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THE COST REDUCTION OF ELECTROLYTICALLY PRODUCED HEAVY WATER AND HYDROGEN IN THE CONTEXT OF SOME NEW PROCESS PARAMETERS

Hydrogen is an extremely important material, which is commonly used in many industrial processes in huge quantities, while its heavy isotopes, deuterium (D) as heavy water, and tritium (T) have great significance for nuclear energetics. Thus, improvements in their production are always of interest.

Electrolysis (sometimes in combination with other methods) is often used for heavy water production or re-enrichment. It is a high energy consuming method at the same time with high isotope separation factors. An efficient way to achieve both, energy savings and a significant increase of the H/D separation factors simultaneously, is applying water electrolysis from alkaline solutions, using catalytic cathode materials made from hypo-hyper-d-electronic combinations of transition metals and electrode in situ activation with tris-(ethylenediamine)-Co(III)-chloride complex. The appropriate conditions were investigated in this study. The dependence of isotope enrichment on the amount of water that must be electrolyzed was calculated using the Rayleigh equation. From that dependence the amounts for obtaining pure heavy water, i.e the corresponding energy savings, were estimated for different values of the separation factor, along with the minimum number of electrolytic stages in an enriching cascade. The method is discussed in a context that assumes heavy water as a by-product of hy drogen/oxygen generation, being an energy storage medium in a certain electroenergetic system during periods of the day when the consumption of energy from the system is reduced. This could be of importance for countries with a high percent of nuclear energy in the system, to avoid plant power reduction. If the discussed conditions are applied, hydrogen/oxygen can be produced at a reduced cost, delivering a D-enriched electrolyte to the subsequent heavy water production cascade.

Hydrogen is an extremely important material. It is commonly used in many industrial processes in huge quantities, such as ammonia production, petrochemistry, food industry, etc. It can also be used as the key medium in "hydrogen energy philosophy" due to its unique "energetic properties" (production for storage, gas—line transport, no environmental damage) that make it an ideal energy carrier or fuel. Hydrogen can be produced in many ways from any energy source, and converted into other forms of energy more efficiently than any other fuel. The main raw material for its production is water which is available in unlimited amounts.

Electric energy can be efficiently stored by making hydrogen, while hydrogen is usually stocked as gas-H₂, liquid-H₂ or metal hydride, depending on further uses and transport convenience. Water electrolysis is the most important way of converting electricity into hydrogen, because it is a technically simple method, although it delivers a relatively expensive product. It is possible to transport hydrogen over large distances through gas-lines or with tankers and use it on location when needed. As a fuel it is usually converted into heat by direct or catalytic combustion, or directly into electric energy in fuel cells [1]. Both methods are environmentally convenient ones since they deliver pure water as the end product. Thus, the hydrogen energy system can become a permanent solution to global energy-environmental problems [2]. One of the possible schemes for massive hydrogen usages in energy

systems of the future (fossil fuels depleted) could be: nuclear power plants for the production of electricity and hydrogen outside cities – gas–line transport to cities and storage there – energy recovery in fuel cells when needed.

Hydrogen heavy isotopes, deuterium (D) and tritium (T), are very important in nuclear energetics. Deuterium in the form of heavy water (D2O) is the neutron moderator. Due advantageous neutron slowing-down properties and very small capture cross section for thermal neutrons. heavy water moderation enables the use of the uranium nuclear fuel having natural isotope concentrations (235U $^{238}U = 0.0071$ 0.9928) in nuclear fission reactors. Thus, uranium enrichment in the ²³⁵U isotope is avoided in the production of reactor fuel. However, isotope separation work must be spent to produce D₂O, which is the investment component of nuclear reactors (no spending during reactor operation). A heavy water nuclear power reactor needs roughly one ton of D2O per megawatt (electric) installed. That is the only large scale use of the D-isotope. Heavy water reactors, most of them are of the PHWR (Pressurized Heavy Water Reactor) type, make about 7% of the worlds' installed nuclear power plants for energy production. The net electrical capacity of nuclear power plants worldwide has been growing from 5 MW in 1955 to about 353 000 MW in 1997. The world nuclear power status in 1997 was about 440 nuclear reactors in operation and about 40 units under construction or being planned [3].

The main raw material for D_2O productions is water. The average natural abundance of deuterium is very low, about 0.00015 atom fractions. A variety of isotope separation methods are now in use for heavy water production.

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Both hydrogen heavy isotopes, D and T, are now seen as fuel components to be used in fusion reactors for energy production in the future. The most promising reactions of thermonuclear fusion, with the evolution of enormous amounts of energy per nucleon, are

$$^{2}_{1}D + ^{3}_{1}T \rightarrow ^{4}_{2}He + n + 17,6 \text{ MeV}$$
 $^{2}_{1}D + ^{2}_{1}D \rightarrow ^{3}_{1}T + ^{1}_{1}H + 4.0 \text{ MeV}$

Tritium is now commonly produced by nuclear reactions between neutron and lithium, or on a smaller scale by isotope separation from the fission reactor's heavy water, in which D is partly transformed into T in nuclear reactions taking place in the moderator.

Finally, we can say that the importance of hydrogen, along with its heavy isotopes, will rapidly increase in the coming decades.

SEPARATION OF ISOTOPES - ELECTROLYSIS

The separation of isotopes from a binary mixture is based on isotope effects, that is on the different properties or behavior of isotopic forms of the same molecular species. The origin of these effects lies in the mass differences between the species. A single element which uses a specific isotope effect for a single—stage separation act is called a separating unit. It is schematically presented in Figure 1.

The principle of any separating unit is that (due to the separating agent) it divides one feed stream into two outgoing streams (phases). It is a convention that the heads stream is partially enriched in the desired isotope (the product stream), while the tails stream is partially depleted (waste). An electrolytic cell for water electrolysis is a separating unit based on the kinetic isotope effect, i.e., on different rates of H₂ and D₂ generation from aqueous electrolytes. An electrolyzer, which contains several parallel—connected cells with the same feed composition, actually gives the same result, but it is usually called a separating stage.

The separating agent in the electrolyzer is electric energy. It decomposes water and delivers a deuterium depleted gas stream on one side, and a deuterium

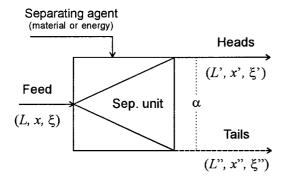


Figure 1. Schematic representation of a separating unit: L – Flow rate, x – Atom fraction of desired isotope, ξ – Abundance ratio, ξ = x / 1 – x.

enriched liquid (electrolyte) phase on the other, both with corresponding concentrations, [D] and [H]. The isotope separation efficiency in a single-stage process is expressed by the separation factor (α) , defined as the ratio of the heads and the tails abundance ratios

$$\alpha = \frac{\xi'}{\xi''} = \frac{x'}{1 - x'} : \frac{x''}{1 - x''} = \frac{\left(\frac{[D]}{[H]}\right)_{iq}}{\left(\frac{[D]}{[H]}\right)_{gas}}.$$
 (1)

Because of the low natural abundance of deuterium, very large amounts of water as the raw-material must be processed using any isotope separation method, to produce a relatively small amount of highly enriched product. The cost of the initial enrichment from the natural abundance to about 1% is much higher than that of the final enrichment, from 1 to > 99%.

Electrolysis which consumes water as the raw material has been used in the first industrial plant for heavy water production in Riukan (Norway) since 1934. However, economical reasons mainly expressed through energy consumption, have reduced its use on a large scale. Recent developments in the field of electrolysis, especially in electrocatalysis, represented by new electrode materials, different ionic electrode activators etc., have led to a remarkable reduction in energy consumption with a simultaneous increase of the separation factor. These improvements can turn electrolysis into an interesting isotope separation process, especially in combination with other "hydrogen-oriented" industries and in the context of "hydrogen energetics". The consideration of these possibilities, keeping in mind some new (basic) results of investigation in this field, is the main aim of the present work. These results are lower energy consumption per generated mass unit of hydrogen, along with improved values of isotope separation factors, obtained simultaneously with specific catalytic cathode materials (hypo-hyper-d-electronic combinations of transition metals) and under the activation of electrodes with some ionic activators.

Cathodes made from mild steel or Fe have been commonly used in water electrolyzers for decades. Their properties are very well known. Thus, they will serve in this work as the reference for comparison with other materials. The analysis, based upon the assumption that heavy water is a by-product of hydrogen/oxygen production in a reversible power plant system, will be made in a very simplified version.

ANALYSIS

The measured values of the D/H isotope separation factors for a number of materials are given in Table 1. The activation of electrodes for the H/D separation efficiency means the addition of a complex

compound into the electrolyte to prepare the surface for efficient development of the process. We have recently shown that the use of *tris-(ethylenediamine)–Co(III)-chloride* complex, the structure of which is given in ref. [1], in 30 wt.% aqueous KOH electrolyte, with some types of electrodes significantly improves the separation factor and simultaneously reduces energy consumption. Very fine Co powder is deposited on electrode surfaces during electrolysis. Experiments with other activators, such as *tris-(trimethylenediamine) -Co(III)-chloride complex*, have given separation factor values higher than 15¹⁾ [5], but these spectacular results must be verified.

Transition elements and their intermetallic phases are good electrocatalysts in hydrogen evolution reactions (HER). In this way the Brewer-Engel intermetallic phases for instance, reduce the energy consumption per evaluated gas by 6-10% [6], [7]. That is actually the final engineering goal in electrocatalysis²⁾. It is usually achieved by lowering the slope of the Tafel lines at higher current densities, ideally to zero. It is well-known that alloys of metals from the left half transition series on one side, and those from the right half series on the other, give well-pronounced synergism in electrocatalysis for hydrogen evolution [7].

Single-stage electrolytic enrichment

The simplest possible way to produce very concentrated (x > 0.99) heavy water from natural water ($x_0 \approx 0.00015$) by electrolysis is to decompose a large initial volume (V_0) to a small amount (V_0) in a single unit, without adding the feed during the process. In such a unit hydrogen is continuously generated and continuously removed from the unit. The electrolyte is progressively enriched in D and is removed at the end of the run. Such an operation is commonly called a Rayleigh operation. It is described by the *Rayleigh equation* [8], [9], which relates the composition of the remaining liquid to the amount of the remaining liquid

$$\frac{x}{x_0} \left(\frac{1 - x_0}{1 - x} \right)^{\frac{1}{\alpha}} = \left(\frac{V_0}{V} \right)^{\frac{\alpha - 1}{\alpha}}$$
 (2)

where x_0 and x are the mole fractions of D in the electrolyte at the beginning and at the end of the process, respectively.

The x value in the above relation depends on the V_0/V ratio. A graphical representation of that dependence when natural water is electrolyzed is displayed in Figure 2a for different values of the separation factor. Figure 2b shows the same type of diagram for partly enriched starting abundances. The

values of α correspond to those obtained for cathodes made from Ni–V alloy, used with and without *in situ* activation ($\alpha=4.7$ and 9.4), and for the Fe cathode ($\alpha=7.9$), respectively (see Table 1). For comparison, the diagrams also contain curves obtained for $\alpha=15$, a value which can be expected, as indicated above.

Figures 2a and 2b clearly show that a significant increase of the separation factor can drastically reduce the necessary amount of water to be decomposed for obtaining pure heavy water ($x \ge 0.997$). For instance, if α

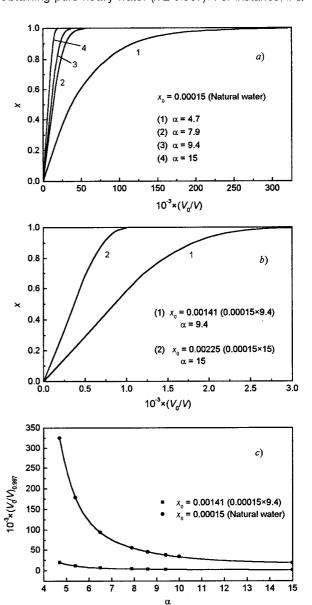


Figure 2. a) Deuterium enrichment of water in simple electrolysis as a function of the electrolyzed amount, calculated using the Rayleigh relation for four different α -values. All curves obtained for natural water ($x_0 = 0.00015$);

¹⁾An α = 19 value was obtained at -20°C, with a nickel (Ni) cathode and a complex concentration of 1 x 10⁻² mol dm⁻³.

²⁾There is even more room for electrocatalysis in the oxygen evolution reaction (OER), about 500 mV at usual current densities.

b) Deuterium enrichment for α -times enriched natural water, calculated using the Rayleigh relation for two different α -values;

c) Dependence of the V_0/V ratio for $x\approx 0.997$ on the separation factor value and the deuterium concentration in the electrolyzed water

is doubled, as in the case of the [Ni–V (70–30)] cathode, that amount falls to about 32 t (for $\alpha=9.4$) instead of 325 t for $\alpha=4.7$, or 55.2 t for $\alpha=7.9$. This dependence on α is more evident in the diagram given in Figure 2c, which is obtained by displaying the (Vo/V) ratios that correspond to x \geq 0.997 as a function of α , also using the Rayleigh formula in an alternate manner.

Besides advanced separation efficiencies, the Ni-V cathode, as a hypo-hyper-d-electronic combination of transition metals (the Brewer-Engel intermetallic phase), has an additional advantage: the energy consumption per mass unit of generated hydrogen is 6-10% lower than that for the Fe-cathode.

Electrolysis with a constant level

Another case worthy of mention is electrolysis with a constant level in the electrolytic cell. Fresh feed water, with a content of desired isotope equal to x_0 , is then continuously introduced into the electrolyzer, while an equivalent amount of gas-phase hydrogen is formed and removed continuously. The content of deuterium which remains in the cell increases to the boundary enrichment (BE) of α times. After that point the leaving hydrogen will contain as much deuterium as the incoming water. The dependence of the content x in the electrolyzer on the added quantity during electrolysis can be calculated using the following relation [8]

$$\ln \frac{\alpha - 1}{\alpha - x/x_0} = \frac{V}{\alpha V_0} \quad \therefore \quad x = x_0 \left[\alpha - \frac{\alpha - 1}{e^{V/(\alpha V_0)}} \right]$$
 (3)

Here $V_0=\mbox{const.}$ is the water quantity in the cell, while V is the quantity of water added.

Figure 3a graphically represents the dependence expressed by equation (3) for $V_0 = 1$ (relative units). Boundary enrichment for a specified α is achieved at $x_{BE} \approx \alpha \cdot x_0$. It requires a certain minimal amount of water that must be electrolyzed (VBE), which can be estimated very easily from the displayed type of diagram. Such an estimation is shown in Figure 3b. The BE value for V linearly depends on α ($V_{BE} \approx c \cdot \alpha$, where c is a proportionality constant), i.e. the higher the α (and thus larger the xBE), the higher the VBE. Therefore, the x_{BE}/V_{BE} ratios remain constant. A larger V_{BE} requires spending more energy, but gives higher enrichment (xBE = V_{BE}/cx₀). Thus, the interest in having higher values of $\alpha_{\mbox{\tiny L}}$ from the energy point of view, lies in the fact that such an "old" electrolyte can efficiently be used as a feed for the subsequent separating stages. The increased deuterium concentration in the latter has a very strong impact on further enrichments. This is illustrated in Figures 2b and 2c for two different feeds.

Cascades

In practice, it is almost impossible to reduce the amounts of electrolyzed water tens of thousands times

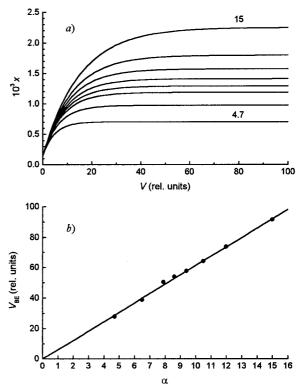


Figure 3. a) The attainment of boundary enrichment (BE) for different values of α (from 4.7 to 15); b) BE amount of water that must be electrolyzed (VBE) as a function of the separation factor α .

in a single unit to obtain the concentrated product. One of the very serious technical problems would be the elimination of excess KOH from the electrolyte, because its concentration increases during the electrolysis. Thus, the enrichment process is usually divided into several stages connected in series, called a cascade. An optimized cascade gives additional possibilities for reducing the amount of water processed as compared to one that follows from the above estimation based on single-stage enrichment. In our analysis we shall not take into account those details in order to ensure a clear and principal approach.

The theory of electrolytic cascades was developed many decades ago and described in detail in several books from that period [10, 11]. Every subsequent stage within the cascade is of much smaller volume. The feed for one stage is the heads fraction from the preceding one. When the depleted (tails) stream has a significant D concentration, it can (not obviously) be returned to the process countercurrently as part of the feed of the preceding section, as illustrated in Figure 4.

Of the many types of cascades that could be designed, the *ideal cascade* is the one in which the heads stream and the tails stream fed to each stage have the same composition: $x_{i+1} = x_{i-1} = x_i$, (i = 2, 3, ..., n-1). It is designed for minimum cost in an isotope-separation plant. If such a cascade produces a certain number of moles of the product enriched in the desired isotope,

Table 1. D/H separation factors for wate electrolysis from alkaline solutions (30% KOH in 0,1% D_2O) without (α) and with in situ activation (α _a) of electrodes by tris–(ethylenediamine)–Co(III)–chloride complex (10^{-2} mol dm⁻³), along with the corresponding minimum number of stages necessary for obtaining pure heavy water, $x_P = 0.997$, in an ideal cascade.

Cathode material	α[14]	α _a [15]	n		na	
			$x_w = 0.000100^{2)}$	$x_w = 0.000846^{3)}$	$x_w = 0.000100^{2)}$	$x_w = 0.000846^{3)}$
Fe	7.9	8.6 ¹⁾	13.5	11.5	13.0	11.0
Ni	7.6	10.0	13.8	11.7	12.0	10.2
V–W–Mo–Fe	6.2	8.9 ¹⁾	15.5	13.1	12.7	10.8
V–Fe	5.4	8.9 ¹⁾	16.8	14.3	12.7	10.8
Ni-W (70-30%)	5.4	7.7 ¹⁾	16.8	14.3	13.7	11.6
Ni-Mo (70-30%)	5.2	6.9 ¹⁾	17.2	14.6	14.5	12.3
Ni-V (70-30%)	4.7	9.4	18.4	15.6	12.4	10.5
Fe-Mo (70-30%)	4.2	6.0	19.9	17.0	15.8	13.4
C (spectr. pure)	5.8	8.6	16.1	13.7	13.0	11.0

¹⁾ t = 24 °C, other values t = 20 °C.

composition x_{P_i} delivering also a defined amount of waste, composition x_{W_i} then the minimum number of stages can be calculated from the following relation [10]

$$n = 2 \frac{|n \frac{x_p (1 - x_w)}{x_w (1 - x_p)}}{|n \alpha|} - 1.$$
 (4)

The number of stages required for a given enrichment is a function of the separation factor α .

DISCUSSION

The values of n calculated using equation (4) for the separation factors listed in Table 1 are shown in columns 4–7 of the same table. The deuterium concentration in the waste hydrogen, x_W , is obtained under the assumption that the raw material utilization is about 33% for the production of pure heavy water from natural contents in an optimized electrolytic cascade as

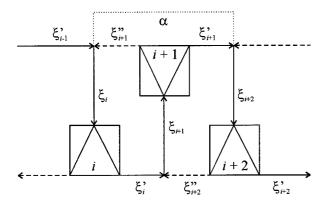


Figure 4. A segment of an ideal cascade.

described in ref. [10], and greater than 40% if the raw material is slightly enriched in D (α -times). This relatively low degree of utilization, which means corresponding recovery, is typical for electrolysis if used alone. Consequently, the amount of produced heavy water is relatively small for the corresponding quantities of water processed. However, if it is combined with another process, such as chemical exchange (between water and hydrogen)3) [12], the utilization can exceed 70%. The utilization can have an impact on the dimensions of the production plant, although those dimensions, usually expressed in m³/(t D₂O y ear¹), are quite small in comparison with other processes, especially in the CECE version. For instance, CECE is 4, GS (chemical exchange between water and hydrogen sulphide which is the most commercial process) 50, water distillation 200, etc.

We can see that an increase of the separation factor significantly lowers the number of stages necessary for the concentration of a given feed to pure heavy water. For the Ni–V cathode, which is an example that expresses both effects (lower energy consumption per mass unit of electrolyzed hydrogen and higher separation efficiency) simultaneously, the number of stages in the cascade is reduced from about 18 to about 12 (n:n_a) for natural contents feed, or from greater than 15 to about 10, for slightly enriched feed. Corresponding numbers for Fe-cathodes are 13:11 in both cases.

Feed = natural water; raw material utilization = 33%; $[x_w = 0.00015 \text{ x } (1 - 0.33)].$

Feed = enriched water, 9.4 times natural; raw material utilization = 0.4; $[x_w = 0.00015 \, x \, 9.4 \, x \, (1 - 0.40)]$.

³⁾Typical combined method is so-called CECE (Combined Electrolysis Catalytic Exchange).

The separation factor, as indicated before (Figure 2 and Table 1), influences both the energy consumption and the number of stages necessary to obtain a given product, through the amount to be processed. Lets analyze that effect briefly for the Ni-V cathode. The amount of (natural) water which must be electrolyzed in order to obtain 1 l of the enriched product (x \geq 0.997 D) is reduced from about 325 t, in the non-activated electrode configuration ($\alpha=4.7$) to about 37.5 t when the tris-(ethylenediamine)-Co(III)-chloride complex is used as the electrode activator ($\alpha_{\rm a}=9.4$), Figure 2a. This is only 11.5% of the primary amount. Compared to the best value for the Fe-cathode of 45.3 t ($\alpha_{\rm a}=8.6$), this is 83%. The energy saving is roughly of the same order of magnitude.

On the other hand, the separation factor, along with the utilization factor, also affects the dimensions of the plant, that is the investment costs (through the reduction of the material processed, i.e. the number of stages), but in principle those effects are not so strong.

An additional energy saving of about 10% comes from the reduction of the energy consumption per mass unit of evaluated hydrogen obtained with the Ni-V cathode, compared to that of the iron (Fe) one. The theoretical energy consumption is the product of the reversible cell voltage and the electrochemical equivalent for the desired gas (3.6 · 10⁶ A · s per 0.418 Nm³ of H₂ and 0.209 Nm³ of O₂). Power is consumed for producing both the products in gaseous form, some water vapor and waste heat. The theoretical cell voltage is 1.23 V, the energy efficiency as observed in practice is 45-65%, so that hydrogen is produced at 14.4-21.6 MJ Nm⁻³. Most industrial type electrolyzers, such as Demag, Bamag, De Nora, CJB etc., are declared to have a consumption of about 16.2 MJ Nm⁻³ of hydrogen. KOH electrolyte (25-30% w/v aqueous solution) along with mild steel, nickel or nickel-plated copper as cathode materials, are commonly used in those electrolyzers.

An analysis made several decades ago [13], and based on a separation factor as low as 10, showed that deuterium-selective electrolysis could be competitive with other processes, provided that power costs could be reduced by certain techniques.

Finally, the suggested context of heavy water production at a low cost is as follows: Heavy water is a by-product of hydrogen and oxygen production. These gases are produced in electrolyzers using excess electrical energy in countries with energetic systems having a high percent of energy from nuclear or hydro plants, during periods of the day when consumption is low. Thus, the primary energy for hydrogen production should be as cheap as possible. Hydrogen and oxygen

can be recombined in periods of maximum consumption in order to give part of the spent energy back to the system, as heat or electricity, depending on needs.

The above hydrogen-generating electrolytic system serves as the primary enrichment plant. It should work under optimal conditions, i.e. with the best available cathodes. made from various hypo-hyper-d-electronic combinations of transition metals, activated with the most efficient activator. Separation factors of more than 10 with an energy saving per mass unit of generated hydrogen of at least 10%, can be expected. It supplies the heavy water plant with a feed significantly enriched in D, as well as the energetic system with cheaper hydrogen. That plant includes all the improvements associated with electrolysis discussed in this study, due to which it has a relatively small number of stages. The power plant system in such a context is actually a reversible one, while the heavy water plant is a parasitic one. It especially could be efficient in combination with chemical exchange (CECE).

Alternatively, this concept can be realized in combination with another hydrogen consuming plant (such as ammonia production). However, such an analysis is beyond the scope of this study.

Concluding remarks. An additional possibility for improving the electrolytic concept of hydrogen and heavy water production is the further development of advanced catalytic cathode materials based on the hypo-hyper-d-electronic combinations of transition metals, along with process optimization by the in situ activation of electrodes and the proper temperature regime. The effects of some promising activators⁴⁾ must be additionally investigated. Activator cost and its decomposition during the process should also be considered, along with products remaining in the electrolyte. Temperature is also an important parameter. It has been known for decades that the separation factor increases as temperature decreases. We have confirmed that result with activated electrodes in the temperature range from -20 to +80°C [15]. Note here for clarity that one should be careful about electrolytic cell cooling in order to increase the separation factor, because it requires additional energy. Thus, these requirements are in some degree conflicting.

It is believed that the achievement of separation factors of about 15 could be possible by careful design, along with a significant catalytic reduction of energy consumed per mass unit of generated hydrogen.

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 $^{^{4)}}$ The tris-(trimethylenediamine)-Co(III)-chloride complex has already been mentioned.

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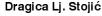
Šćepan S. Miljanić

Šćepan S. Miljanić was born in 1948 in Nikšić, Yugoslavia. He is a Professor and the Head, of the Department of Radiochemistry and Nuclear Chemistry at the Faculty of Physical Chemistry of the University of Belgrade. He teaches Nuclear Chemistry.

Professor Miljanić graduated from the Faculty of Sciences (Department of Physical Chemistry), University of Belgrade, in 1972. He received his M.Sc. degree in 1975 and Ph.D. degree in 1981, both in physical chemistry at the Faculty of Sciences, University of Belgrade. He has spent twenty years doing research at the Vinča Institute of Nuclear Sciences, where he used to be the director of the Department of Physical Chemistry (1993–95). His main research interest is the laser chemistry of isotopes, primarily isotope effects, molecular relaxation in collisions and laser spectroscopy of isotopic species, along with conventional methods of isotope separation (catalytic chemical exchange and electrolysis). He wrote the book en titled **Hydrogen Isotope Effects – Heavy Water** (in Serbian), published in 1996.

He worked with Professor Charles B. Moore at the University of California at Berkeley (1979-80) in the field of molecular relaxation, and Professor B.N. Sergeev (MGU Moscow – 1986), and also had an official cooperation under the EU with the University of Strathclyde (Glasgow) and the Heriot Watt University (Edinburgh) on a new concept of gas lasers.

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Dragica Lj. Stojić graduated from the Faculty of Sciences, Department of Physical Chemistry, University of Belgrade, in 1973. She attained her MSc degree from the same Faculty in 1979. The thesis was part of an investigation in obtaining thermodynamic data on complex formation in anhydrous molten salts mixtures and testing several statistical-mechanical models of ion association based quasi-lattice concept of melts. The interest in the field of X-ray fluorescence spectroscopy derived from the work in the field of environmental protection.

Dragica Stojić is currently mostly interested in electrocatalysis, and her prime contribution is the significant efficiency improvement of the electrolytic separation of hydrogen isotopes obtained by optimizing experimental conditions (cathode materials, ionic activators, temperatures). In that field Dragica Stojić obtained her Ph.D. degree with a thesis entitled "Electrocatalytic effects in the electrolytic separation of hydrogen isotopes". This work resulted in cooperation with the Russian Research Centre "Kurchatov Institute", Electrochemical Department in Moscow.

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