APPLICATION OF ION IMPLANTATION TO ELECTROCHEMICAL STUDIES*

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Abstract

The application of ion implantation to electrochemical studies is illustrated with a study of electrocatalysis of the chlorine evolution reaction at RuO_2 , IrO_2 , TiO_2 mixed oxide anodes in chloride solutions. Electrode/solution interfaces of well defined catalyst composition are generated in a reproducible manner by implantation of Ru (or Ir) into Ti followed by in situ oxidation of the near surface titanium alloys. Ion implantation enables the tailoring on an atomic scale of an electrochemical interface. Analysis by Rutherford backscattering adds the ability of quantitative mechanistic study in terms of actual ion concentration at the interface. In addition, ion implantation, as a processing technique, creates new materials with improved properties which may have future practical use in catalytic materials.

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Ion implantation, which modifies the near-surface of materials by introduction of a controllable amount of ions, appears an ideal tool for studying electrochemical interfaces. Ion implantation was first used in connection with electrochemistry in the field of corrosion studies [1-4]. These early works focused on testing the effects of the radiation damage produced by implantation of heavy inert ions (Xe, Kr) and the chemical effect of the introduction of noble metal ions on passivation. In a study of platinum-implanted titanium [5,6], the combination of ion implantation with Rutherford Backscattering measurements at various times during the electrochemical process lead to a correlation of the hydrogen evolution current with the platinum implant profile. Ion implantation also was recognized as an extremely valuable method for producing and studying catalytic surfaces. Most of the works in this field are listed in the review of G. K. Wolf [7] or in the more recent review of V. V. Poplavskii et al. [8]. The surface can be modified on an atomic scale in order to place controllable amounts of catalyst. The resulting enhancement of the reaction under study can be related quantitatively to the catalyst surface concentration. In this paper we illustrate the potentials of the method with the results [9-12] obtained for the catalysis of the chlorine evolution reaction at Ru- and Ir-implanted titanium anodes in chloride solutions.

1. The Chlorine Reaction

Since the discovery [13] of the RuO_2 , TiO_2/Ti dimensionally stable anode (DSA) with high catalytic activity for the production of chlorine from chloride solutions and with a good corrosion resistance, a large number of electrochemical studies has been reported [14-16]. The industrial electrode

is prepared by applying alcoholic solutions of ruthenium and titanium chlorides on a titanium support. The coating is then baked under an oxygen flow. Several applications are made successively. The final product is a porous layer of mixed oxide with composition, structure and physical properties difficultly predictable or reproducible. Results reported from studies on these electrodes, therefore, have been contradictory and difficult to compare. In contrast, the use of ion implantation to produce electrodes with well defined active area and catalyst content has helped [9] to clarify the mechanism of this important industrial reaction. The charge transfer, $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$, occurring at the electrode is proposed to involve first the adsorption of chloride ions on ruthenium sites, S, at the electrode/solution interface

followed by electrochemical desorption

and by the rate-determining step producing chlorine gas

Under these assumptions, the resulting steady-state current density for chlorine evolution is obtained [9] as

$$i = 2F(S) \frac{A[\text{Cl}^-]^2}{B[\text{Cl}^-] + 1} \exp(3FE/2RT) \quad (4)$$

where (S) is the surface concentration of active adsorption sites, A is the product of the chemical equilibrium constants of (1) and (2) with the chemical

rate constant of (3), and B is the chemical equilibrium constant for (1). In order to accurately test equation (4), current/potential measurements have to be made on electrodes of known area and surface concentration of catalyst.

2. Electrode Preparation and Characterization

The titanium used [9,12] was zone-refined polycrystalline titanium (Materials Research Corporation) polished down to $0.05 \mu\text{m Al}_2\text{O}_3$. In the optical studies [10,11], the titanium foils (Alfa 99.98%) of 0.025 mm thickness were not polished prior to electrochemical treatment. Both kinds of titanium were electrochemically pretreated before implantation in order to remove any oxide layer. The open circuit potential in H_2 -saturated 0.5 M H_2SO_4 and the corrosion potential/maximum current density provided [17,18] a test of the oxide-free surface and a measure of the electrode active surface. Implantation of ^{102}Ru and ^{193}Ir were carried out with an Extrion high current accelerator with a sputter source designed [19] for implantation of high melting point metals. The iridium beam used was double charged.

Figure 1 shows typical ruthenium concentration profiles measured by Rutherford backscattering after implantation of various doses ranging from $1 \times 10^{16} \text{ atom cm}^{-2}$ to $1 \times 10^{17} \text{ atom cm}^{-2}$. A three-energy implantation scheme was used in order to obtain a nearly constant implant concentration over a depth of the order of 20 nm. Thus, electrochemical measurements could be carried out on an electrode surface with a constant and well-defined composition while cutting through the profile. This feature is particularly important for the experimental determination of the reaction order and for the in-situ recording of optical absorption by photoacoustic spectroscopy which both require a few hours. Typically the beam energy was on the order of 100 keV in order to produce implant peak concentrations at a depth of around 25-30 nm.

As is well known, the implantation of low doses generates near-gaussian concentration profiles, therefore few implanted atoms are present at the surface. This can be a drawback in the use of implantation for producing a catalytic surface if there is no way to dissolve the substrate surface. Thus, the pretreatment of the electrode is very important in order to avoid implanting a titanium sample covered with a thick (passive) oxide layer. Formation of oxide at the implanted alloy surface and concurrent metal dissolution were carried out in 1 M $[\text{Cl}^-]$, pH = 1.0 solutions. These conditions were known [9,17] to lead for a titanium surface to a steady-state with a 5 nm thick oxide layer and a corrosion rate of the metal at the oxide/metal interface on the order of 0.4 nm h^{-1} . When these conditions are not fulfilled, it may be impossible to bring to the surface the implanted metal as is suggested by the negative results reported by B. V. Tilak [20] on ruthenium-implanted titanium electrodes. Tilak's choice of a relatively deep implant with a 150 keV Ru^+ beam combined with a chloride solution with a pH of 4 leading to low corrosion rate of titanium may also have prevented the observation of significant ruthenium amounts at the surface in the reported short time of 3 to 6 hours.

3. Chlorine Current/Implant Profile Correlation

In an early study of the hydrogen evolution reaction at platinum-implanted titanium cathodes [5,6,17] the similarity between the variation of the current with time and the implant profile was first pointed out. The explanation was that the hydrogen reaction takes place at noble metal atoms which are brought to the surface during the corrosion of the alloys. However, the noble metal does not dissolve in the solution and platinum was found by Rutherford backscattering measurements to accumulate at the surface of electrodes after corrosion. In order to reconcile the electrochemical

measurements of current and the RBS measurements after corrosion, the authors proposed that the platinum aggregates at the surface are inactive for the electrochemical reaction. The similarity between Ru or Ir implant profiles and the variation with time of the exchange current in the chlorine evolution region has been verified [9-12] on various implanted titanium anodes. Figure 2 compares [10] the exchange current with the ruthenium implant profile of an anode implanted at one energy with a dose of 4.6×10^{16} Ru cm⁻². RBS measurements performed when the exchange current reaches its maximum value (figure 3) or at the end of an experiment when the implant profile is almost exhausted are necessary to test the dissolution process of the electrode. Results in figure 3 show that the ruthenium moves to the surface and the calculated dose, 55% of the initial dose, is consistent with the dissolution of the near gaussian profile up to the maximum. Confirmation of the non-preferential dissolution of the Ru,Ti alloy is given by the Ru profile measurement after a 40 day period of corrosion. The remaining ruthenium dose is 5-6% that of the initial dose and the Ru concentration at the surface is consistent with the measured chlorine current. Similar results are obtained with iridium implanted titanium but the corrosion rates are markedly lower [11-12].

4. Summary of Results

The anodic oxidation of Ru or Ir implanted titanium electrodes produced model electrodes perfectly suited to mechanistic studies of the chlorine evolution reaction. E. J. Kelly [9] made a thorough test of equation (4) which confirmed the reaction mechanism indicated in (1) to (3). A similar study [12] of iridium implanted titanium alloys showed that the same mechanism is present for chlorine production at these electrodes.

For the first time, the chlorine current could be related to the surface concentration of Ru or (Ir) sites at the surface. These results lead [11,12] to the in situ determination of the comparative electrocatalytic activities of Ru and Ir toward the chlorine evolution reaction.

In a parallel study [10-11] these electrodes were examined by photoacoustic spectroscopy for their optical absorption. TiO_2 formed by anodic oxidation of Ti is a semiconductor with bandgap absorption of 3 eV. RuO_2 or IrO_2 are known [21] to be metallic conductors. During the slow dissolution of the anodically oxidized implanted alloys, the bandgap absorption was monitored in terms of the concentration of Ru or Ir in the superficial oxide. Figure 4 shows the collapse of the bandgap absorption, which was interpreted as a semiconductor/metal transition, which occurs for a critical composition of 2.5×10^{21} Ru (or Ir) cm^{-3} in the superficial dioxide. This conclusion is consistent with the measured value of $(dE/d\log i)_{(s),(Cl^-),T}$ which, for concentrations larger than the critical concentration, indicates that the potential change is applied entirely at the electrode/solution interface. The Ru/Ti ratio of near 0.1 at which the implanted electrodes become metallic conductor is lower than the critical ratio of 0.3 [22] for conventional Ru/Ti alloy or mixed oxide powders. The transition for a ratio of 0.3 can be explained in terms of the formation of an infinite cluster of conducting RuO_2 . The lower value of 0.1 in implanted samples suggests that by mixing on an atomic level metallicity is obtained through the spreading of impurity bands and overlap with the conduction band [23].

Ion implantation can produce an unlimited number of new materials, this potentiality yet has to be exploited in connection with electrochemical studies. As an example, coimplantation of Ru and Ir into titanium has been

used [11] to form a RuO_2 , IrO_2 , TiO_2/Ti interface similar to the more recent DSA industrial anodes. Conflicting results have been reported [24-25] on accumulation at the surface of one of the oxides and loss of electrocatalytic activity. Rutherford backscattering measurements of the electrodes indicate that iridium dissolves at lower rate than ruthenium although the global corrosion resistance of the electrode is improved by addition of iridium.

5. Conclusion

Ion implantation with the complementary RBS technique is an unique tool to design electrode surfaces for electrochemical studies. The key advantage lies in the production of accurately controlled surface properties. Therefore the ability to analyze the electrode response in terms of actual concentration of electroactive species allows mechanistic studies of reaction and evaluation of specific activity. In addition, an unlimited number of systems can be generated, including complex systems from coimplantation. This potentiality yet has to be exploited in the search for improved electrode materials.

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Figure Captions

- Figure 1 Ruthenium concentration profiles after implantation into titanium at three energies (40, 70 and 130 keV). The various total doses are indicated.
- Figure 2 Original Ru implant profile in titanium (4.6×10^{16} Ru cm⁻²) and chlorine current recorded with time in 1 M (Cl⁻), pH = 1 and potential of 1.1 V vs SCE. Electrode area = 0.4 cm².
- Figure 3 Rutherford backscattering spectra of Ru-implanted electrode before electrochemical treatment and when the observed chlorine current reaches its peak.
- Figure 4 Dimensionless bandgap absorption measured from photoacoustic (PAS) measurements $(PAS_{300nm} - PAS_{450nm})/PAS_{300nm}$ vs. the surface concentration of noble metal. Reproduced with the authorization of the Journal of the Electrochemical Society.

Fig. 1

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Figure 3

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Figure 4

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