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# *Activation of hydrochloric acid-$CrCl_3 \cdot 6H_2$ solutions with N-alkylamines*

D. SH. CHENG

*Institute of Photographical Chemistry of the Academica Sinica, Peking, China*

A. REINER, E. HOLLAX

*Fraunhofer-Institut für Solare Energiesysteme, Oltmannstraße 22, D-7800 Freiburg, Federal Republic of Germany*

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An economical procedure for the reactivation of aged $CrCl_3 \cdot 6H_2O$ solutions is required for the practical operation of Fe–Cr-redox cells. N-alkylamines of the general form $H_2N{-}CH_2CH_2{-}[NH{-}CH_2CH_2]_nNH_2$ ($n = 0, 1, 2, 3, \ldots$) are suited to this application. The best results were achieved with tetraethylene pentamine ($n = 3$). The technique functions without energy addition for a considerable length of time and is easy to manage. The mechanism of the reactivation is discussed.

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## 1. Introduction

A suitable storage method is a requisite for the utilization of solar, wind or tidal energy in large scale electrical energy production. Until now lead acid batteries have essentially been used for storage. Different parameters (costs, long term stability, raw material situation) confine the extent of utilization. Therefore new storage systems are necessary.

The development of galvanic redox cells [1–10] is advanced. The attractiveness of redox cells results from the spatial separation of the electrical transformation from the storage, and from the fact that negligible self-discharging occurs even in long term storage when pure $Cr^{2+}$ solutions are carefully stored in the absence of air [11]. In addition this spatial separation of transformation and storage allows one to choose the energy and power independent of one another during construction of the redox cell.

Redox cells are presently in the battery test state with the largest advances being made with the redox couple $Fe^{2+}/Fe^{3+} \parallel Cr^{3+}/Cr^{2+}$ [3–10, 12]. During the reaction

$$Cr^{3+} + Fe^{2+} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Cr^{2+} + Fe^{3+} \qquad (1)$$

with 2 M solutions and an average terminal voltage of 1 V, 26.6 kWh $m^{-3}$ can be stored in order to use the principal advantages of theis redox system practically, the chrome electrode must be systematically improved, so that the following research and development tasks must be accomplished:

development of an activation and reactivation technique for the chrome electrode which is both easy to use and economical,

development of a catalyst for the reaction $Cr^{3+} \rightleftharpoons Cr^{2+} + e$,

the shifting of the $H_2$ potential to a more negative value than that of the $Cr^{3+}/Cr^{2+}$-reduction with heavy metals characterized by a higher $H_2$ overvoltage.

We are currently working on all of these problems, but in this paper we discuss the results of work regarding the activation and reactivation of the chrome electrolyte. Work on catalysis will be published in the near future.

## 2. Experimental procedure

### 2.1. *Methods and experimental equipment*

The primary method of investigation used was cyclic voltametry. The apparatus consisted of the Potentioscan Wenking POS 73 (Bank Elektronik, W. Germany), the Omnigraphic 2000 recorder

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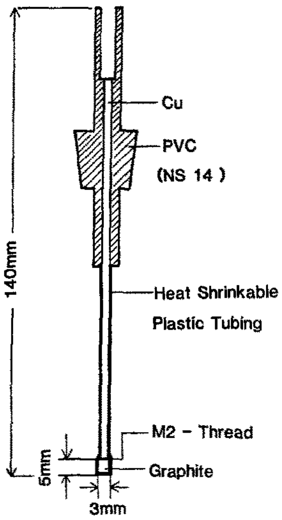


Fig. 1. Working electrode made of high pressure graphite with an exchangeable measuring head.

(Houston Instrument) and the electrolysis cell EA-875-20. The following served as electrodes:

a working electrode of high pressure graphite (developed by the authors) with an exchangeable measuring head with a geometric surface area of 0.113 $cm^2$ (see Fig. 1) and gold electrodes,

a Calomel reference electrode (Model R11, Philips) and

a Pt-counter electrode (Model M13, Philips).

The surface of the graphite electrode was polished with a 2.5 $\mu m$ DB-P-Paste from K&B Instruments. The SEM photographs were taken with a Jeol 35 apparatus with a wave dispersion X-ray spectrometer. A Perkin-Elmer spectrophotometer 330 was used for the UV measurements.

### 2.2. *Electrolyte solutions*

The electrolyte solutions were prepared by dissolving $CrCl_3\cdot 6H_2O$, $PbCl_2$, $HAuCl_4$ and various N-alkylamines in $H_2O$ (double-distilled). The chemicals were of analytical grade from Merck. The solutions for cyclic voltametry were preincubated at 25° C and stored at room temperature until the next measurement. A 30 min bubbling with pure nitrogen removed oxygen from the electrolyte before measurements were taken. After measuring, the working electrode was washed with double-distilled water and acetone and dried. The detachability of the measuring head (see Fig. 1) allowed non-destructive analysis in the scanning electron microscope of the electrode deposits.

## 3. Results and discussion

A wide variety of complexes form as $Cr^{3+}$ salts are dissolved in $HCl/H_2O$. The $Cr^{3+}$ complexes (I), (II) and (III) are significant to the redox cell reactions run with 1–4 N hydrochloric acid.

$$\underset{(I)}{[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O} \rightleftharpoons \underset{(II)}{[Cr(H_2O)_5Cl]Cl_2\cdot H_2O} \rightleftharpoons \underset{(III)}{[Cr(H_2O)_6]Cl_3} \qquad (2)$$

The reaction sequence portrayed in Equation 2 is known as 'hydrate isomerism' [13]. A hydrochloric acid solution of $CrCl_3\cdot 6H_2O$ reacts from (II) to (III) when stored, which considerably reduces the electrochemical reducibility of $Cr^{3+}$ [14]. The decrease of peak current density because of this isomerization is shown in Fig. 2.

It can be seen that the peak current density, $j$, of the reaction

$$Cr^{3+} + e \rightleftharpoons Cr^{2+} \qquad (3)$$

clearly declines after only 5 days. After 200 days $j$ is barely one eighth of its initial value. This deactivation can also be followed spectroscopically in the UV range. The absorption behaviour of the complexes (II) and (III) have already been described [10]. Complex (III), which is difficult to reduce, has bands at 405 and 578 nm. The easily reducible complex (II) absorbs at 435 and 610 nm. We measured the UV spectra of 0.5 M $CrCl_3\cdot 6H_2O$ in 1 N HCl as a function of the age of the solution. The results are shown in Figs. 3 and 4 and in Table 1.

*Table 1. Time dependency of the UV absorption of a 0.5M $CrCl_3\cdot 6H_2O$ solution in 1 N HCl*

| *Complex* | *Age of the $Cr^{3+}$ solution* | *Wavelength (nm)* | *Source* |
|---|---|---|---|
| (II) | | 435 and 610 | [10] |
| (II)–(III)-mixture | 8 days | 428 and 604 | Fig. 3 |
| (II)–(III)-mixture | 31 days | 412 and 587 | Fig. 3 |
| (II)–(III)-mixture | 300 days | 408 and 574 | Fig. 3 |
| (III) | | 405 and 578 | [10] |

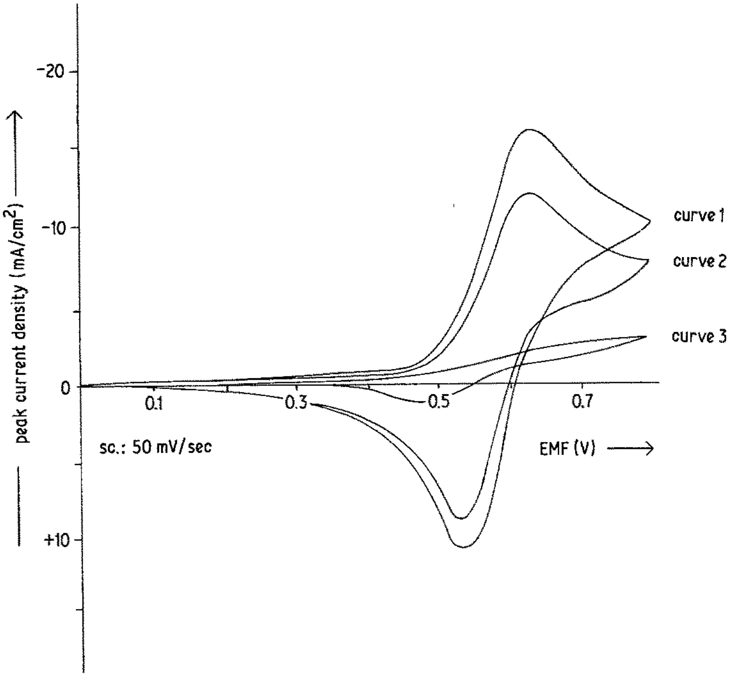


Fig. 2. Cyclic voltammogram of the deactivation of a 2 M $CrCl_3 \cdot 6H_2O$ solution in 1 N HCl measured at 25° C with a gold electrode catalysed with 3.6 × $10^{-4}$ M $PbCl_2$. Curve 1: freshly prepared solution, Curve 2: 5-day-old solution, Curve 3: ⩾ 200-day-old solution.

It can be seen that the UV absorption wavelengths of the $Cr^{3+}$ solutions of increasing age approach those of complex (III). In addition Fig. 3 shows that the older the solution, the smaller the UV intensity becomes. Since $j$ also declines with the increasing age of the solution (see Fig. 2), the peak current densities and UV intensities of solutions of the same age were plotted against one another (see Fig. 5).

There is an apparent proportionality between electrochemical activity and the UV excitation of electrons. It is suggested in the literature [10, 12] that reactivation of aged $CrCl_3 \cdot 6H_2O$ solutions may be achieved by heating to 65° C. The equili-

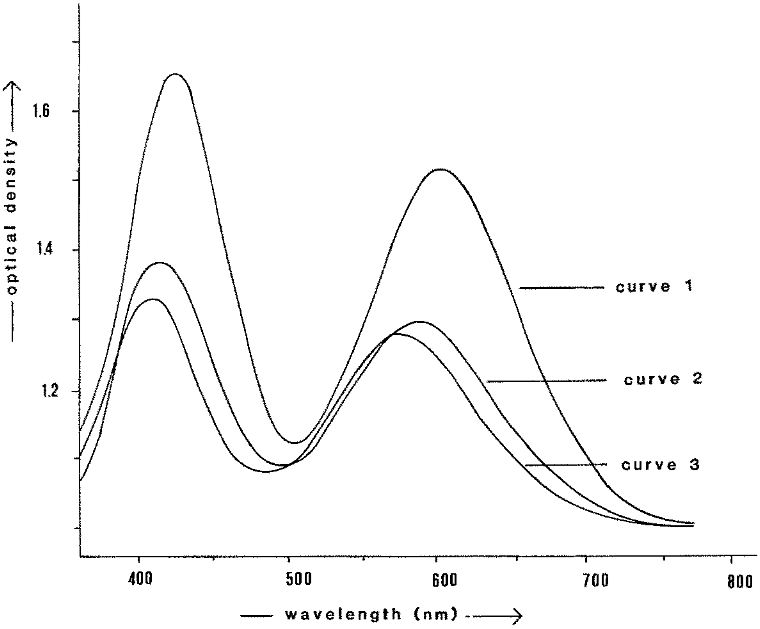


Fig. 3. UV spectroscopic observation of the deactivation of a 0.5 M $CrCl_3 \cdot 6H_2O$ solution in 1 N HCl, path length = 1 mm. Curve 1: 8-day-old solution, Curve 2: 31-day-old solution, Curve 3: 300-day-old solution.

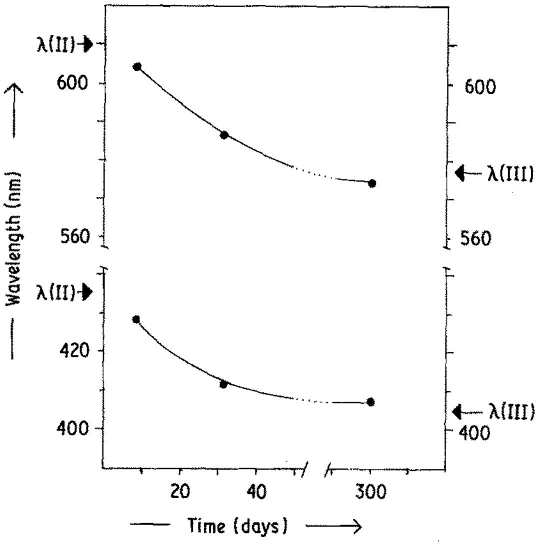


Fig. 4. UV absorption–time dependency of a 0.5 M $CrCl_3 \cdot 6H_2O$ solution in 1 N HCl.

brium position in Reaction 2 would then be shifted to favour complex (II). However, this process is not economically suitable for charging a redox cell connected with a photovoltaic-plant because in Europe overcast weather occurs often and necessitates charging with small currents. Under these conditions only a small warming of the electrolyte will occur. The difference to 65° C has to be supplied by heating. To raise the temperature by only 10° C a thermal energy is used which corresponds to about 40% of the stored electrical energy. Achieving $\Delta T = 23°C$ by external heating corresponds to 100% of the electrically stored energy.

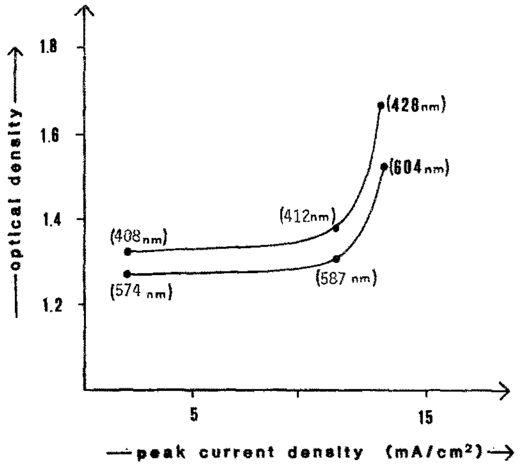


Fig. 5. Proportionality between peak current density, $j$, and peak UV intensity of equally old $CrCl_3 \cdot 6H_2O$ solutions in 1 N HCl.

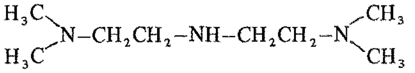
We have therefore attempted to find a reactivation process which needs no further energy addition, which maintains the reducibility of the $Cr^{3+}$ solution for the longest possible time and which is easy to handle. Proceeding on the assumption that the coordination of the six $H_2O$ molecules around the $Cr^{3+}$ ion is responsible for the poor reducibility of complex (III), we looked for ligands which are capable of breaking open the hydrate shell surrounding the $Cr^{3+}$ ion. These ligands must be better electron donors than oxygen in order to displace the water molecules out of the inner coordination sphere. For this reason we tested amines for their ability to prevent the deactivation of the $CrCl_3 \cdot 6H_2O$ solution. We defined the activation factor, $f$, as the measurement of this ability:

$$f = j_a/j_0 \qquad (4)$$

where $j_a$ and $j_0$ are the peak current densities with and without amines. $NH_3$ showed as expected $f = 1$, because the number of $NH_3$ molecules with a free electron pair is increasingly small in 1 N HCl. This means that a negligibly small number of amine ligands exist which are capable of reacting with $Cr^{3+}$. On the other hand a large number of aminoaquohalogenide complexes of $Cr^{3+}$ exist, where an amino group represents, for example, half of a bidentate ligand [15]. One of the simplest bidentate nitrogen ligands is ethylene diamine $H_2N{-}CH_2CH_2{-}NH_2$. Table 2 shows the influence of the addition of $2.2 \times 10^{-2}$ M ethylene diamine to a freshly prepared 0.5 M $CrCl_3 \cdot 6H_2O$ solution in 1 N HCl. $Cr^{3+}$ complexes in aqueous solutions are distinguished by their relatively large kinetic stability [16]. Our investigations showed that several days are necessary after the amine addition before a stable state is reached. Table 2 shows the peak current densities 28 days after the addition of ethylene diamine.

In these 28 days the peak current density did not decrease but even increased by 48%. Ethylene diamine is the first member of the homologous N-alkylamine group $H_2N{-}CH_2CH_2{-}\left[NH{-}CH_2CH_2\right]_nNH_2$ ($n = 0, 1, 2, 3, \ldots$). It was then obvious that we should include other higher members of this group of compounds in our

*Table 2. The activation of 0.5M $CrCl_3 \cdot 6H_2O$ in 1 N HCl with various N-alkylamines*

| *Activator* ($2.2 \times 10^{-2}$ *M*) | *Formula* | $j_0$ (*mA cm*$^{-2}$) | $j_a$ (*mA cm*$^{-2}$) | $j_a/j_0$ |
|---|---|---|---|---|
| Without activator | | 8.8 | 7.0 | 0.81 |
| Ethylene diamine | $H_2N-CH_2CH_2-NH_2$ | 8.8 | 13.0 | 1.48 |
| Diethylene triamine | $H_2N-CH_2CH_2-NH-CH_2CH_2-NH_2$ | 8.8 | 13.6 | 1.55 |
| N,N,N',N'-tetramethyl diethylenetriamine |  $(H_3C)_2N-CH_2CH_2-NH-CH_2CH_2-N(CH_3)_2$ | 8.8 | 14.7 | 1.67 |
| Tetraethylene pentamine | $H_2N-CH_2CH_2 \left[ NH-CH_2CH_2 \right]_3 NH_2$ | 8.8 | 15.7 | 1.78 |

$j_0$: peak current density of a freshly prepared $Cr^{3+}$ solution.
$j_a$: peak current density 28 days after the addition of an activator to the fresh solution.
$j_a/j_0$: activation factor.
Measurements made at 25° C with a gold electrode catalysed with $3.6 \times 10^{-4}$ M $PbCl_2$.

investigations. Table 2 shows that the activation factor increases with the growing chain length of the N-alkylamines. The branched N,N,N',N'-tetramethyl diethylene triamine with its activation factor lies between diethylene triamine and tetraethylene pentamine. The methyl groups apparently overcompensate their steric hindrance of the $\alpha,\omega$-nitrogen through the increase in basicity, which also occurs due to the presence of the $CH_3$-groups. Measurements of the concentration dependency of $j$ in the range $8 \times 10^{-4}$ M $\leqslant c \leqslant 10^{-1}$ M show that tetraethylene pentamine exhibits higher peak current densities in the whole concentration range than all of the other N-alkylamines in Table 2.

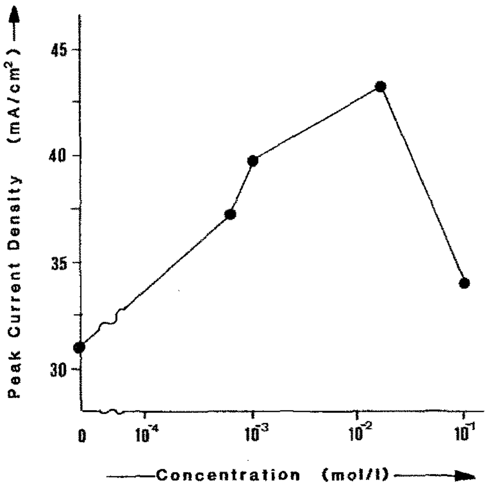


Fig. 6. Concentration dependency of the peak current density of a 1 M $CrCl_3 \cdot 6H_2O$ solution in 1 N HCl activated with tetraethylene pentamine, measured at 25° C with a high pressure graphite electrode catalysed with $3.6 \times 10^{-4}$ M $PbCl_2$ and $4.5 \times 10^{-7}$ M $HAuCl_4 \cdot 4H_2O$.

A concentration of $2.2 \times 10^{-2}$ M resulted in the largest activation (see Fig. 6) with $f = 1.78$ (see Table 2). $2.2 \times 10^{-2}$ M tetraethylene pentamine was therefore chosen for a long term test, the results of which are shown in Fig. 7.

It can be seen that a clear increase of electrochemical activity occurs when tetraethylene pentamine is added even with a freshly prepared $Cr^{3+}$ solution. In addition the deactivation of the $Cr^{3+}$ solution is clearly slowed. Quantitative analysis reveals that with the addition of tetraethylene pentamine to a freshly prepared $Cr^{3+}$ solution, the decline of $j$ after 345 days is only 22% compared with 88% in the activator free $Cr^{3+}$ solution. The actual values of the peak current densities after 345 days are approximately 11 times larger in the activator containing electrolyte than in the activator-free solution. The 22% decline of $j$ of the solution containing the activator is most probably caused by the chemical decomposition of the tetraethylene pentamine. After being stored for months even pure tetraethylene pentamine has a slight odour of $NH_3$. It was therefore reasonable to seek to compensate for the loss by means of renewed addition of the N-alkylamine. The reactivation Curve a in Fig. 7 shows that after two days the value of the initial peak current density is almost reached. From the reactivation Curve b in Fig. 7 it follows that aged, activator-free $Cr^{3+}$ solutions can also be reactivated by tetraethylene pentamine. The reactivation is independent of whether the $Cr^{3+}$ solution already contained an activator or not and is independent of the age of the solution. The activation and reactivation of $CrCl_3 \cdot 6H_2O$ solutions in HCl with

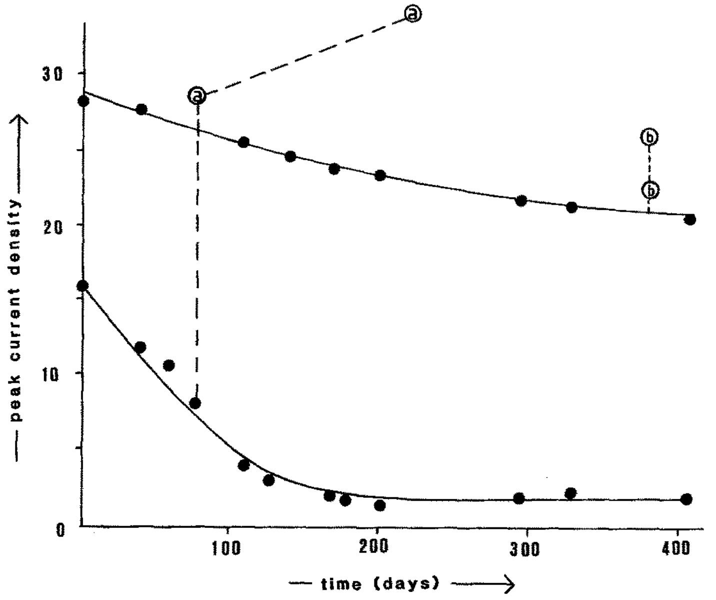


Fig. 7. Long term test of the time dependency of the peak current density of a 2 M $CrCl_3 \cdot 6H_2O$ solution in 1 N HCl. Upper curve: activation by the addition of $2.2 \times 10^{-2}$ M tetraethylene pentamine; lower curve: without activator. – – – ⓐ – – – : reactivation of the activator-free solution by the addition of $2.2 \times 10^{-2}$ M tetraethylene pentamine, – – – ⓑ – – – : reactivation by an addition of $2.2 \times 10^{-2}$ M tetraethylene pentamine of a $Cr^{3+}$ solution slightly deactivated by activator decomposition. Measurements at 25° C with a gold electrode catalysed with $1.8 \times 10^{-4}$ M $PbCl_2$.

tetraethylene pentamine functions without energy addition, lasts for a long period of time and is easy to manage.

Since tetraethylene pentamine is inexpensive, the whole procedure is economically very favourable. The cyclovoltametrically-recorded activation is of course not sufficient proof for operation in redox cells. But we believe that the amines could improve cell performance. The mechanism of the (re)activation with tetraethylene pentamine has not yet been explained in detail. It appears that there are two mechanisms which oppose one another with regard to their effect on the peak current density. The concentration of the N-alkylamine determines which mechanism prevails. Tetraethylene pentamine has an activating effect on the aquohalogenide complexes but, at higher concentrations, reduces the electrochemically active electrode surface. Fig. 6 shows that the optimal state between complex activation and covering of the electrode surface is reached at a concentration of $2.2 \times 10^{-2}$ M. With $10^{-1}$ M tetraethylene pentamine a non-homogeneous catalyst deposition can be seen on SEM photographs. The clusters in Fig. 8 can be identified as Au and Pb.

In order to obtain a high peak current density, a homogeneous catalyst deposition on the electrode surface is necessary. At a high concentration of tetraethylene pentamine a peak current density flows similar to that in the activator-free solution despite cluster formation. This fact suggests that tetraethylene pentamine raises the electrochemical activity of the $Cr^{3+}$-complexes in solution. The activity increase could result either from the shift of equilibrium in Equation 2 from (III) to (II), or to a reaction of the tetraethylene pentamine with one of the $Cr^{3+}$ complexes. The latter mechanism is supported by the results of our UV investigations with two-month-old solutions. Fig. 9 shows the UV spectra of a two-month-old solution of 0.5 M $CrCl_3 \cdot 6H_2O$ in 1 N HCl.

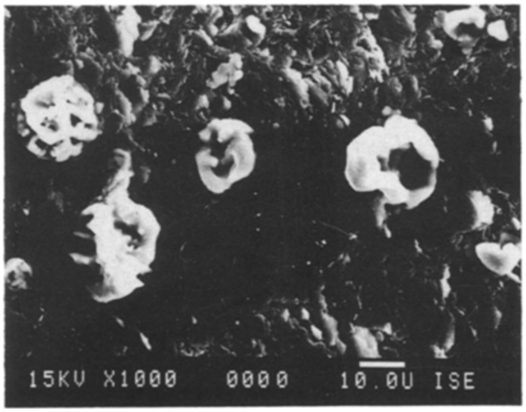


Fig. 8. Inhomogeneous Pb–Au deposition on a high pressure graphite electrode with $10^{-1}$ M tetraethylene pentamine; magnification × 1000, SEM photograph enlargement.

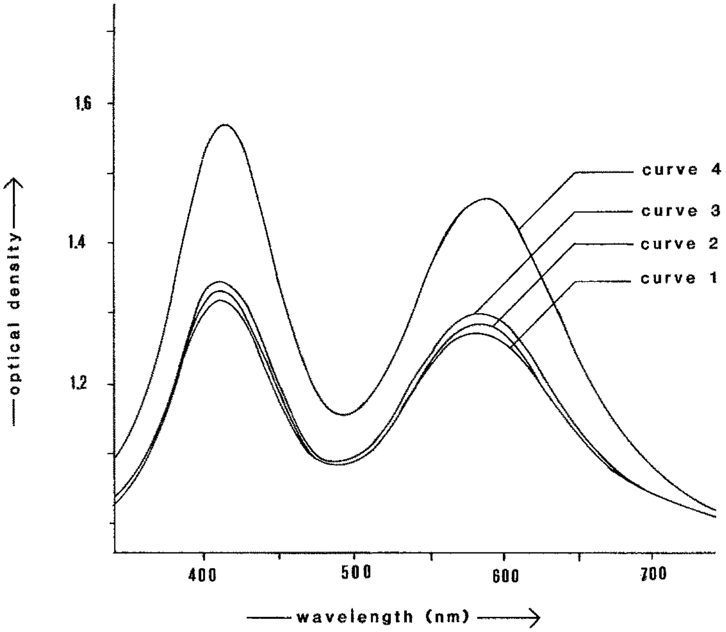


Fig. 9. UV absorptions of a two-month-old solution of 0.5 M $CrCl_3 \cdot 6H_2O$ in 1 N HCl with various N-alkylamines at a concentration of $2.2 \times 10^{-2}$ M. Curve 1: without activator, Curve 2: with $H_2N-CH_2CH_2-NH_2$, Curve 3: with $H_2N-CH_2CH_2-NH-CH_2CH_2-NH_2$, Curve 4: with $H_2N-CH_2CH_2\left[NH-CH_2CH_2\right]_3NH_2$.

The activator free solution (see Curve 1 in Fig. 9) indicates absorptions at 408 and 580 nm. This corresponds to complex (III) in Equation 2. Fig. 9 further shows that through the addition of various N-alkylamines

the UV intensities rise proportionally to the chain length of the N-alkylamine (see Fig. 9, Curves 2, 3 and 4) and

the absorptions shift to longer wavelengths, and this effect is also proportional to the chain length of the N-alkylamines.

Like the peak current density (see Table 2) the UV absorption intensity rises as the chain length of the N-alkylamine increases. These results allow the following to be concluded about the activation mechanism of the $Cr^{3+}/Cr^{2+}$-reduction:

1. In aged solutions the activation does not result from a shift in the chemical equilibrium from (III) to (II) in Equation 2, because the UV spectra of the activator-free solutions do not show absorption bands at 435 and 610 nm.

2. The UV absorptions of the activator containing complexes at 408–414 and 580–585 nm are very similar to those of complex (III) which lie at 405 and 578 nm (see Table 1). The activation itself lies in the reaction of the N-alkylamine with the $Cr^{3+}$ complex (III) to an aminoaquohalogenide complex.

3. The UV absorptions of the aminoaquohalogenide complex are shifted to slightly longer wavelengths relative to the absorption of (III) and are more intensive. It can be assumed from this result and from the proportionality between UV intensity and peak current density (see Fig. 5) that (III), through its reaction with N-alkylamines, maintains an energy term scheme which is more favourable for the $Cr^{3+}/Cr^{2+}$-reduction.

4. The increase of the peak current density with longer chain length of the N-alkylamines could be interpreted as a result of the number of nitrogen ligands which increase as the chain length increases. The number of N-atoms with a free-electron pair indeed increases with the degree of polymerization *n* of N-alkylamine. The pK value for the first deprotonation step is 4.22 for $n = 3$ but 3.37 for $n = 4$ [17]. Another interpretation is to assume a different electrochemical activity of the different amino complexes.

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