

Introduction to Electrochemical Techniques Used in Nuclear Energy Development: Coolant Chemistry Monitoring

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1. Introduction

In the nuclear energy area, most chemical reaction takes place in very severe conditions compared with those in other fields. In reactor coolant system, the operating temperature is over 300°C, much higher than the temperature we are familiar with. For recycling of fuels, fissile elements including uranium in spent fuels are electrochemically reduced and refined in molten salts. Especially, in the next generation reactor systems called GEN-IV, they need lots of chemical information under severe conditions such as high temperature steam, molten metal, supercritical water and so on.

In such severe media, generally two kinds of techniques have been used for the measurement and control of the chemical conditions and reactions. These are the spectroscopy and the electrochemistry techniques. However, the electrochemical technique is only effective method to control chemically the systems. Therefore, lots of electrochemical techniques have been developed and used in nuclear energy areas.

The chemistry of the reactor coolant is one of the most important areas to improve the safety and efficiency of plants operation by electrochemical techniques. Among the chemical factors, the coolant pH is the important one to control the corrosion process of the metal structure. However, the current pH measurement by sampling at room temperature has a limitation for directly monitoring the chemical condition of the coolant at high temperature. Therefore, real-time pH monitoring techniques have developed for last several decades. Macdonald et al.[1-4] have developed many YSZ (yttria stabilized zirconia) pH electrodes. In spite of their endeavor, there are still some difficulties associated with the electrode accuracy and stability. In order to improve the performance of pH measurement at high temperature, we added an enhanced function to the system for the calibration of the measurement devices.

Another chemical factor is a redox potential. Instead of the redox potential, the concentration of dissolved H₂ (DH) has been used to evaluate the redox condition of the coolant. In addition, the electrical conductivity, a chemical factor, depicts the degree of impurities in the coolant. Until now, these two methods, DH and conductivity, have been also used for measuring chemical condition in nuclear reactor coolant. However, these two methods also have the limitation for applying at high temperature, because they have been developed to be used at room temperature.

In order to overcome the current limitation, we developed a real-time chemical measurement system, which can be used in high temperature water, by adding some of electrochemical techniques to the measurement system. This measurement system could be a promising method for directly monitoring the proton (pH) and impurity ions in high temperature coolant.

2. Methods and Results

A high-temperature pH electrode was made by using yttrium stabilized zirconium oxide as an oxygen ion conducting membrane and Ni/NiO mixed powder as an inner electrode[2-3]. A once-through loop system equipped with a pH electrode and an Ag/AgCl reference electrode was used for measuring high temperature pH as shown in Fig. 1. The pH measurement experiments were carried out in various lithium borate buffer solutions under high temperature and high pressure conditions. The pressure and flow rate changes were controlled in the ranges of 100-200 kg·cm⁻² and 5-30 ml·min⁻¹, respectively.

In order to evaluate the impurity ion concentration, an electrochemical experimental system was composed of an electrode system, a once through loop and a potentiostat system. Both working and counter electrodes were made using Pt wires 1 mm in diameter. Potentiodynamic polarization and potential transient techniques were used to detect chloride ions in the hydrogenated solution. The exposed area of the working electrode was 1.0 cm², and an Ag/AgCl electrode was used as an external reference electrode containing 0.1 M KCl as the internal electrolyte.

2.1 Calibration of high temperature pH electrode

Every electrochemical sensor measuring a concentration of a species needs the standardization process by using a standard solution of the species to acquire an accuracy level generally accepted. Even a conventional glass pH electrode used at low temperature needs a calibration of electrode by using a pH buffer solution. Therefore, the high temperature pH electrode also needs the calibration process with a standard pH solution. However, it is difficult to carry out the calibration process under high pressure condition. In order to calibrate the electrode at high temperature and high pressure, we installed a circulating loop with a high pressure injection pump, as shown in Fig. 1. In addition,

a rod-type heater was installed in the loop for maintaining the temperature of coolant constant.

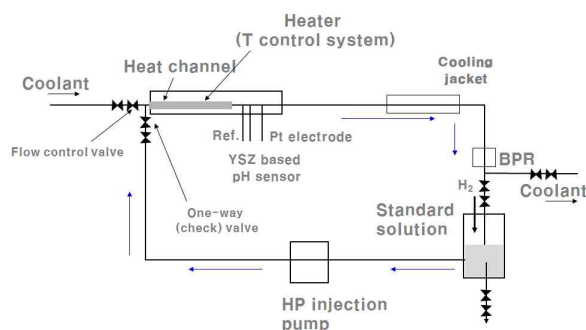


Fig. 1 A high temperature chemistry measurement system with a calibration loop.

2-2. Detection of chloride ions at high temperature

In recent work[5], an oxidation current valley was found at the electrochemical oxidation region of dissolved hydrogen, and it was evaluated to come from the formation of a stable Pt-OH_{ad} (or Pt-O) layer. As the formation of an oxide layer on a metal surface is generally affected by the chloride ion in the exposed solution [6-7], we used this phenomenon to detect the chloride ions. If the applied potential of a Pt electrode is shifted from the open circuit potential to the potential in the valley, the oxidation current of dissolved hydrogen is influenced by the concentration of impure ions, such as chloride ions, in the solution, because the oxidation current is closely related to the oxide layer on the Pt surface.

As shown in Fig. 2, chronoamperometric curves were obtained just after applying the potential of the Pt electrode from -0.65 to $+0.55$ V_{Ag/AgCl}. In order to compare the oxidation current with the concentration of chloride ions, the potential shift experiments were carried out respectively in various concentrations of chloride solutions, up to 100 ppm at 553 K.

The electrochemical oxidation current of dissolved H₂ decreased exponentially as the time increased, after the valley potential applied, at all concentrations of chloride ions. In addition, the initial oxidation current of dissolved hydrogen appeared to increase with an increase in the chloride ion concentration of the test solutions, and the time for reaching the limiting oxidation current was delayed. These results indicate that the oxidation current of dissolved hydrogen could be an indicator of chloride ions, because the formation of the Pt oxide layer is sensitively interfered with the chloride ions.

In plant coolant, there are many other impure ions such as sulfate, nitride, silicate and fluoride ions. And these ions may affect the formation of the Pt oxide layer. In order to develop the chloride ion detection technique with accuracy, we should evaluate the interference of

other impure ions in the formation of the oxide layer at high temperature.

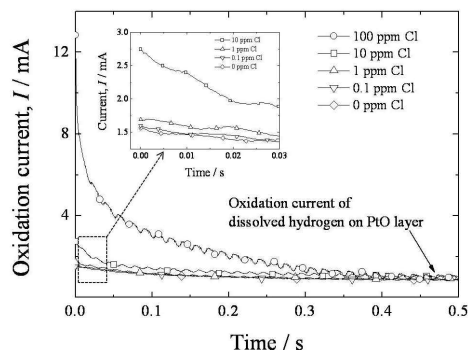


Fig. 2 Chronoamperometric curves obtained at Pt in a 32 mM H₃BO₃ solution containing 0.07 mM LiOH hydrogenated with 3.6 cc H₂/kg at 553 K, the potential shift from OCP to $+0.55$ V_{Ag/AgCl} for Cl ion detection.

3. Conclusions

A water chemistry measurement system equipped with new electrochemical techniques was introduced to monitor the reactor coolant chemistry, which was developed for using at high temperature. The performance of the high temperature pH measurement sensor was improved by installing a by-pass loop for the calibration of the sensor. The impurity detection technique, mainly for chloride detection, was developed from the relationship between the oxidation current of dissolved hydrogen and the concentration of impurity at the Pt-OH_{ad} formation potential. It was confirmed that chloride ions could be detected by 1 ppm in 553 K lithium borate solutions.

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