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Electrochemical behaviour of the Cr(II)/Cr(III) couple on silver, silver amalgam and silver-based mercury film electrodes

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The electrocatalytic activity of silver, mercury, silver-based mercury films, and silver amalgam electrodes for the reduction of Cr(III) ions in acidic solutions is analysed. An enhancement in the activity of the last two electrodes is observed when they are pretreated with high cathodic current polarization or ultrasonic waves. These effects can be explained by the formation of an unstable highly reactive amalgam. The electrocatalytic enhancement is not observed when the same electrode pretreatments are applied to sitting-drop mercury or silver electrodes.

1. Introduction

Chemical reduction of some organic compounds can be carried out with lower energy consumption in emulsified systems (water–organic solvent) using a redox couple as a mediator [1]. The yield of the organic synthesis can be conditioned by factors such as the effective potential for the regeneration of the mediator and the faradaic efficiency of the process, hydrogen evolution being the most significant competitor in aqueous media.

Amalgams, silver and mercury films are among the cathodes with high overvoltage for the hydrogen evolution reaction. If additional cathodization at high potentials in NaOH is applied to such film electrodes, an increase in the overvoltage of the hydrogen evolution is observed although no explanation is given [2].

Cr(II), obtained by the electrochemical reduction of Cr(III), is a typical redox mediator used in many electroorganic reductions [3]. However, the electrochemistry of chromic ion is complicated since, on the one hand, it forms a wide variety of hexacoordinated complexes whose formal reduction potentials range from -0.414 V for the hexa-aqueous complex to -1.28 V when more stabilizing ligands such as cyanide constitute the coordination sphere. The acidic properties of Cr(III) (p*Ka* varies from 2 to 6 according to the ligands) determine whether water molecules or hydroxyls occupy coordination sites at a given pH; species with OH^- groups can develop into polynuclear complexes which polymerize [4]. On the other hand, the electron transfer reaction may proceed through different mechanistic pathways depending on the cathode material and, obviously, on the ligands present in the complex. An outer-sphere mechanism has been diagnosed for the reduction of $Cr(H_2O)_6^{3+}$, $Cr(H_2O)_5F^{2+}$, $Cr(H_2O)_5SO_4^+$ while an inner-sphere one has been indicated for the reduction of a number of ions of the class $[Cr(H_2O)_5X]^{2+}$, ($X = Br^-$, Cl^-, CNS^-, N_3^-, NO_3^-), $[Cr(NH_3)_5X]^{2+}$ ($X = CNS^-$, N_3^-, Cl^-, Br^-), etc. on mercury [5–9], silver [10, 11], gallium, lead and thallium [12]. When the reaction proceeds through an inner-sphere mechanism an enhancement in the reduction rate, which can be explained by a ligand-bridged electron transfer mechanism, is observed. This indicates that the metal surface greatly influences the energy of the process. The differences observed between Ag and Hg for the reduction rate of Cr(III) have been partly attributed to the different values in the zero charge potential for both metals (-0.94 V vs SCE for Ag and -0.46 V vs SCE for Hg) [11]. These values show that the silver surface promotes a greater anion adsorption in the studied potential range, thus favouring the electronic transfer between the complex ion and the silver surface [11].

In the present paper the reduction of $Cr(H_2O)_5Cl^{2+}$ is analysed on different electrodes with the aim of establishing the best conditions for its reduction while keeping the hydrogen evolution as low as possible.

2. Experimental details

A pair of similar electrochemical cells (30 cm^3 volume) with three compartments was used. The counter electrode was a platinum foil of 2 cm^2 geometric area and a calomel electrode in the same solution (1 M Cl^-) was used as reference. All potentials in the text are referred to this electrode. Silver, mercury and silver/mercury amalgams, prepared in different ways, were used as working electrodes. Silver wires ($\phi = 1$ mm) (Koch Light 99.99%) of 0.13 cm^2 geometric area, embedded in a Teflon rod, were employed either directly (previously electropolished according to [13]) or for the preparation of silver-based mercury film

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electrodes (MFE/Ag) and silver–mercury amalgam electrodes (SAE/Ag). The MFE/Ag were prepared by electrodeposition of mercury in 0.1 M $Hg_2(NO_3)_2$ acidic solution (Merck p.a.) at constant cathodic current density ($5\,mA\,cm^{-2}$) for 15 min and rinsed in pure water afterwards. A bright smooth film was obtained. This kind of electrode was prepared immediately prior to use. SAE/Ag were made in the same way as MFE/Ag but waiting until the latter lost its brightness (several hours). A sitting-drop mercury electrode was used as a pure mercury electrode (ME). When indicated, different pretreatments were applied to the working electrodes: (a) cathodization either in 1 M NaOH (Carlo Erba RPE, ACS) or in 1 M HCl (Merck p.a.) at different high constant current densities ($0.5 \leqslant i \leqslant 2.5$) A cm^{-2} for electrolysis times ranging from 10 s to 1 min; (b) ultrasonic vibration at 50 kHz in pure water also for different times.

Solutions were 1 M [NaCl (Merck p.a.)–HCl] of different pH, with or without 10^{-2} M $CrCl_3$ (BDH) prepared with millipore water and degassed with N_2 (99.99%) before each experiment. Chromic solutions were prepared just before use to have a relatively high concentration of the $[Cr(H_2O)_5Cl]^{2+}$ complex [4]. All experiments were performed at room temperature.

Cyclic voltammetry, potential decay at open circuit and microscopic observation of the electrodes were used in order to follow the electrochemical behaviour of the different cathodes. Potentiostatic experiments were performed only for Ag. In all cases, the potential for the onset of hydrogen evolution, E_{H_2}, was determined from potentiodynamic current–potential (i/E) profiles. The potential at which a sudden change occurred in the slope of the E vs log i plots was identified with E_{H_2}. The equipment used was a potentiostat/galvanostat (PAR model 173) (also used galvanostatically during pretreatments), a wave form generator (PAR model 175), a Hewlett Packard *xy* recorder (model 7004B) and a *y–t* recorder (Sargent model MR). An Ultrasonic Cleaner (Cole–Parmer Model 8845 (50 kHz)) was used for ultrasonic vibrating pretreatment.

3. Results

Although metals such as lead, zinc and aluminium, which have a high H_2 overpotential, can reduce Cr(III) [12], the voltammetric experiments showed that after the first cycle, the reduction current falls to very low values.

Mercury and silver were the only metals that maintained their activity along the successive cycles under the experimental conditions used.

3.1. *Chromic ion reduction on silver and mercury*

Figure 1 shows current–potential (i/E) profiles for the Cr(III)/Cr(II) redox couple on silver at three different pHs: 1, 2 and 3, at a potential sweep rate v of $0.100\,V\,s^{-1}$. In the negative potential sweep, two current peaks (p_{c1} and p_{c2}) appeared. Peak reduction potential $E_{p_{c1}} = -0.63$ V was pH independent while $E_{p_{c2}} = -0.90$ V was well defined only for pH = 3. In the positive potential scan, only one oxidation peak, p_a, was observed at $E_{p_a} = -0.56$ V independent of pH.

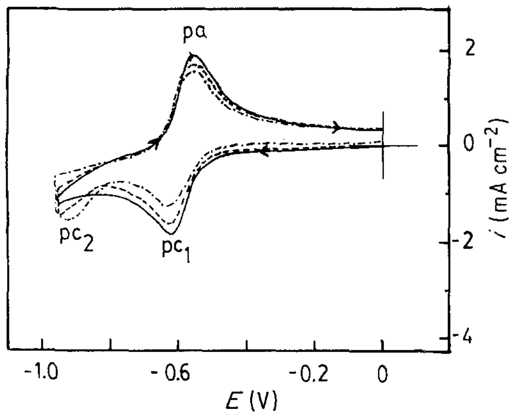

Fig. 1. Potentiodynamic i/E profiles of 10^{-2} M $CrCl_3$ in 1 M (NaCl–HCl) on Ag, at different pH = (——) 1; (– – –) 2; (–·–·–·–) 3. $v = 0.100\,V\,s^{-1}$.

The peak currents $i_{p_{c1}}$ (for pH $\leqslant$ 3) and $i_{p_{c2}}$ (only analysed at pH = 3) varied linearly with the square root of v in the interval ($0.010 \leqslant v \leqslant 0.500$) $V\,s^{-1}$. At pH = 3, $i_{p_a}/(i_{p_{c1}} + i_{p_{c2}})$ was approximately equal to one. This ratio, as well as $E_{p_{c1}}$ and $E_{p_{c2}}$ was independent of v. According to these results, a reversible system $[Cr(H_2O)_5Cl]^{2+}/[Cr(H_2O)_6]^{2+}$ could be characterized on Ag in agreement with the literature [8]. At pH = 3 and $v \leqslant 0.010\,V\,s^{-1}$ the electrode surface became blocked probably by polymeric species similar to those formed in basic media but in this case due to local alkalinization of the interface. The same effect was observed at pH = 2 but only if potentials more negative than 1 V were applied.

The chemical behaviour of the Cr(III) ion requires low pH media for better electrolysis conditions, while higher pHs are necessary in order to minimize the H_2 evolution reaction (HER) competition ($E_{H_2} = -0.70$, -0.76 and -0.82 V at pH 1, 2 and 3, respectively). Taking these facts into account pH = 2 was chosen for the working conditions as an intermediate value between these two opposite requirements.

The irreversibility of the Cr(III) reduction process on mercury can be observed in Fig. 2a where the i/E profile for ME at $0.100\,V\,s^{-1}$ is shown. The reduction current was overlapped by hydrogen evolution at approximately -1.0 V. In the positive potential scan Cr(II) was oxidized with a well-defined peak around -0.200 V.

3.2. *Chromic ion reduction on MFE/Ag and SAE/Ag*

The Cr(II)/Cr(III) redox couple on MFE/Ag showed the same characteristics as on ME, while the HER took place at lower potentials of around -0.95 V. When SAE/Ag was used, significant kinetic changes in both electrochemical processes took place. Figure 2b shows i/E profiles for Cr(II)/Cr(III) and HER at $0.100\,V\,s^{-1}$. For the former process, reduction and

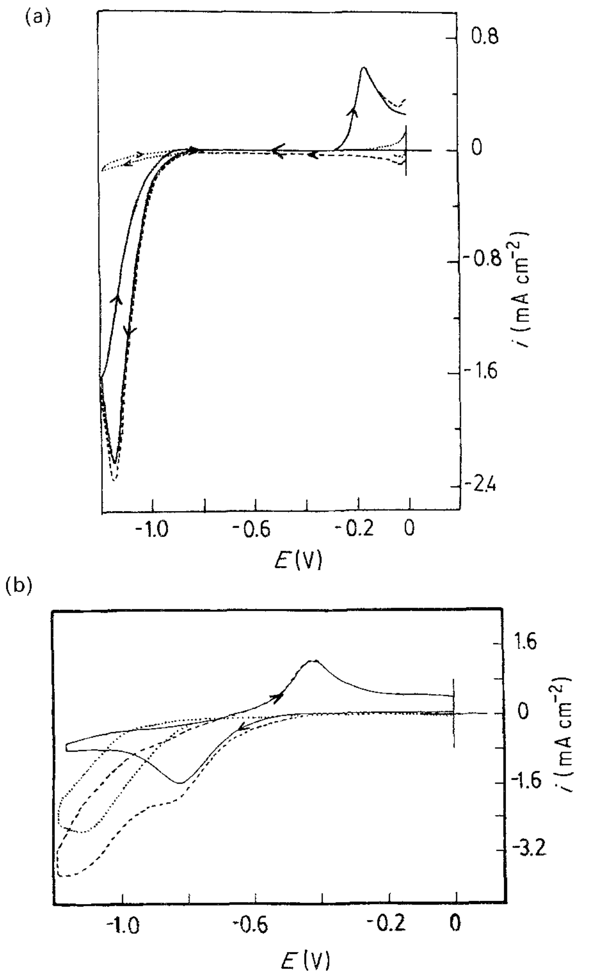

Fig. 2. Potentiodynamic i/E profiles of 1 M (NaCl–HCl), pH = 2 on: (a) sitting-drop mercury electrode (ME); (b) silver amalgam (SAE/Ag) (– – –) with and (· · · ·) without 10^{-2} M $CrCl_3$; (——) voltammetric curve of $CrCl_3$ after correction for the base electrolyte current. v = 0.100 V s^{-1}.

oxidation current peaks were defined. The corresponding peak potentials fell between those observed on Hg and Ag, while E_{H_2} shifted towards less negative values than on MFE/Ag. Nevertheless, peak potentials changed with the time elapsed following the preparation of the electrode, this being an indication that surface changes were still taking place.

3.3. *Chromic ion reduction on pretreated electrodes*

Figure 3 shows i/E profiles at 0.100 V s^{-1} for the Cr(II)/Cr(III) system on MFE/Ag precathodized in NaOH or HCl solutions. It can be observed that the electrode pretreatment in both media produced a remarkable kinetic effect on the redox process.

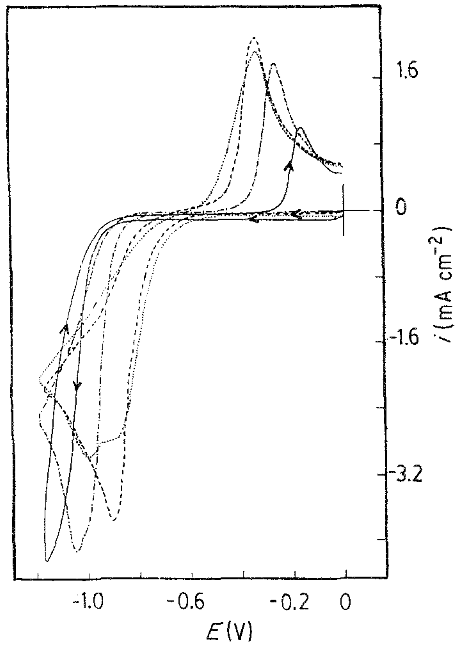

Fig. 3. Effect on Cr(II)/Cr(III) couple of pretreatments on mercury film electrode (MFE/Ag). (——) Without treatment; (–·–·–·–) ultrasonic shake; (– – –) precathodized in 1 M NaOH; (· · · ·) precathodized in 1 M HCl. Solution composition: 10^{-2} M $CrCl_3$, 1 M (NaCl + HCl), pH = 2. v = 0.100 V s^{-1}.

HER was also modified by pretreatments (specially in NaOH) but in an opposite direction (E_{H_2} shifted to -1.20 V) although this effect was easily reversed when N_2 was bubbled through the solution. Figure 4a shows that the increase in reversibility for the Cr(II)/Cr(III) couple was dependent upon the pretreatment conditions. ΔE_p diminished down to a limiting value according to the cathodic current density applied. The activation effect produced by pretreatments decayed at different rates depending on whether it was carried out in NaOH or HCl solution. As shown in Fig. 4b, the change in ΔE_p lasted longer in the former case.

The potential decay at open circuit in NaCl–HCl solution for MFE/Ag and two MFE/Ag electrodes precathodized in NaOH and HCl, respectively, are shown in Fig. 5. The time elapsed until the achievement of a relatively constant potential (1.5 h and 30 min after pretreatments in NaOH and HCl, respectively) was similar to the duration of the activation effect observed in Fig. 4b.

SAE/Ag was also activated towards the Cr(II)/Cr(III) couple by precathodization although the effect of increasing the HER overpotential was less important than on MFE/Ag. When both MFE/Ag and SAE/Ag were ultrasonically vibrated in pure water, an activation

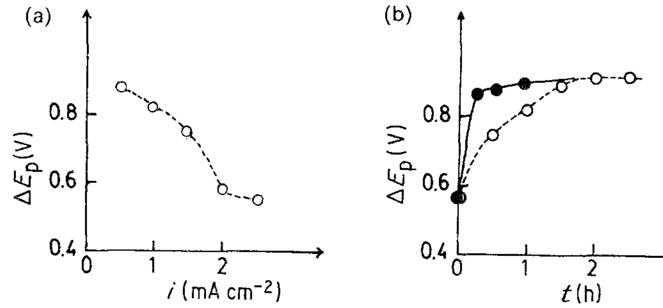

Fig. 4. Activating effect of precathodization on ΔE_p. Solution composition: 10^{-2} M $CrCl_3$ in 1 M (NaCl + HCl), pH = 2. (a) Effect of current density in 1 M NaOH; electrolysis time: 10 s; (b) effect of the time elapsed at open circuit, after pretreatment (cathodic current density of 2.5 A cm^{-2} during 60 s) in: (○) 1 M NaOH; (●) 1 M HCl.

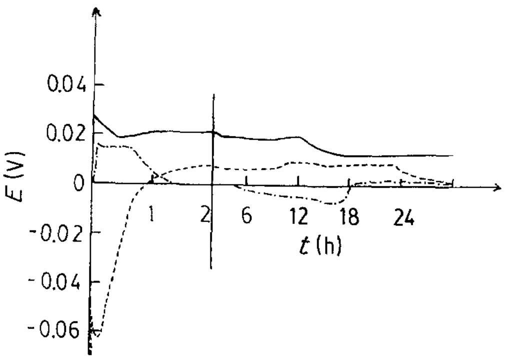

Fig. 5. MFE/Ag potential decay at open circuit in 1 M (NaCl–HCl), pH = 2 after pretreatment. (——) Without pretreatment. Precathodized in: (–·–·–·–) 1 M HCl, (– – –) 1 M NaOH.

effect similar to that produced by precathodization was observed (Figs 3 and 6) though E_{H_2} remained almost unchanged. On the other hand, the ME activity for Cr(III) reduction and HER was not changed when either precathodization (in both NaOH and HCl solutions) or ultrasonic vibration were performed.

4. Discussion

When the MFE/Ag is cathodized in an NaOH solution, a sodium amalgam is formed by reduction of Na^+ ions prior to HER [12]. Afterwards, the following reaction takes place:

$$2NaHg + 2H_2O \longrightarrow$$
$$H_2 + 2Na^+ + 2OH^- + 2Hg$$

and this fact explains the evolution of H_2 observed at open circuit for rather long times after the pretreatment. Furthermore, the solution around the electrode surface becomes red if phenolphthalein is added. The very negative value of open circuit potential immediately after cathodization indicates H_2 accumulation at the electrode–solution interface. The time elapsed at open circuit until a relatively constant potential (0.01 V) is achieved (around 1.5 h) is almost in accordance with the period of enhanced activity towards the Cr(II)/Cr(III) reaction (see Figs 5 and 4b).

It should be observed that if the precathodization is carried out in HCl solution, no H_2 accumulation is produced; nevertheless, the same activating effect was observed.

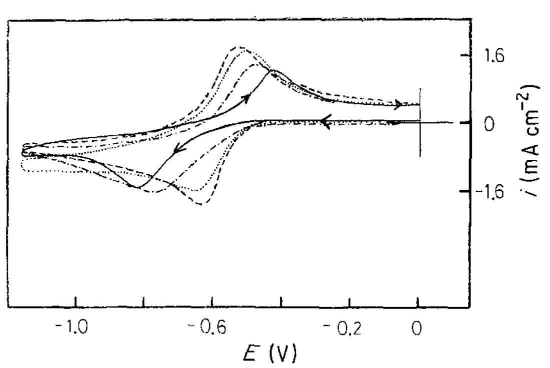

Fig. 6. Effect on Cr(II)/Cr(III) couple of pretreatments on SAE/Ag. (——) Without pretreatment; (–·–·–·–) ultrasonic shake; (– – –) precathodized in 1 M NaOH; (····) precathodized in 1 M HCl. Solution composition: 10^{-2} M $CrCl_3$, 1 M (NaCl + HCl), pH = 2. v = 0.100 V s^{-1}.

Chemical reductors, formed electrolytically during the cathodization, cannot be responsible for electrode activity enhancement because activity is also produced when ultrasonic waves are applied. Thus, Fig. 3 is a clear evidence that whatever pretreatment is performed the same activation (at least at short times) is produced. Movements in the 'liquid' mercury of the film, produced either by ultrasonic vibration or by bubble turbulence, are a possible cause for the electrode modifications observed. Nevertheless, this fact alone cannot account for electrode activation because such an effect is not observed on pretreated ME whatever conditions are applied. Consequently, it is evident that the silver base plays an important role, and it can be concluded that some type of unstable silver amalgam formation is promoted by the inner movement of mercury layers. This amalgam should be more reactive than the one stabilized after some hours.

Microscopic observation of recently pretreated electrodes revealed structural variations with time. These changes were very fast during the early minutes after pretreatment, becoming slower afterwards.

The increase in the HER overpotential observed with NaOH cathodized electrodes might be assigned to diffusional causes (solution near the electrode became saturated in hydrogen). This hypothesis was reinforced by two experimental facts: (a) no effect on E_{H_2} was observed when ultrasonic waves were applied; (b) E_{H_2} returned to less negative values when N_2 was bubbled through the solution. Nevertheless, the same shift in E_{H_2} is observed when precathodization is carried out in HCl solution. As previously stated, no H_2 was produced on the electrode as soon as the cathodization current was interrupted. Thus, the reasons for the E_{H_2} shift produced by precathodization are not yet fully understood.

Although the performance of MFE/Ag and SAE/Ag towards Cr(III) reduction is considerably improved by the described pretreatments, these electrodes are not the best choice when Cr(II) has to be used as redox mediator. Despite the great HER interference Cr(III) reduction on silver cathodes is reversible and proceeds at lower reduction potentials. Polarization curves under potentiostatic conditions demonstrated that long time electrolyses were possible with a good current efficiency at low potentials ($E_{1/2} = -0.55$ V).

Consequently, Cr(II) was used as redox mediator in the electroreduction of dibromonorcarane to the monobromo derivative in an emulsified organic/water medium on a silver cathode. Satisfactory results were obtained [15].

Acknowledgements

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