A Study on Titanium Electrode Fire

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1 Introduction

A series studies on hydrogen production using solid-polymer electrolyte water electrolysis has been carried out since 1993 under the project of International Clean Energy Network using Hydrogen Conversion (WE-NET).

Solid polymer electrolyte water electrolysis has several adventages, compactness of electrolysis cell, simplicity in design, operation, maintenance, and freedom from corrosion problem in comparison with commercially available convensional alkaline water electrolysis. It has a disadovantage of high production cost caused by expensive components, rare metal electrolyst and solid polymer electrolyte membrane [1]. A typical schematic of unit cell is shown in figure 1.

Sintered porous electrodes are used with catalyst. Sintered titanium is used as anode collector [1]. Oxygen gas generated from water electrolysis contacts with anode. Perfluorinated hydrocarbon sulfonate ionomers are used as solid polymer electrolyte membrane, which is known to be chemically unstable at temperatures higher than 100 -150 degree Celsius [1]. The typical thickness of the solid polymer electrolyte membrane is approximately 50 micro meters [2].

The operation pressure of water electrolysis is increasing from the atompspheric pressure to the filling pressure of fuel cell automobile, 35 MPa or 70 MPa. Considering the coexisitence of titanium sintered porous electrode and oxygen gas, water, and perfluorinated hydrocarbon sulfonate, the porous titanium may react with these materials. The operation temperature of water electrolysis was the ambient temperature under normal operation. A review paper describes the dropping of the autoignition temperature of titanium to 100 dgree Celsius at 350 psi (2.3 MPa) in oxygen [3,4]. It was pointed out that the water vapour with 5 % of oxygen was enough to sustain the reaction of titanium at high pressure to 1900 psi (12.6 MPa) [4].

A pilot hydrogen station of this type of 40 MPa operation pressure was constructed in Ito campus of Kyushu University as shown in figure 2. The initial test started from November 15, 2005. An explosion and fire destoried the station on December 7, 2005. Kyushyu University released a preliminary report on the explosion and fire on June 6, 2006. The pressure in the electrolysis module rose above the insturument upper limit within 2 seconds from the initial events [5,6]. The pressure in the electrolysis module lowered to 43 MPa within 10 seconds from the initial events due to the operation of safety devices [5,6]. Another pressure rise started within 20 seconds from the initial events [5,6]. Ruputes of lines of the system was recorded on the monitor video within 40 seconds from the initial events [5,6]. Chemical analysis indicates the presence of HF, TiF_3, TiO, and Ti_2O_3 in samples recovered. Blue colored TiF_3 was seen among black colored dusts in the damaged electrode stack [5,6]. Kyushu University confirms the presence of titanium and floride in the electrode module compornents [5,6]. Kyushu University announced that the pilot hydrogen station of this type will not be used in future research activities [7].

Titanium-water, titanium-oxygen, and titanium-perfluorinated hydrocarbon are well known incompatible mixtures. In this study, the fuel-oxidizer ratio of titanium-water/oxygen gas mixture is determined with a simple model electrode under the operation pressure. Considering the temperature at reaction zone of titanium, water is supercritical or gas.

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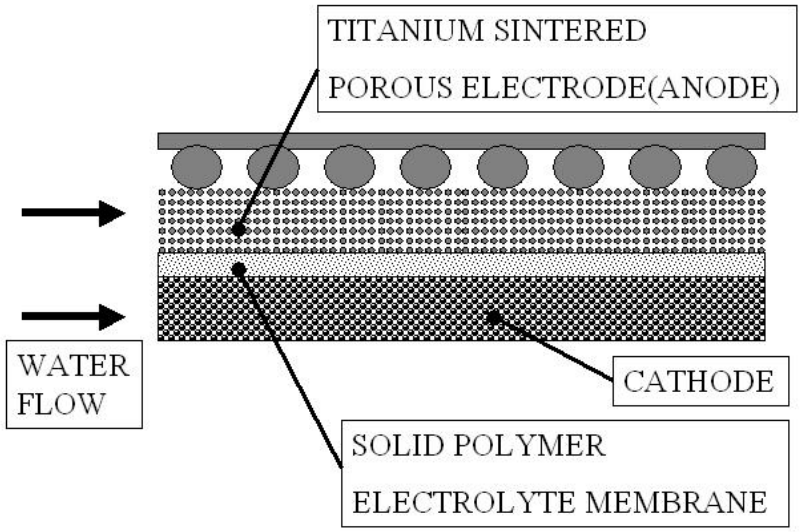

Figure 1 A TYPICAL SCHEMATIC OF UNIT CELL

Figure 2 A PILOT HYDROGEN STATION OF 40 MPa OPERATION PRESSURE

Figure 3 DAMAGED LINES

2 Model of titanium-water/oxygen gas mixture

Titanium sintered porous electrodes have been developed to achieve high efficiency and low production cost.

A simple porous electrode model was used in this study. Assuming that the electrode is constructed with titanium rods of diameter, D with uniform pitch of L, locate on corners as shown in figure 4. The titanium volume ratio, Y is

$$Y = V_{ti} / V_a \qquad (1)$$

The highest titanium volume ratio is 0.8.

After forming the reaction zone of titanium, water is presumed in gas phase due to temperature rise under constant volume condition.

Assuming that the void space is filled with water/ oxygen gas mixture and the volume ratio of oxygen gas, z is uniform in the water/oxygen gas mixture, the ratio of titanium to oxygen atoms, N is expressed with these parameters, the operation pressure, P, titanium and water densities, titanium and water molecular weights.

$$N = (V_{ti}\,\rho_{ti}/M_{ti}) \;/\; \{ (V_a - V_{ti}) (z\,\rho_w/M_w + 2 \times (1 - z)P/RT)\}$$

$$= 9.48 \times 10^4 \;\; Y \;/\; \{ (1 - Y) (P / 1.12 \times 10^3 + z \; (5.56 \times 10^4 - P / 1.12 \times 10^3)) \} \qquad (2)$$

The ratio of titanium and oxygen, N increases with the titanium volume ratio, Y.

The ratio of titanium and oxygen, N increases with the volume ratio of oxygen gas, z below 62 MPa of the operation pressure, P due to the low oxygen density in gas phase. The ratio of titanium to oxygen, N is 1.48 at $z = 0$ and $Y = 0.8$.

Where the operation pressure is lower than this pressure, the ratio of titanium to oxygen, N is

$$N = 1.48 / (1 - z) \qquad (3)$$

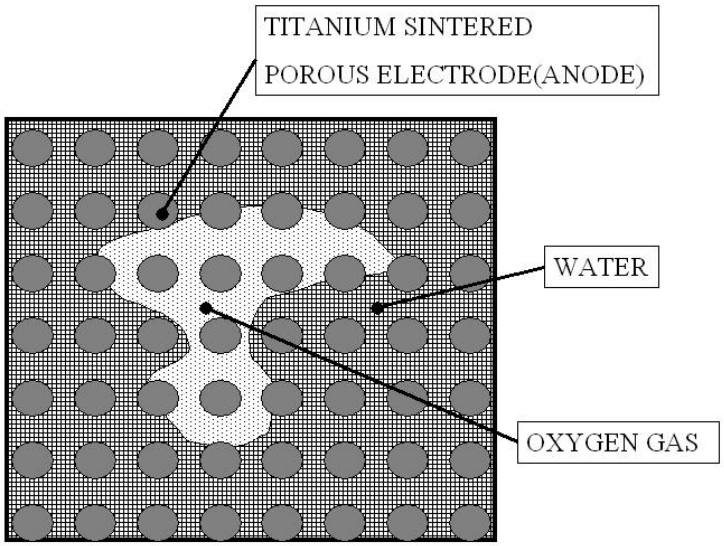

Figure 4 MODEL OF TITANIUM -WATER/OXYGEN GAS UNDER NORMAL OPERATION

3 Results and Discussion

The titanium volume ratio, *Y* of used electrode is estimated around 0.5-0.7. The ratio of titanium to oxygen, *N* is close to 1.0. The ratio of titanium to oxygen is, 1 for TiO, 0.67 for Ti_2O_3, 0.5 for TiO_2. This estimation indicates that the titanium-water/oxygen gas mixture is near the stoichiometric condition and self sustainable reaction may continue. In real systems, there are other water contained volumes around the titanium electrodes. Detailed electrode module drawings have to be reviewed to detremine the real ratio of titanium to oxygen atoms.

The increase of oxygen gas volume at the operation pressure below 62 MPa, do not increase the oxidizer ratio of the titamium-water/oxygen gas mixture. The increase of the oxygen exposed porous titanium may result larger ignition probability.

As shown in reference [4], the titanium exposed to oxygen ignite easily. The self-sustained reaction will continue until the oxygen concentraion drops below the limiting value. However, the test in reference [4] is carried out to determine the propagation limit. The extinction limit have to be tested with further experiments. The oxygen concentration drops due to the consumption by reaction and the generation of hydrogen and water vapour. If the safety device operation lowered the total pressure or water temperature of the system, the oxygen concentration could be recoverd and the self-sustained reaction may contine.

After one year study on the explosion and fire of the hydrogen station accident by Kyushu University, an explosion and fire which destoried the phase I plant on August 28, 2003 was found to be caused with similar process [7]. After a series of modifications, the pase I+ plant was finished on Feburary, 2004 and operated until July, 2004 [7]. The infromation on the explosion and fire of the phase I plant was not released to Kyushu University before the accident on December 7, 2005.

Three pilot hydrogen station of this type of 40 MPa operation pressure were build and two of three stations were lost by explosions and fires. The left one station was decomissioned on March, 2007.

4 Conclusions

The practice of water electrolysis at the filling pressure of fuel cell automobile of 35 MPa or 70 MPa is hazardous based on this simple analysis. Before developing sintered porous electrodes, the safey verification of electrode has to carried out under all operating conditions.

Reviewing the studies on titanium fire, it is found that the use of titanium for porous electrodes is hazardous. Even with a small fracture on the titanium electrode will initiate the reaction of titanium with wet oxygen.

References

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