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CRADA Final Report
for

CRADA Number ORNL95-0331

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RUTHERFORD
BACKSCATTERING
ANALYSIS OF THE FAILURE
OF CHLORINE ANODES

C. E. Vallet
Oak Ridge National Laboratory

B. V. Tilak
Occidental Chemical Corporation

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Chemical and Analytical Sciences Division

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6197
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ABSTRACT

Rutherford Backscattering Spectrometry, carried out at the ORNL Surface Modification And Characterization Collaborative Research Center (SMAC) facility, has been applied to the nondestructive analysis of RuO₂-TiO₂ electrodes of 5000Å, which mimic the DSA anodes in composition and the method of preparation. Occidental Chemical Corporation provided electrodes, which had been subjected to life time testing in H₂SO₄ solution, for analysis by ORNL. The results were used to test the hypothesis of degradation of these, and similar electrodes, from a process involving a decrease in the RuO₂:TiO₂ ratio at and near the electrode surface and the related decrease in the electrode electrical conductivity. The drop in electrode activity is closely linked to a decrease in Ru content, and the measured profiles show that the loss takes place across the thin RuO₂-TiO₂ coating. No build up of a pure TiO₂ layer is apparent. The data agree quantitatively with the critical concentration previously reported by ORNL for materials produced by ion implantation and characterized by Rutherford Backscattering Spectrometry and Photoacoustic Spectrometry. The study has brought a better understanding of the degradation process in electrodes of great technological importance, and has given a more solid background in designing new fabrication procedures for improved electrodes.

STATEMENT OF THE OBJECTIVES OF THE CRADA

The purpose of the CRADA NO 95-0331 between Lockheed Martin Energy Research Corporation and Occidental Chemical Corporation was to obtain insights into the mechanisms of wear and passivation of RuO₂-TiO₂ anodes similar to that used in chlorine/caustic soda production.

The lifetime of anodes, typically fabricated by application of successive coatings of ruthenium and titanium salt mixtures on titanium substrate and oxidation in air at high temperature, depends on the method of preparation, the operating voltage, and the electrolyte brine composition. The mechanisms of failure are still unclear. Failure of the anode may correlate with a loss of RuO₂ at the surface and also is suspected to be related to the formation of a nonconductive TiO₂ layer. The gradual build up of TiO₂ could explain the observed increase in electrode overpotential and the consequent loss in efficiency of the process. The purpose of the collaboration was to test the hypothesis of failure due to changes in electrode composition by nondestructively characterizing the surface of electrodes at different times of use, and therefore with performance ranging from good to that of a failed anode. The objectives of the two parties involved in the project were as follows:

- For Occidental Chemical Corporation, to provide ORNL with electrodes similar to that used in chlorine production, but with thickness compatible to Rutherford Backscattering depth profiling, i.e., much thinner than the electrodes actually used;
- For Occidental Chemical Corporation, to send these electrodes to ORNL for analysis with documented results of life tests and electrochemical measurements of impedance and potentiodynamic analysis in relevant chloride solution;
- For ORNL to analyze the electrode superficial layers over a typical thickness of a few thousand Angstroms by Rutherford Backscattering Spectrometry;
- For ORNL to use and develop a suitable method of numerical analysis of the resulting RBS spectra in order to provide quantitative results of the composition changes as well as the location, within the electrode, at which the composition changes occur;
- For ORNL to prepare manuscript and the final report.

SUCCESS IN MEETING THE OBJECTIVES

Occidental Chemical participant has provided ORNL with samples amenable to measurements by Rutherford backscattering spectrometry on a timely manner. Adjustments in the thickness were made as required from the ORNL contractor. The ORNL contractor was able to deliver analytical results of these samples in the time frame established in the CRADA agreement.

Partial results have been presented at the 18th DOE Surface Science Conference, Oak Ridge, TN, May 10-11, 1995 and at the Electrochemical Society Spring Meeting, Reno, NV May 21-26, 1995. A paper, which is in the clearance process, has been prepared for submission to the Journal of the Electrochemical Society.

BENEFITS TO DOE MATERIALS SCIENCES PROGRAM

The Office of Basic Energy Sciences-Materials Sciences Program has funded an electrocatalysis project for a number of years. ORNL has a number of publications in the literature on the fundamentals of the mechanism of chlorine evolution at Ti/Ru oxide electrodes and has been invited over the years to give papers at international topical meetings such as "Progress in Electrocatalysis: Theory and Practice," Ferrara, Italy (1993). ORNL was solicited by the participant to collaborate in this project because of publications in the open literature

dealing with Rutherford Backscattering Spectrometry used on ion-implanted Ti/Ru model electrodes. ORNL experience, expertise and Surface Modification And Characterization facility (SMAC) were keys to make the collaboration with Chemical Occidental Corp. possible and successful. The focus of ORNL contribution to this project was the characterization of materials with the electrochemistry done entirely by the Occidental Chemical participant. The production of chlor-alkali commodity chemicals is of major importance to the U.S. chemical industry here and abroad particularly in the Pacific region. Improvement to electrode materials could increase efficiency and prolong the life of the electrodes, thus lowering the costs of production. ORNL has unique experience in the fabrication and characterization of model electrodes and applying this experience to "real world" production electrodes substantiates the model and may lead to new procedures for building improved electrodes.

TECHNICAL REPORT

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 $\text{RuO}_2\text{-TiO}_2$ coated titanium electrodes¹, commonly referred to in the industry as DSA (dimensionally stable anode) electrodes^{2,3}. These electrodes have 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 which may lead to the formation of a poorly conducting (TiO_2 -rich) oxide or of an insulating TiO_2 layer.

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 proposed⁴ 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 occurs⁵ 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 observed⁶ by SEM/EDX to assess their porosity and the catalyst distribution 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 active catalytic species displayed. The XPS technique has been the most used⁷⁻¹⁴ 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 oxide⁹. 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^{11,14} to analyze the surface of DSA-like 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 beam¹⁵. Scanning Auger Spectroscopy with a microprobe (0.6 μ m)¹⁵ has recently produced images of RuO₂-TiO₂ anodes which could be related with the topography of SEM images and which were much sharper than EDX elemental mappings. Segregation of RuO₂ 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 simulated¹⁶ by using the stopping powers and ranges of helium in different elements¹⁷, and consequently there is no need for preparing standards of known compositions. The recent application of RBS¹⁸ to a SnO₂-IrO₂ coating gave compositions sustained by analysis by inductively coupled plasma emission spectroscopy (ICPES).

In this study, thin film electrodes, which mimic the DSA anodes in composition and preparation method, have been prepared, tested for their activity toward the chlorine evolution reaction, and subjected to life time testing in sulfuric acid solution. 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).

EXPERIMENTAL

Preparation Procedure

Samples with an oxide layer thickness of a few thousands Angstroms were made 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 sand blasting with SiC, immersion in trichloroethylene, etching by a 10% oxalic acid + 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 H_2SO_4 solution at a constant anodic current of 0.5 A cm^{-2} at 25°C . Samples, removed at different times during the electrolysis, were analyzed by Rutherford Backscattering Spectrometry and subjected to electrochemical tests 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.

TABLE I : Summary of preparation procedures and available characterization data of the RuO_2 - TiO_2/Ti thin film electrodes studied by RBS and A.C. impedance measurements.

Electrode #	Solution Dilution	Number of Coatings	XRF Ru g m^{-2}	Cell* Voltage/V	Electrolysis Time/minute
10-4	1:10	4	58	NA	NA
10-5	1:10	5	77	NA	NA
10-6	1:10	6	73	NA	NA
5-1	1:5	1	58	NA	NA
5-3	1:5	3	81	NA	NA
5-5	1:5	5	1.44	NA	NA
1	1:5	3	81	NA	0
2	1:5	3	NA	3.2	10.
3	1:5	3	NA	3.3	25.
4	1:5	3	NA	3.5	45.
5	1:5	3	NA	4.4	65.
6	1:5	3	NA	7.0	77

*Cell voltage at time of removal after electrolysis at constant current of 0.5 A cm^{-2} in 0.5M H_2SO_4 at 25°C during times indicated in the next column.

Rutherford Backscattering Spectrometry

The Rutherford Backscattering Spectrometry (RBS) technique can probe¹⁶ depths of several thousands Angstroms in a solid by analyzing the energy of a high energy ^4He beam after its interaction with this solid. The results 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 detector has an energy resolution on the order of 20 keV and a solid angle 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 experimental spectra are more difficult to interpret because the ^4He beam penetrates inside the solid and collides with atoms situated at various distances from the surface. The energetic ^4He beam, during its travel in the sample, is slowed down by electronic forces, and consequently the

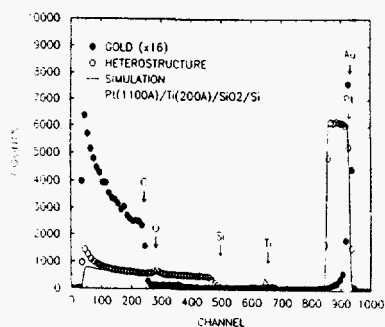


Figure 1 Rutherford Backscattering Spectra obtained with a 2MeV ^4He beam and 160° scattering angle: gold monolayer on graphite; Pt/Ti/SiO₂/Si thin film heterostructure; — simulation. Arrows show energies for indicated surface atoms.

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 calculations 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 edge at channel 200 is due to the carbon substrate. The complex spectrum of the heterostructure, with a Pt peak of about 50 channel half height width, is successfully simulated by taking thicknesses of 1100Å and 200Å for the Pt and Ti upper layers, respectively. However, it should be pointed out that the agreement is not as good in the simulation of the SiO₂/Si substrate interface. The simulation gives a thickness of 2700Å for SiO₂ 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 H₂SO₄ solutions with a EG & G Model 273 potentiostat/galvanostat and a Model 5210 lock-in amplifier. The frequency range employed was from 100 kHz to 1 mHz with a sine wave amplitude of 5 mV.

RESULTS

As-prepared Electrodes

Figure 2 shows RBS data obtained for electrode #5-3 (fabricated with a 1:5 dilution of

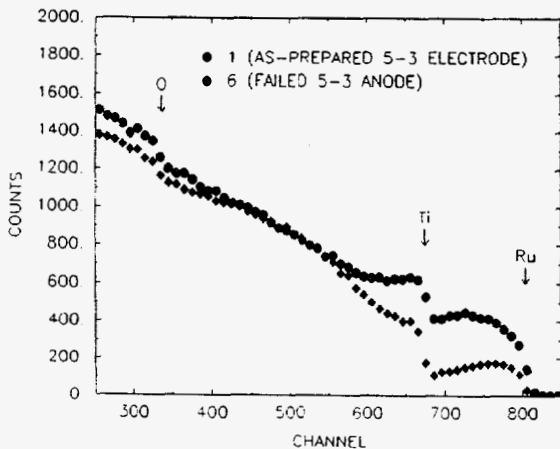


Figure 2 RBS spectra obtained with a 2MeV ^4He beam and 160° scattering angle: • as prepared #5-3 electrode: ♦ failed (after electrolysis) #5-3 anode. Arrows show energies for indicated surface atoms.

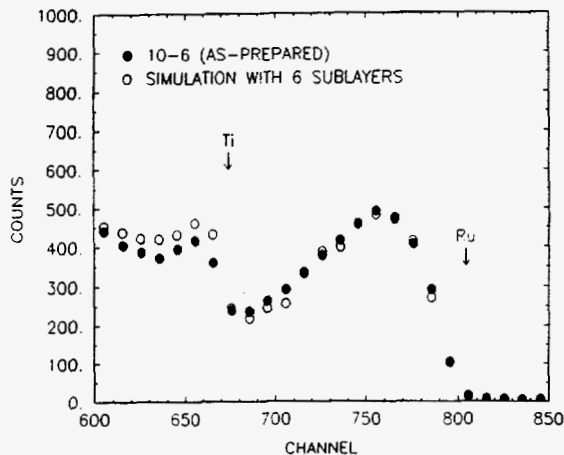


Figure 3 Experimental (•) and calculated (◦) RBS leading edges of Ru and Ti for electrode #10-6. Arrows show energies for indicated surface atoms.

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 the as-prepared 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 atom cm^{-2} and compositions in atom fraction of Ru, Ti and O. The thickness, d , of a sublayer is calculated by

$$d/\text{cm} = \frac{F}{N_{Av}} \left\{ at(\text{Ru})x \frac{M_{\text{RuO}_2}}{\rho_{\text{RuO}_2}} + at(\text{Ti})x \frac{M_{\text{TiO}_2}}{\rho_{\text{TiO}_2}} \right\} \quad (1)$$

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; $\rho_{\text{RuO}_2} = 6.97 \text{ g cm}^{-3}$ and $\rho_{\text{TiO}_2} = 3.84 \text{ g cm}^{-3}$ are the densities of RuO_2 and TiO_2 , respectively.

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

$$C_{Ru}/at\ cm^{-3} = \frac{at(Ru) \times F}{d} \quad (2)$$

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}

$$CL_{Ru}/Ru\ g\ m^{-2} = 10^4 \times \frac{M_{Ru}}{N_{Av}} \sum_{i=1,n} F_i \times at(Ru)_i \quad (3)$$

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 i th 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 calculations, 3 to 6 sublayers have been included. The

TABLE II: RBS analysis of as-prepared RuO_2 - TiO_2 /Ti thin film electrodes.

Electrode	5-1	5-3	5-5	10-4	10-5	10-6
Numbers of Layers, n	6	6	3	4	4	6
Layer 1						
Fluence (at cm^{-2})	1×10^{17}	2.8×10^{17}	4.4×10^{17}	6.0×10^{17}	2.0×10^{17}	2.0×10^{17}
Ru(atom fraction)	0.045	0.07	0.05	0.11	0.025	0.03
C_{Ru} (at cm^{-3})	4.0×10^{21}	6.2×10^{21}	4.4×10^{21}	9.8×10^{21}	2.2×10^{21}	2.6×10^{21}
Layer 2						
Fluence (at cm^{-2})	7.0×10^{17}	2.0×10^{17}	2.0×10^{18}	5.0×10^{17}	9.0×10^{17}	2.7×10^{17}
Ru(atom fraction)	0.055	0.08	0.1	0.07	0.09	0.09
C_{Ru} (at cm^{-3})	4.8×10^{21}	7.1×10^{21}	8.9×10^{21}	6.2×10^{21}	8.0×10^{21}	8.0×10^{21}
Layer 3						
Fluence (at cm^{-2})	4.0×10^{17}	3.0×10^{17}	2.5×10^{18}	4.0×10^{17}	7.0×10^{17}	7.0×10^{17}
Ru(atom fraction)	0.05	0.085	0.07	0.05	0.07	0.115
C_{Ru} (at cm^{-3})	4.4×10^{21}	7.5×10^{21}	6.2×10^{21}	4.4×10^{21}	6.2×10^{21}	1.0×10^{22}
Layer 4						
Fluence (at cm^{-2})	4.0×10^{17}	6.0×10^{17}		1.2×10^{18}	9.0×10^{17}	6.0×10^{17}
Ru(atom fraction)	0.04	0.1		0.015	0.04	0.09
C_{Ru} (at cm^{-3})	3.5×10^{21}	8.9×10^{21}		1.3×10^{21}	3.5×10^{21}	8.0×10^{21}
Layer 5						
Fluence (at cm^{-2})	6.0×10^{17}	5.0×10^{17}				6.0×10^{17}
Ru(atom fraction)	0.035	0.09				0.055
C_{Ru} (at cm^{-3})	3.1×10^{21}	8.0×10^{21}				4.8×10^{21}
Layer 6						
Fluence (at cm^{-2})	8.0×10^{17}	2.7×10^{18}				2.0×10^{18}
Ru(atom fraction)	0.025	0.07				0.04
C_{Ru} (at cm^{-3})	2.2×10^{21}	6.2×10^{21}				3.5×10^{21}
Thickness (Å)	3420	5200	5610	3100	3100	5050
CL_{Ru} (Ru $g\ m^{-2}$)	0.23	0.60	0.67	0.27	0.29	0.42

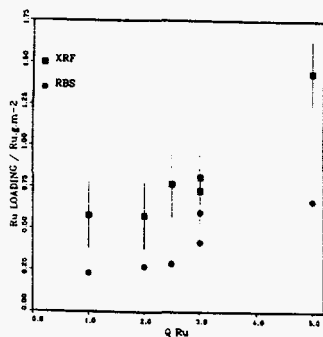


Figure 4 Ruthenium loadings of two sets of electrodes : • measured by RBS; ■ measured by XRF.

attributable to loss and to diffusion during the application of successive layers. These first results suggest that RBS could be used for optimizing the preparation procedure by monitoring the build up of the mixed oxide layer. However, the CL_{Ru} values derived with Equation (3) 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 cm^2

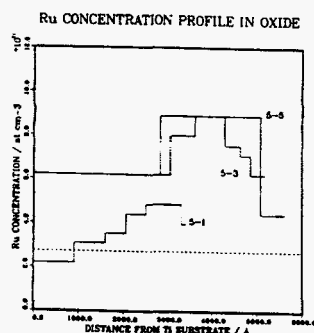


Figure 5 RBS data for #5-1, #5-3 & #5-5. The dashed line is discussed with Fig.7.

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 large difference in masses between Ru and Ti matrix atoms may increase the uncertainty of a linear extrapolation¹⁹.

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 stemming from the fitting of the spectra sloping leading edge attributable to surface roughness and to 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 successive preparation 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 (2×10^{21} at cm^{-3}) to three coatings (6×10^{21} at cm^{-3}).

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 5065Å instead of 5200Å 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 concentrations of Ru assumed in the sublayers vary from 0.015 to 0.115 atom fraction. 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. Thus, the RBS simulation appears to provide very reasonable values for the Ru content in the mixed oxide film. The local fluctuations of composition around the precursor solution composition may be

Used Anodes

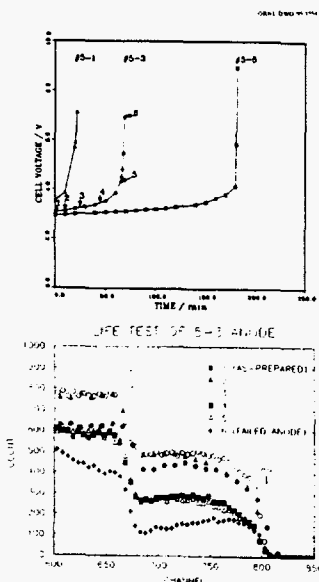


Figure 6(upper): Cell voltage vs. time of electrolysis in a 0.5M H_2SO_4 solution at a constant current of 0.5 A cm^{-2} and at 25°C for anodes #5-1, 5-3 & 5-5; (lower): RBS data (2MeV, 160° scattering angle) of #5-3 after various times of electrolysis: #1: 0., #2: 10., #3: 25., #4: 45., #5: 65., and #6: 77. minutes.

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.

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 H_2SO_4 solution at a constant current of 0.5A 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.

TABLE III: RBS analysis of electrode #5-3 after different times of electrolysis in 0.5M H₂SO₄ at a constant current of 0.5A cm⁻² and at 25°C.

Electrode	1	2 & 3	4 & 5	6
Numbers of Layers. n	5	5	5	5
Layer 1 Fluence (at cm ⁻²) Ru(atom fraction) C _{Ru} (at cm ⁻³)	3.5x10 ¹⁷ 0.065 5.7x10 ⁻²¹	2.0x10 ¹⁷ 0.06 5.3x10 ⁻²¹	2.2x10 ¹⁷ 0.035 3.1x10 ⁻²¹	3.0x10 ¹⁷ 0.03 2.6x10 ⁻²¹
Layer 2 Fluence (at cm ⁻²) Ru(atom fraction) C _{Ru} (at cm ⁻³)	5.0x10 ¹⁷ 0.082 7.5x10 ⁻²¹	3.0x10 ¹⁷ 0.085 7.5x10 ⁻²¹	3.0x10 ¹⁷ 0.055 4.8x10 ⁻²¹	3.0x10 ¹⁷ 0.035 6.2x10 ⁻²¹
Fluence (at cm ⁻²) Ru(atom fraction) C _{Ru} (at cm ⁻³)	5.0x10 ¹⁷ 0.085 7.5x10 ⁻²¹	4.0x10 ¹⁷ 0.095 8.4x10 ⁻²¹	4.0x10 ¹⁷ 0.06 5.3x10 ⁻²¹	6.0x10 ¹⁷ 0.04 3.5x10 ⁻²¹
Layer 4 Fluence (at cm ⁻²) Ru(atom fraction) C _{Ru} (at cm ⁻³)	2.0x10 ¹⁷ 0.092 8.2x10 ⁻²¹	9.0x10 ¹⁷ 0.1 8.9x10 ⁻²¹	8.3x10 ¹⁷ 0.06 5.5x10 ⁻²¹	1.0x10 ¹⁸ 0.034 3.0x10 ⁻²¹
Layer 5 Fluence (at cm ⁻²) Ru(atom fraction) C _{Ru} (at cm ⁻³)	2.2x10 ¹⁷ 0.095 8.4x10 ⁻²¹	2.4x10 ¹⁸ 0.110 9.8x10 ⁻²¹	2.6x10 ¹⁸ 0.065 5.7x10 ⁻²¹	2.8x10 ¹⁸ 0.025 2.2x10 ⁻²¹
Thickness (Å)	4896	4712	4930	5713

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 depletion 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 Spectrometry²⁰ concluded to a critical composition of Ru(IV) in the oxide below which the mixed oxide becomes non-conducting.

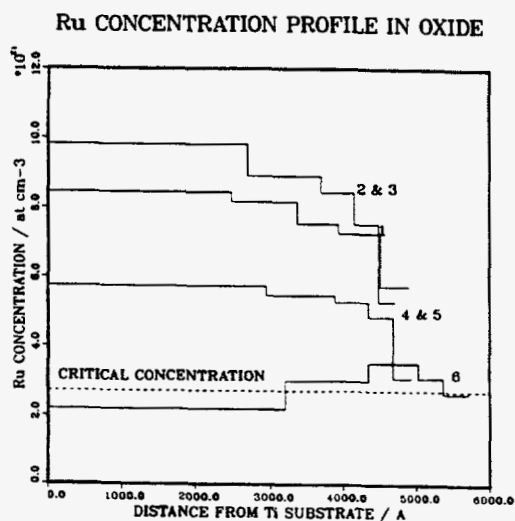


Figure 7 Measured concentration profiles in electrodes #1 to #6. The critical concentration value was obtained for the semiconductor/metal transition in anodic oxide of Ru-implanted titanium alloys¹⁹.

The critical 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 initial cell voltage 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 literature²¹ for $\text{RuO}_2\text{-TiO}_2$ 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_2SO_4 solution for up to 45 minutes at a current density of 0.5 A cm^{-2} ; it suggests that no degradation, detectable by polarization measurements, takes place during the initial period of electrolysis. However, the electrodes after longer times of electrolysis have "Tafel slope" larger than 120mV/decade 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 to the formation of a resistive component during the course of the chlorine evolution reaction.

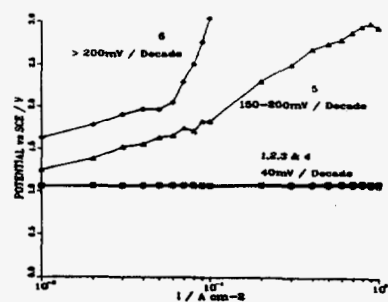


Figure 8 Anodic polarization in 5M NaCl at 70°C and pH 3-4 of electrodes #1 to #6

The decrease in conductivity, suggested by the polarization data, also is evident in Figure 9 from the A.C. impedance data of the progressively deactivated anode (electrodes #1 to #6). 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 be⁵



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 exhibit²² a phase angle of 45° at $\omega \rightarrow \infty$ for the reaction scheme noted in equation (4). Thus, the increase in R_t , suggested by the Tafel slope values, is confirmed by the A.C. impedance data. It should be stated that increased R_t can arise from lowered exchange current density and/or increased matrix resistivity. R_t and C_ϕ values were derived from the Nyquist and Bode plots following the simple procedure outlined in Reference 23, and are presented in Table IV together with the Tafel slope values. These results show that, as the electrode is anodically polarized in H_2SO_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 also consistent with a smaller adsorption pseudocapacitance since this capacitive term results from the $\text{RuO}_2 \rightleftharpoons \text{Ru}_2\text{O}_3$ equilibrium. The electrochemical measurements complemented the RBS data in showing that the deactivation of $\text{RuO}_2\text{-TiO}_2$ thin film electrodes in sulfuric acid solution is a consequence of loss of ruthenium.

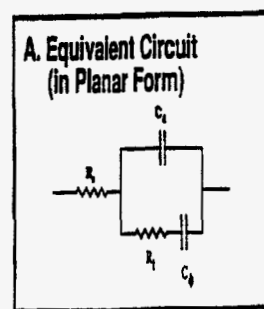
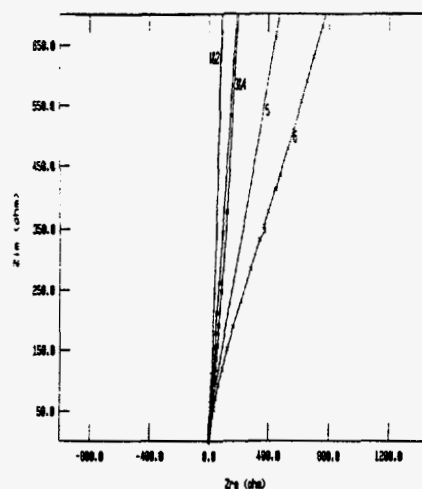


Figure 9 Nyquist plots for electrodes #1 to #6 and equivalent circuit for a planar electrode. R_s solution resistance, C_d double layer capacitance, R_t charge transfer resistance, C_ϕ adsorption pseudocapacitance.

TABLE IV: Summary of data from anodic polarization measurements in H₂SO₄ solution and A.C. impedance measurements in NaCl solution

Time of Electrolysis minute	Tafel slope mV	C ϕ mF cm ⁻²	R, Ω cm ⁻²
0.	40	5.6	0
10.	40	5.6	0
25.	40	5.6	0
45.	40	2.5	0
65.	150-200	0.56	
77.	7200	0.08	3

SUMMARY

The deactivation of RuO₂-TiO₂ 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 linked conclusively to a decrease in the ruthenium content of the electrode. The measured profiles demonstrate that the loss of Ru takes place across the (~5000Å) thin coating, and that failure occurs before the complete depletion of ruthenium and without the formation of a pure TiO₂ layer. Concentrations on the order of 2.7-3. 10²¹ Ru at cm⁻³ in the mixed dioxide are insufficient to sustain the chlorine current. This result quantitatively agrees with the critical composition of 2.7 10²¹ Ru at cm⁻³ determined²⁰ for the metal/semiconductor transition in RuO₂-TiO₂ anodic oxides of Ru,Ti alloy films produced by ion-implantation of Ru into titanium.

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INVENTIONS

No invention was made.

COMMERCIALIZATION POSSIBILITIES

None

PLANS FOR FUTURE COLLABORATION

No plan for further collaboration has been currently initiated by Occidental Chemical Corporation.

CONCLUSIONS

The use of Rutherford Backscattering Spectrometry, in connection with the electrochemical science, is currently not very extensive. However, with the growing interest of electrochemists in experimenting with the wide variety of surface analysis techniques, RBS should not be disregarded because of the cost of the technique.

This study demonstrates the advantages of Rutherford Backscattering Spectrometry (RBS) for characterizing "real life" electrodes. These advantages come from the use of

- nondestructive method
- quantitative method with no need for standards
- method which gives data at the surface and near surface (a few thousands Å).

The latter possibility allows a nondestructive depth profiling of the active region of an electrode. This is particularly advantageous for the study of porous oxides with electrocatalytic properties for various important reactions. The characterization by RBS could serve as a control during the multi step fabrication of the mixed oxide electrodes and help in identifying the best

conditions for building a mixed oxide layer of high electroactive activity and long use.

This study demonstrates that the life time of the actual RuO₂-TiO₂ electrodes is limited by the loss of RuO₂ over a region of at least 5000Å thick leading to a blocking electrode. Since, the failed electrodes retained some ruthenium at the surface and near the surface, it may be possible to use the remaining potential activity by modifying the electrode for increasing its electrical conductivity.

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