§5. Effect of Methane Gas in the Cathode Compartment on the Electrochemical Hydrogen Pump

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From the public acceptance and safety management perspective, we need to monitor the low level of tritium in the discharge gas and work environment. In order to measure lower concentrations of tritium, a number of tritium monitors combining an ionization chamber with semipermeable polymer membranes have been researched and developed. The sensitivity of certain tritium monitors with semipermeable membrane improved by an order of magnitude over that of the tritium monitor without membrane.

To further improve the sensitivity of the tritium monitor, we have proposed new tritium monitor that combines a proportional counter and a closed loop system equipped with a membrane. The proposed system would be useful not only for the elimination of unwanted interference in the proportional counter, but also for the concentration of tritium. It would offer the following advantages over the liquid scintillation counting method: reduction of waste material such as an organic solvent, ease of operation and handling, treatment in the form of gas. As candidate materials for the membrane, we have examined proton conducting oxides, which function as an electrochemical hydrogen pump at elevated temperature. These offer attractive advantages such as hydrogen recovery from hydrogen molecules and hydrogen compounds, control by electric current, no pressurization of supplied gas, hydrogen pump from low to high concentration gas.

In our proposal system, when the proton conducting oxides is used with a proportional counter, argon gas containing methane gas, as it is called “PR gas”, should be passed through the closed loop system for the proper operation of the proportional counter. In this case, PR gas will be also fed to the cathode compartment of hydrogen pump cell. It seems to have some adverse effect on pumping operation. Therefore, the performance tests of the hydrogen pump under water vapor electrolysis were carried out and the effect of methane gas in the cathode compartment on hydrogen pump was evaluated.

From the viewpoint of the practical use, we carried out the performance tests of the one-end-closed tube made of $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ with wide electrode area. The shape of the one end closed test tube was 12 mm inner diameter, 1.0 mm thickness and 200 mm length. The platinum electrode was attached on both sides of the test tube and the effective area on the cathode electrode was 44 cm^2. In this experiment, wet argon gas containing water vapor of 1.2 kPa was fed to the anode. Argon gas containing methane of 10 kPa or dry argon gas was fed to the cathode. These flow rates were 100 cm^3/min. The test tube was heated up to 873 K by an electric furnace. Then, the

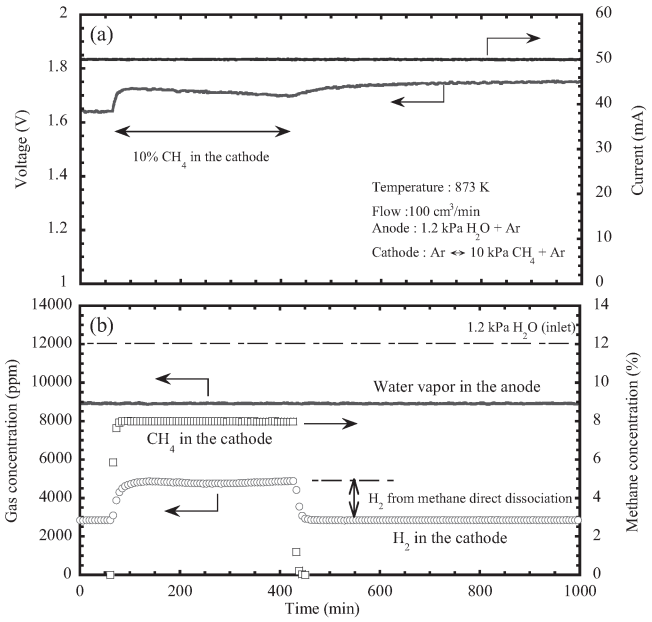

Fig. 1: Time evolution of hydrogen pump (a). current and voltage, (b) gas concentration of water vapor in the anode, hydrogen and methane in the cathode

constant current of 50 mA was passed through between the electrodes by a galvanostat. The gas components in the cathode were analyzed by a gas chromatograph equipped with MS5A separation column and two detectors of TCD (thermal conductivity detector) for hydrogen gas and FID (hydrogen flame ionization detector) for methane gas. Dew point in the anode was measured by a hygrometer.

Figure 1 shows time evolution of hydrogen pump by water vapor electrolysis. Hydrogen pump performance before adding methane gas was stable and hydrogen concentration in the cathode was about 2800 ppm. When methane gas was fed to the cathode, voltage increased from 1.64V to 1.72V and hydrogen concentration also increased about 4900 ppm. However, water vapor concentration in the anode did not change before and after adding methane gas to the cathode compartment. On the other hands, methane concentration in the cathode outlet was less than that in the cathode inlet. It suggested that a part of increased hydrogen concentration in the cathode might come from decomposition of methane according to the following direct methane decomposition reaction:

$$CH_4 \rightarrow C + 2H_2, \qquad (1).$$

In this reaction, carbon is deposited on the oxide. Thus, even after changing to argon gas in the cathode, voltage was kept high value and the effect of methane gas on hydrogen pump might be remained. In conclusion, methane gas in the cathode had adverse effect on hydrogen pump such as an increment of voltage and a deposition of carbon on the oxide by direct methane decomposition reaction. And it continued to exert influence on hydrogen pump performance. Therefore, we are considering new monitor system to avoid contact with methane gas.