Fabrication and Characterization of a Fully Screen-Printed Ag/AgCl Reference Electrode Using Silica Gel Inks Exhibiting Instantaneous Usability and Long-Term Stability

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ABSTRACT
An instantly usable screen-printed Ag/AgCl electrode with long-term stability was fabricated for use as a cost-effective disposable reference electrode. A new silica gel–poly(vinylidene difluoride) ink was prepared to form the hydrophilic liquid junction and electrolyte layer of a planar-type reference electrode and the temporal evolution of its open-circuit potential in different electrolyte solutions was subsequently compared to that of a commercial reference electrode. The potential stabilized within 3 min and remained constant over 20 days. The impedance of the liquid junction was \( \approx 2500 \Omega \), which is close to the value observed for a commercial reference electrode. These results implied that the as-fabricated reference electrode was well-suited for practical measurements.

Keywords : Reference Electrode, Planar-type, Screen-printing, Long-term Stability

1. Introduction
The Ag/AgCl reference electrode is widely used in electrochemical measurements. Commercial Ag/AgCl reference electrodes consist of a Ag/AgCl wire immersed in saturated or 3 M KCl solution contained in a glass tube with a porous ceramic or glass liquid junction that separates the abovementioned constituents from the analyzed solution. Although commercial Ag/AgCl reference electrodes are easy to use, they are rather voluminous and rigid. This has inspired the development of small flexible quasi-Ag/AgCl reference electrodes for use in integrated sensors and total analysis systems. However, the potential of quasi-Ag/AgCl reference electrodes generally changes according to the Cl⁻ ion concentration in a measurement solution.

Thus, recently, flexible planar-type Ag/AgCl reference electrodes with an inner electrolyte layer have been produced by screen-printing, which is a technique that (i) allows one to precisely control the product dimensions, (ii) is highly reproducible, and (iii) can be used for mass production. A typical screen-printed planar-type Ag/AgCl reference electrode (SPRE) comprises a Cl⁻ ion-containing inner electrolyte and a liquid junction layer. In turn, the liquid junction layer commonly features a mixture of KCl powder and polymers such as UV curable resin or poly(vinyl chloride). When an SPRE is immersed in an aqueous medium, the medium penetrates the inner electrolyte layer through the liquid junction to dissolve the KCl powder in the inner electrolyte layer and thus produces a layer of saturated KCl solution. Notably, the open-circuit potential first shifts to more negative values, since the concentration of Cl⁻ increases upon the progressive dissolution of KCl, and then stabilizes as the chloride ion concentration becomes constant. However, the inability of the internal Cl⁻ reserves to offset the dilution-induced decrease of chloride ion concentration with time results in a subsequent potential shift to more positive values.

Most of the previously reported SPREs exhibit long-term stabilities (i.e., lifetimes) of less than several hundred hours and are therefore of only limited practical use. To mitigate this issue, we recently effectively suppressed Cl⁻ dilution by using a poly(dimethylsiloxane) emulsion to form the inner electrolyte layer and the liquid junction. Although the thus obtained SPRE exhibited an increased lifetime of over two months, its initial set-up time, i.e., the time required for the open-circuit potential to stabilize, was still around 2 h.

Rapid water injection is of key importance for set-up time reduction. Recently, we developed a paper-based SPRE to reduce the set-up time. By using a paper-based liquid junction, water was injected very quickly, resulting in the short set-up time (~1 min). Herein, silica gel was used for the first time to construct electrolyte and liquid junction layers in view of its high hydrophilicity, which resulted in the rapid penetration of water into the electrolyte layer. The ability of silica gel to absorb certain ionic species such as Cl⁻ benefited the long-term stability of the fabricated electrode. Specifically, we prepared the liquid junction and electrolyte inks by mixing silica gel with poly(vinylidene difluoride) (PVdF) binder, and these inks were then used to fabricate an SPRE with a set-up time of 2 min and a long-term stability of ~20 days (determined by the two-electrode method). In addition, the as-fabricated SPRE was analyzed by electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1 Materials
Silica gel was purchased from Sigma-Aldrich (Cat. No. 236576), and PVdF was sourced from Kureha (KF polymer #1300). 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU, a good solvent for PVdF) was procured from Tokyo Chemical Industry, and KCl and other reagents were purchased from Wako Pure Chemical. Commercially available Ag ink (ECM-100 AF5000) and solder resist ink (SR-40) were obtained from Taiyo Ink Co. Ltd.

2.2 Ink preparation
Liquid junction ink was prepared by mixing Triton X (1 g), PVdF (0.8 g), DMPU (8.2 g), and silica gel (1.5 g) in a revolving/rotating mixer (ARE-310, Thinky, Japan) followed by 30-min ultrasonic homogenization (PR-01, Thinky, Japan). Electrolyte ink was prepared by mixing silica gel (0.8 g), DMPU (8.2 g), and KCl and other reagents purchased from Wako Pure Chemical.
prepared by dispersing silica gel (1 g) and KCl powder (4 g) in a solution of PVdF (0.8 g) in DMPU (8.2 g) and Triton X (1 g). KCl powder was prepared by pulverization of commercial KCl in a wet ball mill for 8 h followed by ultrasonic homogenization (40 kHz, 140 W) for 3 h. The rheological characteristics of the as-prepared inks were evaluated using a rheometer (MCR-102, Anton Paar, Japan).

2.3 Reference electrode fabrication

Figure 1 illustrates the structure of the fabricated reference electrode, showing that Ag, Ag/AgCl, liquid junction, electrolyte, and resist layers were successively printed on a polyimide substrate using the respective inks. Prior to being overprinted, the layers were dried under the following conditions; Ag and Ag/AgCl inks (150°C, 30 min); liquid junction and electrolyte inks (180°C, 15 min) and resist ink (150°C, 30 min). The shape and surface morphology of the prepared reference electrode were characterized by 3D scanning (VR-3100, Keyence, Japan) and scanning electron microscopy (SEM; VHX-6000, Keyence, Japan).

2.4 Reference electrode characterization

The open-circuit potential change of the reference electrode was monitored by the two-electrode method (Fig. 2) using a potentiostat. Specifically, the as-fabricated reference electrode was used as a working electrode, and a commercial Ag/AgCl reference electrode (RE-1C BAS), in which a porous ceramic material was applied as a liquid junction, was used as a reference electrode. Set-up time was defined as the time required for potential stabilization, and the operational lifetime was defined as the time required for the potential to change by more than 30 mV.16

The performance of the as-fabricated electrode was tested in 1 M NH₄Cl (pH 4), 1 M KNO₃ (pH 7), 1 M NaHCO₃ (pH 9), and 1 M K₂CO₃ (pH 11) solutions. 1 M Na₂SO₄/10 mM K₃[Fe(CN)₆]/10 mM K₄[Fe(CN)₆] was used as the electrolyte for cyclic voltammetry measurements, which were performed using a Au disk (diameter = 1.3 mm) and Pt wire as working and counter electrodes, respectively. The impedance of each printed layer was determined by EIS measurements performed in a frequency range of 1 kHz to 10 mHz at a potential amplitude of ±10 mV, and the acquired data were used to construct Nyquist plots (5 point/decade) that were

![Figure 1](image1.png)

**Figure 1.** (a) Schematic illustration of the fabricated planar Ag/AgCl reference electrode and computer-aided designs of the (b) resist, (c) electrolyte, (d) liquid junction, (e) Ag/AgCl, and (f) Ag layers.

![Figure 2](image2.png)

**Figure 2.** Setup used for (a) time-potential, (b) cyclic voltammetry, and (c) EIS measurements.
fitted using specialized analysis software (EIS, Hokuto Denko, Japan) and a chosen set of parameters.

3. Results and Discussion

3.1 Reference electrode fabrication

To suppress the effusion and concurrent dilution of the internal KCl solution of the as-fabricated reference electrode, the design of the electrolyte layer is a crucial point. It was rationalized that the dimensions of the electrolyte layer would have a considerable effect on the stability of the electrode. In the present study, the size of the electrolyte layer was designed to be larger than that of the liquid junction and Ag/AgCl electrode. The larger electrolyte layer would be able to retain large amounts of KCl powder, resulting in the lowering of Cl⁻ dilution. The KCl powder was sufficiently retained in the electrolyte layer after the potential had stabilized.

Figure 3 shows the photograph and 3D shape of the fabricated reference electrode, confirming the uniformity of Ag and Ag/AgCl layer deposition and revealing that KCl particles initially deposited on the electrolyte layer were stably protected by the resist layer. Cross-sectional SEM imaging of the fabricated electrode revealed the thicknesses of Ag/AgCl, electrolyte, resist, and liquid junction layers as 3, 25, 15, and 20 µm, respectively (Fig. 4).

3.2 Electrochemical measurements

It was considered that the pH of the measurement solution would affect the long-term stability of the electrode. Therefore, we measured the time-potential curves of the as-fabricated reference electrode by using four different solutions, namely, 1 M NH₄Cl (pH 4), 1 M KNO₃ (pH 7), 1 M NaHCO₃ (pH 9), and 1 M K₂CO₃ (pH 11).

Figure 5 shows time-potential curves of the as-fabricated reference electrode recorded in different electrolytes using the commercial saturated KCl/Ag/AgCl electrode as a reference. It was evident that the set-up time in all cases was ~3 min. The set-up time of the as-fabricated reference electrode in NH₄Cl, KNO₃, NaHCO₃, and K₂CO₃ solutions were estimated as 2.8 ± 0.5 min (n = 3), 2.1 ± 1.4 min (n = 4), 0.5 ± 0.1 min (n = 3), and 2.0 ± 0.5 min (n = 4), respectively. It should be noted that the errors were calculated by the standard deviation. Moreover, the long-term stabilities of the as-fabricated reference electrode in NH₄Cl, KNO₃, NaHCO₃, and K₂CO₃ solutions were determined as 430 ± 177 h (18 days, n = 3), 251 ± 76 h (10 days, n = 4), 505 ± 183 h (21 days, n = 3), and 116 ± 91 min (4 days, n = 4), respectively. Thus, the above electrode exhibited good long-term stability and a short set-up time in acidic, neutral, and weakly alkaline media, while rather poor long-term stability was observed in alkaline (K₂CO₃) solution. This
The result was attributed to the formation of AgOH and Ag₂O on the surface of the Ag layer to inhibit the electrode reaction between Ag and AgCl under these conditions. The formation of oxide compounds will be investigated in detail in the near future.

Table 1 compares the performance of the present reference electrode with those of printed reference electrodes (not considering the quasi-reference electrodes) reported previously. The set-up time of the electrode described herein was almost equal to that of our paper-based reference electrode⁰¹° and was much shorter than that of other reference electrodes,¹⁰–¹⁶ while the stability of the as-prepared electrode significantly exceeded that of our paper-based reference electrode and those of almost all other reference electrodes. The hydrophilic surface of silica gel accelerated the penetration of the analyzed solution into the printed film (see SI) and thus decreased the set-up time of the fabricated planar-type Ag/AgCl reference electrode compared to previously reported values.¹⁶ Both the paper-based reference electrode and the present as-fabricated reference electrode showed short set-up time since the test solution can be supplied rapidly into an inner electrolyte layer by using these materials. On the contrary, the silica gel liquid junction suppressed Cl⁻ elution more effectively in comparison with the paper-based liquid junction. Thus, the long-term stability was drastically improved by using the silica gel liquid junction.

Moreover, the decreased set-up time allowed the as-fabricated reference electrode to be employed without prior immersion into a suitable electrolyte solution.

Figure 6 shows the cyclic voltammograms of the as-fabricated (dashed line) and commercial (solid line) reference electrodes in 1 M Na₂SO₄/10 mM K₃[Fe(CN)₆]/10 mM K₄[Fe(CN)₆] at a scan rate of 100 mV s⁻¹. 

3.3 EIS measurements

The estimation of reference electrode resistance is important for alternating-current (e.g., EIS) measurements since this value is known to affect the spectra. For example, when the performance of a gas-evolution electrode was evaluated in a highly conductive solution, the overly high reference electrode resistance resulted in spectral errors in the low-frequency range.⁹,²⁵ Therefore, we estimated the resistance of the prepared reference electrode by EIS, with the obtained Nyquist plot presented in Fig. 7. Notably, a small semicircle representing the charge transfer resistance and electric double layer capacitance was observed in the high-frequency range, while the large semicircle observed in the low-frequency range represented the resistance and capacitance related to ionic conduction in the liquid junction layer.²¹–²⁵
Figure 8. Equivalent circuit used to model the Nyquist plot of the fabricated reference electrode. Table 2 shows that the parameters obtained by curve fitting were in good agreement with those determined experimentally.

Table 2. Parameters obtained by curve-fitting of the impedance shown in Fig. 7 using an equivalent circuit in Fig. 8.

| Parameter                  | Value  |
|----------------------------|--------|
| $R_{sol}/\Omega$           | 1187   |
| $R_{ct}/\Omega$            | 73     |
| $R_{LJ}/\Omega$            | 2428   |
| $CPE_{dl} (p)$             | 0.55   |
| $CPE_{dl} (T/F) s^{(p-1)}$ | $7.58 \times 10^{-4}$ |
| $CPE_{LJ} (p)$             | 0.85   |
| $CPE_{LJ} (T/F) s^{(p-1)}$ | $2.36 \times 10^{-3}$ |
| $Z_w (R_{LJ}/\Omega$       | 79     |
| $Z_w (p)$                  | 0.5    |
| $Z_w (T/F) s^{(p-1)}$      | 0.17   |

The above spectrum was fitted using an equivalent circuit (Fig. 8) comprising the elements of solution resistance $R_{sol}$, charge transfer resistance $R_{ct}$, electric double layer capacitance $CPE_{dl}$, Warburg impedance $Z_w$, ionic conductive resistance $R_{LJ}$, and capacitance $CPE_{LJ}$. Notably, the electric double layer and liquid junction layer capacitances were represented by a constant phase element (CPE) commonly used in the case of inhomogeneous current distribution and described as follows:\(^{26-28}\)

\[
Z_{CPE} = \frac{1}{(Jo)^p T_{CPE}},
\]

where $j$ is an imaginary number, $w$ is angular frequency, and $T_{CPE}$ and $p$ are a parameter associated with the CPE element. Specifically, $R_{LJ}$ was determined to be \(\sim 2500 \Omega\) and was therefore close to the values observed for the liquid junction parts of the commercial reference electrodes made from porous glass or ceramics (typically several thousand $\Omega$),\(^{29}\) which implied that the printed silica gel liquid junction described herein is well suited for alternating-current measurements and should find diverse practical applications in the near future.

4. Conclusions

Herein, we developed electrolyte and liquid junction inks with high mechanical stability and hydrophilicity by combining silica gel and PVdF binder, and used these inks to construct a new printable planar Ag/AgCl reference electrode. The above reference electrode exhibited a short set-up time (3 min), good long-term stability (20 days), and resistance similar to that of a commercial reference electrode, and was thus concluded to be well suited for various electrochemical measurements.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.18-00075.

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