A STUDY OF THE FAILURE MECHANISM OF CHLORINE ANODES

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Thin coating RuO₂-TiO₂ electrodes, which mimic the DSA anodes, have been prepared and tested for their activity toward the chlorine evolution reaction and subjected to lifetime testing. Rutherford Backscattering Spectrometry has been used concurrently with electrochemical measurements to analyze changes in the ruthenium content of the coating. The decrease in electrode activity is found to be closely related to a decrease in Ru content, and the measured profiles indicate that the loss takes place across the thin coating. Failure is observed for electrodes with a Ru content below a critical concentration, but there is no evidence for the build up of a pure TiO₂ layer. AFM imaging of an anode after failure sustained the hypothesis of loss of material.

Keywords: Rutherford Backscattering Spectrometry, A.C. Impedance, AFM, RuO₂, TiO₂
INTRODUCTION

Anodes of the chlorine reaction are typically mixed oxides of Ru, Ir, Ta, Sn and titanium. Ruthenium oxide must be present in large quantity because it is the most efficient catalyst, but other oxides are needed for the stability of the electrode. The most widely used anodes in the chlor-alkali industry are the RuO$_2$-TiO$_2$ coated titanium electrodes$^1$, commonly referred to in the industry as DSA (dimensionally stable anode) electrodes$^2$. These electrodes exhibit a long life and operate at a low chlorine overpotential and at a high efficiency. However, upon prolonged use, deactivation of these anodes occurs resulting in high chlorine overvoltages. The loss of anode activity appears to be related to the loss of RuO$_2$ from the coating resulting in the formation of a poorly conducting TiO$_2$-rich oxide or of an insulating TiO$_2$ layer.

Keywords: Rutherford Backscattering Spectrometry, A.C. Impedance, AFM, RuO$_2$, TiO$_2$
The purpose of this study is to characterize and locate these non-conducting entities in the coating in order to design new preparation procedures for improved electrodes. Because of the technological importance of the reaction, many electrochemical investigations were made and mechanisms were proposed based on observations of effects from various factors related to the electrolyte and the electrode surface such as preparation method, catalyst concentration, surface porosity, etc. However, the most sophisticated electrochemical measurements only can give the overall result of complex mechanisms occurring concurrently and on various time scales at the electrode/solution interface. The electrochemical measurements usually are analyzed in terms of an infinitely thin smooth surface which defines the electrode/solution interface. In reality, the mixed oxide anodes are porous, and the electrochemical reaction occurs at different depths in the porous structure. There is a need for probing the electrode surface by alternative methods sensitive to the chemistry and to the structure of the surface.

Recent progresses in the understanding of anodes performance have been made by concurrent use of various techniques, probing different depths, and/or amenable to depth profiling. Electrode surfaces, "as produced", have been observed by SEM/EDX to assess their porosity and the catalyst repartition at the surface. These investigations showed a cracked-mud structure with cracks deep enough to uncover the titanium support. The EDX mapping of elements gave only a quantitative overview of the local composition at the surface. It should be noted that EDX may probe the material too deep to be relevant to the electrochemical process. Therefore, the relation between an EDX mapping and the performance of an electrode may not be straightforward in terms of number of catalytic species displayed. The XPS technique has been the most used because of its chemical specificity and of its potential for depth profiling. However, XPS analysis is difficult for ruthenium, a key element in chlorine anodes, because of overlapping of the ruthenium and carbon peaks. On the other hand, caution must be exercised with results from depth profiling analysis because the argon sputtering beam reacts with the surface, notably by reducing titanium oxide. Improved results can be expected from this technique with angle resolved measurements and with systems sensitive enough to rely on a secondary ruthenium peak. Auger spectroscopy has been used to analyze the surface of anodes. The method has the
advantage of probing a small volume under the surface, but can not deliver a chemical analysis. Problems with the overlapping of the ruthenium and carbon peaks have been resolved by considering the symmetry of the peaks and by reducing the size of the electron beam\textsuperscript{13}. Scanning Auger Spectroscopy with a microprobe (0.6\(\mu\)m)\textsuperscript{13} has recently produced images of RuO\(_2\)-TiO\(_2\) anodes which could be related with the topography of SEM images and which were much sharper than EDX elemental mappings. Segregation of RuO\(_2\) was studied by this method. Rutherford Backscattering Spectrometry (RBS) has the advantage to allow a non-destructive and accurate depth profiling over a few thousand Angstroms. The method is widely used in studies of layered structures, but rarely in the characterization of mixed oxide anode materials. The experimental spectra can be simulated\textsuperscript{14} by using the stopping powers and ranges of helium in different elements\textsuperscript{14}, and consequently there is no need for preparing standards of known compositions. The recent application of RBS\textsuperscript{16} to a SnO\(_2\)-IrO\(_2\) coating gave compositions sustained by analysis by inductively coupled plasma emission spectroscopy (ICPES).

In this study, electrodes, which mimic the DSA anodes, have been prepared, tested for their activity toward the chlorine evolution reaction, and subjected to life time testing. Electrochemical data, taken at different times during electrolysis, including for an electrode after failure, will be presented and compared to depth profiling analyses of the mixed oxide anode by Rutherford Backscattering Spectrometry (RBS). Finally, Atomic Force Microscopy (AFM) images of the electrodes at different stages of deactivation will provide indications of related surface morphology changes.

**EXPERIMENTAL**

**Preparation procedure**

Samples with an oxide layer thickness of a few thousands Angstroms were prepared on titanium plates. The preparation procedure includes all the steps used for industrial DSA anodes, but was modified in order to produce thinner mixed oxide layers amenable to characterization by RBS. The titanium plate surface first was carefully cleaned by a
combination of beadblasting with SiC, immersion in trichloroethylene, etching by a 10% oxalic + 18% HCl mixture at 90°C and rinsing with water and methanol. Dilute solutions of RuCl₃ and TiCl₃ in ethanol (with 40:60 wt% Ru:Ti) were used to coat the surface. After each coating the samples were fired at 430-450°C. Two sets of electrodes were produced with different dilutions of the chloride solution and different numbers of coatings. They were intended to provide guidelines for controlling the thickness of resulting oxide layers. These electrodes have been analyzed by X-ray fluorescence (XRF) to estimate the Ru concentration (in Ru g m⁻²). One of these electrodes has been submitted to accelerated life tests in a 0.5 M H₂SO₄ solution at a constant anodic current of 0.5A cm⁻² at 25°C. Samples, removed at different times during the electrolysis, were subjected to electrochemical tests and analyzed by Rutherford Backscattering Spectrometry in an effort to correlate the composition changes in the oxide with the observed increase in the cell voltage. Table I lists the electrodes, for which RBS and impedance results will be discussed, together with the preparative procedure and other available characterization data.

**Rutherford Backscattering Spectrometry**

The Rutherford Backscattering Spectrometry (RBS) technique can probe depths of several thousands Angstroms by analyzing the energy of a high energy ⁴He beam after its interaction with a solid. The results presented include the analysis of as-prepared electrodes produced with different procedures, the comparison of RBS estimated Ru loadings to loadings measured by XRF and, the analysis of Ru content in one anode at different times of galvanostatic use.

The Rutherford Backscattering experiments were done with a 2MeV ⁴He beam impinging normally on the electrode surface and an energy sensitive collector placed in such a way that the scattering angle is fixed at 160°. The energy resolution of the detector is on the order of 20 keV and the solid angle of the detector is on the order of 2-3 degrees. In this configuration, the 2 MeV beam, after colliding (elastic collision) with a Ru atom at the surface, typically is detected at an energy of 1.715 MeV. The elastic energy loss decreases with increasing atomic mass and the energy scale can be converted readily into an atomic
mass scale for the scattering surface atoms. In reality, the obtained spectra are more difficult to interpret because the $^4\text{He}$ beam penetrates inside the solid and collides with atoms situated at various distances from the surface. The energetic $^4\text{He}$ beam, during its travel in the sample, is slowed down by electronic forces and consequently the backscattered beam is observed with a variety of energies lower than that corresponding to a surface atom. In fact, the resulting spectra consist of peaks with width and shape reflecting the concentration of scattering atoms below the surface as well as at the surface. The interaction of the beam with a solid can be reasonably well calculated near the surface, but the results become less accurate as the beam is slowed down. Practically, the calculation is good over about 1000 to 2000 Å. Figure 1 illustrates this fact by comparing the spectra obtained for a near-monolayer film of gold deposited on carbon and for a heterostructure including a 1000Å thick platinum film on top of a 200Å thick titanium film. The gold monolayer peak is very sharp with a leading edge reflecting the energy resolution of the detector. The peak at channel 200 is due to the carbon substrate. The complex spectrum of the heterostructure is successfully simulated by taking thicknesses of 1100Å and 200Å for the two upper layers. However, it should be pointed out that the agreement is not as good in the simulation of the SiO$_2$/Si substrate. The simulation gives a thickness of 2700Å for SiO$_2$ instead of the presumed value of 1000Å. The discrepancy may be attributable to the location of the layer, (at more than 1000Å below the surface), and to the fact that the analyzed layer is an oxide with more complex interactions with the probing beam than an elemental metal.

**A.C. impedance measurements**

The measurements were performed in 0.5M H$_2$SO$_4$ solutions with EG & G Model 273 potenstiostat/galvanostat and Model 5210 lock-in amplifier. The frequency range employed was from 100 kHz to 1 mHz with a sine wave amplitude of 5 mV.

**Atomic Force Microscopy imaging**

Images of electrode surfaces were taken in air in the deflection mode with a Nanoscope III AFM microscope. The area scanned were 3 μm$^2$. 

5
RESULTS

As-prepared electrodes

Figure 2 shows RBS data obtained for electrode #5-3 (fabricated with a 1:5 dilution of the solution and with three coats) before use and after electrochemical use up to failure of the electrode. Qualitatively, by comparing the heights of the Ru peaks, it is clear that the as-prepared electrode contains a larger quantity of ruthenium than the failed electrode. The positions of the edges of Ru and of Ti peaks show clearly that Ru and Ti are present at the surface. The oxygen peak appears over a too large background to be of any analytical use. Finally, it should be noted that the samples examined are still thick for the RBS technique.

In order to reproduce fairly well the experimental spectra, the oxide layer had to be arbitrarily cut in portions of different Ru:Ti ratios. Typically the Ru concentration peaks are near or at the surface, and the Ru concentration is the lowest at the Ti substrate interface. Figure 3 shows the experimental and simulated spectra for electrode #10-6. The fit has been obtained by representing the mixed oxide layer with 6 sublayers of different Ru:Ti ratios. The layers are described in the calculations by their fluence in at cm$^{-2}$ and compositions in atom fraction of Ru, Ti and O. The thickness, $d$, of a sublayer is calculated by

$$
\frac{d}{cm} = \frac{F}{N_{Av}} \left\{ at(Ru)x \frac{M_{RuO_2}}{\rho_{RuO_2}} + at(Ti)x \frac{M_{TiO_2}}{\rho_{TiO_2}} \right\}
$$

(1)

Where $at(i)$ is the concentration of $i$ atom in atom fraction; $F$ is the fluence in at cm$^{-2}$; $N_{Av}$ is the Avogadro’s number; $M_{RuO_2}$ and $M_{TiO_2}$ are the molecular weights of RuO$_2$ and TiO$_2$, respectively; $\rho_{RuO_2} = 6.97$ g cm$^{-3}$ and $\rho_{TiO_2} = 3.84$ g cm$^{-3}$ are the densities of RuO$_2$ and TiO$_2$, respectively.

The concentration of Ru in each sublayer, $C_{Ru}$, is calculated with

$$
C_{Ru} \text{ at cm}^{-3} = \frac{at(Ru)x F}{d}
$$

(2)
The simulations of spectra for all the electrodes give total oxide thicknesses in the 3000 to 6000 Å range. Since XRF measurements probe depths on the order of microns, the Ru loadings measured by XRF are compared with the sum of Ru contents over all the sublayers included in the simulations. Equation (3) is used to calculate the electrode ruthenium loading, $CL_{Ru}$

$$CL_{Ru}/Ru \ g \ m^{-2} = 10^4 \times \frac{M_{Ru}}{N_A v} \sum_{i=1,n} F_i \times at(Ru)_i$$

(3)

Where $M_{Ru}$ is the atomic weight of Ru; $n$ is the number of layers in the simulation; $F_i$ and $at(Ru)_i$ are the fluence in at cm$^{-2}$ and the concentration of Ru atom in the ith layer, respectively. Table II summarizes the results of the simulation of RBS spectra for electrodes prepared from the 1:5 and 1:10 solutions. In these simulations, 3 to 6 sublayers have been included. The sensitivity of the simulation to the number of assumed sublayers has been tested by comparing results obtained with two and six sublayers on the #5-3 electrode. The simulation with two sublayers gives a thickness of 5065 Å instead of 5200 Å with six sublayers and a ruthenium loading, $CL_{Ru}$, of 0.72 Ru g m$^{-2}$ instead of 0.60 Ru g m$^{-2}$ with six sublayers. The discrepancy is on the order of magnitude of the uncertainty of 0.2 Ru g m$^{-2}$ generally reported for XRF analysis. The compositions in atom fraction of Ru assumed in the sublayers vary from 0.015 to 0.115. Except for the electrode prepared with one coat, #5-1, the simulation includes one or more sublayers with a composition of 0.08 atom fraction of Ru or higher. The latter value corresponds to the composition in the precursor solution. The RBS simulation appears to provide very reasonable values for the Ru content in the layer. The local fluctuations of composition around the precursor solution composition may be attributable to loss and to diffusion during the firing steps. These first results suggest that RBS could be used for optimizing the firing procedure by monitoring the build up of the mixed oxide layer. However, the $CL_{Ru}$ values derived from the RBS simulations are consistently smaller than those measured by XRF and reported in column 4 of Table I. Both sets of data are plotted versus the quantity of Ru coated on the Ti substrate, $Q_{Ru}$, in Figure 4. $Q_{Ru}$ is expressed in units corresponding to the Ru content of one coat of 1:5 solution on one
cm² surface unit. In these units, the quantity of Ru applied by four coatings with 1:10 solution is 2. The values obtained by the two methods appear to fall on different lines, which may suggest a systematic error. Since the standards used in the XRF measurements have not been examined by RBS, and were outside the range of values used here, the discrepancy may come from incorrect extrapolation.

The distribution of Ru within the oxide layer is shown in Figure 5 for electrodes #5-1, #5-3 and #5-5. The general shape of the profiles is not largely altered by the choice of taking only three layers in the simulation of #5-5. The most superficial layer in the three simulations appears to be slightly depleted in ruthenium. It cannot be ruled out that this result is an artifact from the calculations stemming from the fitting of the spectra sloping leading edge resulting from surface roughness and from the detector resolution. The comparison of profiles in #5-1 and in #5-3 suggests that diffusion of Ru toward the substrate may take place during the firing steps. This would explain the non-uniform concentration of Ru in the oxide and the build up of Ru at the Ti substrate surface from one coating (2x10²¹ at cm⁻³) to three coatings (6x10²¹ at cm⁻³).

**Used anodes**

Electrode #1, prepared with the same procedure as electrode #5-3, i.e., three successive coatings of 1:5 solution, has been examined by RBS at various times during the course of electrolysis in a 0.5M H₂SO₄ solution at a constant current of 0.5 A cm⁻² and at 25°C. Figure 6 shows, in the upper part, the galvanostatic data of cell potential versus time for electrodes 5-1, 5-3, 5-5 fabricated with 1, 3 and 5 coats of a 5:1 solution, respectively. Failure of the electrodes happens when the cell potential increases abruptly. The times, at which the fast surge in potential appears, increase with increasing numbers of coats. On the curve for #5-3 electrode, the voltage/time data before the removing of electrodes #1 to #6 for analysis are indicated with the corresponding electrode label. In the lower part of Figure 6 are the Rutherford backscattering spectra of the as-prepared electrode, #1, together with those of the five electrodes removed after various electrolysis times.

Qualitatively, it appears that with electrodes functioning with a low cell voltage, #2 and #3,
the spectra are similar to that for the as prepared electrode. Spectra for electrodes #4 and #5 show a lower content in ruthenium and are similar. The increase in cell voltage may be related to the decrease in ruthenium content in the electrode. Finally, electrode #6, which was removed from a cell with excessively high voltage, contains the smallest content of ruthenium. However, it should be noted that all spectra indicate ruthenium and titanium at the electrode surface.

The RBS data have been fitted with the assumption of five sublayers of various Ru:Ti ratios in a RuO$_2$-TiO$_2$ mixed oxide, and the values of the parameters are reported in Table III. Figure 7 summarizes the Ru concentration profiles in electrodes #1 to #6. The results do not show a decreasing thickness of the active layer with use, but clearly show a loss of Ru across the whole layer. The data could not be fitted with the assumption of a pure TiO$_2$ layer either at the electrode surface or at the oxide/Ti substrate interface. The deactivation of the electrode is more likely due to the decrease in conductivity of the oxide depleted in conducting RuO$_2$ than to the formation of an insulating pure TiO$_2$ layer. In a related study of anodic oxide films grown on Ru-implanted Ti alloys, electrochemical measurements of Tafel slope and optical absorption measurements by photoacoustic spectrometry$^{17}$ concluded to a critical composition of Ru(IV) in the oxide below which the mixed oxide becomes non-conducting. The critical concentration, measured for these anodic layers, is indicated in Figure 7 by a dashed horizontal line. The concentration profile in the failed electrode lies below and/or very close to the critical concentration line. Similarly, the ruthenium concentration profile measured by RBS and shown in Figure 5 for electrode #5-1 has concentrations lower or close to the critical concentration. These values are consistent with the polarization data for electrode #5-1 shown in Figure 6 where #5-1 exhibits the highest cell voltage at time zero and the shortest life time.

Further indication of changes in the conductivity of electrodes #1 to #6 have been sought independently by measurements of Tafel slope and by A.C. impedance measurements. Anode polarization data were obtained in 5M NaCl solutions at 70°C and pH 3-4. The results, shown in Figure 8, indicate a Tafel slope of 38-40 mV per decade for a fresh electrode (#1); this Tafel slope value is in agreement with the data published in the literature$^{18}$ for RuO$_2$-TiO$_2$ electrodes with a RuO$_2$ content of more than 20-30 mol% in NaCl solutions. The Tafel slope
remained unchanged for electrodes used as anodes during electrolysis in H$_2$SO$_4$ solution for up to 45 minutes at a current density of 0.5A cm$^{-2}$; it suggests that no degradation, detectable by polarization measurements, takes place during the initial period of electrolysis. However, the electrode after longer electrolysis exhibited "Tafel slope" larger than 120mV and reaching much higher values at longer times (i.e., >77min.). The increased value of the slope of the potential / log i curve for used electrodes may point to a change in the reaction mechanism and also to the indication of a resistive component involved during the course of the chlorine evolution reaction at a deactivated anode. The conductivity loss, inferred from the polarization data, also is evident in the A.C. impedance plots of the progressively deactivated anode (electrodes #1 to #6) shown in Figure 9. The A.C. impedance measurements were carried out in a 5M NaCl solution in the non-Faradaic region, where the primary reaction is reported to be

$$2 \text{RuO}_2 + 2 \text{H}^+ + 2e^- \rightarrow \text{Ru}_2\text{O}_3 + \text{H}_2\text{O} \quad (4)$$

Theoretically, reaction (4), at a planar electrode, can be represented by the equivalent circuit (9A). Depending on the magnitude of the exchange current density or charge transfer resistance (R$_t$), the Nyquist plots present a distinctive semicircle interpreted by a finite R$_t$. However, with porous electrodes, the Nyquist plots would exhibit a phase angle of 45° at $\omega \rightarrow \infty$ for the reaction scheme noted in equation (4). Thus, the R$_t$ variations, inferred from the Tafel slope values, can also be deduced from the A.C. impedance plots. It should be stated that increased R$_t$ can arise from lowered exchange current density and/or increased matrix resistivity. R$_t$ and C$_\phi$ values were deduced from the Nyquist and Bode plots following the simple procedure outlined in Reference 20 and presented in Table IV together with the Tafel slope values. These results show that as the electrode is anodically polarized in H$_2$SO$_4$ solution, the electrode develops significant resistivity, presumably as a result of loss of Ru sites from the catalyst surface. The loss of Ru sites is probably also responsible for the lowered adsorption pseudocapacitance as this capacity is a result of the RuO$_2$ $\rightleftharpoons$ Ru$_2$O$_3$ equilibrium.

The electrochemical measurements complemented the Rutherford Backscattering data in showing that the deactivation of RuO$_2$-TiO$_2$ based coatings in H$_2$SO$_4$ is a consequence of loss
of Ru sites on the surface. Studies, in progress to unravel the mechanistic features involved in
the deactivation phenomenon, will be reported in a subsequent communication.

CONCLUSION

The deactivation of RuO$_2$-TiO$_2$ DSA electrodes is readily observable from study of the
electrode performance in the production of chlorine. The failure of the electrodes happens
with little or no progressive decrease in the electrode performance; and accordingly
electrochemical measurements, such as Tafel slope, A.C. impedance measurements, point to
an abrupt decrease in electrode conductivity. In this study, Rutherford Backscattering
Spectrometry has been successful in measuring the ruthenium concentration profile in
electrodes at different times of use. The decrease in electrode activity has been related
conclusively to a decrease in the ruthenium content of the electrode. The measured profiles
demonstrate that the loss of Ru takes place across the thin coating, and that failure occurs
without the formation of a pure TiO$_2$ layer. Concentrations on the order of 2.7-3. $10^{21}$ Ru at
cm$^{-3}$ in the mixed dioxide are insufficient to sustain the chlorine current. This result
quantitatively agrees with the sudden appearance of the TiO$_2$ bandgap absorption in mixed
oxides with less than 2.7 $10^{21}$ Ru at cm$^{-3}$.

Inspection of electrode surfaces of the newly formed surface of #1 and of a failed electrode
#6 by AFM sustained the hypothesis of loss of material. Figure 10 shows the (3$\mu$m x 3$\mu$m)
AFM images of the as-prepared electrode #1 and of the electrode #6 after failure. The Z
scales in the two images are identical in order to provide a qualitative view of the dramatic
change in the aspect of the surface. The failed anode (bottom) shows a etched-like surface
which may come from the preferential corrosion of locations poor in stabilizing TiO$_2$ where
RuO$_2$ dissolves in the solution. A more detailed study of the morphology of the surfaces is in
progress and will be reported elsewhere.
ACKNOWLEDGMENTS

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REFERENCES


FIGURE CAPTIONS

Figure 1 (ORNL-DWG 95-1549)
Rutherford Backscattering Spectra obtained with a 2MeV $^4$He beam and 160° scattering angle: ● gold monolayer on graphite; ○ Pt/Ti/SiO$_2$/Si thin film heterostructure; — simulation. Arrows show energies for indicated surface atoms.

Figure 2 (ORNL-DWG 95-1550)
RBS spectra obtained with a 2MeV $^4$He beam and 160° scattering angle: ● as prepared #5-3 electrode; ♦ failed (after electrolysis) #5-3 anode. Arrows show energies for indicated surface atoms.

Figure 3 (ORNL-DWG 95-1551)
Experimental (●) and calculated (○) RBS leading edges of Ru and Ti for electrode #10-6. Arrows show energies for indicated surface atoms.

Figure 4 (ORNL-DWG 95-1552)
Ruthenium loadings of two sets of electrodes:
● measured by RBS; ■ measured by XRF.

Figure 5 (ORNL-DWG 95-1553)
RBS measured concentration profiles of Ru in electrodes fabricated from the 1:5 precursor solution. The dashed line corresponds to the critical concentration shown and discussed with Figure 7.

Figure 6 (ORNL-DWG 95-1554)
(upper) : Cell voltage versus time of electrolysis in a 0.5 M H$_2$SO$_4$ solution at a constant current of 0.5 A cm$^{-2}$ and at 25°C for anodes #5-1, #5-3 and #5-5.
RBS spectra (2 MeV $^4$He, 160° scattering angle) of anode 5-3 after various times of electrolysis

#1 : 0. minutes; #2 : 10. minutes; #3 : 25. minutes; #4 : 45. minutes; #5 : 65. minutes, and #6 : 77. minutes.

Figure 7 (ORNL-DWG 95-1555)
RBS measured Ru concentration profiles in electrodes #1 to #6. The critical concentration value shown was obtained for the semiconductor/metal transition in anodic oxide of Ru-implanted titanium alloys$^{17}$.

Figure 8 (ORNL-DWG 95-1556)
Anodic polarization in 5 M NaCl at 70°C and pH 3-4 of electrodes #1 to #6.

Figure 9 (ORNL-DWG 95-1581)
Nyquist plots for electrodes #1 to #6 and equivalent circuit for a planar electrode.

- $R_s$ solution resistance
- $C_d$ double layer capacitance
- $R_t$ charge transfer resistance
- $C_\phi$ adsorption pseudocapacitance

Figure 10
AFM images in air of anodes surfaces: upper electrode #1 before electrolysis; lower Electrode #6 after electrolysis and failure.
TABLE I

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<th>Electrode #</th>
<th>Solution Dilution</th>
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*Cell voltage at time of removal after electrolysis at constant current of 0.5A cm⁻² in 0.5M H₂SO₄ at 25°C during times varying from 0.(for electrode #1) to 77 minutes (for electrode #6).
<table>
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<td>6</td>
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<td>( C_{Ru} ) (at cm(^{-3}))</td>
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<td>4.4x10(^{21})</td>
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<td>8.9x10(^{21})</td>
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<td>4.0x10(^{17})</td>
<td>3.0x10(^{17})</td>
<td>2.5x10(^{18})</td>
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<td>1.2x10(^{18})</td>
<td>9.0x10(^{17})</td>
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<td>Fluence (at cm⁻²)</td>
<td>2.2x10¹⁷</td>
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TABLE IV

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<th>Time of Electrolysis/minute</th>
<th>Tafel slope ( \text{mV} )</th>
<th>( C_\Phi ) ( \text{mF cm}^{-2} )</th>
<th>( R_t ) ( \Omega \text{ cm}^{-2} )</th>
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Figure 2

- Solid circles: 1 (As-prepared 5-3 electrode)
- Diamonds: 6 (Failed 5-3 anode)

Channels:
- Ti
- Ru

Counts:
- 2000
- 1800
- 1600
- 1400
- 1200
- 1000
- 800
- 600
- 400
- 200
- 0

Figure 2
LIFE TEST OF 5-3 ANODE

- **CELL VOLTAGE**
  - Time: 0.0 to 250.0 min
  - Voltages: 0.0 to 10.0 V

- **CHANNEL**
  - Ti to Ru
  - Counts: 0 to 1000

- **Samples**:
  - 1 (AS-PREPARED)
  - 2
  - 3
  - 4
  - 5
  - 6 (FAILED ANODE)

Figure 6
Ru CONCENTRATION PROFILE IN OXIDE

Critical Concentration

Ru CONCENTRATION / at cm$^{-3}$

DISTANCE FROM Ti SUBSTRATE / Å
Figure 8

Graph showing potential vs. SCE (vs. SCE) with current density (I / A cm\(^{-2}\)) on the x-axis and potential on the y-axis. The graph displays three distinct regions:

1. **1, 2, 3 & 4**: 40 mV/Decade
2. **5**: 150-200 mV/Decade
3. **6**: > 200 mV/Decade

The data points and trend lines indicate a relationship between potential and current density across these different regions.
A. Equivalent Circuit (in Planar Form)
ELECTRODE#1

ELECTRODE#6