

A Spectral Active Material Interference in the Electrical Conductivity of the Internal Electrolyte and the Potential Shift of the Ag/AgCl Electrode

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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 and stable. For these reasons, the Ag/AgCl electrode has long been used to provide a reliable potential monitoring of ions in a solution [1]. However, when a reference electrode is used in an aqueous solution containing a very low electrolyte for a long period of time, this could cause a considerable potential shift of the reference electrode due to a dilution of the internal electrolyte. If the potential of the reference electrode shifts, undesirable conditions may occur. Therefore, many studies have been applied to improve the long-term performance of the reference electrode. However, these attempts have not completely resolved the problem of an electrolyte dilution by the test solution [2].

In the present study, we developed a creative technique to correct the concentration change of the internal electrolyte by a long-term exposure of the Ag/AgCl electrode in very dilute solutions. We measured the electrical conductivity and UV/VIS absorbance of the internal electrolyte. From these measurements, we observed the linear relationship between KCl concentration and the potential of the Ag/AgCl electrode. In order to accelerate the diffusion of the internal electrolyte into the test solution, an Ag/AgCl electrode with a tiny perforation was used. We confirmed the feasibility of the creative calibration technique.

2. Methods and Results

In order to estimate the potential shift of the Ag/AgCl reference electrode, we tried to estimate the concentration of the diluted internal electrolyte by using two kinds of calibration techniques. The first technique used the relationship between the electrical conductivity and the concentration of the KCl solution. Second was the calibration technique of using the relationship between UV/VIS absorbance of the internal electrolyte added with spectral active material (Triphenylmethane, TPM) and a KCl concentration. The potential shifts of the Ag/AgCl reference electrode were calculated by the Nernst equation, with the estimated KCl concentration from two relationships, respectively.

2.1 Relationship between the Potential Shift and the Diluted Internal Electrolyte.

The electrical conductivity increased linearly with an increase of the KCl concentration, with a logarithmic scale. The UV/VIS absorbance of the KCl solution added with TPM was observed to be quite linear with an increase in the TPM concentration. The potential shift decreased linearly with an increase in the KCl concentration, with a logarithmic scale. From these results, therefore, we derive two kinds of linear relationships. The first relationship was between the electrical conductivity of the internal electrolyte and the potential shift. The second one was a relationship between the UV/VIS absorbance of the internal electrolyte and the potential shift. Therefore, these results show that the potential shift of the Ag/AgCl electrode can be estimated by using the electrical conductivity and the UV/VIS absorbance of the internal electrolyte when the internal electrolyte of the electrode is diluted or contaminated by a long-term exposure in very dilute solutions.

2-2. H_3BO_3 Interference in the Electrical Conductivity, UV/VIS Absorbance and the Potential of the Ag/AgCl Electrode

H_3BO_3 has been used as a chemical additive for a nuclear reactor coolant [4]. In order to describe the contamination of the internal electrolyte by the H_3BO_3 solution, we performed a measurement of the electrical conductivity and the potential shift of the Ag/AgCl electrode in a KCl solution containing H_3BO_3 in the range of 0 - 0.016 M.

Figure 1 shows that the electrical conductivity of the internal electrolyte added with TPM was nearly a constant value for each KCl concentration measured, demonstrating that the electrical conductivity was not affected by TPM. The potential of the Ag/AgCl electrode was also measured with the internal electrolyte containing H_3BO_3 and TPM solution, respectively. The relationship between the logarithm of the KCl concentration and the potential shifts were observed to be quite linear in the KCl concentration range of 0.01 - 1.0 M for both solutions.

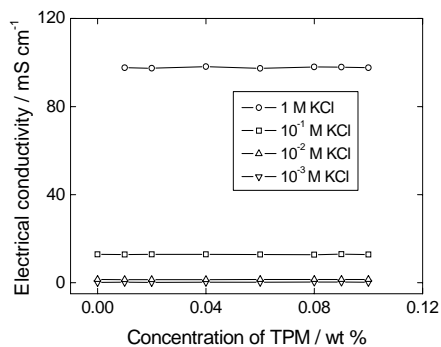


Fig. 1. A spectral active material interference in the electrical conductivities of the internal electrolyte.

2.3 Acceleration Test for a Long-Term Exposure of the Ag/AgCl Electrode in a Diluted Solution

For simulating a long-term exposure of the electrode, we used an Ag/AgCl electrode with a tiny perforation to accelerate the diffusion of the internal electrolyte. First, the Ag/AgCl electrode was filled with 0.1 M KCl solution as an internal electrolyte. During the dilution of the internal electrolyte of the Ag/AgCl electrode, we estimated the diluted concentration of the internal electrolyte by using the electrical conductivity and UV/VIS absorbance, as shown in Fig. 2. The estimated KCl concentration was converted to a potential by the Nernst equation. Consequently, we can simply estimate the potential shift of the Ag/AgCl electrode from the values of the electrical conductivity and UV/VIS absorbance.

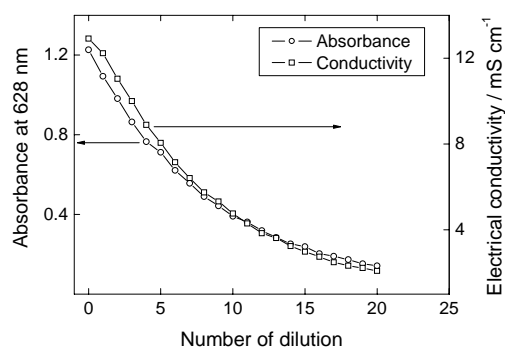


Fig. 2. The electrical conductivity (□) and UV/VIS absorbance (○) with a dilution of the internal electrolyte in distilled water

3. Conclusions

We suggested a correction technique for an Ag/AgCl electrode for a long-term exposure to diluted solutions by using the electrical conductivity and UV/VIS absorbance of the internal electrolyte. By the measurement, it was documented that the electrical conductivity increased with an increase of the

concentration of KCl, and UV/VIS absorbance increased with an increase of TPM concentration. The potential of the Ag/AgCl electrode shifted anodically with a decrease of the concentration of the KCl. There was little interference of the H₃BO₃ and TPM solution on the electrical conductivity and the potential shift of the Ag/AgCl electrode. For confirmation of this technique, an accelerated test was carried out to simulate a long-term exposure of the Ag/AgCl electrode in the presence of H₃BO₃. The collected values of the potential shift with this technique were estimated as less than 3 mV when compared with the experimentally measured ones. Consequently, this correction technique is confirmed to be applicable for the correction of an Ag/AgCl electrode, especially when exposed to non-electrolytic aqueous solutions.

REFERENCES

- [1] D. J. G. Jves, G. J. Janz, Reference Electrode Theory and Practice, Academic Press, New York, 1961.
- [2] J.-W. Yeon, et al., Reference Electrode with Self-Calibrated Function And Automatic Electrochemical Potential Correction Apparatus Using The Same, Korean Patent, 10-2008-0047496.
- [3] R. G. Bates, J. B. Macaskill, Standard Potential of the Silver-Silver Chloride Electrode, Pure & Appl. Chem, Vol.50, pp.1701-1706, 1978.
- [4] J.-W. Yeon, Y. Jung, S.-I. Pyun, Deposition Behaviour of Corrosion Products on the Zircaloy Heat Transfer Surface, J Nucl. Mater, Vol. 354, pp.163, 2006.