An Automatic Calibration Method for a Reference Electrode Using the Relationship between the Electric Conductivity and the Chemical Activity of KCl

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1. Introduction

The Ag/AgCl electrode is a type of reference electrode, commonly used in electrochemical measurements, because it is simple, inexpensive, very stable and non-toxic. For these reasons, the Ag/AgCl electrode has long been used to provide a reliable potential monitoring of ions in a solution [1,2]. However, when a reference electrode is immersed in a solution for a long period of time, this can cause an electrolyte leakage. If the reference electrode does not maintain its reference potential due to an electrolyte leakage, a number of undesirable conditions may occur. As the potential of the Ag/AgCl electrode is determined by the activity of chloride ions in a solution, a number of investigations have been performed on the prevention of an electrolyte leakage. However, these attempts have not resolved the problem of an electrolyte leakage satisfactorily through a junction between a reference electrode and a test solution [3]. In the present work, we demonstrate a new method to calibrate Ag/AgCl reference electrodes. The concept of this method is that the concentration of KCl can be estimated by the electrical conductivity of the electrolyte, and then the potential of the Ag/AgCl reference electrode is calculated by the Nernst equation, with the estimated KCl concentration at a given temperature [4].

2. Methods and Results

The concept of this method is that the concentration of KCl can be estimated by the electrical conductivity of the electrolyte, and then the potential of the Ag/AgCl reference electrode is calculated by the Nernst equation, with the estimated KCl concentration at a given temperature [4].

2.1 Electrical Properties in the KCl Solution

In the solutions with various KCl concentrations, the electrical conductivities of the electrolyte and the potentials of the Ag/AgCl reference electrode were measured. The results were that the conductivities increased with an increase of the KCl concentration. The potentials of the Ag/AgCl reference electrode have a linear relationship to the KCl concentration [5]. Thus, the data represented by the relationship demonstrated that an improvement of the electrode performance could be achieved with this method.

2.2 The Interference Effects of Boric acid

In addition, we examined the electrical properties of KCl solutions in the presence of boric acid and they are shown in Fig. 1. Boric acid has been used as a chemical additive for the coolant of nuclear power plants. Various amounts of boric acid were added to KCl solutions, and the conductivities of these solutions were measured at an ambient temperature. The conductivity values did not directly depend on the addition of the boric acid. This result might be due to the low degree of dissociation of boric acid. These preliminary results indicate that it is possible to calibrate the potential of a reference electrode by monitoring the conductivity of the electrolyte.

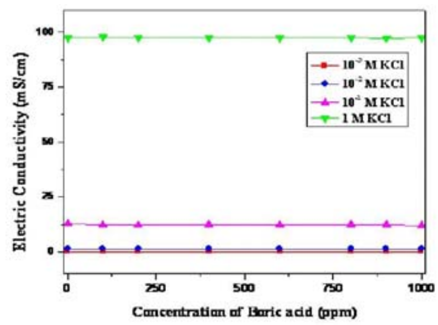

Fig. 1. Conductivity of KCl (0.001~1M) Solution Added Boric Acid.

2.3 Applied Study of Noble Silver/Silver Chloride Electrode

For realizing a long-term potential monitoring, a reference electrode was designed to measure the conductivity of the electrolyte, and electrolyte leakages were intentionally performed. First, the reference electrode was filled with 0.1 M KCl, and the electrode was immersed in water and boric acid, respectively. Conductivity and electrode potential were measured during an electrolyte leakage. The data showed the same trends for both solutions. Consequently, improvements to the reference electrode can be achieved by this new method.

3. Conclusions

We suggested a new calibration method for a Ag/AgCl reference electrode by using the relationship between the electrical conductivity and the potential reference electrode in a solution. The result, the electrical conductivities increase with an increase of the KCl solution. And the potentials of the Ag/AgCl reference electrode decrease with an increase of the KCl concentration. In addition, we tested the electrical properties of the boric acid used as a coolant of nuclear power plants. In the KCl solution added with boric acid, the electrical conductivity values did not directly depend on the addition of the boric acid. Also, for realizing a potential monitoring, a reference electrode was designed to create electrolyte leakages. Consequently, improvements to the reference electrode can be achieved by this new method.

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