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A study of the deactivation and service life of Ir oxide anodes supported on Al substrates

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Abstract

The deactivation of Ir oxides supported on Al substrates has been studied in 0.5 M H_2SO_4. Their electrochemical behaviour and service life was also compared to IrO_2 electrodes, similarly prepared, supported on Ti. The Ir oxides were prepared by thermal decomposition of an Ir salt precursor solution. The service life and other oxide properties were found to be influenced by different factors used for preparation of the Ir oxide electrodes, for example, the temperature used for the decomposition process and the solution used to etch the Al substrate. In contrast to the IrO_2 anodes supported on Ti, the service lives of the IrO_2 anodes supported on Al were found to be very short. The deactivation of the latter anodes appears to be related to poor adhesion between the Ir oxide and the Al substrate. However, it was found that the service life of IrO_2 anodes supported on Al is increased when a layer consisting of iridium is electrochemically deposited onto the Al substrate prior to the thermal formation of the IrO_2.

1. Introduction

The electrosynthesis of N_2O_5 (a nitration reagent used for the synthesis of energetic materials) from N_2O_4 in nitric acid has been of interest since 1910 [1–3]. The basic cell reactions for the electrosynthesis of N_2O_5 are as follows:

Anode reaction

$$N_2O_4 + 2\,HNO_3 \rightarrow 2\,N_2O_5 + 2\,H^+ + 2\,e^- \qquad (1)$$

Cathode reaction

$$2\,HNO_3 + 2\,H^+ + 2\,e^- \rightarrow N_2O_4 + 2\,H_2O \qquad (2)$$

Overall cell reaction

$$2\,HNO_3 \rightarrow N_2O_5 + H_2O \qquad (3)$$

The production of N_2O_5 using this electrochemical route is particularly attractive, as in theory the N_2O_4 produced at the cathode (Reaction 2) can be reused as feed stock for the anode process (Reaction 1). In fact, prior investigations, which included the performance evaluation of a range of electrodes as well as scaling-up studies, have shown that this electrochemical process is very viable [3].

In previous work [3, 4] it was shown that anodes consisting of noble metals and/or noble metal oxides such as platinum and IrO_2 yield the lowest overpotentials for the oxidation of N_2O_4 (i.e., Reaction 1). In fact, IrO_2 showed superior performance for a range of metal oxides studied [3]. IrO_2 electrodes are often prepared by thermal decomposition of an Ir salt onto a Ti substrate and generally exhibit long service lives. However, Ti is incompatible with nitric acid, and the use of anodes consisting of IrO_2 coated onto Ti for the N_2O_5 electrosynthesis has resulted in violent explosion reactions [3]. Scanning electron microscopy (SEM) studies performed on the anode surfaces after such an explosion suggested that the nitric acid penetrated the porous IrO_2 coating, and subsequently, reacted with the underlying Ti. Therefore, other metals have been considered as substrates for the IrO_2 catalyst. The corrosion rate of metals such as Ta, Al and Nb in nitric acid has been estimated showing the corrosion resistance to decrease as follows: $Ta > Nb > Al \gg Ti > Zr$ [3, 4]. However, both Ta and Nb, which were found to have the best corrosion resistance of the above metals, are more costly than Al. Based on these corrosion studies and considering economical factors, Al has been suggested to be the most suitable substrate for the IrO_2 catalyst used in the N_2O_5 electrosynthesis. The service life of the IrO_2 anodes supported on Al was reported to be unsatisfactorily short [4]. The use of IrO_2 anodes, which show a low overpotential and long service life for the electrosynthesis of N_2O_5, could make this process economically more attractive.

In this work the deactivation of IrO_2 anodes prepared by thermal decomposition of an Ir salt precursor solution onto Al substrates was examined. The influence of several factors of the oxide preparation procedure, such as etching and polishing of the Al substrate prior to the thermal decomposition process and the temperature used to thermally decompose the Ir salt, on the anode service life was studied. The results were also compared to IrO_2 anodes coated onto Ti. The service life of IrO_2 supported onto Al substrates, which were electrochemically coated with Ir layers prior to the thermal formation of the IrO_2 coating, was also obtained.

2. Experimental details

2.1. *Preparation of the electrodes*

Iridium oxides (referred to as IrO_2 in this work) were coated onto Ti (99.7% purity, Alfa Aesar) or Al (99.99% purity, Alfa Aesar) circular plates (1.6 cm dia. by 0.089 cm thick). Immediately prior to the formation of the oxide, the metal substrates were polished using sandpaper, ultrasonically cleaned in isopropanol for 20 min, chemically etched at 80 °C and subsequently rinsed with an excessive amount of H_2O. The Ti plates were etched in 10 M HCl for 10 min, while the Al plates were etched in either 10 M HCl, saturated oxalic acid, 3 M HNO_3 or in a solution made of 2.5 g $FeCl_3$ and 1.8 ml HCl in 100 ml H_2O, that is, a '$FeCl_3$-based' solution for 10 min, 1 h, 10 min, and 2 min, respectively. Generally, the Al substrates were etched in 10 M HCl unless otherwise stated. The IrO_2 coatings were formed by thermal decomposition of an Ir salt precursor solution made of 0.1 M $IrCl_4$ (Alfa Aesar) in isopropanol (Fisher). The precursor solution was spread onto the Ti and Al substrates using a Pasteur pipette. After each application of the precursor solution, the electrode was dried at 80 °C for 10 min, and subsequently baked in air at either 350 or 550 °C for 1 h. A total of six IrO_2 layers were generally applied in this manner. The Ti and Al substrates coated with IrO_2 are referred to as Ti/IrO_2 and Al/IrO_2, respectively. In some cases, the temperature used for the thermal decomposition of the precursor solution is given in brackets following the abbreviation of the anode material, for example, an IrO_2 coated onto Al at 550 °C is referred to as Al/IrO_2 (550 °C).

2.2. *Cells and electrodes*

A standard two compartment cell, in which the reference electrode was separated from the working electrode compartment by a Luggin capillary, was generally employed for the electrochemical studies. An electrode holder (model K0105 flat specimen holder kit, EG&G, Inc.) was used, which exposed 1 cm^2 (geometrical area) of the working electrode. A large surface area Pt gauze was employed as counter electrode. A mercury/mercury sulfate electrode (MSE) using 0.5 M H_2SO_4 as electrolyte served as reference for all electrochemical experiments except for the a.c. impedance experiments for which a saturated calomel electrode (SCE) was used. All potentials reported in this paper are referred to the MSE.

2.3. *Techniques and instrumentation*

Electrochemical experiments were performed using an EG&G 273 potentiostat driven by Corrware software program (Scribner, Assoc.). A.c. impedance measurements were carried out using an EG&G model 15210 lock-in amplifier which was interfaced to the EG&G 273 potentiostat and run by model 398 electrochemical impedance software (EG&G Princeton Applied Research). A Jeol JSM-5300 scanning microscope, a Kratos Axis XPS and X-ray diffraction spectrometer (Scintag XRD 2000) equipped with a CuK_α source were also employed to perform surface analytical studies of the oxide electrodes.

2.4. *Acquisition and evaluation of a.c. impedance data*

Electrochemical impedance spectroscopic (EIS) data were acquired for the frequency range of 60 kHz and 1 Hz. Ten points per decade were collected and a root mean square (r.m.s.) amplitude of 5 mV was found to be sufficiently low to yield a linear signal. During the a.c. measurements a d.c. bias potential (E_{dc}) of 0.5 V was applied. A nonlinear least square fitting software program (Equivalent Circuit, version 3.97), written by Boukamp of the University of Twente, was used to analyse and fit the a.c. data. This program also allowed testing the a.c. data for the Kramers Kronig transformation and for several error calculations. The a.c. signals were found to be independent of the applied frequency direction and the error for the Kramers Kronig transformation was satisfactorily small ($\leqslant 10^{-4}$).

2.5. *Solutions*

High resistivity (18 MΩ) H_2O and A.C.S. grade chemicals were used. The electrochemical experiments were performed at room temperature and high purity argon gas was used to deoxygenate the electrolyte solution. 0.5 M H_2SO_4 was employed as electrolyte solution for the electrochemical experiments with the exception of the solutions used to galvanostatically deposit a layer consisting of iridium onto the Al substrates. It is noteworthy that for the electrosynthesis of N_2O_5 highly concentrated HNO_3 solutions are used. However, 0.5 M H_2SO_4 was used to estimate the service lives of all electrodes studied in the present work. The use of 0.5 M H_2SO_4 electrolyte solutions allowed to study IrO_2 anodes supported on Ti substrates and compare them to IrO_2 anodes supported on Al substrates.

3. Results and discussion

3.1. *Electrochemical characteristics and service life estimation for IrO_2 electrodes*

Throughout this work the same procedure was used to study the electrochemical characteristics of the IrO_2

electrodes in 0.5 M H_2SO_4. This involved the recording of potential–time transients (E/t) for the IrO_2 anodes at a constant current of 100 mA cm^{-2}. During this galvanostatic experiment, Oxygen was evolved at the IrO_2 anodes. The galvanostatic experiment was periodically interrupted to record cyclic voltammograms (CVs) of the IrO_2 electrodes at 20 mV s^{-1} between −1.4 and 1.5 V for three complete oxidation/reduction cycles, and subsequently collects a.c. data. CV and a.c. data were also collected for newly prepared (i.e., unused) IrO_2 electrodes.

3.2. *Potential–time transients*

Figure 1 shows a typical E/t curve for an Al/IrO_2 anode operated at 100 mA cm^{-2}. It is seen that the anode potential (E_{anode}) steadily increases with increasing time of electrolysis and, after about 23 h for this particular anode prepared at 550 °C, has increased to very high values. This marked increase in the E_{anode} value is likely related to an increase in the anode resistance. During the galvanostatic experiment, the dark blue IrO_2 coating was observed to flake off the Al substrate, thus partially exposing the Al substrate to the H_2SO_4 solution. It is likely that a nonconductive Al oxide is formed on the Al substrate under these conditions, resulting in an increase of the anode resistance, and E_{anode}, as seen in Figure 1.

The time needed for the anode potential to increase to 10 V has been designated as $t_{breakthrough}$ and is related to the service life of these anodes. In similar work, E/t transients are commonly obtained and used to estimate the service life of Ti/IrO_2 anodes [7, 8]. The breakthrough time will be used to compare differently prepared anodes.

3.3. *CV characteristics*

Figure 2 shows a typical CV profile for an unused Al/IrO_2 (550 °C) electrode in 0.5 M H_2SO_4. The CV characteristics of this Al/IrO_2 are very similar to those found for Ir oxides also prepared using the thermal decomposition method but supported on Ti substrates [7, 9, 10]. It is known that the charge ($Q_{Ir\ oxide}$) passed between about −0.2 and 0.8 V arises largely from the electrochemical conversion of Ir sites within the oxide coating and at the coating/solution interface, and hence, is related to the number of electroactive Ir coating sites [9, 10]. The fact that $Q_{Ir\ oxide}$ remains essentially the same during the first three oxidation/reduction cycles (Figure 2) indicates that this Al/IrO_2 electrode is stable at least during this 'short' experiment. Figure 3 shows the dependence of $Q_{Ir\ oxide}$ on the sweep rate for the same Al/IrO_2 electrode. It is seen that the complete film charge is recovered at sweep rates of 20 mV s^{-1} and lower, therefore, CV data are generally collected at 20 mV s^{-1} in this work. The observed increases in current at very negative ($<\sim -0.65$ V) and positive ($>\sim 0.8$ V) potentials (Figure 2) is due to the evolution of hydrogen (HER) and oxygen (OER), respectively.

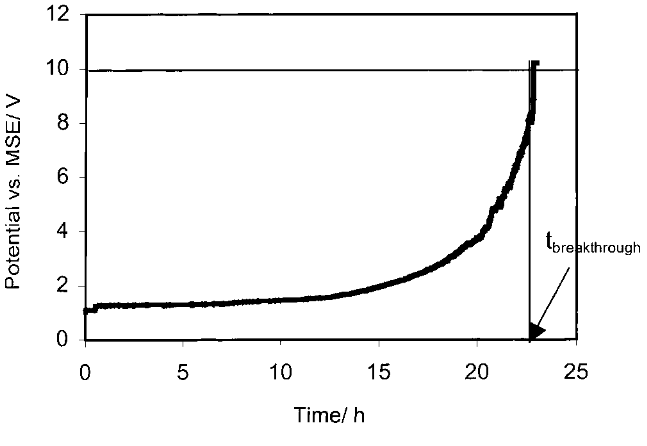

Fig. 1. Typical potential–time transients for a Al/IrO_2 (550 °C) anode at 100 mA cm^{-2} in 0.5 M H_2SO_4.

The CV characteristics of the Al/IrO_2 electrodes were found to be altered as a consequence of using them as anodes at 100 mA cm^{-2}, prolonged anodic electrolysis resulted in a decrease in the $Q_{Ir\ oxide}$ value. For this particular anode clear decreases in the $Q_{Ir\ oxide}$ value of about 20 and 90% were found after 16 and 23 h, respectively, at 100 mA cm^{-2}. This decrease indicates that the number of electroactive Ir sites within the oxide coating decreases consistent with the observed loss of the catalytic IrO_2 coating from the Al substrate. The observed decrease in $Q_{Ir\ oxide}$ with time of electrolysis also correlates well with the increase in the E_{anode} value shown in Figure 1, that is, significant loss of the electroactive Ir sites is observed when E_{anode} clearly increases.

3.4. *A.c. characteristics*

The galvanostatic experiment was interrupted to collect a.c. data for the IrO_2 electrodes at a d.c. bias potential (E_{dc}) of 0.5 V. At 0.5 V, oxygen is not evolved on the

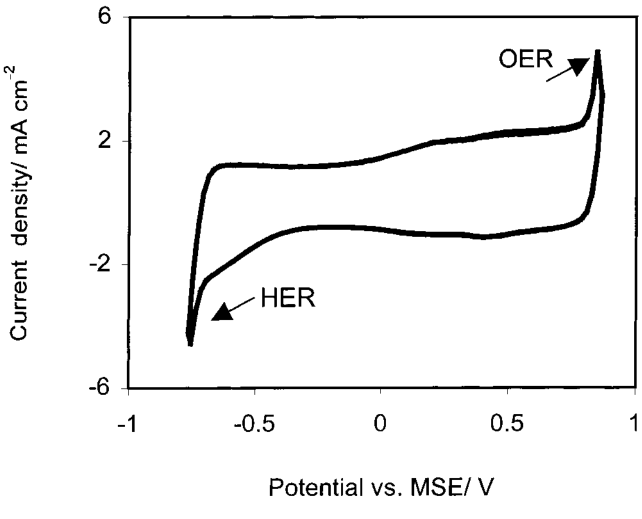

Fig. 2. Typical CVs for an unused Al/IrO_2 (550 °C) electrode recorded at 20 mV s^{-1} in 0.5 M H_2SO_4. First three cycles are shown in Figure 2.

IrO_2 electrodes, and the a.c. data collected at this E_{dc} yield the properties of the IrO_2 coating, the substrate/coating interface and/or the substrate/solution interface. In this work, the raw a.c. data are presented in the form of Nyquist plots, that is, as plots of the imaginary impedance multiplied by −1 ($-Z''$) against the real impedance (Z'). Figure 4 shows a typical set of Nyquist plots for the Al/IrO_2 (550 °C) electrode used in the previous experiments (i.e., Figures 1–3). The Nyquist plots are collected as a function of time that 100 mA cm^{-2} are passed through the Al/IrO_2 anode (i.e., at 0 (□), 0.5 (×), 4 (Δ) and 7 (○) h). It is seen (Figure 4) that the three Nyquist plots collected at 0, 0.5 and 4 h are very similar. Over the entire frequency range, the electrode shows a mainly capacitive behaviour, as indicated in the fact that a straight line is observed with a slope (i.e., $-dZ''/dZ'$) approaching infinity. The raw a.c. data were found to fit a simple equivalent circuit (EQC) shown in Figure 5 which consists of a series combination of a resistor and a constant phase element ($CPE_{Ir\ oxide}$). In this EQC, R_s represents the resistance of the 0.5 M H_2SO_4 present between the Al/IrO_2 and the tip of the Luggin capillary. The $CPE_{Ir\ oxide}$ is believed to result mainly from the faradaic conversion of the electroactive Ir coating sites. Supporting evidence for this assignment is given by the fact that the $Q_{Ir\ oxide}$ value extracted from the CV data and the $CPE_{Ir\ oxide}$ value extracted by fitting the raw ac data to the EQC in Figure 5 are very similar for all the IrO_2 electrodes studied in this work. The fact that the faradaic conversion of Ir coating sites is better presented by a CPE than an ideal capacitor is likely due to the fact that Ir oxides formed by thermal decomposition are typically very heterogeneous, have a rough surface and are likely porous [5, 6, 11, 12]. These properties typically introduce nonideal a.c. behaviours as, for example, a CPE [13, 14].

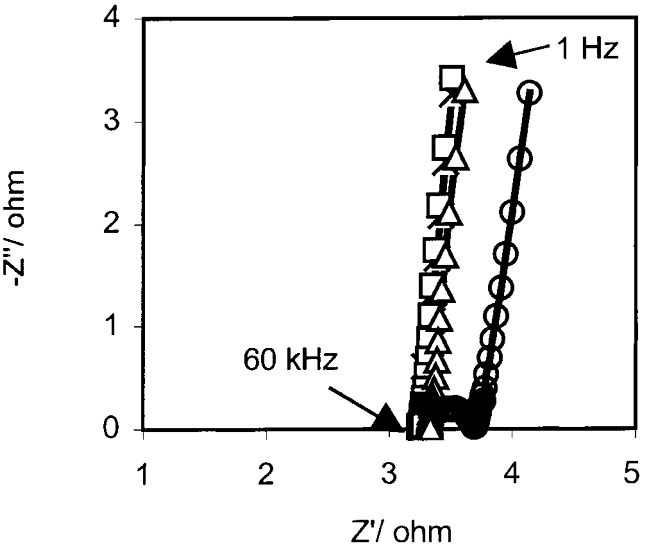

Fig. 4. Family of Nyquist plots for an Al/IrO_2 (550 °C) electrode. The Al/IrO_2 (550 °C) was used for anodic electrolysis at 100 mA cm^{-2} in 0.5 M H_2SO_4. Electrolysis was periodically interrupted at 0 h (×), 1 h (□), 4 h (△) and 7 h (○) to collect a.c. data at a d.c. bias potential of 0.5 V vs. MSE.

Figure 4 also shows that the Nyquist plot characteristics for the Al/IrO_2 are altered after 100 mA cm^{-2} are passed through the oxide anode for a sufficiently long time period, in this case for 7 h. In fact, an additional feature resembling a semicircle is recognizable at high frequencies in the Nyquist plot for the Al/IrO_2 which was used as anode at 100 mA cm^{-2} for 7 h (Figure 4 (○)). This a.c. behavior, which is assigned to represent the properties of Al oxide building up during the anodic electrolysis, is described using a parallel combination of a resistor ($R_{Al\ oxide}$) and a CPE ($CPE_{Al\ oxide}$), as shown in the EQC in Figure 6. The formation of Al oxide may be due to H_2SO_4 accessing the substrate through the cracked and porous structure of the IrO_2 coating (see below). It is also possible that the IrO_2 coating flakes off the Al substrate due to poor adhesion between the oxide and substrate, thus exposing the Al substrate directly to the H_2SO_4 solution. The latter explanation appears more likely, as the service life of these Al/IrO_2 anodes was found to be essentially independent of the thickness of the IrO_2 coating.

It is noteworthy that the $Q_{Ir\ oxide}$, $t_{breakthrough}$, etc. values reported in this work were found to be satisfac-

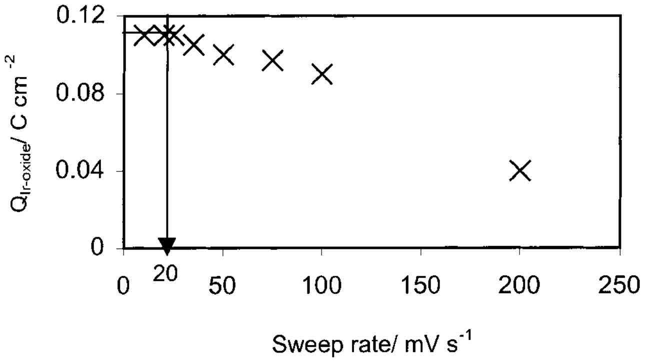

Fig. 3. Dependence of $Q_{Ir\ oxide}$ against the sweep rate for an unused Al/IrO_2 (550 °C) electrode obtained from the CV data in 0.5 M H_2SO_4. $Q_{Ir\ oxide}$ values are equivalent to the anodic charges passed between −0.15 and 0.75 V vs. MSE.

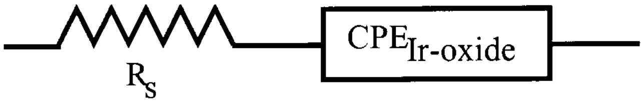

Fig. 5. Equivalent circuit used to fit the raw a.c. data for IrO_2 electrodes at which nonconductive Al oxide is not detectable by EIS.

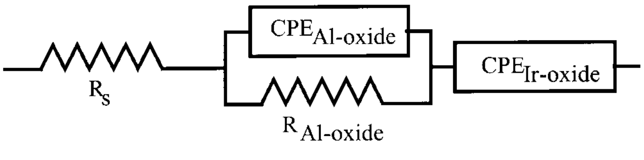

Fig. 6. Equivalent circuit used to fit the raw a.c. data for Al/IrO_2 electrodes which were used for prolonged anodic electrolysis at 100 mA cm^{-2} in 0.5 M H_2SO_4.

torily reproducible for electrodes prepared using the same conditions. The $Q_{\mathrm{Ir\ oxide}}$ and $t_{\mathrm{breakthrough}}$ values for oxide electrodes prepared in the same manner agreed within less than 2 and 8%, respectively.

3.5. *Service life and properties of differently prepared IrO_2 electrodes*

In this Section the electrochemical and structural characteristics, as well as the service life of IrO_2 coated on either Al or Ti substrates, are compared. The influence of the temperature (350 cf. 550 °C) used for the thermal decomposition of the Ir salt precursor solution on the performance of Al/IrO_2 and Ti/IrO_2 anodes is also studied. These temperatures are sufficiently high to decompose the Ir salt, as confirmed by XPS studies.

Table 1 shows data obtained from CV, EIS and galvanostatic experiments for both the Al and Ti 'IrO_2' systems prepared at either 550 or 350 °C. It is seen that over the test period of 60 h at 100 mA cm^{-2}, neither of the IrO_2 anodes supported on the Ti substrates (i.e., Ti/IrO_2 (350 °C) and Ti/IrO_2 (550 °C)) failed. This indicates that the service lives of these anodes are good consistent with previous work [5, 8]. The raw a.c. data collected in this work did not indicate the formation of Ti oxide during the 60 h electrolysis experiment at 100 mA cm^{-2}. In fact, the raw a.c. data of these Ti/IrO_2 anodes fitted the EQC shown in Figure 5, which is the same circuit that also fits the raw a.c. data for the unused Al/IrO_2 electrodes. Table 1 also shows that the service life of the Ti/IrO_2 anodes is markedly better than for any of the Al/IrO_2 anodes studied in this work. This observed influence of the substrate nature on the service life of these IrO_2 anodes could be due to several factors and will now be further discussed.

The service life of the Al/IrO_2 anodes was found to be strongly influenced by the temperature used for the decomposition of the Ir salt. In fact, the service life of the Al/IrO_2 (550 °C) anodes is seen to be almost eight times longer than for the Al/IrO_2 (350 °C) anodes, as indicated in the $t_{\mathrm{breakthrough}}$ values of 23 and 3 h, respectively (Table 1). Furthermore, the raw a.c. data showed that Al oxide was formed after only 0.5 h of electrolysis using the Al/IrO_2 anode prepared at 350 °C, while the formation of Al oxide was only recognizable after 7 h of anodic electrolysis using the Al/IrO_2 formed at 550 °C. The morphology of thermally formed IrO_2 electrodes supported on Ti substrates is known to be influenced by the temperature used for the thermal decomposition of the Ir salt [10]. In this work SEM was employed to study the surface morphology of the differently prepared oxide electrodes. A typical mud-crack structure possibly resulting from the dehydration of the Ir oxide in air and/or in the vacuum chamber is clearly recognizable for the unused Ti/IrO_2 (350 °C) electrode shown in Figure 7(a) [10, 13]. The cracks of the unused oxide formed at 550 °C (Figure 7(b)) are somewhat wider and the oxide structure is slightly more disordered than seen for the oxide formed at 350 °C. These results indicate differences in the oxide morphology consistent with prior studies [10]. This, in turn, influences the number of electroactive Ir sites within the oxide coating, as indicated by the different $Q_{\mathrm{Ir\ oxide}}$ values extracted from the CV data of the two oxides (Table 1). Figure 7(c) shows a typical SEM for a used Ti/IrO_2 (350 °C) obtained after the anodic electrolysis at 100 mA cm^{-2} was carried out for 1 h. The morphologies of the used and unused oxides are clearly different (Figure 7(a) cf. 7(c)). During the anodic electrolysis the oxide appears to 'seal' itself. It is likely that such a sealed oxide coating hinders access of the H_2SO_4 solution to the metal substrate, thereby improving the anode's service life. It is noteworthy that the color of all the Ti/IrO_2 anodes used in this work changed rapidly (within less than 1 h) from blue–black to brown, as a result of passing 100 mA cm^{-2} through these anodes. During this electrolysis experiment oxygen is evolved at the IrO_2 anodes and H_2O is consumed. Therefore, the observed changes of the IrO_2 structure and color could reflect that the oxide is dehydrated during the electrolysis process.

Figure 7(d) and (e) show the SEMs for unused Al/IrO_2 (350 °C) and Al/IrO_2 (550 °C) electrodes. It is seen that the temperature used for the thermal decomposition process influences the morphology of the IrO_2 coating much more strongly when Al is used as a substrate rather than Ti (Figure 7(a) and (b)). The oxide structure for the Al/IrO_2 formed at 350 °C is seen to be very unordered and rough. Furthermore, a large number of the oxide sites are seen as bright SEM images. This

Table 1. Electrochemical characteristics for IrO_2 coated on Al or Ti substrates

Electrode	$t^{*}_{\mathrm{breakthrough}}$ /h	$Q^{\dagger}_{\mathrm{Ir\ oxide}}$ /mC cm^{-2}	Time the IrO_2 is used as anode before Al-oxide or Ti oxide of about 0.5 Ω resistance is formed‡/h
Al/IrO_2 (350 °C)	3	0.06	0.5
Al/IrO_2 (550 °C)	23	0.1	7
Ti/IrO_2 (350 °C)	>60	1.1	>60
Ti/IrO_2 (550 °C)	>60	0.1	>60

* Time equivalent to the service life of the IrO_2 anodes. The $t_{\mathrm{breakthrough}}$ values are obtained from the E/t transients at 100 mA cm^{-2} in 0.5 M H_2SO_4, as shown in Figure 1

† $Q_{\mathrm{Ir\ oxide}}$ values are obtained from CV data of the unused IrO_2 electrodes

‡ Electrochemical impedance spectroscopy at a E_{dc} of 0.5 V was used to estimate the resistance ($R_{\mathrm{Al\ oxide}}$) resulting from the formation of the nonconductive Al oxide

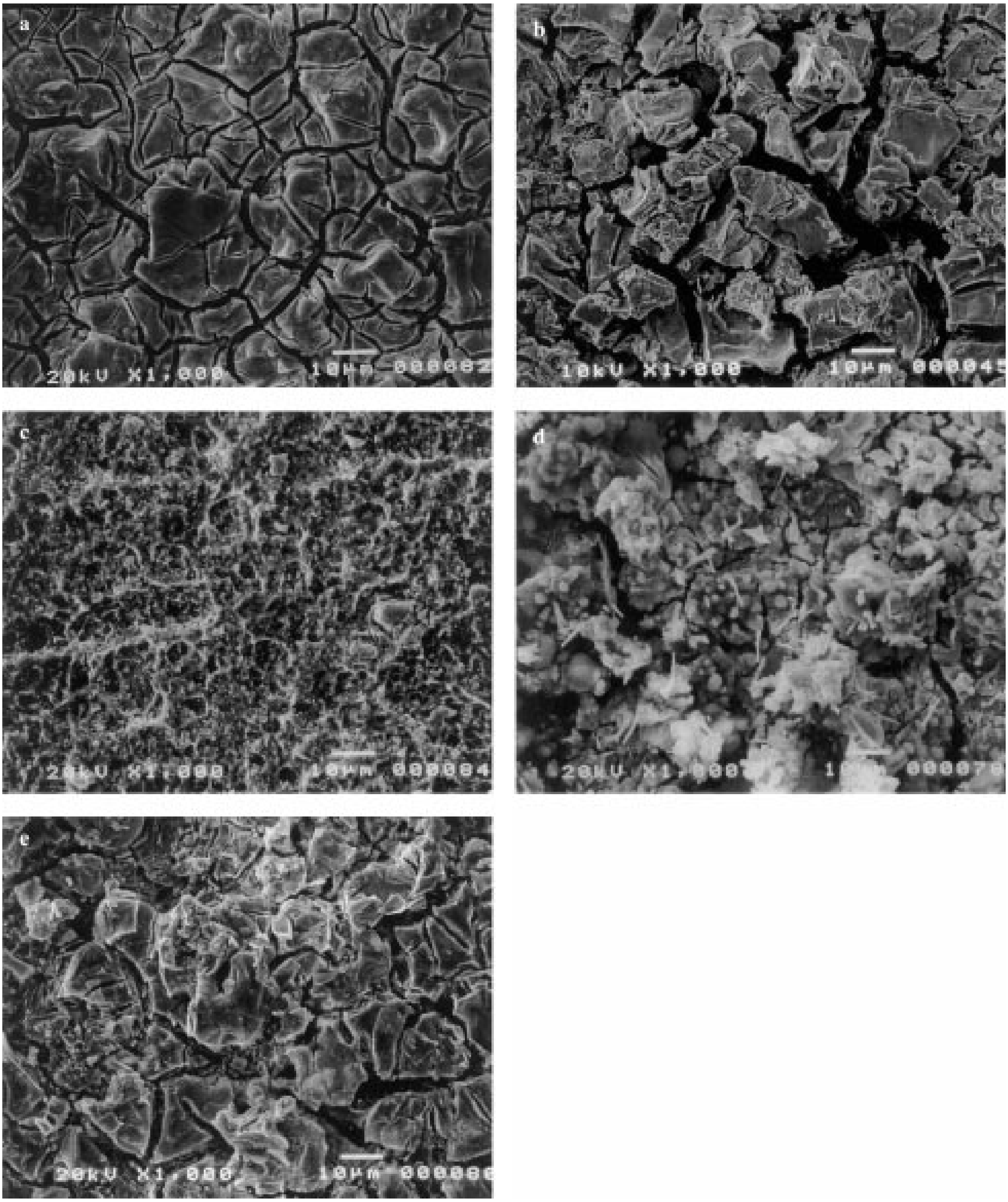

Fig. 7. SEM photographs for IrO_2 electrodes obtained at a 1000 time magnification. Figure 7(a) and (b) show the SEMs for unused Ti/IrO_2 electrodes formed at 350 and 550 °C, respectively, while Figure 7(c) shows the SEM for Ti/IrO_2 (350 °C) used as anode at 100 mA cm^{-2} in 0.5 M H_2SO_4 for 1 h. SEMs for the unused Al/IrO_2 electrodes formed at 350 and 550 °C, respectively, are shown in Figure 7(d) and (e).

could suggest that the IrO_2 is only loosely attached to the Al, and that the electrical connection between the oxide and substrate is poor. Therefore, it is not surprising that the service life of this particular anode is short (Table 1). A poor electrical connection between the IrO_2 and the substrate is likely to reduce the number of electroactive Ir sites, and hence, the value of $Q_{\mathrm{Ir\ oxide}}$. In fact, Table 1 shows that the $Q_{\mathrm{Ir\ oxide}}$ value for the Al/IrO_2 (350 °C) is almost twenty times smaller than for the Ti/IrO_2 also formed at 350 °C. The morphology and the

$Q_{\mathrm{Ir\ oxide}}$ value for the Al/IrO_2 electrode formed at 550 °C are more similar to the Ti/IrO_2 (550 °C) electrodes. However, for both the Al/IrO_2 (350 °C) and Al/IrO_2 (550 °C) electrodes the IrO_2 coating was easily pulled off the Al substrate using scotch tape, while only outer Ir oxide sites (i.e., not exposing the Ti substrate) were removed using Scotch tape for the Ti/IrO_2 electrodes. This suggests that the adhesion between the Al substrate and the IrO_2 is poor, thus likely being at least partly responsible for the short service life of these anodes.

It is noteworthy that the $IrCl_4$ precursor solution made in isopropanol is very acidic (pH < 2). Furthermore, Al (and also Ti) are thermodynamically not stable at open circuit and in acidic solutions [17]. Therefore, the substrate may dissolve partially when the 0.1 M $IrCl_4$ precursor solution is applied which, in turn, could result in poor adhesion between the IrO_2 and the Al substrate. In this work, Al/IrO_2 (550 °C) anodes were also prepared using 0.1 M $IrCl_4$ precursor solutions made in H_2O. The pH of this solution was adjusted to ~7. The service life of this Al/IrO_2 (550 °C) anode was found to be essentially the same ($t_{\mathrm{breakthrough}} = 25$ h), as found for similarly prepared Al/IrO_2 (550 °C) anodes, but using the 0.1 M $IrCl_4$ precursor solution made in isopropanol. These results suggest that the poor adhesion between the IrO_2 and the Al is not related to the low pH of the precursor solution used here. The presence of Cl^- in the precursor solution could assist in the dissolution of Al. However, thermally unstable and chloride free Ir salts are rather rare and very expensive. Hence, the influence of Cl^- on the service life of these IrO_2 anodes was not tested.

3.6. *Influences of polishing and etching on the substrate and oxide properties*

It is common to roughen and etch the metal substrate prior to the formation of the catalytic oxide coating (e.g., IrO_2) to remove oxides from the substrate and to introduce a high surface roughness etc. [5, 7, 8]. It is known that the service life of noble metal oxide anodes is influenced by the procedure used to polish and etch the substrate [5, 7, 8]. For example, a rough surface has been suggested to act as an ‘anchor’ for the oxide coating, thus increasing the service life of these oxide anodes. The substrate morphology (and hence, also the service life of the subsequently prepared oxide anode) is often influenced by the nature of the etching solution [5, 6, 12]. In this work, the influence of different etching procedures on the morphology of the Al substrate was probed and compared to the case of etching Ti substrates. The differently etched Al substrates were also coated with IrO_2 at 550 °C and their service lives were estimated. The service lives of the Al/IrO_2 anodes was found to depend on the etching solution. In fact, the service life of the Al/IrO_2 (550 °C) anodes was longer when HNO_3 rather than HCl was used to etch the Al substrate, as indicated in the $t_{\mathrm{breakthrough}}$ values of 35 and 23 h, respectively. However, the service lives of all these Al/IrO_2 anodes are clearly shorter than for the Ti/IrO_2 anodes. Figure 8(a) and (b) show the SEM photographs for the differently etched Al substrates, that is, Al etched in HCl and Al etched in HNO_3, respectively. Figure 8(c)

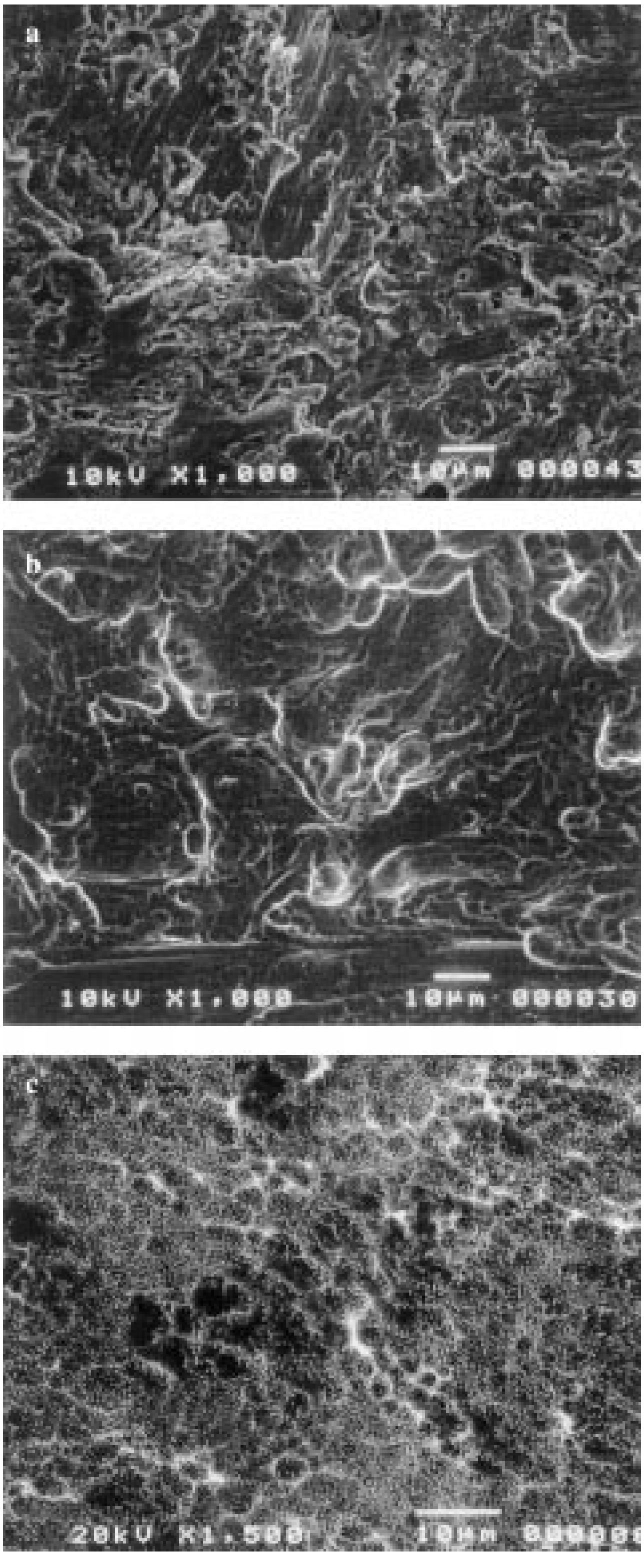

Fig. 8. SEM photographs at a 1000 time magnification for Al and Ti substrates obtained after etching the substrates. Figure 8(a) and (b) show the SEMs for Al substrates etched in 5 M HNO_3 and 10 M HCl, respectively, at 80 °C for 10 min, while the SEM for Ti etched in 10 M HCl at 80 °C for 10 min is shown in Figure 8c.

shows the SEM for a Ti substrate etched in HCl. It is seen that the etching solution influences the morphology of the Al substrate. However, none of these differently etched Al substrates are very rough, and, in fact, both Al substrates show a significantly lower roughness than the Ti substrate. It is to be expected that the higher roughness of the Ti substrate beneficially influences the service life of the IrO_2 anodes. This difference in substrate roughness could be at least partially responsible for the observed dependence of the service life on the substrate nature (Ti cf. Al).

The surface composition of the metal substrate is often altered during the etching process. It has been shown that titanium hydride is formed when Ti is etched in HCl [5, 18, 19]. Furthermore, the titanium hydride (which is thermally unstable [11]) is believed to have a beneficial effect on the service life of the subsequently formed oxide anode [19]. Other etching solutions can influence the surface composition of the substrate similarly, for example, thermally unstable titanium oxalate has been suggested to be formed as a result of etching Ti in oxalic acid [7]. Figure 9 shows the X-ray diffraction (XRD) patterns for Ti substrates that have been polished with sandpaper (a) and etched in HCl (b). The XRD for a Ti/IrO_2 (350 °C) electrode is also shown in Figure 9. It is seen (consistent with previous studies [19]) that titanium hydride is formed as a result of etching the Ti substrate in HCl and the XRD for the Ti/IrO_2 (350 °C) is very similar to previously reported data [19]. Figure 10 shows the XRDs for a sandpaper polished Al substrate and for differently etched (i.e., in HCl, HNO_3 and oxalic acid) Al substrates. The XRD of an Al/IrO_2 (350 °C) is also shown in Figure 10. The XRD spectra for all of the etched Al substrates are essentially the same as for the sandpaper polished Al substrate. Furthermore, XPS studies obtained for the Al substrates etched in either HNO_3 or oxalic acid showed that neither nitrate nor oxalate is present on the etched Al substrates after etching. Therefore, it appears that during the etching procedures used in this work, metal salts on the Al substrate are not formed in contrast to the situation with Ti.

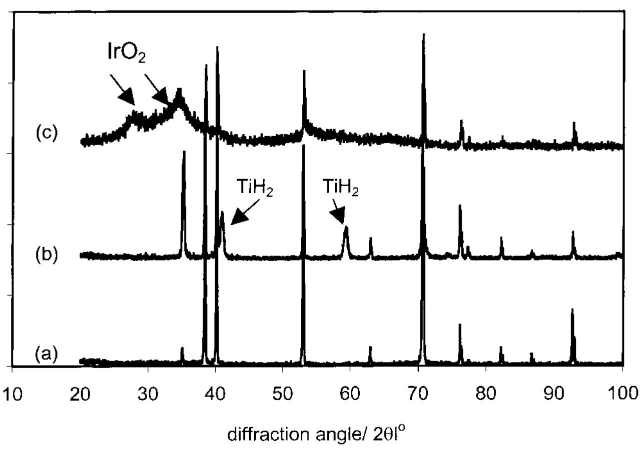

Fig. 9. XRD patterns for (a) a sandpaper polished Ti substrate, (b) a Ti substrate etched in 10 M HCl at 80 °C for 10 min, and (c) an unused Ti/IrO_2 (350 °C). The XRDs were collected using a CuK_α source and a speed of 0.03 deg. s^{-1}.

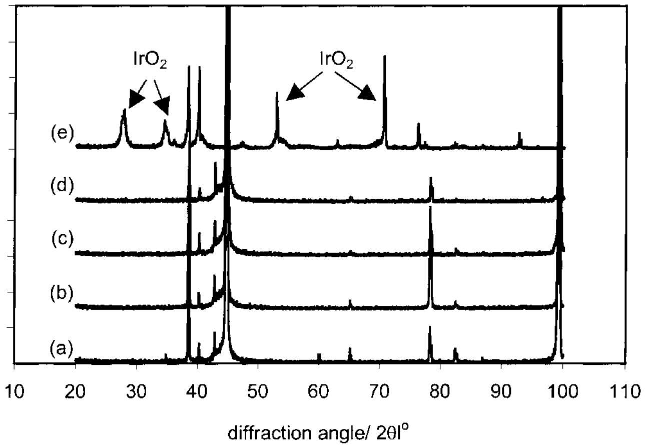

Fig. 10. XRD patterns for (a) a sandpaper polished Al substrate, (b) Al substrates etched in 10 M HCl or (c) 5 M HNO_3 at 80 °C for 10 min, (d) an Al substrate etched in saturated oxalic acid at 80 °C for 1 h, and (e) an unused Al/IrO_2 (350 °C) electrode. The XRDs were collected using a CuK_α source and a speed of 0.03 deg. s^{-1}.

3.7. *Modification of the Al substrate prior to the thermal formation of IrO_2*

In this Section a layer consisting of iridium was electrochemically deposited onto polished and etched Al substrates, before the IrO_2 was formed by thermal decomposition at 550 °C. Electrodes prepared in such a manner are referred to as $Al/Ir/IrO_2$. The iridium layer was deposited using a cathodic current density of -1 μA cm^{-2} from solutions made of low $IrCl_4$ concentrations. Immediately prior to the electrochemical deposition, the Al substrates were etched in the '$FeCl_3$-based' solution. This resulted in smooth Al surfaces as observed in previous work [20]. Different conditions were used for the electrochemical deposition of the iridium layer, as shown in Table 2 which summarizes the most successful experiments carried out in this work. The electrochemically deposited iridium layers have not been characterized. However, these electrochemically deposited layers were bluish, most likely indicating that an iridium oxide, which may be porous, is formed.

The service lives of the $Al/Ir/IrO_2$ anodes tested here (Table 2) were found to be substantially longer than found for the previously tested Al/IrO_2 anodes (see above). Furthermore, the service life of an IrO_2 (550 °C) anode supported on an Al substrate etched in the '$FeCl_3$-based' solution was also found to be shorter ($t_{\mathrm{breakthrough}} = 10$ h) than for the $Al/Ir/IrO_2$ anodes. Therefore, these results strongly suggest that the electrochemically deposited iridium layer acts as a 'protective layer' for the Al substrate, thus slowing down the formation of Al oxide.

The a.c. data collected for the $Al/Ir/IrO_2$ electrodes (Table 2) show that Al oxide was formed during the

Table 2. Experimental conditions used to electrochemically deposit an 'iridium layer' on the Al substrate and its influence on the electrochemical properties of the subsequently prepared IrO_2 electrodes.
A cathodic current density of -1 μA cm^{-2} was used to deposit the iridium layer

Plating solution	Plating time/days	$Q_{\mathrm{Ir\ oxide}}$ for the unused Al/Ir/IrO_2^*/mC cm^{-2}	$t_{\mathrm{breakthrough}}$ for the Al/Ir/$IrO_2^{\dagger}$ anode/h	Time the IrO_2 is used as anode before Al oxide of about 0.5 Ω resistance is formed‡/h
16 μM $IrCl_4$ in phosphate buffer (pH 8)	5	0.95	54	45
16 μM $IrCl_4$ + 10^{-1} M Na_2SO_4	3	0.9	33	22
16 μM $IrCl_4$ + 10^{-1} M Na_2SO_4	5	0.8	98	88

[*] $Q_{\mathrm{Ir\ oxide}}$ values are estimated from the CV data of the unused Al/Ir/IrO_2 electrodes

[†] The $t_{\mathrm{breakthrough}}$ values are obtained from the E/t transients for the Al/Ir/IrO_2 anodes at 100 mA cm^{-2} in 0.5 M H_2SO_4, as shown in Figure 1

[‡] Electrochemical impedance spectroscopy at a E_{dc} of 0.5 V was used to estimate the resistance ($R_{\mathrm{Al\ oxide}}$) resulting from the formation of the nonconductive Al oxide

anodic electrolysis experiment, as was also observed for the Al/IrO_2 anodes. However, for the case of the Al/Ir/IrO_2 anodes, the formation of Al oxide occurred after significantly longer electrolysis times than those needed for the formation of Al oxide using the Al/IrO_2 anodes. Furthermore, the thermally formed IrO_2 coating flaked almost entirely off the Al/Ir/IrO_2 anode significantly earlier (generally after about 25 h of electrolysis) than $t_{\mathrm{breakthrough}}$ was reached and Al oxide was detected. This indicates that the adhesion between the electrochemically deposited iridium layer and the thermally formed IrO_2 is poor. However, these results also suggest that the adhesion between the electrochemically formed iridium layer and the Al substrate is markedly better than between the thermally formed IrO_2 and the Al substrate. The results also suggest that the adhesion between the electrochemical Ir layer and the thermal IrO_2 is poor.

Table 2 also shows that the service life of the Al/Ir/IrO_2 anodes increases as the time for the electrochemical deposition of the iridium layer is made longer. It is likely that the thickness of this iridium layer increases with increasing deposition time. Access of H_2SO_4 to the Al substrate is likely to be slower for a thicker iridium layer and/or a longer time is needed to anodically dissolve the iridium layer, thus enhancing the anode's service life. Furthermore, it was found (Table 2) that Al/Ir/IrO_2 anodes prepared using Al substrates coated with an electrochemically deposited iridium layer from Na_2SO_4 solutions showed the longest service life. However, it is possible that the quality of the electrochemically deposited iridium layer (and hence, also the service life of otherwise similarly prepared Al/Ir/IrO_2 anodes) can be improved using different experimental conditions for the electrochemical deposition process than those used here.

4. Summary and conclusions

The deactivation of Al/IrO_2 anodes, prepared by thermal decomposition of an Ir-precursor solution, was studied during anodic electrolysis at 100 mA cm^{-2} in 0.5 M H_2SO_4. The catalytic IrO_2 coating was found to flake off the Al substrate and nonconductive Al oxide was formed during the electrolysis. The service lives of the Al/IrO_2 anodes was found to be influenced by the temperature used for the thermal decomposition of the Ir salt and the solution used to etch the Al substrate. However, the service lives of all the Al/IrO_2 anodes tested in this work were found to be markedly shorter than for similarly prepared Ti/IrO_2 anodes. Etching in neither HNO_3 nor HCl resulted in a high surface roughness of the Al substrate, in contrast to the etching of Ti substrates in HCl. This difference in surface roughness may at least partly explain the observed differences in the service lives of these IrO_2 anodes.

The surface morphology of the IrO_2 thermally formed at 350 °C was seen to be strongly influenced by the substrate nature (i.e., Al vs. Ti), while the influence of the substrate nature on the IrO_2 surface morphology was less pronounced when 550 °C was used for the thermal decomposition process. Furthermore, SEM and CV data suggest that the electrical connection (and hence, also the adhesion) between the IrO_2 formed at 350 °C and the Al substrate is poor, thus providing a possible explanation for the particularly short service life found for this Al/IrO_2 (350 °C) anode. In general, the adhesion between the IrO_2 formed by thermal decomposition and the Al substrate appears to be poorer than between the IrO_2 and the Ti substrate, as indicated in the fact that the Ir oxide coatings are easily pulled off the Al substrates using Scotch tape.

It was also found that the electrochemical deposition of an 'iridium layer' onto the Al substrate prior to the thermal formation of the IrO_2 coating enhances the service lives of these oxide anodes. This increase in service life is likely due to better adhesion between the electrochemically deposited 'iridium layer' and the Al substrate than between the thermally formed IrO_2 and the Al substrate. However, the service life of these anodes is still short. The quality of the electrochemically deposited 'iridium layer' has to be improved or other methods for the formation of catalytic Ir oxides supported on Al substrates have to be tested.

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