

KINETICS AND MECHANISM OF ANODIC REACTIONS ON OXIDE ELECTRODES

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Electrodes based on electroconductive oxides are gaining importance in industrial electrolysis. Especially, anodes with the active layer of the $\text{RuO}_2\text{-TiO}_2$ solid solutions, which are the best anodic material for electrolytic production of chlorine, are finding widespread application.

The intrinsic features for the chlorine evolution process on the $\text{RuO}_2\text{-TiO}_2$ mixed oxide electrode are: three Tafel slopes 30, 40 and 120mV and the reaction has the first order in respect to chloride ions and the zeroth one to chlorine (at constant potential). The cathodic reduction on Cl_2 proceeds via two parallel routes the main route is characterized by the limiting current equal to the anodic exchange current, the second route has the Tafel slope $\sim 120\text{mV}$. The cathodic process is of the first order with respect to Cl_2 . On pure RuO_2 electrode one of the above mentioned parts of the anodic polarization curve, namely with the slope 30mV, the limiting cathodic currents are absent. The second route characteristics for mixed oxide electrode are quite similar to the characteristics for pure RuO_2 . This is explained by the presence of small quantity of the RuO_2 phase in mixed oxide.

The oxygen evolution on RuO_2 and $\text{RuO}_2\text{-TiO}_2$ obeys the Tafel equation with two slopes 40 and 80-160mV. In the low slope region the reaction order in respect to OH^- is about 1.5 in a wide range of pH (0.5 to 13). Similar regularities are observed for the oxygen evolution on cobalt spinels $\text{M Co}_2\text{O}_4$.

All these regularities may be explained by the following mechanism common for all the reactions considered: quasi equilibrium transfer of the first electron (I) (at not too high overpotentials), rate determining second electron transfer (II) and subsequent fast (sometimes reversible) chemical or electrochemical steps (III)



For chlorine evolution $X = \text{Cl}$, for oxygen evolution $X = \text{OH}$ (in acid solution there is $\text{HX} = \text{H}_2\text{O}$ instead X^- in eqn. (I), the right hand side of this equation includes H^+). The reversible reaction (III) takes place for chlorine electrode only. The Tafel slope is 40mV if the rate determining step (II) is an ordinary reaction ($\beta = 1/2$), the slope 30mV corresponds to a barrierless process ($\beta = 1$). The last case demands an activationless cathodic reaction ($\alpha = 0$) and that explains the existence of the limiting current. More detailed

analysis shows there are quasi barrierless anodic and quasi activationless cathodic processes at the chlorine electrode.

It is pertinent to note that all other reaction schemes proposed show much less accordance with all experimental data available.

Various hypotheses may be put forward concerning the nature of the intermediate $X(+1)$. It seems more probable that the reaction (II) involves not the particle X only, but the whole adsorption complex including the transition metal ion of the oxide.



A noninteger value of the reaction order with respect to OH^- (~ 1.5) may be connected with the change of the protonization degree of the oxide surface due to variations of $p\text{H}$ and hence with the change of the energetics of the surface characteristics.

Keywords : Kinetics & Mechanism; Oxide Electrodes; Industrial Electrolysis; Tafel Equation

INTRODUCTION

ANODIC processes of metal oxides have long been known but only recently this class of reactions has acquired great practical importance. There are two types of electrodes of practical interest—with high and low overpotential for oxygen and chlorine evolution. The first type is represented by lead dioxide which was the object of extensive study by H. V. K. Udupa and his collaborators. A low overpotential is characteristic for many transition metal oxides. Among them one should first mention anodes whose active mass consists of mixed $\text{RuO}_2\text{-TiO}_2$ crystals (henceforth to be referred to as RTO). At the present time, about a half of the world production of chlorine is based on the use of these anodes. Of considerable interest, primarily for electrolysis of alkaline solutions, are anodes with the active mass on the basis of complex oxides of base metals. The object of this study is to discuss and compare the data on the chlorine and oxygen evolution kinetics at two types of transition metal oxides— RuO_2 and RTO on one hand and mixed oxides of the iron group metals as well as some other d -metals on the other.

Without discussing in detail all the relevant literature data, one should note that according to the majority of authors (Faita & Fiori, 1972; Kalinovsky *et al.*, 1972; Erenburg *et al.*, 1972, 1975; Trasatti, 1973; Okamura, 1973; Veselovskaya *et al.*, 1974; Kubasov *et al.*, 1976; Burrous *et al.*, 1977, 1978; Jansen *et al.*, 1977; Arikado *et al.*, 1978a, b; and Krstajic *et al.*, 1979) (only the data of Kuhn and Mortimer, 1973 do not completely fit this picture), chlorine evolution at RTO and pure RuO_2 is characterized by a low Tafel slope about 30mV for RTO^x) and about 40mV for RuO_2 .

Representative data are given in Figs. 1 and 2. For pure RuO_2 the anodic slope is 40mV and the cathodic slope is $\sim 120\text{mV}$. The extrapolated cathodic and anodic exchange currents coincide (Erenburg *et al.*, 1975). For RTO two Tafel slopes are observed: 30 and 40mV (Erenburg *et al.*, 1975) and on the cathodic

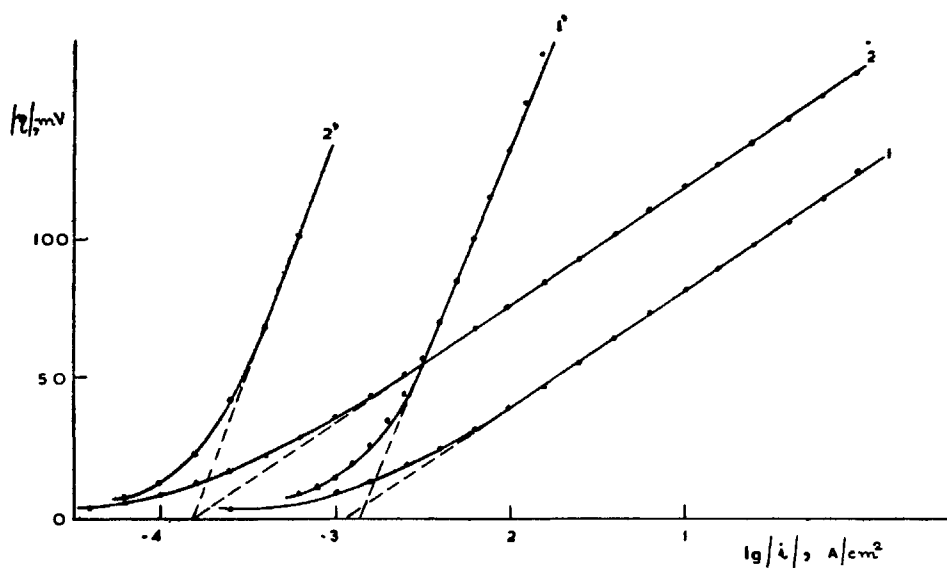


FIG. 1. Anodic (1,2) and cathodic (1',2') polarization curves for 100 per cent RuO_2 . Heat treatment temperature 480°C , solution composition: 1.5M HCl + 2.5M NaCl, P_{Cl_2} : 1, 1'-1; 2, 2'-0.057atm, 30°C .

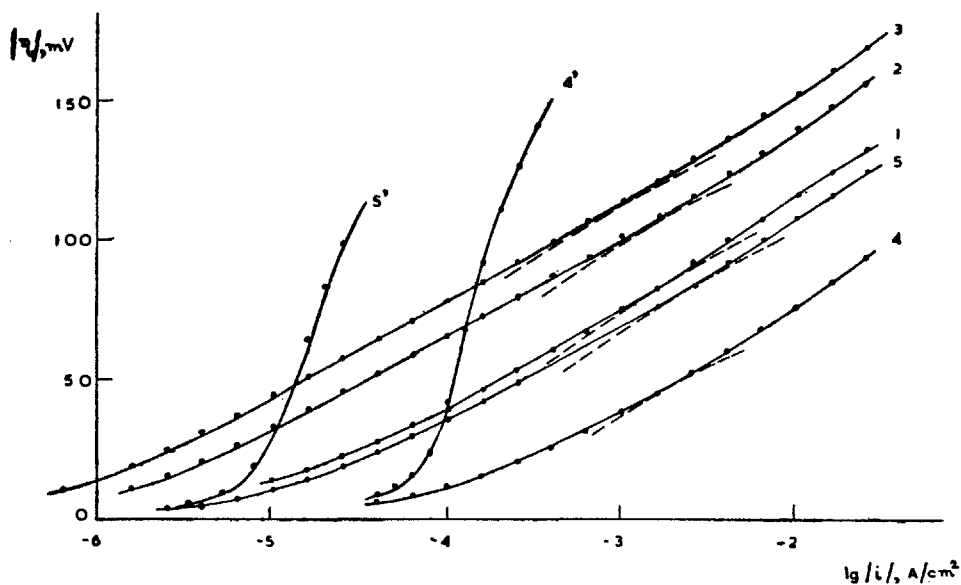


FIG. 2. Anodic (1-5) and cathodic (4',5') polarization curves for RTO. 35 mol. per cent $\sim 0.03 \text{ g/m}^3 \text{ Ru}_{\text{met}}$; heat treatment temperature 420°C . Solution compositions: 1,2,3-1.5M HCl + 2.5M NaCl, 4,4', 5,5'-1.54 M HCl; P_{Cl_2} : 1,4,4'-1, 2-0.1, 3-0.039, 5,5'-0.043 atm; 30°C .

branch we see the limiting current followed by a new current rise and a new Tafel section with the slope $\sim 120\text{mV}$ (sometimes the limiting current and the Tafel section overlap, and instead of a clearly defined limiting current plateau, only an inflection of the curve is observed). The cathodic limiting current is neither a diffusion current nor a kinetic one, but is defined by the electrode reaction rate. Its value practically coincides with that of the exchange current extrapolated from the lower part of the anodic curve.

The electrode capacity determined from the potential decay after switching off the current is $25\text{--}40\text{ mcf/cm}^2$ of true surface; *i.e.*, in its order of magnitude it is close to that of the double* lower slopes (upto 20mV) were observed in (Veselovskaya *et al.*, 1974; and Kubasov *et al.*, 1976), which is possibly associated with the fact that in the experiments carried out in those studies electrolyte was not saturated with chlorine, so that with increasing current density, the dissolved chlorine concentration in the layer adjacent to the electrode rose with the equilibrium potential accordingly increasing. When the Cl_2 concentration, even a very low one, was held constant the Tafel slopes are close to 30mV (Erenburg *et al.*, 1972, 1975).

The slopes $\geq 40\text{mV}$, sensitive to the heat treatment temperature were observed in (Jansen *et al.*, 1977). It is not clear why the results of Jansen *et al.* (1977) are at variance with the data of other studies. This indicates that the surface coverage by an electrochemically active intermediate is low*.

The anodic reaction order with respect to chloride is close to zero when the chloride solution concentration varies from $0.5\text{--}1$ to $4\text{--}5\text{M}$ in the absence of a supporting electrolyte (Faita & Fiori, 1972; Erenburg *et al.*, 1975; and Jansen *et al.*, 1977). At a lower concentration it approaches unity. Such reaction order however cannot be interpreted unambiguously since with increasing concentration, the specific chloride adsorption rises considerably, following to the first approximation the logarithmic adsorption isotherm (Kazarinov & Andreev, 1977). In the case of chlorine evolution at platinum, the process was shown to be inhibited by specifically adsorbed chloride (Kokoulina *et al.*, 1971). Taking all these circumstances into consideration, it is difficult to relate quantitatively the process kinetics to chloride concentration on the surface.

More definite results are obtained in the presence of a sulphuric acid excess, whose anion is more strongly adsorbed than chloride, and practically completely suppresses the specific adsorption of the latter (Kazarinov & Andreev, 1977). Under these conditions the anodic reaction is of the first order with respect to chloride (Fig. 3). The orders of anodic and cathodic reactions with respect to chloride and molecular chlorine in different sections of the polarization curve are listed in (Table I†)

*Another version with the coverage close to unity does not comply with the zero order of the anodic reaction with respect to Cl_2 in combination with a low Tafel slope and the first order with respect to Cl_2 of the limiting cathodic current (Erenburg *et al.*, 1975).

†The reaction orders with respect to Cl_2 similar to those listed in the Table follow from the data of Kuhn and Mortimer (1973). The data in (Burrous *et al.*, 1977) on the process rate in 1M HCl and $0.1\text{M HCl} + 0.9\text{M HClO}_4$ agree with our data on the first order of the anodic reaction with respect to chloride.

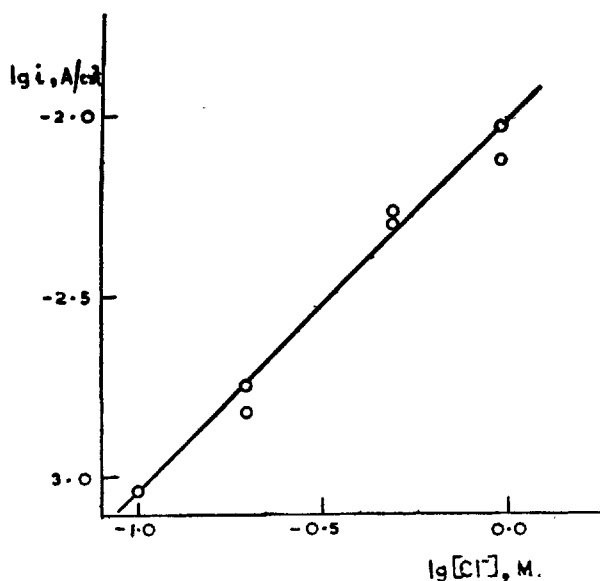


FIG. 3. Dependence of anodic current for RTO on (Cl^-) in the presence of 2M H_2SO_4 as supporting electrolyte. Heat treatment temperature 420 °C, 30 mol. per cent RuO_2 ; $\varphi = 1450\text{mV}$ (N. H. E.); $P_{\text{Cl}_2} = 1$ atm, 30 °C. Slope of the straight line ($\partial \lg I / \partial \lg [\text{Cl}^-]$) $\varphi = 1.00$ (the straight line is drawn with the use of the method of least squares).

TABLE I

Reagent	Main Route		Side Route cathodic reaction
	anodic reaction	cathodic reaction	
Cl^-	1.0 ± 0.1	-0.9 ± 0.1	-0.9 ± 0.1
Cl_2	0.01 ± 0.02	1.04 ± 0.03	0.9 ± 0.1

The complex form of the cathodic polarization curve for RTO is due to the reaction following two parallel routes. The main route gives the limiting current. At more negative potentials the reaction following the side route accelerates to such an extent that it predominates and is responsible for the Tafel section with the slope approaching 120mV. It should be noted that the reaction orders with respect to Cl_2 and Cl^- in this Tafel section are the same as for the limiting current, which indicates that the reaction follows the same scheme.

The presence of parallel reaction routes was confirmed by the stoichiometric numbers criterion for parallel routes obtained by Erenburg (Erenburg, 1973 & 1974).

It should be noted that the cathodic slope for the side route practically coincides with the cathodic curve slope for pure RuO_2 . On the other hand, the X-ray diffraction studies carried out by Roginskaya *et al.* (1977) showed that along with mixed $\text{RuO}_2\text{-TiO}_2$ crystals, an admixture of pure RuO_2 phase was present in the

active mass of RTO. These facts suggest that the main reaction route at RTO is realized on mixed crystals and the side route on the RuO_2 admixture.

The low slope of the anodic polarization curve in combination with the low coverage by the intermediate is an unambiguous indication that transfer of the first electron should be practically reversible, whereas the transfer of the second electron or the subsequent chemical reaction represents the slow step. The first reaction order with respect to chloride makes impossible such mechanisms (usual is explaining the slopes 30 and 40mV) as slow recombination or electrochemical desorption, requiring the second order. Thus the slow step of the anodic reaction consumes a total of two electrons per one Cl^- ion, i.e., it leads formally to the univalent positive chlorine state. Inasmuch as two Cl^- ions are required to form a Cl_2 molecule, the univalent positive chlorine should react with chloride to give Cl_2 . The negative order with respect to chloride of the cathodic Cl_2 reduction reaction means that chloride is formed in the equilibrium step preceding the slow step, i.e., the reaction of $\text{Cl}(+I)$ with Cl^- is reversible. Below is the simplest scheme satisfying these requirements.



The kinetic equations for this scheme are :

$$i_a = k_a [\text{Cl}^-] \exp \frac{(1 + \beta) \varphi F}{RT} \quad \dots(1)$$

$$i_c = k_c \frac{[\text{Cl}_2]}{[\text{Cl}^-]} \exp - \frac{\alpha \varphi F}{RT} \quad \dots(2)$$

It is readily seen that these equations describe the orders of the anodic and cathodic reactions with respect to all components. The anodic slope 30mV corresponds to $\beta = 1$, i.e., to a barrierless reaction. At sufficiently high overvoltages the barrierless reaction should change to an ordinary reaction with $\beta = \frac{1}{2}$ (Krishtalik, 1965 & 1968). Indeed in this particular case, we observed a change to the slope 40mV, i.e., to $\beta = \frac{1}{2}$ (Erenburg *et al.*, 1975a, b, c). It could be assumed that the change of the slope is associated not with the change of the true value of β , but with that of the rate determining step. In such a case, however, should be valid stoichiometric number criterion obtained by Erenburg for a sequence of several steps succeeding one another

$$\sum \frac{\nu_{i0}}{\nu_{i\infty}} = 1 \quad \dots(3)$$

Here ν_{i0} is the true stoichiometric number of the slow step, i.e., the number of its repetitions along the whole reaction route and $\nu_{i\infty}$ is the "extrapolated" stoichio-

metric number calculated with the use of the Horiuti equation (4) from the slope of the $i - \eta$ curve at the equilibrium potential and the extrapolated exchange current value

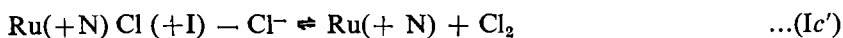
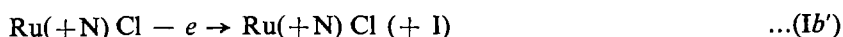
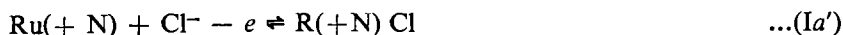
$$v_{ie} = \frac{nF}{RT} i_{oe} \left(\frac{\partial \eta}{\partial i} \right)_{\eta=0} \quad \dots(4)$$

Experiment gave the sum $\frac{1}{v_1} + \frac{1}{v_2} \cong 1.4$. Thus the criterion (3) is not valid and the only explanation left is a change in the true value of β^* .

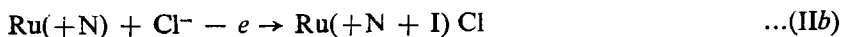
If for the anodic process $\beta = I$, then for the cathodic process $\alpha = 0$ and a barrierless anodic process corresponds to an activationless cathodic one. It is the fact that α is zero which accounts for the cathodic current being independent of potential i.e., for the limiting cathodic current of the electrode reaction proper. As far as we know, this is the first direct observation of an activationless limiting current.

Strictly speaking, the chlorine evolution and ionization reactions are neither barrierless nor activationless reactions in a pure form. Erenburg *et al.* (1975a, b, c) have proved that these are quasi-barrierless and quasi-activationless processes, i.e., they lack a barrier along the solvent coordinate determining the form of the potential dependence of the activation energy, but show a barrier along the chlorine atom coordinate, which gives a constant not potential-depending contribution to the activation energy (Krishtalik, 1969, 1970 & 1979).

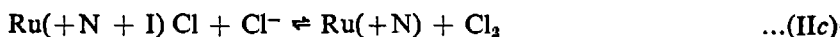
In the above reaction scheme the state of positive univalent chlorine [product of the step (Ib)] cannot be determined to a high precision as yet. This may be the Cl^+ cation or some hypochlorous acid derivative, in which case the oxygen necessary for its formation can come either from water or from the oxide lattice. These possibilities are kinetically indistinguishable. Finally, the step (Ib) can be interpreted not as the oxidation of Cl_{ads} but as a change in the valence state of the adsorption site. Indeed, the reactions (Ia) – (Ic) are written in such a manner that the state of the adsorption site, e.g., a $\text{Ru}(+N)$ atom, is assumed to be constant^a. In an explicit form they can be written as follows :



But the reactions (Ib') – (Ic') can be interpreted otherwise as electrochemical oxidation and chemical reduction of the ruthenium ion

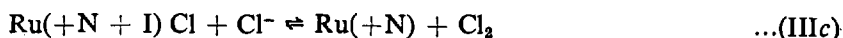
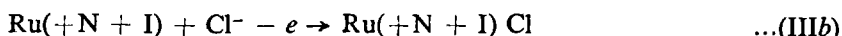


^aThe valence state of Ru on the surface in the potential range of interest can differ from its state in the bulk (+IV). Some data are available in the literature pointing to the valence +VI/(Augustinsky *et al.*, 1978; and Grady *et al.*, 1974). Therefore, we prefer to use the designation $\text{Ru}(+N)$.



Kinetically, this mechanism is indistinguishable from the one given above. As a matter of fact, the difference between them is rather of a formal kind. Indeed, the formulae of $\text{Ru}(+\text{N}) \text{Cl}(+\text{I})$ and $\text{Ru}(+\text{N} + \text{I}) \text{Cl}$ are mainly the extreme methods of writing for one and the same surface complex ($\text{RuCl})(+\text{N} + \text{I})$, the true electron density distribution in it being of an intermediate type.

Inasmuch as we consider the possibilities of oxidation not only of a chlorine atom but also of a catalytically active site $[\text{Ru}(+\text{N})]$, one more mechanism becomes possible, satisfying all the above-mentioned criteria (reversibility of the first electron transfer, first order with respect to chloride of the anodic reaction and the order minus one of the cathodic reactions, a change in the values of α and β) :



As we see, here as well the product of the slow step is the same complex as in the reaction (IIb) (or which is the same, (Ib')). This is no wonder since the overall process in the steps (a + b) is identical—the two-electron oxidation of one chloride ion. The mechanisms (III) and (I) or (II) however, are strictly speaking kinetically different since in the reactions (I), (II) the Cl^- ion participates in the first step while in the reaction (III) it participates only in the second step. Thus we are able to choose between them if we succeed in studying the process kinetics at such high anodic overpotentials at which the first electron transfer becomes the rate-determining step. At present, this problem is under investigation at our laboratory. Some indirect arguments in favour of the first version will be given below in the discussion of the data on the oxygen evolution kinetics.

Typical polarization curves of oxygen evolution at RTO are shown in Fig. 4 (from the data of Kokoulina *et al.*, 1978). The slope of the lower section of the Tafel line is close to 40mV (on the average it is 35mV in acid, in the range 40–50mV in neutral and slightly alkaline and 30–35mV in strongly alkaline solutions). The slope of the upper section rises from 80mV at $\text{pH} \lesssim 2$ to 220mV at $\text{pH} = 10$ and drops to 70mV at $\text{pH} \geq 12^{\#}$. Due to a nonmonotonic change of the slope, an essentially nonmonotonic dependence of overpotential on pH is observed in the upper section of the curve. The increased slope is possibly caused not simply by the change of the limiting step with the mechanism unchanged but by more significant changes of the process mechanism, in particular by the change of the surface composition. This follows from the fact that at the inflection potential the anodic oxide dissolution shows sharp acceleration (Kokoulina *et al.*, 1978).

[#]A low slope of the polarization curves for O_2 evolution at RTO and RuO_2 was observed in several cases (Okamura, 1973; Veselovskaya *et al.*, 1974; Burrous *et al.*, 1978; Augustinsky, 1978; Galizzioli *et al.*, 1974; Iwakura *et al.*, 1977; Bune *et al.*, 1977, 1979; and Lodi *et al.*, 1978). In some cases there was a section with a higher slope.

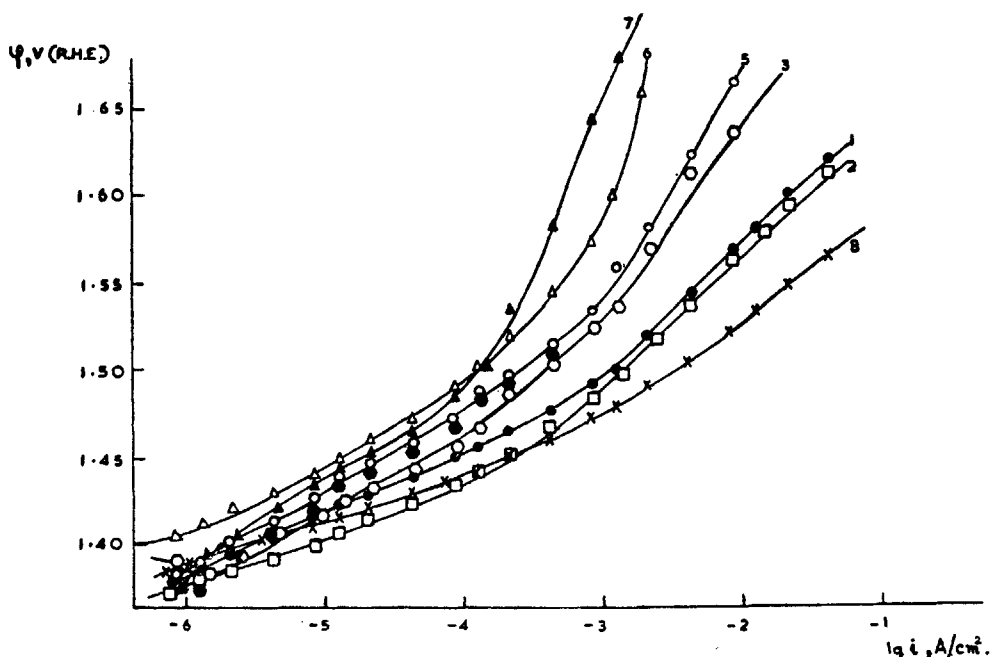


FIG. 4. Polarization curves for oxygen evolution at RTO (RuO_2 concentration in coating 30 mol. per cent, containing 5.4 g/m^2 ruthenium, solution temperature 20°C) at pH : 1-0.5, 2-2.0, 3-3.2, 4-6.5, 5-7.0, 6-8.3, 7-10.0, 8-12.4 and 13.

In the low Tafel slope section, overpotential is practically independent of pH . Overpotential increases slightly at medium pH values. It is not clear, however, whether this effect should be caused by the phosphate buffer as the phosphate anion is more strongly adsorbed than the SO_4^{2-} ion used in strongly acid solutions (Kazarinov & Andreev, 1977). It is impossible, however, to make measurements in nonbuffer solutions due to strong acid accumulation in electrode pores (Krishtalik, 1979). As has been already mentioned, to the first approximation, overpotential does not depend on the solution pH , i.e., the electrode potential in the presence of current depends on pH as the potential of an equilibrium electrode, i.e., with the slope $\sim 60\text{mV}$. At the average Tafel slope 40mV , this corresponds to the reaction order 1.5 with respect to the OH^- ion at constant potential. It is important to emphasize that the reaction order proves to be practically the same in a wide pH range (0.3-13).^a

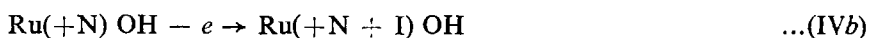
The slope $\sim 40\text{mV}$ is usually explained by the assumption of a slow reaction of the electrochemical desorption type. But this explanation seems to us to be unlikely. Such mechanism suggests the first order with respect to OH^- in acid solutions when

^aSimilar results but in a narrow range of pH were obtained in (Augustinsky *et al.* 1978; Bune *et al.*, 1977, 1979; and Lodi *et al.*, 1978).

H₂O participates in the slow step, and the dependence on *pH* is completely defined by the Nernst dependence of the surface coverage with intermediate particles formed by the equilibrium discharge reaction. In alkaline solutions the reaction should be of the second order with respect to the OH⁻ ion: the ion participating in the slow step. The experimental data are at variance with these conclusions. It is important that the difference is not only quantitative (the appearance of a noninteger order itself requires a special explanation, see below), but qualitative—the experimental order with respect to OH⁻ is the same in strongly acid and in alkaline solutions, whereas the mechanism in question necessitates an essentially different order in these two kinds of solutions. The same order in the whole *pH* range is to be expected for a mechanism similar to the reactions (I) or (II) for chlorine evolution:



or



The step (IVb) is followed by a series of faster reactions ultimately transforming OH to O₂.^a

With this mechanism, the dependence on *pH* is completely determined by the preequilibrium (IVa) or (IVa'). In the slow step (IVb), however, no particle from solution participates and therefore, there are no differences in the kinetics in acid and alkaline solutions. To be sure, the mechanism (IV) is not substantiated in such detail as the mechanism (I) for chlorine evolution, which is primarily associated with a greater complexity of the oxygen evolution reaction and with the impracticability of an equilibrium oxygen electrode. It should be noted however, that the mechanism (IV) agrees much better with all experimental evidence than all other mechanisms, at any rate, one relatively simple ones.

The absence of any variation in the kinetics over a wide *pH* range allows a choice to be made between the mechanism (IV) and a mechanism similar to (III), i.e., a mechanism including the ruthenium atom oxidation as the first step



or



Here the species from solution participate in the slow step and, therefore, one would expect different reaction orders with respect to OH⁻ in acid (zeroth order) and in alkaline solutions (first order). Thus the mechanism in question proves to be inconsistent with experimental data.

^aA similar oxygen evolution mechanism based only on the data for alkaline solutions was suggested by Grady *et al.*, (1974).

Oxygen evolution in acid solutions and chlorine evolution occur in overlapping potential ranges. If the oxidation of Ru(+N) without ligand addition from solution (Reaction Va) proves to be less advantageous than the oxidation after hydroxyl addition (IVa-IVb), then one may suppose that a similar situation will be encountered in chloride solutions as well i.e., the mechanism (I), or (II), seems to be more likely than (III).

The mechanism (IV) presupposes the first order with respect to the OH^- ion over the whole pH range, but in experiment the order close to 1.5 is observed. This fact cannot be unambiguously explained as yet. It is expedient to mention that the reaction order higher than 1 may be explained if one takes into account that the oxide surface is hydrated, that surface groups are ionized and that the ionized O^- groups influence the energy of the adsorbed particles OH and OH^+ . Assuming the Temkin logarithmic isotherm it can be shown that the reaction order equals to $1 + K\beta$, where the coefficient K is determined by the relation between the effects of the O^- coverage on the adsorption energies of O^- , OH and OH^+ . With the sound assumption that the O^- influence on the un-charged particles OH is substantially smaller than on the charged ones (O^- and OH^+) being for both latter of the same order of magnitude one obtains $K \approx 1$ and hence the reaction order $\approx 1 + \beta$ in accordance with the experiment. In the framework of the same approach one obtains the reaction order $\sim 1 - \beta$ in the case of slow first step.

The kinetics of chlorine and oxygen reactions at basic metal oxides are much less known than for RuO_2 . At our laboratory, Morozov and Mostkova obtained the polarization curves in sulphuric acid, alkali and chloride for a number of complex oxides with the structure of perovskite ABO_3 , pyrochlore $\text{A}_2\text{B}_2\text{O}_7$ and spinels AB_2O_4 .

Low chlorine and oxygen overpotentials were observed for perovskites $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ and LaNiO_3 possessing metallic conductivity. Perovskites of this type also have similar potential values when La^{+3} is substituted by another rare earth cation or by a triply-charged nontransition metal cation. Part of a triply-charged cation A may be substituted by a doubly-charged one without essentially affecting the electrochemical characteristics. The slope of the polarization curve of chlorine evolution is $\sim 30\text{mV}$ and that of oxygen evolution $\sim 60\text{mV}$ in alkaline medium. Similar data on chlorine evolution at some perovskites were obtained also by Arikado *et al.* (1978a, b).

Among pyrochlores, a low oxygen overpotential is characteristic of rhenium salts, e.g., $\text{Ni}_2\text{Re}_2\text{O}_7$. The slope of the polarization curve of oxygen evolution in alkaline solution is $\leq 40\text{mV}$.

Oxides of spinel type have received the maximum attention and study. Low chlorine and oxygen overpotentials proved to be characteristic of cobaltites ACo_2O_4 and chromites ACr_2O_4 , the nature of the bivalent cation ($\text{A} = \text{Co}, \text{Ni}, \text{Cd}, \text{Mg}$) having little effect on the process kinetics. At the same time, the use of iron as a trivalent metal B leads to a significant potential increase and a varying, rapidly increasing with potential, Tafel slope (up to $\sim 300\text{mV}$). For low over-potential processes, low polarization curve slopes are typical. Thus in (Morozov & Mostkova, 1978) for chlorine evolution at Ni, Cd and Mg cobaltites a slope of about 30mV was

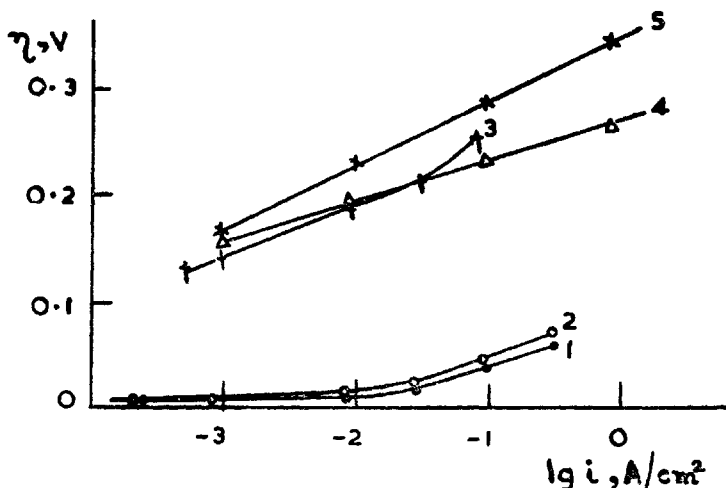


FIG. 5. Polarization curves for chlorine (4.3N NaCl, curves 1,2) and oxygen (6N KOH, curves 3-5) evolution on NiCo_2O_4 (1, 3), CdCo_2O_4 (2) $\text{Ni}_3\text{Re}_2\text{O}_{7-x}$ (4) $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (5) 80 °C.

found (for NiCo_2O_4 in HCl at higher current densities an increase in the slope to $\sim 120\text{mV}$ was observed). Low slopes were also found in (Konovalov *et al.*, 1976; and Agapova & Kokhanov, 1976): about 30mV at $70\text{--}90^\circ$ for anodes with the active mass from Co_3O_4 . According to (Morozov & Mostkova, 1978) oxygen evolution at cobaltites in alkaline medium shows a slope of $50\text{--}60\text{mV}$, subsequently increased to $100\text{--}120\text{mV}$. Tarasevich and Efremov obtained curves with the slopes 50 and $90\text{--}100\text{mV}$ in alkaline medium at 60° (for Co, Ni, Mn cobaltites on a gold substrate). The data of several other authors are for titanium substrate (Morozov & Mostkova, 1978; Konovalov *et al.*, 1976; Agapova & Kokhanov, 1976; Singh *et al.*, 1976; Shub *et al.*, 1978; and Shalaginov *et al.*, 1978) or ceramic anodes (Arikado *et al.*, 1978; and Morozov & Mostkova, 1978). A still lower slope was obtained in (Singh *et al.*, 1976) (45mV , 80° , 30 per cent KOH). The slope 60mV in acid medium with subsequent increase was observed for Co_3O_4 in (Shub *et al.*, 1978; and Shalaginov *et al.*, 1978) ascribe the slope 60mV to the depletion of the semiconductor surface layer in current carriers—holes. The semiconductor nature of the electrode is evident from its relatively low capacity value and the characteristic dependence of capacity on potential. It should be mentioned however that lower polarization curve slopes observed by some authors show that at any rate in the cases considered by them spinels behave virtually as metals. In this sense it is characteristic that e.g., Co_3O_4 and NiCo_2O_4 have very similar properties though the forbidden band width for Co_3O_4 is $0.2\text{--}0.3\text{eV}$ and for NiCo_2O_4 only $0.03\text{--}0.06\text{eV}$ (Trunov *et al.*, 1975, 1979). Probably for these strongly degenerated semiconductors, anodic polarization is attended by significant surface metallization.

The semiconducting properties of spinels can significantly affect the behaviour of their contact with the substrate from a valve metal—titanium. The characteristics of anodes with Co_3O_4 are known to be very sensitive to pretreatment of titanium

surface (Agapova & Kokhanov, 1976). It is interesting that more "metal-like" spinel NiCo_2O_4 proved to be less sensitive to substrate preparation. In this connection, it should be emphasized that the lowest slope values obtained in (Morozov & Mostkova, 1978; Konovalov *et al.*, 1976; Agapova & Kokhanov, 1976; and Tarasevich & Efremov, 1980) are for electrodes with a substrate from a non-valve metal, or from titanium treated in such a manner that its contact resistance became vanishingly small, as evidenced by their properties being identical to those of electrodes with an intermediate layer of platinum or $\text{RuO}_2\text{-TiO}_2$.

The dependence of the reaction rate on the solution composition was systematically studied only in (Morozov & Mostkova, 1978) for electrodes from Co_3O_4 , NiCo_2O_4 and MnCo_2O_4 in alkaline solutions. In the presence and absence of a supporting electrolyte, the authors of (Morozov & Mostkova, 1978) observed the order with respect to the OH^- ions equal to 1.3 at $b = 50$ and to 0.7 at $b = 90 - 100\text{mV}$. The explanation of these reaction orders similar to the above may be used here too, namely, the noninteger value may be due to the influence of the ionized surface hydroxyls on the adsorption energies of various groups.

We believe that the scheme (IV) and similar schemes (I) and (II), which have been rather strongly substantiated for electrodes from RuO_2 and RTO can be considered as convenient working hypotheses in studying anodic processes at spinels and other transition metal oxides. The rather scattered data available now on the chlorine evolution reaction and the behaviour of other oxides are not inconsistent with these schemes. On the whole, oxide electrodes of the type under consideration can be said to possess a number of common features with the system $\text{RuO}_2\text{-TiO}_2$.

It is to be hoped that the studies in the next few years will fill up the gap in our knowledge and lead us to more definite conclusions about the mechanism of these important and interesting reactions.

In this study we have restricted ourselves to treatment of some possible reaction schemes and have not considered the reasons of the important electrocatalytic effects shown by oxides, in particular, their connection with the electrophysical and structural characteristics of electrodes (for an interesting review on this subject see Kolotyркиn *et al.* (1979). This problem also offers a wide field of research.

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