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Bifunctional electrochemical systems

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Abstract. The electrochemical reduction and oxidation of metal ions accompanied by the formation of a film at the electrode–electrolyte boundary is discussed. The formation of a film having a mixed conduction type and consisting of oxide–hydroxide compounds of the metal denotes the presence of a new system: the electrode–film–electrolyte system, called a bifunctional electrochemical system because it can act as an electrolyte and as an electrode simultaneously. The bibliography includes 112 references.

I. Introduction

Interest in the electrochemical reduction and oxidation of transition metals has increased continuously for many decades, in spite of the extensive fundamental studies which have already been reported. This can be attributed to the complexity of the relevant electrochemical reactions, especially in systems containing multivalent metal ions.

When the pH of the cathodic film on an electrode surface differs significantly from its value in the bulk of the electrolyte[3] the intermediate reduction products (compounds of a metal being deposited in lower states of oxidation or compounds of a metal being dissolved in higher states of oxidation) form a cathodic or anodic film whose composition includes compounds able to be discharged directly to the metal.

The formation of this film denotes the presence of a new electrode system (now called a bifunctional system because electrode processes can take place on both sides of the film). The film possesses both electronic and ionic conductivity: the ionic conductivity supports the electrolysis on the side of the electrode and the electronic conductivity supports it on the side of the electrolyte. Hence the film behaves as an electrode towards the electrolyte and as an electrolyte towards the electrode, thus fulfilling two functions simultaneously.

It is therefore of interest to examine electrochemical reduction and oxidation processes from the standpoint of assessing their degree of bifunctionality towards various systems.

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II. Formation of a film at the electrode–electrolyte interface

1. Cathodic processes

The presence of a cathodic film was first suggested in the 1920s following a study of one of the most complex of these processes: the electrodeposition of chromium from solutions of chromic acid. The existence of such a film during the electrodeposition of chromium is now generally accepted, and has been confirmed by electrochemical[4–8] and optical methods, by microscopic observations with both still and ciné-film recording,[7–9] and also by an analysis of the zone adjacent to the electrode using special apparatus.[10, 11]

Two types of film (primary and secondary) have been defined, formed on the cathode in a solution of chromic acid in the absence of current and under polarisation respectively.[12, 13] They differ both in their composition and properties and in the mechanism of their formation.

The primary films, formed on the electrode surface before the current is applied, are very thin (~0.02 μm) and almost free from pores; they cover the cathode uniformly and they have an electronic conductivity.[5, 12] The metal atoms of the cathode contribute to their formation, and as a result the primary films formed on different cathodes have different compositions. This explains the effect of the cathode material and of the state of the surface on the nature and structure of the films.[11, 12, 14]

The secondary (truly cathodic) films are formed by the electrochemical reduction of the chromic acid. These films are porous and thicker than the primary films, and they can grow to macroscopic dimensions (~0.1 μm) (0.1 mm? Ed.).[10–12]

Obviously, the properties of the secondary films are independent of the initial state of the electrode surface. It has been suggested[5] that the secondary films have semiconducting properties.

Whereas the presence of a cathodic film is now no longer in doubt there is still a divergence of opinions concerning the influence of foreign ions on the film (and therefore also on the cathodic process). We know[12] that chromium is not deposited from solutions of chromic acid except in the presence of small quantities of H_2SO_4, H_2SiF_6, HF, or HCl. Interest in explaining the role of inorganic acids in the formation of the film was also stimulated by the widely held view[4, 5, 15–18] that chromium is reduced to the metal on the cathode from the film itself.

The direct study of the composition and of the behaviour of the cathodic film during *in situ* electrolysis is a complex problem. Consequently most judgements on the nature of the films have

been based on indirect experimental data.[4, 5] Thus it has been shown[19, 20] that irrespective of the $CrO_3 : H_2SO_4$ ratio in the bulk of the electrolyte this ratio is constant within the film, suggesting the formation of chemical compounds between CrO_3 and H_2SO_4 which are then discharged on the cathode. Possible explanations include the formation[21] of CrO_4^{2-} and Cr^{3+} compounds, complex particles $CrCrO_4^+$ and $CrCrO_4H$, and also the formation of complex compounds of chromium with chromium anions[22-24] and cations, connected through an oxygen bridge: Cr(III)–O–Cr(IV).[19, 22]

Studies of the composition of the cathodic film and of the reduction of chromic acid led many workers to conclude that the layer of liquid adjacent to the cathode may contain Cr^{2+}. This suggestion was first made[25] in the 1930s. In more recent work it has received both indirect and direct confirmation[10, 12]

The presence of bivalent chromium ions in solution denotes their interaction with the chromic acid, which should produce the dimer and hexa-aquo (tervalent) chromium ions (observed experimentally). These results led to the conclusion that the discharge as far as the metallic state is initiated by the bivalent chromium ions, and that the formation of tervalent chromium ions is the result of a secondary chemical reaction.[26]

Since the electrochemical reduction of chromic acid is accompanied by the reduction of H^+ the solution in the layer adjacent to the cathode becomes strongly alkaline, with formation[3, 12, 27] of chromium hydroxides [$Cr(OH)_3$] on the cathode surface by the reaction

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O ,$$

together with a small quantity of $Cr(OH)_2$. Thus the nature of the cathodic film is determined by the character of the interaction of the solid phase of the newly produced hydroxide $Cr(OH)_3$ with the divalent chromium ions and with the ions of the additives (SO_4^{2-}, SiF_6^{2-}, F^-, etc.).[12] The conversion of a finely divided sol into a solution with a molecular degree of dispersion, which has been called[12] a 'phase transformation', is accelerated by a factor of 6–94 in the presence of additive ions, depending on their concentration.

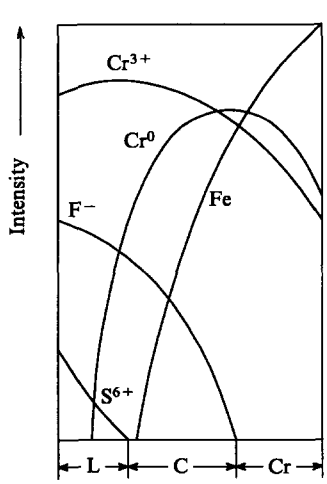


Figure 1. Distribution of the ions in the bulk of the film. Composition of the electrolyte/g dm^{-3}: CrO_3 180; H_2SO_4 0.54; Na_2SiF_6 54; T = 50 °C; i_c = 70 A dm^{-2}; τ = 2 s.

With the aid of recently developed apparatus[10] it was established that the cathodic film formed at the deposition potential of metallic chromium (−1.2 V) consists of two layers (Fig. 1): a dense, sparingly soluble internal layer (the C Layer) and a looser, more soluble external layer (the L layer). The ratio of the L and C layer thicknesses was found[10] to be 10 : 1. In spite of the small thickness of the dense C layer the largest potential drop occurs across this layer because this part of the film has the highest electrical resistance. Some interesting results on the distribution of the ions in the cathodic film have also been reported.[10] Since the electrolyte being studied contained mixed additive ions (SO_4^{2-} and SiF_6^{2-}) the film was found to contain sulfur and F^- ions, but the concentration of F^- decreased sharply on going from the looser to the denser layer, making the interface easily detectable.

A study of the reduction of the CrO_4^{2-} ions in the presence of CH_3COOH by the optical phase contrast method[15] additionally confirmed the presence of at least two layers in the vicinity of the electrode. It was found that if the thickness of the whole film is ~100 μm the main electrode process is confined to a small fraction (~0.01%–0.02%) of the total thickness.

The formation of bivalent chromium compounds which are reduced to the metal during the electrodeposition of chromium in the presence of H_3BO_3 has been established by Auger spectroscopy.[28] It was concluded[28] that the catalytic action of H_3BO_3 consists in the formation of a complex of tetrahydroxy $B(OH)_4^-$ ions with Cr^{3+}, which is then reduced to $Cr(OH)_2$. The latter is dehydrated, forming CrO, which then proceeds to form a complex with the $B(OH)_4^-$ ion, is adsorbed on the cathode surface, and is reduced to the metal. Thus the role of $B(OH)_4^-$ is similar to that of HSO_4^-, but since the hydrolysis constant of H_3BO_3 is small (pK = 9.00) the concentration of $B(OH)_4^-$ ions is also small. This explains the relatively low effect of $B(OH)_4^-$ as compared with that of HSO_4^-.

We may conclude from these observations that the cathodic film formed during the electrochemical reduction of the Cr^{6+} ions consists of lower-valency compounds of chromium formed by an intermediate reduction step.

The products of an intermediate reduction are observed in studies of many cathode processes. Especially interesting in this respect is the electrochemical reduction of the anionic forms of metals, whose deposition takes place with a current yield significantly lower than 100%.

These processes include the electrochemical reduction of the ReO_4^-, MoO_4^{2-}, WO_4^{2-}, and VO_4^{3-} ions. Detailed studies of these systems have established[29] the electrolysis conditions leading to the formation of products of the intermediate reduction of the transition metal ions (in the form of sparingly soluble, often powdery deposits), and also the composition and properties of these compounds. From the totality of the available information it was concluded that the composition of the compounds is described by the general formula $A_2O \cdot xMO_n \cdot yMO_{n-q} \cdot zH_2O$, where A is an alkali metal, ammonium, or hydrogen. The presence of water and of hydroxyl groups connected by hydrogen bonds of various strengths has been demonstrated.[29] The fraction of the current taken up by the formation of these oxygen compounds can be determined from the electrodeposition parameters.[30, 31] For the reduction of the ReO_4^- ions it was shown that the finely divided black deposits are rhenium compounds of various valencies. Since the average of the observed valencies of rhenium was close to 4 it was concluded that both more oxidised and more reduced forms must be present. In the electrochemical reduction of ReO_4^- ions from electrolytes with pH 1–2 the average valency of the rhenium is less than 4: this is attributed[29] to the presence of metallic rhenium in the cathodic deposit.

The formation of rhenium oxide from an aqueous electrolyte of pH ~1.65 has been reported.[32] Polarisation and X-ray diffraction studies have shown that the reduction process takes place in two steps. The first steps produces a film of partially reduced rhenium oxide, whereas in the second step the reduction proceeds to the metallic state. The composition of the oxide is determined by the cathode potential: shifting the potential towards more positive values produces black deposits of rhenium oxides in a higher state of oxidation. The deposition of metallic rhenium (with hydrogen evolution) takes place at potentials below −0.4 V.

Under ordinary conditions metals such as Mo, W, V, Zr and Nb are not deposited from aqueous electrolytes. The products of the incomplete reduction of molybdenum and tungsten have been studied in the greatest detail: the intermediates in the reduction of the MoO_4^{2-} ions are formed sequentially through a series of steps (giving quinque-, quadri-, and tervalent ions respectively), depending on the potential of the electrode, on the composition and temperature of the electrolyte, and on other factors.[33]

In the electrolysis of neutral and of weakly acid solutions of alkali metal molybdates or of ammonium molybdate a black deposit of composition $Mo_2O_3 \cdot 3H_2O$ is formed on the cathode.[29] The kinetics of the deposition and composition of the cathodic films formed in the reduction of MoO_4^{2-} ions have been studied in detail.[29, 34] The average valency of the molybdenum (4.96) was determined by chemical analysis, and the formula $xMoO_{2.4+z} \cdot yH_2O$ was assigned[29] to the compound deposited on the cathode (where $x:y = 1$ and $z = 0.1$). Similar results were obtained in studies of the reduction of molybdates from aqueous chloride solutions. Molybdenum blue, formed on a cathode, was given the formula[35] $MoO_{2.89} \cdot xH_2O$. This nonstoichiometric compound is a semiconductor,[36] and its conductivity is determined by the degree of dehydration.

The formation of a film of insoluble molybdenum oxides and hydroxides in a lower valency state on a cathode has been noted also in studies of the reduction in the presence of metals of the iron subgroup.[37] Experimental data lead to the conclusion that a film consisting of molybdenum compounds in a lower valency state [for example, Mo(III)] is permeable to Fe^{2+} and Ni^{2+} ions even if relatively thick. Introducing these into the film alters its structure and composition: the Mo–O bonds become weaker, bonds between the molybdenum, the iron, and the nickel are formed, and as a result the molybdenum is reduced to the metal with formation of an alloy. The reduction of the iron and of the nickel is also stepwise,[37] and increasing their concentration in the electrolyte increases the rate of reduction of the film.

Molybdenum oxides in a lower state of oxidation formed on a cathode are easily identified and can be used in practice. Thus molybdenum oxide prepared electrochemically has been used as a catalyst[38] and as a functional coating.[38, 39]

The reduction of the WO_4^{2-} ion from acid and from alkaline electrolytes takes place with deposition on the cathode of the lower oxides of tungsten or of a mixture of the oxide and the metal.[40] The composition $Na_2O \cdot nW_2O_5 \cdot mWO_3 \cdot qH_2O$ has been assigned[29] to the cathodic deposit obtained from a solution of Na_2WO_4.

The formation of intermediate reduction products takes place also in the electrochemical reduction of cationic forms of the metal. Thus, in the electrochemical reduction of copper from sulfate[41] and diphosphate[42] electrolytes† on a cathode, sparingly soluble copper compounds have been detected. In the sulfate electrolyte Cu_2O was detected on the cathode[41] in amounts increasing as the current density was decreased. In diphosphate electrolytes also a cathode film was detected:[42, 43] it was formed at all values of the electrode polarisation, and the film itself consisted entirely of univalent copper compounds. In these compounds copper can be reduced to the metallic state during cathodic polarisation in a supporting electrolyte not containing copper.

The presence of a film containing Cu_2O has been observed in a diphosphate electrolyte during a study of the interface by the electroreflectance method.[44] In this case the film was detected, as in a later patent,[45] only at relatively low polarisations (up to −0.1 V). At higher values of the cathodic polarisation the electroreflectance spectra had the characteristic shape of the spectra for metallic copper.

The formation of copper oxides has been established also in sulfate electrolytes at pH > 3 by measurements of the photoelectrochemical effect.[46, 47] It was assumed that the film with *n*-type conduction on the surface of a copper electrode consists of copper oxide. The change in the conductivity type at a well defined potential was attributed to the reduction of CuO to Cu_2O.

The formation of sparingly soluble compounds of the oxide-hydroxide type has been noted[48, 49] in studies of the fluorosilicate copper-plating electrolytes. The role of the concentration of hydrogen ions in the formation of these compounds has been studied by electrochemical reduction methods and by electron-diffraction studies of their composition. As a result it was established that Cu_2O, CuO, and $Cu(OH)_2$ are formed on the copper electrode surface. The relative amounts of these compounds are determined by the pH of the electrolyte: the content of $Cu(OH)_2$ increases with the pH of the solution, and in electrolytes with a low pH value no oxygen compounds are formed (as a rule) on the surface of the copper electrode.

At low current densities $Cu(OH)_2$ is formed in these electrolytes, but the fraction of the current used in this process is small.[48] The most significant process is the reduction of the Cu^{2+} ions. It has been suggested that the increase in the cathodic polarisation is caused by the blocking of the electrode surface by these compounds.[49]

The formation of sparingly soluble copper compounds on the cathode surface increases the cathodic polarisation also in fluoroborate electrolytes.[50]

A solid phase (black zinc) is formed in the electrochemical reduction zinc from a sulfate electrolyte under certain conditions.[51] X-ray diffraction analysis has shown that black zinc consists of finely divided metallic zinc, ZnO, and a small amount of inorganic salt absorbed from the electrolyte. The formation of oxides during the deposition of zinc has also been reported very recently.[52]

Studies of the mechanism of the cathodic deposition of nickel[53] and cadmium[54] have also led to the conclusion that a solid phase is formed on the cathode surface.

The electrolysis of solutions containing $FeCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, and $PbCl_2$ has produced loose black deposits of composition α–FeOOH, $Ni(OH)_2$, Cu_2O, ZnO, and $PbO \cdot 0.5H_2O$ respectively on the cathode.[55]

The presence of a film of hydroxide on the electrode surface has been established also in the deposition of cobalt from diphosphate electrolytes.[56] In this case the reaction is not the discharge of the unstable diphosphate complex anions $[Co(P_2O_7)_2]^{6-}$ or $[Co(P_2O_7)]^{2-}$, but their dissociation in the cathode layer as a result of the increase in the pH, with formation of a substantial amount of $Co(OH)_2$. Thus, in the electrochemical reduction of cobalt ions the formation of a relatively thick film can be visually observed. The formation of a finely divided sol of composition $\{x[Co(OH)_2] \cdot z[Co(OH)^+]\}$ during the dissociation of the diphosphate cobalt complexes passivates the electrode surface and strongly influences the cathodic process even when the formation of a film cannot be detected visually.[57] A study of the electrocrystallisation of cobalt by the impedance method has shown[58] that the discharge process involves several steps, ultimately leading to the formation of partially reduced cobalt compounds of the $Co(OH)_{ads}$ type, as in the reduction of the Cu^{2+} and Ag^+ ions. This effect is responsible for the inductive component of the Faraday impedance in the low frequency region. On the other hand the composition of the film is determined by the electrolysis conditions.[59]

A study of the polarisation during the electrodeposition of antimony from fluoride electrolytes led to the conclusion[60] that a partially hydrolysed atom of the metal, not containing F^- ions, is contributing to the cathodic process. The retardation of the process at low current densities is attributed to passivation of the surface by oxides, which makes a multistage mechanism possible.[61]

† The term pyrophosphate for these compounds is now obsolete.

Black deposits containing oxides have been observed[62] in the deposition of manganese at potentials up to −0.88 V. The total metal content of these compounds is not more than 70%–80%.

A passivating layer has also been detected on the surface of a gold electrode in weakly acid or in alkaline solutions of $KAu(CN)_2$ by using ellipsometry, Auger spectroscopy, and spectroscopy in the UV and the visible region.[63, 64]

A cathodic film obtained during the deposition of gold from a weakly acid electrolyte consists of $Au(OH)_3$ or Au_2O_3, adsorbed $KAu(CN)_2$, and metallic gold. As reported,[64] the formation of compounds of tervalent gold is due to a disproportionation reaction, involving an unstable compound of univalent gold, induced by the development of alkalinity in the layer of solution adjacent to the cathode. The element composition of the surface layers formed at potentials of −0.33 and −0.88 V, which characterise the initial step of the chemical and the electrochemical gold-plating process respectively, has been determined by Auger spectroscopy. The surface layer formed at −0.88 V is richer in gold than the layer formed at −0.38 V. Under these conditions the total concentration of impurity elements cannot account for complete compound formation by the surface gold, thus showing that metallic gold must be present in the film. After the beginning of the electrolysis the pH of the layer of solution adjacent to the cathode increases from 5.5 to 9.0, thus producing conditions favourable to the formation of insoluble $Au(OH)_3$ on the cathode surface. The compound is initially formed by the oxidation of a univalent gold surface ion by adsorbed and by chemisorbed oxygen. These unstable compounds of univalent gold are subsequently disproportionated to give tervalent gold.

During the initial stage of the electrodeposition of gold from alkaline cyanide solutions the electrode reaction is retarded by the formation of a sparingly soluble film of overall composition $Au_x(OH)_y(CN)_z$ on the cathode. It has been shown by ellipsometric measurements[65] that the thickness of this film of poorly conducting material increases with the concentration of $KAu(CN)_2$. Under these conditions not only the concentration of CN^- ions but also the pH of the electrolyte can strongly influence the coverage of the electrode surface by a film. The maximum coverage is 0.9 monolayer, reached at pH 13.6 and a potential of −0.2 V.

The formation of oxides has been suggested also in the electrodeposition of uranium from an ammonium fluoride solution.[66, 67] The uranium oxide UO_2 is formed on the cathode as a result of the discharge and dissociation of the complex species $UO_2(L)^{n+}$ formed in solution, which migrate to the cathode

$$UO_2(L)^{n+} + ne \rightleftharpoons UO_2 + L ,$$

where L is the ligand of a complexing agent. Since hydrogen evolution takes place simultaneously with metal deposition it is reasonable to assume that the oxide can be reduced by atomic hydrogen:

$$H^+ + e \longrightarrow H^\cdot ,$$

$$UO_2 + 4H^\cdot = U + 2H_2O .$$

Under these conditions (and at low current densities) the metal is deposited together with oxygen-deficient oxides because of the low rate of discharge of H^+. Increasing the current density increases the rate of discharge of hydrogen and of reduction of UO_2 to the metal.

A study of the kinetics and mechanism of the passivation of the electrode during the electrodeposition of gallium from chloride electrolytes[68] has shown that the passivation is due mainly to the formation on the gallium surface of a film of sparingly soluble compounds, described by the general formula $Ga_x O_y H_z Cl_m$.

The cathodic reduction of the TcO_4^- ion has been shown[69–71] to be a multistage process leading to the formation of both compounds of technetium in a lower valence state and metallic technetium. The cathodic processes (deposition of technetium and formation of partial reduction products) take place in parallel, but there is no clear correspondence between changes in their rates.[71]

2. Anodic processes

Films are formed at the electrode–electrolyte interface also during the oxidation of metals, the preparation of oxides, anodic etching, electropolishing, and the chemical machining of metals. In these operations (as in cathodic processes) the film consists of products of variable composition of the oxide-hydroxide type.

A typical example is the oxidation of manganese in alkaline media. The compounds MnO, $Mn(OH)_2$, and MnOOH can be formed on the electrode surface, depending on the pH of the solution and on the polarisation of the electrode.[72] The oxidation process takes place in the solid phase through the interconversion of the different oxide phases:

$$MnO \longrightarrow Mn(OH)_2 \longrightarrow MnOOH \longrightarrow MnO_2 .$$

According to the results[73] of impedance measurements, of the analysis of chronoamperograms, and of measurements with a rotating disk electrode the mechanism of the electrochemical deposition of MnO_2 form solutions of bivalent manganese compounds consists in the formation of intermediate compounds such as MnOOH, Mn_2O_3, and $Mn(OH)_4$, and finally MnO_2. If the rate of conversion of these compounds into MnO_2 is smaller than their rate of formation a layer of intermediates is seen to grow on the outer surface. This layer hinders the transport of the Mn^{2+} ions from the bulk of the electrolyte to the electrode–electrolyte interface. As the thickness of the layer increases, the rate of diffusion of the Mn^{2+} ions changes towards a value comparable to the rate of transformation of the MnOOH and Mn_2O_3 intermediates into MnO_2. This creates a dynamic equilibrium in the electrode–film–electrolyte system.

Film formation takes place also during metal polishing. The electropolishing process depends on the ratio of the rates of formation of the oxide film (on the metal side) and of dissolution of the film (on the electrolyte side). The predominance of either reaction controls the character of the process, i.e. it determines whether etching or polishing is achieved. The highest surface brightness is obtained when he oxide film is as thin as possible (though thick enough to suppress the etching action of the electrolyte). This situation is found under conditions of dynamic equilibrium in the system, when the rates of the electrochemical formation of the film and of its chemical dissolution are equal.[74]

Studies of the capacitance and of the polarisation resistance at the metal–solution boundary during the polishing of steel have shown that under the optimum conditions a capacity minimum is obtained together with a large increase in resistance. This suggests the formation of an oxide film on the metal, since the presence of a salt film could not account for such large changes in the parameters of the electrode–electrolyte boundary.[74] The polishing process is usually carried out in relatively aggressive media, and therefore the ligand composition plays an important role in the dissolution of the film formed on the anode.

The electrochemical treatment of nickel also produces an oxide film (*p*-type) of nonstoichiometric composition on the metal surface. An analysis of the polarisation measurements and of activation energy data has indicated[75] anodic dissolution of the metal within the surface film, and therefore it is reasonable to interpret the role of the formation of films at the electrode–electrolyte boundary as rate-determining in the dissolution.

A similar picture of film formation applies to the polishing and electrochemical machining of metal surfaces. Thus, on the potentiostatic anodic dissolution curves of titanium in alkaline

solutions we observe a decrease in the rate of the process at potentials between −0.5 and −0.7 V, due to the saturation of the anodic layer by the reaction products and to the formation of a porous film of complex composition on the electrode surface.[76]

The oscillations in the electrode potential observed in various cathodic or anodic processes are a consequence of the formation and dissolution of the film. It should be noted that the best polishing results are obtained in the self-oscillatory regime.[77]

III. Modelling of bifunctional electrochemical systems

As was pointed out above, the first step in any electrochemical reduction involving aquo ions of metals (or their complexes with various ligands) or in the electrochemical oxidation of metals is the formation of a film at the electrode–electrolyte interface. The film is a dynamic multilayer system,[78] containing reducible or oxidisable substances in intermediate states of oxidation. The application of a range of research methods to the layer adjacent to the electrode has demonstrated the formation of a film at the phase boundary and its existence for finite times during electrode processes in aqueous and in molten media.

The fundamental property of the films formed at the electrode–electrolyte phase boundary is the presence of a well defined quantitative relationship between the amounts of ionic and of electronic conductivity, which determines the character and the features of the electron transfer process in the electrode–electrolyte system. On the external side of the film (towards the electrolyte) we observe parallel reactions of partial electrochemical reduction of the metal ions being discharged, or their oxidation to the highest oxidation state allowed in the given conditions, or the chemical dissolution of the film by interaction with the components of the solution. On the inner side of the film (towards the electrode) a topochemical process[79] takes place: the further electrochemical reduction to the metal or the electrochemical oxidation of the metal (Fig. 2).

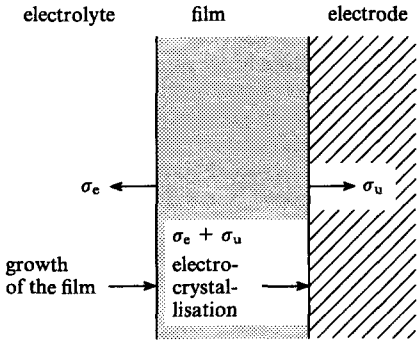


Figure 2. Model of the bifunctional electrochemical system.

The film formed on the electrode surface contributes directly to the electrochemical reactions, which are determined by the physicochemical properties of the film, including its chemical stability towards the reaction medium. A film is formed if the rate of its electrochemical production is greater than the rate of the heterogeneous chemical dissolution process.[80, 81]

The difficulties met in direct studies of the film during its formation and operation stimulated attempts to develop suitable models on the basis of the suggested similarity criteria.[82]

1. Phenomenological description of a model of the bifunctional electrochemical system

Along the normal to the electrode the film is characterised by the nonuniformity of its composition and of its physicochemical properties. We should stress that it is not easy to establish whether a given nonuniformity leads to the formation of discrete phases or whether it merely causes gradual changes in properties. In the former case the model should describe the formation of a sequence of bifunctional systems having a mixed conductivity type. Under these conditions each interface can be associated with one of the successive steps of the electrochemical reduction or oxidation process.

In general the electrochemical step of a cathodic process can be described by the reaction

$$M^{(z-q_{j-1})+} + p_j e \xrightarrow{k_j} M^{(z-q_{j-1}-p_j)+}, \quad (1)$$

where

$$q_{j-1} = \sum_{i=1}^{j-1} p_i$$

is the total number of electrons transferred to an ion during the previous $j-1$ steps of the process; p_j is the number of electrons taking part in the jth step; k_j is the rate constant of the electrochemical process. The reaction products formed under these conditions as a result of the chemical process dissolve on the side of the electrolyte at a constant rate k_j'.

Each of the intermediate phases (from $j = 1$ to $j = m-1$, Fig. 3) is characterised by the average concentration c_j of the partially reduced multivalent metal $M^{(z-q_j)+}$, which is included in the composition of the compounds forming this phase. The electrochemical process leading to the partial solid-phase reduction of the multivalent ions (and to their full reduction at

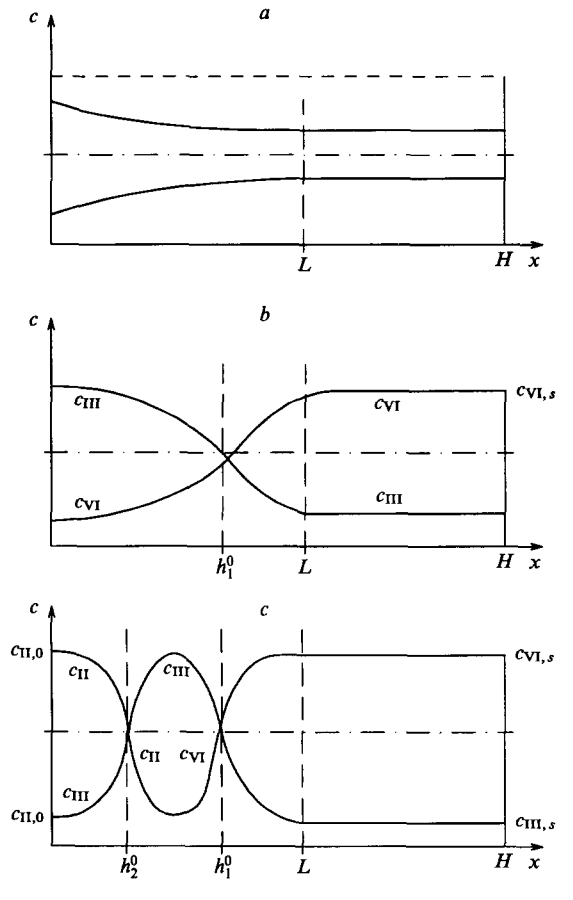


Figure 3. Concentration profile of the partial reduction products in a bifunctional electrochemical system. (*a*) smooth distribution; (*b*) with one boundary ($h_1^0 < L$); (*c*) with two boundaries ($h_2^0 < h_1^0 < L$).

the electrode–film boundary) takes place at increasingly negative potentials of each successive step in the process. The dynamical behaviour of this multilayer structure has recently been described.[78]

The reactions (1), which take place at the interfaces, can lead to changes in the volume of the intermediate phases. For a constant concentration of multivalent metal ions in each layer of thickness h_j the process can be described as follows:

$$c_j \frac{\partial h_j(t)}{\partial t} = Q_{j-1,j} - Q_{j,j+1}\,; \quad j = 1,2,\ldots,(m-1)\,. \tag{2}$$

Here

$$Q_{j,j'} = k_{j,j'} c_j n_{j,j'}^{p_j} - k'_{j,j'} c_j\,; \quad h_j(t)|_{t=0} = 0\,, \tag{3}$$

where $Q_{j,j'}$ is the flux, defined by the total number of multivalent $M^{(z-q_j)^+}$ ions formed in one second as a result of the electrochemical and the chemical processes per unit area of the boundary between phases j and j'; $n_{j,j'}$ is the concentration of conduction electrons in the jth phase near the boundary with phase j'. According to the Tafel equation the rate constant of the electrochemical reaction at the phase boundary is

$$k_{j,j'} = \tilde{k}_{j,j'} \exp(\alpha_{j,j'} e\beta\delta E_{j,j'})\,, \tag{4}$$

where $\alpha_{j,j'}$ is the transfer coefficient; $\beta^{-1} = k_B T$, where k_B is Boltzmann's constant; δ is the average distance between the charge localisation centres; $E_{j,j'}$ is the strength of the electric field at the phase boundary.

Increasing the current I_0 (in the galvanostatic regime) increases the field E_0 at the electrode–electrolyte boundary. When the potential reaches the value corresponding to the electrochemical reduction (1) (which is the first step of the discharge of the metal ions) the ions are reduced to the first intermediate state $M^{(z-p_1)^+}$.

A space charge layer is formed at the metal–semiconductor interface during the growth of the film: the presence of uncompensated charge affects the intensity of the electric field in a volume defined by the space charge region, whose size (in the case of semiconductors) is 10^{-5} to 10^{-4} cm.

The dependence of the electric field intensity on the distance to the cathode surface (where $x = 0$) produces a dependence on x of the rate constant of the electrochemical process, which determines the separation of the phases in space in the bifunctional system for the multistage discharge of multivalent metal ions. The space charge region at the metal–semiconductor interface (bifunctional films usually have semiconductor properties) has been described[80] in terms of the Schottky model on the assumption that the space charge is due mainly to the charge of uniformly distributed ionised donors with a concentration n_0. In this case when the film thickness H is greater than the thickness of the Schottky layer L the field strength in the space charge region ($x < L$) is given by the expression

$$E(x) = E_0 - \frac{en_0}{\varepsilon}(L-x)\,\mathrm{H}(L-x)\,, \tag{5}$$

where

$$L = \left(\frac{2\varepsilon\Delta\varphi}{e^2 n_0}\right)^{1/2}.$$

Here E_0 is the uniform field strength; H is the Heaviside function; ε is the permittivity of the semiconductor; $\Delta\varphi$ is the height of the barrier at the metal–semiconductor interface.

In the region of $0 < x < L$ the concentration of electrons $c_e(x)$ is also dependent on the x coordinate:[83]

$$c_e(x) = n_0 \exp[-\beta\varphi(x)]\,,$$

where

$$\varphi(x) = eE_0(x-L) + \frac{e^2 n_0}{2\varepsilon}(L-x)\,\mathrm{H}(L-x)\,. \tag{6}$$

The presence of a strong electric field $E(x)$ [Eqn (5)] allows the reduction of the multivalent metal ions to proceed in the bulk of the film. The steady state of the film corresponds to equality of the fluxes at the electrolyte–film and electrode–film phase boundaries ($Q_S = Q_0$). The intermediate reduction products are formed when $Q_0 > Q_S$ and the growth rate of the film is

$$V = Q_0 - Q_S\,. \tag{7}$$

When the chemical processes play a dominant role in comparison with the charge transfer process the film is not formed, and therefore the metal deposition is suppressed. This system can be dynamically unstable. The region giving a stable state is determined by the ratio of the rate of the electrochemical process (which depends on the current density) to the rate of the chemical dissolution process (which depends on concentration of the ligand, its nature, the electrolyte temperature, and other parameters).

The mechanism of formation of the bifunctional structure has been examined[80] for the case of the most widely studied of these processes: the electrochemical reduction of the CrO_4^{2-} ions. In this case the kinetic equations which describe processes of type (1) can be written as the following system of equations:

$$\begin{aligned} \frac{dc_{III}(x)}{dt} &= k_1(x)\,c_{VI}(x)\,c_e^3(x) - k'_1 c_{III}(x)\,,\\ \frac{dc_{II}(x)}{dt} &= k_2(x)\,c_{III}(x)\,c_e(x) - k'_2 c_{II}(x)\,,\\ c_{III}(x,t)|_{t=0} &= c_{II}(x,t)|_{t=0} = 0\,, \end{aligned} \tag{8}$$

where k_i, $k_{j'}$ are the rate constants of the reaction, describing the ith process in the discharge of the chromium ions; $k_i(x) = \tilde{k}_i \exp[\alpha_i\beta\delta E(x)]$; $c_{VI}(x,t)$, $c_{III}(x,t)$, $c_{II}(x,t)$ are the concentrations of the chromium ions with a valency of six, three, and two respectively.

The operating regime of the electrochemical system depends on the current flowing through the system. Depending on $E(x)$, i.e. on the current in the system, on the parameters of the Schottky layer, etc., and also on the concentration of the multivalent metal ions at the surface of the film (determined by the rate of the electrochemical processes at the electrolyte–film and the electrode–film boundary), the system of equations (8) can have two solutions, one solution, or no solution.

In the case of large currents, when the field E_0 created by the polarisation of the electrode exceeds the internal field of the Schottky layer, the ion distributions c_{III} and c_{VI} in the film are only slightly dependent on the distance to the electrode (Fig. 3*a*). Decreasing the current brings the field E_0 closer to the field of the electrical double layer, and the system of equations gives successively one solution (Fig. 3*b*) and two solutions (Fig. 3*c*), i.e. an internal multilayer structure is formed in the film under the influence of the field. A further decrease in the current lowers the rate of the electrochemical reaction on the outer surface of the film, and the dissolution of the film becomes the dominant process. The following are the existence criteria of a multilayer structure in the stationary state: for $\tilde{k}_1 c_e < k'$ and $k_2 c_e < k'_2$ the chemical process is dominant in comparison with the electrochemical reduction, and the film is not formed. When the system reaches the $V = 0$ state we observe periodic variations in the rates of growth and dissolution of the film,[84] which leads to oscillations in the potential with a frequency ω_{cr}. In this regime no metal is deposited, as has been observed[82] experimentally. The parameters h_1^0, h_2^0, ω_{cr}, and others, which determine the dynamical behaviour of the bifunctional system, are strongly dependent on the dissolution constants k'_1 and k'_2. In

its turn the parameter k_1' is determined by the nature and concentration c_L of the ligand in the electrolyte and in the bulk of the film, so that the operation of the system can be controlled fairly easily by varying c_L.

The most suitable model of a bifunctional electrochemical system, which allows as fully as possible for all its properties and special features, is provided by the compounds formed on the electrode when the charge transfer process is fixed at an intermediate stage during electrochemical reduction or oxidation. These compounds form a complex electrically conducting heterogeneous system containing the oxides and hydroxides of the appropriate metal in a lower or a higher state of oxidation than in the bulk of the electrolyte, and therefore able to undergo reduction or oxidation. Thus the following similarity criteria between the experimental model and the films actually present on the electrode can be adopted:[85] the presence of low-valency compounds of a mixed conductivity type, and the ability to undergo electrochemical reduction in the solid phase.

2. The presence of low-valency compounds

Let us examine fluorine-containing electrolytes. The rate of formation of partial reduction compounds is determined mainly by the concentration of the F^- ion in the electrolyte and also (to a much lesser degree) by the electrolysis parameters.[86-90] For chromium, nickel, and manganese, which are fairly easily deposited from aqueous solutions, we can define an optimum concentration of the ligand in the electrolyte, offering the maximum rate of formation of the solid phase on the cathode. For molybdenum and zirconium, whose electrode position from aqueous solutions is more difficult, we note a gradual decrease in the rate of deposition of the intermediate reduction products, depending on the concentration of the ligand.

The extent of reduction of the ion being discharged, quantitatively expressed as the total concentration of metal in the solid phase, depends on the concentration of ligand in the electrolyte. In the case of chromium and rhenium it has been shown[91] that this parameter is affected also by changes in the temperature of the electrolyte. An increase in the amount of metal in the deposit produces changes in its properties (colour, microhardness, corrosion resistance). In all the systems which have been examined, including molybdenum and zirconium, a ligand concentration which gives complete reduction to the metal can be identified.

Table 1. Formation conditions and composition of lower-valency oxides.

Metal being discharged	Content of F^- ions in the electrolyte (%)	Total concentration of metal in compound (%)	Phase composition (%)					
			M^0	M^+	M^{2+}	M^{3+}	OH^-	H_2O
Copper	5	92	28	28	–	–	trace	7
	10	95	54	40	–	–		4
	25	97	71	25	–	–		2
	50	99	79	19	–	–		1
Nickel	1	–	85	–	–	–	1.5	1.5
	2	–	90	–	–	–	1.5	1.0
	3	–	98	–	–	–	1.0	1.0
Zinc	2	79	29	–	–	–	8	2
	4	84	40	–	–	–	7	2
	6	87	47	–	–	–	7	1
	8	88	53	–	–	–	6	1
Rhenium	5	66	–	–	–	–	5	4
	10	72	–	–	–	–	4	3.5
	20	88	–	–	–	–	3	3.5
	25	98	–	–	–	–	1	1
Manganese	2	72	25	–	18	29[a]	5	2
	5	83	37	–	19	27[a]	4	2
	8	88	–	–	–	–	4	1
	12	95	–	–	–	–	4	1
Chromium(III)	0	39	7	–	3	29	6	5
	1	42	11	–	4	27	5	4
	2	42	12	–	4	24	4	4
	5	60	21	–	8	31	3	3
Chromium(VI)	0.2	70	30	–	18	22	6	5
	0.4	73	41	–	13	19	5	4.5
	0.6	75	49	–	11	15	5	4.5
	0.8	83	–	–	–	–	4	4
	1.2	90	–	–	–	–	3	4
	2.0	100	–	–	–	–	–	–
Molybdenum	5	56	–	–	–	–	14	9
	10	58	–	–	–	–	13	7
	25	61	–	–	–	–	12	6
Zirconium	5	25	–	–	–	–	–	–
	10	38	–	–	–	–	–	–
	15	58	–	–	–	–	–	–

[a] The total amounts of three- and four-valent manganese are quoted.

Table 2. Composition and rate of oxidation of chromium black.

Valency of chromium	Concentration of chromium in deposits (%)				Rate of deposition/ μm min^{-1}
	Cr_{tot}	Cr^{3+}	Cr^{2+}	Cr^{0}	
II	45–55	10–11	20–27	12–17	3–5
III	45–55	30–35	5–10	5–15	4–5
VI	65–80	7–25	10–20	20–60	0.5–1

The composition of the partial reduction products of various metals is shown in Table 1. We may conclude from these data that the concentration of ligand in the electrolyte determines the amount of metal in the deposit. Thus, for chromium the concentration of metal in the deposits obtained from an electrolyte containing six-valent chromium is higher than in the deposits from tervalent and bivalent chromium electrolytes (Table 2). This effect is produced by a change in the ratio of the rates of (1) the electrochemical formation of lower-valency metal compounds and (2) their further reduction to the metal. The higher the rate of formation of these compounds as compared with the rate of the electrochemical reaction leading to their further reduction, the lower must be the metal content of the deposit. Under these conditions we observe the electrochemical deposition of partially reduced compounds, as indicated by the data in Table 1. Thus the products of the partial reduction of rhenium and molybdenum ions are characterised by the presence of compounds in which the average valency of rhenium is 3 and that of molybdenum is 4.

The metal deposition takes place under conditions of dynamic equilibrium between the processes leading to the formation and to the further reduction of the substances in the cathode film. The presence of low-valency compounds in the solid phase suggests that these compounds exist in the layer adjacent to the cathode and act as a barrier between the bulk of the electrolyte and the reaction zone. At high concentrations of the ligand in solution the lower-valency compounds in the film are electrochemically reduced to the metal, and at low concentrations of the ligand some partial reduction products are formed. By varying the ligand concentration in the electrolyte we can easily control the cathodic process at the partial or the complete reduction stage.

The identical structures and compositions of the intermediate reduction compounds of the chromium, rhenium, manganese, molybdenum, zirconium, copper, nickel, and zinc ions suggest that their reduction processes from aqueous solutions have identical mechanisms irrespective of the form in which the ions exist in the bulk of the electrolyte.

3. Conductivity of the partial reduction products of the metal ions

According to our model of the bifunctional electrochemical system the film should have a mixed (ionic and electronic) conductivity. A quantitative assessment of the relative contributions from the ionic and the electronic conductivity has been made[92] by the pulse method (Table 3).

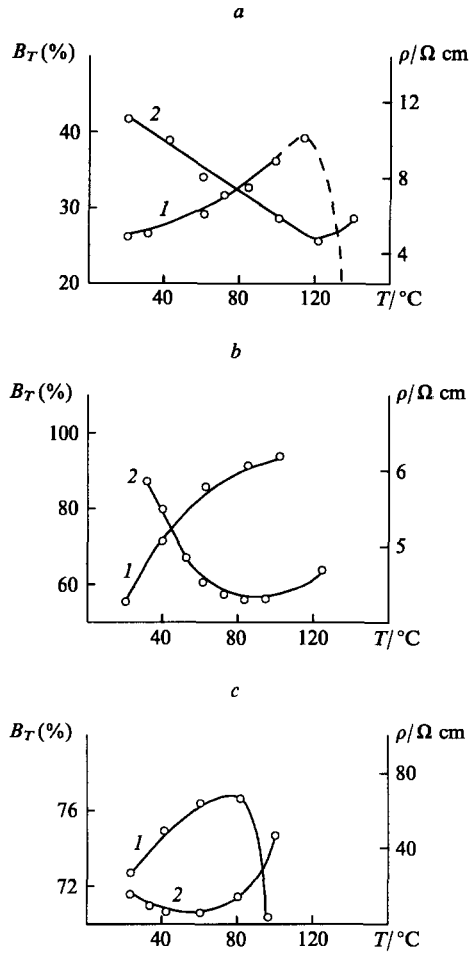


Figure 4. Temperature dependences of the current yield of metal (*1*) and of the resistivity (*2*) of the partial reduction products of chromium (*a*), nickel (*b*), and manganese (*c*).

The results of a study of the temperature dependence of the conductivity by alternating current methods are summarised in Fig. 4. The curves show either a maximum or a minimum, depending on the nature of the system. The systems in which the ionic component makes the larger contribution to the total conductivity (molybdenum, tungsten) show a minimum on the $\ln\sigma = f(T)$ curves, whereas systems in which the ionic conductivity plays a minor role have a maximum (manganese, chromium, nickel) or tend towards a maximum (copper).

A thermogravimetric analysis of these systems at 120 to 160 °C (the upper limit being set by the onset of substantial structural changes in these materials at higher temperatures) revealed the presence of an endothermic effect at 80–120 °C. These effects have only a small influence on the overall conductivity, since an extremum in one of the types of electrical

Table 3. Electrophysical parameters of the cathodic film.

Metal in the system	Temperature of change in slope of the $\ln\sigma-(1/T)$ dependence	Thermogravimetric analysis results: temperature of effects/°C	Total conductivity/Ω^{-1} cm^{-1}		Fraction of ionic conductivity (%)
			alternating current	direct current	
Copper	140	130–140	$2.9\cdot10^{-6}$	$2.6\cdot10^{-6}$	4
Nickel	80–90	80–90	0.22	0.18	8
Manganese	60	60–80	$0.9\cdot10^{-5}$	$0.2\cdot10^{-5}$	10
Chromium	120	120–130	0.25	0.80	11
Molybdenum	90–100	100–120	$1.3\cdot10^{-6}$	$2.4\cdot10^{-6}$	17
Tungsten	110–120	110–130	$0.3\cdot10^{-4}$	$1.5\cdot10^{-4}$	22

conductivity would have been produced if the influence had been large.

The temperature dependence of the conductivity is due to the structural changes associated with the removal of the water of crystallisation and of the OH^- groups, as shown by the correlation with the thermogravimetric analysis results (see Table 3).

Comparing the temperature dependences of the current yield of metal (B_T) deposited under normal conditions and of the resistivity (ρ) of the incompletely reduced compounds also showed a correlation[92] from which it is clear that the higher the electrical conductivity of the system, the higher is the current yield of the metal. This is evidence of a direct dependence of the technological parameters of the electrolysis (rate of deposition of the metals, and current yield) on the physicochemical properties of the cathode film.

4. Electrochemical reduction in the solid phase

An important contribution to the study of cathodic reduction was made by Gorbunova et al.,[93-97] who used a range of electrochemical and structural methods to establish the mechanism of the solid-phase reduction of sparingly soluble compounds (oxides and salts) in protic electrolytes. By applying the Avrami–Erofeev heterogeneous kinetics equation[98] they were able to characterise the process quantitatively. The same approach was used successfully by other workers.[99, 100]

Studies of solid-phase reduction processes have identified diffusional limitations in the solid phase, and also a dependence of the rate of the process on the concentration gradient of oxygen in the phase. Structural studies have established that the process begins at the solution interface and gradually spreads throughout the bulk of the oxide. Under these conditions the composition of the compounds deviates from stoichiometry.[97] Electric fields are formed in the region of the boundary[101, 102] as a result of the changes in concentration and structure.

The process leading to the formation of a metallic phase is localised in the bulk of the compounds of intermediate composition.[103-105]

The possibility of electrochemically reducing compounds of the partial reduction of metals in the anionic (chromium) and the cationic form (copper) in supporting electrolytes not containing ions in common with the solid phase has been demonstrated.[106-108]

The electrochemical reduction[106-108] and the chemical dissolution[109] of these compounds in a supporting electrolyte can be described by the Avrami–Erofeev heterogeneous kinetics equation. The kinetic parameters of these processes for various systems are summarised in Table 4. The rate constants of the electrochemical reduction and of the dissolution of all the compounds used to model the cathodic film are higher in hydrofluoric acid than in sulfuric acid. These data explain the formation of lower-valency compounds only at low concentrations in a hydrofluoric acid electrolyte[82] and the decrease in the rate of the process caused by increasing the concentration of ligand in the electrolyte.

Comparing the rate constants for the heterogeneous dissolution of the lower-valency oxides of chromium and copper in hydrofluoric and in sulfuric acid with the constants of the topochemical electro-reduction of these compounds in the same supporting electrolytes[109] allows us to calculate the role of the chemical processes in the control of bifunctional electrochemical systems.[110, 111]

In the electrodeposition of chromium the contribution of the chemical dissolution reactions of the cathodic film is small, as shown by the small value of the formal rate constant of this process. This accounts for the marked accumulation of film material on the electrode, which can be easily detected, even visually: not surprisingly, cathodic films were first detected in the electroplating of chromium. An entirely different situation is found in the electroplating of copper, because the rates of the chemical dissolution of the cathodic film and of the electrochemical reduction of the film material to the metal are comparable. Evidently, in this case the presence of a film can be detected only under conditions which make the rate of the formation reaction greater than the rates of both the above processes. It is clear that in the electrodeposition of copper film material is difficult to identify and to collect in all electrolytes except those containing fluorine,[112] since the required redistribution of the reaction rates can be achieved only in the latter electrolytes.

Thus the reduction mechanism is determined by the physicochemical properties of the compound: its electrical conductivity and its chemical stability towards the medium chosen for the process. The direct reduction of sparingly soluble compounds in the solid phase is achieved when the electrical conductivity of the substance is reasonably high. In cases of low electrical conductivity reduction takes place only at the points of direct contact between the compound to be reduced and the surface of the current lead. Whether a solid-phase or a liquid-phase mechanism is established depends on the rate of the chemical reaction in the chosen electrolyte: the higher the rate, the greater is the probability of controlling the process through a preliminary dissolution stage.

At a well defined ratio of the rates of the chemical and the electrochemical process the electrochemical reduction becomes possible by both mechanisms. Their relative contributions are determined by the properties of the substance itself and by the composition of the solution, and especially by the nature of the ligand.

IV. Principles of the control of the electrochemical reduction of transition metals

The concept of a bifunctional electrochemical system and the theoretical description of the special features of processes taking place in these systems have allowed us to formulate a set of principles for controlling the electrochemical reduction of transition metals.

Basically the control of electrochemical processes consists in regulating the composition (and therefore also the properties) of the bifunctional electrochemical system by controlled changes in the external factors such as the composition of the electrolyte, the nature and concentration of the ligand, the temperature of the electrolyte, and the current density. These parameters allow us to vary the rate of the electrochemical and of the chemical processes at the electrode–film and electrolyte–film interfaces, and the rates of deposition or of dissolution of the metals (as well as their current yield).

Table 4. Rates of the chemical and of the electrochemical processes in a bifunctional electrochemical system.

System	HF			H_2SO_4		
	K_{chem}/ cm s^{-1}	K_{ec}/ cm s^{-1}	$\lg\beta$	K_{chem}/ cm s^{-1}	K_{ec}/ cm s^{-1}	$\lg\beta$
Copper	$4.41 \cdot 10^{-2}$	$5.8 \cdot 10^{-2}$	0.85	$2.75 \cdot 10^{-2}$	$4.3 \cdot 10^{-2}$	0.50
Molybdenum	$5.07 \cdot 10^{-2}$	–	3.90	$5.01 \cdot 10^{-3}$	–	2.16
Manganese	$5.31 \cdot 10^{-2}$	–	5.48	$3.02 \cdot 10^{-2}$	–	2.30
Chromium	$8.10 \cdot 10^{-6}$	$3.22 \cdot 10^{-1}$	4.4	$1.20 \cdot 10^{-6}$	$9.1 \cdot 10^{-2}$	1.76

Nature and concentration of the ligand. The rates of the electrochemical and of the chemical reactions at the electrode–film and electrolyte–film interfaces are determined by the nature of the ligand and by its concentration, since the stability of the resulting complexes and the rate of dissolution of the partial reduction products are strongly dependent on these factors. We can define an optimum concentration of the ligand in the electrolyte ($c_{L,opt}$) which offers the appropriate ratio of the rates of the electrochemical and the chemical processes.

According to Eqn (7) at concentrations $c_L < c_{L,opt}$ the rate of the electrochemical processes exceeds the rate of the chemical processes. Partial reduction products are formed near the electrode, and are accumulated there. At concentrations $c_L \gg c_{L,opt}$ the rate of the chemical reactions becomes much greater than the rate of the electrochemical reactions, the film cannot be formed, and the new phase is not detected.

Electrodeposition of the metal is observed only for ligand concentrations close to the optimum, i.e. under conditions such that a dynamic equilibrium between the film formation processes and the further reduction of the film material to the metal can be established, i.e. when the equality $Q_S = Q_0$ is obeyed.

On the whole, however, and all other conditions being equal, departures (on either side) of the ligand concentration from the optimum value allow us to vary the composition of the compound formed on the electrode and to create conditions favouring either the electrodeposition or the dissolution of the metal or of its intermediate valency compounds. By varying the metal content of the partial reduction products we can control the ratio of the ionic and the electronic contributions to the electrical conductivity.

Current density. The rate of the electrochemical reactions at the electrode-film and at the electrolyte-film interfaces and within the film itself is determined by the current density. By varying this easily controllable parameter we can impose the required operating regime on the bifunctional electrochemical system. At any given concentration of the ligand we can identify an optimum value of the current density.

For $c_L < c_{L,opt}$ the rate of formation of a new phase on the electrode can be markedly increased by increasing the current density. Because of the relatively small rate of the chemical process at the electrolyte–film interface we can expect the formation of partial reduction products containing a higher proportion of low-valency compounds and a lower proportion of metallic phase. Under these conditions the contribution of the ionic component of the conductivity in the resulting oxides is increased.

For $c_L > c_{L,opt}$ the rate of the chemical process is high, and in order to suppress it (so as to obtain a new phase) we must increase the rate of the electrochemical process, i.e. we must increase the current density.

Electrolyte temperature. Other conditions being equal this factor affects the electrode process less markedly than does the concentration and nature of the ligand, or the current density.

For $c_L < c_{L,opt}$ the rate of the chemical reactions is usually small. Increasing the temperature of the electrolyte increases the rate of the electrochemical reduction processes. The result is an increase in the rate of formation of intermediate-valency compounds on the electrode, and an increase in their content of metallic phase.

For $c_L \gg c_{L,opt}$ increasing the temperature of the electrolyte usually produces predominance of the chemical processes over the electrochemical. As a result a large increase in the current density is needed to bring the bifunctional electrochemical system into dynamic equilibrium. Therefore the temperature dependence of the critical parameters of the process is qualitatively similar to their dependence on concentrations of the ligand.

V. Conclusions

It follows from our discussion that the necessary condition for the electrodeposition or the electrodissolution of the transition metals is the formation of a bifunctional electrochemical system consisting of compounds of the metal ion having a high or a low valency state and a mixed conductivity type. At the electrolyte–film interface the film is formed by the reduction of the metal ions being discharged or by the dissolution of the metal to an intermediate state of oxidation, and at the electrode–film interface the material of the film is consumed by being further reduced to the metal or oxidised to higher valency forms. As a result of the simultaneous occurrence of these processes the film remains continuously in a state of dynamic equilibrium.

Our ability to vary controllably the rate of the processes taking place at the two phase separation boundaries allows the bifunctional electrochemical system to be accurately controlled.

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