

Fabrication and Characterization of a Solid State Reference Electrode for Electroanalysis of Natural Waters with Ultramicroelectrodes

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As an alternative to standard commercial reference electrodes, a solid state reference electrode is fabricated for in situ voltammetric analysis in solutions containing little or no added supporting electrolyte. In the fabrication process, a Ag/AgCl wire is coated with an electrolyte immobilized and protected with Nafion or polyurethane. The electrode potential is measured as a function of time, ionic strength, and pH. A stable potential is obtained for Nafion and polyurethane within 30–35 min in water. Both the polyurethane and Nafion solid state reference electrodes are stable for at least 90 days, but the Nafion electrode fluctuates more than the polyurethane electrode. The electrode is demonstrated using square wave anodic stripping voltammetry at a large electrode (3 mm), an ultramicroelectrode (10 μm), and an array of ultramicroelectrodes.

Recently, interest in using various types of ultramicroelectrodes (UMEs) for the analysis of aqueous samples in which there is very little or no added supporting electrolyte has been increasing.^{1–5} When UMEs are used for analysis of such samples, especially in situ environmental samples, it becomes imperative that the reference electrode itself does not introduce any significant amount of electrolyte into the measurement volume or near the microelectrode. For example, a typical saturated calomel reference electrode with a porous fiber junction will increase the Cl^- concentration in a 25 mL electrochemical cell from nil to about 1 μM or more in the course of a 4–6 h experiment. This can produce a significant perturbation in the voltammetric response of an UME while attempting to measure micromolar quantities of an analyte using techniques such as square wave anodic stripping voltammetry (SWASV). Chloride leakage from the reference electrode can also lead to metal complexation as in the cases of lead and mercury. As a result, the voltammetric peak may shift or decrease and make it difficult to obtain quantitative data for these metals. To avoid leakage problems, it would be desirable to use a reference electrode that does not contain an internal liquid electrolyte and/or is protected by a polymer layer to prevent the escape of the electrolyte into the sample.

Over the years, there have been several reports on the fabrication of various types of solid state reference electrodes

(SSREs). SSREs have been fabricated three different ways: (1) a Ag/AgCl wire immersed in a pressed pellet containing KCl, alumina, and PTFE,^{6–8} (2) a PVC tubing with a PTFE glass membrane containing a paste of mercury, calomel, KCl and graphite,^{9–11} and (3) electrodes coated with a swollen conducting polymer.^{12–14} In these cases, the reported electrodes do not easily lend themselves for use with ultramicroelectrodes or are difficult to fabricate. We report here a convenient and reliable method for fabricating a solid state reference electrode.

For in situ measurements, the ionic strength of the sample cannot be altered. Thus, an immobilized electrolyte is desirable so that the potential is not influenced by changes in ionic strength. In this work, the electrolyte is immobilized on a Ag/AgCl wire from a solution consisting of a halogenated polymer (poly(vinyl chloride)) which is saturated with sodium chloride. The electrolyte is protected by an outer polymer layer. This protective polymer layer prevents the migration of the electrolyte.

Two polymers, Nafion and polyurethane, were evaluated as possible protective layers. Nafion was chosen because it is a cation-exchange polymer that prevents anion exchange. Thus, transport of chloride ions through the Nafion film is blocked and leakage eliminated. Another important advantage is that Nafion discriminates against organic species.¹⁵ Nafion stability is greatly enhanced by thermal curing,^{14–16} which protects the reference electrode and provides increased reproducibility and stability.

Polyurethane was chosen because it exhibits a lack of degradation and a negligible drift in potential when used to protect a Ag/AgCl reference electrode, as shown by the work of Bindra et al.¹⁷ and Moussy and Harrison.¹⁴ Polyurethane is, in principle, neutral; thus, cations and anions should be equally impeded by the coating.¹⁴ Even though very different from Nafion, the polyurethane coating provides protection similar to that achieved by thermally cured Nafion.

EXPERIMENTAL SECTION

Reagents. Pure silver wire (99.9+%) was used for the fabrication of all SSREs. All solutions were prepared with 18 M Ω

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deionized water from a Barnstead Nanopure system. Polishing supplies were obtained from Buehler. Buffer solutions were prepared from 99.99+% ammonium acetate and glacial acetic acid (Aldrich Chemical Co.). Metal solutions for voltammetric experiments were prepared from 99.999% $\text{Hg}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, and $\text{Cd}(\text{NO}_3)_2$ (ALFA-Johnson Matthey). All other metal solutions were prepared from ACS reagent grade chemicals.

Nafion 117 (5% w/w) was obtained from Fluka. Tetrahydrofuran (THF, Aldrich) was tested for peroxides before being used. Low molecular weight poly(vinyl chloride) (PVC) was purchased from Sigma. *N,N*-Dimethylformamide (DMF, AVACADRO-Johnson Matthey) was distilled over calcium hydride (AVACADRO-Johnson Matthey) under reduced pressure and stored over 3 Å molecular sieves (Aldrich). Polyurethane (SG 85A) was obtained from Theremedics, Inc. (Woburn, MA).

Apparatus. Electrode potentials were measured versus a standard $\text{Ag}/\text{AgCl}/(3\text{ M})$ NaCl reference electrode (Bioanalytical Systems, Inc.) using an Escort (EDM 1111A or EDM 1105A) digital multimeter. Chronoamperometry and square wave anodic stripping voltammetry (SWASV) were performed using an EG&G PAR Model 273 potentiostat/galvanostat (EG&G PAR, Princeton, NJ) interfaced to a digital DECpc 420sx with EG&G M270 electrochemical software.

Fabrication of the SSRE. Silver wires were encapsulated with heat-shrink tubing, leaving 1 cm exposed. The tip and sides of the exposed wires were successively polished with 180, 400, 600, and fine grit sandpaper, 30 and 6 μm diamond paste, and 5 and 0.05 μm alumina to ensure a new and clean silver surface. A layer of silver chloride was formed on the silver wires by applying +0.5 V for 50 s in a 0.1 M KCl solution.¹⁸ Stability tests were performed on these electrodes while they were stored in water and a saturated AgCl solution. The electrodes stored in water were stable for 10 days, while those stored in saturated AgCl lasted 20 days. Thereafter, Ag/AgCl wires were stored only in a saturated AgCl solution. Before coating of the immobilized electrolyte on the wires, their potentials were measured in 3 M NaCl , and if accurate, they were used in the fabrication process.

In all cases, the immobilized electrolyte was freshly prepared by saturating 12 mL of THF with NaCl at room temperature and then adding 0.4 g of PVC. The Ag/AgCl wires were dip-coated in the immobilized electrolyte solution. After dipping, the electrodes were dried in a desiccator for 48 h to evaporate the solvent.¹⁹

After the electrodes were dried, they were dip-coated with a protective polymer layer to prevent the leakage of chloride ions. The two protective polymers used and compared in this study were polyurethane and Nafion.

For the polyurethane layer, the electrodes were dip-coated three times in a solution of 5% polyurethane in 98% THF/2% DMF.¹⁴ These electrodes were dried in a desiccator overnight and stored in 15 mL of 18 M Ω water for 24 h. These electrodes were then transferred back to a desiccator, and the water was tested for chloride leakage by adding two drops of 0.1 M AgNO_3 .

Three different Nafion-coated electrodes were fabricated and compared. The electrodes were each dip-coated three times. The types of Nafion electrodes produced depended on the curing process. One set of electrodes were not cured but were dried in a desiccator overnight. Another set of electrodes were cured at

80 °C for 1 h. The last set of electrodes were cured at 120 °C for 1 h.¹⁴ After curing, these electrodes were stored in a desiccator overnight and then placed in 18 M Ω water for 24 h. The water was tested for chloride leakage, as above, and the electrodes were stored in a desiccator.

If an electrode tested positive for chloride leakage, it was not included in the stabilization and characterization studies. All the studies were performed in triplicate.

RESULTS AND DISCUSSION

Stability. The potentials of each of the four types of electrodes were measured for 1 h in 18 M Ω water to determine their stabilities. The uncured Nafion was not reproducible and fluctuated in potential. When the SSREs were cured at 80 °C, their potential fluctuated and was not reproducible, varying from 44.5 to 129.9 mV. The SSREs cured at 120 °C showed the best reproducibility (167.9 ± 8.9 mV) and stability (± 1.1 mV) of the three Nafion electrodes. As expected, the cured Nafion SSREs were more stable and demonstrated better reproducibility than the uncured Nafion electrodes. The polyurethane SSREs demonstrated the best reproducibility (146.6 ± 2.7 mV), but their stability (± 3.4 mV) was less than that of the Nafion SSREs cured at 120 °C.

A longer 8 h evaluation of the four different electrodes was performed to determine the potential drift during a typical length of an experiment. The drift in potential was most likely due to an insufficient amount¹² or loss of electrolyte. The loss of electrolyte could be from the commercial reference electrode or the SSRE. The Nafion SSREs cured at 80 °C demonstrated the least amount of drifting (16.4 ± 8.2 mV), but as discussed above, they were not reproducible. The greatest amount of drift was shown by the uncured Nafion SSREs (50.0 ± 22.8 mV). The Nafion cured at 120 °C (28.3 ± 4.6 mV) and the polyurethane (29.0 ± 4.8 mV) SSREs yielded comparable results. Characterization studies were performed on these two types of SSREs.

The potentials of the Nafion (cured at 120 °C) and the polyurethane SSREs were measured as a function of time in 18 M Ω water to determine the lifetime of the electrodes. Three different media were tested for storage: 18 M Ω water, 3 M NaCl , and a desiccator. When the electrodes were stored in water, chloride leakage increased and the lifetime of the SSREs was, on average, only 10 days. The other set of electrodes, stored in 3 M NaCl , became unstable, as indicated by their fluctuating potential. Storing the electrodes in a desiccator was preferred since it decreased chloride leakage and increased the lifetime of the SSREs. The electrodes stored in a desiccator needed a certain amount of time in water before the potential stabilized. The potentials of the Nafion and polyurethane SSREs were stable after 30 and 35 min, respectively, in water.

As shown in Figure 1, the polyurethane SSREs fluctuated somewhat initially, but their potential remained in the range of 120–180 mV for the first 20 days. Bindra et al.¹⁷ found that polyurethane-coated sensors increased in response for the first few days as a result of the swelling of the polyurethane as the residual solvents were replaced with water. Since the SSREs were stored in a desiccator, more time was needed to obtain a stable potential. The electrodes stabilized over the next 70 days and demonstrated the best stability in the last 40 days of testing. Testing was stopped after 90 days, even though the electrodes remained useable. Thus, the lifetime of the polyurethane SSREs was at least 90 days.

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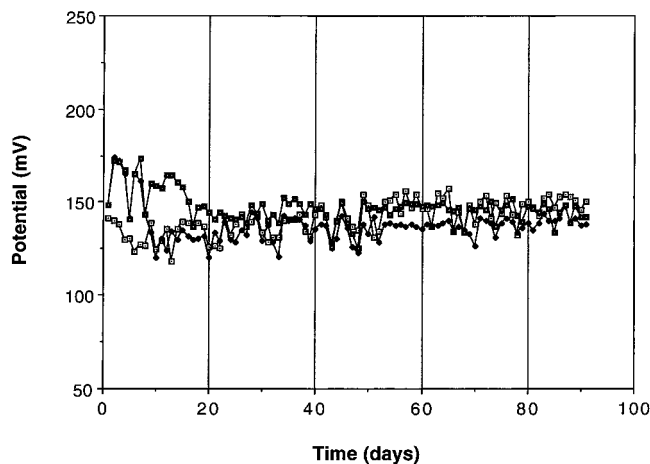


Figure 1. Lifetime test of three polyurethane SSREs. Potential vs time (days).

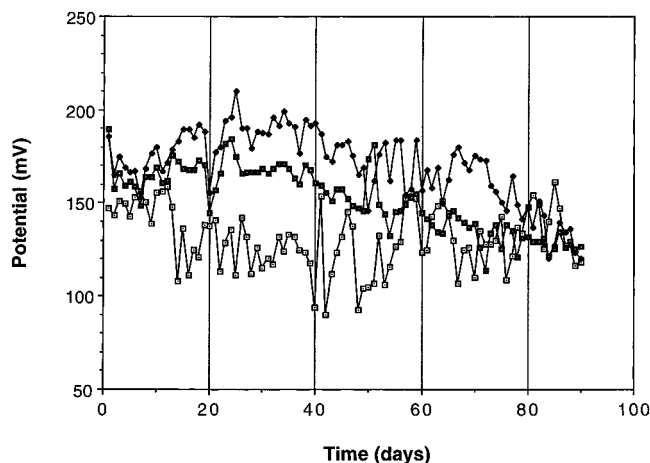


Figure 2. Lifetime test of three Nafion SSREs. Potential vs time (days).

Figure 2 shows the potential of the Nafion SSREs remained in the range of 90 to 180 mV for the 90 days. However, their potentials fluctuated dramatically over the 90 days. The initial drift in the potential was probably due to the equilibration of the Ag/AgCl wire and the immobilized electrolyte. The later drifts are probably the effects of aging on the immobilized electrolyte and the Nafion layer.

Different Electrolyte Solutions. The potentials of the SSREs were measured in several different electrolytes (KNO_3 , $\text{Cu}(\text{NO}_3)_2$, and $\text{Al}(\text{NO}_3)_3$) at varying concentrations. Figure 3 shows the potentials plotted as a function of ionic strength. When the ionic strength was less than 1, the potential was independent of the ionic strength for the polyurethane electrodes. The potential increased approximately 50 mV when the ionic strength was above 1. Because both anions and cations are impeded by the polyurethane layer, its potential was independent of the nature of the electrolyte.

Since Nafion is a cation-exchange polymer, its potential was dependent on the nature of the electrolyte as shown in Figure 4. The potential of the Nafion SSREs in potassium nitrate was independent of the ionic strength. When copper nitrate was used as the electrolyte, the potential was lower than that for potassium nitrate, and the potential increased with increasing ionic strength. In aluminum nitrate, the potential was higher by approximately 40 mV than that measured in potassium nitrate. The potential in aluminum nitrate was independent of ionic strength above 0.005.

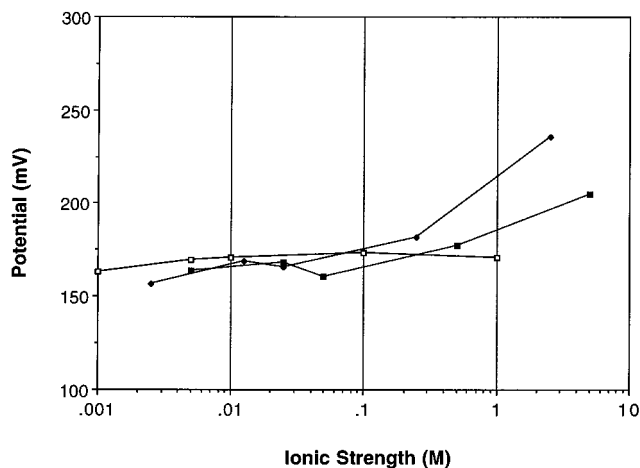


Figure 3. Polyurethane SSREs potential response to different electrolytes of varying concentrations. \square , KNO_3 ; \blacklozenge , $\text{Cu}(\text{NO}_3)_2$; and \blacksquare , $\text{Al}(\text{NO}_3)_3$.

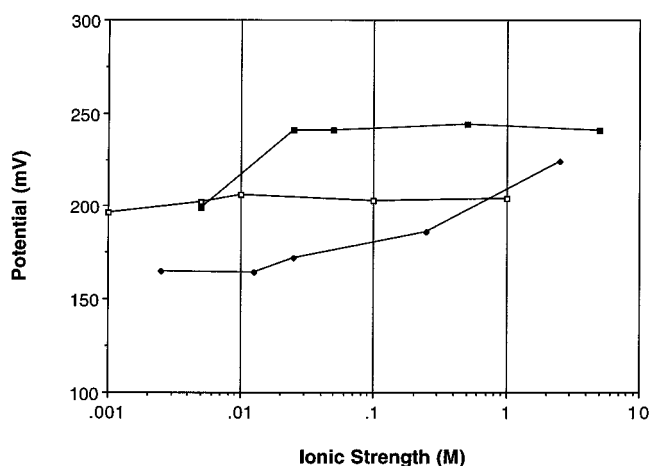


Figure 4. Nafion SSREs potential response to different electrolytes of varying concentrations. \square , KNO_3 ; \blacklozenge , $\text{Cu}(\text{NO}_3)_2$; and \blacksquare , $\text{Al}(\text{NO}_3)_3$.

The Nafion-coated electrodes demonstrated higher potentials than the polyurethane electrodes in the solutions.

Potential vs Chloride Ion Concentration. The potentials of the SSREs were measured in chloride solutions of different concentrations. Both the polyurethane and the Nafion electrodes demonstrated a decrease in potential as the concentration of chloride ions increased. With chloride concentrations lower than 0.01 M, the polymer sufficiently blocked the chloride ions. On a logarithmic scale, a linear plot was obtained with a slope of -41.8 and -39.5 mV/log I for the polyurethane and Nafion SSREs, respectively. The large slope could be due to chloride diffusion into the immobilized electrolyte. This should not present a problem for in situ measurements.

Different pH. The pH response of the SSREs was measured in a 0.1 M acetate buffer with the pH ranging from 4 to 10. As can be seen in Figure 5, both the polyurethane and Nafion electrodes were slightly dependent on the pH. The Nafion electrodes varied by approximately 13 mV over the pH range. The polyurethane electrodes showed more of a dependence on the pH. Their potential decreased by almost 35 mV as the pH increased. Thus, the Nafion electrodes were less affected by the pH than the polyurethane electrodes.

Analytical Characterization. The Nafion and polyurethane SSREs were used in the laboratory in conjunction with a large glassy carbon electrode coated with a gold film, a glassy carbon

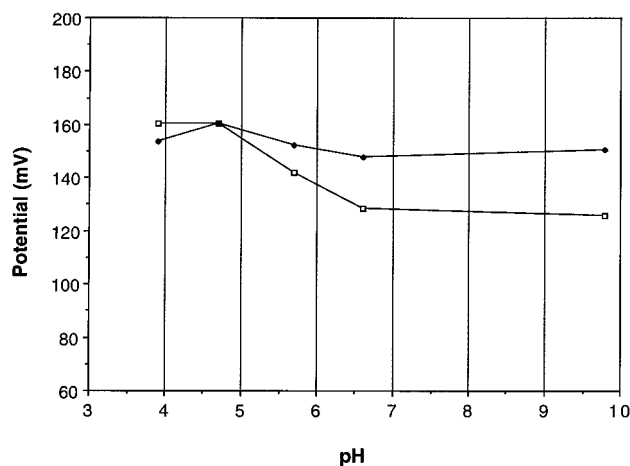


Figure 5. Potential vs pH for polyurethane (□) and Nafion (◆) SSREs.

ultramicroelectrode coated with a mercury film, and an array of iridium ultramicroelectrodes^{5,20} coated with a mercury film to detect mercury, lead, and cadmium, respectively. The Ag/AgCl/(3 M) NaCl commercial reference, the Nafion SSRE, and the polyurethane SSRE were each used in three separate experiments with each working electrode.

Unless otherwise noted, SWASV was used for all analytical characterizations with a SW frequency of 60 Hz and pulse height of 25 mV. The preconcentration time for mercury, lead, and cadmium was 240, 180, and 360 s, respectively. A platinum wire was used as a counter electrode.

Mercury (10–40 ppb) was measured in a 0.005 M KCl and 0.025 M sulfuric acid electrolyte solution. The potential drift during the experiment for the commercial reference was 10 mV, larger than that for both the Nafion (4 mV) and polyurethane (8 mV) SSREs. The potential difference between the commercial and Nafion SSRE was 185.0 mV. For the polyurethane SSRE, the potential difference was 161.9 mV. Since the chloride concentration was low, no decrease in potential from the SSREs was observed.

For the determination of lead, the standard addition method was utilized to demonstrate the effect of chloride leakage from the reference electrode on the resulting peak current. The results indicate that the chloride ions from the commercial reference electrode diffused into the sample solution and complexed with

the lead. Thus, the resulting currents for both of the SSREs were larger than the current measured with the commercial reference electrode, indicating that either the SSREs did not contaminate the sample with chloride leakage or the contamination was less than that by the commercial reference. The average potential difference relative to the commercial reference was 187.9 and 167.0 mV for the Nafion and polyurethane SSREs, respectively.

Cadmium was measured in a 0.02 M acetate buffer (pH 4.1). The potential drift of the peak for the commercial reference (26.2 mV) was less than that for the Nafion SSRE (35.3 mV) but greater than that for the polyurethane SSRE (24.7 mV). Both leakage of chloride ions from the reference electrode and fluctuation of the reference potential could have caused the potential shift of the cadmium peak. For this experiment, the potential difference of the Nafion and polyurethane SSREs with respect to the commercial reference was 211.2 and 181.9 mV, respectively. These potentials are somewhat higher than expected from the characterization data.

CONCLUSION

The stability of the reference electrode is an important factor in any electroanalytical procedure since any variation can affect the response of the working electrode. In all experiments, the Nafion and polyurethane SSREs demonstrated equal or better stability than the commercial reference. The polymer coating appears to be very effective in protecting and stabilizing the electrode. Both polyurethane and Nafion are reasonably effective, but from these studies the polyurethane demonstrated slightly better overall stability than the Nafion electrode. In addition, the polyurethane SSREs were less influenced by the nature of the solution, except at a high pH. It appears clear that both SSREs can be used in solutions with no added electrolyte, such as natural water samples, to perform on-site and in situ analysis.

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