An Application of a Porous Charcoal Junction to a Reference Electrode in Acidic and Alkaline Solutions

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ABSTRACT

Charcoal is used as a salt bridge at the end of the Ag/AgCl reference electrode in acid and alkaline solutions. The impedance and the phase shift of the Ag/AgCl wire with the use of the charcoal junction are stable in all solutions, while those with the use of the glass frit show instability in the strong acid and alkaline solutions. Electrochemical impedance spectroscopic results on type 304 stainless steel surfaces are successfully obtained using the reference electrode with the charcoal junction, while the glass frit in strong acid and alkaline solutions shows inconsistency on the steel surfaces.

1. Introduction

A salt bridge is an ionic channel between the solution in a reference electrode and the solution of the electrolyte. It is essential to use the salt bridge for electrochemical experiments. The type of porous materials for the salt bridge is widely selected, such as aluminum oxide, glass, polyethylene, and Teflon. The aluminum oxide and glass are chemically stable in acidic and neutral solutions. However, those materials are chemically dissolved in an alkaline solution. For the reason of the degradation of glass and aluminum oxide in alkaline solutions, porous polyethylene and Teflon are applied in alkaline solutions. Unfortunately, the contamination rate of the reference solution by the electrolyte through these materials is relatively higher than that through the glass materials due to the large pore size of the materials. It is necessary to develop a salt bridge in various solutions of pH.

Porous carbon materials, such as pencil lead and charcoal, are chemically inert in an acid as well as an alkaline solution, while pencil lead cannot be used in an alkaline solution due to the possibility of the dissolution of the clay (silicon oxide) inside. Charcoal is a candidate for chemically-stable porous material for a salt bridge at a reference electrode in acidic and alkaline solutions. However, the use of the charcoal salt bridge in acidic as well as alkaline solutions has not been reported. In this study, the electrochemical measurements using the Ag/AgCl reference electrode with a charcoal or a commercial glass frit was compared in acid and alkaline solutions.

2. Experiment

The natural charcoal (11740, Faber-Castell) was used as a salt bridge of the Ag/AgCl reference electrode in saturated KCl (SSE). After ten cycles of polarization from −0.5 to 0.5 V_{SSE}, the Ag wire with a diameter of 200 μm was anodically polarized at 0.1 V_{SSE} for 1800 s in 1 mol dm⁻³ KCl. The Ag/AgCl wire was inserted into a polyurethane (PU) tube with an inner and an outer diameter of 2 mm and 4 mm, respectively, and then the end of the tube was clogged with the charcoal or the glass frit (Vycor®) with a diameter and length of 4 mm and 6 mm, respectively. The charcoal or glass frit was tied up to the heat shrink tube, and then the PU tube was filled with a sat. KCl reference solution. Figure 1 shows the schematic image of the fabricated reference electrode and the photographs of the charcoal and the glass frit. Since the charcoal was made from a natural willow branch, the porosity of the charcoal was difficult to estimate. However, the pore size of the glass frit was reported to be less than 10 nm.

The electrochemical impedance spectroscopy (EIS) of the fabricated Ag/AgCl electrode was conducted at the open circuit electrode potential with a perturbation of 1 mV rms in the sat. KCl, 0.1 mol dm⁻³ H₂SO₄ (pH 1.1), 0.1 mol dm⁻³ Na₂SO₄ (pH 7.4), boric-borate buffer (pH 8.4), and 0.01 mol dm⁻³ KOH (pH 11.2) solutions, while the EIS of the type 304 stainless steel electrode (0.03 cm²) was carried out at passivation potential −0.1 V_{SSE} with a perturbation of 10 mV rms at the frequency from 10⁷ to 10⁻² Hz in 0.1 mol dm⁻³ H₂SO₄, 0.1 mol dm⁻³ Na₂SO₄, boric-borate buffer, and 0.01 mol dm⁻³ KOH solutions. The EIS for the fabricated Ag/AgCl
electrode was carried out in a three electrochemical cell with a graphite counter electrode (1 cm²), the commercial type of Ag/AgCl reference electrode with a salt bridge made of Teflon, and the fabricated Ag/AgCl electrode with the charcoal or the glass frit salt bridge as a working electrode.

After applying $-0.7 \text{V}_{\text{SSE}}$ to the steel surfaces for 600 s, the potentiodynamic polarization of the steel surface was conducted from $-0.7$ to $1.2 \text{V}_{\text{SSE}}$ with a scan rate of $1 \text{mV s}^{-1}$ in those solutions.

3. Results and Discussion

Figure 2 shows Bode plots of the fabricated Ag/AgCl with the charcoal junction in reference and electrolyte solution of saturated KCl.

![Figure 2](image-url)

Figure 3 shows Bode plots of the fabricated Ag/AgCl electrode with the use of charcoal or glass frit as a salt bridge junction in (a) $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, (b) $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$, (c) boric-borate buffer, and (d) $0.01 \text{ mol dm}^{-3} \text{ KOH}$. In all types of junction, the impedance increases with a decrease in the frequency regardless of pH. The impedance value for the use of charcoal is lower than that of the glass frit in all pH of solutions. The phase shift value for the charcoal junction is measured in the value lower than $-5^\circ$, while the value for the glass frit is measured in the value lower than $-10^\circ$. In the acidic solution of pH 1, the phase shift value exceeds $-15^\circ$, and the impedance value also sharply increases to $940 \Omega$ in the use of glass frit at the frequency range lower than $10^4 \text{ Hz}$. In the alkaline solution of pH 11 used for the glass frit, the EIS measurements were not successful in obtaining impedance or phase shift values due to the overload error signal from the potentiostat, which resulted from the dissolved or damaged glass frit in between the reference solution and the experimental solution.

These changes in the impedance and the phase shift are supposed to result from the chemical/electrochemical instability of the glass frit in strong acid and strong alkaline solutions. However, when the charcoal junction is used as the salt bridge in the electrode, the respective, were working. The impedance values are lower than $400 \Omega$ in all frequency range irrespective of the type of salt bridge. However, the impedance value in the case of the use of glass frit is slightly higher than the use of charcoal frit at a frequency lower than $100 \text{ Hz}$. The phase shift does not exceed $-15^\circ$ in all frequency ranges irrespective of the type of salt bridge, while the phase shift change in the case of the use of the glass frit, higher than the charcoal junction’s, is shown. The charge transfer or mass transport resistance is thought to be relatively higher in the case of the use of charcoal junction than glass frit. The change in the impedance and the phase shift indicates that the charcoal and the glass frit junction at the end of the fabricated Ag/AgCl electrode does not act as a significant electrochemical resistance between the reference and the electrolyte solution.

![Figure 3](image-url)

Electrochemistry, (in press)
electrode shows a significantly stabilized state in all pH ranges of the solutions.

Figure 4 shows Bode plots of type 304 stainless steel surface in 0.1 mol dm\(^{-3}\) H\(_2\)SO\(_4\), 0.1 mol dm\(^{-3}\) Na\(_2\)SO\(_4\), boric-borate buffer, and 0.01 mol dm\(^{-3}\) KOH with the use of the glass frit and the charcoal junction at the end of the reference electrode. Bode plots show that two capacitive layers are formed on the steel surfaces in all types of the junctions, irrespective of the pH of the solutions. There seems to be no significant difference in the plots of the impedance and the phase shift for all types of junctions in the neutral and weak alkaline solutions. However, for the use of the glass frit, the impedance and the phase shift does not seem to be a similar value at the frequency lower than 10\(^{5}\) Hz in the solution pH 1. It is thought that the electrochemical or chemical instability of the glass frit itself influences the electrochemical measurements. The measurement in the strong alkaline solution was difficult to obtain, along with its results for the Bode plot in the use of the glass frit at the reference electrode.

4. Conclusions

The charcoal junction as a salt bridge at the tip of the Ag/AgCl reference electrode was used. When the charcoal was used as a salt bridge between the reference and the electrolyte solution, the impedance and the phase shift of the Ag/AgCl electrode was not significantly changed as a function of the frequency. Potentiodynamic polarization and electrochemical impedance spectroscopy measurements were carried out on type 304 stainless steel surfaces, and the results of the experiments showed that the salt bridge of the charcoal allows conducting those electrochemical measurements in acidic as well as alkaline solutions. However, the glass frit does not allow one to obtain a stable electrochemical result in strong acid and strong alkaline solutions. On the one hand, the use of the glass frit as a salt bridge is recommended to apply in a solution of a weak acid, neutral, or a weak alkaline solution. On the other hand, the charcoal junction is possible to apply as a salt bridge to the reference electrode in all range of pH from the strong acid to a strong alkaline solution.

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