

Ionic activators in the electrolytic production of hydrogen—cost reduction-analysis of the cathode

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Abstract

As recent technology progress makes hydrogen a realistic long-term energy option with little or no pollution, development of new methods for its production and improvement of conventional technology is important. In spite of the fact that, among overall world technologies for hydrogen production today, only 4% is produced by electrolysis, this is the most promising method in the future as a consequence of the high existing water supply. The limitation factor for its use on the large scale is well known-high energy consumption.

In this work, methods for increasing efficiency and lowering the energy consumption in the electrolytic hydrogen production are presented. The stability of ionic activators, as an indicator of capital cost, are also shown, as are an analysis of composition, structure and morphology characteristic of cathode, formed in the presence as ionic activators.

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1. Introduction

Hydrogen production *via* water electrolysis promises to be of great future importance, especially in countries with cheap electrical energy. Therefore, the development of high-efficiency electrolytic method represents the first step towards the improvement of the hydrogen economy.

There were various attempts to improve the electrolytic process with increasing efficiency and lowering carbon emissions, and to make electrolysis an acceptable method for hydrogen production, with the idea to adjust all aspects of “hydrogen philosophy” with sustainable development.

In our previous work [1], we investigated methods for improvement in the electrolytic method for hydrogen production from alkalyne solution and Ni-based electrodes, by adding ionic activators into the electrolyte and changing cell geometries. Two types of activators, either tris(ethylenediamine)Co(III) chloride complex on tris(trimethylenediamine)Co(III) chloride complex, gave the best effect in combination with Na–molybdate. It is also known from the literature that the combination of these two d-metals (Co–Mo), from the two branches of Balandin’s volcano

curve [2], creates a remarkable electrocatalytic effect for the hydrogen evolution reaction (HER), most particularly when added *in situ* during the electrolytic process [3–5]. This is a very simple method for increasing the efficiency of the electrolytic process that does not require high technology.

As the result of our previous work [1] activation with these combinations of ionic activators reduces the energy needs per mass unit of hydrogen produced by more than 10% in some cases, compared with those of non-activated electrolytes.

The idea of this work was to investigate the activator’s stability in order to estimate the true energy consumption and cost reduction in the electrolytic production of hydrogen and possible use of this method on a large scale. In addition, our previous results, connected with the reduction of energy consumption, allow an analysis of the composition, structure and morphology characteristic of cathode and an exact determination of the influence of the added ionic activator on the mechanism of electrolytic hydrogen production.

1.1. Theoretical consideration

The catalytic activity of various metals for the HER is a periodic function of the atomic number within the three long transition periods of the Periodic Table of Elements [6,7],

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the exchange current density being the measure of it. Thus it has been qualitatively noted from the electronic configuration of outer shells of the elements in their ground state that the catalytic activity first increases with the increase of the d-electrons, reaches its maximum at nearly filled d-orbital (at about d^8 -electrons), then 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- and subsequent d-orbitals.

It has been shown that there is synergism in the catalytic activity for HER in the combination of two or more d-metals from different part of transition series, one from the left and the other from the right half. Besides this synergetic effect, the proper co-deposition of such d-metals (from two branches of Balandin's volcano curve) improves and even exceeds the electrocatalytic activity of the platinum group of metals and provides a large surface area of active centers [4,5,8–11]. Cobalt, both in the metallic lattice and in its individual cationic and complex forms, appears to be a good proton transferring species [12].

2. Experimental

All experiments have been carried out similarly to ones described previously [1]. The experimental set-up consisted of the electrolytic cell (a simple glass-made cell of defined geometry), a thermostat/cryostat and a power supply.

In the experiments, the time of evolution of a certain volume of cathodically evolved hydrogen was measured using a U-tube water manometer, along with overall voltage across the cell at proposed temperatures and current densities. All these values were recorded to calculate the corresponding energy consumption.

Nickel electrodes were used. The standard electrolyte was 30 wt.% KOH. As the ionic activator, based on our previous results [1], the following combination was used: $1 \times 10^{-3} \text{ mol dm}^{-3}$ tris(ethylenediamine)cobalt(III) chloride, $[\text{Co}(\text{en})_3]\text{Cl}_3$, and $1 \times 10^{-2} \text{ mol dm}^{-3}$ sodium molybdate, Na_2MoO_4 , in standard electrolyte.

Scanning electron microscopy (SEM), energy dispersive X-ray fluorescence analysis (EDXRF) and UV-Vis spectrophotometry were used to characterize the cathode and changes in the electrolyte after the electrolytic process.

The morphology characteristics of cathode were investigated using JSM-35 scanning electron microscope (SEM). The tilt angle was between 0 and 30° and the magnification was up to $10,000\times$.

The apparatus for energy dispersive X-ray fluorescence spectrometry (EDXRF) comprised a lithium-drifted silicon detector with a Be window and multichannel analyzer (manufactured by Canberra Ind.) connected to a computer for automatic data handling. The detector's resolution was 156 eV (FWHM at 5.9 keV). The samples are excited by the radiation from radioisotopes ^{109}Cd (22.1 keV) and ^{241}Am (59.6 keV), and the intensities of characteris-

tic X-rays, emitted from the samples are related to their concentrations.

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

3. Results and discussion

The experimental conditions were as follows: current range from 100 to 280 mA (current density range: from 14.7 to 41.1 mA cm^{-2}); the temperatures were from 255.5 to 323 K (from -17.5 to $+50^\circ\text{C}$).

The data obtained are divided in two parts.

3.1. Long-term run electrolysis

We have shown here that one fill of the activator at low concentration as given above, can maintain the energy consumption at a level which is lower than in the non-activated case by up to 10% (Fig. 1). Actually, that consumption decreases to the value typical for the 'activated systems' immediately after the activator is added, and stays at that level for the next 16 days at a current of 250 mA. Under these conditions, the calibration vessel of 30 cm^3 volume was filled with hydrogen within 16.5 min. After all the activator is spent the energy consumption exhibits a steep rise to the 'non-activated' level. Refilling with the starting concentration of ionic activators, calculated for the 70 ml volume of the electrolytic cell, three times during the 50-day experiment, recovers the efficiency of the system entirely. This means that the electrolytic system remains stable with time. A simple calculation has shown that the consumption of activators, including the starting concentration and three additions of activators, is roughly 0.04 g of tris(ethylenediamine)Co(III) chloride complex and 0.25 g of Na-molybdate per 0.13 m^3 (about 6 mole) of hydrogen generated since this is the total amount of hydrogen produced during 50 days, at the specified current of 250 mA.

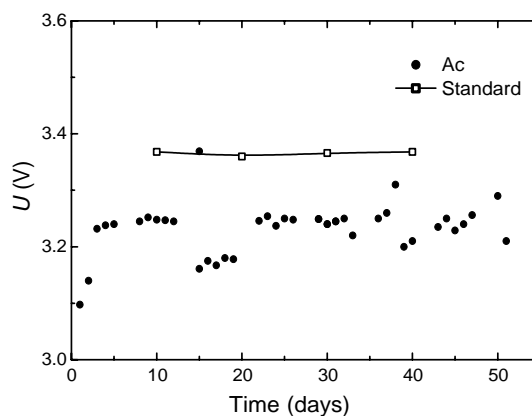
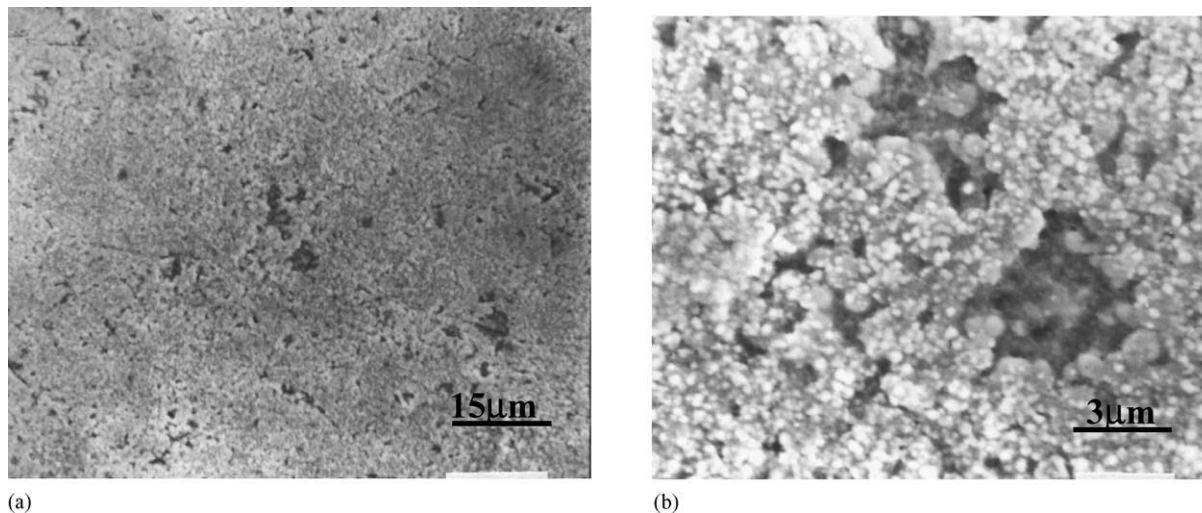


Fig. 1. Long-term run electrolysis ($I = 250 \text{ mA}$). Illustration of the stability of the ionic activator.

Table 1

Cost reduction in the electrolytic hydrogen production, using the ionic activator presence; $I = 250$ mA

Energy consumption: about 4.5–5 kWh/m ³ _n H ₂ (electricity price \cong 0.1 €/kWh ^a)	10% of reducing consumption: about 0.45–0.50 kWh/m ³ _n H ₂
Investment (technical chemicals; large amounts): 0.01 €/m ³ _n H ₂	Cost reduction (in the energetic sense): 0.05 €/m ³ _n H ₂ + Co-powder

^a Data sources: Eurostat, Energy Market.Fig. 2. SEM microphotographs of the cathode: (a) magnification 670 \times and (b) magnification 3300 \times .

The price for the activator is about 0.01 €/m³_n H₂.¹ Since the quantities added are very small, they do not have any significant influence on the economy of the process (as shown in Table 1) against the energy saving obtained.

The calculated savings in the electrolytic hydrogen evolution process, due to the use of the ionic activator, were 0.04 €. From the economical aspect it is interesting that the cathode surface (when [Co(en)₃]Cl₃ is used as ionic activator) is comprised at α -Co with hexagonal close-packed (h.c.p) crystalline structure, (obtained by XRD method (X-ray diffraction) in our previous work [13]). The cobalt powder could be a by-product of the electrolytic hydrogen evolution process. The approximate quantity of cobalt powder for the fifty-day experiment duration, based on XRF spectra and a calibration curve, is estimated to be about 0.02 g. The price for this quantity of cobalt powder is 0.005 € (250 €/kg Co., Aldrich, Catalog Handbook of Fine Chemicals, 2000).

3.2. Analyses of the cathode and changes in the electrolyte after the electrolytic process

Following the electrolytic process the cathodes were coated with a fine, black coating. Since this coating is likely to be involved in the possible mechanisms through which

the activator decrease energy consumption, its characterization is necessary.

A structural characterization of the coating on the Ni cathode was carried out by EDXRF and SEM. The electrolyte, after the electrolytic process, was investigated by UV-Vis spectrophotometry.

The morphological characteristic of the cathode and anode surfaces on the nickel are presented in the SEM microphotographs, Figs. 2 and 3. The cathode surface (Fig. 2a and b) exhibits a regular arrangement of small spherical grains. Besides the existence of these very fine particles, nickel is also visible. The anode surface (Fig. 3a and b) exhibits both needle- and plate-like zones. These zones look like a cascade erosion of the cathode material (Fig. 3a) with a significant distribution of particles on the edges. The distribution of particles is linear, homogenous and grouped with an approximate dimension of 1 μ m (Fig. 3b).

The EDXRF spectra, presented in Fig. 4a and b, indicate the presence of Co and Mo in cathode surface layer, resulting from their successive reductions during the electrolytic process. The results, obtained by EDXRF analysis, for the cathode and the standard, are presented in Table 2. On the basis of the results obtained, and the calculated detector efficiency (from the standard sample), the estimation of the cobalt/molybdenum ratio indicates the presence of cobalt in larger quantity than molybdenum, approximately 100:1.

The investigation of the electrolyte after the electrolytic process is also necessary in order to determine the role of different influences on the reduction of energy consumption.

¹ Estimated money amount based on the activator price (technical grade chemicals) of around 50 €/kg for both components.

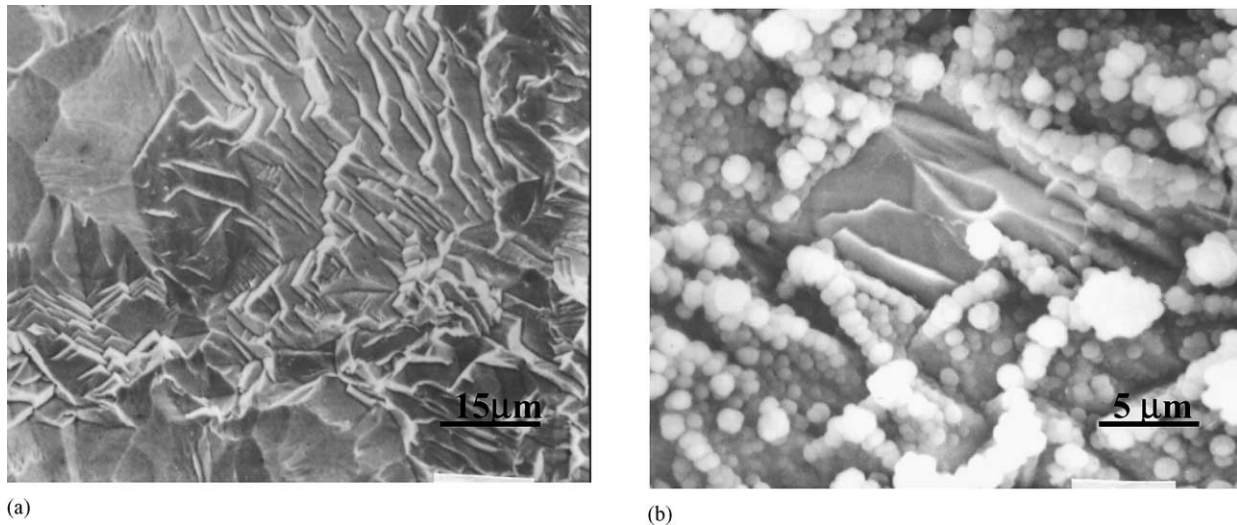


Fig. 3. SEM microphotographs the anode: (a) magnification 670 \times and (b) magnification 2000 \times .

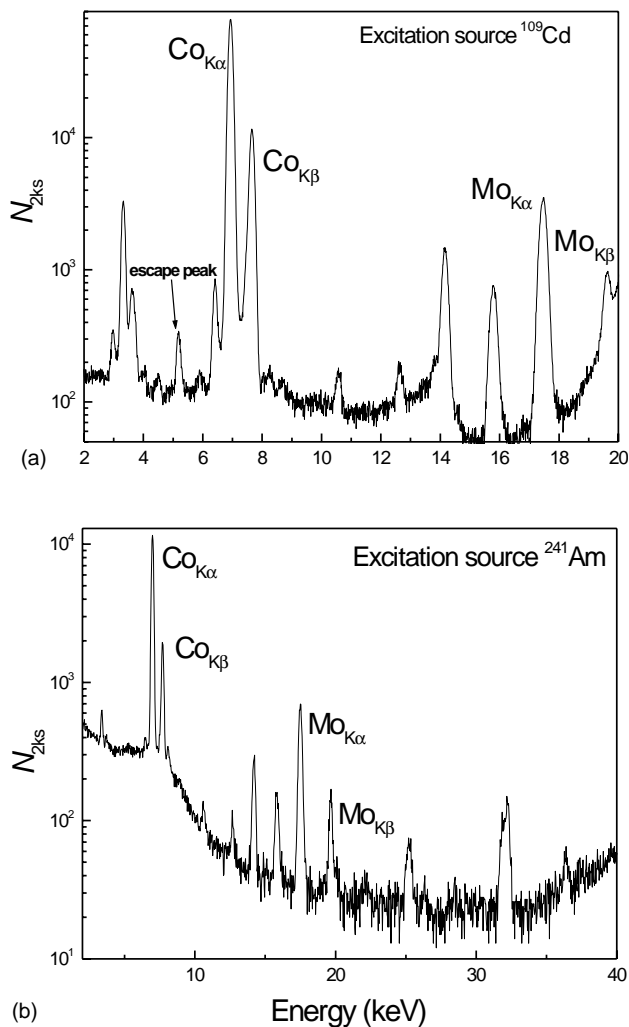


Fig. 4. EDXRF spectrum of the cathode: (a) ^{109}Cd excitation and (b) ^{241}Am excitation.

The absorption spectra obtained in UV-Vis region, are shown in Fig. 5. As a result of the electrolytic process, and consequently cathode surface coating formation, a decrease in the complex concentration is noted (Fig. 5).

Numerous effects of individual and/or composite influences of ionic activators added into the electrolyte could make specific contributions to the possible mechanism of the electrolytic efficiency increase.

As a consequence of Rowland's effect [14], the active electrode surface becomes more developed, due to the presence of ethylenediamine ligand, which cleans the electrode surface and prepares it for the deposition of metals.

An explanation of the mechanism must be valid for a decrease of energy consumption when the ionic activator, with a concentration of $1 \times 10^{-3} \text{ mol dm}^{-3}$ tris(ethylenediamine)cobalt(III) chloride, $[\text{Co}(\text{en})_3]\text{Cl}_3$, and $1 \times 10^{-2} \text{ mol dm}^{-3}$ sodium molybdate, Na_2MoO_4 , in standard electrolyte, was used. The presence of Co and Mo in the cathode surface (Fig. 4a and b), as a consequence of the electrolytic process, and appearance of SEM microphotographs (Fig. 2a and b) suggest that an alloy created at the cathode substrate surface is extremely active, providing a very large surface area of active centers. The role of the transition complex as a "bridge" for hydrogen transfer from the electrolyte to the metal surface is also significant.

All these influences place a part in the overall mechanism of energy consumption decrease obtained in this work.

Table 2
The results of EDXRF analysis

Sample	^{109}Cd ($N/2ks$)		^{241}Am ($N/2ks$)	
	Co K α	Mo K α	Co K α	Mo K α
Standard (15 wt.% Co, 16.2 wt.% Mo)	51062	287719	15874	122946
Cathode	78449	3529	11580	697

Excitation sources: ^{109}Cd and ^{241}Am ; N : intensity for measuring time of 2000 s.

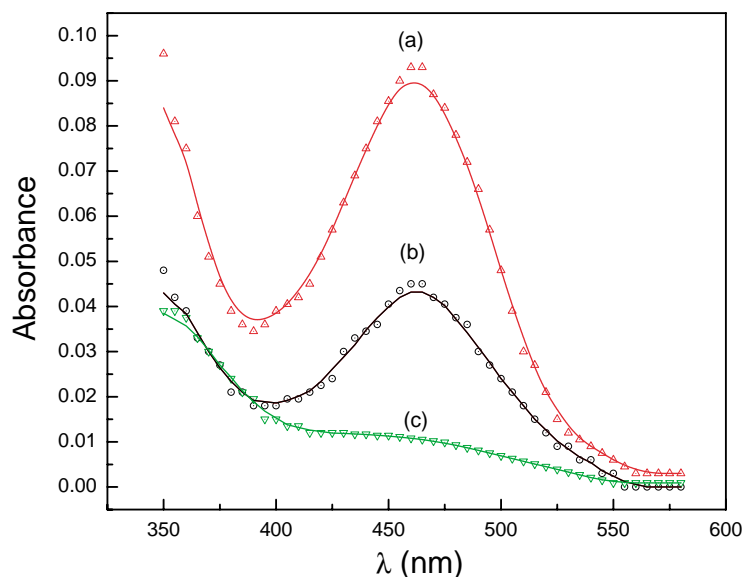


Fig. 5. UV-Vis absorption spectrum of: electrolyte (a); catholyte (b) and anolyte (c) after the electrolytic process.

4. Conclusion

A Co–Mo co-deposit formed in situ during hydrogen evolution appears extremely active. This electrocatalytic achievement appears valuable in view of the significant cost reduction that is presented here through the investigation of the activator stability which is relevant for the possible use of this method on a large scale.

Structural and morphological characterisation of the cathode surface layer and an analysis of the electrolyte indicate a combined influence of different effects on the decrease of energy consumption in the electrolytic production of hydrogen.

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