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**SYNERGETIC
ELECTROCATALYTIC EFFECTS OF d-METALS ON
THE HYDROGEN EVOLUTION REACTION IN
INDUSTRIALLY IMPORTANT
ELECTROCHEMICAL PROCESSES^{*)}**

By

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Abstract

An electrocatalytic method has been developed for depolarization of the hydrogen evolution reaction (h. e. r.) on graphite, iron, steel, nickel and both plain- and palladium alloyed-titanium substrate surfaces. It is useful in industrially important electrolytic processes, such as chlorine (membrane and diaphragm) and chlorate cells, water and sea-water electrolysis, alkali amalgam decomposers and electro-organic syntheses. The combination of two d-metals from the two branches of Balandin's volcano curve for the h.e.r. has created a remarkable electrocatalytic effect, most particularly for molybdenum and cobalt which have been added in situ as their *anionic or complex species* during the electrolytic process (molybdate and tris-Ethylenediamine cobalt (III) chloride). The alloy activity appears shifted to values representative of precious metals, the effect being above 400 mV over the entire current density range important for industrial applications. In other words, the alloy created at the cathode substrate surface is extremely active, even more so than precious metals, providing current densities more than two orders of magnitude higher at the same potential and dissolving with vigorous hydrogen evolution instantaneously after the cathodic protection ceases. The synergetic electrocatalytic effects and the improvements in polarization are illustrated by linear potential sweep voltammograms and steady-state Tafel lines. The duration (the life-time) and reactivation of the combined d-metal catalytic activity are given too. Some theoretical consideration concerning synergism in transition metal electrocatalysis and the state of catalytically active coatings have also been presented. Engineering aspects and applications were considered too.

*) Paper partly presented at 31st ISE-Meeting, Venice, Italy, 1980 and the partial fulfilment of the M. S. thesis (Č. M. Lačnjevac), and the basis for the plenary lecture to be presented at International Meeting on Electrocatalysis, Erlangen, 1983.

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Introduction

For almost twenty years, molybdate anions have been used for *in situ* activation of mercury cell decomposers with remarkable electrocatalytic effect¹⁾: either the concentration of produced caustic soda has been increased from 45 to 66%, or the throughput of the electrolyser was doubled without any change in the decomposer size.²⁾ The activation method has now been applied world-wide.^{3~5)} Hund⁵⁾ indicates two months as the electrocatalytic life-time for high load electrolyzers before reactivation, while the best achievements for horizontal decomposers at lower capacity has been almost eight months.^{1,*)}

A further electrocatalytic contribution has been based on the improvement of graphite polarization characteristics for the hydrogen evolution reaction (h. e. r.) by deposition of small amounts of cobalt.⁶⁾ Contrary to the previous method, the latter has not found application in the activation of decomposers because of cobalt precipitation with hydroxide. In other words, it requires a separate graphite plating. The aim of the present paper is to present further advances in electrocatalysis for the h. e. r. obtained by the synergetic effect of two or more d-metal ions on graphite, iron, nickel or titanium substrates and its application in industrially important electrolytic processes.

Theoretical considerations

As pointed out by Kita,⁸⁾ the catalytic activity of various metals for the

*) One of the best examples of interfacial turbulence (Marangoni rippling motion) has been found at the surface between sodium amalgam and neutral molybdate solution¹⁾: brown-black particles form all over the interface during molybdate reduction and *visibly move* towards the edges of the mercury surface. In other words, the variation with potential of the interfacial tension at the mercury-solution phase boundary has had a most remarkable effect: if two points on an amalgam surface have different potentials owing to the presence of reduced molybdenum particles, (and therefore different interfacial tensions), the mercury moves from points of higher- to points of lower-tension, tending to equalize them. The swirling motion of the mercury surface has been so vigorous that ripples formed as if from violent stirring and the reduced molybdenum particles were carried to the edges of mercury surface where they adhered to the solid boundary (bottle glass, or graphite grids in amalgam decomposers). The rippling mercury and the movement of the molybdenum particles are visual evidence of the motion imparted by the interfacial tension gradient, which motion appears much greater than in case of any diffusion flow. It is worth noting here that whereas tungstate and vanadate exhibit almost the same effect on amalgam decomposition, the product of molybdate reduction ($\text{MoO}_2/\text{MoO}_3$ mixture) *adheres* to the solid phase boundary and undergoes further reduction to the metallic state by the intense hydrogen evolution (the effect of absorbed atomic hydrogen intermediates).

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h. e. r. is a periodic function of the atomic number within three long periods, the exchange current density being the measure of the former. Thus it has been qualitatively noted⁸⁾ from the electronic configuration of outer shells of the elements that the catalytic activity first increases with the increase of the d-electrons, reaches its maximum at a nearly filled d-orbital, sharply decreases after its completion with one or two electrons in the s-orbital, and then increases again with successive additions of electrons to the p-orbitals. Whereas the sp-metals appear characterized by a weak positive field perpendicular to the surface and a strong positive field in the lateral direction, most d-metals exhibit spherical ion cores with a symmetrical positive field; the electronic distribution on the surface for the latter being much smoothed and rather homogeneous.¹⁰⁾ Miles and Thomason⁹⁾ have also shown periodic variations of hydrogen overvoltage with the atomic numbers of the electrode metal, the former being scanned at constant current density by cyclic volt-ammerty both in acidic and alkaline solutions. It has been pointed out in the same context that the periodic trends observed for hydrogen overvoltages show a high correlation with the work functions of the transition metals [9, cf. (12, 13)]. The relationship between the electronic configuration of substrate metals and their activity for the h. e. r. has thereby been demonstrated.

A theoretical consideration of the fundamental kinetic equations for the h. e. r. has led Parsons¹¹⁾ to predict the existence of a Balandin's type volcano curve in the plot of the logarithm of the exchange current density versus the enthalpy of hydrogen adsorption for various metals (cf. ref. 14). Trasatti¹²⁾ confirmed the existence of the volcano type curve in the dependence of the former on the intermediate metal—hydrogen bond strengths recalculated from overpotential data (cf. ref. 9, 13). Similar volcano curves, moreover, have already been found for the logarithm of the exchange current density as a function of some other physical properties *depending on the metal electronic configuration* too, such as melting and boiling point, heat of fusion, sublimation, and vaporization (cf. ref. 8). Trasatti¹²⁾ has also pointed out that the equilibrium rate of the h. e. r. ($\log i_0$) as a plot of the electron work function separates various substrate metals into two parallel straight line plots: group (a) comprises all transition d-metals and sp-metals with positively charged surfaces, whereas group (b) consists of sp-metals with negatively charged surfaces, mercury being an exception (cf. ref. 9). In other words, the experimental evidence points to an interdependence between the exchange current density as the main kinetic parameter of the electrode activity, and the electronic configuration of the substrate metal.

Parsons¹⁴ has also considered theoretically the possibility that an increased reaction rate could be achieved by using a dual-site electrode, *i. e.* one with two types of active surface with different adsorption properties. Enhancement of the h. e. r. rate by transfer of the intermediate (adsorbed hydrogen atom) between sites of different adsorption energy was considered, but the approach did not predict any appreciable electrocatalytic effect resulting therefrom.

The next step was naturally to look for some synergism in the combination of two or more d-metals selected for their mutual interorbital electronic effect for h. e. r. electrocatalysis, and electrodeposited together onto a substrate. Thus the leading question has been :

Could we make hybrid bonding structures behaving like precious metals in electrocatalysis by proper alloying of d-metals to form a dual-site microcosm as a consequence of the partial delocalization of d-electron orbitals in transition metals and the excellent overlap of their far-reaching outer-shell sp-orbitals. In other words, may we expect that proper codeposition of two or more d-metals from two branches of Balandin's volcano curve, could improve and even exceed their individual electrocatalytic properties especially when applied *in situ* during the process of electrolytic hydrogen evolution, which would provide a very large surface area of active centers. Their combined activity may thus be brought closer to the top of the volcano curve among the precious metals. The periodicity in the activity of individual metal catalysts,^{8,9} which certainly reflects the electronic state of their outermost orbitals and changes with the number of electrons in the outer-shells, suggests that their inter-electronic combinations may exert some synergism in their electrocatalytic effects and approach or even exceed the properties of the platinum group of metals.

For weak hydrogen adsorption the activity of an individual electrode increases with increasing metal-hydrogen bond strength (left branch of the volcano curve,¹¹⁻¹⁴) while for strong adsorption (right branch), the activity decreases as the metal-intermediate bond strength increases. One might thus expect that the dual-site combination of two metals from the two branches could provide a mutual interchange of adatoms, causing instability phenomena within the double layer and thereby an enhancement of the overall electrode reaction rate (cf. ref. 14). In such a context cobalt both in the metallic lattice and in its individual cationic and complex forms appears as a good proton transferring species, while molybdenum has been widely used both for hydrogenation and even dehydrogenation catalysts.

Electrocatalysis by underpotential deposition, which appears as function

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of the adatom coverage, has also been based on the mutual interelectronic configuration effects of two distinct metals.¹⁵⁾ Thus it turns out that an isolated adatom on a foreign substrate surface appears deprived of its outermost electrons and thus loses its chemical identity, creating a new entity whose catalytic properties depend on its atomic nature and surface concentration.¹⁶⁾ Sometimes the electrode characteristics of an adatom resemble the properties of the element preceding it in the Periodic table, for example, gold in submonolayer amounts behaves like platinum, and the latter behaves like iridium, and so on.¹⁶⁾ The electronic structure and the corresponding adatom properties apparently differ from the ones for transition metals both in their metallic and atomic states. The latter arises as the effect of a chemical binding between adatoms and the substrate and thereby affects the binding energy of adsorbing proton species.

The foregoing theoretical path has consequently led to the combination of cobalt and molybdenum, and brought a considerable catalytic improvement to both graphite and titanium substrates¹⁷⁾: Tafel lines have been shifted to much more positive values than the two metals provided in their individual electrocatalytic action. Darlington¹⁸⁾ recently pointed out that a codeposit of cobalt-tungsten-phosphorus shifts the polarization characteristics of mild steel almost to the reversible potential of the hydrogen electrode. The Co-W-P alloy was chemically deposited, using sodium hypophosphite as a reducing agent, and heated further for 24~72 hours at 400~450 degrees centigrade in an oxidizing atmosphere to activate the surface.

Brown *et al.*³³⁾ have recently achieved the pronounced synergetic electrocatalytic effect for the h. e. r. by another couple from two branches of Balandin's volcano curve (Mo-Ni), that perfectly well agrees with above line of theoretical consideration.

It has also been shown recently that an appropriate combination of molybdate with iron (Fe(II)) provides a remarkable extension of their individual cathodic activities for the h. e. r.,¹⁹⁾ as one would expect for two d-metals from two different branches of the volcano curve.

Kitamura *et al.*³⁶⁾ have recently also pointed out that combination of Lanthanum or other rare earth mischmetals with Cobalt or Nickel, the most particularly LaNi₅ provides the approach almost to the reversible hydrogen evolution potential within the wide range of current density, that perfectly agrees with the theory displayed in the present paper and supports the latter.

It seems that the first synergetic electrocatalytic effect for the h. e. r. was observed by Westrip,²⁰⁾ who pointed out that a considerable amount of copper depresses the overvoltage of the alloying zinc cathode below its indi-

vidual potential values.

Stender *et al.*²¹⁾ have shown that the hydrogen overpotential for zinc-cobalt alloys exactly reflects the crystal structure and the composition of the latter. Thus, cathodically formed alloys exhibit the same shape of polarization curve as thermally made alloys, but have higher hydrogen overvoltages as a function of cobalt content. However, after thermal treatment the former alloys increase their content of $\text{Co}_5\text{Zn}_{21}$ and thereby approach the latter in their electrode properties (cf. ref. 33).

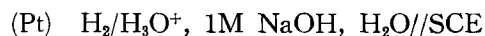
Recent requirements for energy savings have stimulated numerous papers dealing with the electrocatalysis of the h. e. r.^{18,17,22~25)} There is great promise that the reversible hydrogen electrode potential can be approached over a very wide range of current density while employing only cheap and available metals as the catalysts.

Experimental

All experiments have been carried out in classical way and similarly to the ones formerly described^{1,6)}. The cell for cathodic polarization was a simple glass vessel (about 250 cm³) with double wall mantle to provide thermostatic temperature control (± 0.2 K). Squared plates of one cm² exposed apparent surface area on both sides acted as the cathode in vertical position, centered and situated to be surrounded by Winkler platinum gauze anode. Cathode potentials were measured vs. SCE by means of VTVM (Keithly 610 C). The tip of Luggin capillary was about 0.03 cm diameter and touched the cathode, reducing pseudo-ohmic polarization at higher current densities to low values. The electrode potentials were corrected for ohmic losses by the interrupter technique and therefrom represent true overpotentials for hydrogen evolution. The electrolyte was either 1 M or 40% sodium hydroxide solution and the intention has been to achieve conditions as close as possible to those in water electrolysis and amalgam decomposers of mercury cells. Special precautions such as pre-electrolytic purification were not undertaken since, in the range of current densities (1 to 300 mA·cm⁻²), the effect of impurities in reagent-grade caustic soda with twice distilled water can be neglected. On other hand, the present work reveals only the electrocatalytic effect and achievements and does not intend to enter in kinetic parameters at lower current densities. Tafel lines were obtained for various temperatures ranging from 298 to 363 K. Reproducibility of Tafel plots in ascending and descending direction of measurements repeated several times successively was better than ± 10 mV. Every measurement was undertaken after long time prepolarization, sometimes, as indicated, of two days duration.

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The emf of galvanic cell



as a function of temperature was measured for evaluation of overpotentials, and can be expressed by

$$\text{emf} = 1068 - (T - 273)$$

where T is the temperature in K and the emf is in mV. The SCE was maintained at room temperature in all measurements and overvoltages were calculated by subtracting the values according to above relationship from the measured ones.

Some measurements were carried out in 1 M NaCl at about pH 7 in reagent grade purity and under conditions close to the chlorate cell process.

Long time polarization measurements to assess the life-time of electrocatalysts were carried out in the same vessel providing all the time constant cell load, temperature and electrolyte concentration. Measurements of linear potential sweep voltammograms, as well as steady-state Tafel plots were carried out in the same cell.

Various cathodic materials were employed to assess the electrocatalytic effects onto various substrates of importance for industrial application: mild steel, electrolytic nickel (99.99% purity), titanium for industrial electrodes (Tikrutan-12 of high purity, Krupp product) and pyrolytic graphite (Union Carbide).

Ionic Synergetic Electrocatalytic Effects of d-Metals

Cobalt and nickel cations appear useless for in situ electrocatalytic action because of their precipitation in alkaline solutions. As the diffusion layer for h. e. r. is usually alkaline even in acidic bulk and buffered solutions, particles of metal hydroxides adhere to the electrode surface, block the latter, and thereby decrease the synergetic electrocatalytic effect of cobalt and nickel in combination with molybdate and tungstate. Thus, an earlier endeavour to improve the electrocatalytic properties of industrially important electrode materials such as iron, steel, nickel, titanium and even graphite for the h. e. r. has finally been achieved by using the *anionic or complex* forms of the d-metals (molybdate, tungstate, cobalt and nickel amino complex) chosen from the two branches of Balandin's volcano curve.²⁵⁾ The greatest improvement so far has been obtained with tris-ethylenediamine-cobalt (III) chloride $\{[\text{Co}/\text{C}_2\text{H}_4(\text{NH}_2)_2/3] \text{Cl}_3\}$ (see Appendix) in synergetic combination with molybdate (Fig. 1, 2, 3 and 4).

Steady-state Tafel lines on nickel, steel, titanium and graphite, both

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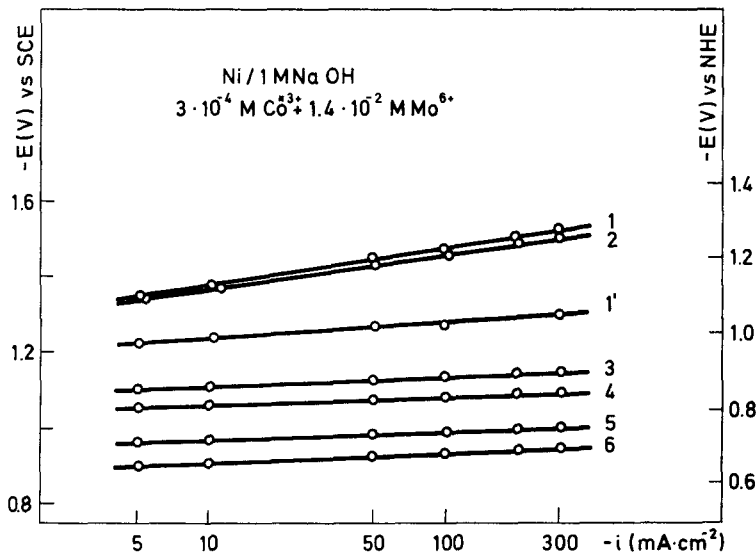


Fig. 1 a. Individual and synergetic electrocatalytic effects of anionic molybdate and Co (tris) complex species in a solution of caustic soda (1M NaOH) on nickel substrate, compared with the polarization characteristics of pure nickel for the h. e. r. 1 and 1'-pure nickel at 20 and 80°C, respectively, 2- the individual effect of molybdate, 3, 4, 5 and 6, the synergetic Co-Mo effect at 20, 40, 60 and 80°C, respectively.

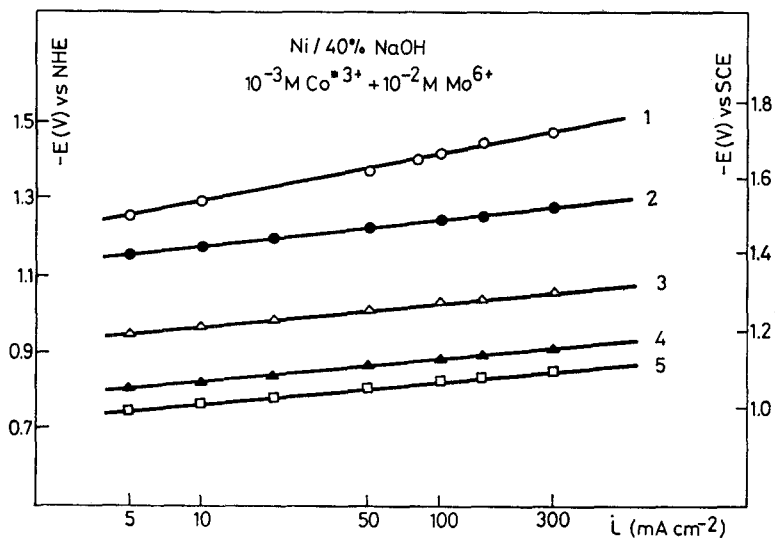


Fig. 1 b. Individual and synergetic electrocatalytic effects of anionic molybdate and Co (tris) complex species in a solution of caustic soda (40% NaOH) onto nickel substrate, compared with the polarization characteristics of pure nickel for the h. e. r. 1 and 2-pure nickel at 25 and 80°C, respectively, 3, 4 and 5-the synergetic Co-Mo effect at 25, 60 and 80°C, respectively.

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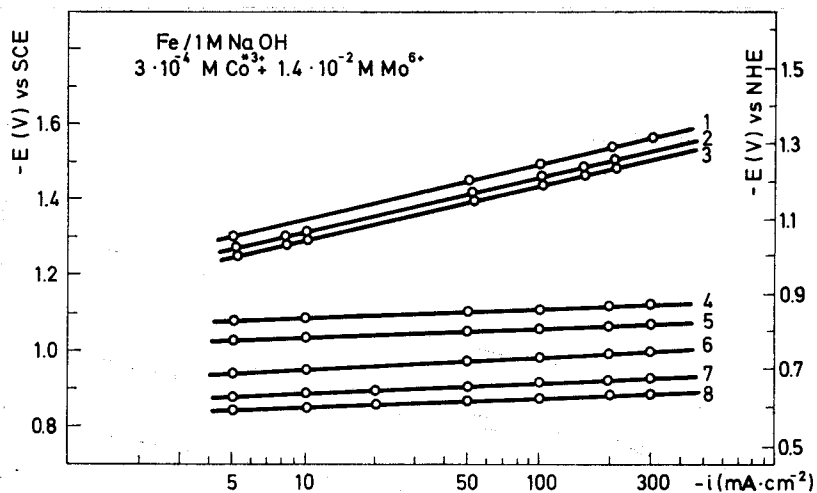


Fig. 2 a. Polarization characteristics and the electrocatalytic depolarization effects for the h. e. r. in 1M caustic soda solution: 1-mild steel, 2-the cobaltized mild steel, 3-the molybdenized mild steel, 4, 5, 6, 7 and 8, the synergetic Co-Mo effect on mild steel at 20, 40, 60, 80 and 90°C, respectively.*)

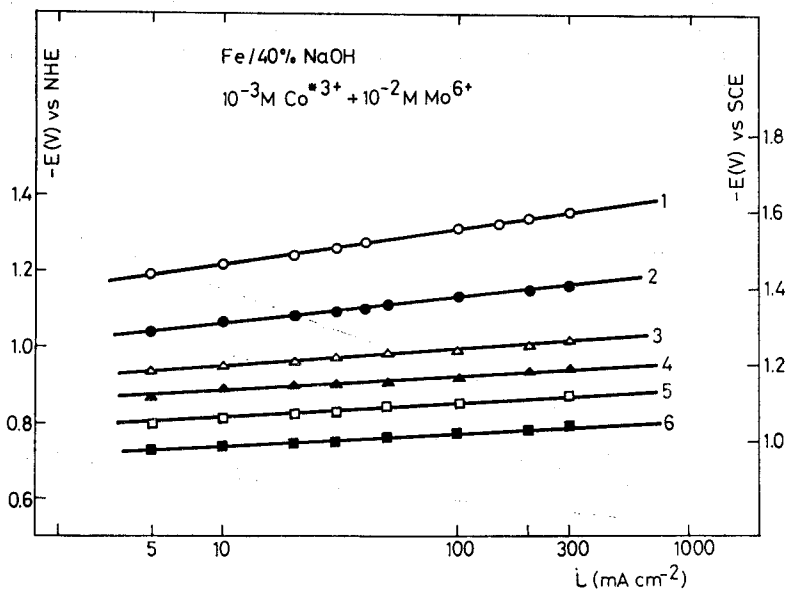


Fig. 2 b. Polarization characteristics and the electrocatalytic depolarization effects for the h. e. r. in 40% caustic soda solution: 1 and 2-mild steel at 20 and 80°C, respectively, 3, 4, 5 and 6, the synergetic Co-Mo effect on mild steel at 20, 40, 60 and 80°C, respectively.

*) All measurements throughout the Figures relates to 20°C except when stated otherwise.

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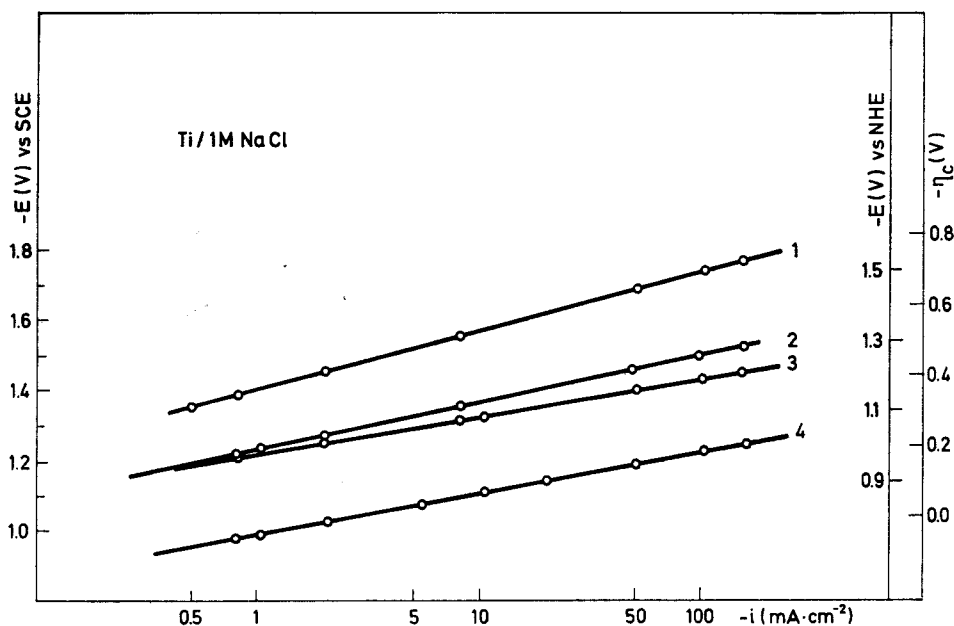


Fig. 3. Individual and synergetic electrocatalytic effects of molybdate and Co (tris) complex ionic species in brine on a titanium electrode substrate at 20°C: 1-pure titanium, 2-the cobaltized titanium, 3-the molybdenized titanium, and 4-the synergetic Mo-Co effect on titanium.

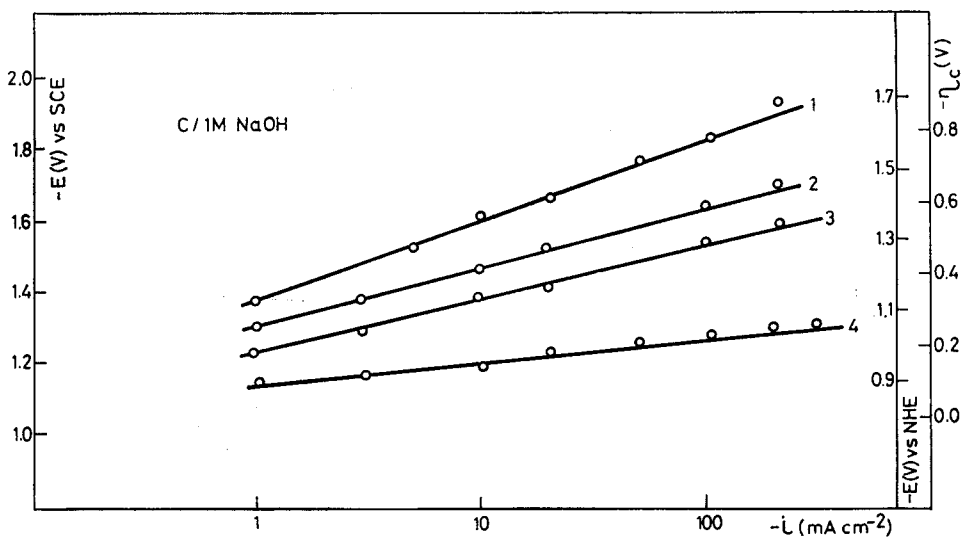


Fig. 4. Individual and combined electrocatalytic effects of Co (tris) and molybdate ionic species on graphite compared with the plain substrate cathode for the h.e.r. at 20°C in caustic soda: 1-plain graphite, 2-cobaltized graphite, 3-molybdenized graphite, and 4-the mutual Co-Mo anionic effect.

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in acidic sodium chloride (pH between 6 and 7) and caustic soda solutions have remarkably been shifted towards much more positive potential values with slopes sometimes even below 30 mV/decade, which implies that the electrodes tend towards reversible behaviour for the h. e. r. within a wider current density range. Actually, potentials even more positive than the equilibrium value for the hydrogen electrode apparently occur at lower current densities because of the pronounced contribution of partial metal codeposition within the low electrode reaction rates.

It has been shown that dual and even triple d-metal combinations, most particularly Mo-Co and W-Co (cf. ref 18) alloying compositions shift the polarization characteristics of substrate cathodic materials to even better electrode properties than those of any of the platinum group of metals, even when one component is present in negligible amounts (Fig. 5). This electrocatalytic achievement appears even more pronounced at the higher current densities important for industrial applications. It seems that the main goal of electrocatalysis has been nearly reached by this approach; *i. e.*, to replace precious metals as catalysts by cheaper and more available metallic species of improved electrode polarization characteristics. Eventually the ultimate

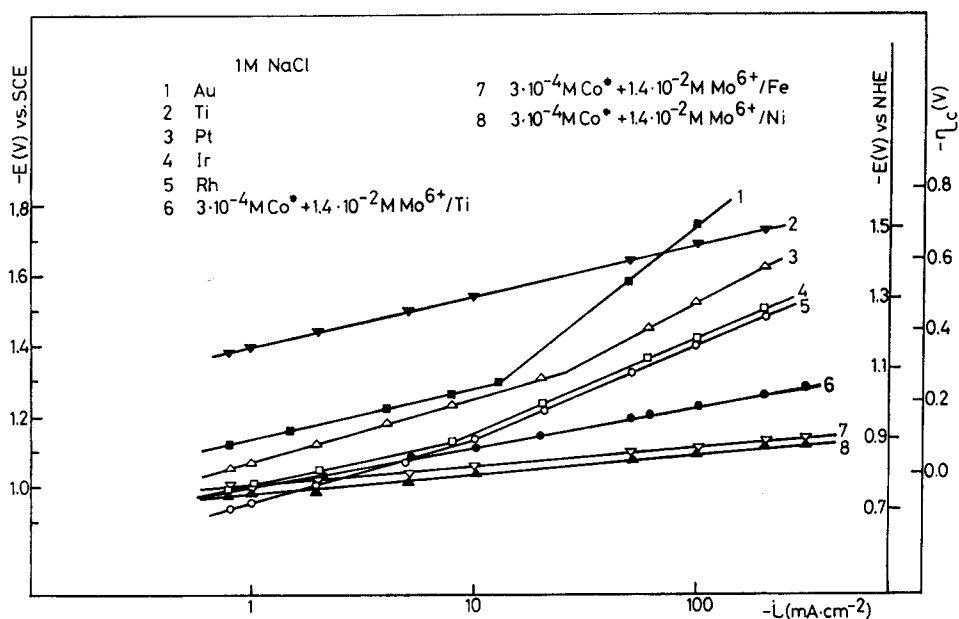


Fig. 5. Individual polarization characteristics of various precious metals and titanium for the h. e. r. and the electrocatalytic effect of Co-Mo ionic species on titanium, mild steel and nickel in 1M NaCl solution at 20°C.

achievement in electrocatalysis for hydrogen evolution has been possible: to improve the synergetic action of d-metals so that their cathode properties lie amongst those of the precious metals on Balandin's curve, and may even exceed them. In other words, not only iron and nickel, but almost to the same extent titanium and even graphite substrates have been shifted among the platinum group of metals in their polarization properties for the h. e. r.

It has recently been shown that the ionic synergetic combination of tris—molybdate even succeeds to improve the polarization properties of gold itself for more than 250 mV within the wide range of current density (over 300 mA/cm²) in the electrocatalytic action for the h. e. r.

While the individual electrocatalytic effects of molybdenum and cobalt were both close to 250 mV, their synergetic effect on titanium and graphite over the whole current density range amounted to about 400 mV and even more. Whereas the effect of molybdate by itself was progressively inhibited by the presence of dichromate ions (the chlorate cell process), as well as the precipitation of magnesium and calcium hydroxides onto the cathode surface, the combined activity of cobalt and molybdenum showed a smaller partial inhibition in slightly acidic and neutral chloride solutions.

A Mo-Co synergetic codeposit formed in situ during hydrogen evolution appears extremely active and is cathodically protected as long as the current flows. When the current stops, the active centers immediately dissolve with hydrogen evolution, similarly to Raney alloys. Individual application of cobalt or molybdenum approaches the maximal electrocatalytic effect for the h. e. r. at about 10⁻² molar ionic content in solution.⁷⁾ However, five times less, and even more less concentration of either one in combination with another (the synergetic effect) appears enough almost to double the former individual activity of each one and bring the substrate electrode amongst the precious metals in its polarization properties, the presence of molybdenum even being the most essential. It is almost irrelevant for their electrocatalytic synergism which one has been added first or whether one is added a long time after the other or both were introduced together.

It is necessary to note that the codeposit in Co-Mo electroplating,²⁶⁾ regardless of the alloy thickness, appears far from providing an electrocatalytic effect similar to the one achieved by the negligible amounts of Co or Mo anionic species added in situ during hydrogen evolution.

Although the synergetic electrocatalytic effect has been considerable and of the same order of magnitude for all substrate materials tried, it is important to point out a remarkable and decisive contribution of the base electrode material to the entire catalytic synergism; that is the triple-site effect.

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This causes the slopes of the Tafel lines to decrease and the latter appear shifted towards successively more positive potential values in the following substrate order : graphite < titanium < iron < nickel (Fig. 1, 2, 3 and 4). The experimental evidence thus unambiguously suggests that a proper synergetic combination of several d-metals on some appropriate substrate electrode material, most particularly nickel, could exhibit the reversible cathodic behaviour for the h.e.r. within a very wide current density range. In such a context it is especially worthwhile to observe that whereas the individual electrocatalytic effects of both anionic molybdate and cobalt complex species were rather small on iron and nickel surface, their combined catalytic action brought the substrate electrode close to the reversible potential of the hydrogen electrode within the entire current density interval important for industrial application ; such an electrode appears even better in its cathodic properties than the individual precious metals themselves. In addition, it is noteworthy that the activity on iron and most particularly nickel substrate electrodes is stable for a rather long time.

**The State and Activity of the Synergetic d-Metals (Mo-Co)
Electrocatalyst**

Successive voltammograms of linear potential sweep polarization of titanium in molybdate solution reveal two cathodic and two corresponding anodic peaks, which progressively extend with cycling (Fig. 6). Kolthoff and Hodara²⁷⁾ also observed two distinct polarographic waves, the first one associated with the reduction of molybdenum (VI) to molybdenum (V), while the second was ascribed in the further reduction of the latter to molybdenum (III) and had a height twice that of the first one. Augustinski²⁸⁾ detected two distinct molybdenum species in compact blackbrown coloured "molybdate film" on an aluminium surface by X-ray photoelectron spectroscopy (XPS), the first, of variable composition assigned to MoO_x ($2 < x < 3$), and the second being the basic molybdate ion (MoO_4^{2-}) (see Fig. 5 in ref. 28 for the X-ray photoelectron spectrum of the Mo 3d level).

The scanned area of the anodic peaks (Fig. 6) is remarkably small compared to the corresponding one for cathodic molybdate reduction in the voltammogram although both grow with time and cycling. This means that the anodic oxidation does not remove the whole cathodic deposit during each cycle, and hence the latter grows. However, the growth does not continue to the complete exhaustion of molybdate ions, but rather approaches a steady-state value. Thus, the molybdate consumption appears rather negligible. Once the voltammogram reaches the potential of intense hydrogen evolution, both cathodic and anodic peaks keep reasonably steady-state values.

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This experimental evidence agrees with Wagner's theory²⁰⁾ for the cathodic reduction of anions, which states that there exists some critical reaction rate for the main electrode process (hydrogen evolution) when the adverse potential gradient across the boundary layer becomes sufficient to repel all anionic species, and thereby to suppress completely their codeposition. As a result, the electrocatalytic deposit which grows out of anionic codeposition, progressively increases both the h.e.r. rate and the electric field for further anionic repulsion. Each time the electrode is in the range of intense hydrogen evolution (each longer hold on the voltammogram), there is a progressive shift towards more positive potential values. This also means that the deposit

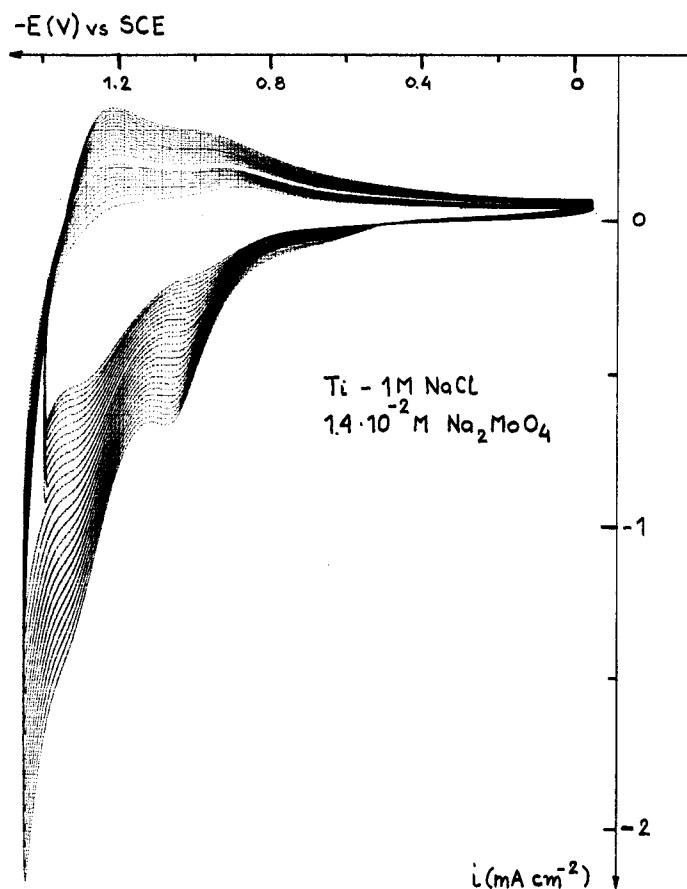


Fig. 6. The successive linear potential sweep voltammograms of a titanium substrate electrode for brine solution (1M NaCl) in the presence of molybdate ions. Potential sweep 100 mV/sec.

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undergoes further cathodic reduction and thereby increases its catalytic activity for the h. e. r. Finally, the latter approaches some steady state when the electric field according to Wagner²⁹⁾ is high enough for efficient repulsion of all further anionic species. After every long "hold" in the voltammogram

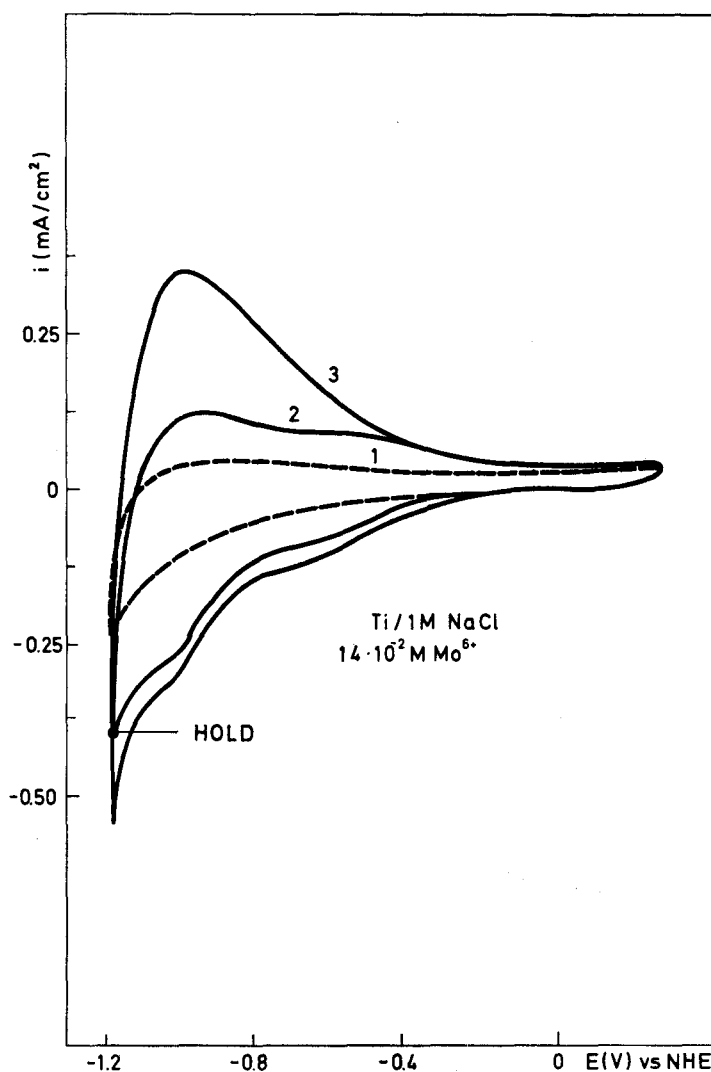


Fig. 7. The linear potential sweep voltammograms in 1M NaCl solution: 1-pure titanium, 2-Ti in presence of $1.4 \cdot 10^{-2}$ M molybdate, and 3-the same as the latter with 60 seconds hold in the range of hydrogen evolution. The sweep rate 100 mV/sec.

there appears just one distinct peak in the anodic potential range, which points to another state of the active deposit (Fig. 7).

By itself cobalt exhibits a similar behaviour with distinct peaks of deposition and dissolution successively growing in multilayer plating during recycling in the potential sweep as long as the cathodic value approaches hydrogen evolution, but eventually dying away and finally disappearing completely (Fig. 8 a). For voltammograms taken up to the negative potential at which hydrogen starts evolving, the scanned peaks ascribed to cobalt deposition roughly match the corresponding anodic surface area scan for its dissolution (Fig. 8 b). However, once hydrogen evolution takes place at a little more negative potentials, the peaks characteristic of cobalt deposition and its dissolution progressively vanish. The electrocatalytic activity meanwhile keeps its previous magnitude. It is, however, hard to explain such an effect of cationic cobalt species. One tentative explanation is that cobalt adatoms

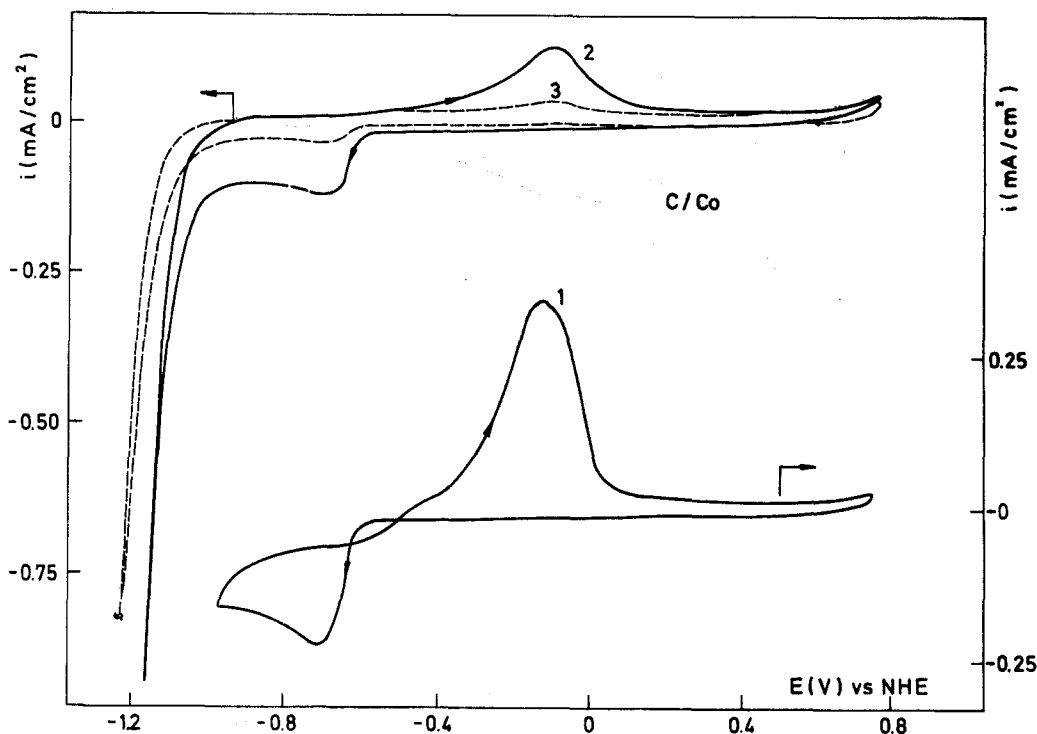


Fig. 8 a. The linear potential sweeps of the graphite electrode in the presence of Co^{2+} cationic species in 1M NaCl solution: 1-the voltammogram without hydrogen evolution, 2-the first voltammogram with the h. e. r., and 3-the second one after hydrogen evolution. Potential sweep 100 mV/sec.

Synergetic Effects in the Hydrogen Evolution Reaction

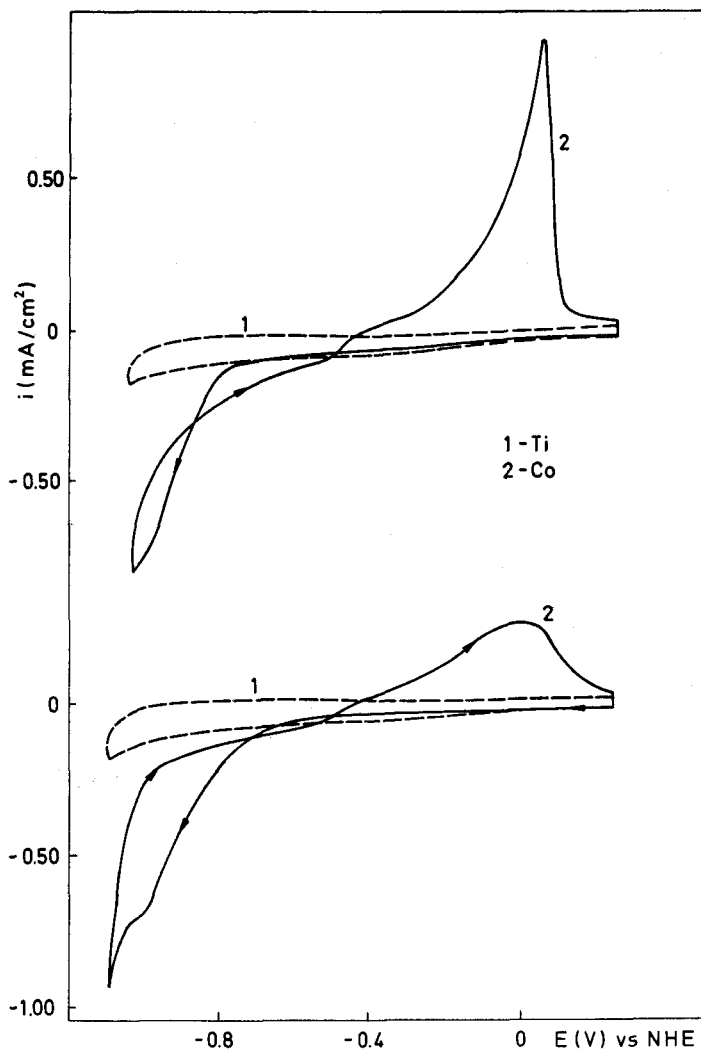


Fig. 8 b. The linear potential sweep voltammograms for the plain-(dashed lines) and cobaltized-(fill line) titanium before (lower-curves) and after hydrogen evolution (upper-curves). Potential sweep 100 mV/sec, $1 \cdot 10^{-2}$ M Co (II) in 1M NaCl.

deposited earlier undergo hydride formation during hydrogen evolution, which protects them from anodic dissolution during potential sweeps, and at the same time is catalytically active for further cathodic reaction.

It is important to note that even the cathodic peaks for molybdate reduction disappear in the synergetic action due to additional cobalt (tris)

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when the potential approaches the range of intense hydrogen evolution, while the catalytic activity progressively extends to its steady-state high value (Fig. 9).

It has been observed that the electrocatalytic action of both molybdate and its synergetic combination with cobalt reach their maximum activities after one or two days of continuous cathodic polarization with intense hydrogen evolution and keep them for a rather long period of time (Fig. 10) if the current is uninterrupted. The molybdate concentration does not change

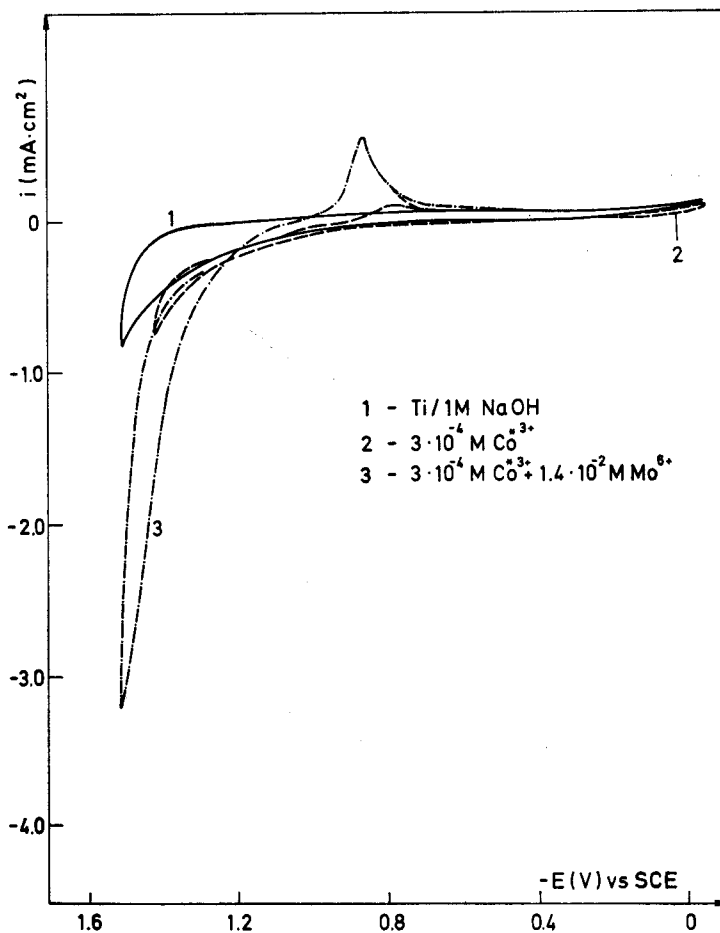


Fig. 9. Voltammogram presentations of the individual and synergetic electrocatalytic effects of tris (Co) and molybdate ionic species, compared with the plain titanium electrode for the h. e. r. in 1M NaOH at the sweep rate 100 mV/sec.

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noticeably throughout, but its presence in rather small amounts (0.2 ppm) appears essential for maintaining the catalytic activity. In amalgam decomposers with stable mercury flow, the activity remains unaltered for up to 6 months¹⁾ with no readdition of molybdate in the input water stream. However, once the activity more or less drops, the potential becomes successively more negative and molybdate anions undergo further cathodic reduction as the activity approaches the initial state.

It may be asked "What is the active state in molybdate reduction for h.e.r. electrocatalysis and why does it take a while to reach that state".

Pure metallic molybdenum has not yet been produced electrolytically with any appreciable current efficiency even from its fused salts and appears only as the codeposited alloy at higher contents with cobalt, iron, and nickel²⁹⁾. Two distinct products of the molybdate cathodic reduction arise simultaneously in various ratios depending on the electrode reaction conditions, 1: brown colour MoO_2 , which is electrically conductive, appears catalytically active and exhibits a metallic lustre during continuous cathodic polarization with hydrogen evolution, and 2: black MoO_3 , which is inactive and stable¹⁾ (cf. ref. 28). All Tafel lines continuously shift with time of polarization

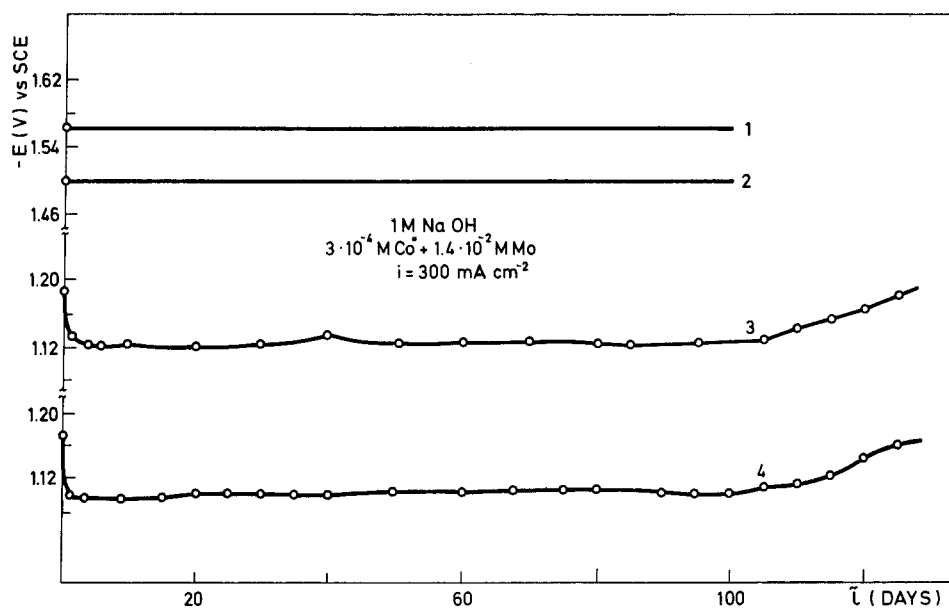


Fig. 10 a. Time dependence of the synergetic electrocatalytic effect of tris (Co) and molybdate ionic species in 1M NaOH at 300 mA/cm² obtained in situ on mild steel-3, and nickel-4, and compared with the substrate electrodes (1-Fe, 2-Ni) for the h. e. r. at 20°C.

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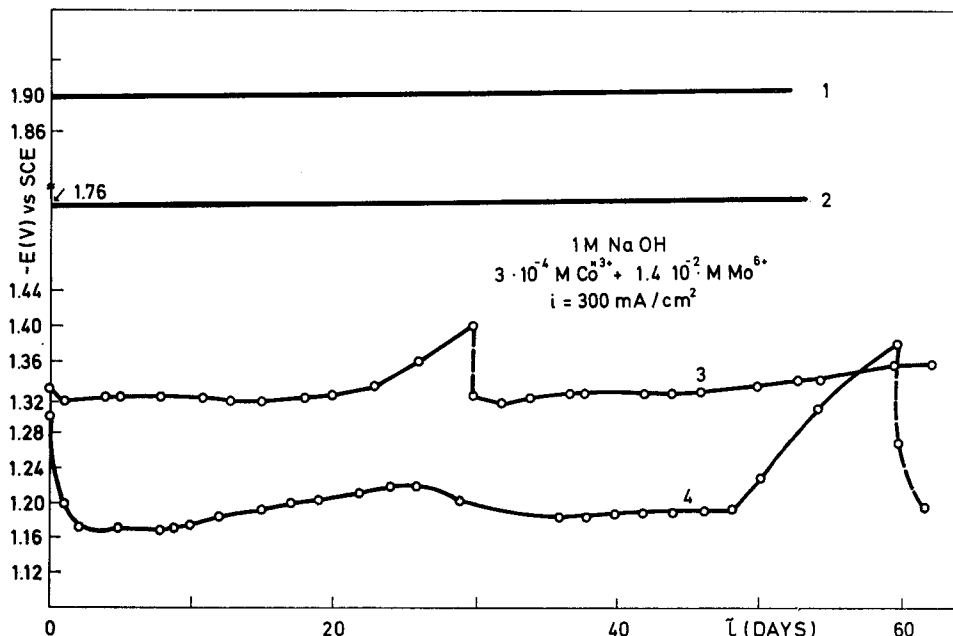


Fig. 10 b. Time dependence of the synergetic electrocatalytic effects of tris (Co) and molybdate anionic species in 1M NaOH solution at 300 mA/cm², obtained on graphite-3, and titanium-4 electrodes, and compared with the plain graphite cathode-1, and titanium-2 substrate for the h. e. r., Dashed lines represent the reactivation of cathodes.

towards more and more positive potentials and after about two days of uninterrupted current flow approach their final steady-state positions (cf. ref. 1). Although all steady-state polarization measurements presented throughout this paper have been taken after long term prepolarization, it is certain that the true electrode properties of molybdate are slightly better; *i. e.*, these measurements have been scanned at a quasi steady-state. The time dependence of the electrocatalytic activity undoubtedly proves that the final state of the electrocatalytic action of molybdate anions corresponds to extremely active *metallic form* of molybdenum. It would be rather difficult, however, to investigate the deposit experimentally since it dissolves immediately after any interruption in the cathodic polarization and optical methods could not be used in situ because of the intense gas evolution.

Linear potential sweep scans show a straightforward transition from MoO_2 to hydrogen evolution without any peak for metallic molybdenum deposition. However, the potential of hydrogen evolution at constant current density takes progressively more positive values until steady-state is established.

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Therefore, the electrocatalytically active metallic molybdenum must arise from direct reduction of molybdenum oxides by adsorbed protons during the intense hydrogen evolution. The activity extends over rather long time intervals (about four months), while the simple in situ reactivation takes place directly during the uninterrupted electrolytic process (Fig. 10).

The final state in molybdate—tris catalytic action certainly represents a codeposited submonolayer alloy of cobalt and molybdenum. Cobalt adatoms undoubtedly contribute to proton transfer and stimulate the total molybdate reduction to its final metallic state during their mutual codeposition with hydrogen evolution, both the activity and the surface area of the catalytic codeposit being increased and determined by the latter.

Electrocatalytic d-Metal Synergism in Practical Industrial Application

The synergetic electrocatalytic effect of two d-metals, molybdenum and cobalt, can be used in situ during the electrolytic process both in membrane and diaphragm chlorine cells by the simple addition of molybdate and tris in rather small amounts. Remarkably better polarization characteristics, especially at higher current densities can be achieved on nickel and nickel—plated iron compared to steel, titanium and graphite cathode substrates. An appropriate triple ionic combination of molybdate, tungstate and tris on a nickel substrate promises to give a cathode even closer to the reversible potential for the h. e. r., most particularly at higher electrode reaction rates, and this would be the main application (cf. ref. 18). Simple instantaneous reactivation and almost perfect polarization properties even for the dual Mo-Co anionic combination, comprises the most favourable advantage of this method in comparison with the other ones already described in the available literature.

The method can also be directly applied with equal catalytic effect in water electrolysis, preferably with a nickel cathode. More than 200 mV in voltage reduction has already been achieved by the described method.³⁶⁾

The tris—molybdate reactivation method could certainly greatly improve the individual molybdenum catalytic effect formerly achieved in mercury cell decomposers.¹⁾ The effect would be a higher concentration of caustic soda product approaching 73% NaOH, provided that either heat is supplied or heat losses are sufficiently decreased. Another benefit would be a considerable reduction in decomposer sizes, and thence in the mercury content. The best catalytic effect may be obtained by the impregnation of graphite cathode pieces with tris—molybdate mixture supplemented by continuous reactivation by adding not more than 0.2 ppm of molybdate to the demineralized water supply.

Titanium has recently become an important anode material for many

industrial electrolytic processes : membrane, diaphragm and mercury chlorine cells, water and sea water electrolysis, the chlorate cell process, hypochlorite production, organic electrosynthesis and bioelectrochemical reactions. Many bipolar cell designs require titanium to be used for the cathode material. Unfortunately, titanium is a poor electrocatalyst for the h. e. r. and suffers from hydriding embrittlement. The combination of tris and molybdate may solve both problems at the same time. In other words, titanium would operate as a current conductor of the first kind, and as a substrate for Co-Mo active centers, the entire electrode process being carried out by the latter while titanium is protected from hydriding. No significant decrease in titanium substrate weight, has been observed at 25°C during many months of continuous electrolytic hydrogen evolution with Mo-Co activation. Titanium both as the cathode and anode has recently become particularly important for bipolar chlorate cells and sea water electrolysis. Kuchinski and Kohanov³⁰⁾ have earlier pointed out that hypochlorite ions also efficiently suppress hydriding of titanium, iron and even tantalum especially at higher temperature. Thus the problem of titanium hydride formation during cathodic hydrogen evolution has been overcome to some extent.

The catalytic activation of the h. e. r. on various cathodic substrates in chlorate cells has so far been one of the most attractive goals in electrocatalysis and all achievements reported here were obtained in the search for the former. However, whatever is catalytically active for the h. e. r., is at the same time, equally or even more active for decomposition of the available chlorine and because of this side reaction, the goal has still not been attained. Some other anionic cobalt complexes, which were expected to be inactive for available chlorine degradation have also been tried, *e. g.*, cobalt-tetraphenylporphirin (Co-Pr) and cobalt-phthalocyanin (Co-PC), but tris has exhibited the best catalytic properties for the h. e. r. Moreover Co-Pr undergoes chlorination and thus could hardly be used in an environment of available and most particularly elemental chlorine. At the same time, whatever the behaviour of complex cobalt species in the solution, the resulting active metallic form on the cathode surface instantaneously dissolves whenever any interruption in the cathodic protection occurs, and Co (II) ionic species which arise therefrom, appear to be a strong catalyst for both available chlorine and chlorate decomposition. It is important to observe here that although iridium ions appear as even stronger catalysts for available chlorine degradation, metallic iridium alloyed with platinum has recently been used for coating catalytic titanium anodes. In the course of chlorine evolution, iridium dissolves in rather small amounts as colloidal particles and appears harmless

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for the available chlorine. Therefore, to use any d-metal catalytic combination in the chlorate cell process with continuous electrolyte recirculation, one has to solve the problem of keeping it permanently in the catalytically active state even when cathodic protection ceases.

Another problem arises associated with the dichromate ions which are almost unavoidable for chlorate production. The latter undergoes partial cathodic reduction to a semipermeable polyoxide membrane, which effectively suppresses cathodic hypochlorite reduction, but at the same time progressively reduces the catalytic activity of molybdenum.⁷⁾ Dichromate partially inactivates even the synergetic Co-Mo combination and therefore, according to Wagner's theory²⁹⁾, the electrode exhibits a certain selectivity amongst anionic species due to which the chromate overcomes the effect of molybdate. At the same time a much higher effective current density on the active centers of the catalyst means an efficiently suppressed cathodic hypochlorite reduction^{31,32)} regardless of the dichromate. Thus, one might either replace dichromate with another suitable buffer system like phosphate, or reduce the chromate content and provide a proper d-metal synergetic electrocatalytic effect. Therefore, the catalysis of the h. e. r. in the chlorate cell process still seems far from a solution. A combination of Mo-W with extremely small amounts of cobalt anionic complexes in the solution, just for the activation, may be harmless for available chlorine decomposition, and promises to be a possible way to improve the polarization properties of the chlorate cell cathode.

The tris—molybdate activation method appears particularly simple and efficient for sea water electrolysis and hypochlorite production, which is characterised by low temperature and continuous single stage flow (no recirculation). The method could equally well be applied to all anodic electro-organic processes accompanied by cathodic hydrogen evolution regardless of the substrate electrode material.

The effect of any dual and triple synergetic d-metals could improve the electrocatalytic properties of some substrate electrode materials for the h. e. r. even in acidic media if the flux of hydroxyl ions from the cathode exceeds the hydronium ionic flux towards it, *i. e.*, if hydrogen evolution takes place from an alkaline diffusion layer and represents the reduction of water molecules. However, when the flux of hydronium ions predominates, the catalyst will not be cathodically protected from dissolution. This is the reason why the method reported in this paper could not be used in the electrolysis of hydrochloric acid.

Some Engineering Aspects of Electrocatalysis and Concluding Remarks

The exchange current density is the main kinetic parameter to classify electrodes from the electrocatalytic point of view. Thus, almost all fundamental conclusions in electrocatalysis have been derived under zero current conditions close to the reversible potential of the unpolarized electrode. On the other hand, the engineering approach takes into account the polarization properties and depolarization effects at definite reaction rates (the current density). An ideal electrode from both the engineering and the fundamental viewpoints would be one that has a potential close to the reversible value within a wide range of the current density. The final electrochemical engineering goal in electrocatalysis for practical application is to lower the slope of the Tafel lines at higher current densities, ideally to zero. However, the lower the slope, the lower also is the intercept and therefore the lower the exchange current density. Therefore, the engineering approach to electrode properties is mainly based on the value and the rate of overpotential change vs. definite current densities and, hence, has to fill the gap between fundamental criteria and practical parameters in applied electrocatalysis. In other words, the basic engineering criterion for electrocatalytic achievements should be the polarization gradient of the Tafel line $(\partial\eta/\partial \ln i)_i$ at constant reaction rate rather than the exchange current density. Reversible electrode behaviour therefore would be characterised by $(\partial\eta/\partial \ln i)_i=0$, regardless of the value of the latter (i_0). According to the just stated criterion the nickel substrate electrode has been brought nearly to perfect reversible behaviour by the synergetic electrocatalytic effect of dual d-metals combination (Mo-Co) in alkaline solutions.

In the final conclusion one could state that the synergetic d-metal electrocatalytic activation method provides better polarization characteristics for the h. e. r. than any individual metal could exhibit, even exceeding precious metals themselves. What further could be done? The present method has traced the path to approach a zero slope Tafel line by a proper combination of triple d-metals so that the current density range will correspond to a reaction rate of 1,000 mA/cm², in other words to achieve a true reversible electrode for the h. e. r. at reasonably high current densities. Such an achievement, as well as the theoretical predictions for the electrocatalytic behaviour of various d-metals combinations, based on their interelectronic structure and interorbital synergism, will be presented elsewhere.

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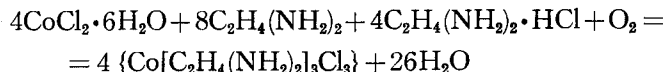
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Appendix

The synthesis of tris-ethylenediamine cobalt (III) chloride was carried out as follows: First, 60 gr 30% ethylenediamine solution was partially neutralized in a 500 cm³ reagent flask with 15 cm³ of 6 N hydrochloric acid followed by addition of CoCl₂·6H₂O (about 0.1 mol) dissolved in about 80 cm³ of water. Second, Cobalt (II) was further oxidized to Co (III) by aeration with a mild stream of air for about 90 minutes. Third, the solution was evaporated in a water bath until a membranous film formed on the top, and then about 15 cm³ of concentrated hydrochloric acid and 30 cm³ ethanol was added. After cooling, tris crystals were separated on Buchner funnel and washed until the filtrate became colorless. Finally, the product was washed with ether and dried. The yield was about 90%.

Tris-ethylenediamine cobalt (III) chloride was in the form of orangeyellow needle-shaped crystals which easily dissolved in water, but were insoluble in many common organic solvents.

The reaction stoichiometry :



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