

# *High-temperature Proton Conductor Hydrogen Sensor for Tritium Monitoring*

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**Abstract:** In order to develop the trace tritium monitoring technologies in exhaust gas of nuclear power plants and other tritium apparatus, a high-temperature proton conductor ceramic  $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\alpha}$  was used as a hydrogen sensor for tritium monitoring. The trace hydrogen extraction characteristics of an electrochemical hydrogen isotopes sensor using a one-closed  $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\alpha}$  proton conductor tube were studied in case of helium with 100 ppm and 10ppm levels of hydrogen, respectively. These results indicated that about 99% of hydrogen at anode was recovered to the cathode, and the electrochemical hydrogen sensor will be one of potential trace tritium extraction and monitoring technologies. The driving force of extracting hydrogen in the hydrogen sensor was a potential difference without pressurization, so the hydrogen sensor can extract hydrogen isotopes from a low-pressure hydrogen isotope gas by only loading direct current voltage.

## 1. Introduction

Tritium is an important radioactive material which is the only radioactive isotope of the element hydrogen to be handled as one of fuels in D-T fusion reactors to produce electricity. Tritium emission must be within regulatory control requirements specified by International Commission on Radiological Protection and the most governments' strict environmental limits.

In order to ensure radiation safety for staffs and the public around tritium handling facilities, tritium monitoring at room, stack, and process system is essential with respect to protecting the environment around the fusion reactors. However, tritium is a difficult nuclide to monitor directly due to its low beta energy and other radiations interference from coexisting short-lived radionuclides. Tritium monitors such as gas-flow ionization chambers, proportional counters, and liquid scintillation counters are selected widely. In order to directly monitor of lower concentrations of tritium, a new tritium monitoring system which combined a high-temperature proton conductor (HTPC) ceramic used as the tritium separation membrane with a high-sensitivity proportional counter used as tritium sensor has been proposed, which can not only capture and enrich tritium but also monitor tritium. Dense ceramic membranes had received much interest due to their low cost

and high efficiency from the fundamental points of view as well as from applied points of view in hydrogen separation and production [1]. For their effective application in tritium handling facilities such as fusion reactors, the extraction of hydrogen and tritium were demonstrated for fusion engineering applications [2]. However, the experimental results have indicated that building a more compact loop system and investigating the tritium extraction characteristics using trace tritium for practical use of the tritium monitoring system was necessary[2].

The present authors also have investigated some hydrogen extraction performance of  $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\alpha}$  under the conditions of trace hydrogen pumping or water vapor electrolysis [3]. In this paper, attention was focused on the trace hydrogen extraction performance of a  $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\alpha}$  tube. A new tritium monitoring system which combined a  $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\alpha}$  tube used as the membrane separator with a high-sensitivity proportional counter used as tritium sensor has been proposed. For the practical fundamental application feasibility, an integrated a loop system using a proportional counter and a proton conductor was constructed.

## 2. Experimental

### 2.1. High-temperature proton-conducting tube

A one-end closed  $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\alpha}$  ceramic tube ( $\varnothing 19.6 \text{ mm} \times 1.8 \text{ mm} \times L 520 \text{ mm}$ ) was used in this work, and the porous Pt electrodes were coated on the surface of the inner and outer tube. High-temperature proton-conducting tube was used as the electrolytes for electrochemical hydrogen sensor as shown in Fig.1, the driving force for hydrogen (or tritium) motion is the external electric field applied across the two electrodes on the HTPC membrane, so tritium can be extracted from pumping of dilute tritium, electrolysis of tritiated water vapor, and decomposition of tritiated methane.

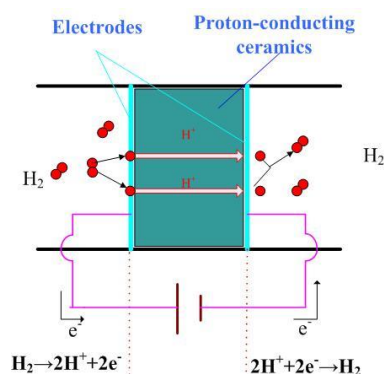


Figure 1: The schematic of an electrochemical HTPC hydrogen sensor.

### 2.2. Experimental apparatus and procedures

A schematic diagram of the experimental apparatus for tritium monitoring is shown in Fig.2. Tritium balanced with helium was supplied to the anode of hydrogen sensor. When the voltage was applied between outer and inner surface electrode of the proton conductor ceramic tube, hydrogen isotopes in anode were pumped to the cathode and were swept by helium.

The experimental procedures were carried out as follows. At first, the hydrogen extraction experiment was carried out and similarly described in our previous report [3]. Then the hydrogen and tritium balanced helium was fed into the anode side, the tritium was extracted into the cathode side and enriched in the closed cathode loop. The HTPC tube was heated to 1073K under purge gas passing. Hydrogen concentration in the introduced gas was about 1000ppm. The hydrogen

concentration was analysed by a gas chromatograph (USA GOW MAC, 816). Water vapor was monitored by a dew point hygrometer (UK SHAW, DS-3000). Tritium was monitored by a proportional counter. DC voltage was applied by a potentiostat (Keysight technologies, B2961A). The current and voltage were recorded by a Data Acquisition / Switch Unit (Keysight technologies, 34972A). The experimental conditions were shown in table 1.

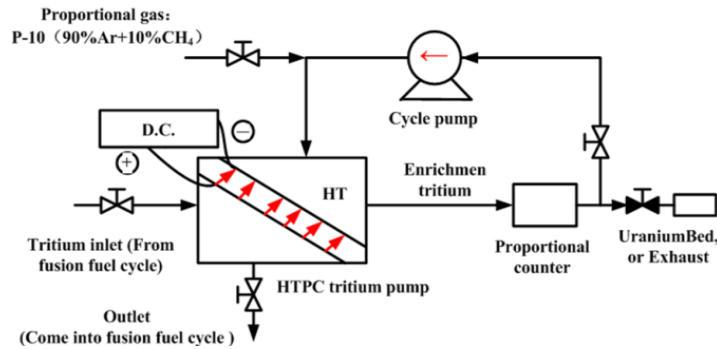


Figure 2: A flow diagram of experimental system.

Table 1: A list of experimental conditions.

	Anode inlet	Cathode inlet
Gas fed	H <sub>2</sub> /He	He
Pressure [kPa]	99-101	99-101
H <sub>2</sub> [ppm]	10-100	-
Flow rate [ml/min]	10-200	10-200

### 3. Results and discussion

#### 3.1. Hydrogen extraction performance

Fig.3 shows change in gas concentration and voltage as a function of current at 1023K and the supply gas of anode containing 100 ppm H<sub>2</sub>. When 0.78 V DC was applied to the hydrogen sensor, hydrogen concentration of cathode export was 99.37ppm, hydrogen concentration of anode fell from 100ppm to 0.01ppm. These results indicated that about 99% of hydrogen supplied was extracted.

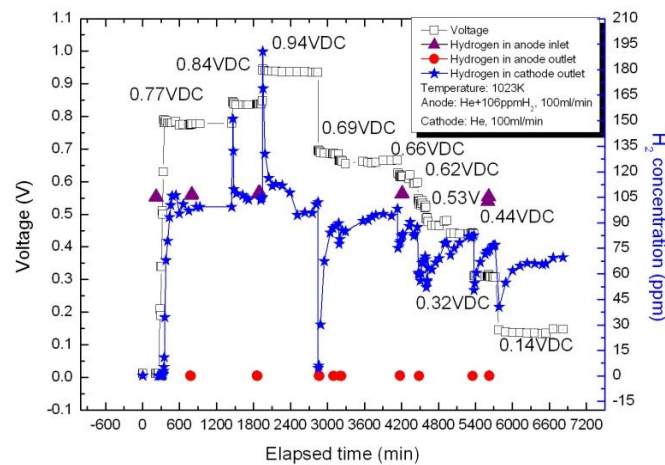


Figure 3: Change in gas concentration and voltage at 1023K and anode supplying 100ppm H<sub>2</sub>.

Fig. 4 shows change in gas concentration and voltage as a function of current at 1023K and the supply gas of anode containing 10 ppm H<sub>2</sub>. When 1.27 V DC was applied to the hydrogen sensor,

hydrogen concentration of anode export was less than 0.12ppm. These results indicated that about 99% of hydrogen supplied was extracted.

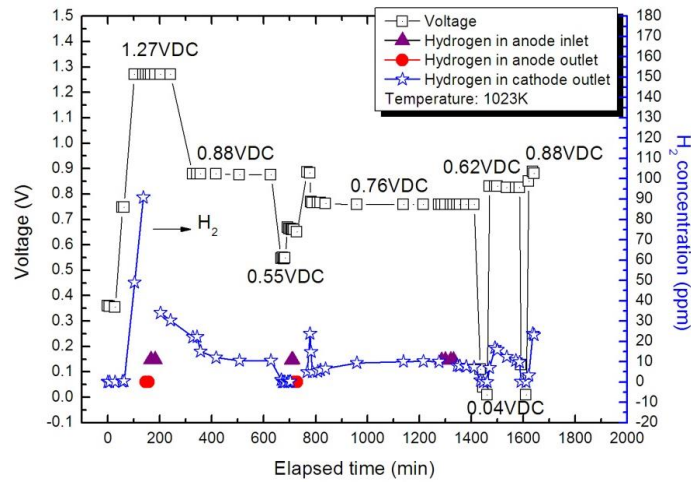


Figure 4: Change in gas concentration and voltage at 1023K and anode supplying 10ppm H<sub>2</sub>.

### 3.2. Preliminary feasibility analysis of the application

Aiming at the practical application environment, the feasibility experiment and analysis of the extended application of proton conductor ceramic electrochemical hydrogen sensor was carried out under the simulated condition of 0.12% H<sub>2</sub> in He. The relationship curves of hydrogen concentration at the outlet of anode and cathode to current were shown in Fig. 5 and Fig. 6 respectively. With the increase of loading voltage, H<sub>2</sub> concentration at anode outlet gradually decreases to ppm, H<sub>2</sub> concentration at cathode outlet gradually increased, and the hydrogen separation and recovery efficiency reached 100%, which verifies the technical feasibility of hydrogen separation and recovery by high-temperature proton conductor ceramic electrochemical hydrogen sensor, and the electrochemical hydrogen isotopes sensor will be one of potential trace tritium extraction and monitoring technologies.

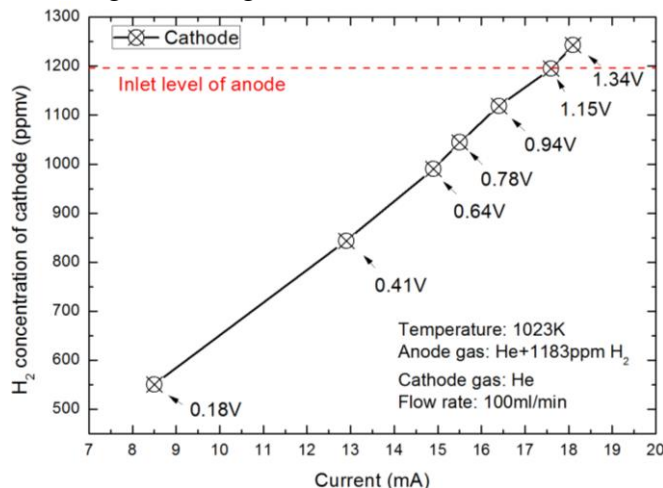


Figure 5: Concentration changes at the outlet of the cathode as a function of current at 1023 K and 1000 ppm H<sub>2</sub>.

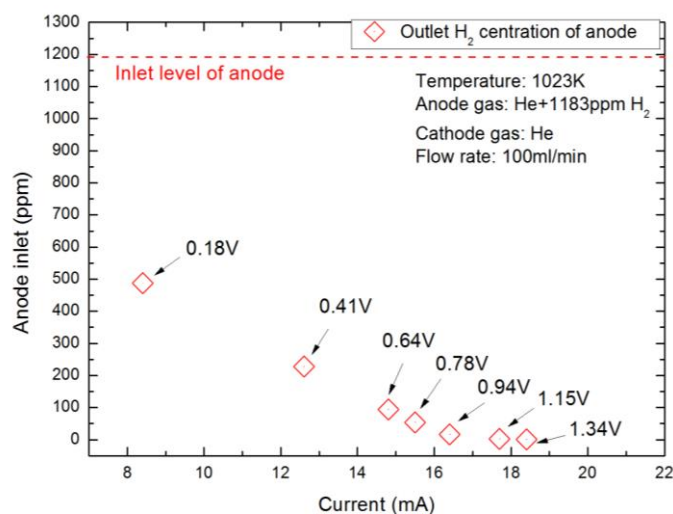


Figure 6: Concentration changes at the outlet of the anode as a function of current at 1023 K and 0.12% H<sub>2</sub>.

#### 4. Conclusion

The trace hydrogen extraction characteristics of an electrochemical hydrogen isotopes sensor using a one-closed tube of CaZr<sub>0.9</sub>In<sub>0.1</sub>O<sub>3- $\alpha$</sub>  proton conductor were studied in case of helium with 100 ppm and 10ppm levels of hydrogen, respectively. These results indicated that about 99% of hydrogen supplied was recovered. Aiming at the practical application environment, the feasibility experiment and analysis of the extended application of proton conductor ceramic electrochemical hydrogen sensor was carried out under the simulated condition of 0.12% H<sub>2</sub> in He, the hydrogen separation and recovery efficiency reached 100%, which verifies the technical feasibility of hydrogen separation and recovery by high-temperature proton conductor ceramic electrochemical hydrogen sensor, and the electrochemical hydrogen isotopes sensor will be one of potential trace tritium extraction and monitoring technologies.

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