Cathodes for chlorate electrolysis with nanocrystalline Ti–Ru–Fe–O catalyst

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Abstract

Cathodes for chlorate electrolysis were prepared by mixing nanocrystalline Ti–Ru–Fe–O catalyst powder with small amounts of Teflon and subsequent hot pressing on a carbon–Teflon sublayer. Initially, the electrode materials were characterized by SEM, EDX, XRD and BET measurements. The behaviour of electrodes with catalyst loadings from 300 mg cm^{-2} reduced to 10 mg cm^{-2} was investigated in chlorate electrolyte with pH 6.5 and in part, for comparison, in 1 M sodium hydroxide solution at 70 °C. Several methods have been used: cyclic voltammetry for the determination of double layer capacitance, Tafel plot analysis, cathodic potentiodynamic polarization and potentiostatic tests at $i = -250$ mA cm^{-2}. The as-milled catalyst powder electrodes showed a high activity for the HER in chlorate electrolyte particularly expressed in low overpotentials of about 580 mV at -250 mA cm^{-2} for catalyst loadings down to 20 mg cm^{-2} and high double layer capacitances in the freshly prepared state. These electrodes show increased activity at low polarization. The long-term stability during electrolysis was also analysed.

1. Introduction

In chlorate electrolysis about one half of the total production cost is due to the high electrical energy consumption. Many efforts have been directed towards a reduction of the overall cell voltage, particularly by lowering anodic and cathodic overpotentials. The introduction of the dimensionally stable anode (DSA) has allowed a decrease in overvoltage to a small value of 50 mV at 250 mA cm^{-2}. Then, most of the energy losses occur at the cathode. Mild steel cathodes are mostly used presently but they exhibit high overpotentials (850 to 1100 mV) at -250 mA cm^{-2}. On the other hand, under open circuit conditions (o.c.p.), that is, during standstill periods, steel-based cathodes are not stable in chlorate electrolyte. This results in a relatively short cathode lifetime. It has been shown that titanium cathodes are stable at o.c.p. but suffer from hydrogen embrittlement during electrolysis [1, 2]. To date, no stable cathodes are available for industrial chlorate electrolysis. There is, thus, an urgent requirement in the development of new cathode materials with lower potentials for HER and more stability in chlorate electrolyte. The cathodic performance of ruthenium oxide (RuO$_2$) coated electrodes prepared by thermal decomposition of RuCl$_3$ on Ti

substrates [3, 4] and on Ni substrates [5] and by electro-codeposition of RuO$_2$ powder with Ni [4] has been investigated in 1 M sodium hydroxide solution and partly in chlorate electrolyte. Their electrocatalytic activity for HER after preactivation was found to be significantly improved compared to that of steel. However, RuO$_2$ is thermodynamically unstable, that is, shows disposition for partial reduction to lower oxidation states [4]. Furthermore, RuO$_2$ coated electrodes were eroded by strong gas evolution [3]. Thus, long-term stability of those electrodes cannot be expected in industrial atmospheres.

Recently, nanocrystalline Ti–Ru–Fe–O alloys [2, 6] (and Ti–Ru–Fe–Cr–O alloys [7]) have been developed as new cathode materials for chlorate electrolysis. It was shown that they can easily be prepared by high energy ball milling of pure Ti and RuO$_2$ powder under formation of a fine mixture of two new phases [2]: a hcp Ru-like phase and cubic RuTi(Fe)O were obtained. Iron is usually incorporated by wear debris of the milling tools and is additionally alloyed into the material. It has been shown that iron does not significantly affect the excellent catalytic parameters of the HER for electrodes based on those nanocrystalline alloys [2]. Depending on the Ti/RuO$_2$ ratio, overpotentials at -250 mA cm^{-2} of only 550 to 600 mV were

obtained. These values are about 300 mV lower than those obtained on mild-steel based cathodes. The typical catalyst loading of the electrodes was 300 mg cm^{-2}. This loading has been optimized previously [2, 6]. The high catalytic activity of the alloys was attributed to the formation of new phases during milling and/or to the strongly reduced crystal size providing a large surface area. Further fundamental studies are performed to answer the question, whether the intrinsic or the extrinsic factors are dominating [8]. Initial investigations indicated that the presence of the component ruthenium is essential for the high catalytic activity for HER. On the other side, the titanium and oxygen components were found to be responsible for the excellent resistance of the nanocrystalline Ti–Ru–Fe–O alloys to the chemical attack of the chlorate electrolyte [2, 6]. Even when those first fundamental studies showed the high capacity of nanocrystalline Ti–Ru–Fe–O powders for application as HER electrode materials in chlorate electrolyte, there are still several problems that must be solved before an introduction of the catalyst into industrial electrolysis processes is possible. One of these aspects is the reduction of the catalyst loading of the electrodes without the decrease of their performances. This is an important point because the most cost intensive factor in the Ti–Ru–Fe–O catalyst powder preparation is the expensive RuO$_2$. Therefore, the catalyst loading of the cathode must be as small as possible if one expects to keep production costs of these new electrodes in reasonable limits. This suggests the preparation of electrodes consisting of a metal substrate coated with a thin layer of catalyst powder, which provides a large surface for HER, that is, which exhibits a high surface roughness or/and active surface sites. At the same time, the metal substrate must resist to degradation processes in the chlorate electrolysis bath. To realise those electrodes two approaches can be used: (i) Searching for new highly degradation resistant metal substrates, which are coated with a catalyst powder layer forming a highly adhesive junction between the bulk substrate and the powder grains. (ii) Keeping the conventionally used mild steel or titanium cathode materials as substrate and introducing a thin, conductive, adhesive sublayer that supports on one side the catalyst powder layer, and, on the other side, protects the substrate against the attack of the chlorate electrolyte. The present work is related to the improvement of the electrocatalytic properties of the electrodes based on the second approach (ii).

The aim of this work is to study the effect of an inactive sublayer between the catalyst layer and the substrate on the electrode performance for the HER in chlorate medium. Thus, double layered electrodes fixed on a metal substrate were prepared. The inactive sublayer was adapted from gas diffusion electrode technique [9]. The effect of the Ti–Ru–Fe–O catalyst powder loading on the electrocatalytic activity of the electrode for the HER in chlorate electrolyte was investigated.

2. Experimental details

2.1. Catalyst powder preparation

The catalyst was based on nanocrystalline Ti$_2$RuFeO$_2$ powder. The alloy preparation by high energy ball milling and studies on phase transformation processes during the mechanical alloying process have been described elsewhere [2, 6]. As-milled powders were characterised by scanning electron microscopy (SEM), EDX analysis, X-ray diffraction (XRD) and BET measurements.

2.2. Electrode preparation

The catalyst powder was mixed with 5 wt% PTFE (Teflon) powder forming a highly conductive and wettable paste. A sublayer material was created by mixing carbon Vulcan XC72 powder with PTFE powder in a weight ratio of 2:1. Pretests revealed that this sublayer material is highly conductive, similar to the catalyst–Teflon mixture, and it is almost completely hydrophobic (water uptake at 25 °C and 70 °C lower than 1 wt%). Both materials were simultaneously pressed on a substrate at 250 °C and three tons forming a double layered pellet with an area of $A = 1.44$ cm^2. This assembly was embedded in epoxy resin for electrochemical tests. In this way, electrodes with catalyst loadings from 300 to 10 mg cm^{-2} were prepared. The morphology of those double-layered pellets was investigated before and after electrochemical treatments by SEM and EDX analysis.

2.3. Electrochemical investigations

Electrochemical measurements have been performed in a stationary 2 dm^3 cell with a DSA as an anode electrode and an external Calomel reference electrode ($U_H = 0.241$ V vs SCE). The electrolyte was a synthetic chlorate electrolyte formed of 550 g dm^{-3} NaClO$_3$, 110 g dm^{-3} NaCl, 1 g dm^{-3} NaClO, 3 g dm^{-3} Na$_2$Cr$_2$O$_7$ at pH 6.5 and 70 °C. For comparison, the electrodes have also been characterized in 1 M sodium hydroxide solution at 70 °C. The measuring equipment consisted of an EG&G PAR potentiostat/galvanostat 273A and a Schlumberger/Solartron frequency response analyser 1255. After immersion of the sample into the electrolyte and stabilisation of the open circuit potential over about 1 h, various potentiodynamic methods and galvanostatic polarization tests were done at a current density of $i = -250$ mA cm^{-2} to characterize the electrode behaviour. For calculation of overpotentials, ohmic resistance values were determined from impedance spectroscopy data. The spectra were recorded at the open circuit potential with an amplitude of 10 mV in a frequency range from 100 kHz to 10 mHz before and after electrochemical polarization tests, respectively.

3. Results and discussion

3.1. Powder and pellet characterization

Figure 1 shows SEM pictures of as-milled Ti–Ru–Fe–O catalyst powder. It showed that the catalyst consists of irregular shaped particles with sizes in the range from 1 to 200 μm. The corresponding BET surface area of 0.42 m^2 g^{-1} was found. The XRD pattern taken from the powders revealed that the nanocrystalline Ti–Ru–Fe–O alloy was formed after millings.

The catalyst powders were mixed with small amounts of organic Teflon as a binder and hot pressed at moderate pressure on the sublayer material. Figure 1(b) shows the SEM image of the fractured cross-sectional area of such a double-layered pellet with a catalyst loading of 20 mg cm^{-2}. The catalyst layer is formed by a high porous structure of dispersed Ti–Ru–Fe–O particles with wide space in between. The Teflon forms a spider web structure connecting the catalyst particles. The thickness of this layer is about 40 μm but it can increase up to 800 μm for catalyst loadings of 300 mg cm^{-2}. A fine-grained, homogeneous and dense sublayer of a mixture of very small sized Teflon particles and carbon Vulcan XC72 powder was also produced. It may be seen from Figure 1(b) that a very good interlocking of the two layers was obtained. The interface shows a continuous transition zone between catalyst layer and hydrophobic material. The total thickness of the fabricated pellets varies from about 1400 μm for the highest catalyst loading to 600 μm for samples with only 10 mg cm^{-2} catalyst powder.
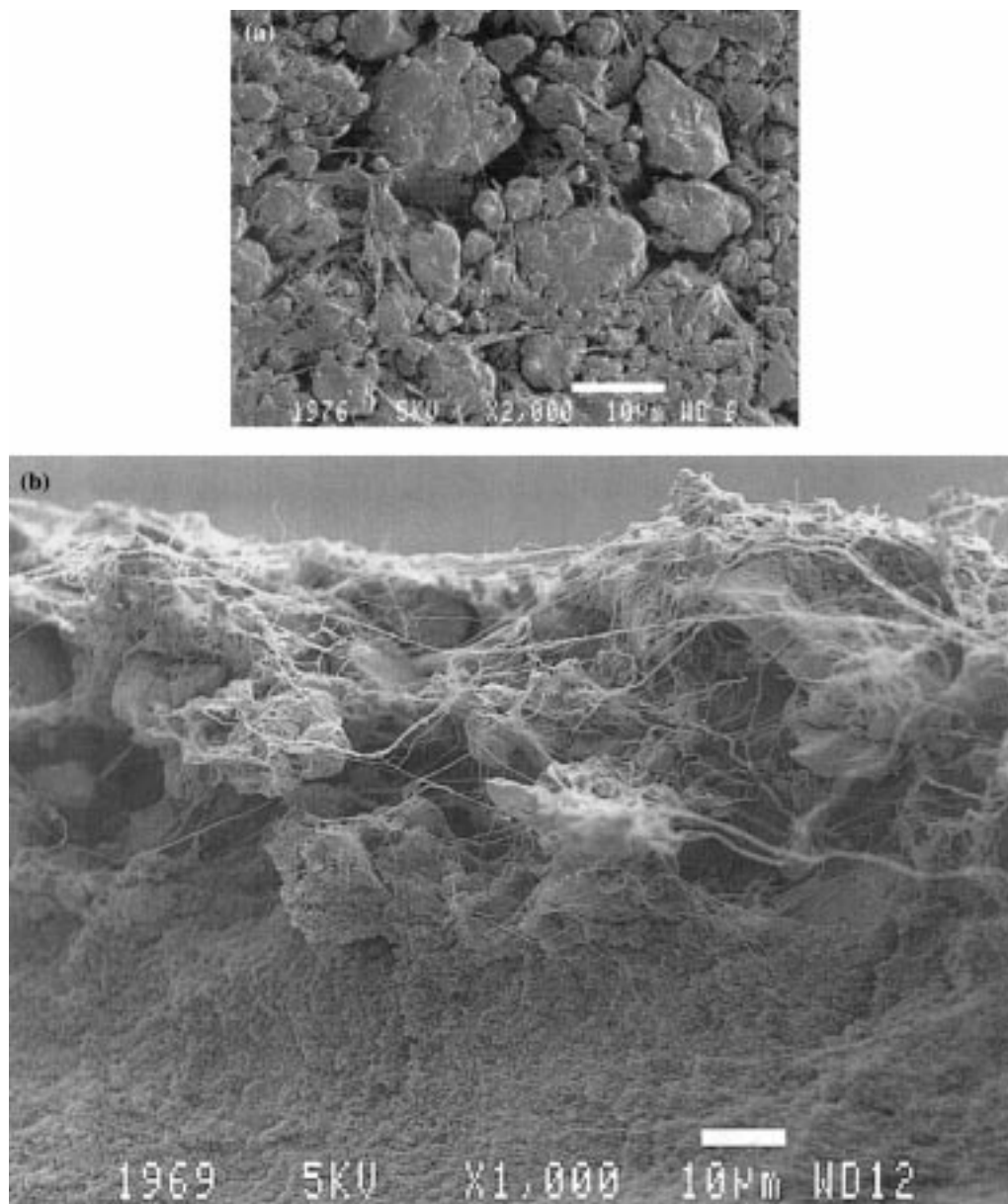

Fig. 1. SEM images of a hot pressed double-layered electrode pellet with a catalyst loading of 20 mg cm^{-2}. (a) catalyst layer surface (b) fractured cross-sectional area of the pellet. Scalebars 10 μm.

3.2. *Electrochemical studies*

To obtain information on the active surface area of our electrodes in chlorate electrolyte, the cyclic voltammetric method [4, 8, 10, 11] has been applied to determine capacity values based on the relation:

$$I_c = AC_{dl}v \tag{1}$$

where I_c is the capacitive current, A is the apparent electrode surface area, C_{dl} is the double layer capacity and v is the scan rate. Voltammograms have been recorded for freshly prepared electrodes in two cycles in a potential range of 60 mV around the open circuit potential at varying scan rates from 200 to 0.2 mV s^{-1} depending on the electrode composition. The data of the symmetrically shaped second cycle were only considered for further analysis. A typical example of the voltammograms is shown in Figure 2. The recorded current is the capacitive current. We obtained curves with almost horizontal sections with approximately the same anodic and cathodic currents when scan rates between 50 and 5 mV s^{-1} were used. Figure 3 shows the linear dependence of the capacitive currents on the scan rate. The slope of the linear fitting curve corresponds to the capacity value of the electrode for a given mass of the catalyst. The double layer capacity values determined from cyclic voltammetric measurements in chlorate electrolyte are plotted in Figure 4 as a function of the mass of the as-milled catalyst powder. A linear dependence of the double layer capacity with the catalyst mass was obtained. The curve fitting gives a slope of 0.0485 F g^{-1} (Table 1). With a geometric surface of 1.44 cm^2 for each electrode, the double layer capacity values obtained from voltammetric measurements were 33.68 mF g^{-1} cm^{-2} for these electrodes.

The calculation of the capacities referred to the BET surface area of the catalyst powders gives 11.72 μF cm^{-2} for these electrodes. The C_{dl} value calculated from BET measurement data is lower than that referred to the

Fig. 3. Capacitive currents as a function of the scan rate of cyclovoltammetric measurements performed for an electrode with a catalyst mass of 432 mg (300 mg cm^{-2}) in chlorate electrolyte at o.c.p. ($\pm$30 mV).
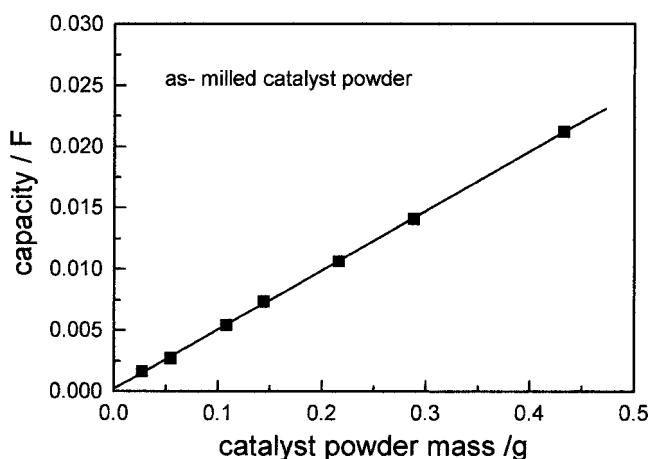
Fig. 4. Capacity values of electrodes in chlorate electrolyte as a function of the catalyst powder mass.

geometric surface area. The double layer capacities obtained in this work are lower than those obtained on pure pc-Ru catalyst in 1 M NaOH (e.g., 202 μF cm^{-2}) for a BET surface area similar to that of Ti–Fe–Ru–O) [8]. They are also lower to those obtained on RuO$_2$ coated electrodes (e.g., 142 μF cm^{-2}) [12]. These differences between the results obtained in this work and those in the literature may be attributed to the difference of electrolyte used in this work and in the literature. For the same electrode, sodium hydroxide 1 M may lead to higher double layer capacities than in chlorate medium at pH 6.5.
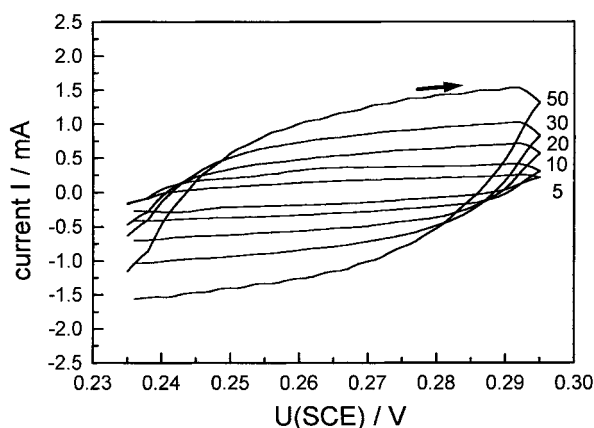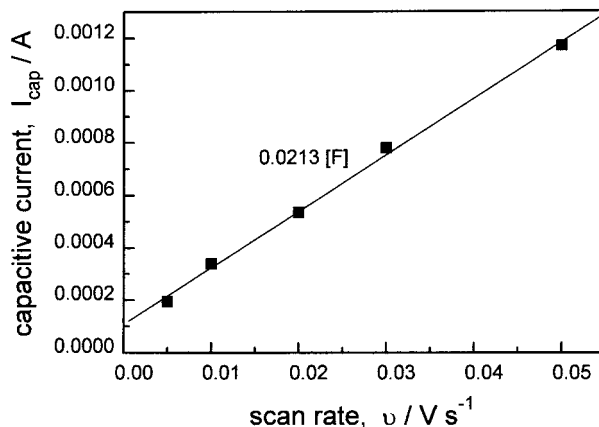

Fig. 2. Cyclovoltammograms recorded for a catalyst powder electrode with a catalyst mass of 432 mg (300 mg cm^{-2}) in chlorate electrolyte at different scan rates in the potential region near the o.c.p. ($\pm$30 mV). Scan rate labels (curves) in mV s^{-1}.

Table 1. Capacity data for Ti–Ru–Fe–O catalyst powder electrodes in chlorate electrolyte determined from cyclovoltammetric measurements (from Figure 4)

Capacity/mass of catalyst powder	Capacity/geometric electrode surface area	Capacity/BET surface of catalyst powder
0.0485 F g^{-1}	33.68 mF g^{-1} cm^{-2}	11.72 μF cm^{-2}

The electrocatalytic activity of the above double-layered electrodes was characterized by potentiodynamic polarization studies. Figure 5 shows Tafel plots of electrodes based on as-milled catalyst powder loaded at 150 mg cm^{-2}. The curves were recorded at 0.1 mV s^{-1}, starting from the anodic region, and come from the chlorate electrolyte after 15 h of cathodic prepolarization at -50 mA cm^{-2}. This pretreatment supports the formation of a chromium oxide film, which is necessary to suppress undesirable side reactions like hypochlorite and chlorate reduction [3, 13]. The electrolyte was purged with nitrogen before and during the measurements. For comparison, Tafel plots of the electrodes containing nitrogen purged 1 M sodium hydroxide solution at 70 °C were recorded. The different parameters deduced from the Tafel slopes are shown in Table 2. Tafel slopes were determined, one in the low overpotential region (up to about -50 mV) and another in the higher overpotential region (up to about -150 mV). The Tafel slopes of the HER on the electrodes obtained in 1 M sodium hydroxide solution was 67 mV (decade)$^{-1}$ in the low overpotential region (at $\eta = -30$ mV) and 160 mV (decade)$^{-1}$ in the high overpotential region (at $\eta = -130$ mV). The corresponding exchange current density was 0.547 mA cm^{-2} for the low overpotential region. This current density value is slightly lower than that (2.3 mA cm^{-2}) obtained on preactivated ruthenium oxide coated electrodes under comparable electrolyte conditions [4] and lower than the value (5.8 mA cm^{-2}) determined on pure Ru catalyst intercalated into graphite in 1 M potassium hydroxide solution [14]. From measurements performed on the electrodes based on Ti–Ru–Fe–O catalyst powder in chlorate electrolyte at pH 6.5 after prepolarization, it was shown that the electrocatalytic parameters of the
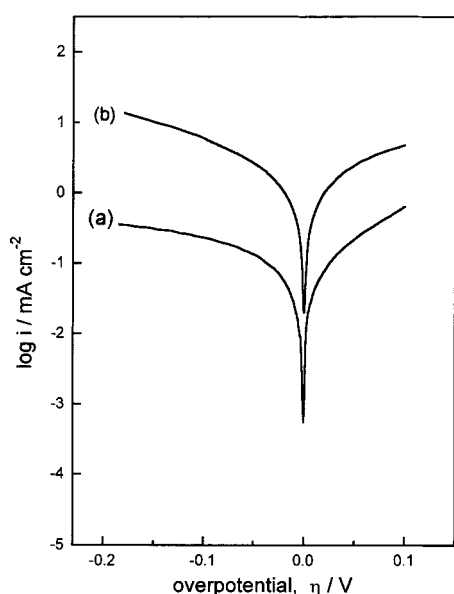
Table 2. Kinetic parameters determined from Tafel plots shown in Figure 6 and capacity values for electrodes with 150 mg cm^{-2} loading (from Figure 5)

	b_c (low η) /mV dec^{-1}	b_c (high η) /mV dec^{-1}	i_0 /mA cm^{-2}	C_{geom} /mF cm^{-2}
Powder electrodes in 1 M NaOH	67	160	0.547	
Powder electrodes in chlorate electrolyte after prepolarization	79	220	0.034	7.4

electrodes for the HER are much lower than those in hydroxide solution at pH 14. It was found that, in chlorate electrolyte, the Tafel slopes of the cathodic reactions on electrodes based on as-milled catalyst were larger than the values determined in hydroxide solution (Table 2). An exchange current density of 34 μA cm^{-2} was obtained in chlorate electrolyte. This may be due to the coverage of the catalyst surface by a chromium oxide layer formed during the prepolarisation and resulted in the reduction of the catalyst active surface area.

The electrodes behaviour has also been investigated in a high cathodic current density region. Figure 6 shows the potentiodynamic curves of electrodes based on different loadings. The potentiodynamic polarization curves of the electrodes containing chlorate electrolyte have been recorded at a scan rate of 1 mV s^{-1} up to a potential value that corresponds to a cathodic current density of -250 mA cm^{-2}. As it may be seen, the polarization curves of the electrodes based on catalyst loadings of 300 g cm^{-2} and 37.5 g cm^{-2} are similar with a slightly improved curve for the electrode loaded with 37.5 g cm^{-2}. The maximum current density of -250 mA cm^{-2} is reached at potentials between -1.45 and -1.65 V vs SCE. For the electrode based on a catalyst loading of 13 mg cm^{-2}, the polarization curve shifted to more negative potential regions. Thus, the
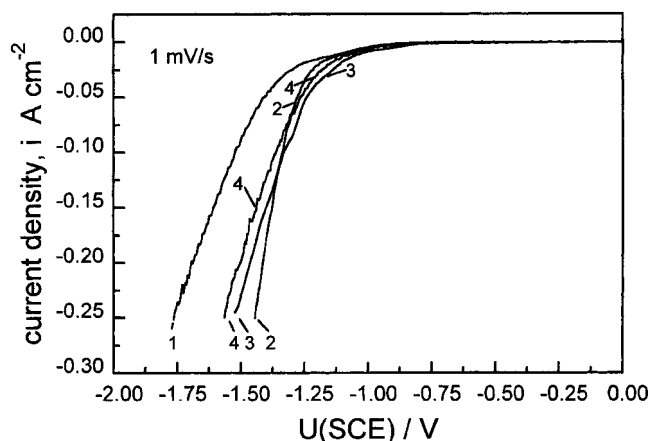

Fig. 5. Tafel-plots recorded at a scanrate of 0.1 mV s^{-1} for powder electrodes with a catalyst loading of 150 mg cm^{-2} in (a) chlorate electrolyte after cathodic prepolarization and in (b) 1 M sodium hydroxide solution at 70 °C.

Fig. 6. Potentiodynamic cathodic polarization curves recorded at a scan rate of 1 mV s^{-1} for catalyst powder electrodes with different catalyst loadings in chlorate electrolyte. Key: (1) 13, (2) 37.5, (3) 150 and (4) 300 mg cm^{-2}.

cathodic reaction on this electrode is less efficient than on electrodes with loadings of 300 g cm^{-2} or 37.5 g cm^{-2}. For overpotential more negative than -1.3 V vs SCE, the potentiodynamic polarization of electrodes are similar for the different loadings. This might be explained by the formation of a chromium oxide film during polarization, which may block active sites on the catalyst surface. Another explanation may come from the mechanism for the HER. It has been shown elsewhere [2, 7] that the rate determining step of the mechanism of the HER at high cathodic polarization in chlorate electrolyte on electrodes based on Ti–Ru–Fe–O powders was the Heyrovsky step. This step corresponds to the combination of a hydrated proton with an adsorbed hydrogen. Here, the experimental Tafel slope is 220 mV being much higher than the 120 mV for the Heyrowsky step and at an almost covered electrode surface. This is an indication that the Heyrowsky step may not be used here as an explanation. The explanation may be found from the structure of the electrode. In this type of electrode, the hydrogen gas that is evolved on the porous catalyst layer can accumulate in the micropores of the layer and so, the active surface in these pores is not available for the electrochemical reaction since the electrolyte cannot penetrate. This also explains, why electrodes with high catalyst loadings, that is, with high catalyst layer thickness, show similar HER activity like those with only very thin catalyst layer corresponding to a low loading (Figure 7).

After the potentiodynamic measurements, the electrodes were polarised galvanostatically at -250 mA cm^{-2} for 1 h. From these short-term tests, overpotentials for the HER were determined. Ohmic resistance values for the potential (IR) drops calculation were obtained from impedance measurements which were performed initially and, also, for comparison, after recording the polarization curves. For the investigated
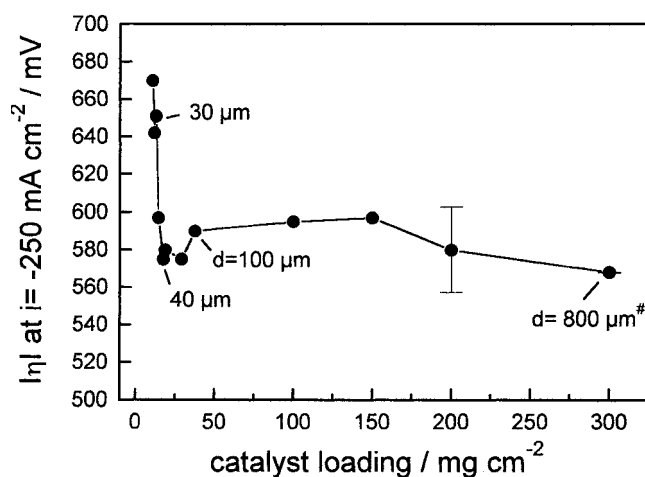
electrodes, ohmic resistances of 0.5–0.6 Ω were determined. Figure 7 shows the variation of the overpotential for HER with the electrode catalyst loading. From this plot it may be seen that the catalyst loading can be reduced from 300 to 20 mg cm^{-2} while keeping a low overpotential of about 580 mV ($\pm$20 mV). For loadings less than 20 mg cm^{-2} an increase in overpotential was observed suggesting that at this charge, the quantity of catalyst material is too small to provide sufficient active surface area which is necessary for the HER at high current densities. The optimum catalyst loading (20 mg cm^{-2}) for the electrodes corresponds to a catalyst layer of 40 μm only. The multilayer structures of the electrodes prepared in this work may imply an increase in the active surface sites concentration for the HER [15]. The same efficiency obtained here for the HER at -250 mA cm^{-2} on electrodes based on different catalyst powder loadings support this interpretation.

The long-term galvanostatic behaviour of the electrodes at -250 mA cm^{-2} conducted in an industrial chlorate electrolyte is shown in Figure 8. As it may be seen, three types of behaviour were obtained: (i) nondegraded electrodes after 18 h polarization (curve A); (ii) cracked electrodes after 10 h of polarization (curve B) and (iii) blistered and cracked electrodes after 10 h of polarization (curve C). After 18 h of polarization, the electrode surface was covered with a thick, porous, white-orange precipitation layer. EDX analysis revealed that this layer contains mainly chromium oxide species. Furthermore, traces of calcium, magnesium and molybdenium compounds were detected as it was found for cold pressed Ti–Ru–Fe–O electrodes after 1000 h of electrolysis [2]. Unfortunately, in this work, most of the electrodes failed before this extended period of time. Microscopic investigations of the long-term polarized samples revealed no apparent degradation of the catalyst layer containing small amounts of Teflon. But, during electrode preparation, crack formation in the
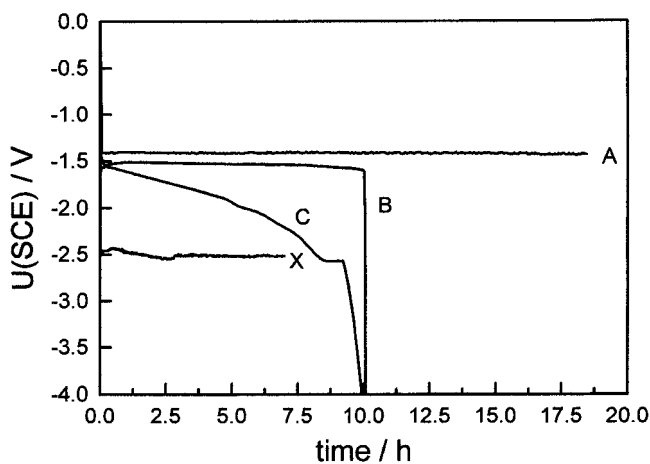

Fig. 7. Effect of reduction of catalyst loading or catalyst layer thickness (d) on the overpotential at $i = -250$ mA cm^{-2} after 1 h in chlorate electrolyte. Points (●).

Fig. 8. Results of galvanostatic long-term tests performed at $i = -250$ mA cm^{-2} in an industrial chlorate electrolyte. Key: (A) nondegraded electrode; (B) electrode cracked; (C) electrode blistered, cracked; (X) sublayer material.

catalyst layer is possible due to the difference in elasticity of this layer and that of the high Teflon containing sublayer. During electrolysis, those cracks may grow and the electrolyte can locally penetrate in the sublayer up to the metal substrate. Furthermore, hydrogen which is produced in the catalytic layer, can diffuse into the carbon–Teflon sublayer and form channels, through which electrolyte can penetrate. Electrode breakdown due to crack formation is associated to a sudden potential drop in the polarization curve as shown in curve B. The cathodic potential of the carbon–Teflon sublayer material in chlorate electrolyte at -250 mA cm^{-2} is about 1 V more negative than that of the catalyst (curve X). When chlorate electrolyte penetrates into the sublayer during the polarization, hydrogen evolution occurs within the layer and results in a strong blistering of this layer affecting also the catalyst layer integrity. The blistering process is responsible of the gradual drop of the potential seen on the galvanostatic curve (curve C). These observations suggest that the substitution of this sublayer material by a more suitable material may, of course, help in the stability and efficiency of the catalyst. This is the case observed in previous studies for the HER on graphite powder electrodes. Thus, it was recommended to use inorganic binders, like LaPO$_4$, instead of organic binders to make a cathode with higher mechanical stability to support large hydrogen flow at high current densities [14, 16]. Unfortunately, electrode preparation with those inorganic binders included a final heat treatment step at temperatures higher than the temperature stability range of the nanocrystalline Ti–Ru–Fe–O alloys.

4. Conclusions

Based on the results obtained in this work, the following conclusions are drawn:

(i) Electrocatalysts based on ball milled nanocrystalline Ti–Ru–Fe–O catalyst powder exhibited a high activity for hydrogen evolution in chlorate electrolyte.

(ii) Electrocatalytic electrodes were fabricated by hot pressing a mixture of the catalyst powder with small amounts of Teflon on a hydrophobic carbon–Teflon sublayer. The catalyst loading of these electrodes can be reduced to 20 mg cm^{-2} while maintaining high electrocatalytic efficiency for the HER.

(iii) The multilayer structure of the electrodes may be responsible for the high catalytic activity for the HER. This structure resulted in high electrochemically active surface area or/and a high number of active sites.

(iv) In high current density regions, the activity of electrodes with low catalyst powder loadings is similar to that of electrodes fabricated with high catalyst powder loadings. As an example, the overpotential at -250 mA cm^{-2} was 580 mV $\pm$ 20 mV for electrodes based on low and high catalyst powder loadings.

(v) The long-term tests of the electrodes conducted for several hours at -250 mA cm^{-2} in industrial chlorate electrolyte showed significant deterioration in performance. This was mainly due to the degradation of the sublayer.

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