

Electrolytic Deuterium/Hydrogen Isotope Separation: Temperature Dependence and *In Situ* Activation Effects

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Electrolytic separation of hydrogen isotopes has been investigated as a function of temperature and *in situ* activation of electrodes. A tris(ethylenediamine)cobalt(III) chloride complex was used as the activating agent. Several methods, such as XRF, XRD, SEM and both IR and UV–VIS spectrophotometry, have been employed to characterize electrodes and electrolyte. On this basis possible mechanisms have been suggested and their contribution to the values of the isotope separation factors is discussed.

The subject of the present article is an investigation of isotope separation (H/D) by water electrolysis in alkaline electrolytes and with *in situ* activation of the electrodes. Such an activation was substantiated by employing tris(ethylenediamine)cobalt(III) chloride as the activating agent. The main purpose of this work was to indicate a possible interpretation of *in situ* activation mechanisms and their contribution to the isotope separation factors achieved.

Various authors have applied different techniques to improve the efficiency of electrolysis as an isotope separation method. The purity of the cathodic surface plays an important role in the electrolytic separation of isotopes,^{1,2} although it is impossible to maintain the surface in a perfectly clean state all the time. Methods involving scavengers or displacement¹ were developed to maintain and control the surface conditions.

It has also been shown³ that the addition of some carbon- and nitrogen-containing compounds with polarizable π -bonds to the electrolyte increases the separation factor, apparently because the active compounds are adsorbed on the cathode surface and interfere with the exchange process.

Experimental

The experimental setup, consisting of an electrolytic cell, an evolved-hydrogen dryer, a sample cell, a cryostat and a power supply, has been described in detail elsewhere,⁴ as has the electrolytic process.

The electrolyte was a 30 wt % aqueous solution of KOH in which the deuterium concentration was about 1000 ppm. Each electrode, before entering the electrolytic cell, was

carefully prepared. It was first mechanically cleaned, then treated chemically with hydrochloric acid (1 + 5, v/v). Nickel electrodes were polished with metallographic carborundum paper, and the treatment was finished by successively increasing the fineness of the grist to 600 mesh. Finally, all electrodes were washed in ethanol.

A mass spectrometer, model SIRA 12(VG-ISOGAS), was used for the isotopic analysis. The precision of the mass spectrometry method was within ± 0.2 ppm. D. Isotope separation factors were determined with an error of $\pm 5\%$.

Several methods, such as X-ray fluorescence analysis (XRF), X-ray diffraction (XRD), infrared absorption spectroscopy (IR), scanning electron microscopy (SEM) and UV–VIS spectrophotometry were used to investigate changes on the electrode surfaces (the deposits obtained) and electrolyte in the electrolytic process.

The apparatus for XRF comprised a lithium-drifted silicon detector and a Canberra Omega multichannel analyser which was connected, through an interface, to a personal computer for automatic data handling.⁵ The detector's resolution was 250 eV (FWHM at 5900 eV). The excitation source was a radioisotope, ¹⁰⁹Cd.

XRD measurements were made using a Siemens Crystalloflex 4 X-ray diffractometer. A direct beam from a copper tube (35 kV, 18 mA, Ni filter) was used for the excitation of the sample's characteristic X-rays.

IR spectra were recorded with a 983 G Perkin Elmer spectrophotometer using the KBr pellet technique.

The morphology of the deposit was investigated using a JSM-35 scanning electron microscope (SEM). The tilt angle was between 0 and 30° and the magnification was up to $\times 10000$.

A spectrophotometric analysis of the electrolyte used in the process was performed using a Beckman 5260 spectrophotometer with a 1.00 cm silica cell.

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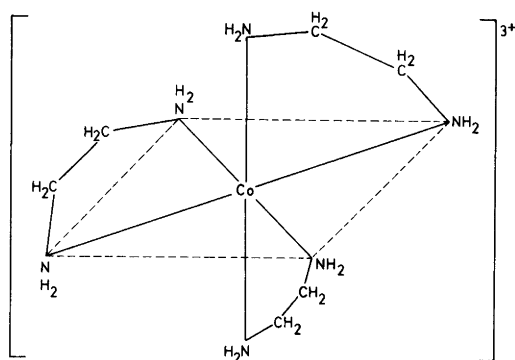


Fig. 1. Structural formula of the tris(ethylenediamine)cobalt(III) ion.

Experiments were carried out at specified temperatures. If not specified, the temperature was 20°C and the current density was 25 mA cm⁻² (for the Ni cathode only). The ionic activator used for *in situ* activation was the tris(ethylenediamine)cobalt(III) chloride complex (Fig. 1). This is an octahedral, low-spin (*t_{2g}*) stable complex with three bidentate ligands. The experiments were carried out with both a commercial sample and one synthesized in our laboratory.⁶

Results and discussion

All values of the separation factors were evaluated from the concentration data obtained after at least 6 h of continuous electrolytic processing, a length of time that was sufficient to establish steady-state conditions [Fig. 2 (Δ)]. The results obtained with various cathode materials are collected in Table 1.

Some of the intermetallics used as cathodes in alkaline water electrolysis increased the initial values of the separation factors significantly (one even doubled it) when activated *in situ* with the tris(ethylenediamine)cobalt(III) chloride complex. These increases in separation factors are of theoretical and practical significance and deserve serious theoretical consideration. The best results were obtained with a concentration of 10⁻² mol dm⁻³ tris-Co complex [Fig. 2 (\circ)].

Owing to electrolysis the cathodes were coated with fine, black deposits and the electrolyte became discoloured. At the same time the separation factors increased. Characterization of these deposits and of the electrolyte after the electrolysis could be the key to determining possible mech-

Table 1. Comparison of the electrolytic separation factors.

Cathode	α	α_1^a	α_1/α
Ni	7.6	10.0	1.32
Ni-V (70–30 %)	4.7	9.4	2.00
Fe-Mo (70–30 %)	4.2	6.0	1.43
Fe-Mo (60–40 %)	4.0	6.8	1.70

^a α_1 – *In situ* activation with tris-Co complex ($C/10^{-2}$ mol dm⁻³).

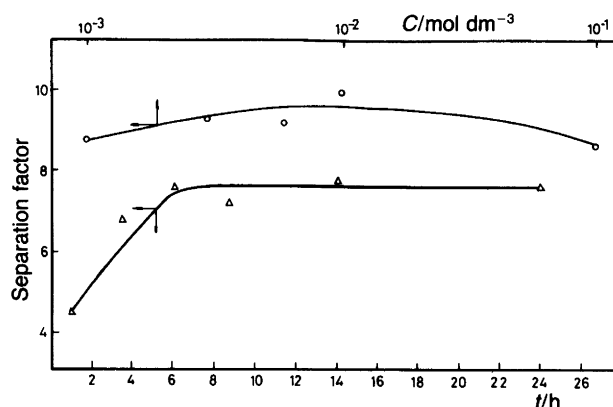


Fig. 2. \circ , Separation factor of cathodes activated *in situ* as a function of tris-Co complex concentration. Δ , Separation factor as a function of time, without *in situ* activation.

anisms to improve the separation factors by the choice of the complex compound added.

A structural characterization of a typical black deposit on a Ni substrate, resulting from cathodic reduction of the tris-Co complex, was carried out by XRF, XRD, IR spectroscopy and SEM. The electrolyte was investigated by UV-VIS spectrophotometry.

The XRF spectrum (Fig. 3) indicated only the presence of Co in the cathode deposit, resulting from successive reductions of Co(III) during the electrolytic process and its attachment to the cathode surface.

XRD (Fig. 4) indicated, on the basis of the (100), (002) and (101) reflections of Co, the presence of α -Co with a hexagonal close-packed (h.c.p.) crystalline structure.

In the IR absorption spectra (Fig. 5), in addition to the strong band at about 3400 cm⁻¹ and the band at 1600 cm⁻¹, which correspond to the stretching and bending OH vibrations of lattice water, and/or aquo- (H₂O-) complexes, a few weak bands below 1200 cm⁻¹ are present. These bands

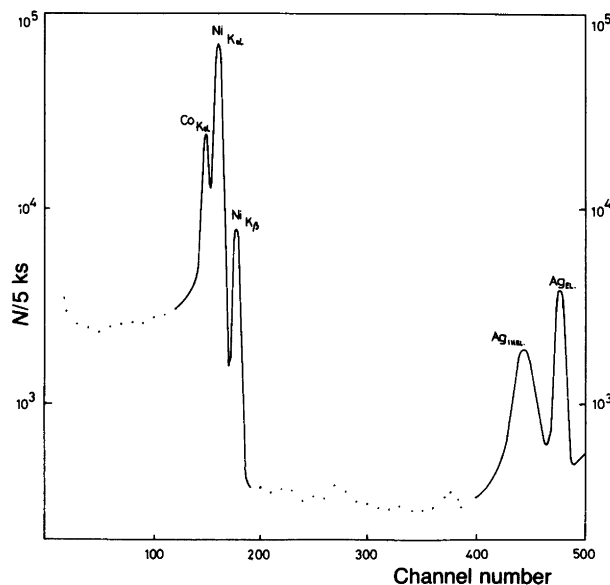


Fig. 3. XRF spectrum of nickel cathode with deposit.

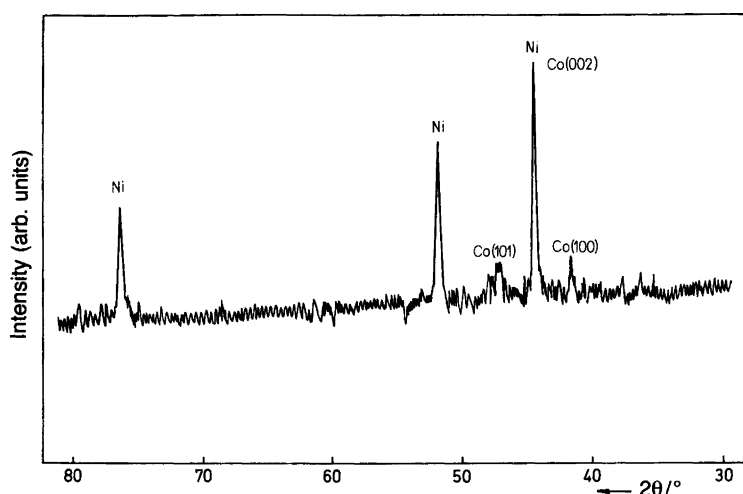


Fig. 4. XRD spectrum of nickel cathode with deposit.

could be assigned to coordinated water and/or OH groups in hydroxo complexes.

In general, hydroxo complexes exhibit $\nu(\text{OH})$, $\delta(\text{MOH})$ and $\nu(\text{MO})$ bands at 3760–3000, 1200–700 and 900–300 cm^{-1} , respectively.^{7,8}

Some parallel reactions, such as nucleophilic substitution of the ligands with OH^- ions from the electrolyte to form a hydroxo complex (with greater probability than the aquo complex in the solution described), and the successive reduction of Co^{3+} followed by its attachment to the electrode surface together with the electrolyte constituents, could be assumed. Those constituents, like water, could be trapped (occlusion) in the h.c.p. crystalline lattice of cobalt attached to the cathode surface. This is a possible explanation of the presence of IR bands beyond 1100 cm^{-1} and bands at about 3400 and 1600 cm^{-1} , respectively.

The morphological characteristics of different cathodic and anodic products arising from tris-Co reduction and oxidation are shown in SEM microphotographs (Fig. 6). Cathodic deposits exhibit a regular spherical shape (a), while the anodic ones are both needle- and plate-like particles (b).

The dimensions of spherically shaped deposited particles decrease with decreasing temperature [Figs. 6 (c) and (d)], a result that may be associated with the higher separation factors at lower temperatures (Table 2), as obtained at the Ni cathode activated *in situ* with 10^{-2} mol dm^{-3} tris-Co complex. The negative temperature coefficient of the separation factor is in accordance with theoretical considerations.⁹

The similarity between the absorption spectra of the tris(ethylenediamine)cobalt(III) chloride complex in distilled water and in a strong alkaline solution $C_{\text{KOH}}/5.4$ M, $H_- = 15.6$,¹⁰ at the time of preparation and after 14 months [Figs. 7 (a)–(c)] demonstrated its high stability. As a result of the electrolytic process during a long period of time, a decrease in the complex concentration, owing to the electrolytic reduction of Co^{3+} , is correspondingly noted [Fig. 7 (d)].

The data presented in the paper show a general agreement with those obtained in similar attempts by other authors.^{1,2,3,11} First, it means that the separation factor α depends on the mutual effect of cathode features and electrolyte composition. Secondly, a cleaned cathode surface

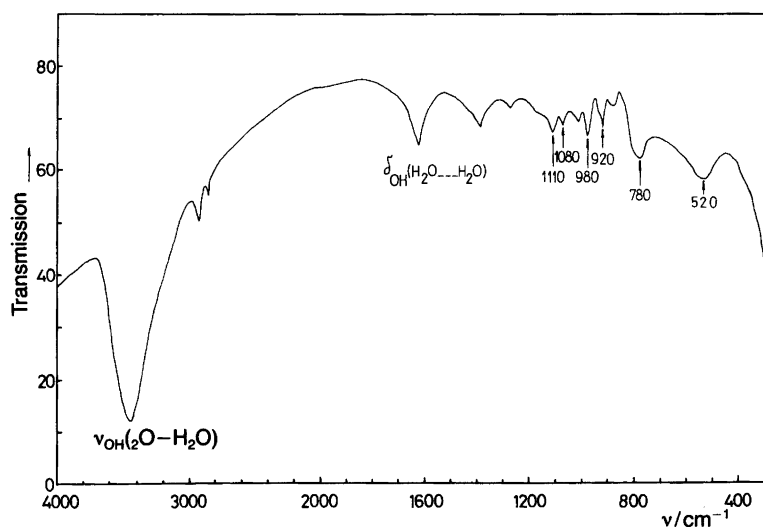


Fig. 5. IR spectrum of cathode deposit.

Table 2. Temperature dependence of electrolytic separation factors obtained at Ni cathode activated *in situ* by tris-Co.

$T/^{\circ}\text{C}$	α
-20	11.9
-15	11.5
-10	11.6
0	11.0
10	10.6
15	9.4
20	10.0
23	8.8
30	8.9

gives higher separation factors. Thus it is important to maintain the electrodes in appropriate conditions. One method frequently employed is to make a continuously growing surface of freshly deposited metal (the 'scavenger'

effect), or to remove or displace other impurities from the surface by adding a certain 'undermining' agent (the 'displacement' method). A group of activating agents of the above types is listed in Ref. 1.

On the basis of a similar idea various compounds were employed in the present work⁴ for the *in situ* activation of electrodes, and correspondingly remarkable increases of α with the tris-Co complex were obtained (Table 1). In addition to a significant electrocatalytic effect in the overpotential (for HER, the hydrogen evolution reaction), a decrease has also been achieved by *in situ* addition of the same complex to the alkaline electrolyte.¹² A possible mechanism for H/D separation probably consists of an alteration of the overvoltages for H and D evolution by the freshly deposited and cleaned metal from the activating complex, and more particularly the difference in overvoltages which leads to higher separation factors.

The Rowland effect^{1,2,11} of an *in situ* cleaning ('under-

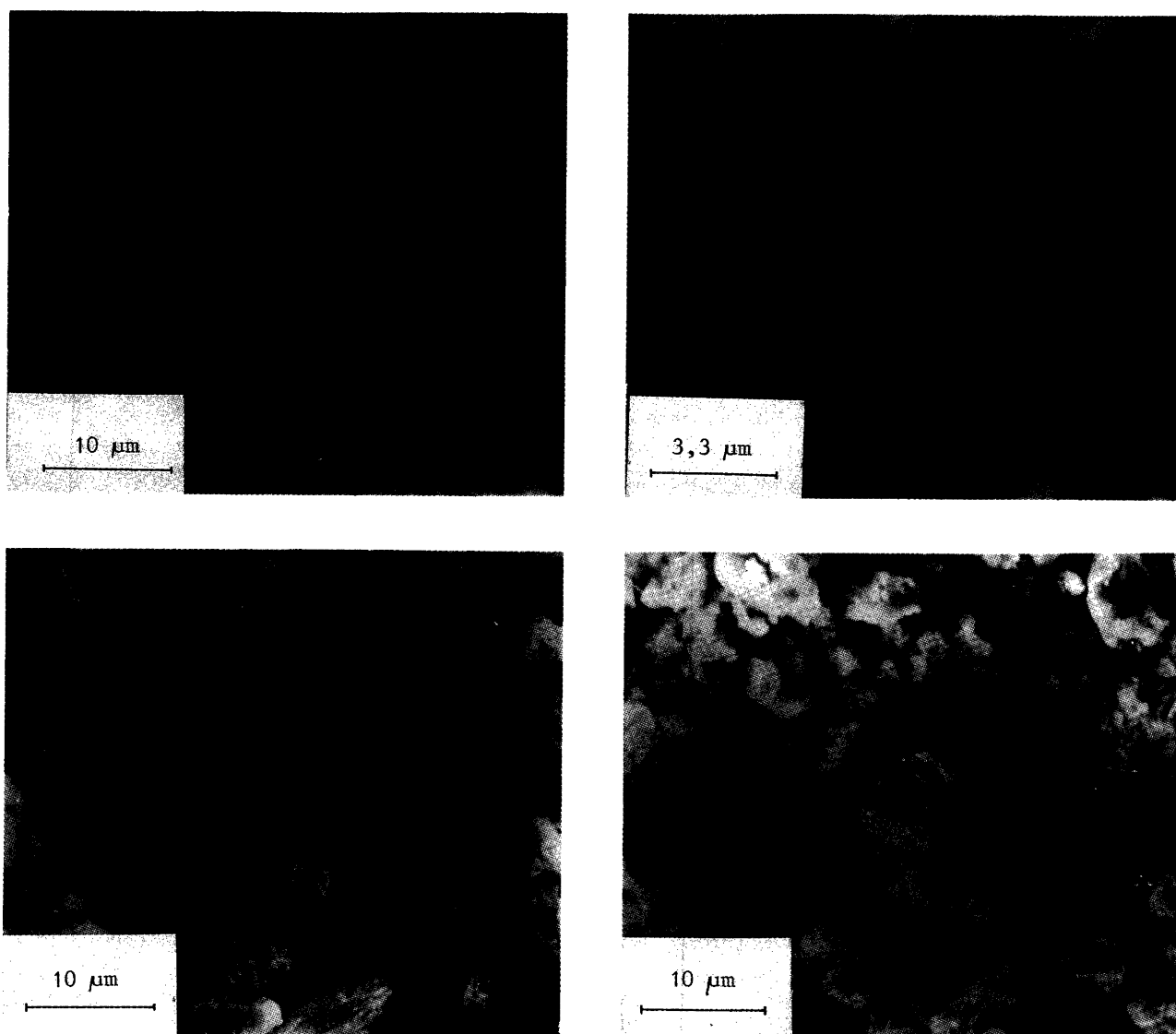


Fig. 6. SEM microphotographs of electrode deposits: (a) cathode deposit, (b) anode deposit, (c) cathode deposit ($T = -15^{\circ}\text{C}$), (d) cathode deposit ($T = -20^{\circ}\text{C}$).

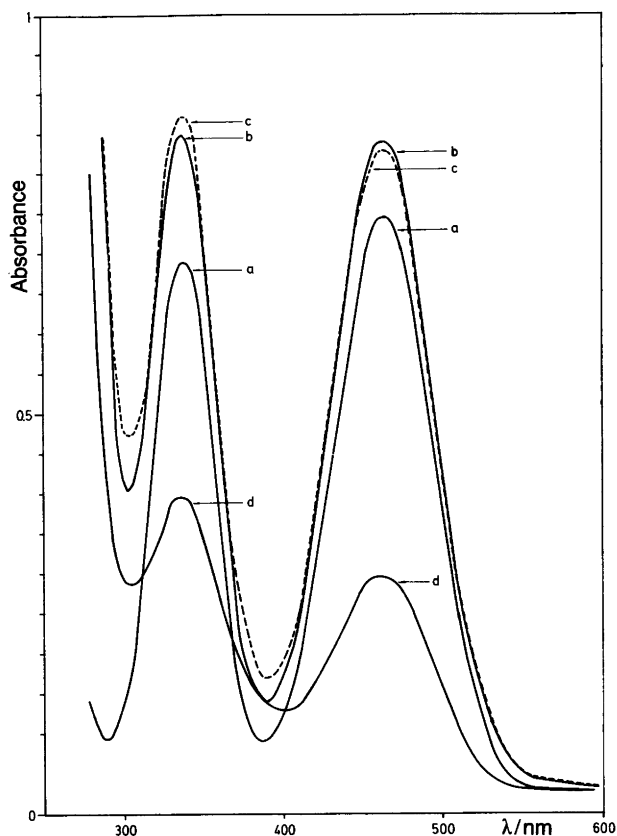


Fig. 7. UV-VIS absorption spectra of: (a) tris-Co complex (10^{-2} mol dm^{-3}) in distilled water; (b) tris-Co complex (10^{-2} mol dm^{-3}) in 30 wt % KOH, 0.1 mol % D_2O for electrolyte in process; (c) tris-Co complex (10^{-2} mol dm^{-3}) after 14 months; (d) catholyte after the electrolytic process.

mining') of oxide layers on the electrode substrate, achieved by the complex chelating action of EDTA (ethylenediamine tetraacetic acid), has now been advanced by the tris-Co complex. In other words, the ethylenediamine ligand of the tris-Co complex takes the role of an *in situ* cleaner of a particular site. At the same time, cobalt is electrodeposited from the same complex molecule, providing an extremely fine structure and developed surface that exhibits highly active electrocatalytic properties.⁴

Brewer intermetallic phases of hypo-hyper-d-electronic combinations of transition metals, which exhibit highly active synergetic electrocatalytic properties for hydrogen evolution,^{13,14} have often been advanced in D/H separation by the tris-Co complex, even in doubling the separation effect.

The answers to many of the questions posed here should be found in separate measurements and comparisons of

overvoltages for hydrogen and deuterium evolution in pure light and pure heavy water with and without *in situ* activation; this is the next step of the presented investigation.

In all electrolytic isotope separation experiments special care should be devoted to the possible consecutive reactions of isotope exchange between hydrogen and water [eqn. (1)] which takes place only in the presence of a catalyst.



If electrodes are made from a catalytic material the overall separation factor should be a function of the two processes, electrolysis and the chemical exchange of isotopes. One list of such materials, along with their catalytic efficiencies for reactions of the above type, is given in Ref. 15. A comparative study is in progress.

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