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IAEA
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Vienna, Austria

UNIVERSITY OF LATVIA

Extraction And Separation Of Tritium, The Nuclear Fusion Fuel And The By-product Of Fission

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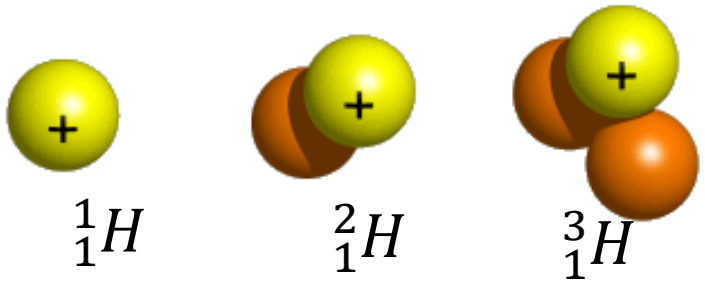
Outline

- Tritium in fission and fusion
- The need of separation of hydrogen isotopes
- Existing methods
- Concept of the graphene based electrochemical pumping
- Scope of the study
- Implementation steps into practice



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:

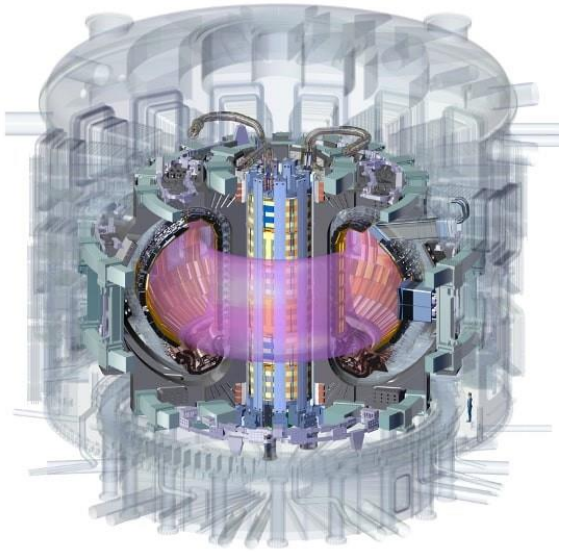
- **boron** in water and control rods $^{10}_5B + {}^1_0n \rightarrow \mathbf{^3_1H} + {}^4_2He + {}^4_2He$
- **heavy wate**r moderator and coolant (e.g. CANDU type reactors) $^2_1H + {}^1_0n \rightarrow \mathbf{^3_1H} + \gamma$

In **FUSION** tritium is foreseen as a **nuclear fuel** $^2_1H + {}^3_1H \rightarrow \mathbf{^4_2He} + n \quad (17.6MeV)$

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



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The need of tritium separation

There is a constant risk of T release into the environment from the nuclear facilities such as pressurized water reactors, irradiated fuel and recycling plants and based on T production during waste dispose, small incidents or nuclear accidents such as as the case of Fukushima Daiichi that caused significant emission of T into the environment.

Tritium separation is crucial in following applications:

- Tritium extraction from air in case of its **industrial contamination** if containment fails resulting in tritium emissions (nuclear industry, production plants, research institutions);
- 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;

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

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
Electrolysis	15	6	5
Adsorption Processes	1.4	4.5	6

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.

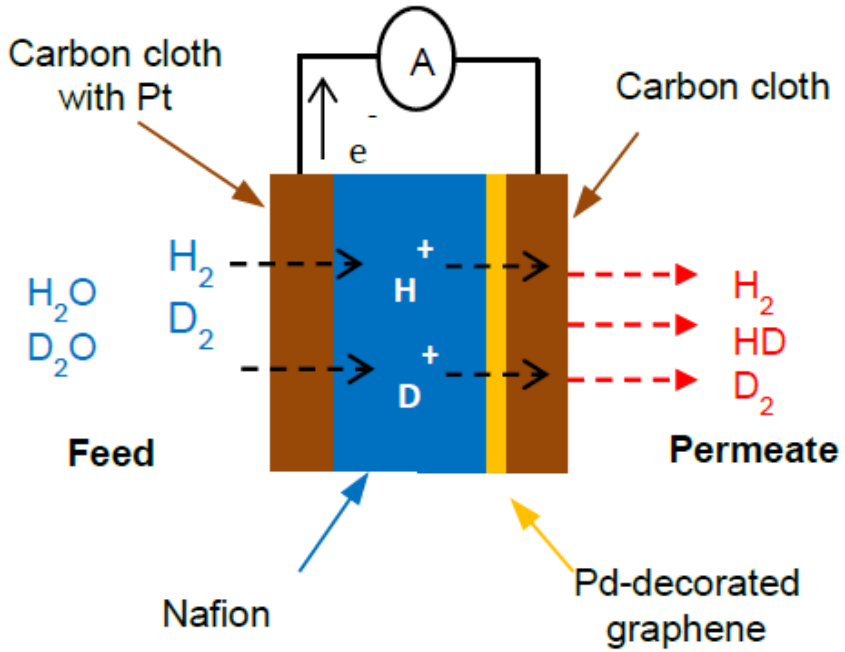
Graphene based electrochemical pumping

Electrochemical pumping applies fuel cell principle – the membrane-electrode assembly consists of two catalytic electrodes deposited on a proton conducting membrane.

Hydrogen gas or water is split on one side to the **proton and electron**, which combines on the other side of membrane.

Additionally, graphene coating is introduced on the proton conducting membrane as a quantum sieve

It is expected that proposed technique could reach separation factor **~30 for protium-tritium** separation that is significant improvement compared to the existing methods

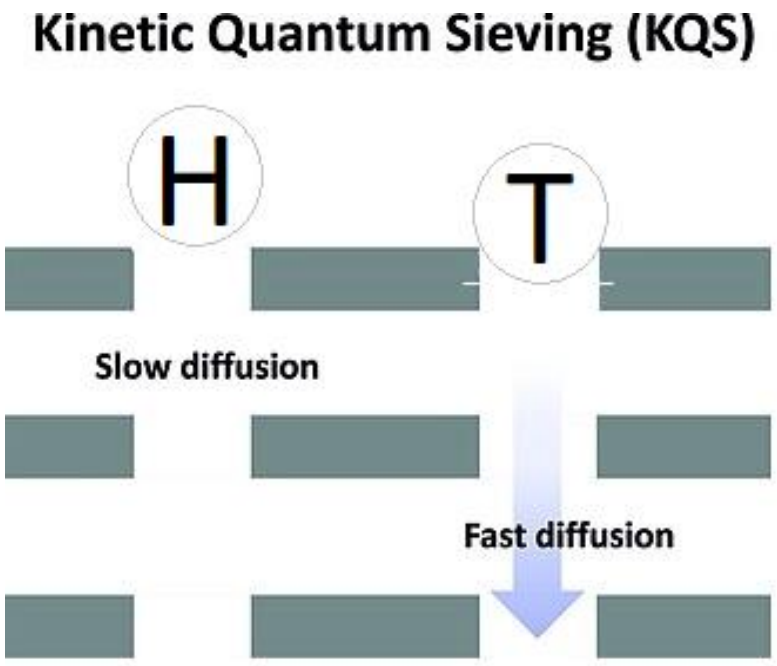


Schematics of deuterium separation device proposed by Hildalgo et al

Lozada-Hidalgo, S. Zhang et al, Scalable and efficient separation of hydrogen isotopes using graphene-based electrochemical pumping, Nature Communications, 8 (2017) 15215.

Quantum sieving

Atoms start behaving as waves rather than classical particles if confined in spaces comparable with their de Broglie wavelength



Adopted from Oh, H. and Hirscher, M. (2016), Quantum Sieving for Separation of Hydrogen Isotopes Using MOFs. Eur. J. Inorg. Chem., 2016: 4278-4289

At thermal energies De Broglie wavelength can be calculated as follows:

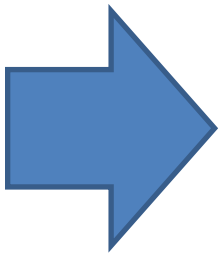
$$\lambda_B = \frac{h}{\sqrt{3mkT}}$$

h- Planck constant
m – particle mass
k – Boltzmann constant
T – temperature
De Broglie wave length for the hydrogen isotopes at different temperatures are as follows:

Isotope	Mass, kg	Wavelenght, nm		
		4K	298K	350K
^1H **(H)**	$1{,}67 \cdot 10^{-27}$	1,24	0,146	0,134
^2H **(D)**	$3{,}34 \cdot 10^{-27}$	0,87	0,103	0,095
^3H **(T)**	$5{,}01 \cdot 10^{-27}$	0,71	0,084	0,077

Expected advantages

GRAPHENE-BASED ELECTROCHEMICAL PUMPING

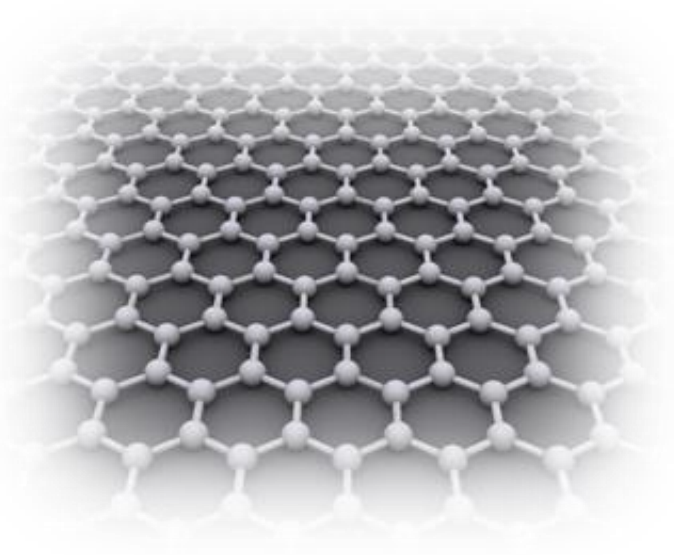


- **High separation fac**tor
- Reduced number of steps
- Reduced energy consumption
- Exploitation in **harsh radiation environments**
- Possibility to **develop remote controlled** device

The aim of the study

Development of a set-up for separation of tritium both from water and gas based on the concept described above which includes the **design** and implementation of the **test system** for separation measurement, **demonstratio**n 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 test under potential exposure conditions



Steps & Challenges for practical implementation

Radiation resistant membrane

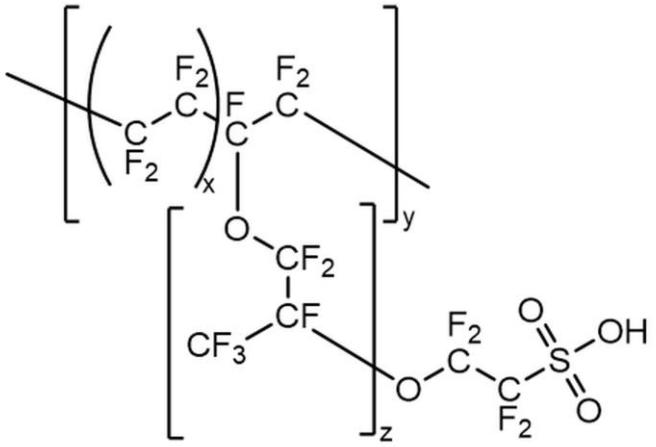
Graphene synthesis and transfer onto the membrane

Insertion of the membrane/graphene composite into the Membrane Electrode Assembly

- Construction
- Feeding
- Output
- Containment
- Pressure

Reliable measurement of the separation factor

Radiation stability - commercial membranes



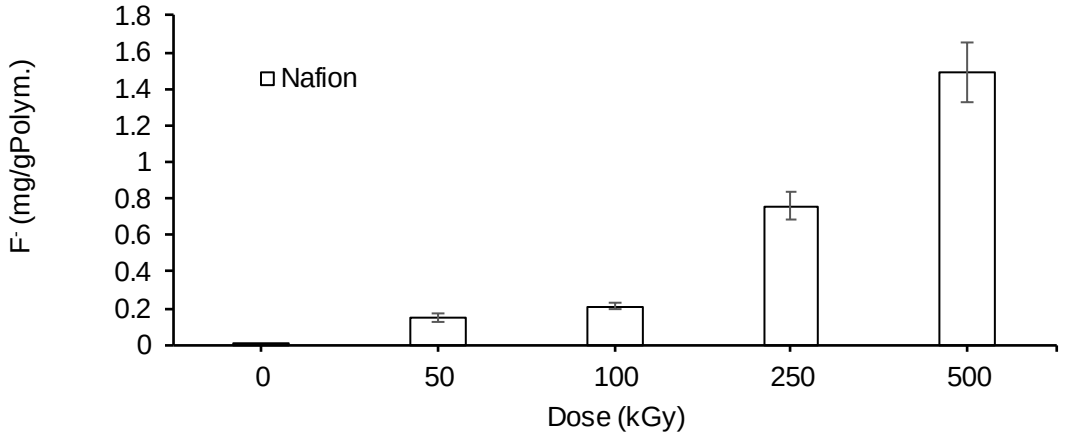
Nafion®

Sulfonated tetrafluoroethylene - based fluoropolymer–copolymer

First synthesised by the DuPoint™ is a standard membrane material used for polymer electrolyte membrane (PEM) applications

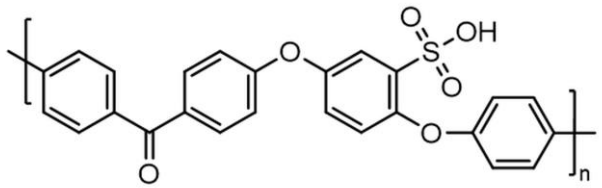
Electron beam irradiation (6MeV) in dose range from 50 to 500kGy was used to evaluate the effects of radiation on the physico-chemical and mechanical properties

Methods: Fourier-transform infrared (FTIR) spectroscopy and FTIR-TGA, Ion chromatography, Differential scanning calorimetry (DSC), Mechanical properties Dynamic mechanical analysis (DMA) , Electron paramagnetic resonance (EPR) spectroscopy

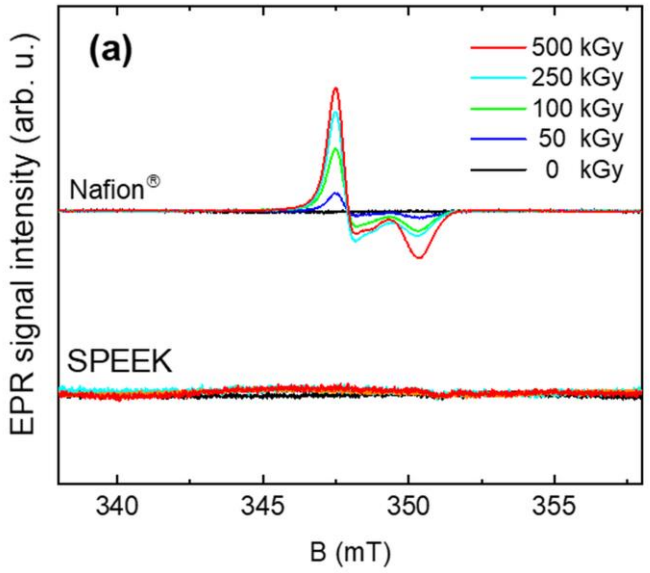


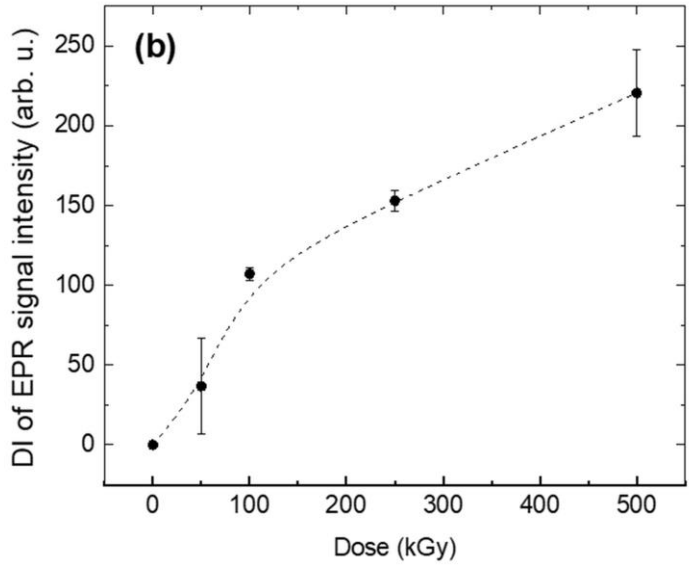
E. Pajuste, I. Reinholds, G. Vaivars, et al, Evaluation of radiation stability of electron beam irradiated Nafion® and sulfonated poly(ether ether ketone) membranes, Polymer Degradation and Stability 200 (2022) 109970. https://doi.org/10.1016/j.polymdegradstab.2022.109970

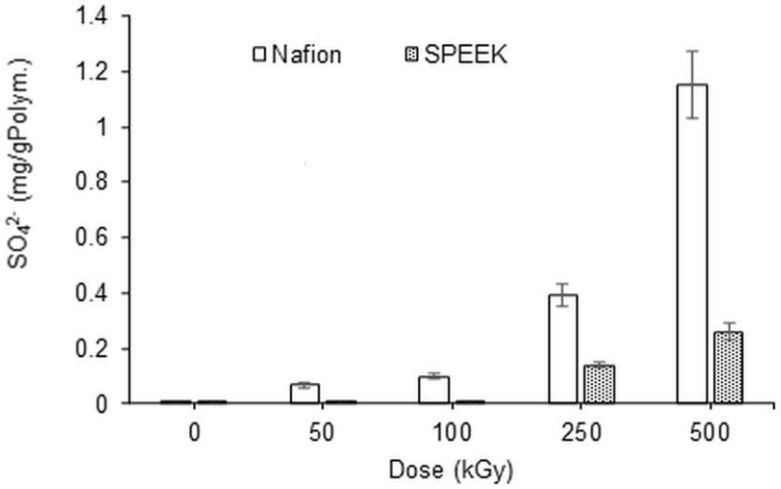
Radiation stability - comparison with alternative membrane

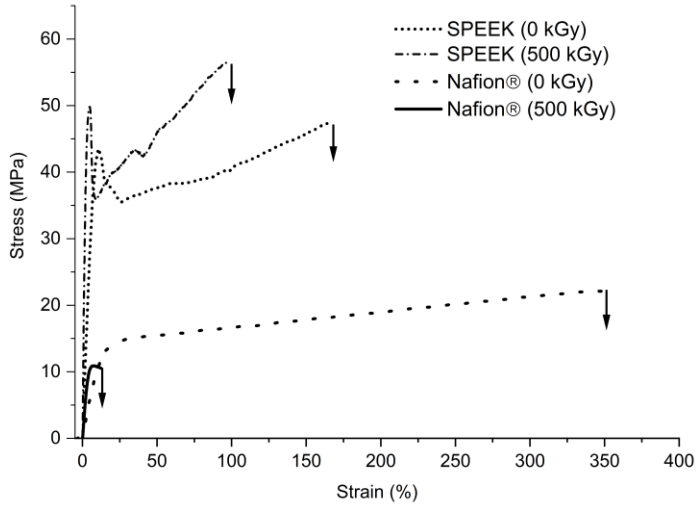


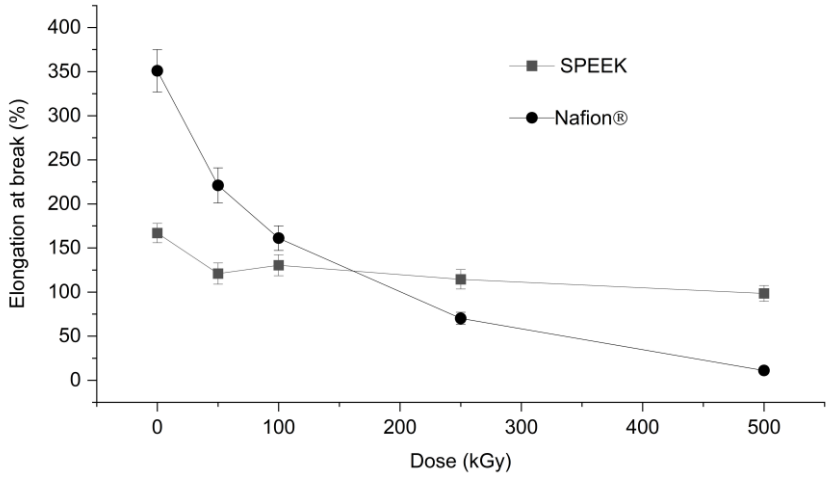
SPEEK
Sulfonated polyether-ether ketone











Graphene synthesis and transfere

Graphene synthesis was performed on the catalytic copper surface using Chemical vapour deposition CVD reactor according to the methodology developed by X. Li, et al. (Science, 324 (2009) 1312-1314)

Several approaches of graphene transfer to the membrane have been tested and most effective one chosen for further activities.

Polymer PMMA (used as a framework) coating on graphene synthetized on Cu substrate, Cu dissolution either by 20% $FeCl_3$ or 1 M ammonium per sulphate and then graphene transfer to membrane by dissolution of polymer in acetone not possible due to the membrane properties

Membrane formation on the surface of the Cu substrate from suspension, Cu dissolution either by 20% FeCl3 or 1M ammonium persulfate

Transfer using hot pressing from Cu substrate followed by dissolution of Cu substrate ammonium persulfate (method from literature) or detached mechanically

Quality control of the transfere

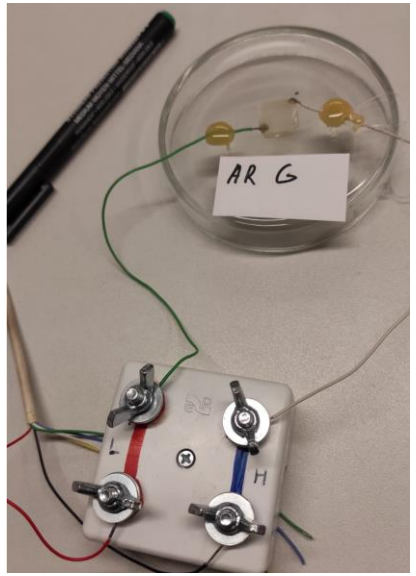
RAMAN Spectroscopy - not possible due to the membrane properties

Graphene coated surface electrical resistance

Graphene acting as a barrier - water permeation change (T tracer method)

Graphene on membrane surface

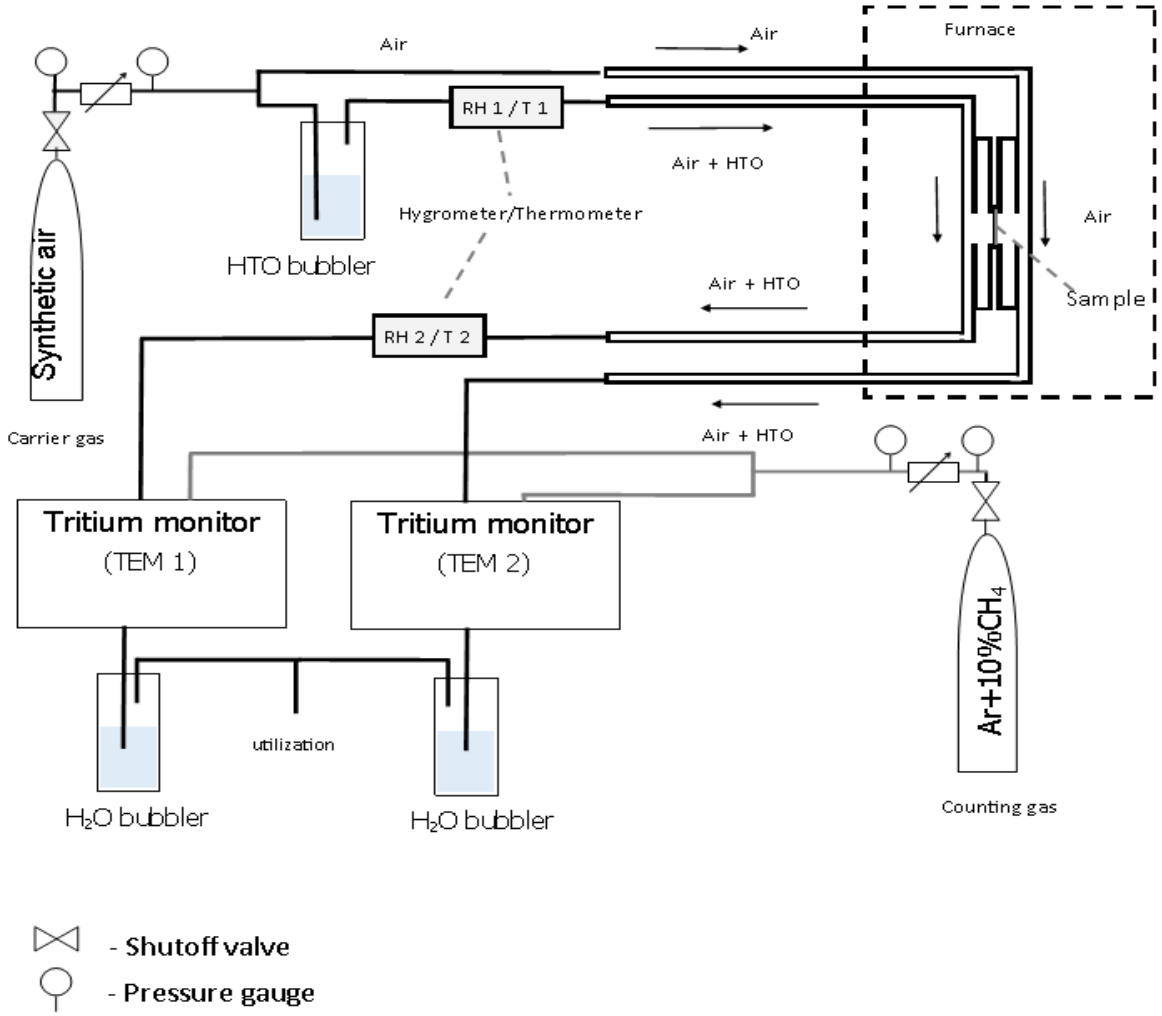
Electric resistivity measurement



Without graphene > 20 MΩ
With graphene 240±10 kΩ

(SPEEK)

Tritiated water or water vapour permeation measurements



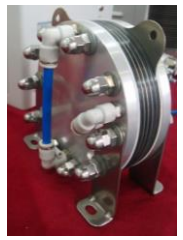
Tritium measurement - electrolysis of HTO

$$\mathrm{A}(+)\colon 2\,H_2O_{(l)} \longrightarrow O_{2(g)} + 4\,H^+_{(aq)} + 4\,e^-$$

$$\mathrm{C}(-)\colon 4\,H^+_{(aq)} + 4\,e^- \longrightarrow 2\,H_{2(g)}$$

$$\boldsymbol{2\,H_2O_{(l)} \longrightarrow 2\,H_{2(g)} + O_{2(g)}}$$

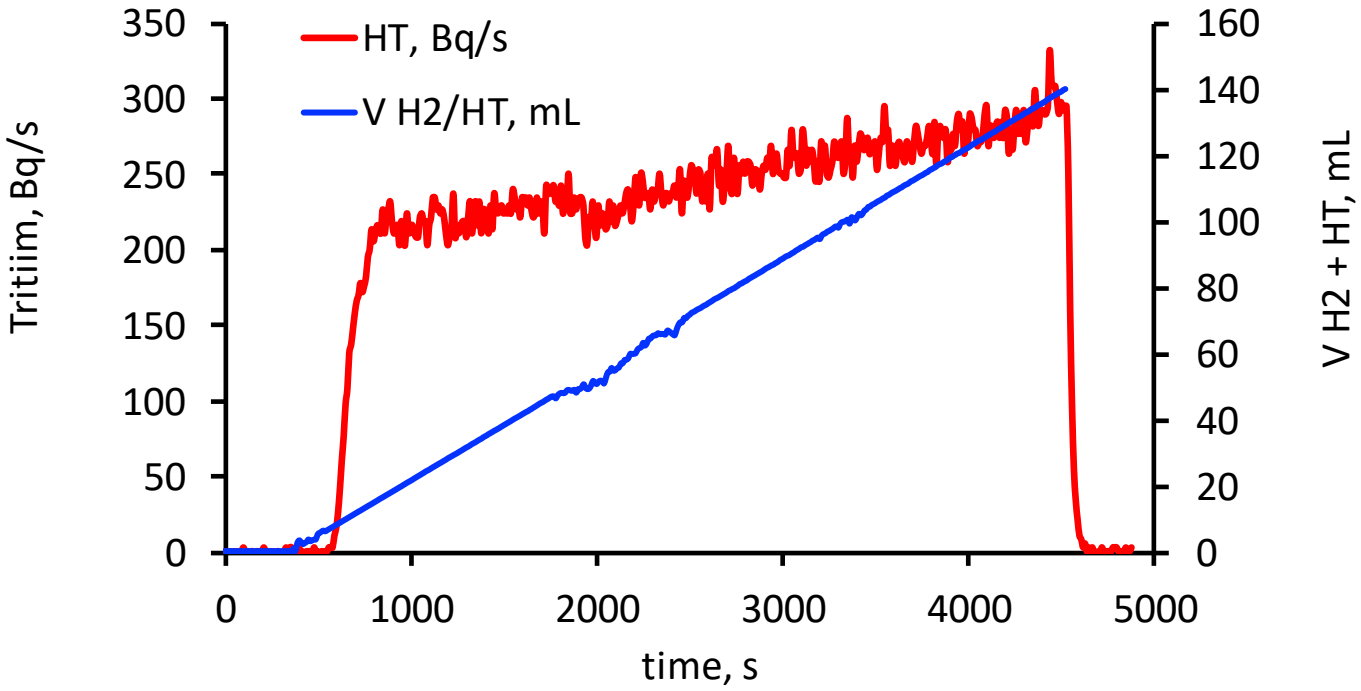
$$V_{H_2} = \frac{R \cdot T \cdot 10^3 \cdot \int_0^t I(t)dt}{2 \cdot F \cdot p}$$



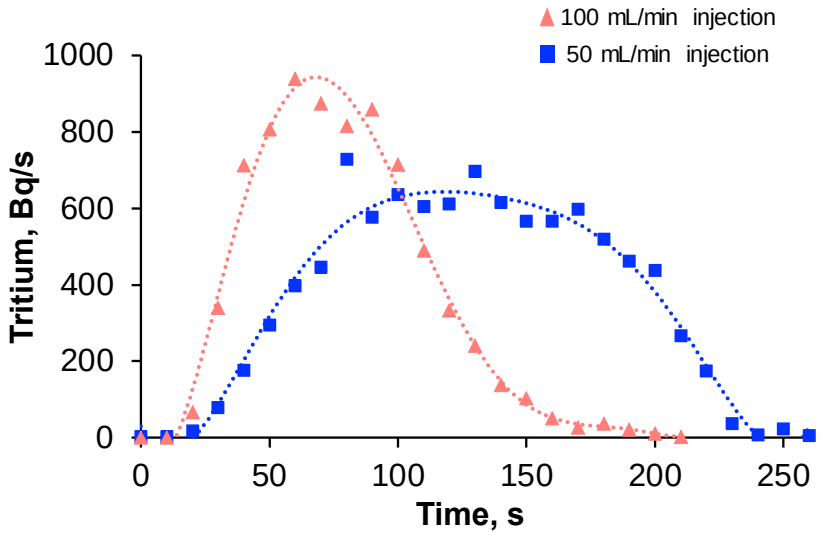
FuelCellStore, US

Electrolysis of **tritiated water** performed at **2,1V DC** (source *UNI-T* UTP3315TFL-II, 30 V ± 0,5%, 5 A ± 0,5%) in *H-TEC* 1-Cell Rebuildable PEM Electrolyzer **up to 1,0 A.**

Produced H_2+HT gas was collected in Tedlar bags (and an gas aliquot taken afterwards) or introduced directly in the flow of the purge gas to tritium monitor.

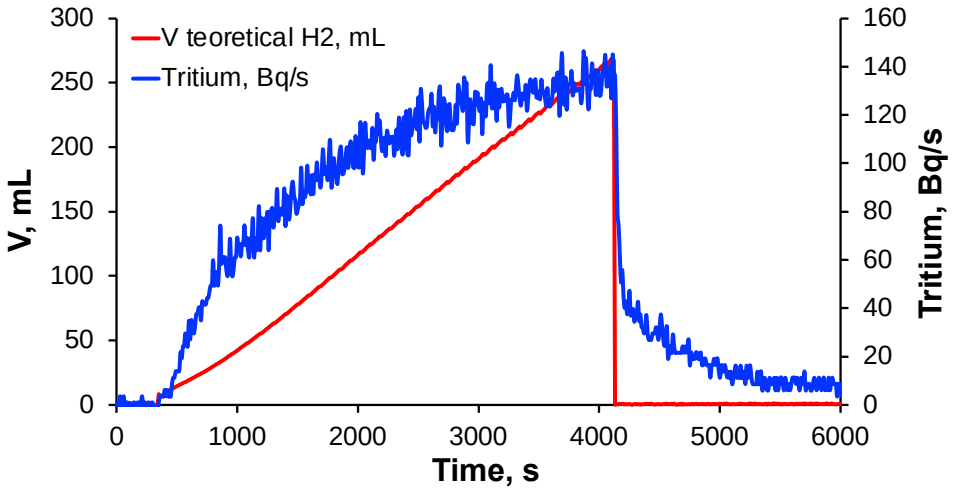


Comparison of measurment approaches



Syringe injection in TEM through Tedlar gas storage bag

Theoretical volume of hydrogen generated	0,100 L	0,100 L
Gas injection speed	100 mL/min	50 mL/min
Theoretical activity of tritium (in gas volume)	105 256 Bq	105 256 Bq
Practically measured activity (TEM data)	75 730 Bq	95 490 Bq
Relative yield	72%	91 %



Direct injection in TEM

Theoretical volume of hydrogen generated	0,267 L
Theoretical activity of tritium (in gas volume)	431 677 Bq
Practically measured activity (TEM data)	409 230 Bq
Relative yield	95 %

Next steps

- Measurement approach for fuel cell (HT to HTO) - based of liquid scintillation
- Construction of MEA with graphene coated membranes
- Electrolysis and HT oxidation using graphene coated membranes

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”

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Thank you for your attention!

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