

# Hydrogen generation from water electrolysis—possibilities of energy saving

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## Abstract

Hydrogen production via electrolysis of water from alkaline aqueous electrolytes is a well-established conventional technology. However, due to high energy requirements of about 4.5–5 kWh/m<sup>3</sup> H<sub>2</sub> in most industrial electrolyzers, the cost of hydrogen produced in such a way is high. This is a limiting factor for the use of this method on a large scale, except in countries where the electricity is very cheap.

There were various attempts to improve this process, like zero-gap cell geometry, development of new diaphragm materials, development of new electrocatalytic materials for electrodes, etc. We tried here to use ionic activators to reduce energy consumption.

Two types of activators, both ethylenediamine complexes of cobalt, were used separately or in combination with some molybdates.

The activation energies were significantly decreased in the presence of single ionic activators. However, the best results regarding the activation energy reduction were obtained when combinations with the molybdate were used.

On the basis of the results of our experiments there is a strong indication that the activation with ionic activators reduces energy needs per mass unit of hydrogen produced for more than 10% in some cases, compared to those of non-activated electrolytes.

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**Keywords:** Electrolysis; Hydrogen; Catalysis; Ionic activators; Energy consumption

## 1. Introduction

Hydrogen's energetic potential lies in its ability to serve as an energy source and medium, convenient for efficient energy storage, transport and manipulation, with little or no pollution. Additionally, it can be directly converted into heat, using different techniques, or into electricity, in fuel cells, at the place of use. The latter conversion principle offers much higher efficiencies of hydrogen utilization to produce electricity (up to 60%), than via its combustion in a thermal machine like thermoelectrical power plant [1]. Similarly, if it is burned in an internally combustion engine to obtain useful work, for instance to produce motion of a vehicle, its usefulness would be quite low. However, if this is done by converting the hydrogen energy into the electrical one in fuel cells, and then this energy is used for motion of an electrical motor, the usefulness can be very much increased. Thus, hydrogen can be very attractive in this way, because hydrogen produced to simply burn would be too expensive.

Hydrogen energy is becoming increasingly important as recent technology progress makes hydrogen a realistic energy option. It is a long-term energy option, which means one of “fuels of the future” for buildings, transportation, portable application, vehicles and propellant for space mission, etc. Hydrogen can be used as a storage medium for intermittent and seasonal renewable technologies. It is also used for upgrading many metallurgical processes, as well as a chemical in different kind of industries, like synthesis of ammonia, methanol, oil refinery processes, etc.

Hydrogen will join electricity in the 21st century as a primary energy carrier in the sustainable energy future. When we speak of hydrogen, we are talking about its production, storage and utilization. Both electricity and hydrogen in the future will be mostly derived from either renewable or nuclear energy sources. Meanwhile, fossil fuels may serve as a transitional resource.

Although hydrogen is generally considered to be a clean fuel, it is important to recognize that the steps involved in producing it may have negative impacts on the environment in some cases. There are about 90 hydrogen production routes that can be divided into four categories: biological, chemical, electrochemical (water electrolysis;

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photoelectrochemical; halide electrolysis, H<sub>2</sub>S electrolysis) and thermal technologies [2].

In a view of economical requirements, water electrolysis has not had a significant commercial impact because it has not been cost-effective, due to high electricity consumption (4.5–5 kWh/m<sup>3</sup> H<sub>2</sub> in most industrial electrolyzers), although it is technologically very simple and delivers very clean gases. Electricity is known to be the most expensive form of energy. In addition to that its production is not a carbon-free process in most cases, because carbon fuels are often used. Moreover, electricity is not a primary energy but must be produced using fossil fuels, nuclear fuels, or renewable energy. Considering the fact that production of electricity has an average efficiency of around 30–40% with respect to primary energy, the overall efficiency of the electrolyser is generally below 40%. Thus, it is of the highest interest for the future hydrogen economy to reduce the hydrogen production price as much as possible.

There are many attempts to make the electrolytical production to become the attractive one. We can divide them in two categories: one is reduction of energy required in the water electrolytical process by different approaches, like zero-gap cell geometry, development of new diaphragm materials, and especially development of new electrocatalytic materials for electrodes. The other is making the electricity used as cheap as possible. Sometimes, in some countries there are great amounts of an excess electrical energy at a low price (especially over night). That is characteristic of countries where the nuclear (these plants could not go to lower power easily in a short time) or hydropower share of the energy in the electropower system is high.

The aim of this work was the attempt to reduce energy consumption in the electrolytic hydrogen production by using ionic activators added in situ to the standard electrolyte during the electrolysis. The effect expected to be obtained in this way is principally based on catalysis of

the gas evolution reactions via electrolysis (electrocatalytic effects). Two types of activators, both ethylenediamine complexes of cobalt, tris(ethylenediamine)cobalt(III) chloride complex and the tris(trimethylenediamine)cobalt(III) chloride complex, were used either solely or in combination with the Na-molybdate, Na<sub>2</sub>MoO<sub>4</sub>. For simplicity the two complexes will be further in the text assigned as [Co(en)<sub>3</sub>]Cl<sub>3</sub> and [Co(tn)<sub>3</sub>]Cl<sub>3</sub>, respectively. The standard electrolyte was the aqueous solution of 30 wt.% KOH. We investigated the efficiency of the activators for different concentrations, for a number of current densities in a wide temperature range.

## 2. Experimental

All experiments were performed with either cell of two designed to match our goals: (i) a simple glass-made cell of defined geometry. It was constructed as a “three finger” tube having three compartments, the catholite, the anolite, and the central one for temperature reading and addition of electrolyte. Thus, evolved gases (hydrogen and oxygen) were separated; (ii) a Plexiglas-made cell with more precisely defined geometry and with no more than one compartment of very small volume, to ensure collection of both gases in the same measuring volume, in order to increase the rate and accuracy of recording. It had much smaller gap between electrodes than the first one. Both cells along with the accompanied equipments are presented in Fig. 1.

In both cells the nickel electrodes were utilized. In the first one they were rectangularly shaped, while in the second the electrodes were of disk form. Before entering the cell each electrode was polished to the near mirror quality, then carefully cleaned mechanically and finally treated chemically with HCl (1 + 5 v/v). It was followed by washing in ethanol and finally in distilled water. Each electrode was attached to the cell via its own holder.

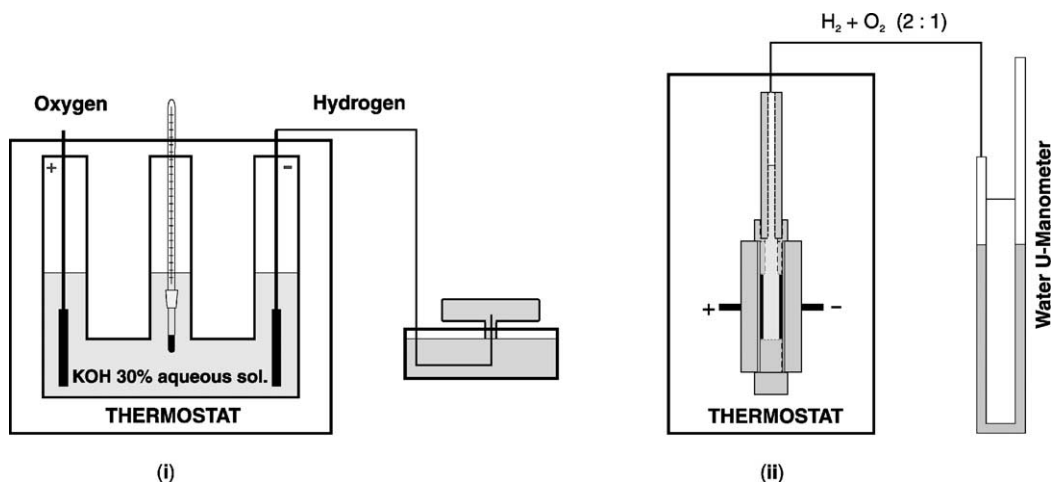


Fig. 1. Experimental setups used for measuring energy consumption per mass unit of hydrogen evolved: (i) “three finger” glass cell apparatus (gap between electrodes, 77 mm); (ii) small gap Plexiglas cell apparatus (gap between electrodes, 5 mm).

The cell was thermostated at a desired temperature with an accuracy of  $\pm 0.3$  °C, by employing a water ultrathermostat for temperatures beyond 5 °C and an alcohol cryostat for those below 5 °C.

In experiments with the cell (i), cathodically evolved hydrogen gas under its own pressure continuously filled the vessel, which was previously filled with water. Time of evolution of a defined volume of hydrogen, as well as the voltage on the electrodes, were measured at a certain temperature and the constant current density.

Similarly, time of evolution of a certain volume of hydrogen + oxygen (2:1), which here was measured using a U-tube water manometer, along with the voltage in the cell (ii), were recorded to calculate corresponding energy consumption at a temperature and a current density. Relative ratios of consumptions were of primary interest, although the apparatus allows measuring absolute values.

In all experiments the BRUKER-EI 30 Potentio/Galvanostat, as a constant current source was used. Voltage was measured with either Hewlett-Packard—Model 3478A MULTIMETER or PANCONTROL KT-25 voltmeter.

The KOH used was of p.a. grade, dissolved in bidistilled water. Both ionic activators were laboratory made from p.a. chemicals. The procedure of this synthesis was described elsewhere [3].

### 3. Results and discussion

The energy requirement for the electrolytic process run was calculated using the relation:

$$Q = I U t$$

where  $I$  (A) and  $U$  (V) are overall current and voltage through the cell, and  $t$  (s) is the time of evolution of a certain volume of hydrogen.

All experiments were done in the current range from 60 to 250 mA, which means the current density range from 10.5 to 43.8 mA cm<sup>-2</sup> for the cell (i), and from 9.1 to 37.9 mA cm<sup>-2</sup> for the cell (ii). The applied temperatures were from 253 to 353 K (from -20 to +80 °C).

The results obtained with the standard electrolyte are presented in Figs. 2 and 3 (upper diagrams). It shows an expected type of dependence: the energy requirement decreases with increasing temperature. In principal, that means the higher the temperature the higher the reaction rate, thus the higher the current density for the voltage applied, or the lower voltage requested for a certain current density.

We investigated concentration dependence of energy consumption for both complex activators, used in the standard electrolyte either solely or in combination with Na-molybdate. From a number of data obtained, we selected the optimal ones in respect to the energy requirements, which are presented in Table 1.

It can be seen that all of the ionic activators used show some electrocatalytic effects, in comparison with the

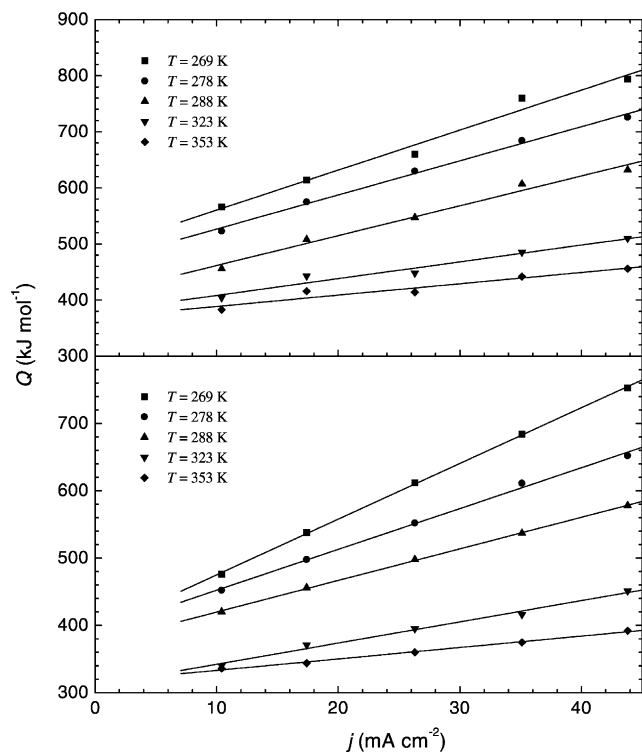


Fig. 2. Energy consumption per 1 mol of hydrogen evolved as a function of the current density at different temperatures, measured with the cell (i): upper diagram—standard electrolyte; lower diagram—the electrolyte that is  $1 \times 10^{-3}$  mol dm<sup>-3</sup> and  $1 \times 10^{-2}$  mol dm<sup>-3</sup> in respect to [Co(en)<sub>3</sub>]Cl<sub>3</sub> complex and Na-molybdate, respectively.

standard electrolyte. However, the best results were obtained with the following combination:  $1 \times 10^{-3}$  mol dm<sup>-3</sup> of [(Co(en)<sub>3</sub>]Cl<sub>3</sub> complex and  $1 \times 10^{-2}$  mol dm<sup>-3</sup> of Na-molybdate in the standard electrolyte. Thus, all further measurements were done with this combination.

The results obtained with the above combination of ionic activators are presented in Figs. 2 and 3 (lower diagrams). Energy saving is higher at higher temperatures, as it was observed also in the standard electrolyte. Basically, both the ionic activation and temperature act as accelerating factors of the electrolytic process. That is clearly illustrated in the three-dimensional diagram shown in Fig. 4, where the specific energy consumption is represented as a function of temperature and current density.

Table 1  
Energy consumption per 1 mol of hydrogen produced at the current density of  $j = 43.8$  mA cm<sup>-2</sup> and temperature of 323 K

Electrolyte	$Q$ (kJ mol <sup>-1</sup> )
30% KOH in distilled water (standard electrolyte)	510.3
$1 \times 10^{-3}$ M [Co(en) <sub>3</sub> ]Cl <sub>3</sub> in the standard electrolyte	497.1
$1 \times 10^{-3}$ M [Co(en) <sub>3</sub> ]Cl <sub>3</sub> in the standard electrolyte	487.7
$1 \times 10^{-3}$ M [Co(en) <sub>3</sub> ]Cl <sub>3</sub> + $1 \times 10^{-2}$ M Na <sub>2</sub> MoO <sub>4</sub> in the standard electrolyte	454.6
$1 \times 10^{-3}$ M [Co(en) <sub>3</sub> ]Cl <sub>3</sub> + $1 \times 10^{-2}$ M Na <sub>2</sub> MoO <sub>4</sub> in the standard electrolyte	450.9

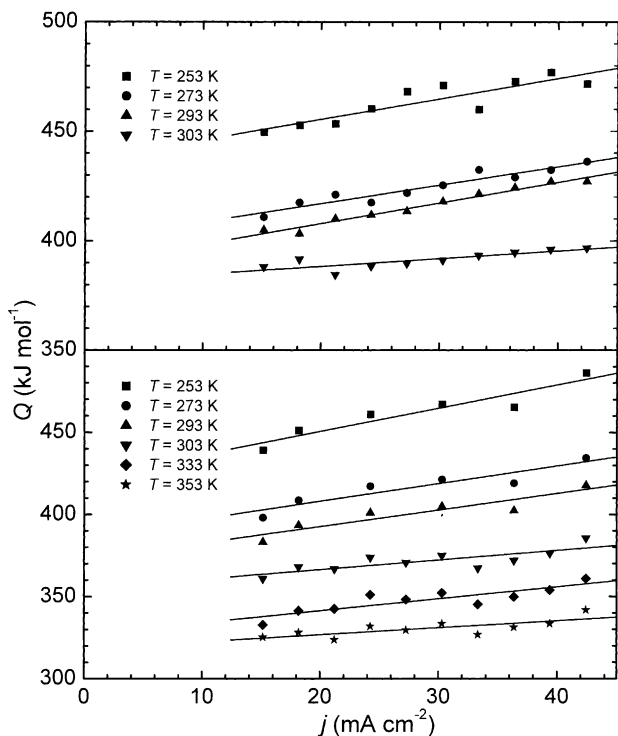


Fig. 3. Energy consumption per 1 mol of hydrogen evolved as a function of the current density at different temperatures, measured with the cell (ii): upper diagram—standard electrolyte; lower diagram—the electrolyte that is  $1 \times 10^{-3} \text{ mol dm}^{-3}$  and  $1 \times 10^{-2} \text{ mol dm}^{-3}$  in respect to  $[\text{Co}(\text{en})_3]\text{Cl}_3$  complex and Na-molybdate, respectively.

Figs. 2–4 indicate also the role of the cell geometry in energy consumption. That means the smaller the gap between electrodes, the lower the requirement, as also demonstrated in [4]. Thus, the “zero-gap” geometry is highly recommended in practical uses.

We can see in the figures presented that energy saving with the activators used is beyond 10% in some cases. If that effect is accompanied with the temperature and geometry of the cell influences to optimize the process, one can expect significant reduction of price of electrolytically produced hydrogen.

Possible mechanism through which ionic activators increase electrolytic efficiency is very complex. It includes different effects, with their specific contributions. One of them could be the electrocatalytic effect of either one individual metal (Co), or combination of two metals (Co–Mo), deposited on the electrode surface (powder like deposition observed also in this work and our previous investigation [5,6]), providing at the same time very large surface area of active centers. However, the catalytic effects of ethylenediamine, or trimethylenediamine ligands, which are present in the electrolyte after decomposition of the corresponding complex and deposition of metals on the surface, has its own role in that mechanism. Therefore, there arises a kind of double electrocatalytic effect caused by metals and the complex ligands [7]. That role is not quite clear, but it looks like that it is similar to the effect of EDTA (Rowland’s effect [8,9]). It cleans the surface by destroying and removing the oxide film from the cathode surface, preparing it for deposition of metals. As a consequence, the active electrode surface becomes more developed. All of this usually leads to a lower overpotential, as it had shown in some of our previous works [10,11]. Further, hydrogen atoms are transported to the metal via an exchange with the electrolyte, and this will also have the effect of decreasing the activation energy and hence the overvoltage. In accordance with the transition state theory, it was suggested [9] that the transition complex acts as a “bridge” for hydrogen transfer from the electrolyte to the metal surface.

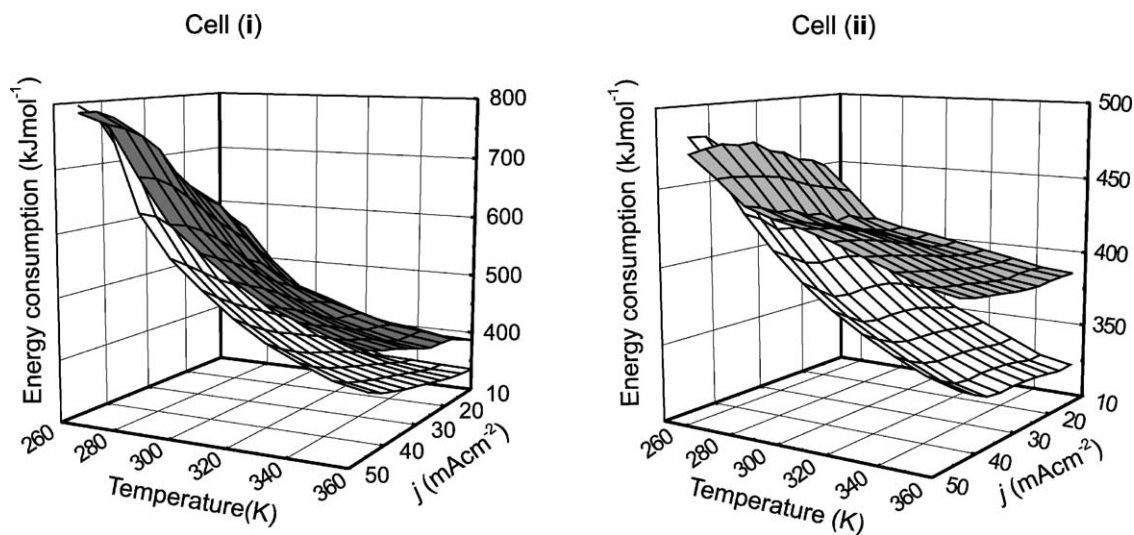


Fig. 4. Three-dimensional diagrams of energy consumption per 1 mol of hydrogen evolved vs. the current density and temperature: upper planes—standard electrolyte; lower planes—the electrolyte that is  $1 \times 10^{-3} \text{ mol dm}^{-3}$  and  $1 \times 10^{-2} \text{ mol dm}^{-3}$  in respect to  $[\text{Co}(\text{en})_3]\text{Cl}_3$  complex and Na-molybdate, respectively.

#### 4. Conclusion

Ionic activators used in this work have shown significant electrocatalytic effects and thus corresponding energy savings per mass unit of electrolytically evolved hydrogen from alkaline aqueous solutions. We pointed out in our experiments that these savings can be beyond 10% in some cases, compared to those of non-activated (“standard”) electrolytes. This investigation also proved positive effects of temperature rise and gap (between electrodes) reduction on the energy saving.

#### Acknowledgements

The financial support for this study was provided by the Ministry of Science, Technologies and Development of The Republic of Serbia, Projects No. 1995 (Spectroscopic & Isotopic Investigation of Systems) and 1318. The authors are grateful to Prof. Milan Jaksic for always valuable discussions of the subject.

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