

Introduction to the High Temperature pH Measurement System Equipped with New Electrochemical Techniques

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1. Introduction

In a reactor coolant system, the need for reliable pH measurement system at the high temperature has resulted from interests in the corrosion and corrosion product behaviors of the structural materials. In developing the measurement system for monitoring pH at the high temperature, it is necessary to consider two important issues: the stability of pH measurement against various sample supply conditions, and an electrode's integrity for one fuel exchange period. Over the past decade Macdonald et al. [1-4] have developed many YSZ (yttria stabilized zirconia) pH electrodes. However, there are still many difficulties associated with the properties of ceramic electrode. In order to enhance the performance of pH measurement system, it is necessary to add enhanced functions to the measurement system.

In present study, we introduced the pH measurement system with new technologies: Reinforced stability of pH measurement under the discrete sample supply condition, long-term performance of reference electrode, and enhanced homogeneity of pH electrode materials.

2. Methods and Results

2.1 Reinforced stability in pH measurement system

The YSZ based pH electrode was found to take over 2 hours to put on the reliable pH values after approaching the operating temperature of the electrode, above 180°C. If the temperature of the supplied coolant sample is below the temperature value, the system needs another several hours to return to the normal measurement condition.

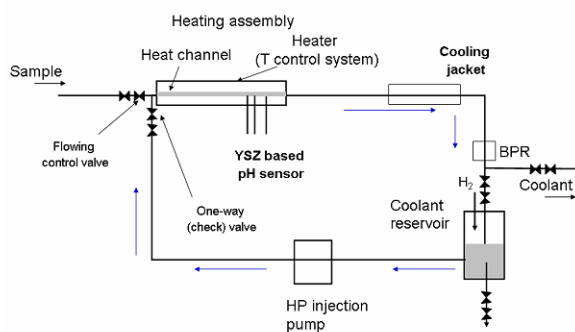


Fig. 1. A high temperature pH measurement system with a circulating by-pass loop.

In order to overcome the limitation of the pH electrode on the sample supply condition, we installed a circulating loop with an extra heater for the measurement system, as shown in Fig. 1.

In addition, in the case of the stopping of the sample supply, the high temperature lithium borate buffer solution would be supplied from the circulating loop for maintaining the constant operating temperature.

2.2 Long-term performance of reference electrode

The pH measurement system was designed to operate for one fuel exchange cycle without any maintenance. Even though the ceramic pH electrode is robust enough for working during the period, the reference electrode needs the calibration due to the dilution of internal electrolyte. For the calibration of the reference electrode, we used the relationship between the electrical conductivity and the concentration of the KCl solution.

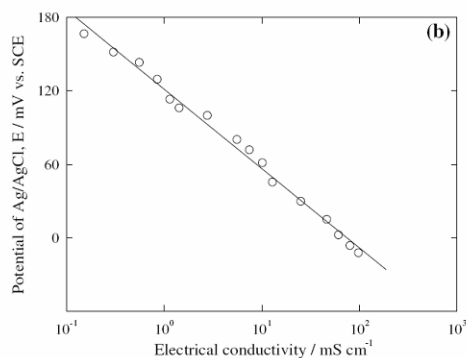
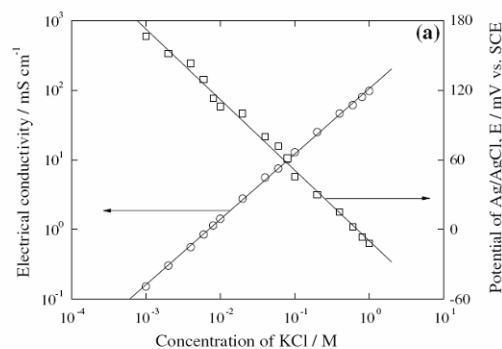


Fig. 2. (a) Relationship between the electrical conductivity (open circle) of the KCl solution and the potential (open square) of the Ag/AgCl electrode in the 0.001–1 M KCl solutions and (b) a linear relationship between the electrical conductivity and the potential of the Ag/AgCl electrode [5]

In Fig. 2a, the electrical conductivity and the potential of the Ag/AgCl electrode were respectively plotted against the KCl concentration. Both linear relationships were observed against the logarithm concentration of the KCl. The electrical conductivity increased linearly and the potential shift decreased linearly, respectively, with an increase of the KCl concentration, with a logarithmic scale. From the two linear relationships as shown in Fig. 2a, we can derive a linear relationship between the electrical conductivity and the potential of the Ag/AgCl electrode as shown in Fig. 2b. Therefore, this result shows that the potential shift of the Ag/AgCl electrode can be estimated by using the electrical conductivity of the internal electrolyte, when the internal electrolyte of the electrode is diluted or contaminated by a long-term exposure in very dilute solutions.

2.3 Enhanced homogeneity of pH electrode materials

The Ni/NiO mixed oxide powder has been used for the pH electrode material. To obtain high homogeneity of the electrode material, the Ni and NiO powder were mixed over 20 hours with mixing bottle. It takes long time and unexpected oxidation of Ni metal during the mixing process of the powder. To develop the advanced process for making the electrode material, we made a heat treatment of Ni powder at various temperatures. It was observed that the Ni powder treated at 600°C was partially oxidized and gave the equivalent structure compared with the Ni/NiO mixed powder. This method could be applicable to make the electrode material.

3. Conclusions

A pH measurement system was introduced with the enhanced techniques such as the stand-by circulating loop system, the self-calibrated reference electrode, and the enhanced homogeneity of pH electrode materials. The performances of these techniques were confirmed by the separated experiments.

Acknowledgments

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