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Behaviour of tungsten carbide hydrogen-diffusion electrodes in chloride etching solutions

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Studies were performed of tungsten carbide hydrogen-diffusion electrodes operating as anodes in electrolytic baths for regeneration of etching solutions of $CuCl_2$ and $FeCl_3$. Under conditions of electrolytic regeneration of copper chloride solutions ($i = 40\,mA\,cm^{-2}$, 40° C) after 1500 h operation the electrode polarization increased by about 200 mV. Maximum current efficiency of 60–65% was obtained at $I_k = 80\,mA\,cm^{-2}$. It is demonstrated that the replacement of the standard carbon anodes with tungsten carbide hydrogen-diffusion electrodes and the elimination of the ion exchange membrane separating the anodic from the cathodic space leads to a 2–4 V decrease of the electrolytic bath voltage. The regenerated solutions of $CuCl_2$ and $FeCl_3$ can be reused as etching agents after adding 7–10 ml 30% solution of hydrogen peroxide per litre.

1. Introduction

In industrial plants the chemical etching of printed circuits and profile metal components is an important part of the production processes. Salts of heavy metals such as $CuCl_2$ and $FeCl_3$ are used as etching solutions. Their presence in the waste waters causes grave ecological problems. It is well known that heavy metals strongly hamper the effectiveness of biological methods for waste water treatment.

It is evident that instead of transporting used etching solutions as waste materials it is more profitable to develop a method for their regeneration, which also allows copper recuperation.

Etching solutions of $CuCl_2$ normally contain about 60–70 g dm^{-3} copper ions. Their etching capability is due to the content of Cu(II) ions, which are converted into Cu(I) during the process.

$$\begin{aligned} Cu + Cu^{2+} + 2Cl^- &\rightarrow 2CuCl \\ Cu + Cu^{2+} &= 2Cu^+ \end{aligned} \tag{1}$$

The equilibrium constant of the reverse reaction of Cu^+ disproportionating in the chloride solutions has a value of 16×10^{-6} [1] and obviously the equilibrium of Reaction 1 is shifted to the right towards the formation of CuCl. Since copper (I) chloride is a compound with low solubility, Cu(I) is present in the solution as a component of highly soluble complexes containing Cl^- ions.:

$$CuCl + (x-1)Cl^- \rightarrow CuCl_x^{(x-1)-} \tag{2}$$

where $x = 2, 3, 4$, depending on the Cl^- concentration [2].

As a result the solution is enriched mainly with Cu(I) ions. When the copper ion concentration exceeds 120–150 g dm^{-3}, the etching rate decreases significantly. The regeneration of these solutions is performed by electrolysis, and the process continues until the copper ion concentration drops to the initial 60–70 g dm^{-3}.

Besides hydrochloric acidic solutions of copper dichloride, etching solutions of $FeCl_3$ (400–500 g dm^{-3} $FeCl_3$) are also used. In this case also, during the etching process the copper ion concentration increases, while simultaneously the Fe(III) concentration drops in favour of Fe(II) ions.

$$Fe^{3+} + Cu \rightarrow Fe^{2+} + Cu^+ \tag{3}$$

At a copper ion concentration of 80–90 g dm^{-3} the etching rate decreases sharply. The electrolytic regeneration of such solutions is aimed toward complete extraction of the copper ions.

The proposed technical procedures for regeneration of copper chloride etching solutions [3, 4] are based on the following electrochemical reactions:

cathode

$$Cu^+ + e^- \rightarrow Cu \quad E = 0.137\,V[5] \tag{4}$$

anode

$$\begin{aligned} Cu^+ &\rightarrow Cu^{2+} + e^- \\ 2Cu^+ &\rightarrow Cu + Cu^{2+} \end{aligned} \tag{5}$$

Depending on the electrode potential, the following reactions may also take place:

$$Cu^{2+} + e^- \rightarrow Cu^+ \quad E = 0.522\,V[5] \tag{6}$$

cathode

$$Cu^{2+} + 2e^- \rightarrow Cu \quad E = 0.337\,V[6] \tag{7}$$

anode

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \tag{8}$$

and in the electrolyte

$$2Cu^+ + \tfrac{1}{2}O_2 + 2H^+ \rightarrow 2Cu^{2+} + H_2O \tag{9}$$

During regeneration of copper ferrichloride electrolytes besides Reactions 4 to 8 the following also occur:

anode

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \tag{10}$$

cathode

$$2H^+ + e^- \rightarrow H_2 \tag{11}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{12}$$

Several technical procedures for electrochemical regeneration of copper chloride solutions have been described in the literature [3,4]. Generally, the anodes are carbon electrodes on which the oxygen evolution proceeds, and if precautions are not taken to separate the anodic from the cathodic space by an ion exchange membrane, chloride evolution may also occur.

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{13}$$

All this leads to a complicated and expensive design and construction of the electrolytic cell and significant energy consumption due to the ohmic losses in the membrane and the high potential of the anodic reaction.

A new technical solution of the problem is the utilization of hydrogen-diffusion anodes (HDAs). It is known that hydrogen oxidation occurs at remarkably lower potentials than the oxygen reduction, leading to a decreased energy consumption. Moreover, the use of an ion exchange membrane is not necessary in this case, which allows simplification of the cell construction.

The aim of the present work was to investigate the feasibility of this type of electrode, catalysed with tungsten carbide, for regeneration of chloride etching solutions.

2. Experimental details

The performance of two-layer HDAs [7] has been studied. The active layer consisted of $400\,mg\,cm^{-2}$ tungsten carbide [8–10] and Teflonized carbon black (TCB), and the gas supplying one contained TCB. Carbide synthesized in the Central Laboratory of Electrochemical Power Sources from WO_3 with $S_{BET} = 3\,m^2\,g^{-1}$ was used. This carbide was preferred since, according to our previous studies, carbides synthesized from WO_3 with relatively small specific surface areas displayed the best corrosion resistance and the most stable electrochemical characteristics [11, 12].

The studies were performed in chloride electrolytes containing $110\,g\,dm^{-3}$ $CuCl_2$ and $65\,g\,dm^{-3}$ HCl; 20–$40\,g\,dm^{-3}$ Cu^{2+}, 60–$80\,g\,dm^{-3}$ Cu^+ and $110\,g\,dm^{-3}$ $FeCl_3$ (industrial grade) at 40° C on electrodes with surface areas of $10\,cm^2$ and $225\,cm^2$, mounted in plastic gas chambers. For comparative measurements, hydrochloric and sulphate solutions such as H_2SO_4, $CuSO_4$, $FeSO_4$ were used.

The current–voltage measurements and long term tests were carried out under galvanostatic conditions. The potential was measured against a Ag/AgCl reference electrode during operation in chloride solutions and against a Hg/$HgSO_4$ reference in sulphate solutions.

3. Results

The steady state potential of the hydrogen tungsten carbide electrodes in copper chloride and copper ferrichloride solutions is about +270 mV (HE).

To determine whether the copper and chloride ions are responsible for this, the steady state potentials of HDAs were measured in different electrolytes: 2 M HCl, $CuCl_2$, H_2SO_4, $CuSO_4$, and $FeSO_4$. The results show that the copper ions determine the high anodic potentials. This can be attributed to the following reaction occurring on the HDAs catalysed with tungsten carbide.

$$Cu^{2+} + H_2 \rightarrow Cu + 2H^+ \tag{14}$$

It was established that this process actually takes place in both types of electrolyte and the copper is deposited in the pores of the active layer of the electrodes. On switching on the electric circuit the potential of the HDA is shifted in the anodic direction and a reverse process starts, i.e. dissolution of the deposited copper. The studies shows that after 4–5 such cycles the active layer of the electrodes starts disintegrating. To avoid this, the HDAs in the copper chloride baths should always be under load.

Figure 1 shows the anodic current–voltage curves of these electrodes, measured in both types of solution used for etching of copper pieces – copper chloride and copper ferrichloride. For comparison, the electrode performances in copper sulphate and iron sulphate are also included. It can be seen that the replacement of sulphate by chloride ions leads to a significant deterioration of the current–voltage characteristics. A plausible explanation of this effect may be the blocking of the electrode surface by the adsorbed ions, the adsorption being stronger for Cl^- as compared with SO_4^{2+}, as in the case of platinum electrodes [13].

Despite the worse characteristics displayed by the hydrogen tungsten carbide electrodes in hydrochloric acid solutions, their use has some advantages. A comparison of the conditions under which conventional regeneration of electrolytes is performed [3, 4] shows that the change in the anodic reaction and the absence of an ion exchange membrane leads to a decrease of the cell voltage by 2–4 V, as well as to a remarkable simplification of the cell construction.

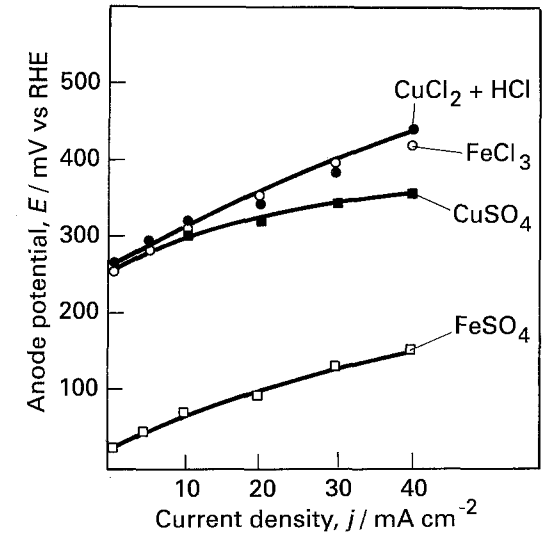

Fig. 1. Current–voltage curves of tungsten carbide hydrogen-diffusion electrodes with an active layer composed of 400 mg cm^{-1} tungsten carbide and 47 mg cm^{-2} Teflonized carbon black in electrolytes containing: (□) 556 g dm^{-3}, $FeSO_4 \cdot 7H_2O$; 40° C; (2 M $FeSO_4 \cdot 7H_2O$). (■) 500 g dm^{-3} $CuSO_4 \cdot 5H_2O$; (2 M $CuSO_4 \cdot 5H_2O$). (○) 118 g dm^{-3} $FeCl_3$; 40° C. (●) 110 g dm^{-3} $CuCl_2$; 65 g dm^{-3} HCl; 40° C.

Figure 2 shows the dependence of the copper current efficiency on the cathodic current density, j_c measured in a copper chloride electrolyte at anodic current density of 40 mA cm^{-2} and 40° C. All measurements were conducted in electrolyte with constant initial composition for 24 h. Constant cathodic current density was maintained by mechanical removal of the cathode deposit at regular 30 min intervals. The copper current efficiency rises to $j_c = 80$ mA cm^{-2}, the maximum not exceeding 60–65%. This shape of the curve can be explained as follows.

With the increase in the cathodic current density the cathode potential decreases owing to the reduction of the Cu^{2+} concentration (Fig. 3) by Reactions 6 and 7.

At $j_c = 100$ mA cm^{-2}, the cathode potential is sufficiently negative to allow hydrogen evolution. Evidence for this process is the porous structure of the copper deposited. This leads to a decrease of the copper current efficiency. A similar phenomenon was observed during the electrolysis of copper sulphate solutions at $j_c > 100$ mA cm^{-2} [14].

The comparison of this result with the current efficiency during conventional electrolysis shows that the latter is 10–15% higher. This is probably due to the use of an ion exchange membrane which limits, to a certain extent, the diffusion of the Cu(I) from the cathode towards the anode.

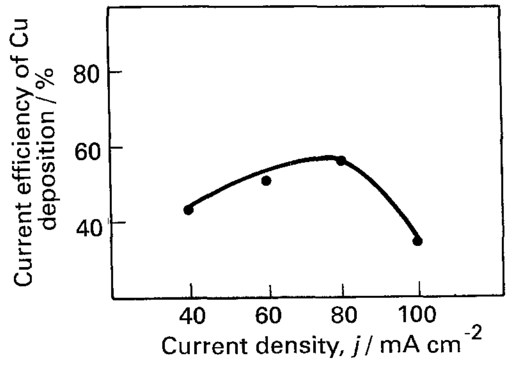

Fig. 2. Dependence of the current efficiency on the cathodic current density. 110 g dm^{-3} $CuCl_2 \cdot 2H_2O$; 65 g dm^{-3} HCl; 40° C.

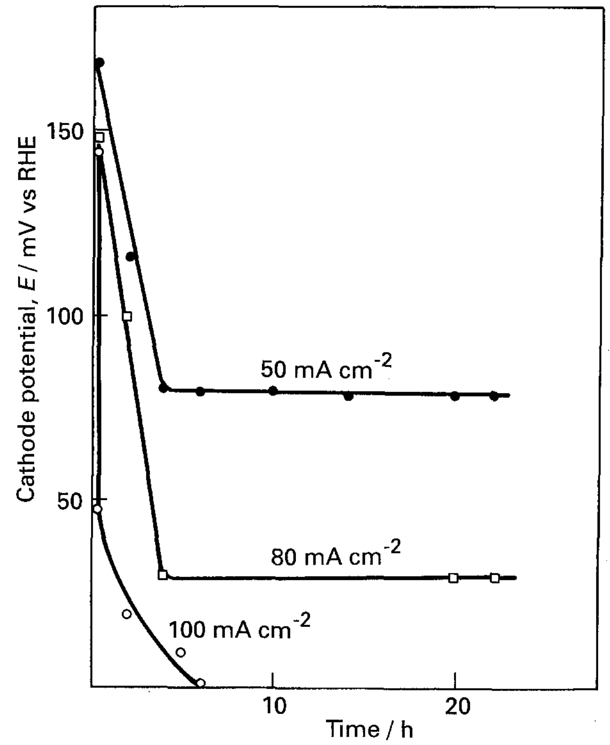

Fig. 3. Change of the cathode potential with time at various cathodic current densities, j_c: (●) 50; (□) 80; and (○) 100 mA cm^{-2}. 110 g dm^{-3} $CuCl_2 \cdot 2H_2O$; 65 g cm^{-1} HCl; 40° C.

Chemical analysis of the copper chloride solutions regenerated by both methods shows high copper ion content (30–60 g dm^{-3}). This is probably due to the formation of stable cuprocomplexes in the acid electrolyte.

The regeneration of copper ferrichloride solutions requires almost complete extraction of copper from the electrolyte. For this reason, conditions are created at the end of the electrolysis for hydrogen evolution, even at $j_c < 80$ mA cm^{-2}. Furthermore, Fe^{3+} reduction is also possible at the cathode. These cathode processes occur independently of the anode type and the presence or absence of a membrane between the cathode and anode. Thus, both during conventional regeneration of copper ferrichloride solutions, and regeneration using hydrogen-diffusion anodes, the current efficiency is nearly the same, not exceeding 40%.

Unlike copper chloride solutions, complete extraction of the copper ions is achieved during regeneration of ferrichloride solutions. The chemical analysis performed after regeneration of copper ferrichloride solution shows a copper content of 1–1.5 g dm^{-3}. Reduction of Fe(III) to Fe(II) occurs simultaneously.

It is obvious that in both cases, copper chloride and ferrichloride solutions, the use of an oxidizing agent is necessary to restore their etching properties. An appropriate agent is hydrogen peroxide, which has strong oxidizing properties, capable of oxidizing Fe(II) and Cu(I) to Fe(III) and Cu(II), respectively,

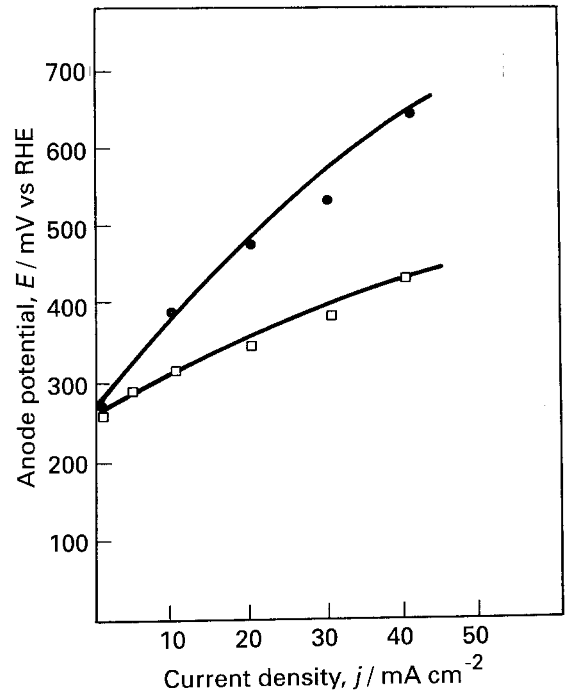

Fig. 4. Current–voltage curves of tungsten carbide hydrogen-diffusion electrodes with an active layer composed of 400 mg cm^{-2} tungsten carbide and 47 mg cm^{-2} Teflonized carbon black. (□) Initial curve, (●) after 1000 h. 110 g dm^{-3} $CuCl_2 \cdot 2H_2O$; 65 g dm^{-3} HCl; 40° C; $S_{-1} = 10\,cm^2$.

without changes in the electrolyte composition. Both electrolytes can be regenerated by adding 7–10 ml 30% solution of hydrogen peroxide per litre electrolyte. Such an amount of peroxide should also be added after conventional electrochemical extraction of copper ions from these electrolytes; therefore this circumstance cannot lead to preference of any of the methods discussed.

Long-term tests of the tungsten carbide HDAs have been performed in copper chloride electrolytes. Figure 4 shows two current–voltage curves of such electrodes; the initial one and one taken after 1000 h operation at a current density of 40 mA cm^{-2} (used during the conventional regeneration of copper chloride solutions as well).

It can be seen from the figure that the electrode polarization after 1000 h operation rose by about 200 mV at $j_c = 40\,mA\,cm^{-2}$. From Fig. 5 showing the change in the electrode potential with time, recorded *versus* HE in the same solution, it is clear that the observed increase of the polarization occurs during the initial 500 h. To elucidate this phenomenon, the following experiments were carried out:

Table 1. WO_x content in tungsten carbide samples after various storage times in copper chloride electrolyte

τ/h	WO_x/wt %	E/mV(HE)
0	> 1	580–640
500	6–7	600–680
1500	8–12	630–700

1. Tablets of Teflonized carbon black (TCB) were produced (150 mg cm^{-2}), with the collector grid pressed into it. They were immersed in copper chloride and copper sulphate electrolytes and taken out at intervals to check the grid. After 180 h the grid of the tablet immersed in the chloride solution started to corrode, and after 350–400 h its corrosion was complete. The grid of the tablet placed in the sulphate solution did not exhibit any changes even after 1000 h storage in the electrolyte.
2. Samples of tungsten carbide were kept in copper chloride and copper ferrichloride solutions. The steady state potential and degree of corrosion were regularly checked by X-ray diffraction and chemical analysis [11]. The results of the analyses are given in Table 1.

WO_2 and WO_3 are formed during the corrosion. Their amounts are given as WO_x in the table, since there are no analytical methods to determine them separately.

As can be seen, after 1500 h storage in chloride solution at $E = +600$–$700\,mV(HE)$ the carbides did not corrode significantly. X-ray diffractograms were taken and chemical analysis was also performed on the tungsten carbide electrodes after 1500 h operation in copper chloride solutions ($E = 500$–$600\,mV(HE)$).

The content of the tungsten oxides in the active layer was found to be 15 wt %, an amount almost equal to that of the oxides in the samples immersed

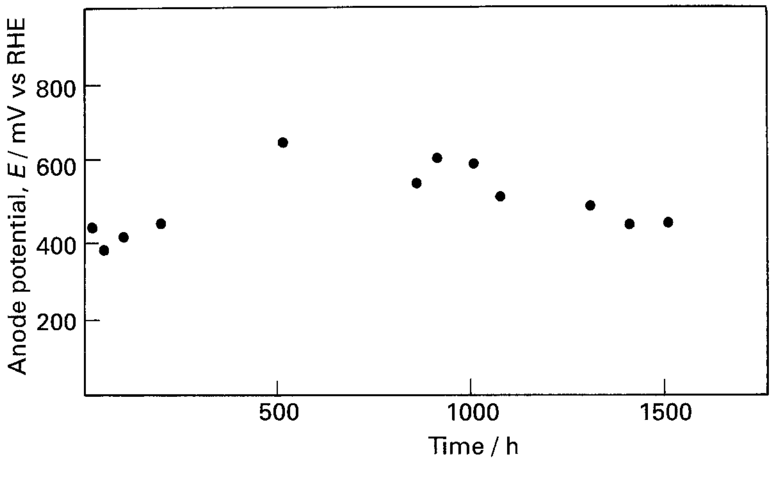

Fig. 5. Long-term tests of tungsten carbide hydrogen-diffusion electrodes with an active layer composed of 400 mg cm^{-2} tungsten carbide and 47 mg cm^{-2} Teflonized carbon black. 110 g dm^{-3} $CuCl_2 \cdot 2H_2O$; 65 g dm^{-3} HCl; 40° C; $S_{-1} = 10\,cm^2$.

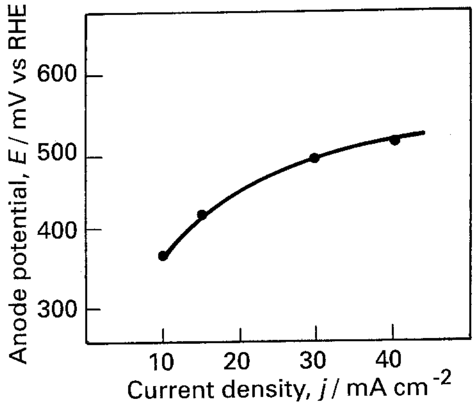

Fig. 6. Current–voltage curves of an electrode ($S = 225\,\text{cm}^2$) with an active layer composed of $400\,\text{mg}\,\text{cm}^{-2}$ tungsten carbide and $47\,\text{mg}\,\text{cm}^{-2}$ Teflonized carbon black. $110\,\text{g}\,\text{dm}^{-3}$ $CuCl_2 \cdot 2H_2O$; $65\,\text{g}\,\text{dm}^{-3}$ HCl; 40° C; $S_{-1} = 225\,\text{cm}^2$.

in electrolyte (Table 1). This shows that the hydrogen contact with the carbide did not compensate for the corrosive effect of the chloride electrolyte.

Our previous results showed that such amounts of oxide should not affect the current–voltage characteristics of the HDAs significantly [12].

From the results of the corrosion studies performed on the gas-diffusion layer wherein the collector grid was pressed, and the tungsten carbide studies, it was concluded that the deterioration of the hydrogen-diffusion anode performance during the initial 300–400 h during regeneration of copper chloride solutions is due to the collector grid corrosion. After 300–400 h it corrodes altogether and the role of a current conductor is performed by the TCB gas supplying layer. That this is actually possible is demonstrated by the resistivity of a TCB tablet, without grid, 1.75 Ω, of dimensions $10\,\text{cm}^2$ (containing $135\,\text{mg}\,\text{cm}^{-2}$ TCB).

Owing to the comparatively low resistivity of the TCB tablet and its small size ($10\,\text{cm}^2$), after the grid corrosion the HDAs continue to operate at about the same performance. The picture would be different for large electrodes. To verify these conclusions, a series of tungsten carbide electrodes with $S = 225\,\text{cm}^2$ ($15 \times 15\,\text{cm}$) were tested. The current–voltage curve of such electrodes (Fig. 6) shows that their initial activity differs little from that of small electrodes, as expected. During the first 100 h of operation there is no increase in polarization. Subsequently, it starts rising gradually by more than 200 mV, unlike the small electrode behaviour. Furthermore, a new phenomenon was observed – after 200–300 h operation cracks appeared on the electrode surface, through which the electrolyte started to penetrate into the gas chamber. It was established that the cracks occurred in regions where the collector grid had fully corroded.

In conclusion, the use of tungsten carbide hydrogen-diffusion electrodes as anodes for the regeneration of copper chloride and copper ferrichloride electrolytes can lead to a significant decrease in the energy consumption at nearly the conventional copper current efficiency and to a simplification of the electrolyser construction, if the problem of the collector grid corrosion is solved.

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