

Fabrication and Evaluation of a New High-Temperature pH Sensor for Use in PWR Nuclear Power Plants

Yongju Jung* and Jei-Won Yeon†*

Department of Applied Chemical Engineering, Korea University of Technology and Education, Cheonan 330-708, Korea

*E-mail: yjung@kut.ac.kr

†Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Daejeon 305-353, Korea

*E-mail: yeonysy@kaeri.re.kr

Received July 20, 2010, Accepted August 31, 2010

A new high-temperature pH sensor has been successfully developed by reforming the internal reference systems of the pH sensors based on oxygen-ion conducting ceramic membrane. The conventional internal reference system, a mixture of Ni and NiO, has been replaced with partially oxidized Ni powders, where Ni and NiO coexist on the surface of particles, in order to avoid the cumbersome mixing step of Ni and NiO particles. The partially oxidized Ni particles were made by oxidizing Ni under air atmosphere at 600 °C and characterized by X-ray diffraction (XRD) and FTIR spectroscopy. The viability of the pH sensor developed was assessed in boric acid (1000 ppm-B) / lithium hydroxide (1 to 3 ppm-Li) buffer solutions at 280 °C. The pH sensor showed excellent accuracy with a small error less than ± 0.2 pH units.

Key Words: High-temperature pH sensor

Introduction

It is of significant importance to control and measure pH of coolants in pressurized water reactor (PWR) primary system in order to minimize the generation of corrosion products within the primary coolant loop. For the measurements of pH in high-temperature aqueous systems such as nuclear power plants, four types of pH sensors have been proposed, including platinum-based hydrogen electrodes,¹ palladium hydride electrodes,^{2,3} metal/metal oxide electrodes,^{4,5} and ceramic membrane electrodes (e.g., the yttria-stabilized zirconia (YSZ) membrane electrode).⁶⁻⁹ In case of hydrogen electrodes, however, it is not easy to practically use them because molecular hydrogen should exist in a test system.¹⁰ For palladium hydride electrodes, they cannot be used in a system containing oxidants.¹⁰ Above all, the three systems except ceramic membrane electrodes show a mixed potential in case that electrochemically active species exist in a system. For this reason, they have not been used in the area of nuclear power plants. On the other hand, ceramic membrane electrodes such as YSZ, which can be used under various chemical environments containing other redox species due to oxygen-ion selectivity, have attracted much attention as a reliable sensor for high-temperature pH measurements.¹⁰ The YSZ membrane electrodes consist of the following two parts: 1) YSZ membranes that play role of an oxygen-ion conductor and 2) metal/metal oxide internal reference systems (e.g., Cu/CuO, Ni/NiO, Hg/HgO) inside the YSZ membrane. The proton (H^+) activity in the test solutions makes an influence on the oxygen vacancy of the ceramic lattice and finally the equilibrium of the metal/metal oxide systems. So far, metal/metal oxide systems were made through homogeneous mixing of metal and metal oxide particles, which has been considered as a cumbersome and time-consuming process.

In this study, we present a new YSZ membrane-based pH sensor using partially NiO-coated Ni particles instead of a con-

ventional internal reference system, a mixture of Ni and NiO particles, in order to simplify manufacturing process and increase reproducibility. The new high-temperature pH sensor has been constructed by filling YSZ membrane tube with a NiO-coated Ni powders which were made by a simple oxidation method. The surface of Ni powders was oxidized under air atmosphere at 600 °C. The resulting Ni powders were analyzed using X-ray diffraction (XRD) and FTIR spectroscopy. The performance of the pH sensors was evaluated in aqueous solutions containing LiOH and boric acid at 280 °C, which are a general composition of primary coolant systems. Furthermore, the influence of trace elements (e.g., Fe, Ni, Zn, Cr) on pH of coolant systems was examined at 280 °C.

Experimental

Once-through loop system for high-temperature pH measurement. Stainless steel (SUS 316) with excellent mechanical properties was used as structural materials for a once-through loop system. To protect the corrosion on stainless steel at high-temperature solutions, the interior of the main body was coated with titanium metal which is considered to be physiologically inert and stable under severe chemical environments. Titanium metal was placed by inserting a titanium tube (34.8 mm in inside diameter with a wall thickness of 1.64 mm) to the inside of the main body right after a titanium tube was cooled to shrink at a temperature of -196 °C. For mechanical integrity between titanium tube and SUS 316 body, the main body was heated at 200 °C for 5 h. The flow rate and pressure of the once-through loop system were controlled by a high-pressure diaphragm pump (Teikoku EKMs-1) and a back-pressure regulator (Tescom 6000 PSIG), respectively. In this study, the loop system was operated with a flow rate of 10 cc min^{-1} at 120 atm.

Development of a new pH sensor using partially oxidized Ni powders. To determine an appropriate oxidation temperature,

Ni foil was exposed to an air at 400 and 600 °C for 12 h to make NiO on the surface of the Ni foil. The resulting Ni foil was analyzed by X-ray diffraction (XRD) and FTIR spectroscopy. It was observed that both Ni and NiO coexist at 600 °C. So, partially oxidized Ni powders were prepared by heating Ni powders under air atmosphere at 600 °C for 12 h.

Ytria-stabilized zirconia (YSZ) tube (Friatec AG, Germany) was used as a ceramic membrane with oxygen-ion conductivity. The tube (200 mm long and 5 mm in inside diameter with a wall thickness of 1.5 mm) was stabilized with 8.5 wt % Y_2O_3 . The partially oxidized Ni powders as internal reference elements were placed at the bottom part of YSZ tube. For insulation and sealing, the rest part of the YSZ tube was sequentially filled with zirconia sand, ceramic sealant and epoxy adhesive (Fig. 3a). Finally, the pH sensing electrode was assembled using stainless steel fittings and epoxy adhesives for installation in the once-through loop system, as shown in Fig. 3b. The pH measurement system consisted of a pH electrode and an external Ag/AgCl reference electrode. In general, the activation step is needed for the normal operation of the pH sensor. For this, the pH sensor was heat-treated in distilled water at 300 °C for 3 days.

The viability of the pH sensor developed in this study was assessed in synthetic coolant solution of 1 ~ 3 ppm-Li and 1000 ppm-B. LiOH (Aldrich) and H_3BO_3 (Aldrich) were used as the source of Li and B, respectively. The pH of each solution was recorded every second for 1 h. Generally, the fluctuation in pH values was less than 0.1 pH units and the pH data reported here were the average of all pH values measured for 1 h. Furthermore, the effect of trace elements on pH of coolant systems was checked at 280 °C. $Fe(NO_3)_2$, $Ni(NO_3)_2$, $Cr(NO_3)_3$ and $Zn(NO_3)_2$ were used as sources of trace elements. Electrochemical measurements were carried out at 120 atm and 280 °C. The temperature of test solutions was controlled by a cartridge heater with Zircaloy cladding and monitored by thermocouple which was installed between Ag/AgCl reference electrode and pH sensor. All potentials were measured using a Keithley electrometer (M6514) with a high input impedance of 200 T Ω and were recorded by a data acquisition system.

Results and Discussion

Fig. 1 shows the schematic of the once-through loop system for pH measurement at high temperature. In case of stainless steel, when it was exposed to high-temperature solution, corrosion products are generated to make a change in solution pH. For this reason, titanium metal with strong corrosion resistance was used in the high-temperature region exposed to test solutions in order to protect contamination of test solutions by corrosion products generated from the structural materials at high temperature and maintain the purity of solutions. To remove impurities in the loop system, the system was operated with distilled water at 300 °C for 3 days. After that, the chemical composition of distilled water passing through the loop system was analyzed by ICP-AES. Metallic elements except Ni were not detected. Only Ni was detected at a few ppb levels, indicating that the loop system was not affected at all by high-temperature corrosion.

A Ni foil was oxidized under air atmosphere at the tempera-

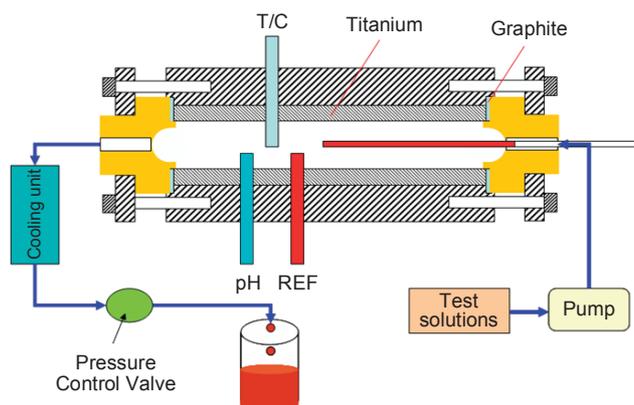


Figure 1. Schematic of the once-through loop system for pH measurement at high temperature.

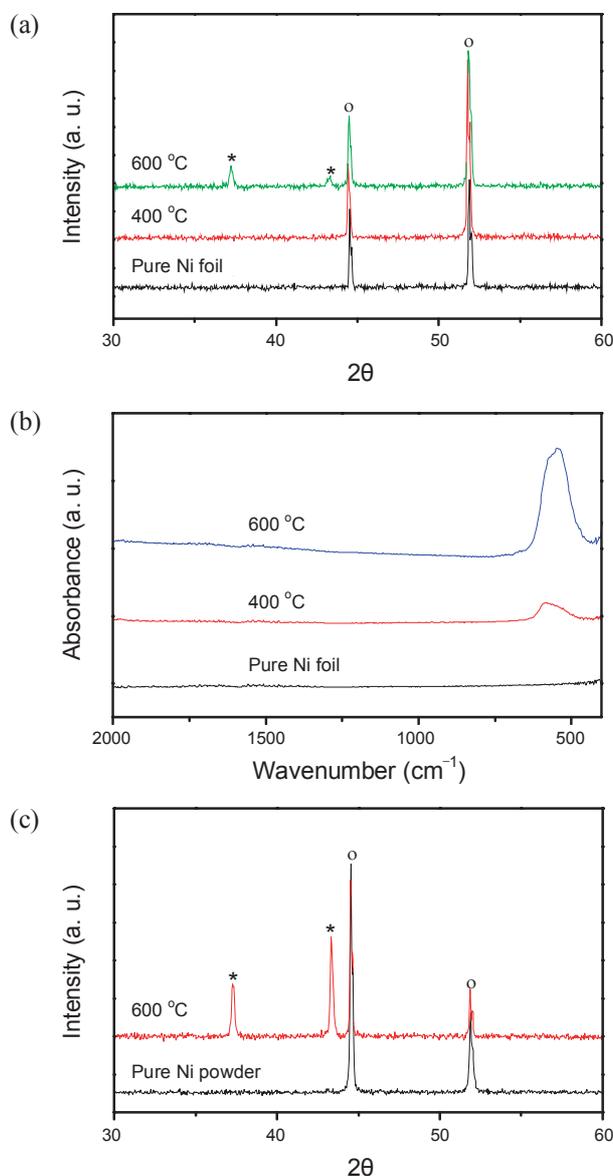
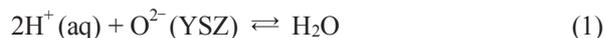


Figure 2. (a) XRD patterns of Ni foil and heat-treated Ni foils: Ni *open circle* and NiO *asterisk*; (b) FTIR spectra of Ni foil and heat-treated Ni foils; and (c) XRD patterns of Ni powders and heat-treated Ni powders: Ni *open circle* and NiO *asterisk*.

ture of 400 and 600 °C to get a partially NiO-coated Ni foil so that both Ni and NiO exist simultaneously on the surface of the Ni foil. It was examined from XRD patterns that NiO did not form on Ni foil at 400 °C but well form at 600 °C (Fig. 2a). However, it was revealed from more surface-sensitive FTIR analysis that a small amount of NiO (450 ~ 600 cm⁻¹) could be produced even at 400 °C (Fig. 2b). So, Ni powders were oxidized at 600 °C to get NiO-coated Ni powders (Ni-NiO) which would be used in pH sensors. Fig. 2c shows that XRD patterns of Ni powders heat-treated at 600 °C were similar to that of Ni foil, except intensity ratio of NiO to Ni. NiO peaks of Ni powders were relatively more intense compared to those of Ni foil. It is thought that this can be attributed to the higher surface area of Ni powders.

NiO-coated Ni powders were placed with a Pt wire current collector at the bottom part of YSZ membrane tube as shown in Fig. 3a. Above the internal reference system, quartz wool and ZrO₂ sand were added. Finally, the rest of YSZ tube was filled with two kinds of sealing materials, ceramic sealant and epoxy, to completely seal the pH electrode. For easy installation in once-through loop system, the YSZ membrane was assembled using a home-made fitting method as shown in Fig. 3b.

For the electrochemical system, Ni-NiO/YSZ membrane/H⁺, H₂O (test solution), the operation principle of the pH sensor is based on the YSZ membrane that acts as an oxygen-ion conductor at temperature higher than 185 °C and the following two kinds of reactions: chemical reaction at external interface of the membrane and electrode reaction at the internal interface of the membrane.⁹ The chemical equilibrium occurring outside YSZ membrane and electrode reaction inside YSZ membrane are expressed by equation 1 and equation 2, respectively.



These equations mean that proton activity in solution side affects the oxygen ion vacancy within YSZ membrane and

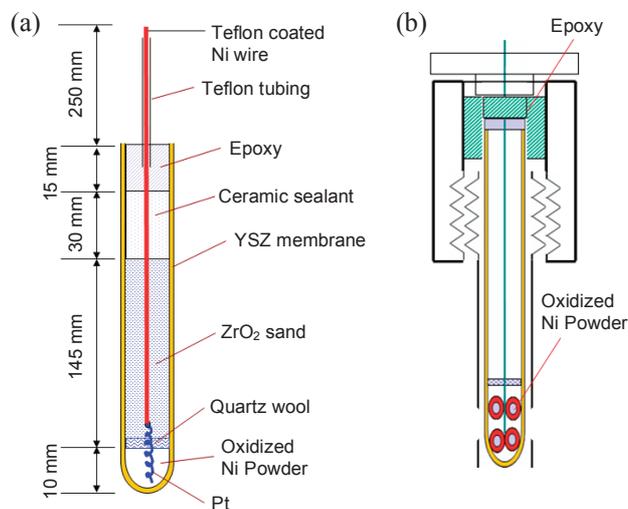


Figure 3. (a) YSZ-based pH sensor using partially oxidized Ni powders (Ni-NiO) and (b) pH sensor assembly with stainless steel fittings.

finally the electrode reaction of Ni/NiO redox couple.

As a result, overall reaction (eq. 1 + eq. 2) is given by the following equation 3:



From the overall reaction, potential (E) measured at the pH sensor can be described as a function of pH by equation 4.

$$E(T) = E_{\text{Ni/NiO}}^{\circ}(T) - (2.303RT/F)\text{pH} \quad (4)$$

where $E(T)$ is the potential measured at a temperature T , $E_{\text{Ni/NiO}}^{\circ}(T)$ is the standard potential for the Ni/NiO redox couple at a temperature T , and, F is Faraday constant.

To assess the viability of the new pH sensor, its performance tests were performed in the synthetic PWR primary coolants consisting of LiOH (1.0, 2.0, 3.0 ppm-Li) and H₃BO₃ (1000 ppm-B) at 120 atm and 280 °C. Fig. 4 shows that the pH values measured by the pH sensor applying partially oxidized Ni powders as an internal reference system were very similar to theoretical values, implying that the pH sensor was successfully developed. It was observed that the measurement error by the pH sensor was less than ±0.2 pH units.

In addition, the effect of trace elements on pH of the synthetic coolants was investigated. Table 1 shows pHs measured in solutions of 3 ppm-M in synthetic coolants (3 ppm-Li + 1000 ppm-B) at 280 °C, where Fe, Ni, Cr and Zn were used as M. The concentration level of 3 ppm, which is 1000 times higher than the general concentration of corrosion products in a real

Table 1. The effect of trace elements on the pH of coolant solution at 280 °C.

Solution	pH
3 ppm-Li + 1000 ppm-B	7.05
3 ppm-Fe + 3 ppm-Li + 1000 ppm-B	6.93
3 ppm-Ni + 3 ppm-Li + 1000 ppm-B	6.79
3 ppm-Zn + 3 ppm-Li + 1000 ppm-B	6.90
3 ppm-Cr + 3 ppm-Li + 1000 ppm-B	6.99

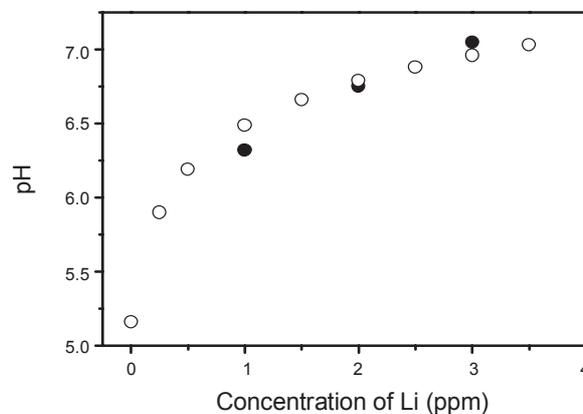


Figure 4. The pH values measured by the developed pH sensor in the synthetic coolant solutions consisting of LiOH (1.0, 2.0, 3.0 ppm-Li) and H₃BO₃ (1000 ppm-B) at 280 °C: the measured values filled circle and the theoretical values open circle.

primary coolant system, was used to observe an obvious pH change. It was found that coolants pH slightly decreased from 7.05 to 6.79. This result suggests that the corrosion products at a real primary circuit have little influence on the pH of coolant, because their concentration is as low as a few ppb.

Conclusions

A new YSZ membrane-based pH sensor has been successfully fabricated by using partially oxidized Ni powders as an internal reference system instead of the conventional internal reference system, a mixture of Ni and NiO. For making the partially oxidized Ni particles, study on the oxidation of Ni foil was carried out to determine an appropriate oxidation temperature. It was found from X-ray diffraction (XRD) and FTIR spectroscopy that Ni and NiO exist simultaneously on the surface of Ni particles, when they were heat-treated under air atmosphere at 600 °C. The performance of the pH sensor developed was examined in the synthetic coolants (1 ~ 3 ppm-Li + 1000 ppm-B) at 280 °C. The pH sensor showed excellent accuracy with a small error less than ± 0.2 pH units. In addition, the effect of trace metal elements on the pH of coolant solutions was investigated in solutions consisting of 3 ppm-M, 3 ppm-Li, and 1000 ppm-B at 280 °C, where Fe, Ni, Cr and Zn were used as M. It was found that coolants pH slightly decreased from 7.05 to 6.79, suggesting that corrosion products at a real primary cir-

cuit have little influence on the pH of coolant, because their concentration is as low as a few ppb.

Acknowledgments. This work was supported by the nuclear R&D program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology.

References

1. Macdonald, D. D.; Butler, P.; Owen, D. *Can. J. Chem.* **1973**, *51*, 2590.
2. Tsuruta, T.; Macdonald, D. D. *J. Electrochem. Soc.* **1981**, *128*, 1199.
3. Macdonald, D. D.; Wentzcek, P. R.; Scott, A. C. *J. Electrochem. Soc.* **1980**, *127*, 1745.
4. Kriksunov, L. B.; Macdonald, D. D.; Millett, P. J. *J. Electrochem. Soc.* **1994**, *141*, 3002.
5. Macdonald, D. D.; Liu, J.; Lee, D. *J. Appl. Electrochem.* **2004**, *34*, 577.
6. Macdonald, D. D.; Hettiarachchi, S.; Lenhart, S. *J. Solution. Chem.* **1988**, *17*, 719.
7. Niedrach, L. *Science* **1980**, *207*, 1200.
8. Danielson, M. J.; Koski, O. H.; Meyers, J. *J. Electrochem. Soc.* **1985**, *132*, 296.
9. Lvov, S. N.; Zhou, X. Y.; Ulmer, G. C.; Barnes, H. L.; Macdonald, D. D.; Ulyanov, S. M.; Benning, L. G.; Grandstaff, D. E.; Manna, M.; Vicenzi, E. *Chem. Geol.* **2003**, *198*, 141.
10. Eklund, K.; Lvov, S. N.; Macdonald, D. D. *J. Electroanal. Chem.* **1997**, *10*, 99.