher than those of the Ru–Ti type. The latter result can be partially explained by the fact that Ru–Sn binary electrodes possess higher surface area and higher conductivities due to lower crystallinities and smoother, more compact morphologies, respectively than their Ru–Ti counterparts [24]. In addition, RuO_2 experiences a closer, more intimate mixing with TiO_2 due to similar lattice parameters [24] than with SnO_2; a result that depresses activity in the former system [25,26].

The magnitudes of the regression equation coefficients compared to their estimated standard errors are used as a basis for judging statistical significance and illustrate the relative effects of linear and nonlinear blending properties on the current densities for oxy-

Table 3. The analysis of variance for the fit of current densities for electrodes that had been calcined at 500° C ($z = 1$).

Source	d.f.	Sum of squares	Mean square	F value
Model	8	188.78	23.60	413.91
Error	8	0.46	0.06	
Total	16	189.24		

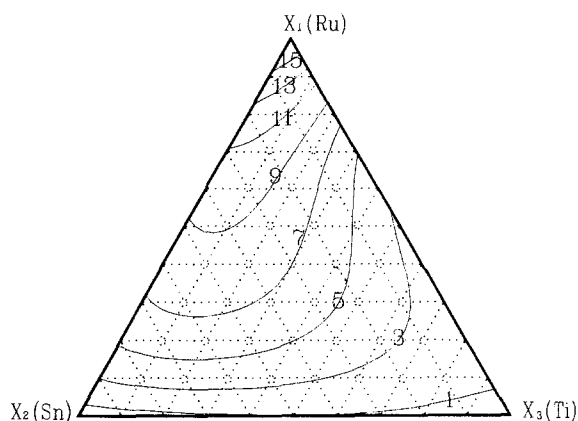$R^2 = 0.9976$; $R^2_{adj} = 0.9951$

Fig. 1. Constant current density ($mA\,cm^{-2}$) contour lines against Ru–Sn–Ti ternary oxide electrode compositions (calcined at 400° C). Current was measured at 1.6 V/RHE in 0.5 M H_2SO_4 at 25° C.

gen evolution. The main effect of RuO_2 on current density is indicated by the magnitude of the coefficient associated with the x_1 term, which is 17.64 and 7.24 for i_{400} and i_{500}, respectively, while for TiO_2, the main effect is represented by the magnitude of the coefficients associated with the $x_1 x_3$ and $x_1 x_3 (x_1 - x_3)$ terms, which are -24.43, -24.60 and -5.98, -5.12 for i_{400} and i_{500}, respectively. Similarly, the main effect of SnO_2 on current density, indicated by the magnitude of the coefficients associated with the $x_1 x_2 (x_1 - x_2)$ term, is -17.71 and 3.95 for i_{400} and i_{500}, respectively. An examination of these coefficients reveals that the addition of Ti into an Ru oxide based electrode decreases current density (oxygen evolving activity) to a much greater degree than does the introduction of Sn. This result is also corroborated by the electrode cycle voltammetric behaviour illustrated in Fig. 3. In the transition region, both the Ru–Sn binary and the RuO_2 electrodes exhibit two pairs of peaks, p_1 and p_2, which represent the Ru(III)/Ru(IV) and Ru(IV)/Ru(VI) redox reactions, respectively. Note however, that although those peaks resulting from the former electrode are retarded somewhat in comparison
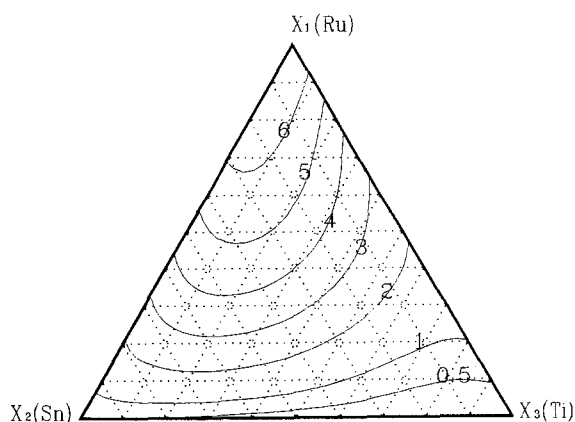

Fig. 2. Constant current density ($mA\,cm^{-2}$) contour lines against Ru–Sn–Ti ternary oxide electrode compositions (calcined at 500° C). Current was measured at 1.6 V/RHE in 0.5 M H_2SO_4 at 25° C.
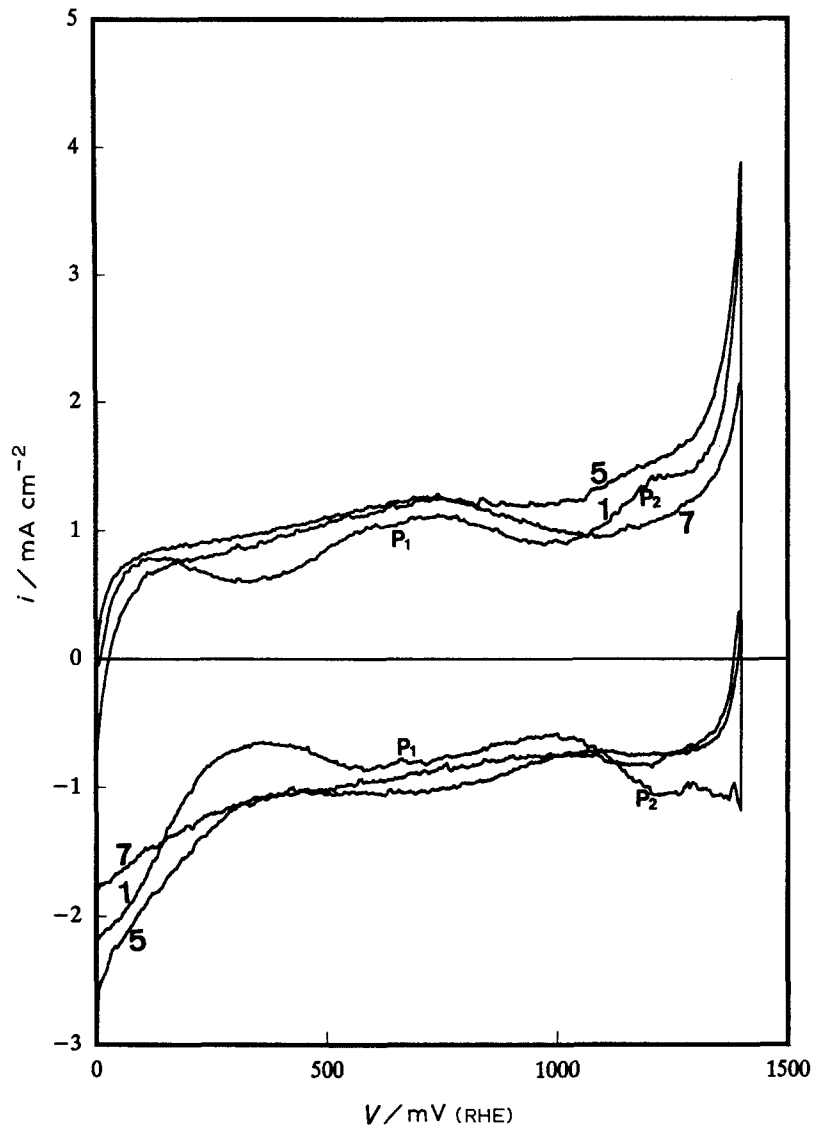
Fig. 3. Cyclic voltammograms of RuO_2, $RuO_2 + SnO_2$ and $RuO_2 + TiO_2$ electrodes with a scan rate of $100\,mV\,s^{-1}$. The curve numbers indicate the following different electrode compositions: (1) pure RuO_2; (5) RuO_2 55% + SnO_2 45% (7) RuO_2 55% + TiO_2 45% (from Table 1).

to the latter, for the Ru–Ti binary electrodes, the Ru(III)/Ru(IV) redox reaction is depressed to a much greater degree, while the Ru(IV)/Ru(VI) transition, which is thought to catalyse oxygen evolution [3,35], is absent. These results are similar to those obtained previously by Trassatti *et al.* [25].

In order to illustrate the effect of calcination temperature on linear and nonlinear blending properties of the components, a model combining process variables and composition was constructed and subjected to regression analysis.

A stepwise regression procedure was utilized in determining the 'best' regression model [36]; the selection of which was based on correlation coefficient (R^2) and C_P criteria and gave the following regression equation:

$$i = 12.34x_1 + 0.88x_2 - 14.34x_1x_3$$
$$(0.34) \quad (0.88) \quad (1.45)$$

$$- 13.06x_1x_3(x_1 - x_3) + 160.04x_1x_2^2x_3$$
$$(3.14) \quad (29.08)$$

$$- 5.54x_1z + 3.74x_1x_2z + 9.98x_1x_3z$$
$$(0.45) \quad (1.61) \quad (1.61)$$

$$- 32.57x_1x_2x_3z + 10.78x_1x_2(x_1 - x_2)z$$
$$(11.42) \quad (3.17)$$

$$+ 10.32x_1x_3(x_1 - x_3)z \quad (3)$$
$$(3.17)$$

The analysis of variance is summarized in Table 4. The values of the test statistics, F and R^2_{adj}, indicate that the regression model is statistically significant. The C_P

Table 4. The analysis of variance for the combined model of current density, involving calcination temperature and coating solution composition

Source	d.f.	Sum of squares	Mean square	F value
Model	11	957.12	87.01	209.564
Error	21	8.72	0.42	
Total	32	965.84		

$R^2 = 0.9910$; $R^2_{adj} = 0.9862$; $C_P = 10.91$

Table 5. The analysis of variance for the reparameterized model of current density, involving calcination temperature and coating solution composition

Source	d.f.	Sum of squares	Mean square	F value
Model	13	957.68	73.67	171.58
Error	19	8.16	0.43	
Total	32	965.84		

$R^2 = 0.9916$; $R^2_{adj} = 0.9858$; $C_P = 13.56$

statistic, defined as

$$C_P = \frac{RSS_P}{s^2} - (N - 2P)$$

where RSS_P is the residual sum of squares of the regression model containing P terms, and s^2 is an estimate of the error variance, gives an indication of regression model bias. Since the value of C_P (10.91) is close to the number of terms ($P = 11$), the regression model is considered to possess negligible bias.

The coefficients associated with the terms, $x_1 x_i z$ and $x_1 x_i (x_1 - x_i) z$ ($i = 2, 3$) (see Equation 3) effectively model the binary oxide system in which depression of current density in electrodes calcined at 400°C is greater among the different (binary) compositions than in those calcined at 500°C (refer to Table 1). In order to isolate the main effect of the process variable, a reparameterized form of the combined model was undertaken. Substitution of $(1 - x_2 - x_3)z$ for $x_1 z$ in Equation 3, allows x_1 to serve as a baseline from which the effects of the process variable can be referenced. The same regression procedure used in Equation 3, generated the following equation:

$$
\begin{aligned}
i = & -5.52z + 5.23x_2 z + 5.35x_3 z + 4.41x_1 x_2 z \\
& (0.45) \quad (0.58) \quad\;\; (0.58) \quad\;\; (1.84) \\[4pt]
& + 10.36x_1 x_3 z - 30.53x_1 x_2 x_3 z \\
& \;(1.84) \quad\quad\;\; (11.75) \\[4pt]
& + 9.82x_1 x_2 (x_1 - x_2)z + 9.72x_1 x_3 (x_1 - x_3)z \\
& \;(3.42) \quad\quad\quad\quad\quad\;\; (3.42) \\[4pt]
& + 12.34x_1 + 0.88x_2 - 14.34x_1 x_3 \\
& \;(0.34) \quad\;\; (0.29) \quad\;\; (1.47) \\[4pt]
& - 13.06x_1 x_3 (x_1 - x_3) + 160.04x_1 x_2^2 x_3 \quad (4) \\
& \;(3.20) \quad\quad\quad\quad\quad (29.57)
\end{aligned}
$$

The analysis of variance is summarized in Table 5. The -5.52 coefficient value of the process variable reflects the fact that a pure RuO_2 electrode's catalytic oxygen evolving activity decreases as the calcination temperature increases from 400 to 500°C. At high temperature (500°C), this result is attributed to the fact that the surface area of an RuO_2 coated electrode decreases [35] and to the growth of an insulating film on the Ti support resulting from interdiffusion at the solid/solid interface during calcination [37]. The coefficient associated with the terms, $x_i z$ ($i = 2, 3$) (see Equation 4) effectively model the situation in which the relative difference in current densities, corresponding to a depression in current densities between RuO_2

Table 6. The analysis of variance for the fit of service life for electrodes that had been calcined at 400°C ($z = -1$)

Source	d.f.	Sum of squares	Mean square	F value
Model	6	713.00	118.83	115.218
Error	10	10.31	1.03	
Total	16	723.31		

$R^2 = 0.9857$; $R^2_{adj} = 0.9772$

electrodes calcined at 400 and 500°C, is greater than in Ru10% − Sn 90% as well as Ru10% − Ti 90% systems calcined at the above temperatures (refer to Table 1).

4.2. Coating stability

The results of the accelerated coating stability tests are given in the last column of Table 1. The regression equations for the service life of the electrodes fabricated at calcination temperatures of 400 and 500°C are of the following forms:

$$
\begin{aligned}
SL_{400} = & \;6.45x_1 + 2.79x_2 + 2.17x_3 + 33.89x_1 x_2 \\
& (0.87) \quad\;\; (0.87) \quad\;\; (0.87) \quad\;\; (3.84) \\[4pt]
& - 0.57x_1 x_3 - 3.91x_2 x_3 \quad\quad\quad\quad (5) \\
& \;(3.84) \quad\quad\; (3.84)
\end{aligned}
$$

$$
\begin{aligned}
SL_{500} = & \;3.19x_1 + 2.14x_2 + 126.94x_1 x_2 + 19.98x_1 x_3 \\
& (1.03) \quad\;\; (0.81) \quad\;\; (4.32) \quad\quad\;\; (3.89) \\[4pt]
& + 343.58x_1 x_2 x_3 - 124.13x_1 x_2 (x_1 - x_2) \\
& \;(63.12) \quad\quad\quad\; (8.86) \\[4pt]
& - 1422.04x_1 x_2^2 x_3 \quad\quad\quad\quad\quad\quad\quad (6) \\
& \;(167.69)
\end{aligned}
$$

The analysis of variance is summarized in Tables 6 and 7. The value of the test statistics, F and R^2_{adj}, indicate that the regression model is statistically significant.

The dependence of the service life of electrodes fabricated at calcination temperatures of 400 and 500°C on composition for Ru–Sn–Ti ternary oxide systems are shown in Figs 4 and 5, respectively. An examination of Fig. 4 reveals that a 13 h maximum electrode service life occurs midway along the line that represents an Ru–Sn binary electrode; in other words, at an approximate electrode composition of 50% in both Ru and Sn. Note that electrode service life decreases with increasing Ti content. In Fig. 5, note that electrode (calcined at 500°C) service life contour

Table 7. The analysis of variance for the fit of service life for electrodes that had been calcined at 500°C ($z = 1$)

Source	d.f.	Sum of squares	Mean square	F value
Model	7	3558.23	508.32	411.71
Error	9	11.11	1.23	
Total	16	3569.34		

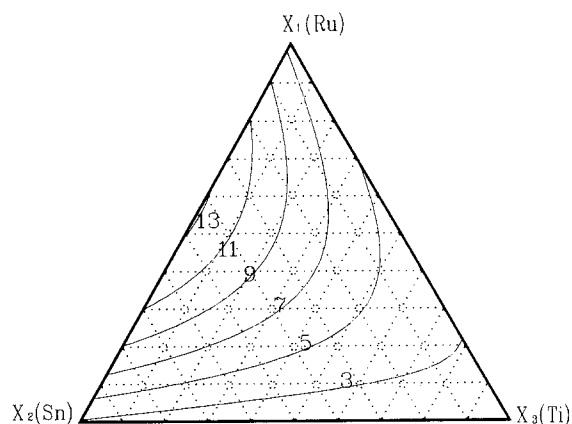$R^2 = 0.9969$; $R^2_{adj} = 0.9945$

Fig. 4. Constant service life (h) contour lines against Ru–Sn–Ti ternary oxide electrode compositions (calcined at 400° C), under an anodic current density of 500 mA cm^{-2} in 1 M H$_2$SO$_4$ at 30° C.

lines cover a much greater range than those in Fig. 4, reaching a maximum value of about 30 h in Ru–Sn binary systems possessing 30 $\sim$ 55% Ru composition. Also, note that in all cases (Figs 4 and 5), the service life of Ru–Ti binary electrodes are lower than their Ru–Sn counterparts. As scanning electron microscope (SEM) photographs attest [9], the morphology of an Ru–Sn binary electrode is smoother and more compact than that of a Ru–Ti system, contributing to a longer life by depressing penetration and migration of electrolytes and oxygen through surface pores and cracks [6,38]. The formation of a non-conducting oxide layer due to oxygen chemisorption during anodic oxygen evolution, is a serious cause of activity loss in RuO$_2$–TiO$_2$ binary electrodes [6,7].

Equation 5 accurately describes the service life of an electrode calcined at 400° C. The magnitude of the coefficient associated with the $x_1 x_2$ term (33.89) represents the synergistic effect of composition ($x_1 = x_2 = 1/2$) on the service life (13 h) of this particular binary oxide system. In Equation 6, where calcination temperature is now 500° C, the magnitude of the coefficients associated with the $x_1 x_2$ and $x_1 x_2 (x_1 - x_2)$ terms (126.94 and -124.13, respectively) effectively model the situation in which the maximum value of
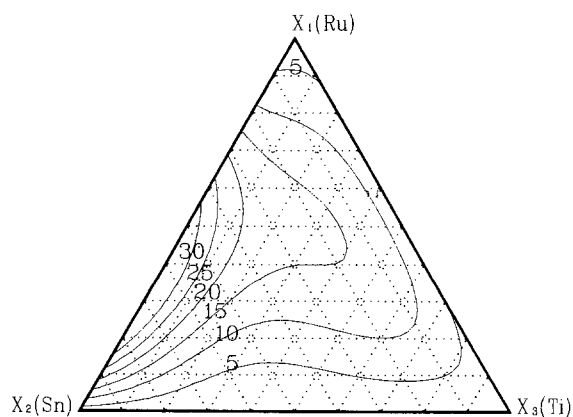

Fig. 5. Constant service life (h) contour lines against Ru–Sn–Ti ternary oxide electrode compositions (calcined at 500° C), under an anodic current density of 500 mA cm^{-2} in 1 M H$_2$SO$_4$ at 30° C.

Table 8. The analysis of variance for the combined model of service life, involving calcination temperature and coating solution composition

Source	d.f.	Sum of squares	Mean square	F value
Model	13	4267.13	328.24	244.30
Error	19	25.53	1.34	
Total	32	4292.66		

$R^2 = 0.9941$; $R^2_{adj} = 0.9900$; $C_P = 12.72$

service life in the Ru–Sn binary system occurs in the $x_1 = 25 \sim 50\%$ (Ru $= 32.5 \sim 55\%$) compositional range. The magnitude of the coefficient associated with the $x_1 x_2^2 x_3$ term (-1422.04) accurately describes the depression in the service life contour plot at the composition $x_1 = x_3 = 1/6, x_2 = 2/3$, indicating that the addition of Ti into Ru–Sn binary oxide systems depresses their service lives significantly. According to the above discussions, the enhancement of service life in Ru–Sn binary oxides can be attributed to: (i) the surface morphology; and (ii) the formation of a stable Ru–Sn compound [9] that supresses the dissolution of the active layer.

A stepwise regression model combining calcination temperature and compositional effects on electrode service life generated the following equation:

$$SL = 5.04x_1 + 1.86x_2 + 1.52x_3 + 82.30x_1 x_2$$
$$\quad (0.76) \quad (0.63) \quad (0.60) \quad (3.19)$$

$$+ 9.08x_1 x_3 - 61.66x_1 x_2(x_1 - x_2)$$
$$\quad (3.23) \quad (6.19)$$

$$- 471.64x_1 x_2^2 x_3 + 213.96x_1 x_2 x_3^2$$
$$\quad (74.42) \quad (73.88)$$

$$+ 41.79x_1 x_2 z - 62.93x_1 x_2(x_1 - x_2)z$$
$$\quad (2.24) \quad (6.18)$$

$$+ 203.99x_1^2 x_2 x_3 z - 556.45x_1 x_2^2 x_3 z$$
$$\quad (84.18) \quad (84.18)$$

$$+ 240.06x_1 x_2 x_3^2 z \qquad\qquad (7)$$
$$\quad (74.27)$$

The analysis of variance is summarized in Table 8. Both F and R^2_{adj} values indicate that the regression model is statistically significant. In addition, the C_P statistic ($C_P = 12.72$) indicates that the fitted model possess negligible bias.

The influence of calcination temperature on electrode service life appeared in the binary [$x_1 x_2 z$, $x_1 x_2 (x_1 - x_2)z$] and the ternary [$x_1^2 x_2 x_3 z$, $x_1 x_2^2 x_3 z$, $x_1 x_2 x_3^2 z$] blending properties of these ternary systems. Since, the effect of temperature on the service life of pure components (x_i, $i = 1, 2, 3$) is negligible, the $x_i z$ were not included in Equation 7.

The service life of the oxide-coated electrodes depends not only on the composition of coating solution but also on the calcination temperature. Maximum electrode service life occurs predominately in Ru–Sn binary systems. For electrodes that had been calcined at 400° C, 55 $\sim$ 60% Ru content generated maximum service life values (13 h), while for those that had been

calcined at 500°C, only 30 ~ 55% Ru content was necessary for long service lives (30 h). Iwakura *et al.* [9] reported that for an electrode that had been calcined at 450°C a maximum service life of 12 h was obtained with an aqueous coating solution composition of 30% Ru–70% Sn. The high service life value at a low Ru composition achieved in Iwakura's electrode may have resulted from: (i) different calcination temperatures and (ii) different decompositional yields of SnO_2 [39] obtained from $SnCl_2 \cdot 2H_2O$ in a non-aqueous solution (this work) and $SnCl_4$ in an aqueous solution in Iwakura's case. In both cases, it is believed that a stable compound of Ru–Sn binary oxide may form, leading to depression of active layer anodic dissolution [9].

5. Conclusions

The results of the mixture design method were subjected to regression analysis. These results, plotted as contour diagrams, were extremely useful in studying the effects of calcination temperature and coating solution composition on the service life and activity of Ru–Sn–Ti ternary oxide-coated electrodes. The catalytic oxygen evolving activity of an RuO_2 coated electrode decreases with increasing Ti and Sn content, with the activity of a Ru–Sn binary electrode being higher than that of its Ru–Ti counterpart. The coefficients associated with the binary terms in regression Equation 3 (see text) effectively model the binary oxide system in which depression of current density in electrodes calcined at 400°C is greater among the different (binary) compositions than in those calcined at 500°C. The effect of calcination temperature on activity can be separated from the reparameterized model of regression Equation 4 (see text), the coefficient of which indicates that oxygen evolving catalytic activity of pure RuO_2 electrode decreases as the calcination temperature increases. In all cases, the service lives of Ru–Sn binary electrodes are consistently higher than their Ru–Ti counterparts. Maximum electrode service life occurs predominately in Ru–Sn binary systems. For electrodes that had been calcined at 400°C, 55 ~ 60% Ru content generated maximum service life values, while for those that had been calcined at 500°C, only 30 ~ 55% Ru content was necessary for long service lives. In all cases, service life decreased with increasing Ti electrode content.

Acknowledgement

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