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Ruthenium dioxide as a hydrogen-evolving cathode

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Ruthenium dioxide was investigated as a cathode material for hydrogen evolution in acid media. In 1 N H_2SO_4 a Tafel slope of 40 mV was obtained and an exchange current density of $6 \times 10^{-5}\,A\,cm^{-2}$, which is about one order of magnitude lower than that for platinum. XPS analysis showed that only partial reduction of the oxide occurred during hydrogen evolution. RuO_2 cathodes are almost insensitive to poisoning by metal ions in solution. This observation is in contrast to the behaviour of platinum and can be correlated to the underpotential deposition phenomenon which does not occur on RuO_2. The performance of RuO_2 cathodes in lab-scale Membrel* water electrolysis cells is demonstrated and compared to that of platinum cathodes.

1. Introduction

Ruthenium dioxide has gained much attention in recent years as an electrode material for Cl_2 and O_2 evolution. The invention of the dimensionally stable anode which is based on RuO_2 has had a major impact on the development of chlor-alkali cell technology. For O_2 evolution in acid media RuO_2 is the best material with respect to catalytic activity.

In contrast, almost no attention has been drawn to the use of RuO_2 as a cathode material since the early general investigations of this electrode material by Trasatti and co-workers [1]. The only exception so far is the study by Yeager and co-workers [2] who investigated RuO_2 electrodes for O_2 reduction. The investigation demonstrated, however, that RuO_2 is not a good cathode for this purpose.

The reasons for the lack of investigations of RuO_2 as a cathode material are obvious. Firstly, oxides in general are non-conducting or semiconducting which makes them less attractive as electrode materials. Secondly, noble metal oxides are expected to be reduced to the metal by hydrogen *in statu nascendi* which will lower their long-term stability. There is, however, one aspect which makes oxides interesting for applications as a cathode material. As a consequence of the different surface chemistry of oxides, as compared to the respective metals, oxides may be less sensitive to poisoning by metal deposits. For metals like platinum or nickel, poisoning by metal deposits is well known. The poisoning of cathodes for H_2 evolution in alkaline media has been investigated recently by Nidola and Schira [3] and it was shown that oxidative treatment of the cathode material could lead to a relative improvement of the cathode performance [4]. In addition these investigations [3, 4] gave rise to some patents where RuO_2 has been claimed as a cathode component.

In acid media, where platinum is the best electrocatalyst for hydrogen evolution, the increase in H_2 evolution potential with increasing coverage of the electrode by foreign metals is well established [5, 6]. This extreme sensitivity of platinum poisoning can be correlated to the underpotential deposition (UPD) phenomenon. In order to get around this problem of platinum cathode poisoning we investigated RuO_2 [7] which has a different surface chemistry.

In the first part of this paper the performance of RuO_2 as a H_2-evolving cathode in H_2SO_4 is investigated. The effect of metal ions in solution on the hydrogen evolution reaction will be treated in the second part where platinum and RuO_2 are compared. Finally, some data will be given for the performance of RuO_2 in Membrel water electrolysis cells where a proton-conducting polymer serves as the electrolyte.

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* Membrel is the registered trade mark of Brown Boveri water electrolysis technology.

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2. Experimental details

RuO_2 electrodes were prepared by reactive sputtering onto etched titanium or glass substrates [8]; the film thickness was 0.2 μm. These electrodes were used without any further pretreatment. For use in Membrel cells, RuO_2 powders were prepared according to the procedure given by Adams and Shriner [9]. The platinum electrode was a foil with a geometric surface area of 1 cm^2, spot welded to a platinum wire. The platinum electrode was cleaned by etching in boiling aqua regia.

Potentiostatic and galvanostatic polarization curves were recorded using the standard three-electrode arrangement with a platinum wire as the counter electrode and a saturated calomel electrode as a reference. All solutions were prepared from reagent grade chemicals and triply distilled water. XPS measurements were performed in a Kratos ES 300 electron spectrometer using MG–Kα radiation. RuO_2 powders are used as the cathode material in Membrel electrolysis cells. The design of these electrolyser cells has been given elsewhere [10].

3. Results and discussion

3.1. *Hydrogen evolution*

In Fig. 1, current versus potential plots obtained during hydrogen evolution on RuO_2 and platinum in 1 N H_2SO_4 are compared. For the hydrogen evolution reaction on reactively sputtered RuO_2 a Tafel slope of 40 mV per decade was found and the exchange current density was determined to be $6 \times 10^{-5}\,A\,cm^{-2}$. The values for platinum are in good agreement with the literature (30 mV per decade and $4 \times 10^{-4}\,cm^{-2}$) [11].

Thus the activity of RuO_2 for hydrogen evolution in acid electrolytes is lower than that of platinum leading to an increased overpotential by 50 mV at a current density of $0.1\,A\,cm^{-2}$. Our data for RuO_2 compare well with those determined by Trasatti and co-workers [1, 12]. For RuO_2 electrodes prepared by thermal decomposition of the chlorides at 300° C these investigators found a Tafel slope of 40–60 mV dec and an exchange current density of $0.3\,mA\,cm^{-2}$. These data were, however, dependent on the preparation temperature [12].

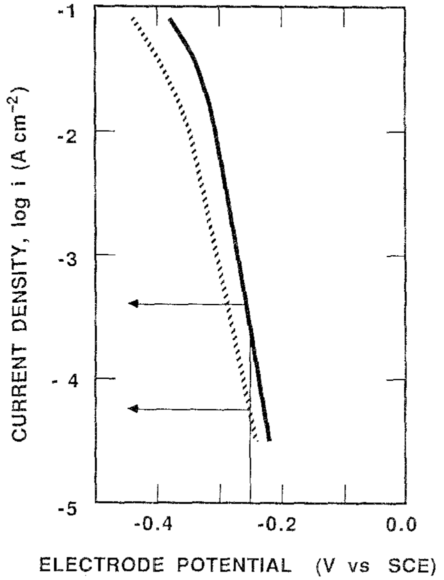

Fig. 1. Logarithmic current–potential curves for platinum (——) and RuO_2 (– – –) in 1 N H_2SO_4. Electrode area, 1 cm^2.

In order to estimate the absolute difference in H_2 evolution activity between platinum and RuO_2 the true surface area of the RuO_2 electrode has to be known. The roughness of the RuO_2 electrode is mainly determined by the roughness of the etched titanium substrate which is comparable to that of the etched platinum electrode. The extreme pseudo-capacitance of the dimensionally stable anode-type RuO_2 electrodes prepared by thermal decomposition is not observed on our sputtered electrodes. (This is also evidenced by the voltammograms of ruthenium and RuO_2 of Fig. 6 which show comparable double layer capacities.)

Possible changes of the electrode surface during hydrogen evolution were checked by XPS analysis. Fig. 2 shows the XPS spectra of the RuO_2 electrode as prepared and after H_2 evolution at room temperature and at 80° C. While the Ru 3d level stays constant at a binding energy of 280.7 eV the O1s level shifts from 529.8 eV to a higher binding energy of 531.3 eV. The shift in binding energy of the O1s level most probably indicates the formation of OH bonds [13]. The valence state of the metal, however, stays constant as is indicated by the Ru3d level

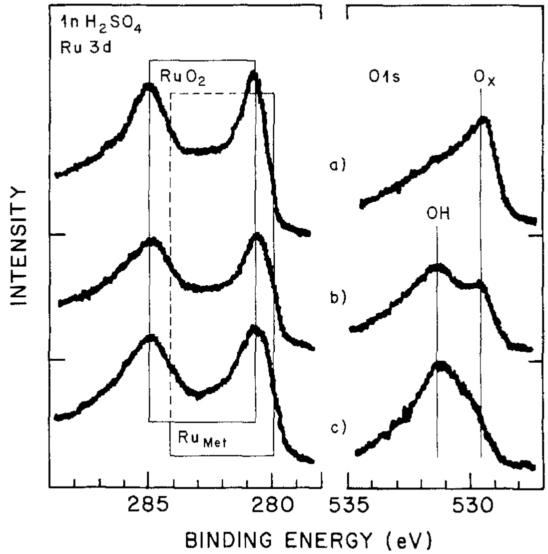

Fig. 2. XPS intensities of Ru3d and O1s levels for a RuO_2 electrode (a) as received, (b) after 15 min of H_2 evolution in 1 N H_2SO_4 at a current density of $50\,mA\,cm^{-2}$ at 25°C and (c) as for (b) but at 80°C.

at 280.7 eV [14]. The Ru3d level of metallic ruthenium has a binding energy of 280.0 eV [14]. The characteristic binding energy of the O1s level in hydroxides is about 531.5 eV [13]. Therefore it can be stated that during H_2 evolution the RuO_2 electrode surface is only partly reduced to some oxy-hydroxide, but reduction to the metal does not occur. Penetration of hydrogen was also observed by Rizzi in his early experiments [12].

3.2. *Poisoning of platinum by metal ions in solution*

Increasing cell voltages that result from the increase in H_2 evolution overpotentials at platinum cathodes are a severe problem in water and brine electrolysis. Due to the excellent catalytic activity of platinum for H_2 evolution, any other metal deposited on to the surface will increase the overpotential. In order to gain some insight into this problem we have reinvestigated the poisoning of platinum during H_2 evolution in the presence of metal ions in the electrolyte. The influence of several metal ions such as Ti, Cr, Mn, Co, Ni, Cu, Mo, Ag, Cd, Sn and Pb on the H_2 evolution reaction on platinum in acid electrolytes was investigated and it was found that only Cu, Mo, Ag, Cd, Sn, Pb led to a considerable poisoning of the cathode. Poisoning of platinum by silver and copper is expected because the reversible potential for the electrodeposition of these metals is positive of the H_2 evolution potential. However, poisoning of platinum by cadmium is surprising if only deposition at potentials negative of the reversible potential, which is -0.4 V (RHE) for Cd^{2+}/Cd, is considered.

The situation becomes different if the so-called underpotential deposition is taken into account. According to the Kolb–Gerischer model, half of the difference between substrate and adsorbate work functions determines the potential at which a considerable fraction (presumably half) of the first monolayer can be deposited onto a polycrystalline substrate [15]. Taking this effect into account, the potentials at which metal deposition starts are shifted towards more positive values. As a consequence of the relatively high work function of platinum, the UPD shifts are relatively large. This can be seen in Fig. 3 where the reversible potentials [16] and the corresponding UPD shifts (half of the work

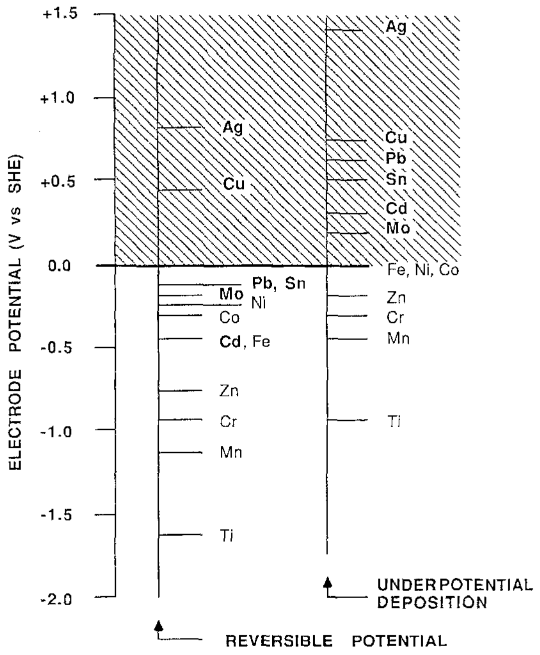

Fig. 3. Reversible potentials for several metal ions in solution and potentials of the UPD maximum according to the Kolb–Gerischer model. Elements which were found to poison platinum during H_2 evolution are printed bold. Work functions were taken from [22].

function differences, see [23]) are considered. From Fig. 3 we can see that those metals which we found to be poisons for H_2 evolution on platinum appear in a potential range positive of the hydrogen potential only after accounting for the UPD shift.

Besides the effect of shifted deposition potentials, the UPD effect has another important influence on the poisoning of platinum by metal ions. It is known that in those cases where UPD occurs, the growth process of the adsorbate is a monolayer by monolayer mechanism in contrast to cluster growth [17]. Monolayer growth in an UPD system is a consequence of an adsorbate–substrate interaction which is stronger than the corresponding adsorbate–adsorbate interaction. Therefore rather small amounts of metal ions in solution are sufficient to cover, and thus poison, the substrate completely. The experimental verification of this behaviour is given in Figs 4 and 5. Fig. 4 shows the potential versus time plot for a platinum electrode during hydrogen evolution with 100 mA cm^{-2} in the presence of different amounts of Cu^{2+} ions in the electrolyte. It was found that the maximum increase in electrode potential of 300 mV is independent of the Cu^{2+} concentration. At low concentrations, however, the time needed to reach the final potential value increases. The dashed line in Fig. 4 indicates the potential increase without intentional additions of copper ions.

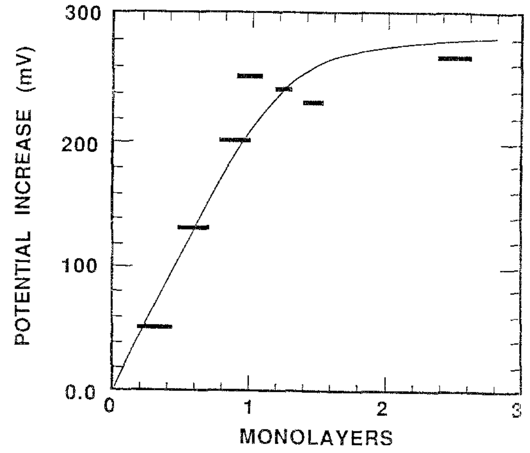

Fig. 5. Increase of the H_2 evolution potential of platinum at 100 mA cm^{-2} as a function of copper coverage measured in Cu^{2+}-free electrolyte (1 N H_2SO_4) at 100 mA cm^{-2}. The curve shown serves only as a guide line.

The fact that, in principle, only one monolayer of copper is sufficient to poison the platinum electrode is seen in Fig. 5, where the H_2 evolution potential is plotted as a function of copper coverage, ϕ. After deposition of copper in a Cu^{2+}-containing solution the electrode was transferred to a Cu^{2+}-free electrolyte where the H_2 evolution potential at 100 mA cm^{-2} was measured. The amount of copper on the surface was determined afterwards using stripping voltammetry. The H_2 evolution overpotential increases linearly for coverages $0 < \phi < 1$ and starts to level off for $\phi > 1$. Similar results were obtained by Motoo *et al.* [5, 6]. These authors found that the poisoning effect also depends on the potential at which the metal is deposited. The slight difference in potential increase between Figs 4 and 5 may be due to the different conditions of copper deposition in both

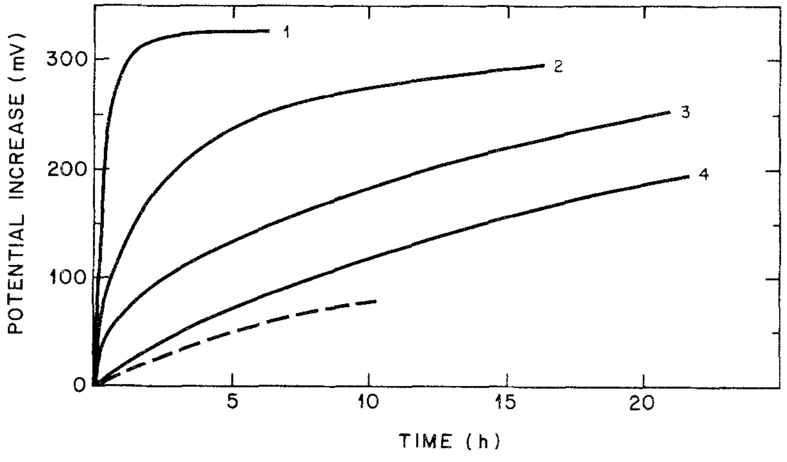

Fig. 4. Deactivation of a platinum electrode during H_2 evolution in the presence of Cu^{2+} ions in 1 N H_2SO_4 at 100 mA cm^{-2}. Cu^{2+} concentration: (1) 5×10^{-4} M, (2) 5×10^{-5} M, (3) 1×10^{-5} M, (4) 1×10^{-6} M. Dashed line, potential increase in 1 N H_2SO_4 (purum, pro analysi grade) no Cu^{2+} added.

experiments. In addition it cannot be excluded that a further potential increase would be observed in Fig. 5 at higher ($\phi > 3$) coverages. Bulk properties of the UPD film are expected to be achieved at roughly 10 monolayers [17].

From the above it is obvious that the UPD phenomenon is of twofold importance for the poisoning of platinum during H_2 evolution. First, the UPD effect makes poisoning of the electrode possible by metals whose reversible potentials are negative of the H_2 evolution potential. Second, only a few monolayers are sufficient to poison the electrode completely because UPD favours an initial monolayer by monolayer growth mechanism.

3.3. *H_2 evolution on RuO_2 in the presence of metal ions*

In order to prove the importance of UPD for poisoning of platinum during H_2 evolution – and eventually to get around it – we have looked for an alternative electrode material. According to the Kolb–Gerischer model, UPD only occurs if the work function of the substrate is higher than that of the adsorbate [15]. Thus choosing a low work function electrode material will prevent UPD in most cases. Unfortunately, however, the activity for H_2 evolution is correlated to the work function of the material, giving rise to low activity for low work function materials [18]. This seems to rule out the combination of good catalytic activity with low sensitivity to poisoning.

A better approach to the solution of the problem is the choice of an electrode material other than a metal. It is known that UPD does not occur on semiconductors or oxides [19]. The requirement, that a technically promising electrode material should be a reasonably good conductor leaves us with metallically conducting oxides like RuO_2 or IrO_2.

The difference in surface chemistry of ruthenium and RuO_2 with respect to metal deposition is demonstrated in Fig. 6. While the cyclic voltammogram of ruthenium in Cu^{2+}-containing H_2SO_4 exhibits the well-known current maximum for the stripping of bulk and monolayer copper at +10 mV and +160 mV respectively, the monolayer peak at 160 mV is totally missing on RuO_2 in the same solution. The cyclic voltammogram of ruthenium is in good agreement with data published by Quiroz *et al.* [20]. The relatively small UPD shift of 150 mV observed for the system Ru–Cu is a consequence of the small difference in work functions (Ru: 4.7 eV

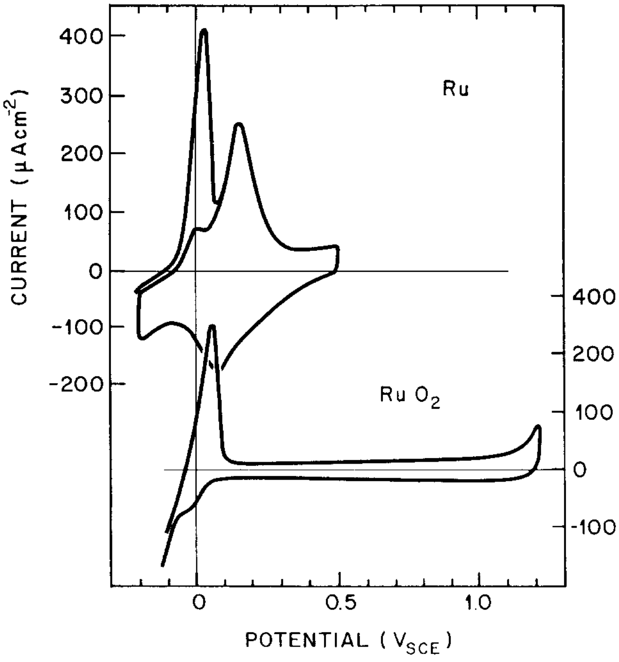

Fig. 6. Cyclic voltammogram of ruthenium and RuO_2 in 1 N H_2SO_4 + 1.6 × 10^{-3} M $CuSO_4$, at a scan rate of 50 mV s^{-1}.

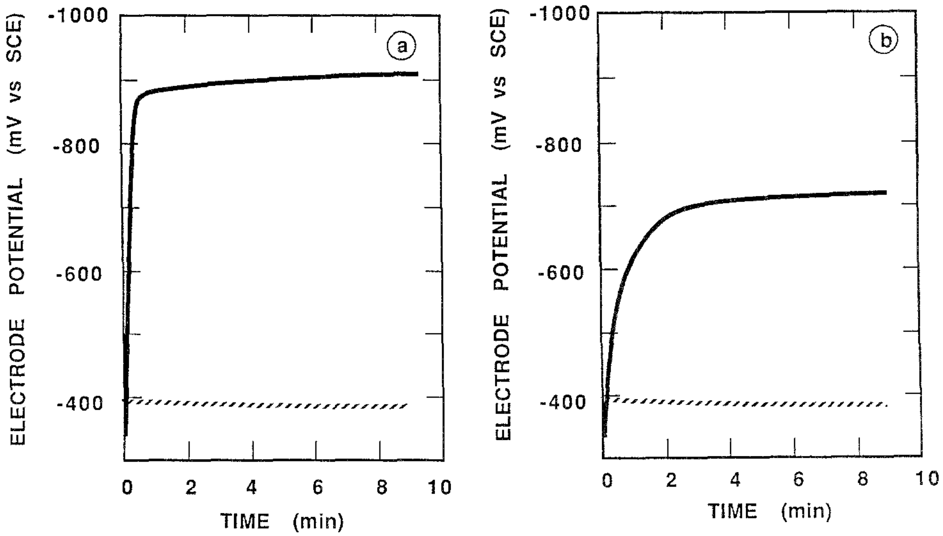

Fig. 7. Electrode potential as a function of time for platinum (——) and RuO_2 (– – –) during H_2 evolution in 1 N H_2SO_4 with (a) 3 × 10^{-4} M Cd^{2+} or (b) 5 × 10^{-4} M Cu^{2+}. Current density, 50 mA cm^{-2}.

[21, 22]; Cu: 4.5 eV [22, 23]). The voltammogram of the RuO_2 electrode appears to be rather featureless at the current scale chosen in Fig. 6. In a magnified version of the voltammogram [24] the valence state change of Ru from (III) to (IV) is clearly visible.

If UPD is of fundamental importance for the deactivation of H_2-evolving cathodes, significant differences between platinum and RuO_2 should be observed. As can be seen in Figs. 7a and b the results for platinum and RuO_2 are strikingly different. Poisoning of platinum during H_2 evolution in acid media in the presence of Cd^{2+} or Cu^{2+} ions occurs immediately, as is evidenced by the steep increase in overpotential. In contrast, the H_2 evolution potential on RuO_2 in the very same solution stays constant. On both electrodes deposition of copper is visible as a colour change after prolonged electrolysis. The somewhat higher initial overpotential of RuO_2 compared with platinum is in agreement with Fig. 1. The initial ($t = 0$) potentials are −345 mV and −390 mV versus SCE for platinum and RuO_2, respectively. For the RuO_2 electrode an initial increase in hydrogen evolution activity is observed which levels off after 10–20 min and has no influence on the long-term performance as can be seen in Fig. 8.

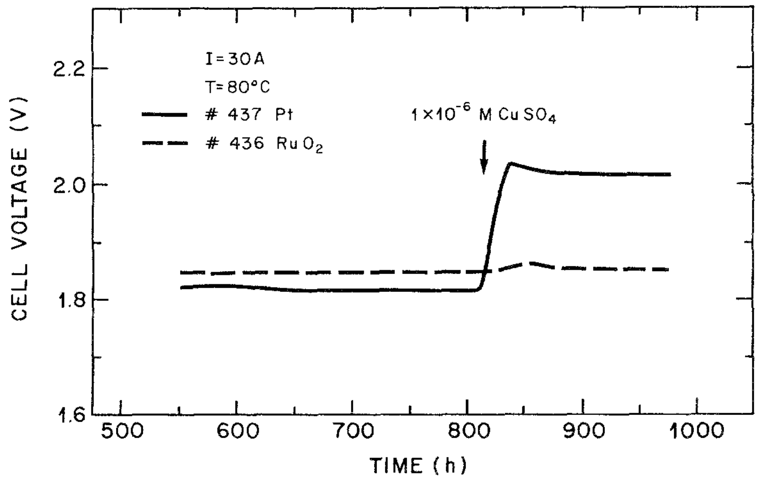

Fig. 8. Cell voltage of two Membrel electrolysis cells as a function of operation time. One cell was equipped with a platinum cathode (——) the other with a RuO_2 cathode (– – –). After 800 h of operation Cu^{2+} was added to the common water circulation system.

A similar increase in catalytic activity with time has been observed for RuO_2 single crystals by Hepel *et al.* [25].

According to Fig. 3 Cd^{2+} and Cu^{2+} represent two extreme cases with respect to the reversible potential of metal deposition. In the case of cadmium the initial H_2 evolution potential on platinum is anodic of the reversible potential for cadmium deposition, making bulk deposition impossible. The first monolayer, however, can be deposited causing a gradual shift of the H_2 evolution potential towards more negative values where, eventually, bulk deposition becomes possible. For copper the situation is different, because here the H_2 evolution potential on clean platinum is cathodic of the reversible potential for metal deposition. Thus, copper deposition takes place in the overpotential deposition range. In both cases, however, H_2 evolution on RuO_2 is not influenced which, in our opinion, must be correlated to UPD suppression. XPS analysis of platinum and RuO_2 electrodes after 5 min of H_2 evolution at a current density of $50\,mA\,cm^{-2}$ in metal ion containing H_2SO_4 confirms the above ideas (Figs. 9a and b). While copper is deposited in almost equal amounts on platinum and RuO_2, cadmium is only deposited onto platinum while no cadmium could be detected on RuO_2.

This result demonstrates again the importance of suppressed UPD on RuO_2. In the case of cadmium the reversible potential is too low for overpotential metal deposition (without UPD). In the case of copper only a different growth mechanism (cluster growth without UPD) can explain the stunning result. Besides the UPD phenomenon there are other important factors influencing the poisoning of the H_2 evolution reaction by metal deposition, such as the geometry of the adsorption site of the metal, the nature of the chemical bond or the hydrogen evolution mechanism. These factors, however, should preferably be investigated on single-crystal RuO_2 electrodes [26] which is beyond the scope of this present study of polycrystalline electrodes of technical relevance.

3.4. *Performance of RuO_2 in Membrel electrolysis cells*

In order to test the performance of RuO_2 in a Membrel cell, RuO_2 powders were prepared according to the procedure described by Adams and Shriner [9] and applied as the cathode catalyst. The construction and general features of Membrel cells for hydrogen production have been described earlier [10].

Long-term experiments have demonstrated the stability of RuO_2 cathodes for more than 4000 h at a current density of $1\,A\,cm^{-2}$ and a temperature of 80° C. The measured cell voltage of 1.85 V is about 50 mV higher than the respective voltage obtained with our proprietary platinum cathode and a Nafion 120 membrane. The

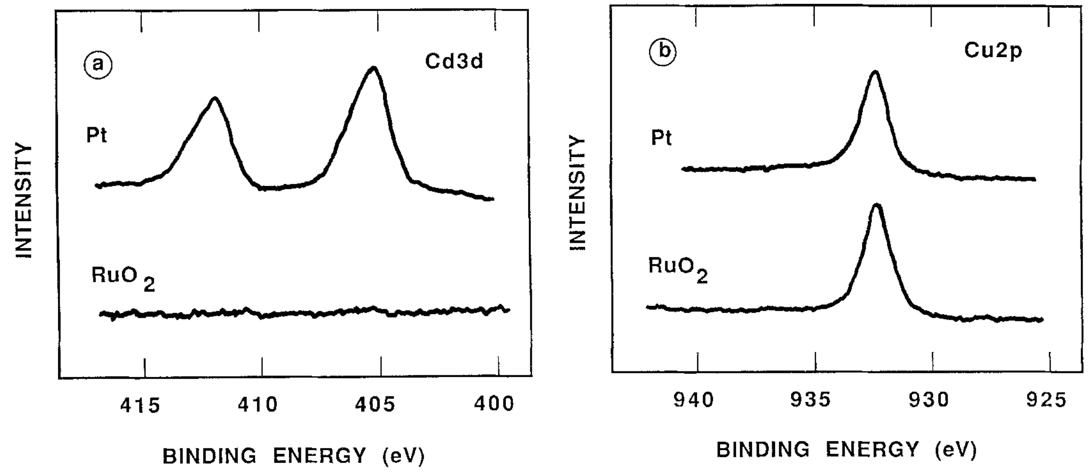

Fig. 9. XPS emission intensities of the (a) Cd3d level and (b) the Cu2p level for a platinum and a RuO_2 electrode after 5 min of H_2 evolution in 1 N H_2SO_4 with (a) 1×10^{-3} M Cd^{2+} or (b) 1×10^{-3} M Cu^{2+}. Current density, $50\,mA\,cm^{-2}$.

fact that the striking insensitivity of RuO_2 towards poisoning is also maintained during operation in a Membrel cell is seen in Fig. 8. After 800 h of operation 10^{-6} M Cu^{2+} ions were added to the *common* feed water circulation system of two Membrel cells – one equipped with a platinum cathode, the other with a RuO_2 cathode. While the platinum is immediately poisoned, the RuO_2 cathode ignores the presence of the metal ions.

4. Conclusions

We have demonstrated for the first time that metallic oxides like RuO_2 are insensitive towards poisoning by metal deposition during hydrogen evolution in acid media. In addition, the catalytic activity of RuO_2 for H_2 evolution falls between those of platinum and nickel. The exchange current density of 6×10^{-5} A cm^{-2} in combination with a Tafel slope of 40 mV per decade results in an overpotential for the hydrogen evolution reaction which is about 50 mV higher than that of platinum at a current density of 0.1 A cm^{-2}.

XPS analysis of RuO_2 film electrodes after H_2 evolution reveals a partial reduction of the oxide surface only, probably a result of hydrogen penetration. The partial reduction of the oxide does not seem to affect the hydrogen evolution reaction.

In technical Membrel electrolysis cells the stability of the RuO_2 cathode has been demonstrated for more than 4000 h. The insensitivity of RuO_2 towards poisoning by metal ions is maintained in Membrel electrolysis cells.

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