15th International Symposium on Fusion Nuclear Technology

September 10 - 16, 2023,
Las Palmas, Grand Canaria

Graphene-based electrochemical system for radioactive hydrogen isotope enrichment

E. Pajuste, G. Vaivars, I. Reinholds, A. Lescinskis, A. Kizilovs, R.J. Zabolockis, M. Sondars

LATVIJAS UNIVERSITĀTE

LATVIJAS UNIVERSITĀTE

OUTLINE

- Tritium in fission and fusion
- The need of separation of hydrogen isotopes
- Existing methods
- Concept of the graphene based electrochemical separation
- Aim of the study
- Steps for method development
- Separation factor
- Set-up concept & prototype
- Summary and outlook

$^{1}_{1}H$ $^{2}_{1}H$ $^{3}_{1}H$

LATVIJAS UNIVERSITĀTE

TRITIUM IN FISSION AND FUSION

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

$$^3_1H \rightarrow ^3_2He + \beta^- + \bar{\nu}$$

T is primary produced by ternary **FISSION** in nuclear weapon tests and **nuclear power reactor**s by neutron activation reactions with:

- **boron** in water and control rods $^{10}_5B + ^1_0n \rightarrow \mathbf{^3_1H} + ^4_2He + ^4_2He$
- **heavy wate**r moderator and coolant (e.g. CANDU type reactors) $^2_1H + ^1_0n \rightarrow \mathbf{^3_1H} + \gamma$

In **FUSION** tritium is foreseen as a **nuclear fuel** $^2_1H + ^3_1H \rightarrow \mathbf{^4_2He} + n$

T will be produced on site from lithium $^6_3Li + ^1_0n \rightarrow \mathbf{^3_1H} + ^4_2He$

Additionally, it is also produced by the:

- Deuterium – deuterium reactions $^2_1H + ^2_1H \rightarrow ^3_1H + ^1_1H$
- beryllium activation

www.iter.org

LATVIJAS UNIVERSITĀTE

THE NEED OF TRITIUM SEPARATION

Tritium separation is crucial in following applications:

- tritium **extraction from cooling water** of nuclear fission and fusion reactors in order to decrease amount and class of radioactive waste;

- tritium **recovering and purification for its further use** in fusion devices or industrial applications;

- **decrease of tritium contamination** of natural water sources in case of accidental tritium water leakages;

LATVIJAS UNIVERSITĀTE

EXISTING AND EVOLVING METHODS

Existing methods for T separation are mostly either time and energy consuming or expensive. New separation methods with larger separation factors, reduced number of stages and energy consumption are needed[1]

Method	Separation factor, H/T	Costs, $/1L	TRL
Water Distillation	1.059	5	7
Cryogenic Distillation	1.8	2.5	6
Girdler Sulfide	3.6	3	7
Ammonia Bithermal	16.1	44	7
Catalytic Exchange	5.3	2	7
Electrochemical	**15**	**6**	**5**
Adsorption Processes	1.4	4.5	6

[1]*K. Brooks , G. Sevigny, E. Love Review and Evaluation of Water Detritiation Technologies for Watts Bar Primary Cooling Wate, in, Pacific Northwest National Laboratory, Richland, WA 99352, 2017.*

LATVIJAS UNIVERSITĀTE

ELECTROLYSIS & POLYMER ELECTROLYTE MEMBRANES

Isotopic effects in the electrochemical processes of water is based on the differences in the kinetics of the hydrogen evolution reaction of different isotopes.

Electrolysis had been the first widely used method for deuterium enrichment and currently is used in combination with catalytic isotope exchange

Use of the solid polymer electrolyte membrane (or proton exchange membrane) PEM instead of electrolytic solutions has number of advantages:

- absence of any impurities - ultrapure gas production;
- no risk of explosive gas mixture formation since hydrogen and oxygen are emitted by separate outputs
- lower specific energy consumption
- PEM's and equipment is scalable

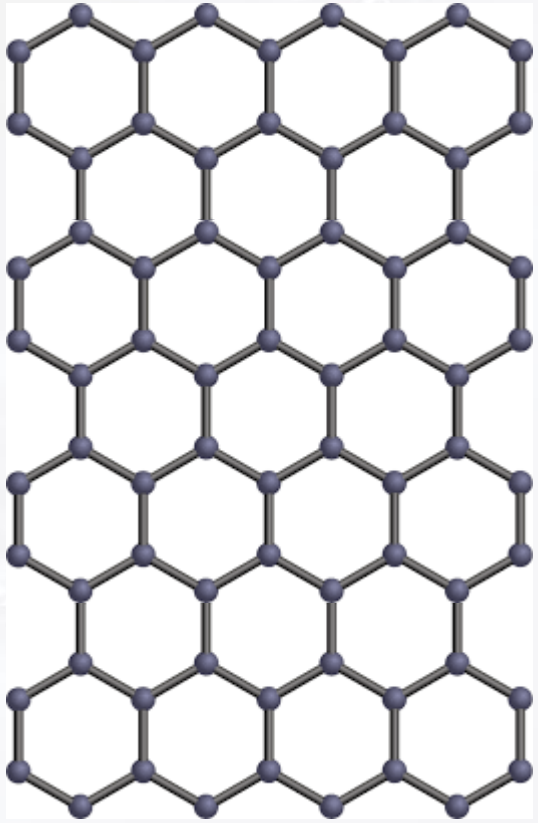
GRAPHENE IN ELECTROCHEMICAL SEPARATION

Polymer Nafion™ membrane coated with graphene layer has been proposed by Hidalgo et al[2] for enhanced isotope separation.

It has been demonstrated that deuterons permeate through graphene much slower than protons, resulting in a separation factor of ≈10 at room temperature.

Authors suggest that the proposed technique could reach separation factor ~30 for protium-tritium separation that is a significant improvement compared to the existing methods[2]

The isotope effect is assumed to be attributed to a difference of ≈60 meV between zero-point energies of incident protons and deuterons, which translates into the equivalent difference in the activation barriers posed by two-dimensional crystals.



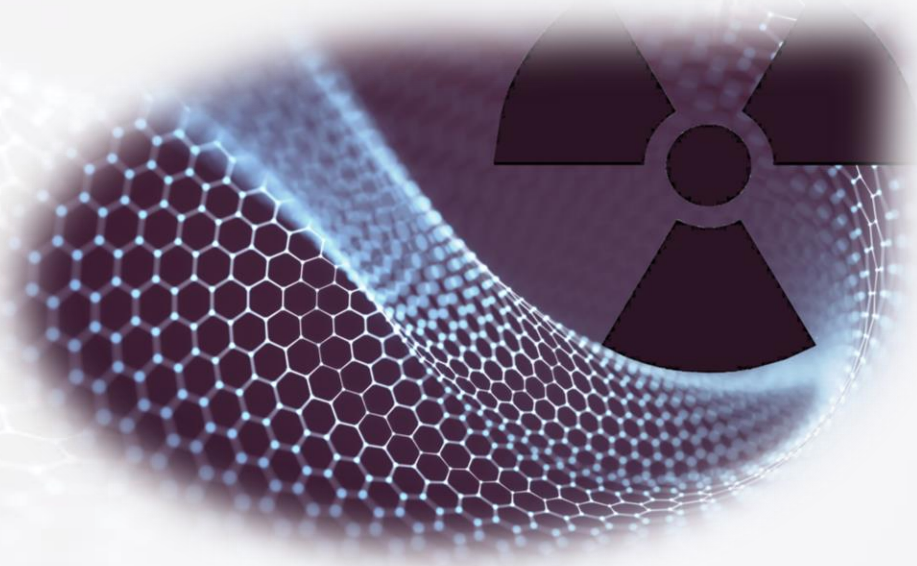
2 Lozada-Hidalgo, M., et al., Scalable and efficient separation of hydrogen isotopes using graphene-based electrochemical pumping. Nature Communications, 2017. 8(1): p. 15215.

LATVIJAS UNIVERSITĀTE

THE AIM OF THE STUDY

Development of a set-up for separation of tritium based on the concept described above which includes the **design** and implementation of the **test system** for separation measurement, **demonstration** of the practical application of the concept.

Additionally, special attention is dedicated to evaluation of the **radiation stability** of the developed system, thus choice of radiation stabile materials and tests under potential exposure conditions.



LATVIJAS UNIVERSITĀTE

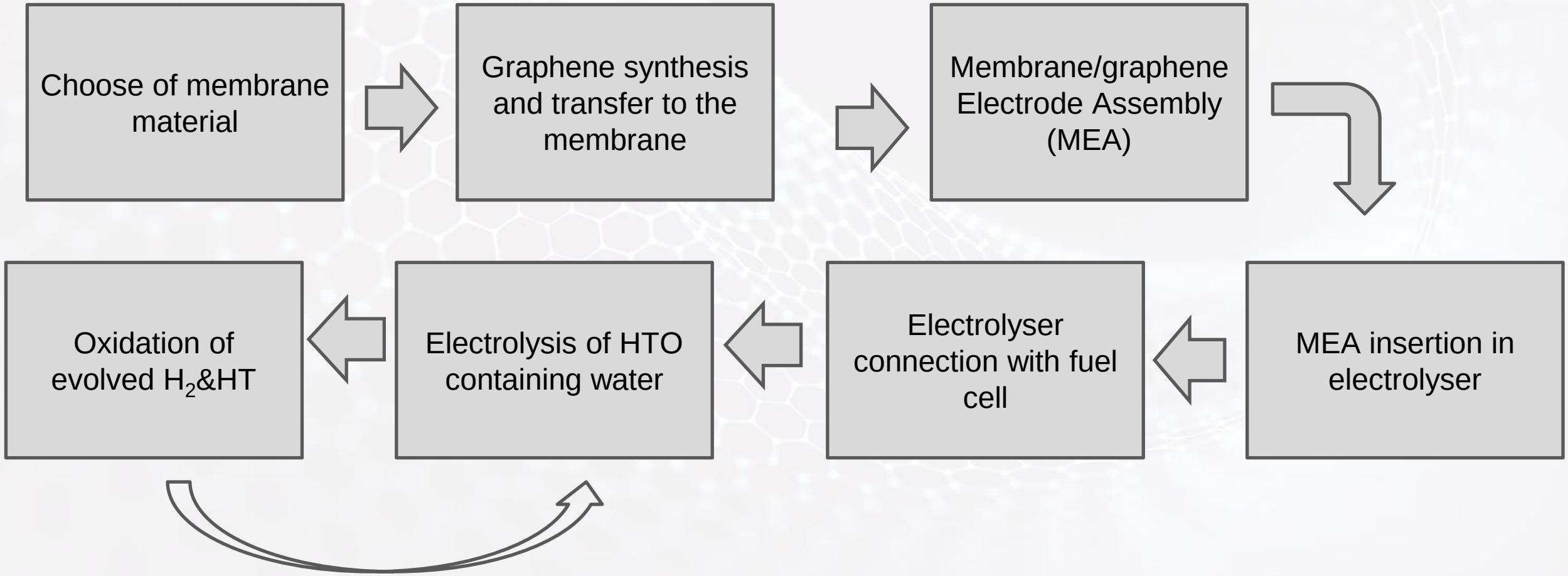
EXPECTED ADVANTAGES

Graphene-based electrochemical separation

- **High separation factor**
- Reduced number of steps
- Reduced energy consumption
- Exploitation in **harsh radiation environments**

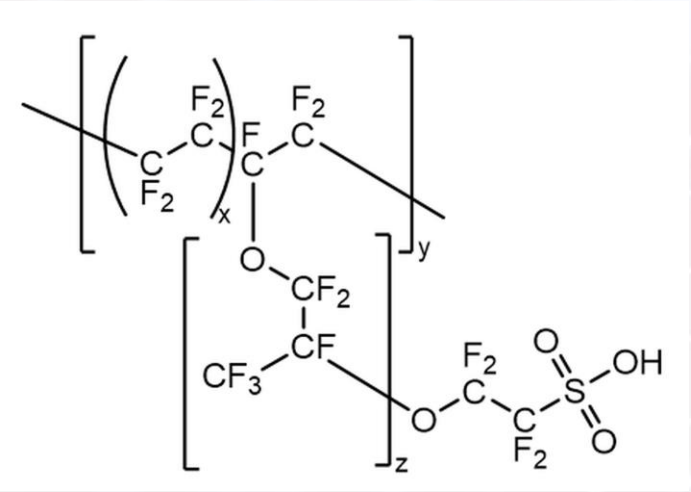
LATVIJAS UNIVERSITĀTE

Steps of system development



PROTON EXCHANGE MEMBRANES (PEM)

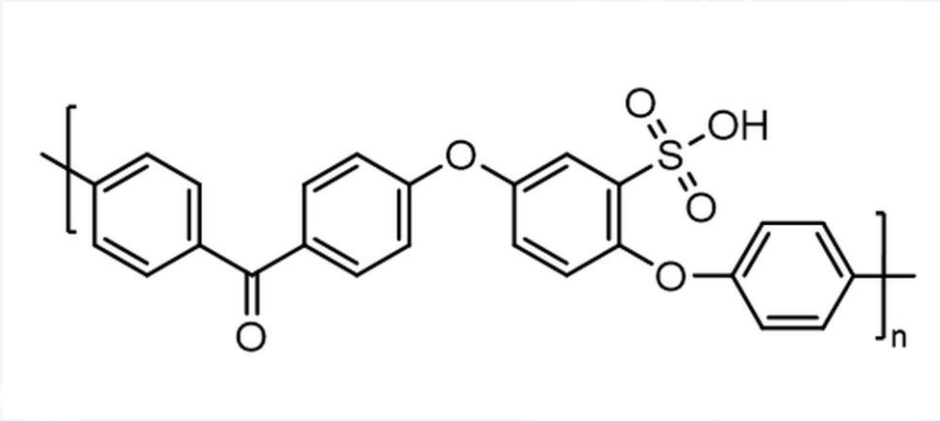
Commercial



Nafion®
Sulfonated tetrafluoroethylene - based fluoropolymer–copolymer

- Thermally and mechanically stable
- Low cost
- Radiation stable

Laboratory synthesized alternative

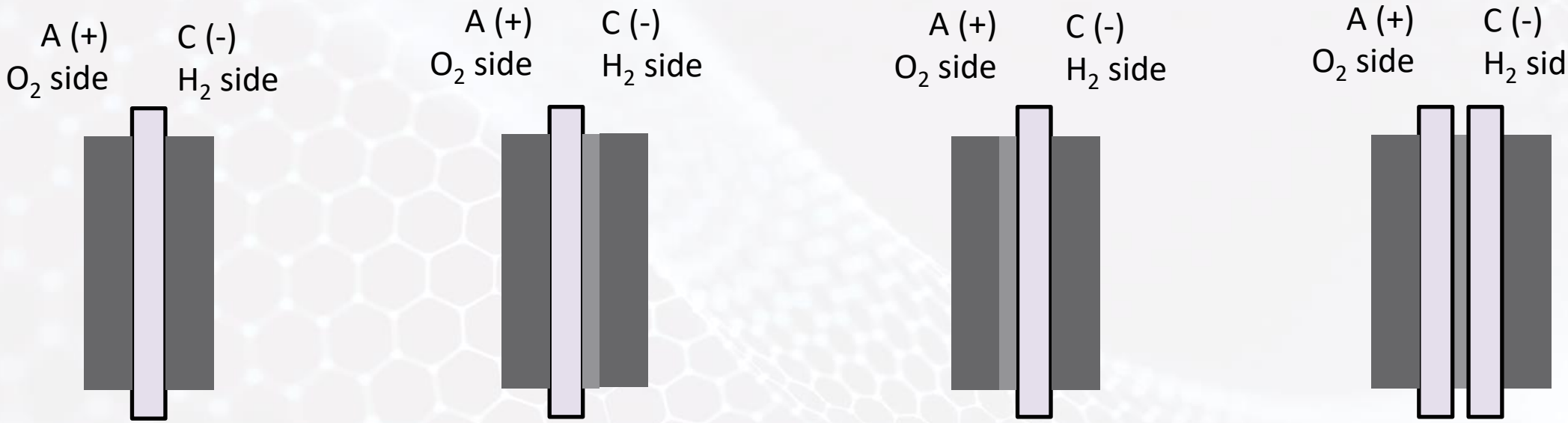


SPEEK
Sulfonated polyether-ether ketone

E. Pajuste, I. Reinholds, G. Vaivars, et al, Evaluation of radiation stability of electron beam irradiated Nafion® and sulfonated poly(ether ether ketone) membranes, Polymer Degradation and Stability 200 (2022) 109970. https://doi.org/10.1016/j.polymdegradstab.2022.109970

LATVIJAS UNIVERSITĀTE

Graphene/PEM composites

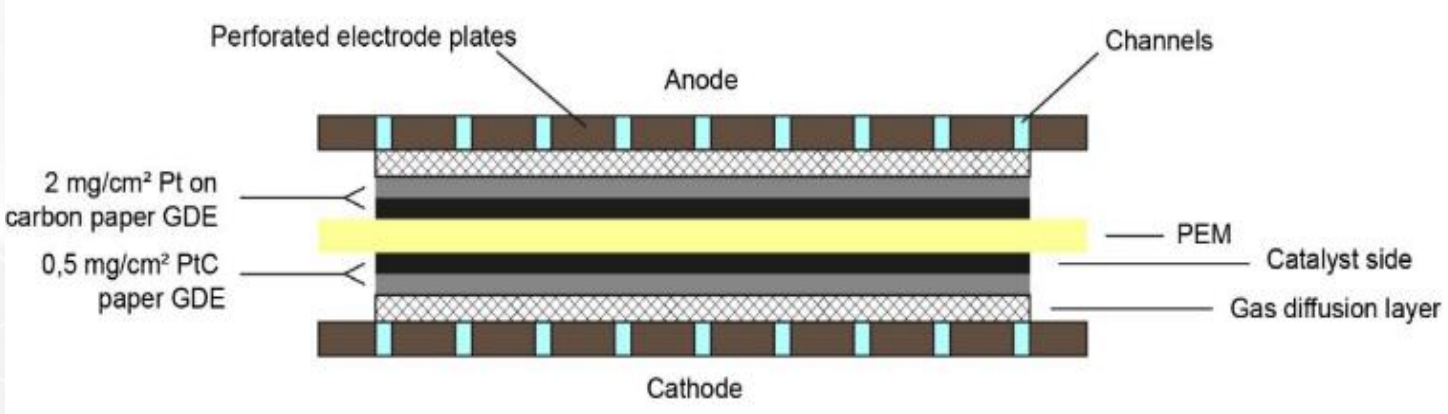


Transfer on the membranes were done by hot pressing with graphene-coated copper foils (180°C,11.8 kN) followed by Cu dissolution with nitric acid and persulfate

Membrane Electrode Assembly (MEA)

The MEA consists of:

- PEM
- Catalysts on both sides
- Cathode
- Anode
- Gas diffusion layer (GDL).



0.5 mg/cm² 60% Platinum on Vulcan and 2 mg/cm² Platinum Black - Carbon Paper Electrodes were used, with the GDL Sigracet 22 BB (thickness 215 microns). The components were hot pressed together.

LATVIJAS UNIVERSITĀTE

Separation factors

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

- Measurement of T in gaseous phase evolved as a result of tritiated water electrolysis has been done by the means of tritium monitor TEM 2100A with gas flow proportional detector DDH32.
- In water phase the tritiated water aliquots were mixed with liquid scintillation cocktail and analysed by Ultima Gold Tri-Carb 2900TR liquid scintillation counter (Perkin Elmer Inc., Ultima Gold), 20mL high density polyethylene vials are used for the scintillation measurements.

As the number of atoms of protium and tritium (ratio) is known the tritium separation factor can be calculated as follows:

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

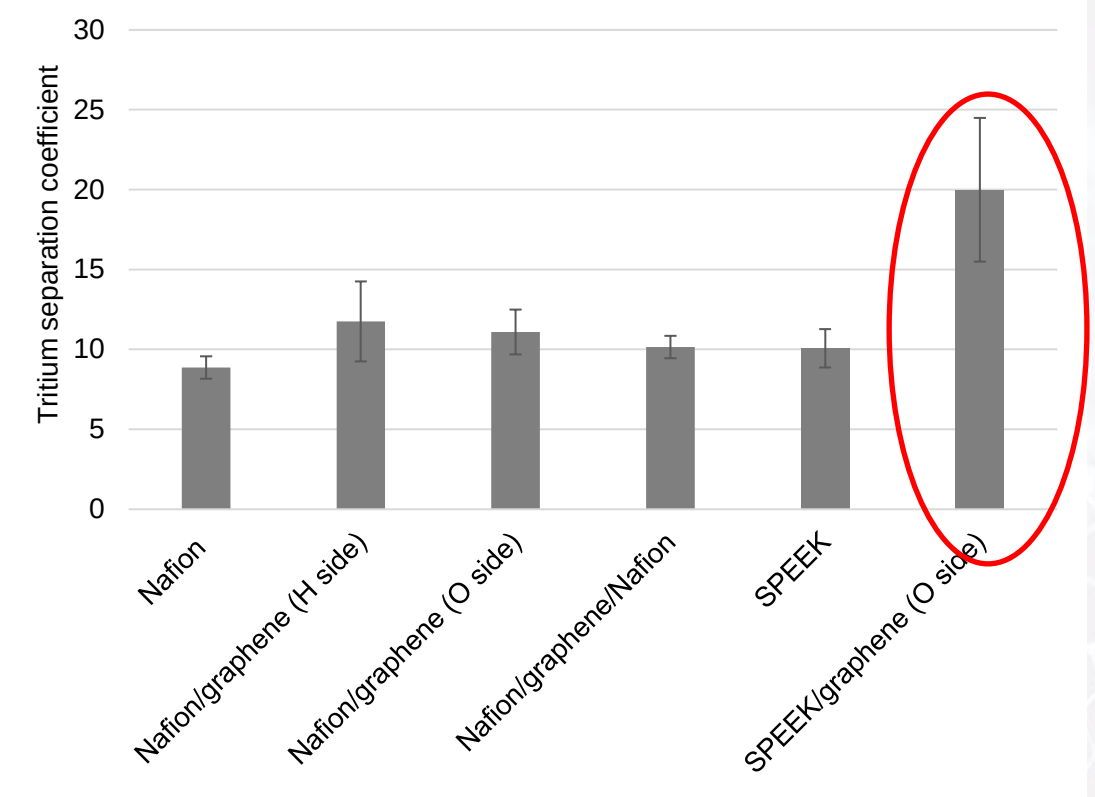
where $\left({}^{N_H}/_{N_T}\right)_{(g)}$ *– ratio of protium to tritium atoms in gaseous phase;*

$\left({}^{N_H}/_{N_T}\right)_{(l)}$ *– ratio of protium to tritium atoms in liquid phase;*

β *– tritium separation factor (H/T)*

LATVIJAS UNIVERSITĀTE

Separation factor in elecotrlysis



According to the literature, the separation factor using electrolysis process can reach value up to 15 which is higher that obtained by the proposed setup. However, the initial aim of the system is to comparatively test different membranes and their modifications

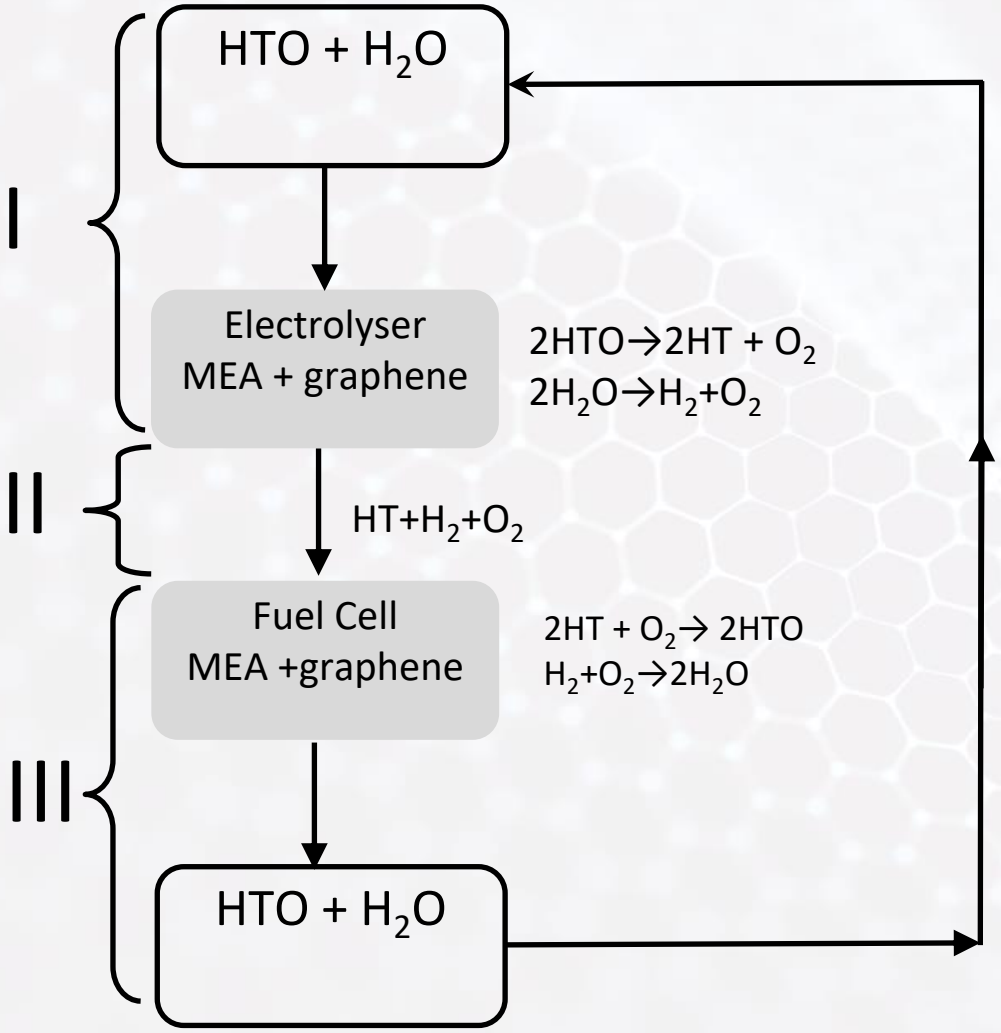
PEM electrolysis using non-modified membranes gave separation factors 8.9±0.7 and 10±1 for Nafion™ and SPEEK, respectively.

In the case of Nafion™ based system slight increase of separation factor was observed - up to 12±3, providing maximum increase of 33%.

The SPEEK/graphene combination provided the highest increase of the separation factors up to 20±4, which means by 98% compared to SPEEK and **125%** comparing with the Nafion™ membrane-based electrolyser system.

LATVIJAS UNIVERSITĀTE

SET-UP CONCEPT



The separation/enrichment system is based on combination of PEM electrolyser with an exchangeable membrane assembly and a fuel cell where generated hydrogen gas is turned back into the water.

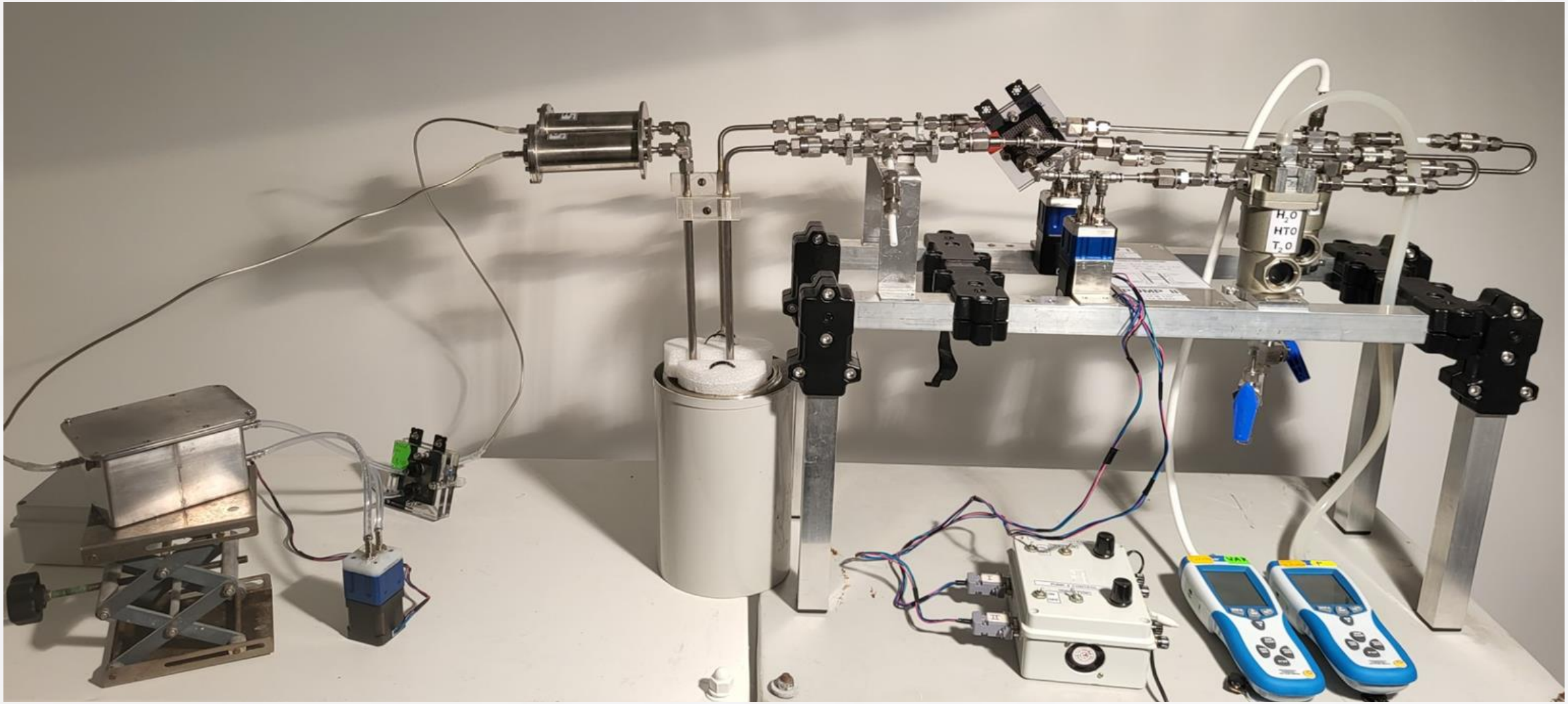
Main separation is expected to take place in the electrolyser based on both differences in the kinetics of the hydrogen evolution reaction and transport through graphene layer of different isotopes.

Water is, thereby, enriched with tritium.

However, evolved hydrogen still contains heavy isotopes. Therefore, the **fuel cel**l is introduced to turn hydrogen into water which can be **electrolysed again** until required T enrichment is achieved.

LATVIJAS UNIVERSITĀTE

PROTOTYPE



Separation factor

LATVIJAS UNIVERSITĀTE

System opereation

- In the electrolyser – 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 produced tritium containing water can be collected and recycled to the electrolyser
- On average, the fuel cell achieved power output of ~ 0.1 W, which can be stored by a battery or directly applied to the electrolyser (consumption 0.4 – 1.2 W).

LATVIJAS UNIVERSITĀTE

SUMMARY AND OUTLOOK

- If sulfonated poly ether ether ketone (SPEEK) membrane with graphene coating is used as a PEM in electrolysis cell, tritium separation factor could be increased by up to 125% compared to commercial membrane materials, such as Nafion™
- SPEEK membranes as alternative materials have benefits for such applications compared to the commercial membranes also regarding their cost and radiation stablity.
- Further experiments are requied in order to obtain more detailed information of other parameters affecting the separation efficiency in the case of such SPEEK based systems and the possibilities to upscale the developed tritium enrichment system.

LATVIJAS UNIVERSITĀTE

Acknowledgements

The research was supported by European Regional Development Fund Project No.1.1.1.1/19/137 “Graphene-based electrochemical pumping system for radioactive hydrogen isotope separation”

NATIONAL DEVELOPMENT PLAN 2020

EUROPEAN UNION
European Regional Development Fund

INVESTING IN YOUR FUTURE

JYVÄSKYLÄN YLIOPISTO
UNIVERSITY OF JYVÄSKYLÄ

INSTITUTE OF SOLID STATE PHYSICS
UNIVERSITY OF LATVIA

BSI BALTIC SCIENTIFIC INSTRUMENTS

Thank you for your attention!

LATVIJAS UNIVERSITĀTE