*Transactions of the Korean Nuclear Society Spring Meeting*
*Gwangju, Korea, May 30-31, 2013*

# Development of Iridium Solid-state Reference Electrode for the Water Chemistry Status Measurement in Nuclear Power Plants

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## 1. Introduction

Various metallic materials used in a nuclear power plant have been exposed to a variety of water chemistry environments and the corrosion of metallic materials occurs due to the reactions between metal structures and water chemistry environments. Therefore, the management of the water chemistry factors is needed to prevent corrosion. The chemical factors affecting the corrosion are pH and Electrochemical Corrosion Potential (ECP).

The world-wide studies suggest that ECP and pH are effective indicators for preventing the material damage from water chemistry condition [1,2,3]. ECP and pH should be measured as the reference electrodes, and should show stable potential characteristics with fast responses.

In this study, the iridium reference electrodes using a solid-state metal oxide electrode has been developed to measure effective indicators such as ECP and pH.

## 2. Methods and Measurement Mechanism

This section describes the development methods and the operating principles of the iridium solid-state metal oxide electrodes.

### *2.1 Solid-state Metal Oxide Electrodes*

$IrO_x$, $PtO_2$, $Ta_2O_4$, $TiO_2$ and $RuO_2$ are the metal-metal oxide widely used in the production of the pH-sensing electrode. Especially, $IrO_x$, $RuO_2$ and $SnO_2$ show better characteristics related to the sensitivity, responsiveness, range of motion and performances.

Among the various electrodes made of above mentioned materials, it is known that the electrode using $IrO_x$ shows stable performance in the wide range of temperature and rapid response in the broad range of pH and low sensitivity against the interference by other redox reaction.

Typical fabrication methods of the iridium Solid-State Reference Electrode (SSRE) are the high-temperature oxidation process, sputtering and direct electrolytic coating methods. However, the sputtering method is expensive and the high temperature oxidation method has a problem such as cracks caused by high temperature (T>500℃) processing. Direct electrolytic coating method of the iridium metal oxide is made by a iridium coating on the Ti wire. The Advantages of this method are 1) easily coated with iridium, 2) Nafion coating, to form a cation permselective membrane able to perform a electrode surface protection. The iridium direct electrolytic coating method was announced by Yamanaka and developed by Marzouk in 1989 [1].

In this study, iridium(SSRE) reference electrode has been developed, which is applying the iridium electrode development method by Marzouk, for low temperature (T<120℃) ECP and pH measurement.

### *2.2 pH Measurement Mechanism of Iridium Electrode*

The stable oxidation products of iridium are $Ir_2O_3$ and $IrO_2$, and electrode potential is determined by electrochemical reactions [3] below.

$$\begin{aligned} Ir_2O_3 + 6H^+ + 6e^- &= 2Ir + 3H_2O \\ IrO_2 + 4H^+ + 4e^- &= Ir + 2H_2O \\ 2IrO_2 + 2H^+ + 2e^- &= Ir_2O_3 + H_2O \end{aligned} \quad (1)$$

The above equation is represented by the Nernst equation for pH.

$$E = E^0 + \frac{2.303RT}{nF}\log\frac{[IrO_2]^2}{[Ir_2O_3]} + \frac{2.303RT}{nF}\log[H^+] \quad (2)$$

The activity of 1 is applied to above equation because $Ir_2O_3$ and $IrO_2$ are metal. Then, it shows equation as follow.

$$E = E^0 + \frac{2.303RT}{nF}pH \quad (3)$$

Where T is temperature with K of unit. The coefficient of above pH term at 25℃ is 0.059. The electrode potential of iridium (SSRE) in pH titration test is 59mV/pH.

In this study, Ag/AgCl solid reference electrode was used when measuring ECP developed for reference electrode and theoretical standard potential with iridium oxide is 577mV.

### *2.3 Methods*

The iridium (SSRE) reference electrode was fabricated with 1) electrodeposition of iridium oxide film on a etched Ti wire with Pt wire for 10 minute at 2mA/cm$^2$ (0.00127mA) and 2) coating with Nafion for protecting irdium oxide film and 3) heat treatment for 1hour at 120℃. The deposition procedure was produced according to Marzouk procedures. Table 1 is materials for fabricated iridium (SSRE) reference electrodes.

Table 1. Materials of fabricated iridium (SSRE) reference electrodes.

| | Materials |
|---|---|
| Coating substrate | Ti wire |
| Eching solution | $H_2SO_4$ |
| Coating solution | $IrCl_4 \cdot H_2O$ |
| | 30% $H_2O_2$ |
| | Potassium oxalate hydrate |
| | $KCO_3$ |
| Protecting solution | Nafion 117 |

## 3. Results

### *3.1 Data of the stabilization of iridium metal oxide electrodes*

Electrode potential of fabricated iridium (SSRE) reference electrode was measured with commercial Ag/AgCl (Orion 90-02) electrode for 117 hours in a solution (Buffer 7). Figure 1 shows the stable electrode potential of iridium (SSRE) reference electrodes. The stable electrode potentials of iridium (SSRE) reference electrodes are 155mV and 160mV, respectively.

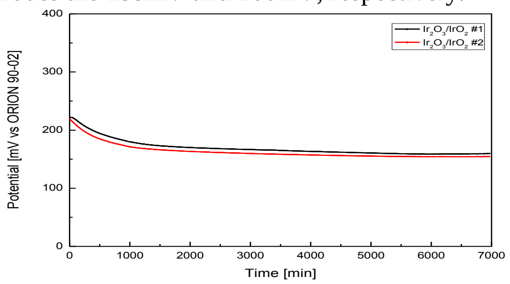


Fig. 1. Result of stable potential of iridium (SSRE) reference electrodes.

### *3.2 Response of iridium metal oxide electrodes*

The pH titration tests were performed for identifying characteristics of pH on the responses of iridium (SSRE) reference electrodes in HCl – NaOH solution. This test was performed with fabricated Ag/AgCl (SSRE) reference electrode and the test pH range was 2 to 14. Figure 2 shows the pH titration test of iridium (SSRE) reference electrode. The curve-fitting result of the Figure 2 data was obtained from the slope -63.12mV/pH.

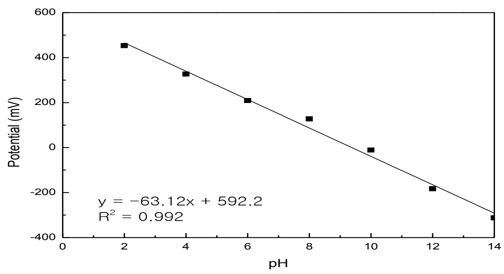


Fig. 2. Response on the pH-titration of iridium (SSRE) reference electrodes

### *3.3 Measurement of ECP*

Figure 3 shows the ECP of pipe materials (carbon steel) in nuclear power plants. The result is represented orange color square in pourbaix diagram. Measurement range of the test is 6.3 to 9.3 of pH. The ECP value of steel materials is about -0.370V and the values tends to decline in accordance with the increase of pH.

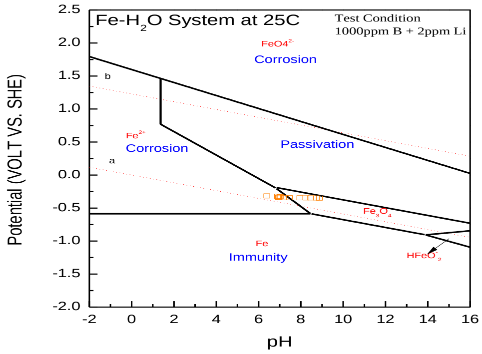


Fig. 3. Result of measurement ECP of steel in pourbaix diagram

## 4. Conclusions

The iridium (SSRE) reference electrode for the ECP measurement in water chemistry environment of nuclear power plants has been developed. A calibration for water chemistry measurement was performed by potential measurement of iridium (SSRE) reference electrode with Ag/AgCl (SSRE) reference electrode. The result exhibited a stable potential for 117 hours and a super-Nernstian response with 63.12mV/pH.

In this study, the iridium (SSRE) reference electrode shows super-Nernstian characteristic and it may be caused by the property of electrolytically coated iridium oxide. Considering the long-term stability of the developed electrode, it is possible to apply as a reference electrode through calibration procedure.

The result of ECP measurement of piping material in nuclear power plant at low temperature using the developed iridium (SSRE) reference electrode is approximately -0.370V . Based on the various results of this study, the developed iridium (SSRE) reference electrode can be applied to the water chemistry environments of nuclear power plant.

## ACKNOWLEDGMENTS

This work was supported by Small & Medium Sized Business R&D Program of the Small & Medium Business Administration(SMBA)

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