Short Communication

Carbon-Based Membrane Materials to a Silver/Silver Chloride Reference Electrode

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Carbon-based membrane materials made of natural charcoal and pencil lead were attempted as an ion-exchange membrane to a silver-silver chloride reference electrode in sulfuric acid, hydrofluoric acid, sodium sulfate, boric-borate buffer, and potassium hydroxide solutions. During the immersion in ultrapure water, the potential shift towards the positive potential direction revealed that the KCl reference solution is diluted through the membranes. Electrochemical impedance spectroscopy showed that the pencil lead membrane is more electrochemically resistive than the charcoal membrane in all the pH solutions. The relatively high resistance of the pencil lead compared to the charcoal membrane is thought to be due to its pore structure and the presence of clay as an ingredient of pencil lead. The charcoal membrane could be a more suitable material than the pencil lead as a salt bridge to the reference electrode in aqueous solutions.

1. INTRODUCTION

A porous membrane is widely used as a salt bridge at the end of a reference electrode in electrochemical experiments with an ionic channel between a reference electrode solution and an experimental electrolyte. These membranes are porous glass [1, 2], alumina oxide [3, 4], and Teflon [5]. The glass and alumina membranes are difficult to use in alkaline and fluoride solutions due to their chemical and/or electrochemical instability. Teflon has chemical stability in pH solutions as well as hydrofluoric acid. However, the relatively large pore size and few micrometers of the membrane lead to contamination in the reference solution from the experimental solution [5]. Recently, it was proposed that a carbon membrane made of natural charcoal is applied to the salt bridge of a reference electrode in an acidic and alkaline solution [6, 7]. The charcoal membrane shows more stable electrochemical

behavior than a glass membrane in an alkaline solution. Another carbon membrane of pencil lead, a mixture of graphite and clay, can be used as a membrane in the application of a reference electrode. However, the electrochemical use of porous carbon materials, charcoal and pencil lead, as a membrane not only in various solutions of pH but also in hydrofluoric acid, has not been reported. In this study, natural charcoal and a pencil lead were used as a membrane for fabricating silver (Ag)-silver chloride (AgCl) reference electrode in various aqueous solutions.

2. EXPERIMENTAL SECTION

The porous carbon materials of charcoal (11740, Faber-Castell) and a graphite pencil lead (119008, Faber-Castell) were prepared. The silver wire (AG-401265, Nilaco) with a diameter of 200 μm was polarized with 10 cycles from –0.5 to 0.5 $V_{Silver\text{-}Silver\ chloride\ electrode\ in\ sat.\ KCl\ (SSE)}$ of 0.1 V s^{-1} scan rate in 1 mol dm^{-3} KCl. After the polarization, the Ag wire was anodically polarized at 0.1 V_{SSE} for 1800 s in 1 mol dm^{-3} KCl. The carbon materials are prepared with a diameter of 3 mm and used as a salt bridge for clogging the silver/silver chloride reference electrode in saturated KCl to electrolyte solutions. Finally, the Ag/AgCl wire was inserted in a polyurethane tube, which was filled in a saturated KCl solution. These bundles of the Ag/AgCl wire, the KCl-filled tube, and the carbon material terminal were referred to the carbon-plugged Ag/AgCl electrode in this study.

After the monitoring of the electrode potential of the Ag/AgCl wire in sat. KCl solution, the wire was removed from the polyurethane tube to the other saturated KCl solution. The terminal of the polyurethane tube with the carbon materials was dipping into 0.05 dm^{-3} of ultrapure water (18.2 MΩ m^{-2}). The concentration of the KCl in the tube without the wire was changed through the carbon materials. After the immersion, the wire was replugged into the tube, and the electrode potential of the wire was monitored in a saturated KCl solution.

The electrochemical cell with two private solution baths of 0.015 dm^{-3} was fabricated by a 3D-Printer (M200, Zortrax). The previous study [6, 7] was carried out in a single solution bath was used. For the use of the bath, both commercial and the prepared reference electrode are immersed in the experimental solution of 0.1 mol dm^{-3} KOH. Thus, the contamination in the commercial reference electrode is difficult to negligible. In order to improve the electrochemical system, in this study, the separate solution bath for the commercial and the prepared reference electrode was prepared. The one and the other bath contained a saturated KCl and various solutions of pH; 0.1 mol dm^{-3} H$_2$SO$_4$ (pH 1.1), 0.1 mol dm^{-3} HF (pH 2.3), 0.1 mol dm^{-3} Na$_2$SO$_4$ (pH 7.4), boric-borate buffer (pH 8.4), or 0.1 mol dm^{-3} KOH (pH 13.4) solution, respectively. The three-electrode system with a commercial reference electrode of Ag/AgCl in saturated KCl was immersed in the KCl bath, while the carbon-plugged Ag/AgCl electrode and a platinum counter electrode coil of 200 μm were used as a working and counter electrode, respectively, in the other bath. The electrochemical impedance spectroscopy (EIS) of the carbon-plugged Ag/AgCl electrode was carried out at the open circuit potential with 1 mV rms at frequency from 10^5 to 10^{-2} Hz in the solutions.
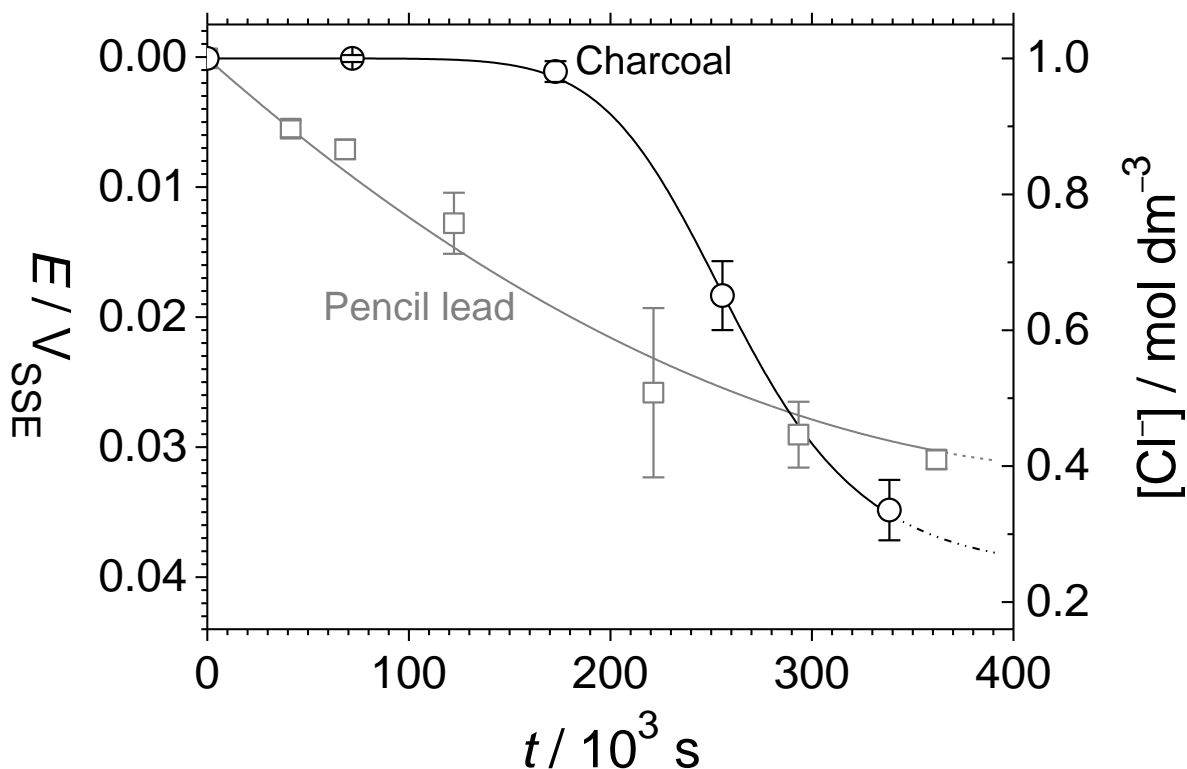
3. RESULTS AND DISCUSSION

Figure 1. Bode plot of the carbon-plugged Ag/AgCl electrode with the charcoal [4] and pencil lead junction in reference and electrolyte solution of saturated KCl

Figure 1 shows the electrode potential change with the immersion time for the carbon-plugged Ag/AgCl electrode. The electrode potential was converted to the concentration of chloride ions using the Nernst equation:

$$AgCl + e = Ag + Cl^- \qquad\qquad (1)$$
$$E_{SSE} = -0.059\log[Cl^-] \qquad\qquad (2)$$

Although the $[Cl^-]$ of the saturated KCl solution is higher than 1 mol dm^{-3}, the $[Cl^-]$ at the electrode potential of 0.00 V_{SSE} refers to 1 mol dm^{-3}. The electrode potential of the carbon-plugged Ag/AgCl electrode is shifted towards the positive potential direction during the immersion in the ultrapure water regardless of the carbon materials, indicating that a dilution of a saturated KCl in the electrode occurs through the porous carbon membranes.

On the one hand, during the immersion for 201×10^3 s, the potential with charcoal-containing electrode gently shifts to 0.001 V_{SSE}, indicating that the $[Cl^-]$ decreases from 1 mol dm^{-3} to 0.96 mol dm^{-3}. After the immersion for 201×10^3 s, the potential drastically shifts to 0.018 V_{SSE} for 340×10^3 s, which means that the $[Cl^-]$ also decreases to 0.33 mol dm^{-3}. On the other hand, the potential for the pencil lead-containing electrode gradually shifts from 0.00 V_{SSE} to 0.024 V_{SSE} for 362×10^3 s. During the immersion, the potential is shifted to 0.001 V_{SSE} for 13.7×10^3 s, supposing that a dilution rate of the

KCl solution through the pencil lead is approximately 15 times faster than that through the charcoal membrane. This dilution rate difference might be related to a micro-pore structure difference between nature charcoal and pencil lead. The structure of the pore in natural charcoal was challenging to estimate because of its random network structure of pore made from willow branches, while the pore structure of a pencil lead is reported as < 5 μm of diameter [8].
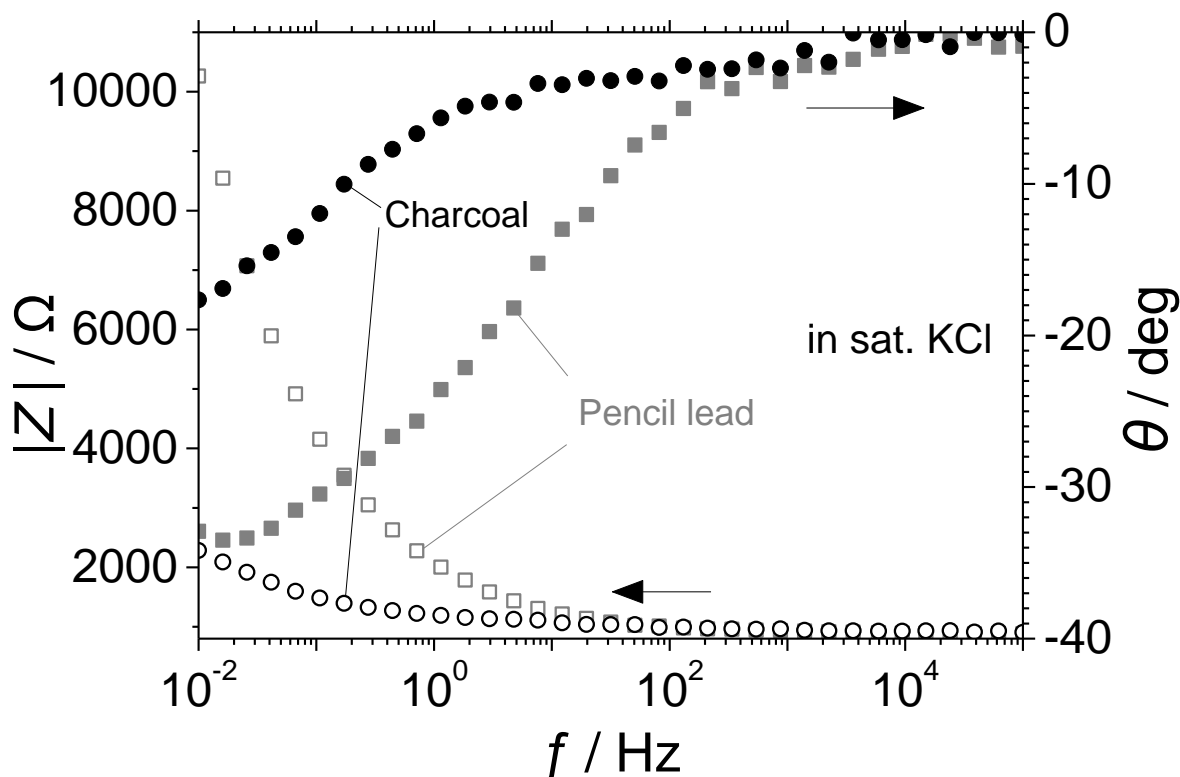

Figure 2. Bode plots of the carbon-plugged Ag/AgCl electrode with the charcoal or pencil lead in a saturated KCl solution

Figure 2 shows Bode plots of the carbon-plugged Ag/AgCl electrode with charcoal and pencil lead in a saturated KCl solution. The phase shift of the carbon-plugged Ag/AgCl electrode is lower than −40° indicating that the carbon membrane does not significantly contribute to the capacitive property at/in the membrane between the solution. The phase shift for the pencil lead electrode is more significant than for the charcoal electrode. The solution resistance does not show a significant difference irrespective of the carbon materials. For the pencil lead electrode, the resistance drastically increases at the frequency lower than 10^2 Hz and reaches the resistance value to 10,300 Ω at 10^{-2} Hz, though the resistance of the charcoal electrode slightly increases as 2,300 Ω at 10^{-2} Hz. It is demonstrated that the charcoal electrode is less electrochemically resistive than the pencil lead electrode.

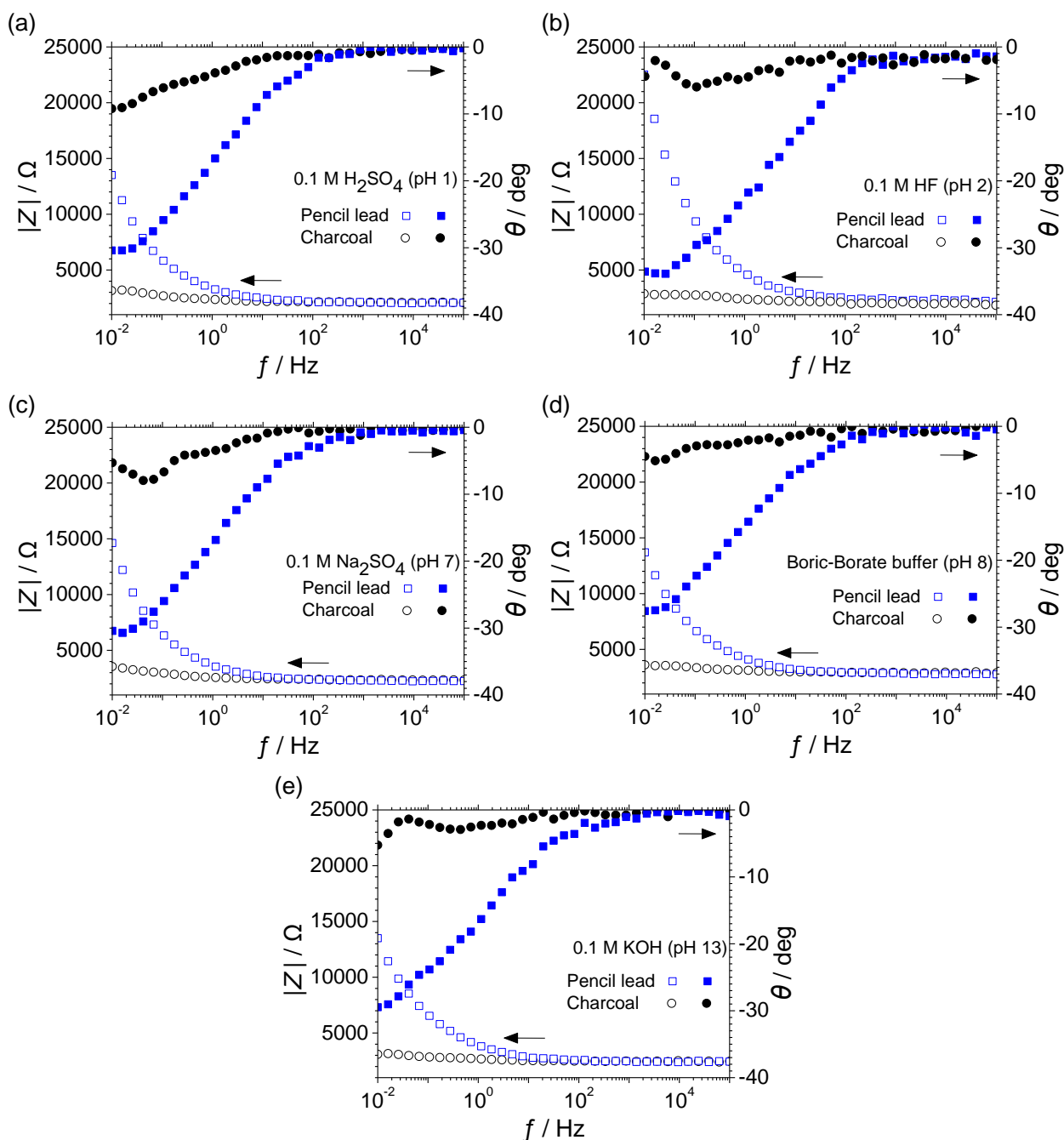**Figure 3.** Bode plots of the carbon-plugged Ag/AgCl electrode with the charcoal or pencil lead salt bridge in (a) 0.1 mol dm^{-3} H$_2$SO$_4$, (b) 0.1 mol dm^{-3} HF, (c) 0.1 mol dm^{-3} Na$_2$SO$_4$, (d) boric-borate buffer, and (e) 0.1 mol dm^{-3} KOH

Figure 3 shows Bode plots of the carbon-plugged Ag/AgCl electrode in 0.1 mol dm^{-3} H$_2$SO$_4$, 0.1 mol dm^{-3} HF, 0.1 mol dm^{-3} Na$_2$SO$_4$, pH 8.4 boric-borate buffer, and 0.1 mol dm^{-3} KOH. In all solutions of pH, the solution resistance is almost similar, with values approximately 2,500 Ω. The resistance value of the charcoal electrode is almost constant at less than 4,000 Ω regardless of the solution pH and frequencies. However, in all pH solutions, the resistance for the pencil lead electrode increases from a frequency lower than 10^0 Hz and reaches approximately 15,000 Ω at 10^{-2} Hz. Especially for the pencil lead electrode in the HF solution, the resistance significantly increases to 23,000 Ω at 10^{-2} Hz. The phase shift of the charcoal electrode is almost constant at less than −10º in all pH solutions irrespective of

frequency, while the pencil lead experiences a higher phase shift than the charcoal electrode in all pH solutions at a lower frequency than 10^2 Hz. Those electrochemical resistance differences between the charcoal and the pencil lead are thought to be related to the chemical or electrochemical interaction of clay (almost silicon oxide) as an ingredient of the pencil lead.

Compare to the previous studies [4, 5], the resistance increased in all frequencies regardless of the solution pH because of the electrochemical cell system—the separate solution bath with agar salt bride for the solutions of sat. KCl and the experimental solutions lead to the increase of the resistance during the EIS measurements. The charcoal is less resistive and electrochemically stable than the pencil lead and can be used as a salt bridge at the end of the reference electrode in all pH solutions. The charcoal salt bridge can also be stable in the HF solution.

4. CONCLUSIONS

Natural charcoal and pencil lead were applied as a membrane to a silver-silver chloride reference electrode in acidic, neutral, and alkaline solutions. The contamination of the KCl solution by ultrapure water through a membrane was relatively severe in the case of the pencil lead than the charcoal. Electrochemical impedance spectroscopy revealed that the charcoal membrane electrode was electrochemically less resistive than the pencil lead electrode regardless of the solution pH. The presence of ingredients of pencil lead such as clay affected the electrochemical or chemical instability of the pencil lead electrode.

References

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