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ORIGINAL PAPER

A calibration technique for an Ag/AgCl reference electrode utilizing the relationship between the electrical conductivity and the KCl concentration of the internal electrolyte

**Myung-Hee Yun · Jei-Won Yeon · Jaesik Hwang ·
Chang Seop Hong · Kyuseok Song**

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Abstract For ensuring the long-term performance of an Ag/AgCl reference electrode, a calibration technique was developed by using the linear relationship between the electrical conductivity and the KCl concentration of an internal electrolyte. It was observed that the electrical conductivities increased with an increase of the KCl concentration of the internal electrolyte, and the potentials of the Ag/AgCl electrode shifted anodically with a decrease of the KCl concentration. For simulating a long-term exposure of the electrode, we designed a reference electrode with a tiny perforation to accelerate the diffusion of the internal electrolyte. During the acceleration tests, the potentials of the Ag/AgCl electrode were shifted by almost the same amount as the potentials calculated from the change of the electrical conductivity of the internal electrolyte. Consequently, this technique was confirmed to be applicable for the calibration of an Ag/AgCl electrode, especially when exposed to non-electrolytic aqueous solutions.

Keywords Ag/AgCl · Reference electrode · Calibration · Electrical conductivity · Long-term exposure

1 Introduction

The Ag/AgCl reference electrode is commonly used in electrochemical measurements, because it is simple, compact, stable, and non-toxic. For these reasons, the Ag/AgCl electrode has long been used to provide a reliable potential monitoring in aqueous solutions [1–8]. As the potential of the Ag/AgCl electrode is determined by the activity of the Cl^- ions [9–11], it is important to maintain the Cl^- ions at a constant concentration in the internal electrolyte of the reference electrode. However, when a reference electrode is used in an aqueous solution containing little electrolyte such as de-mineralized water or natural water 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 reference electrode does not maintain its reference potential, a number of undesirable conditions may occur [12].

In order to improve the long-term performance of the reference electrode, many techniques have been applied for its development. Most techniques [13–16] have focused on preventing a dilution of the internal electrolyte of the electrode. In one example [13], the micro-valve for the nano-fluid was constituted to the electrode system for reducing the consumption of KCl during the measurement. In another example [14–16], a polymer material was used as a membrane to inhibit an electrolyte dilution. And the KCl electrolyte of low concentration has been used in order to minimize the dilution of the internal electrolyte [17]. However, these attempts have not satisfactorily resolved the problem of an electrolyte dilution through a junction between a reference electrode and a test solution.

In the present study, we developed a creative technique for a promising long-term performance of the reference electrode. The concept of the technique is to calibrate the

M.-H. Yun · J.-W. Yeon (✉) · J. Hwang · K. Song
Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Daeduk daero 1045, Yuseong-gu, Daejeon 305-353, Republic of Korea
e-mail: yeonysy@kaeri.re.kr

C. S. Hong
Department of Chemistry, Korea University, Anam-dong Seongbuk-Gu, Seoul 136-701, Republic of Korea

change of the internal electrolyte by its electrical conductivity, rather than focusing on reducing the dilution of the internal electrolyte. We confirmed the linear relationship between the electrical conductivity and the KCl concentration of the electrolyte. From the relationship, the KCl concentration can be estimated to determine the potential of the Ag/AgCl electrode. The long-term exposure tests were carried out by using a modified Ag/AgCl reference electrode with a tiny perforation to accelerate the diffusion of the internal electrolyte into the test solution. We confirmed the feasibility of the suggested calibration technique from the good agreement between the estimated and measured potential values.

2 Experimental

Two types of Ag/AgCl electrode were used as shown in Fig. 1a and b, respectively. Both were made from glass tubes of 4 mm in diameter. One was a typical Ag/AgCl electrode with a Vycor frit. Using this electrode, we measured the relationship between the potentials of the Ag/AgCl electrode and the electrical conductivity of the KCl solutions. The second electrode was designed for simulating a long-term exposure in a dilute solution. Therefore, the tip of the electrode was treated with a tiny perforation as a junction. The perforation of the electrode accelerates the diffusion of the internal electrolyte into the test solution.

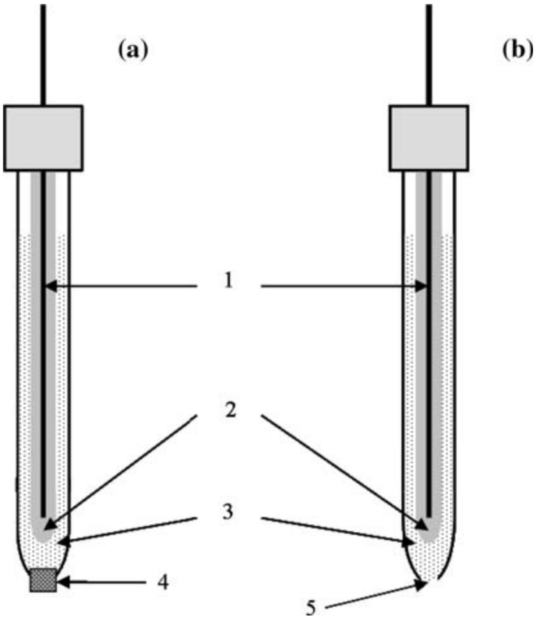

Fig. 1 Scheme of the Ag/AgCl electrodes (**a**) typical Ag/AgCl electrode with a Vycor tip and (**b**) Ag/AgCl electrode with a tiny perforation to accelerate the diffusion of the internal electrolyte into the test solution: 1, Ag wire; 2, AgCl layer; 3, KCl solution; 4, porous Vycor; 5, perforation

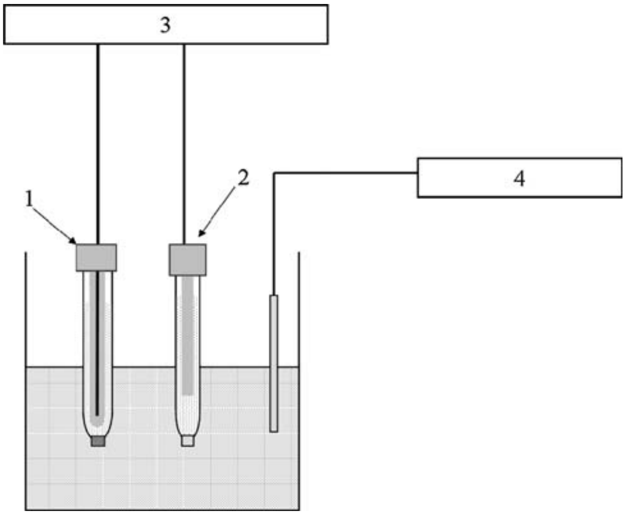

Fig. 2 The electrochemical measurement system of the potential difference between the Ag/AgCl electrode and SCE: 1, Ag/AgCl electrode; 2, SCE; 3, high input impedance electrometer; 4, thermometer

The Ag/AgCl electrode was made in the laboratory by an electrochemical oxidation of a silver (99.9%) wire of 1 mm in diameter in an HCl solution. For the determination of the conductivity of the KCl solution, a typical two-electrode type conductivity meter (Tacussel CD778) was used. As shown in Fig. 2, the potentials of Ag/AgCl electrode were measured against a SCE (saturated calomel electrode). A high in-put impedance electrometer (Keithley Model 6514) was used to measure the potential difference between the electrodes. All chemicals used in this study were analytical reagent grade. And the experiments were carried out at temperature of 25 ± 1 °C.

3 Results and discussion

3.1 Relationship between the electrical conductivity of the internal electrolyte and the potential of the Ag/AgCl electrode

The internal electrolyte of the reference electrode can be diluted by the concentration gradient, when the electrode is exposed to a diluted solution. Moreover, under the condition of a long-term exposure in those environments, the degree of dilution would be more severe. As a dilution of the internal electrolyte causes a potential shift of the reference electrode, we have to examine the change of the reference electrode during the use of the electrode. In order to estimate the potential shift of the Ag/AgCl reference electrode reasonably, we tried to utilize the linear relationship between the electrical conductivity and the concentration of the KCl solution.

In Fig. 3a, the electrical conductivity and the potential of the Ag/AgCl electrode were respectively plotted against the KCl concentration in a range including 0.001 to 1.0 M. 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. 3a, we can derive a linear relationship between the electrical conductivity and the potential of the Ag/AgCl electrode as shown in Fig. 3b. In general, both the electrical conductivity and the potential of the Ag/AgCl electrode are influenced by the activity coefficient depending on the given KCl concentration [9–11, 18, 19]. In the range of the KCl concentration between 0.001 and 1.0 M, however, it was thought that the effect of the activity coefficient is not considerable for the potential of the Ag/AgCl electrode.

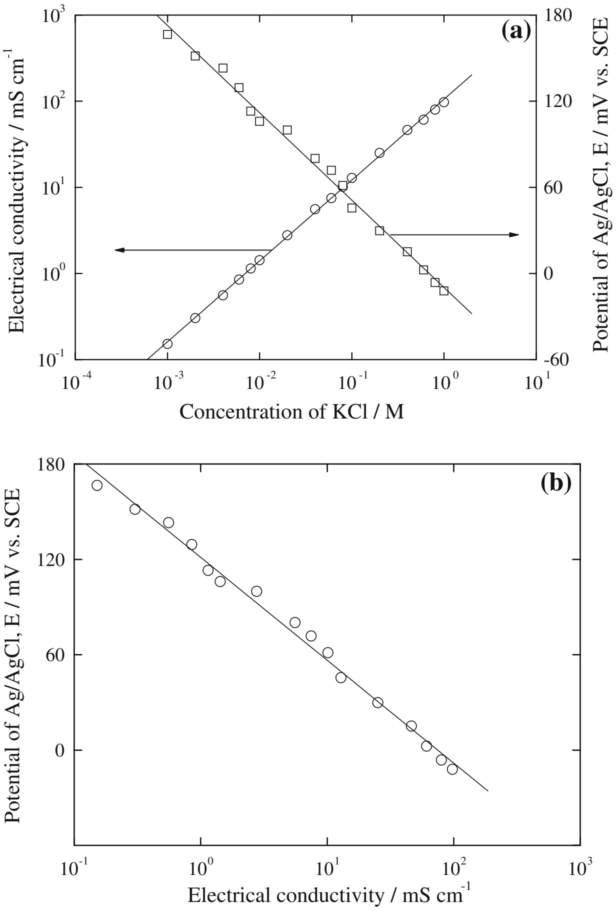

Fig. 3 (**a**) Relationship between the electrical conductivity (*open circle*) of the KCl solution and the potential (*open square*) of the Ag/AgCl electrode in the 0.001–1 M KCl solutions and (**b**) a linear relationship between the electrical conductivity and the potential of the Ag/AgCl electrode

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.

3.2 The interference effect of H_3BO_3 on the electrical conductivity of the KCl solution and the potential of the Ag/AgCl electrode

H_3BO_3 has been used as a chemical additive for a nuclear reactor coolant [20]. 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 of the Ag/AgCl electrode in a KCl solution containing H_3BO_3. The H_3BO_3 in the range of 0–0.016 M was added into the KCl internal electrolyte of the Ag/AgCl electrode, and then the electrical conductivity and the potential of the Ag/AgCl electrode were measured, respectively. Figure 4 shows that the electrical conductivity of the internal electrolyte solution was nearly a constant value for each KCl concentration measured, demonstrating that the electrical conductivity is not affected by the H_3BO_3. This result might be explained due to the low dissociation constant of the H_3BO_3 [21].

The potential of the Ag/AgCl electrode was also measured with the internal electrolyte containing H_3BO_3 up to a concentration of 0.016 M. Figure 5 shows the potential of the Ag/AgCl electrode as a function of the KCl concentration of the internal electrolyte. The relationship between the logarithm of the KCl concentration and the potential was observed to be quite linear in the KCl concentration range of 0.01–1.0 M at all H_3BO_3 concentrations, while

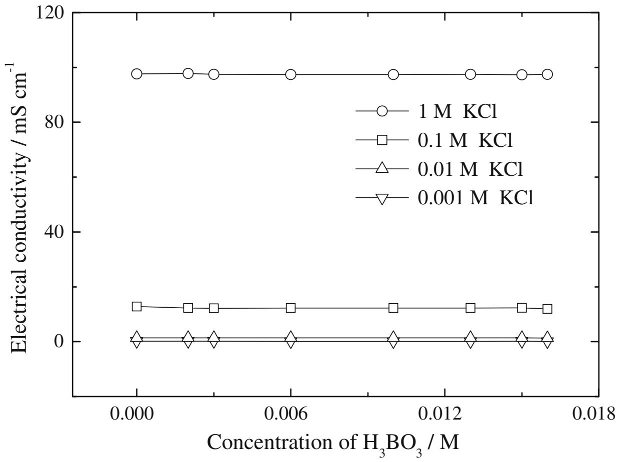

Fig. 4 Interference effect of H_3BO_3 on the electrical conductivities of KCl solutions with various concentrations; 1 M (*open circle*), 0.1 M (*open square*), 0.01 M (*open triangle*), 0.001 M (*inverted open triangle*) KCl

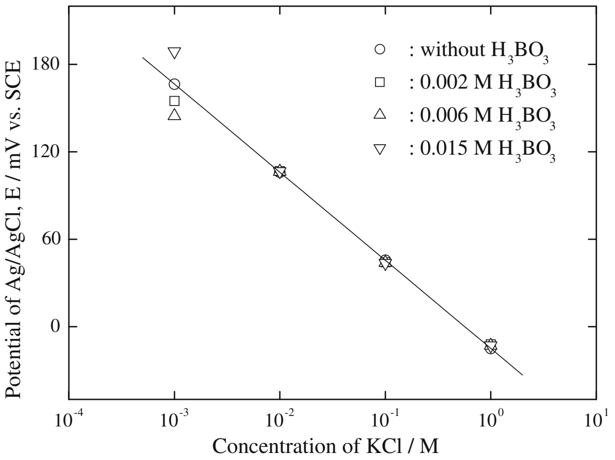

Fig. 5 The potential of the Ag/AgCl electrode with various concentration (0.001–1 M) of the KCl solutions containing various concentrations of H_3BO_3; without H_3BO_3 (*open circle*), 0.002 M (*open square*), 0.006 M (*open triangle*), 0.015 M (*inverted open triangle*) H_3BO_3

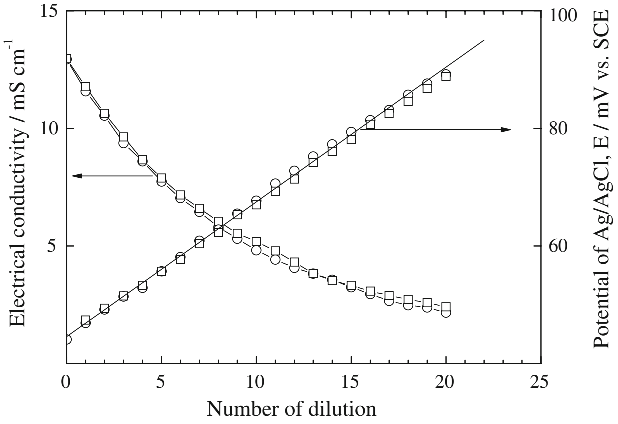

Fig. 6 Electrical conductivities of the internal electrolyte and the potential shift of the Ag/AgCl electrode with a dilution of the internal electrolyte in distilled water (*open circle*) and a 0.016 M H_3BO_3 (*open square*) solution, respectively

there were some irregular deviations from the linearity at 0.001 M KCl.

The deviation of the potential at 0.001 M KCl provides a meaningful result. It is apparent that the deviation comes from the interference of H_3BO_3. Therefore, when the Ag/AgCl electrode is used in the H_3BO_3 solution for a long time, the KCl concentration of the internal electrolyte should be above 0.01 M to ensure the correct potential of the Ag/AgCl electrode.

3.3 Acceleration test for a long-term exposure of the Ag/AgCl electrode in a diluted solution

In order to confirm the applicability of this calibration technique, we carried out long-term exposure tests 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 internal electrolyte. Then, the Ag/AgCl electrode was immersed in the diluted solutions, which were the distilled water and a 0.016 M H_3BO_3 solution, respectively. The internal electrolyte of the Ag/AgCl electrode was exchanged with each test solution by 1.0 ml (about 10% of total volume of the internal electrolyte) at every dilution step. At each dilution step, we measured for the electrical conductivity and the potential of the Ag/AgCl electrode, respectively.

Figure 6 shows the changes in the electrical conductivity and the potential of the Ag/AgCl electrode as a function of the dilution factor. The electrical conductivity decreased exponentially and the potential of the Ag/AgCl electrode increased linearly as the internal electrolyte was diluted in distilled water and the H_3BO_3 solution, respectively. It was observed that there was little difference, less than 0.5 mS cm^{-1}, in the measured results for both solutions.

Under these conditions, the dilution profile of the internal electrolyte can be expressed by a simple differential equation as follows:

$$dC/dt = -x\,C, \quad d\ln C = -x\,dt \tag{1}$$

where C is the concentration of the internal electrolyte, x is a dilution constant and t is time. Therefore, the concentration of the internal electrolyte decreases exponentially with the dilution factor. The potential determined by the Nernst equation [19] is linearly proportional to the logarithm of the KCl concentration. The dilution profiles of the electrical conductivity and the potential, plotted in Fig. 6, are in good agreement with the theoretical relationships. In addition, as shown in Fig. 6, the dilution trend when exposed to distilled water is almost the same as that observed for the 0.016 M H_3BO_3 solution. Therefore, the electrode behavior, when contaminated by H_3BO_3 solutions, can be regarded as the same as that observed for the effects of a dilution in distilled water.

In the previous section 3.1, we derived a linear relationship between the electrical conductivity and the KCl concentration. With this relationship, we can simply estimate the potential shift of the Ag/AgCl electrode from the value of the electrical conductivity. Besides the above method using the obtained relationship experimentally, there is another method to determine the concentration of a salt from its electrical conductivity. Since, the electrical conductivity of an aqueous solution is highly dependent on the concentration of the dissolved salts, the concentration of a salt can be calculated by using a known equation [22] regarding the relationship between the electrical conductivity and the concentration:

$$K_{cal} = \sum_i |\mathrm{Z_i}|(\lambda_i)(\mathrm{C}_i)\gamma^2 \quad (2)$$

where K_{cal} is the calculated electrical conductivity of a solution of ions, C_i is the concentration of the ion, $\mathrm{Z_i}$ is the charge number of the ion, λ_i is equivalent ionic conductivity, and, γ is ionic activity coefficient.

We used both methods to determine the concentrations of KCl from the values of the electrical conductivity. The values of the calculated KCl concentration were plotted, respectively, in Fig. 7. In both results, the two correlation lines between the electrical conductivity and the KCl concentration show a complete linearity. The two correlation lines were almost elapsed in a low concentration region. However, the lines deviated from each other with an increase in the KCl concentration. The small gap between the estimated concentrations in the high conductivity region is thought to arise from a difference in the application of the activity coefficient term in Eq. 2.

From the two kinds of KCl concentrations obtained in Fig. 7, the potential shifts of the Ag/AgCl electrode were estimated separately. The KCl concentration was estimated by using the experimental relationship between the KCl concentration and the electrical conductivity in Fig. 3a. The KCl concentration calculated by Eq. 2 was converted to a potential by the Nernst equation. Hence, the two kinds of converted potentials were plotted in Fig. 8, respectively.

During the dilution of the internal electrolyte of the Ag/AgCl electrode, the concentrations of the KCl were diluted from 0.1 M to approximately 0.01 M. Within the concentration range, the potentials converted from the experimentally obtained relationships were almost the same, less than a 3 mV difference, when compared with the directly measured potential shifts. Another converted potential calculated by the Nernst equation was observed to deviate more from the measured values. However, the deviated potential values were less than 5 mV. They were still good enough values (pH deviation: 0.08), however, to calibrate the Ag/AgCl electrode. Consequently, this technique is applicable to calibrate the Ag/AgCl electrode when the internal electrolyte is diluted or contaminated by a long-term exposure in a non-electrolyte media such as de-mineralized water and natural water.

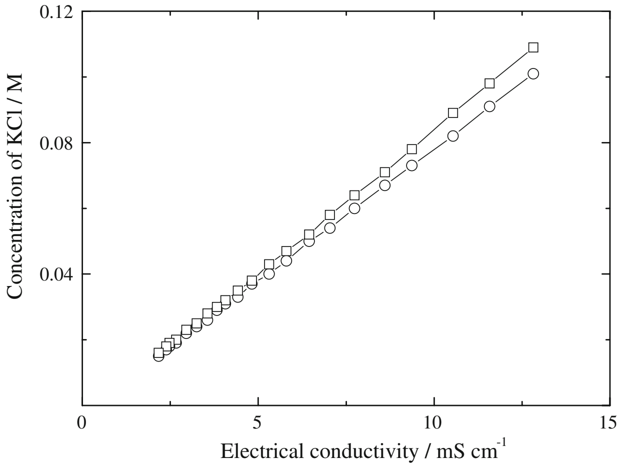

Fig. 7 The correlation lines between the electrical conductivity and the KCl concentration; the values (*open circle*) of the KCl concentration estimated by using the experimental relationship and the values (*open square*) of the KCl concentration calculated by Eq. 2

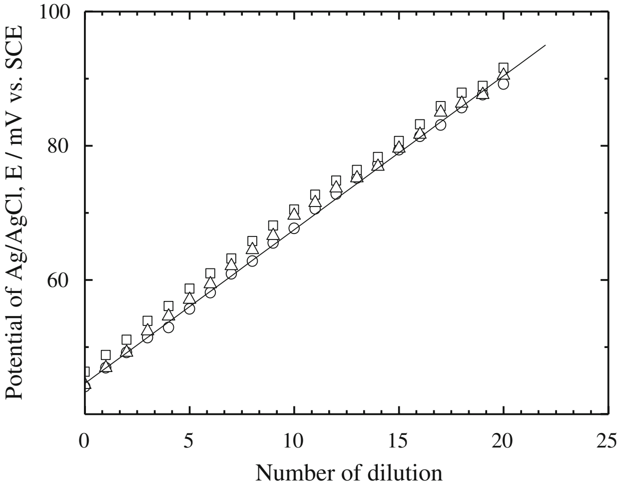

Fig. 8 The potential shift of the Ag/AgCl electrode with a dilution of the internal electrolyte in distilled water; the experimentally measured potential shift (*open circle*), the estimated potential shift (*open square*) by using the linear relationship between the electrical conductivity and the KCl concentrations in Fig. 3a and the potential shift (*open triangle*) calculated by using the KCl concentration calculated by Eq. 2

4 Conclusions

In the present study, we established a calibration technique for an Ag/AgCl electrode for a long-term exposure to diluted solutions by using the relationship between the electrical conductivity and the KCl concentration of the internal electrolyte. By the measurement, it was documented that the electrical conductivity decreased with a decrease of the concentration of the KCl. A linear correlation was observed between the electrical conductivity and the KCl concentration between 10^{-3} and 1.0 M. In addition, the potential of the Ag/AgCl electrode shifted anodically with a decrease of the concentration of the KCl. We observed that the potential had a good correlation with the logarithm of the KCl concentration between 10^{-3} and 1.0 M. There was little interference of the H_3BO_3 up to 0.016 M on the electrical conductivity and the potential shift of the Ag/AgCl electrode. However, in the presence of H_3BO_3, a reliable potential value was observed in the range above 10^{-2} M KCl. For the confirmation of this technique, an accelerated test was carried out to simulate a long-term exposure of the Ag/AgCl electrode in distilled water. The collected values of the potential with this technique were estimated as less than 3 mV, when compared with the experimentally measured ones. Moreover, from collected values calculated by the known equations, a conversion equation and Nernst's equation, the difference of the potential shift did not exceed more than 5 mV. Consequently, this technique is confirmed to be applicable for the calibration of an Ag/AgCl electrode, especially when exposed to non-electrolytic aqueous solutions.

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