Life Time of an SPM Electrolyser in a Water Detritiation System

Ion Cristescu

Forschungszentrum Karlsruhe, Postfach 3640 D-76021 Karlsruhe, Germany,

+ 49 7247 82 3757 e-mail: ion.cristescu@hvt.fzk.de

The Combined Electrolysis Catalytic Exchange (CECE) method in combination with Cryogenic Distillation (CD) was chosen for tritium recovery from tritiated water which will be produced during ITER operation. One of the key components with impact to both the tritium inventory and safety is the electrolyser. The solid polymer electrolyser type is proposed but the main concern is the life time in tritium environment. On overview of main activities devoted to the life time of a SPM and carried out at Mound facility-US, TPL JAERI and TL Karlsruhe are presented in this paper.

I. Introduction

For ITER, the Water Detritiation System (WDS) is one of the key systems to recover as much tritium as possible and consequently to minimize any potential impact to the environment. The most suitable process for water detritiation and tritium recovery is the well known CECE process in combination with CD process for final tritium enrichment [1].

In a WDS facility based on the CECE process, the electrolysis unit contains almost the entire amount of tritium involved in the separation process. Usually the water hold-up of the electrolysis unit based on solid polymer membrane (SPM) electrolyte is three to five times larger than the water hold-up of the Liquid Phase Catalytic Exchange (LPCE) column.

One of the key issues related to the SPM electrolyser is the lifetime under tritiated water processing. Studies that have been conducted to mathematically predict long-term performance of the cells have, for the most part, relied on the time-independent virgin properties of the polymeric materials. However, SPM properties can significantly change as functions of time and exposure to elevated temperatures due to degradation and/or aging. This provides numerous motivations for different kind of investigations [2].

Another important aspect under consideration, which can be effectively demonstrated on different types of SPM, is the effect of sulfonation on their properties. Since changes in the level of sulfonation lead to dramatic changes in the physical properties of the material, the investigation in this area is increasing in the last years.

The following issues have to be considered for operation of a SPM:

- Water also travels across the membrane in the direction of proton movement. This makes it necessary to periodically pump the transported water back to the anode side.

- Other metal cations will also occupy the proton sites in the SPM. The metal cations bond more strongly to the SPM and therefore are difficult to be removed. This cause the cell to develop a high resistance across the SPM, therefore requiring a higher voltage difference to maintain a given current through the cell. This, in turn, results in parasitic heat losses due to ohmic heating and can result in overheating and burn up of the SPM.
- Water is necessary to the structure of the polymer. If the material is dried out, the resistance first goes up, then the material become brittle and cracks easily.

In addition to these issues which are specifically for electrolysers in service with normal water, the damage which may be produced by the tritium environment has to be quantified and the life time estimated as function of provided dose.

II. Electrolysis of Tritiated Water in Solid-polymer Electrolyte Cells at Mound Facility US

An investigation of the electrolysis of tritiated water using General Electric Company solid polymer electrolyte (SPE) cells was carried out at MRC-Mound [3]. Several operating systems were built and tests done on three types of cell designs. The experimental rig to measure the lifetime of a SPE is shown in Figure 1. The main components are the electrolysis cell, pump for water circulation, two reservoirs for hydrogen and oxygen respectively, and an ion exchange column. Water circulating in this system goes out of the bottom of the H_2O-O_2 reservoir, through the pump, filters and ion exchange column, flow meter, and cell, and back into the side of the H_2O-O_2 reservoir. The gases are gravity separated from the water inside the reservoirs on both the H2 and O2 sides of the system.

Three types of electrolysis cells have been tested: one test with a regenerative cell, five tests with a screen hardware cell, and three tests with a pneumatic seal cell.

Tritium concentrations of 1 to 300 $Ciml^{-1}$ in a single addition of tritiated water were used in the first four tests. Total cell operating time until SPE failure was recorded for these tests. The final five tests were designed to measure SPE life time at tritium concentration of 1, 10, and 100 $Ciml^{-1}$.

The experimental results are presented in Table 1, and the outcomes can be summarized as follow:

- No precise determination of the useful SPM lifetime can be made from the data gathered in tests; several additional parameters affecting the lifetime were not sufficiently controlled.
- The presence of iron and other impurities affected the electrical resistance of the SPM. At high tritium level, such impurities will always be present due to radiolysis of the metallic materials of system construction. Even with a ion exchange resin provided in the last experiments, lowering the concentration of Fe+3 , the Nafion itself is an ion exchange material and will increase the resistance and heating inside the SPM.
- Another issue is the electrical and water circulation parameters as they combine to cause heating of the SPM. For non tritiated water 2.6 V were required to maintain 50 A compared with 3.6 V when tritiated water was processed. To lower

the effects of resistance heating, the water flow rate can be increased and/or add refrigeration to the circulation loop.

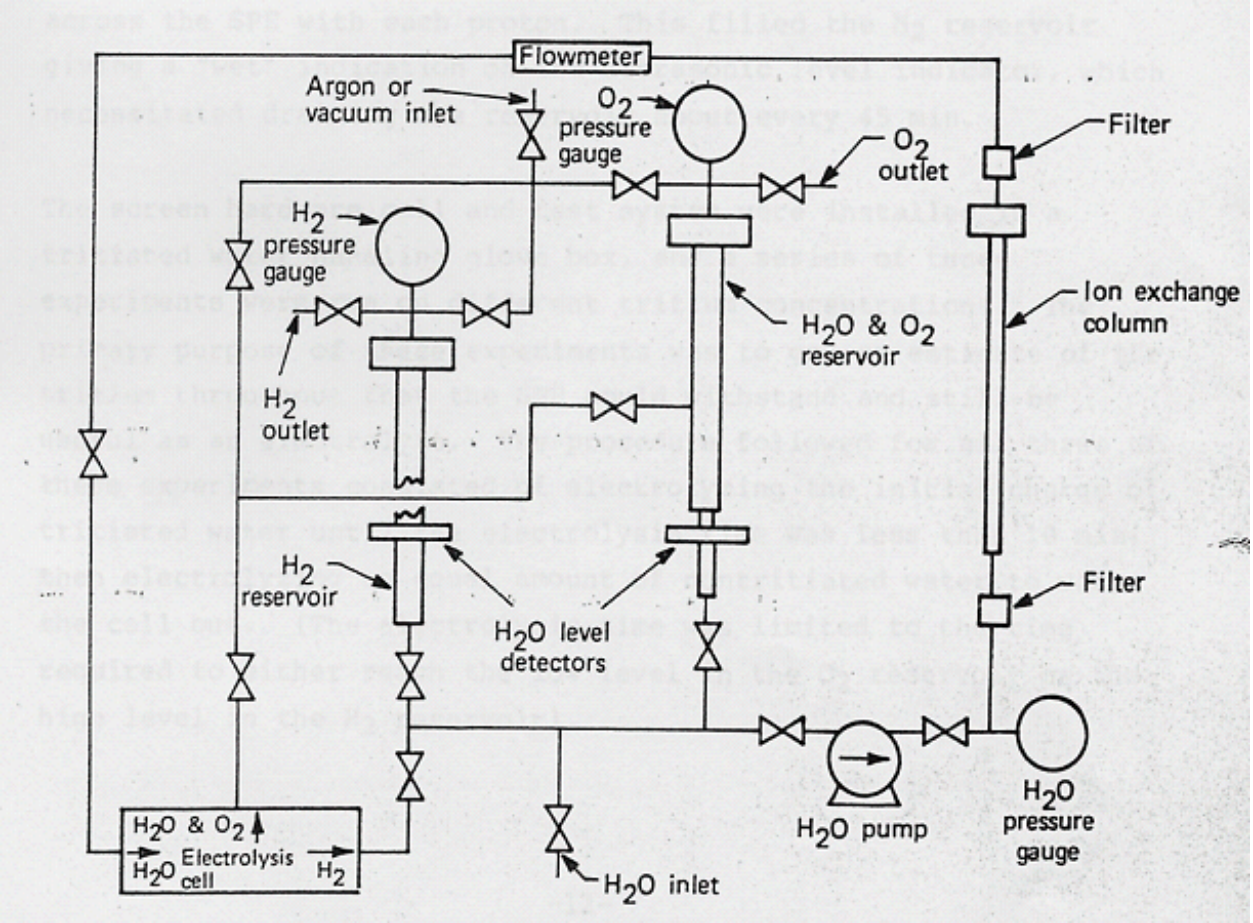

Figure 1. The experimental rig at Mound facility

Table 1. Experimental results of SPM lifetime at Mound facility

Test No.	Tritium concentration ($Ciml^{-1}$)	Cell operating time (min)	Exposure time (days)	SPM Lifetime (days)	Total Dose (Mrad)
1	300	765			
2	1	366			
3	10	498			
4	150	373			
5	1		70	273	24.5
6	10		203		84.4
7	10		49	49	59.1
8	10		111	111	134
9	100		22	22	265

III. Life Time Investigation of SPM at Tritium Process Laboratory (TPL) -JAERI and Toshiba Corporation

Detailed Investigations have been carried out at TPL-JAERI in order to estimate the life time of a SPM [4]. The outcome of these experiments was necessary to develop a maintenance procedure for the electrolysers to be used in ITER. Components of an electrolyser have been gamma ray irradiated and the effects evaluated.

Three main organic compounds of the electrolysis cell have been tested: SPM membrane, gaskets and electric insulators. A piece of these compounds was irradiated by the gamma ray up to 850 kGy. The reference for this dose is based on the fact that tritiated water of 250 $Cikg^{-1}$ provides in two years a dose of 530 kGy. The dose of 850 kGy is a conservative figure for the foreseen working time of one year for each electrolyser from ITER WDS. The durability was evaluated as a series of tensile strength, and as an ion exchange capacity of the membrane.

No serious damages for the strength and the ion exchange capacity of the membrane (Nafion) have been observed up to 850 kGy. For gasket materials (AFLAS) also, no damage was observed up to 500 kGy. The insulator materials (PFA and FEP) lost their strength at 200 kGy and 300 kGy, respectively. As far as tensile strength and ion exchange capacity of the membrane is concerned the electrolysis cell could be used for two years under the ITER conditions, in the case where PFA and FEP are replaced by the other materials such as polyimide resin.

Additional tests have been carried out to measure the effect of dose on the water uptake and fluorine released. Since the branch of sulfonic acid in SPM is hydrophilic, the water uptake may be correlated with the ion exchange capacity. The influence of dose on the water uptake is shown in Figure 2, and as can be seen no serious deterioration is observed in the case where the irradiation dose is less than 600 kGy.

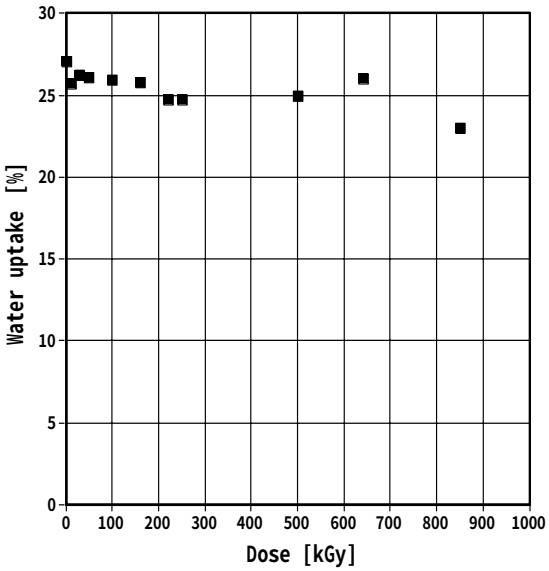

Figure 2. SPM water uptake versus dose

One of the irradiation effects is the releasing of fluorine and therefore the dose provided to a SPM can be quantified as well by the amount of fluorine released. As is shown in Figure 3, the amount of the fluorine ions dissolved is almost linear with the dose. This correlation may be used during functioning of the SPM electrolyser to find out the dose provided to the membrane.

During development of different SPM for various applications, the possibility of improving the structure of SPM by radiation exposure was considered as well. A correlation between the in

purpose dose provided to SPM and the dose provided by tritiated water environment can be done. Close to ITER-WDS situation is one surface treatment carried out by Toshiba Corporation with the aim modifying the surface structure of the commercial Nafion117, by low dose electron beam (EB) exposure [5].

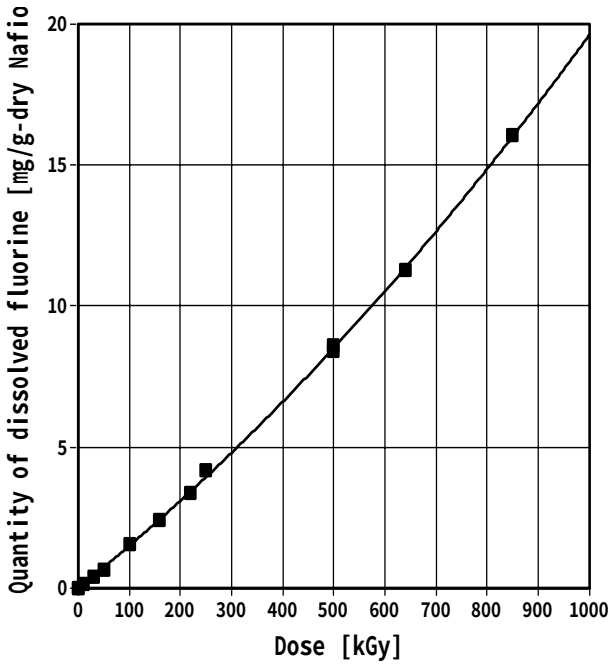

Figure 3. Dissolved fluorine versus dose

Low dose EB treatment was shown to be effective in the reduction of methanol crossover, 600 μC/cm2 exposure reducing crossover to 7% of that of the parent material and an improvement of up to 51% in the maximum power when used in a fuel cell was found compared with an untreated material

The calculated time to get an equivalent exposure of 600 μCcm^{-2} but coming from tritiated water of 250 $Cikg^{-1}$and considering 5.9 keV the average energy for beta decay is more than 5 years.

IV. Activities on SPM Lifetime at TLK Karlsruhe

An experimental rig with the aim to investigate the behavior of a small electrolysis cell based on SPM has been developed at TLK [6]. The process was conceived in order to allow operation of tritiated water in a closed loop. Therefore, in addition to the electrolysis cell, which produces tritiated hydrogen and oxygen, a catalyst bed was inserted along the process with the aim to convert the products of the electrolysis cell to water. The catalyst bed was tested for one month continuous operation with demineralized water. A scheme of this experimental rig is shown in Figure 4. Several buffer vessels are in the experimental rig in order to allow to feed and empty the process. The water circulation between different components of the experimental rig is realized only gravitationally, therefore the relative elevation between components was carefully adjusted.

The experiments performed at TLK have been focused on the following issues:

- To investigate the behaviour of a small electrolyser cell based on a SPM over a long period functioning with tritiated water, with tritium activity of 1.2 $Cikg^{-1}$
- To compare the mechanical properties such as tensile strength and elongation for a solid polymer membrane before and after exposure to tritiated and demineralized water.

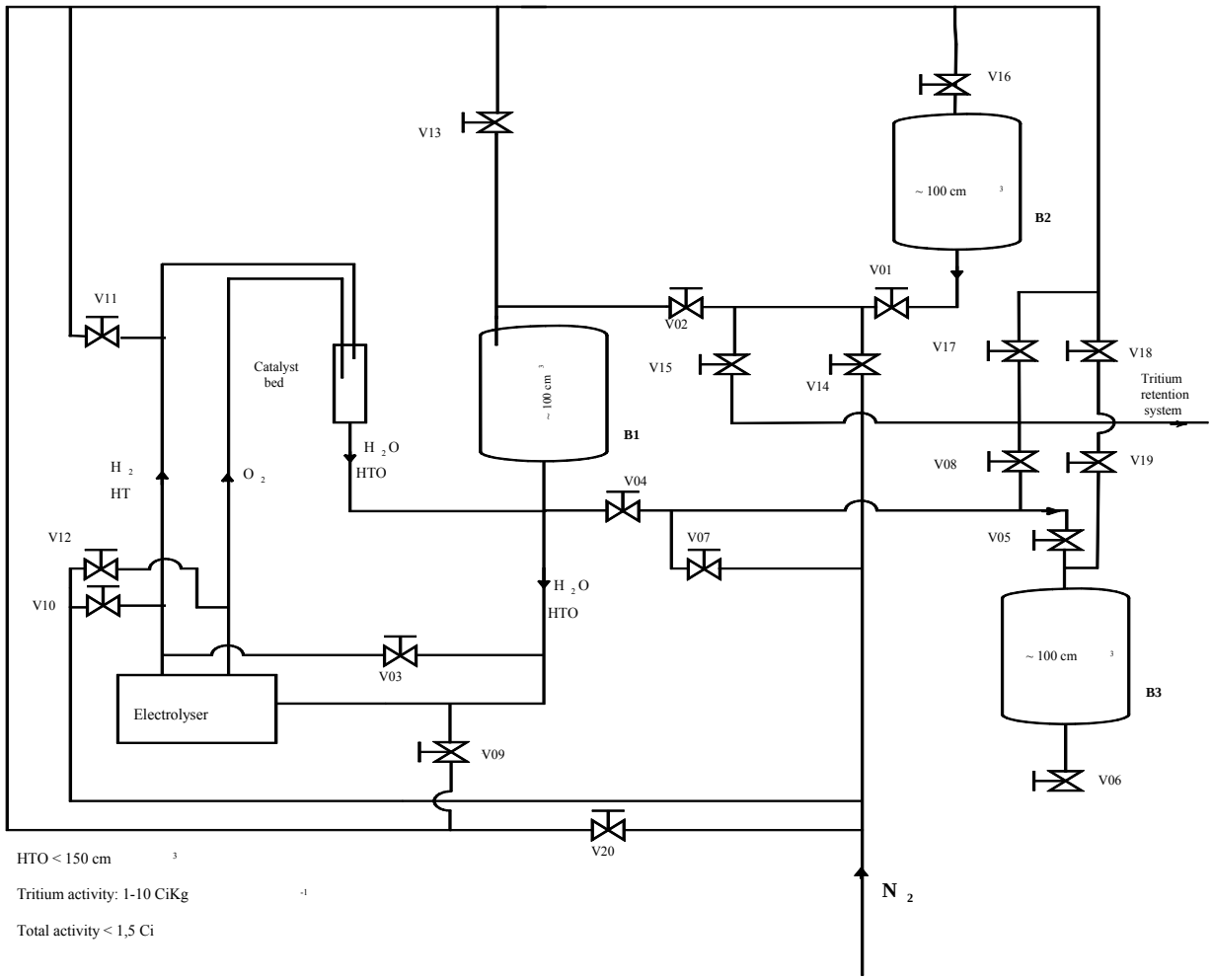

Figure 4. The TLK experimental rig for SPM life time measurement

During six months continuous operation of the experimental rig, the voltage drop applied on the electrolysis cell was maintained constant and the current through the electrolysis cell was continuously recorded. A similar electrolysis cell was in function with demineralised water in the same working conditions. For this second set-up the current through the electrolysis cell was also continuously recorded. In Figure 5, the behaviour of the cell current of the two electrolyser cells over six months functioning period is shown. The current in both electrolysis cells had a similar behaviour, the instabilities due to the relative movement of the electrodes when pressure fluctuation occurred.

The chemical composition of tritiated water processed in the first experimental rig was measured after two and six months operation. In Table 2, the chemical composition of tritiated water withdrawn from the experimental rig after two and six months operation is presented. The amount of cations in the tritiated water changed very slight after three months operation. The

general trend is to decrease, probably due to their fixation within the SPM.

The mechanical properties such as tensile strength and elongation of the membranes used at TLK during the investigation of the two small electrolysis cell in operation with tritiated and demineralized water have been measured. In Table 3, the average values for tensile strength and elongation for the SPM used in the two electrolysis cell and for one virgin SPM cells are presented. The differences of tensile strength and elongation between the two SPM in service with tritiated and demineralised water are very small and there is not reason to consider them as provoked by β radiation of tritium.

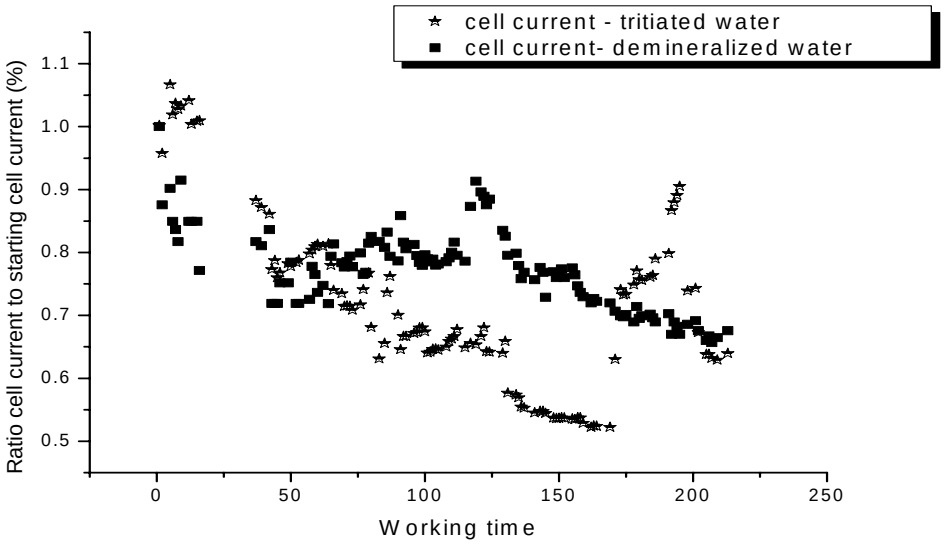

Figure 5. Cell current behaviour of the two electrolysis cells

Table 2. Chemical composition of tritiated water after two and six months operation

Kation/Anion (mgl^{-1})	Feeding water (mgl^{-1})	After two month operation (mgl^{-1})	After six month operation (mgl^{-1})
Al	< 0.2	6.1	5.0
Ca	0.11	4.9	3.3
Fe	<0.05	2.6	0.87
P	<0.5	6.0	4.1
S	<0.5	4.3	4.7
Si	0.68	7.8	8.9
Ti	<0.5	4.2	0.4
Chloride	0.09	6.99	3.2
Fluoride	0.45	37.6	22.7
Phosphate	0.15	7.8	8.4
Sulfate	0.26	9.1	10.9
pH	5.5	3.0	3.8

Table 3. Comparison of tensile strength and elongation of the three SPM

	Virgin SPM	SPM in operation with demineralized water	SPM in operation with tritiated water
Tensile strength when force was in the fibre direction (MPa)	26.8	20.1	19.1
Elongation when force was in the fibre direction (mm)	61.1	26.6	30.5
Tensile strength when force was right angles to the fibre direction (MPa)	21.1	18.9	18.1
Elongation when force was right angles to the fibre direction (mm)	42.7	22.7	22.7

V. Conclusions

Beside some manufacturing aspects, such that improper selections of cell assembly parameters as compression and gasket design could give rise to premature membrane failure, many parameters including fuel cell operation temperature, pressure, and relative humidity may have a significant effect on membrane life. However, within a given set of operation conditions, certain intrinsic membrane characteristics could affect membrane durability dramatically.

The available experimental results may constitute a good basis to consider that the replacement of the electrolysis cells in ITER should not be required before one year full operation. Nevertheless, further investigation are needed for a better understanding of the damage mechanism of different SPM and experimentally proven of an ITER relevant scale electrolyser in service with tritium.

VI. References

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