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Graphene-based electrochemical system for tritium enrichment

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Abstract

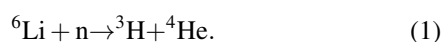
In this study, a tritium enrichment system in the water phase has been developed based on the combination of a proton exchange membrane (PEM) electrolysis cell and a fuel cell. As the PEM, NafionTM and laboratory-synthesized sulfonated poly(ether ether ketone) membranes modified with an additional graphene layer in order to enhance the tritium separation factor were used. Both differences in the kinetics of the hydrogen evolution reaction and transport through the graphene layer of different isotopes are the driving factors expected to affect the separation of hydrogen isotopes. The separation factor was measured both during the electrolysis and fuel cell stage using different membranes. The facilitating effect of the graphene on the separation efficiency was determined during the study. The separation factor obtained by the proposed method was evidently higher than that obtained by other conventional methods.

Keywords: tritium, proton exchange membrane, graphene, electrolysis, fuel cell

(Some figures may appear in colour only in the online journal)

1. Introduction

Tritium, denoted as ³H or T, is a beta-emitting radioactive isotope of hydrogen produced in very small quantities in the atmosphere as a result of cosmic radiation-induced nuclear transmutations [1]. In nuclear fusion processes, T is used as a nuclear fuel and is planned to be produced on site from lithium according to:

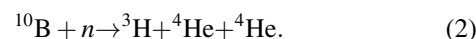


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Tritium is produced also in nuclear power reactors (yield ranging between 0.01 and 0.02%) by neutron activation reactions with boron in water and control rods:



Large commercial nuclear power reactors produce about 2 g of T per year, generally incorporated in the nuclear fuel and cladding leading to the permeation of T in the spent fuel, construction materials, and coolant [2]. In CANDU-type fission reactors, T is generated through the reaction of fission neutrons with the heavy water moderator and coolant [3]. Since T is produced in the fission reactors as a by-product, it can be extracted and used as a fuel in nuclear fusion reactors.

Tritium separation is crucial in the following applications:

- Extraction from cooling water of nuclear fission and fusion reactors in order to decrease the amount and class of radioactive waste [4];
- Recovery and purification for its further use in fusion devices or industrial applications as mentioned above;
- Decrease of T contamination in natural water sources in case of accidental tritium water leakages in case of industrial contamination (nuclear industry, production plants, research institutions).

The existing methods for T separation are mostly either time- and energy-consuming or expensive. New separation methods with larger separation factors, and a reduced number of stages and energy consumption are needed. Moreover, a mobile, remote controlled device capable of operating in harsh environments could be of great importance in case of nuclear/radiation accidents.

Isotopic effects in the electrochemical processes of water have been reported broadly, starting from the early era of nuclear technologies up to today [5–11]. The effect is based on the differences in the kinetics of the hydrogen evolution reaction of different isotopes, and can be used for heavy hydrogen isotope separation [12]. Electrolysis was the first widely used method for deuterium enrichment and is currently used in combination with the catalytic isotope exchange technique, in which >99% of separation is reached in the isotope exchange step [7]. This combination is used for tritium extraction from CANDU reactors [13, 14] and foreseen in the nuclear fusion demonstration reactor DEMO [15]. However, this technique involves high energy consumption. As an alternative to the electrolysis/catalytic isotope exchange technique, an electrolysis/fuel cell combination has been discussed recently [6]. Additionally, the effects of additional separation in the fuel cell are of great interest, since the kinetic isotope effect of the hydrogen oxidation reaction has also been observed in polymer electrolyte fuel cells (PEFCs) [16–18].

Membranes with fixed negatively charged sites facilitating selective transport of positively charged species such as protons can be used in electrolyzers as solid electrolytes [19]. The membrane–electrode assembly consists of two catalytic electrodes deposited on a proton-conducting membrane. Hydrogen gas or water is split on one side into protons and electrons, which recombine on the other side of the membrane. The use of a solid polymer electrolyte membrane or proton exchange membrane (PEM) instead of electrolytic solutions has a number of advantages, including a lower specific energy consumption, minimal amount of electrolyte in the device, absence of any impurities [7], and no risk of explosive gas mixture formation since hydrogen and oxygen can be emitted by separate outputs [18]. However, one of the disadvantages could be the exploitation lifetime due to the deteriorating effect on the membrane material of the radiation environment [20]. An alternative membrane material can be used with higher radiation stability, such as sulfonated poly(ether ether ketone) (SPEEK) membrane [20].

Hydrogen gas produced during the electrolysis still contains a considerable fraction of the heavier isotopes, therefore

the introduction of the fuel cell into the systems allows this gas to be continuously reprocessed into the water, enriching it with deuterium or tritium.

The use of a PEFC for isotopic separation of deuterium (D) was reported by Matsushima *et al.* Facilitated exchange of D with protium (H) in H₂O by a Pt catalyst was observed, and the water produced during the operation of the PEFC was enriched in D [21]. In the experimental work of Ogata *et al* it was demonstrated that the heaviest hydrogen isotope, tritium, was concentrated in the water phase in all experimental setups [22].

Fuel cells with NafionTM membrane coated with a graphene layer were proposed by Rozenkevich and Rastunova [7] for enhanced isotope separation. Hydrons are expected to have a high energy barrier for transfer through the pristine graphene; however, the experimentally measured value is reported to be 0.78 eV, which is considerably lower than that predicted by electronic structure calculations [23, 24]. According to [25, 26], the hydrogenation process of graphene can lead to a decrease in the barrier to less than 1 eV, which may explain the experimental observations [25, 26], and as a result, the graphene membrane could serve simultaneously as a semi-transparent hydron barrier and a drain electrode for hydrons [27]. However, in order to separate deuterium and tritium, isotopic effects must be present. It has been demonstrated that deuterons permeate through graphene much slower than protons, resulting in a separation factor of ≈ 10 at room temperature. The isotope effect is assumed to be attributed to a difference of ≈ 60 milli-electron volts between the zero-point energies of incident protons and deuterons, which translates into an equivalent difference in the activation barriers posed by two-dimensional crystals. The authors suggest that the proposed technique could reach a separation factor of ~ 30 for protium–tritium separation, which is a significant improvement compared to the existing methods [28]. Additionally, quantum tunneling has been proposed as a contributing mechanism for hydrogen isotope separation based on the theory that protons can undergo quantum tunneling at a much higher probability than its heavier isotopes, deuterium and tritium [23].

The present study reports on the development of a system for the separation of T in the water phase based on a combined PEM electrolysis cell and fuel cell enrichment system. Special attention during this study was dedicated to the selection of radiation-stable materials for the system according to previous research [20]. Pristine and graphene-coated commercial-grade NafionTM PEM and laboratory-synthesized SPEEK membrane as a radiation-stable alternative material were used as a test material for comparison of their performance characteristics.

2. Experiment

2.1. Enrichment system

The enrichment system is based on the combination of a PEM electrolyzer with an exchangeable membrane assembly and a fuel cell where the generated hydrogen gas is turned back into water (figure 1). The main separation is expected to take

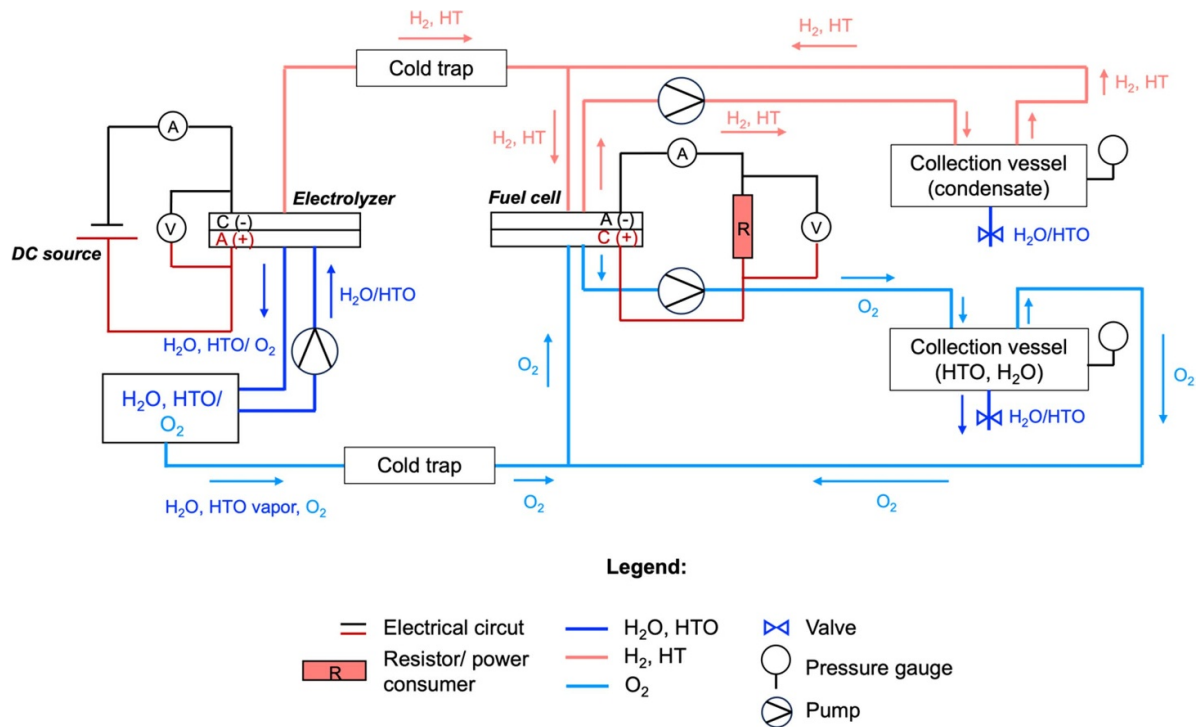


Figure 1. Schematics of tritium enrichment system.

place in the electrolyzer based on both differences in the kinetics of the hydrogen evolution reaction and transport through the graphene layer of different isotopes. Water is, thereby, enriched with tritium. However, the evolved hydrogen still contains heavy isotopes. Therefore, the fuel cell is introduced to turn hydrogen into water, which can be electrolyzed again until the required T enrichment is achieved. The electrolysis process for tritium separation was carried out for 2 h per experiment, amounting to a total of around 48 h.

The system consists of stainless steel (SS316) tubing, Swagelok connectors, and valves. Cold traps were constructed as U-shape SS316 tubes that were placed into cooling bath dewars. Collection vessels were SS316 with glass windows for visual water-level inspection. Both the electrolyzer and fuel cell were connected to an Agilent multimeter for data registration, and the pressure was recorded by a PeakTech manometer (output to PC). TCL Micropumps (R404-BL) pumps were controlled by voltage, set to a precise rpm, and monitored by the Agilent output.

To ensure that no tritiated water vapor was fed parasitically into the system, electrolysis cold traps were set up immediately after using an acetone/liquid nitrogen mixture (-78°C).

2.2. PEM

NafionTM 212 membranes of $50.8\ \mu\text{m}$ thickness were purchased from Chemours Company (Wilmington, Delaware, USA). Poly(ether ether ketone) (PEEK) granules were obtained from Sigma Aldrich (MO, USA).

In order to prepare SPEEK membranes, the PEEK pellets were dried in a vacuum oven at 100°C overnight. Then, the

appropriate weight (10 g) of PEEK was dissolved in 200 ml of concentrated sulfuric acid (98%) and vigorously stirred at room temperature for 24 h. Afterward, the obtained polymer solution was placed in a thermostat and heated at 36°C for 24 h. The polymer suspension was slowly poured into a large amount of cool deionized water. The precipitated SPEEK yarns were filtered, washed with deionized water until reaching a neutral pH, and dried at 80°C for 24 h. The procedure was repeated to obtain the necessary samples for membrane replicates.

SPEEK membranes were obtained by the solvent cast method as follows: 0.5 g of the SPEEK polymer was dissolved in 20 ml of dimethylformamide followed by stirring at 100°C for 1 h. Then, the polymer solution was cast into a Petri dish and dried for 24 h at 80°C to remove the solvent.

2.3. Graphene synthesis and transfer

Graphene synthesis was performed on a catalytic copper surface using a chemical vapor deposition (CVD) reactor according to the methodology developed by Li *et al* [29]. Graphene films were synthesized using a First Nano Easy tube 101 CVD reactor. Polycrystalline copper foil of $25\ \mu\text{m}$ thickness was used as the catalyst. Before the synthesis, the foil was cleaned with acetone, isopropanol (IPA), and deionized water, then electrochemically polished in a cooled mixture of nitric acid and IPA (1:9). Before the synthesis, the copper foil was annealed at 1000°C for 30 min in 20 sccm hydrogen flow at 0.5 Torr pressure. After the annealing, the graphene was synthesized for 1 h at 1000°C in the presence of CH_4 and

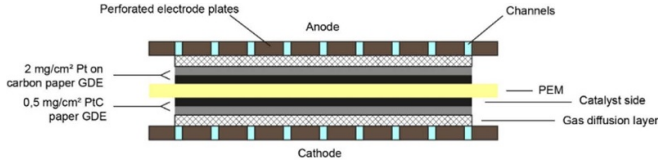


Figure 2. Schematics of MEA.

H₂ gas flow at a rate of 20 and 35 sccm, respectively. The synthesized graphene was used only for transfer method tests and optimization.

For membrane electrode assembly (MEA), preparation of commercially available graphene on Cu substrate provided by Graphenea was provided due to the sample size restriction of the First Nano Easy tube 101 CVD reactor. Graphene from Graphenea was CVD synthesized, one layer thin with a theoretical thickness of 0.345 nm and AFM measurement <1 nm, with grain sizes up to 20 μm.

Transfer onto the membranes was done by hot pressing from Cu substrate followed by dissolution of Cu substrate with nitric acid and ammonium persulfate. Graphene-coated copper foils were placed on membranes between two sheets of Teflon and placed in a hot press (Carver 3851-0) heated to a temperature of 180 °C before the experiment. Samples were subjected to a press force of 11.8 kN (1.2 t) for 3 min, then removed and allowed to cool. In the case of sandwich-like samples after the graphene transfer, an additional membrane was pressed on the graphene side.

2.4. Preparation of MEA

The MEA consists of PEM, layers of catalysts on both sides, a cathode, an anode, and a gas diffusion layer. A total of 0.5 mg cm⁻² 60% Platinum on Vulcan and 2 mg cm⁻² platinum black carbon paper electrodes were used, with the gas diffusion layer Sigracet 22 BB, which was 215 μm thick. The components were hot pressed together. The schematics of the assembly are shown in figure 2.

2.5. Fuel cells and electrolyzers

We used an H-TEC SYSTEMS GmbH 1-cell rebuildable PEM fuel cell, which can be completely disassembled and then reassembled. The PEM fuel cell can be run in hydrogen/oxygen or hydrogen/air operation modes. In hydrogen and oxygen mode, which was used in this study, it can generate up to 1 W power. The electrode area is 16 cm² and a DC voltage from 0.4 V to 0.96 V can be generated.

We also used an H-TEC SYSTEMS GmbH 1-cell rebuildable PEM electrolyzer, which can be completely disassembled and then reassembled. The PEM electrolyzer can generate hydrogen and oxygen gas from de-ionized water (or distilled water) with the aid of a DC power supply. With room-temperature de-ionized water (20 °C–23 °C), electrical voltage input of up to 2.0 V and an electrical current of up to 4.0 A can be achieved (current density up to 250 mA cm⁻²). The electrode area for electrolyzers is 16 cm².

2.6. Membrane electrochemical performance tests

Since non-commercial and modified membranes are used, their electrochemical performance was tested. The performance of the membranes was assessed based on Faraday efficiency measurement, where the theoretically generated volume of hydrogen was compared with the measured amount. The theoretical volume of hydrogen evolved as a result of electrolysis was calculated as follows:

$$V_{\text{H}_2\text{theor}} = \frac{qRT}{2F(p_{\text{atm}} - p_{\text{H}_2\text{O}})} \quad (3)$$

$V_{\text{H}_2\text{theor}}$ —volume of theoretically generated hydrogen, m³;
 q —total electric charge, C;
 R —universal gas constant, 8.3145 m³ Pa K⁻¹ mol⁻¹;
 T —room temperature, K;
 F —Faraday's constant, 96 485 C mol⁻¹;
 p_{atm} —atmospheric pressure; Pa;
 $p_{\text{H}_2\text{O}}$ —water vapor pressure; Pa

2.7. Tritium water

Tritiated water was purchased from RC TriTec AG (catalog no. RCTT0075), specific activity 9 MBq ml⁻¹ on the date of production. A solution of (4.05 ± 0.01) MBq ml⁻¹ tritiated water was used.

2.8. Tritium measurement

In order to estimate the separation steps and overall factor of T measurements, tests in both the water and gaseous phases were performed.

The measurement of T in the gaseous phase evolved as a result of tritiated water electrolysis was carried out using the tritium monitor TEM 2100 A with the gas flow proportional detector DDH32. Generated hydrogen was introduced into the monitor using argon as a purge gas. The overall hydrogen amount was estimated according to the Faraday law:

$$Q = \int I(dt) dt \quad (4)$$

The T gas monitor provides signals in counts per second (cps), which are integrated over the given period (10 s) and an average number is given as an output. The average T release rate at a given integration period in becquerels (Bq) can be calculated as follows:

$$r_i = \frac{v_{\text{gas}} \cdot A_i}{3600 \cdot 1000} \quad (5)$$

where v_{gas} is the purge gas flow, l h⁻¹ (3600 · 1000 is used to recalculate to m³ s⁻¹)

A_i is the tritium average activity in the purge gas at the time moment, Bq m⁻³

$$A_i = v_{\text{gas}} \cdot K \cdot (R_i - R_0) \quad (6)$$

where K is the calibration coefficient, $\frac{\text{Bq}}{\text{m}^3 \text{ cps}}$

R_i is the average counting rate, counts per second (cps)

R_0 is the background counting rate, counts per second (cps)

To obtain the total tritium amount, the signal is integrated by time:

$$A_{\text{total}} = \int_0^t f(A_i) dt \quad (7)$$

where $t = 0$ is the start of the experiment and $t = t$ is the time when the signal reaches the background level after the experiment.

In order to recalculate the amount of tritium into the number of atoms, the decay constant λ was used:

$$N_T = \frac{A_{\text{total}}}{\lambda} \quad (8)$$

where the decay constant $\lambda = 1.78 \cdot 10^{-9} \text{ S}^{-1}$

In order to measure the tritium concentration in the water phase, tritiated water aliquots were mixed with liquid scintillation cocktail and analyzed by an Ultima Gold Tri-Carb 2900TR liquid scintillation counter (Perkin Elmer Inc., Ultima Gold). 20 ml high-density polyethylene vials were used for the scintillation measurements. 5 ml of tritium-containing water solution was mixed together with 15 ml scintillation cocktail. In the cases when the total volume of the tritium-containing water did not reach 5 ml, the sample was diluted to 5 ml, and this procedure was considered in the calculations. The scanning time in the scintillating device was 1 min, and up to five scans were made per sample. The liquid scintillator provides signals in counts per minute. The actual tritium activity in the measured volume was then calculated applying the registration efficiency of the device. The registration efficiency was regularly monitored using standard solutions (Perkin Elmer Inc.).

2.9. Tritium separation factor

As the number of atoms of protium and tritium (ratio) in tritiated water is known (liquid scintillation counter (LSC) measurement and manufacturer's data sheet), the tritium separation factor can be calculated as follows:

$$\beta = \frac{\left(\frac{N_H}{N_T}\right)_{(g)}}{\left(\frac{N_H}{N_T}\right)_{(l)}} \quad (9)$$

where $\left(\frac{N_H}{N_T}\right)_{(g)}$ is the ratio of protium to tritium atoms in the gaseous phase;

$\left(\frac{N_H}{N_T}\right)_{(l)}$ is the ratio of protium to tritium atoms in the liquid phase;

β is the tritium separation factor (H/T)

3. Results and discussion

3.1. Membrane electrochemical performance tests

Commercial membrane NafionTM, its modifications with graphene and radiation-stable alternative SPEEK membrane, and its modifications with graphene were tested by

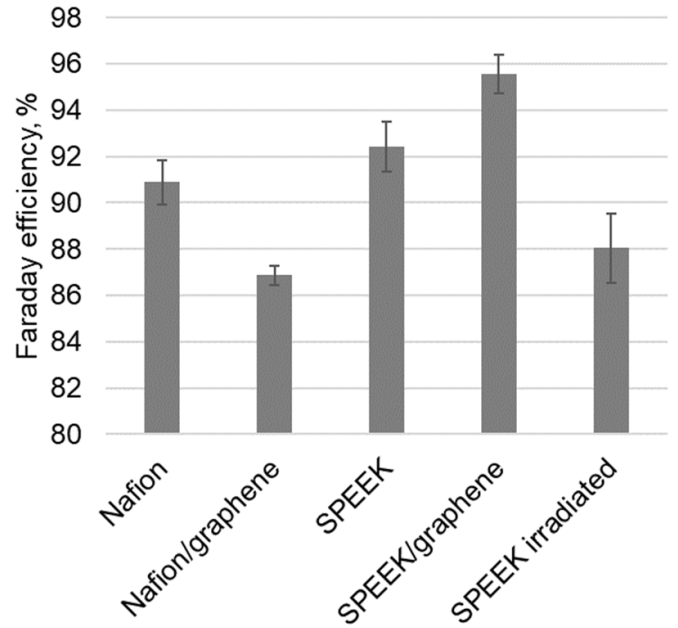


Figure 3. Membrane electrochemical performance.

measuring Faraday efficiency in water electrolysis (figure 3). Additionally, electron beam-irradiated (10 MeV, 500 kGy) membranes were also tested.

The results show that the SPEEK membrane both with and without graphene had a better performance compared to the commercial NafionTM membrane. Graphene addition increased the Faraday efficiency for the SPEEK membrane but decreased it for NafionTM. However, it must be noted that this performance will be affected by irradiation, which is an important aspect since use in the radiation environment is planned.

3.2. Tritium separation factor—electrolysis

Tritium separation in the electrolysis process was assessed. PEM electrolysis using non-modified membranes gave separation factors of 8.9 ± 0.7 and 10 ± 1 for NafionTM and SPEEK, respectively (figure 4). Uncertainties in these measurements were calculated as a combination of systematic and random errors (multiple measurements for each combination performed).

Electrostatic interaction between oxygen in the sulfonate group and hydrogen in hydroxonium ions has been reported to be much stronger in SPEEK than in NafionTM, leading to a lower diffusion coefficient of H_3O^+ in SPEEK [30]. A slower diffusion process through the membrane can lead to a better separation due to the contribution of the isotopic effect in electrostatic interactions [31] in addition to the kinetics of the hydrogen evolution reaction of different isotopes [12]. Therefore, a higher separation factor using SPEEK as a PEM was expected.

According to the literature, the separation factor using the electrolysis process can reach values of up to 15, which is higher than that obtained by the proposed setup. However, the initial aim of the system was to comparatively test different

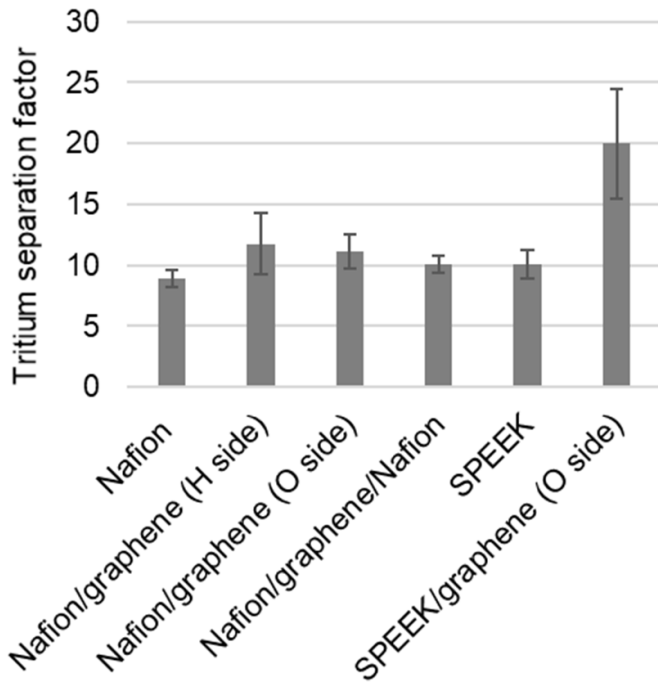


Figure 4. Tritium separation factor during PEM electrolysis using different membranes and their modifications.

membranes and their modifications. Several options to incorporate a graphene layer have been tested using Nafion™ as the membrane material. The results show no significant difference if the graphene is transferred onto the O or H sides between the two membranes. Therefore, for the SPEEK-based system, only one configuration was tested. In the case of the Nafion™-based system, a slight increase in the separation factor was observed—up to 12 ± 3 , providing a maximum increase of 33%. The SPEEK/graphene combination provided the highest increase in the separation factor up to 20 ± 4 , which means by 98% compared with SPEEK and 125% compared with the Nafion™ membrane-based electrolyzer system (figure 4). The increased separation factor in the SPEEK/graphene combination can be explained as a synergetic result of isotopic effects in the diffusion process through the polymeric membrane, permeation through the graphene layer, and the kinetics of the hydrogen evolution reaction.

The results show that graphene-coated SPEEK membranes are a promising material for hydrogen isotope separation by means of PEM electrolysis. Further studies and experiments should be dedicated to a detailed analysis of the parameter optimization in order to approach the theoretically predicted separation factor that can reach the value of 30. Work on the system scale-up is also expected during future studies.

3.3. Electrolyzer–fuel cell system

A tritium enrichment system has been successfully constructed and tested. The main advantage of the system is the reduction of radioactive waste and electric power regeneration using a fuel cell. On average, the fuel cell achieved a power output

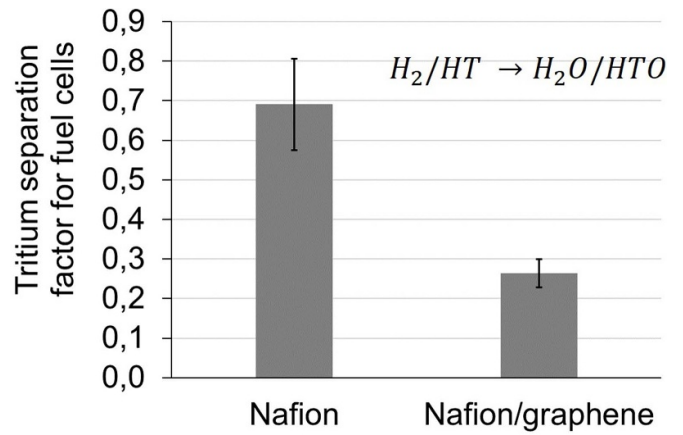


Figure 5. Tritium separation factor for fuel cells in the electrolyzer–fuel cell experimental setup.

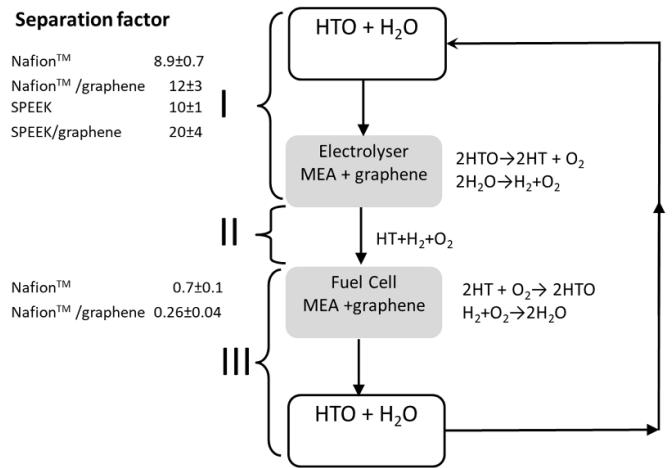


Figure 6. Tritium separation factor in different separation phases.

of ~0.1 W, which can be stored by a battery or directly applied to the electrolyzer (consumption 0.4–1.2 W).

The tritium separation factor for Nafion™ membranes showed a value of 0.69 ± 0.12 , whereas graphene-coated Nafion™ membranes showed 0.26 ± 0.04 . These results are explained by the tritium separation factor equation (equation (9)), which measures the ability to concentrate tritium in the liquid phase. For fuel cells, the opposite effect is present—tritium is concentrated in the gaseous phase as graphene acts like a sieve for HT/H₂ mixture, letting through more of the lighter isotope H than T [27]. Therefore, the lower the separation factor (as per equation (9)) for fuel cells, the higher the activity of T in the gaseous phase due to the function of the fuel cell. The tritium separation factor for fuel cells is shown in figure 5.

The experimental system (figure 6) showed that it is possible to simultaneously produce both enriched tritiated water as well as T-enriched H gas. Meanwhile, all the T is recycled:

- In the electrolyzer—tritium-enriched HTO is produced (first and main product) and tritium-containing hydrogen gas is used further in the system by the fuel cell;

- In the fuel cell—the tritium-containing hydrogen gas is enriched (second product) and can be pressurized into gas cylinders, whereas the produced tritium-containing water can be collected and recycled to the electrolyzer.

More research is needed regarding the electrolyzer–fuel cell system parameter optimization, as it was discovered that a recirculating flow within the system can increase the fuel cell performance by up to 50%, and the pressure is a good indicator of the overall system behavior.

4. Conclusions

If SPEEK membrane with graphene coating is used as a PEM in electrolysis cells, the tritium separation factor could be increased by up to 125% compared to commercial membrane materials, such as Nafion™, used in fuel cell systems, which may have problems with reduced performance due to the effect of radioactive hydrogen isotope interaction with the membrane material. SPEEK membranes as alternative materials have benefits for such applications compared to commercial membranes.

Further experiments are required in order to obtain more detailed information on other parameters affecting the separation efficiency in the case of such SPEEK-based systems and possibilities to upscale the developed tritium enrichment system.

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