Microporous Ag/AgCl on a Titanium Scaffold for Use in Capillary Reference Electrodes

Emily E. A. Robinson, Blair K. Troudt, and Philippe Bühlmann*

Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis MN 55455, USA

*Corresponding author E-mail: buhlmann@umn.edu

Abstract

Thermal-electrolytically fabricated AgCl-coated silver can be used to prepare more reproducible reference electrodes than Ag/AgCl prepared with alternative methods, such as electrolytic and chemical AgCl deposition or thermal fabrication. However, thermal-electrolytic fabrication requires a scaffold material to build the layers upon. Platinum and rhodium have been used for this purpose as they are mechanically strong and chemically inert but their cost is prohibitive for wider application. Herein, we report the stability of Ag/AgCl reference electrodes built atop a titanium scaffold using the thermal-electrolytic method, and the use of these Ti/Ag/AgCl constructs in capillary-based reference electrodes. Electrochemical characterization shows that the probable presence of small amounts of oxygen at the Ti/Ag interface does not affect the reference electrode performance; in particular, over a wide pH range, the half-cell potential is pH independent. The electrical resistance of the Ti/Ag/AgCl/KCl system is dominated by the charge transfer resistance at the interface of the AgCl to KCl solution but is kept very small by the large AgCl surface area and a high solution concentration of chloride. The resulting high exchange current minimizes the effect of system impurities on the reference half-cell potential. Capillary-based reference electrodes comprising Ti/Ag/AgCl show exceptionally low potential drifts (as low as 0.03 ± 2.01 μV/h) and standard deviations of the potential at or below ± 0.5 mV over a 60 h period. These capillary-based reference electrodes are suitable for very small sample volumes while still providing for a free-flowing liquid junction that prevents reference electrode contamination.

Introduction

Conventional reference electrodes that were once adequate for routine electroanalytical measurements often do not meet the requirements of long-term monitoring with the deployable, wearable, and implantable potentiometric sensors proposed in recent years. Reference electrodes with half-cell potentials, E^o, reproducible to ≤0.1 mV are few, with the notable example of the Ag/AgCl electrode.[1–3] Indeed, Ag/AgCl reference electrodes are often the electrode of choice, given the availability of a number of straightforward methods to manufacture them, the comparatively low dependence of their E^o on temperature, and the low toxicity of silver.[4,5] However, while in the past emphasis was often placed on the electrode-to-electrode reproducibility of E^o, the increased desire for calibration-free long-term monitoring is also creating a need for reference electrodes that exhibit low long-term E^o drift, a characteristic rarely addressed in the older literature. Factors that must be considered in this context include electrode polarization, potential changes caused by electrode contamination, and potential biases when a current (i) flows through the reference electrode. The latter add an iR term to E^o, where the resistance, R, is likely dominated by charge transfer resistance at the interface of the AgCl phase and the surrounding chloride solution.

The fabrication methods available for Ag/AgCl electrodes range from 3D printing to electrolytic deposition and chemical coating.[1,6,7] With most of these methods, a AgCl layer is deposited atop a planar Ag substrate, resulting in a flat surface Ag/AgCl electrode.[8] However, the limited surface area of a planar Ag/AgCl surface results in a comparatively low exchange current, which has been associated with increased electrode potential drift.[8–11] Thermal-electrolytically fabricated Ag/AgCl electrodes circumvent this with a microporous structure[10,12,13] and are fabricated in a two-step process based on (1) thermal decomposition of a Ag_2O paste to form a highly porous Ag layer atop a scaffold provided by another metal, as Ag_2O is a thermodynamically unstable form of silver at high temperatures,[14,15] and (2) the anodization of part of the Ag layer in HCl to produce a AgCl coating on the porous Ag. The microporosity of the AgCl layer results in a very high surface area of the AgCl, minimizing the charge transfer resistance at the electrode/solution interface.[10] This is expected to result in the fast establishment of chemical equilibria at the electrode surface and, therefore, small temperature hysteresis.[2,11] The use of microporous Ag greatly increases the surface area while still maintaining a small electrode body.[3,11,17–19] Importantly, the large surface area is also expected to minimize any effects impurities entering the inner filling solution might have on the potential stability of the reference electrode.

Previous literature on the thermal-electrolytic fabrication process and the reproducibility and long-term potential stability of reference electrodes prepared with this method is quite limited.[8,9,18–21] This work relied on the use of platinum[9] or rhodium[18] as a scaffold on which the microporous Ag/AgCl was deposited, leading to high material cost. To enable the wider use of the thermal-electrolytic fabrication method, a different scaffold is required, one that is chemically inert and allows electron conduction across the scaffold/Ag interface. We are proposing here titanium as a new scaffold material for the thermal-electrolytic fabrication of Ag/AgCl. Titanium has been used frequently in both medical and industrial applications due to its high biocompatibility and its resistance to corrosion in chloride-containing solutions.[22,23] Prior work has shown successful use of Ti as a support for iridium oxide-based pH sensors,[24] but Ti has not been used for the fabrication of reference electrodes in the past. Its relatively low cost and high natural abundance[25] make Ti an attractive and sustainable alternative to precious metals such as platinum and rhodium. While the oxide layer that forms under ambient conditions on Ti may be of concern for other applications, the thinness and slow growth of this oxide layer at room temperature allows for fast electron transfer between Ti and many substrates atop it, as evident from its previous success in pH sensors[24,26,27] and as also seen in this work.

Herein, we report on thermal-electrolytically fabricated Ag/AgCl reference electrodes built upon a titanium scaffold. When these reference electrodes were directly immersed into chloride containing sample solutions, i.e., without a salt bridge separating the sample from the electrolyte solution surrounding the Ag/AgCl electrode, drifts as low as -0.2 ± 0.8 μV/h, standard deviations of E^{o} from electrode to electrode of ± 0.14 mV, and, for individual electrodes, a standard deviation of the measured potential, E_{meas}, over 90 h below 25 μV were observed. Moreover, the potential did not depend on pH over a large pH range. Ti/Ag/AgCl inner reference elements were also built into capillary-based reference electrodes, which are notable for their highly stable and contaminant-resistant free-flowing liquid junction that is compatible with very small sample volumes.[28] For reference electrodes with such exceptionally low drift of the half-cell potential, it is important that the potentiometer itself can be excluded as a significant contributor to drift, which is why in this work the contribution of potentiometer to such drift was also quantified.

Experimental Section

Materials. Reagents were purchased from the following sources: Ag_2O from Oakwood Chemical (99% purity, Estill, SC, USA), Ti rods (3.175 mm diameter, ultra-corrosion-resistant grade 2, 99% purity, Rockwell B65 hardness) and Ti sheets (ultra-corrosion-resistant grade 2, 99% purity, Rockwell B65 hardness) from McMaster-Carr (Atlanta, GA, USA), KCl, and AgCl (≥ 98% purity) from Sigma-Aldrich (St. Louis, MO, USA), and Ag wire (0.5 mm diameter, ≥ 99.9% purity) and Pt wire (0.25 mm diameter, ≥ 99.9% purity) from Alfa Aesar (Tewksbury, MA, USA). Deionized water was purified with a Milli-Q PLUS reagent grade water filtration system at 18.2 MΩ/cm (Millipore, Bedford, MA, USA) and was used for all aqueous experiments.

Ag/AgCl Electrolytic Fabrication. Ag wires were cut to 5 cm and electrolytically coated with AgCl by submerging wires into a solution of 1.0 M HCl and applying a constant current of 0.4 mA/cm^2 against a Pt wire.[29]

Ag/AgCl Chemical Coating Fabrication. Ag wires were cut to 5 cm. Half of each wire was submerged in a solution of 1 M $FeCl_3 \cdot 6H_2O$ for 10 min before being rinsed off with DI water. For further conditioning, the electrodes were then stored for 7 days in the dark in water saturated with AgCl.

Pt/Ag/AgCl Thermal-Electrolytic Fabrication. Pt wires were cut into 5 cm segments and rinsed with 1.0 M HNO_3 before being polished with a polishing cloth using an aqueous suspension of alumina powder (0.3 and 0.05 μm, Buehler, Lake Bluff, IL, USA). Wires were sonicated in water and ethanol for 5 min each. The dried wires were coated with ~5 mg of Ag_2O paste (0.5 mg/ml H_2O), made by grinding the Ag_2O with a mortar and pestle, adding water, and sonicating the mixture. This paste was applied using a paintbrush, and the thus treated wires were heated in a tube furnace at 450 °C for 20 min under a constant flow of house-line nitrogen. The coating and heating were repeated an additional two times. The Ag wires thus coated with microporous Ag were stored under argon in the dark overnight before electrodeposition of a AgCl layer was performed by immersion into 1.0 M HCl and application of a 1 mA current over 1.0 h, using a Pt wire counter electrode. For conditioning, the wires were then stored in water saturated with AgCl in the dark for 7 days.

Ti/Ag/AgCl Thermal-Electrolytic Fabrication. Titanium rods were cut with a grinding wheel into 6 cm segments, which were rinsed with 0.1 M HCl before being lightly sanded with 60, 150, and 600 grit sandpaper and individually polished with a polishing cloth using alumina powder (0.3 and 0.05 μm, Buehler) and water. Of note, the oxide layer on Ti can be minimized by sanding the outer layer if discoloration occurs, as the change in color gives an estimate of the size of the oxide layer.[30] The rods were then sonicated in water and ethanol for 5 min each. Upon drying, they were coated with ~15 mg of Ag_2O paste (0.5 g/ml H_2O, prepared as described above), leaving 2 cm of the rod at one end bare. The rods were then heated in a tube furnace at 450 °C for 20 min under nitrogen. The coating and heating steps were repeated an additional two times. After storage of the rods under an inert atmosphere in the dark overnight, electrodeposition of the AgCl layer was performed by converting 15% of the thermally coated Ag to AgCl.[20] This was achieved by immersion into 1.0 M HCl and application of a 1 mA current for 2.35 h, as determined using Faraday's laws of electrolysis.[31] The thus prepared Ti/Ag/AgCl electrodes were stored for conditioning in the dark for 72 h in 0.1 mM HCl saturated with AgCl.

For observation with scanning electron microscopy (SEM), grade 2 Ti sheets (1 cm^2) were cut and thermally coated with Ag using the same method as for the rods. After coating with Ag, 15% of the thermally coated Ag was converted electrochemically in 1.0 M HCl to AgCl, with a constant 1 mA current. SEM images were obtained with a Hitachi SU8230 Field Emission Gun Scanning Electron Microscope (FEGSEM) at the UMN Characterization Facility.

Incorporation of Thermal-Electrolytically Fabricated Ti/Ag/AgCl Electrodes into Capillary-Based Reference Half Cells. Ti/Ag/AgCl rods (3 mm diameter) fabricated with the thermal-electrolytic method were mounted into reference half cells with a Polymicro Flexible Fused Silica capillary (inner diameter 10μm, outer diameter 150μm capillary; Molex, Lisle, IL, USA; secured in Tygon tubing filled with epoxy adhesive) as the liquid junction and 3.0 M KCl saturated with AgCl as the inner filling solution.[32] A Ti/Ag/AgCl rod was mounted into a hollowed out PVC rod, and glued in place with a THF/PVC mixture. A barbed hose adaptor was connected to the in-house nitrogen line and pressure gauge, and a MF-Millipore filter was added above the capillary area to prevent AgCl particles from clogging the capillary (see Figure S1).

To improve the tightness of the pressurized reference electrodes, a Ti/Ag/AgCl electrode was incorporated at a later stage of this work into a polyacrylate body, which was filled with internal filling solution (3.0 M KCl saturated with AgCl) and connected to an in-house nitrogen line for pressure application. See the Supplementary Information for apparatus details.

Potential Measurements. Electrode potential studies were conducted with an EMF 16-channel high-impedance potentiometer (Lawson Laboratories, Malvern, PA, USA) with 1.0 TΩ input impedance, controlled with EMF Suite 1.03 software. Measurements were performed in a Faraday cage at a constant 25 °C using a temperature-controlled box with heating elements and a fan controlled by a Watlow EZ-ZONE PM Panel Mount PID Controller (Watlow, St. Louis, MO, USA).

The potentiometer's contribution to potential drift was assessed by connecting measurement channels through a 10 MΩ resistor to the reference channel. The thus determined drift was 0.09 ± 0.06 μV/h over 24 h, showing that the potentiometer itself did not contribute significantly to emf drift (see the Supplementary Information for more details).

The long-term stability of Ti/Ag/AgCl electrodes was assessed by measurements in a 1.0 M KCl solution against an electrode of the same batch. The long-term potential stability of capillary-based reference electrodes with thermal-electrolytically fabricated Ti/Ag/AgCl rods was measured in 100 mM KCl against an electrolytically coated Ag/AgCl wire. Responses to Cl^{-} and Ag^{+} were determined in KCl and $AgNO_3$ solutions, respectively, against a free-flowing LiOAc double-junction reference electrode (Mettler Toledo, Columbus, OH, USA).[33]

Ion activities were calculated with an extended Debye–Hückel approximation.[34] Liquid junction potential calculations and corrections were performed with the Henderson equation.[35] Electrode responses to pH change were studied by incremental additions of 1.0 M HCl or 1.0 M KOH aliquots to a 1.0 M KCl solution.

Resistance Measurements. Ag/AgCl and Ti/Ag/AgCl electrode resistances were measured with symmetric electrochemical cells made of two electrodes of the same batch immersed into 100 mM KCl, using a Metrohm Autolab PGSTAT204 potentiostat/galvanostat system equipped with an EIS module (Metrohm, Herisau, Switzerland).[35] Alternatively, Ti/Ag/AgCl electrode resistances were also measured in a symmetric cell in 10 mM and in 1.0 M KCl, each with a constant 1.0 M Na_2SO_4 background. A Fluke 77 Series II Multimeter (Fluke Corporation, Everett, WA, USA) was used to measure the resistance between two electrodes separated from one another by 0.1, 1.0, or 3.0 cm.

Results/Discussion

Fabrication of Porous Ag/AgCl Electrodes. High porosity Ag coatings on Ti were produced by deposition of Ag_2O paste onto a Ti scaffold, and a fraction of the porous Ag layer thus formed was electrochemically converted to AgCl by application of a constant current. To assess the structure of the thus formed Ag and AgCl layers, SEM images were taken of both thermally produced Ag (Figures 1A and 1B) and partially anodized Ag/AgCl (Figures 1C and 1D) prepared on a planar sheet of titanium as scaffold. Following anodization, the growth of AgCl particles can be seen as small substructures atop the thermally produced Ag, with the microporous structure from the thermal decomposition step still maintained. This level of porosity is not found in electrolytic coatings as there is no porous substructure of the Ag substrate to begin with.[8]

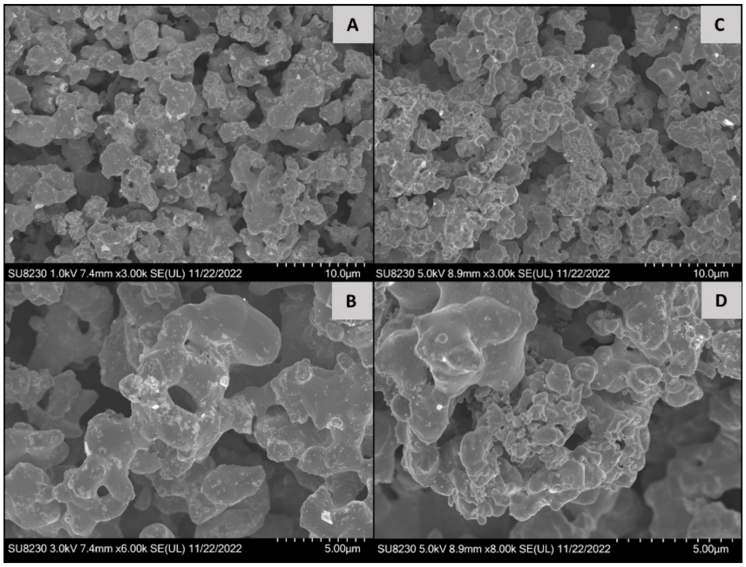


Figure 1: SEM images showing the porosity of a Ag layer thermally formed atop a titanium substrate (left, A and B) and the persistence of the porous structure after partial conversion of the Ag to AgCl (right, C and D).

Performance of Thermal-Electrolytically Fabricated Ti/Ag/AgCl Electrodes. In a reliable reference electrode, all phase boundary potentials must be well defined and reproducible. To this end, it is of interest whether the thin oxide layer on the surface of the Ti scaffold on which the porous Ag is deposited affects the performance of the Ti/Ag/AgCl reference electrodes prepared in this work. A layer of $TiO_{2,}$, which is an semiconducting material,[22,36] is naturally present on the surface of Ti metal, typically with a thickness of about 5 nm.[37]

Ti/Ag/AgCl electrodes immersed into 100 mM KCl exhibited a very small half-cell resistance of 150 Ω, which originates almost entirely from solution resistance and interfacial resistance at the solution/AgCl interface. The likely presence of a small amount of oxide at the Ti/Ag interface contributes only minimally to the total half-cell resistance, as shown by the following experiment. The electrical resistance between the back ends of two Ag-coated Ti rods that touched one another at their Ag-coated front ends was determined with a multimeter to be 6.5 Ω. This setup comprises two Ti/Ag interfaces, which are protected in this resistance measurement from physical damage by the overlying Ag layers, confirming that the resistance of the Ti/Ag interface is a few ohms at most.

Moreover, the resistance of two Ti/Ag/AgCl electrodes measured at differing distances from one another in 10 mM and 1.0 M KCl solutions (each with a constant 1.0 M Na_2SO_4 electrolyte background) confirmed that most of the measured total resistance comes from the AgCl/sample interface. This is evident from the large increase in resistance upon dilution of the KCl, while for the 1.0 M KCl solution the distance between the electrodes affected the resistance to a much lesser extent (Table 1).

Table 1: Resistance of a symmetrical electrochemical cell with two Ti/Ag/AgCl electrodes immersed into 10 mM or 1.0 M KCl solution (each with a constant background electrolyte concentration of 1.0 M Na_2SO_4) as a function of the distance between the two electrodes.

KCl concentration	Distance between electrodes		
	0.1 cm	1 cm	3 cm
10 mM	52.1 Ω	65.2 Ω	84.6 Ω
1.0 M	18.4 Ω	19.3 Ω	22.2 Ω

These observations show that the presence of oxygen at the Ti/Ag interface, whether present in minuscule or more substantial amounts, is not interfering to a considerable extent with electron conduction across the Ti/Ag interface. Further experiments were performed to assess whether oxide present at the Ti/Ag interface, whether present to a sizeable amount or not, does affect the potentiometric Ag^+ and Cl^- responses expected of the AgCl surface and whether it induces sensitivity to pH.

The potentiometric responses of Ti/Ag/AgCl electrodes to Ag^+ and Cl^- were measured against a double-junction reference electrode with LiOAc as salt bridge, using varying concentrations of $AgNO_3$ or KCl (see Figure 2). Linear slopes of 55.8 ± 0.2 and -61.5 ± 0.5 mV decade were observed for the responses to Ag^+ and Cl^-, respectively. This confirms that the use of titanium as a scaffold does not interfere with the expected ion responses of the AgCl top layer of these electrodes.

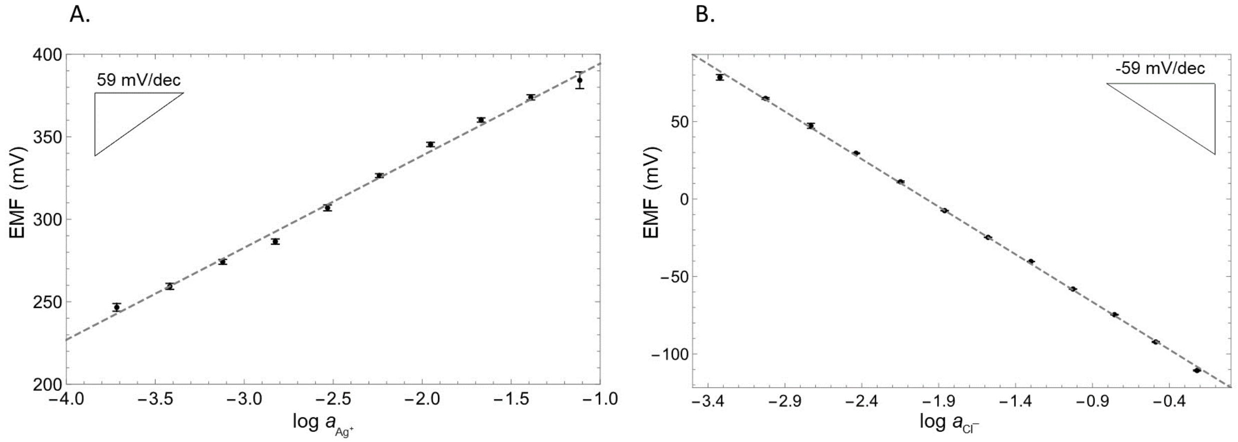


Figure 2: (A) Potentiometric response of Ti/Ag/AgCl electrodes to Ag^+ (A) and Cl^- (B), as measured against a free-flowing LiOAc double-junction reference electrode (n=4, 23 °C; shown with standard deviation).

We suspected a sensitivity of uncoated Ti electrodes to pH as electrodes made from other metals with a surface oxide layer, such as antimony, iridium, or palladium, are well known to exhibit potentiometric responses to pH.[16,38] Indeed, pH sensitivity was observed for clean, sanded Ti rods when they were immersed into 1.0 M KCl solution and the pH was varied between pH 2 to 12 by addition KOH or HCl (see Figure S4). As expected, the Ti rods showed a change in potential of -36.7 ± 1.7 mV per pH unit.

To test whether the Ti scaffold indeed makes the Ti/Ag/AgCl half cell sensitive to acids and bases or whether the microporous Ag/AgCl layer suppresses that effect, the measured potential was studied in the pH range of 2 to 12. To do so, a 1.0 M KCl solution was acidified with HCl down to pH 2, followed by the addition of KOH to increase the pH to 12. As shown in Figure 3, the response of the Ti/Ag/AgCl electrode was minimal with a change in response of 0.07 ± 0.02 mV per unit pH change, and the EMF over the entire pH range is characterized by a standard deviation of ± 0.3 mV, a result that may be the effect of a very minor fluctuation in the liquid junction potential between the sample and the conventional reference electrode. Whether oxygen is present at the Ti/Ag interface or not, a pH sensitivity clearly cannot be seen.

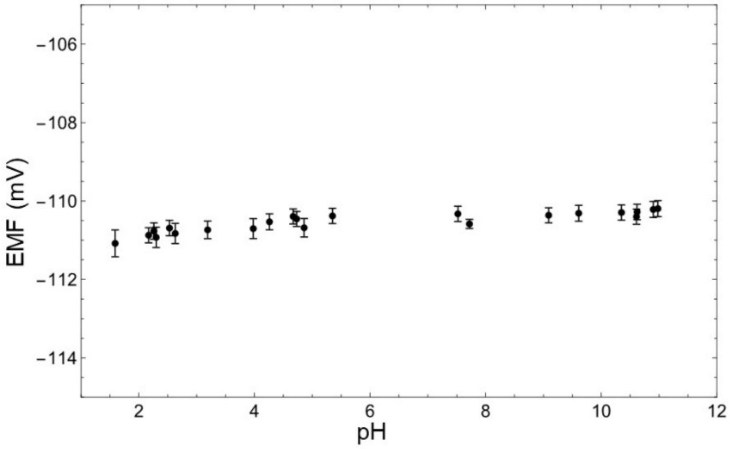


Figure 3: pH response of thermal-electrolytically fabricated Ti/Ag/AgCl electrodes in 1.0 M KCl (pH monitored with a pH glass electrode and adjusted by first adding aliquots of 1.0 M HCl, then 1.0 M KOH, n=4, shown with standard deviations).

We also note that attempts to build analogous reference electrodes with a stainless steel scaffold coated with Pt, porous Ag, and electrochemically deposited AgCl failed. Immersion of these stainless steel/Pt/Ag/AgCl electrodes into 1.0 M KCl solutions for several hours resulted in extensive corrosion, as apparent from discoloration of the solutions to deep red. In contrast, no corrosion was apparent for the Ti/Ag/AgCl electrodes, consistent with the well-known corrosion resistance of Ti.[39] The difference between stainless steel/Ag/AgCl electrodes and Ti/Ag/AgCl electrodes is notable, as apparently neither the Pt nor Ag/AgCl coating fully protected the stainless steel from corrosion, while the Ag/AgCl coating is effective in suppressing any possible effect of exposed Ti or TiO_2.

To test the long-term stability of Ti/Ag/AgCl reference electrodes, four electrodes of this type were immersed into 1.0 M KCl, and the potentials of three of these electrodes were measured with respect to the fourth one in a temperature-controlled cage at 25 °C over 90 h. Results of this Harned cell system showed an average potential drift of -0.2 ± 0.8 μV/h and a standard deviation of the potential over the entire 90 h of $\pm$ 23.1, $\pm$ 7.1, and $\pm$ 8.5 μV for electrodes 1, 2, and 3, respectively (see Figure 4). This is an extraordinarily low value for potential drift and is indeed on a very similar order of magnitude as the potential drift that we observed when short-circuiting the measurement and reference channel of our high input impedance potentiometer with a 10 MΩ resistor (0.09 ± 0.06 μV/h over 24 h for a six channel measurement; see the Supplementary Information). This confirms the exceptional stability of the Ti/Ag/AgCl reference electrodes.

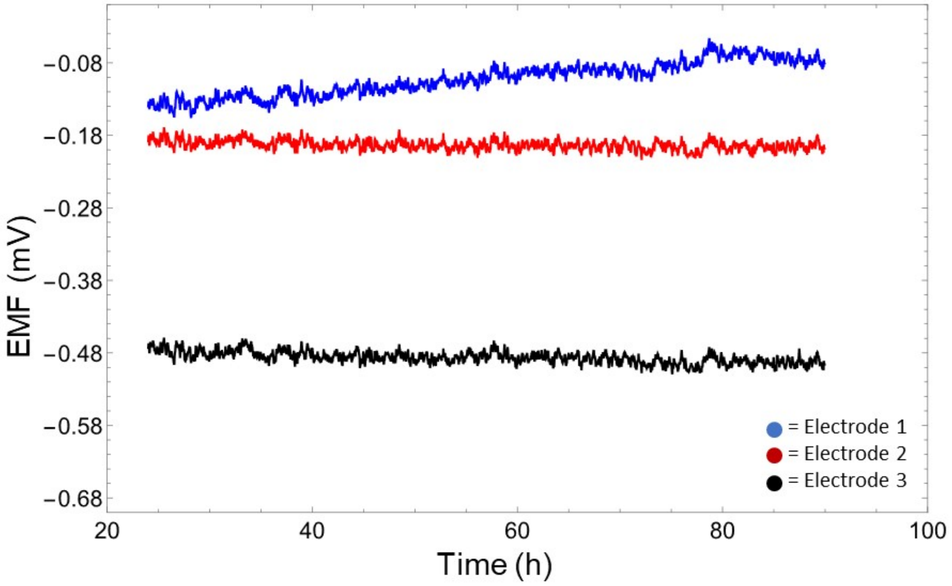


Figure 4: Potential stability of thermal-electrolytically coated Ti/Ag/AgCl measured against an electrode of the same batch in 1.0 M KCl at 26 °C inside a temperature-controlled cage.

The reader may wonder why we measured the stability of the Ti/Ag/AgCl reference electrodes with respect to one another, rather than measuring their stability with respect to a conventional reference electrode, such as a commercial free-flowing liquid junction reference electrode. We note, however, that in our hands measurements of commercial free-flowing liquid junction reference electrode versus another free-flowing liquid junction reference electrode typically give drifts on the order of several microvolts per hour, likely caused by instabilities of the liquid junction. Clearly, characterizing a new reference electrode with respect to a less stable reference electrode is hardly meaningful. As no electrochemical cell can consist of one half cell only, it is unavoidable that the very best reference electrode cannot be tested with respect to a better reference electrode and, therefore, have to be tested with respect to one another.

It is evident, though, that a Ti/Ag/AgCl electrode cannot be used by direct immersion into samples unless the chloride concentration in the sample is known and constant over time. To that end, we also used Ti/Ag/AgCl electrodes as the internal half-cell element for capillary-based reference electrodes.

Incorporation of Thermal-Electrolytically Fabricated Ag/AgCl Electrodes into Capillary-Based Reference Electrode System. The capillary-based reference electrode system with constant external pressure provides a few notable advantages. First, the external pressure allows for a well-controlled continuous flow of inner filling solution into the sample with a high linear flow rate (estimated to be 1.2 m/h for capillary-based reference electrodes with inner capillary diameters as discussed here[32]), preventing both backflow of sample into the capillary as well as diffusion of sample components from into the inner filling solution and, thereby, preventing contamination and dilution of the bridge electrolyte separating the sample from the reference electrode. Second, because the use of a small capillary minimizes volumetric flow, reference electrodes can be used for time periods as long as several months without the need for solution refilling.[32]

Ti/Ag/AgCl rods were incorporated into capillary-based reference electrode bodies as reported previously.[32] For this purpose, Ti/Ag/AgCl rods were mounted each into a 1 cm long PVC rod with a central hole drilled to fit the Ti/Ag/AgCl rod, using a PVC/THF mixture as an adhesive to seal any gaps between the Ti and the PVC. Tygon tubing was used to connect the reference electrode body to a source of N_2 gas with a constant pressure of 10 kPa pressure to ensure continuous flow of the inner filling solution towards sample solutions. Following immersion of the capillary tip into 1.0 M KCl solution and thermal equilibration of the reference electrode for 24 h, capillary-based reference electrode potentials were measured for several days against an electrolytically coated Ag/AgCl wire (see Figure 5). Over 65 h, the measured potential exhibited a very small drift of 0.03 ± 2.01 μV/h, with the standard deviations of the measured potential during this time being ± 0.13, ± 0.53, and ± 0.06 mV for electrodes 1, 2, and 3, respectively (see Figure 5). This is an improvement over previously reported work[32] on capillary-based reference electrodes with electrolytically coated Ag/AgCl electrodes, whose potentials exhibited drifts of 6 ± 3 μV/h and reproducibility within ± 2 mV. To put this performance into a practically relevant context, consider the monitoring of K^+ for clinical applications. As of July 2024, the acceptable error for such a measurement as determined by United States federal regulations is 0.3 mM.[40] Assuming a drift of 2 μV/h, which corresponds to the standard deviation of the drift observed in this work, this would allow for a Ti/Ag/AgCl reference electrode to be used for 6 years and still be within acceptable error for K^+ detection.

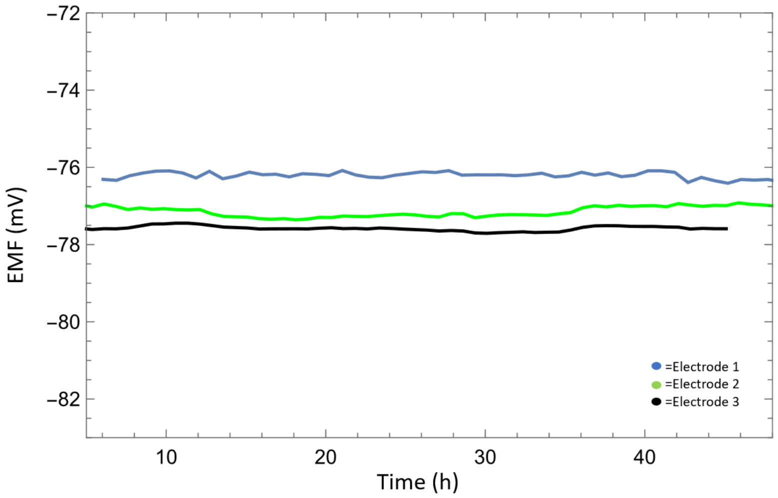


Figure 5: Potential stability of Ti/Ag/AgCl electrode incorporated into capillary-based reference electrode system in 100 mM KCl measured against an Ag/AgCl wire.

Capillary-based reference electrodes were also prepared by mounting thermal-electrolytically fabricated Ti/Ag/AgCl rods into a new polyacrylate body designed to minimize leakage upon pressurization with nitrogen gas (see Figures S5 to S7). This design takes advantage of the large diameter of the Ti rods used in this work, made possible by the low cost of Ti. It makes it easy to connect the Ti rods to the polyacrylate block with commercially available male nuts and ferrules. Similarly, chromatography-type fittings and sleeves were used to mount the capillary, avoiding the need for any glue in the assembly of the reference electrode. Consequently, these electrodes can also be disassembled readily if needed. The reliability of this new body surpasses that of the previous bodies, and preliminary long-term stability testing showed drifts of the measured potentials in line with that of the previous electrode body design (see Figure S8). One might consider the use of Pt/Ag/AgCl reference elements instead of Ti/Ag/AgCl. However, the cost of a large Pt rod, or the cost of coating a metal rod of an alternative metal with Pt prior to the application of Ag and AgCl, surpasses that of the use of a Ti rod greatly. For more details on Ti/Ag/AgCl reference electrode bodies with the polyacrylate body, see the Supplementary Information.

Comparison of Ag/AgCl Fabrication Methods in View of Potential Stability. The Ti/Ag/AgCl electrodes as described above were also compared to Pt/Ag/AgCl reference electrodes prepared with the thermal-electrolytic fabrication method a well as Ag electrodes coated chemically or electrolytically. Criteria considered were the standard deviation of the half-cell potential, potential drift, and the standard deviation of the measured potential, E_{meas}, of individual electrodes over 72 h. Table 2 shows that the drift for the two types of thermal-electrolytically fabricated electrodes is an order of magnitude smaller than for Ag/AgCl electrodes prepared with the chemical coating method and one-fourth of that for Ag/AgCl electrodes prepared with electrolytic coating. This good performance of the Ti/Ag/AgCl and Pt/Ag/AgCl electrodes is likely owed to the increased Ag/AgCl surface area and, consequently, the minimization of the charge transfer resistance that results from the microporous structure not seen in either the chemically-coated or electrolytically fabricated electrodes. The Ti/Ag/AgCl electrodes stand out with a particularly low standard deviation of E_{meas} over 72 h, even better than the Pt/Ag/AgCl electrodes. Of note, the standard deviation of E^{o} for the different fabrication methods do not differ largely, with all at or below ± 0.15 mV.

Table 2: Comparison key characteristics of Ag/AgCl electrodes in 1.0 M KCl for different fabrication procedures: standard deviation (SD) of E^{o} and long-term potential drift over 72 h as well as SD of the measured potential of individual electrodes over 72 h.

	chemical coating (Ag/AgCl)	electrolytic coating (Ag/AgCl)	thermal-electrolytic coating (Ti/Ag/AgCl)	thermal-electrolytic coating (Pt/Ag/AgCl)
SD of E^{o} (mV)[a]	0.11	0.15	0.15	0.08
drift (µV/h)[b]	1.80 ± 0.64	-0.83 ± 1.04	-0.24 ± 0.78	0.22 ± 0.28
SD of E_{meas} over 72 h (mV)[c]	0.08[d]	0.15[e]	0.01	0.08[f]

[a] Determined from the potentials of 3 electrodes as measured against a fourth electrode prepared with the same fabrication method and in the same batch. [b] Drift over 72 h of electrodes as measured against an electrode of the same batch (n=3). [c] SD of the measured potential, E_{meas}, of individual electrodes over a period of 72 h; shown here are averages of these values from 3 electrodes. [d] SD of E_{meas} of individual electrodes: 0.07, 0.09, and 0.09 mV. [e] SD of E_{meas} of individual electrodes: 0.18, 0.13, and 0.13 mV. [f] SD of E_{meas} of individual electrodes: 0.08, 0.12, 0.07, and 0.05 mV.

Conclusions

Thermal-electrolytically fabricated Ag/AgCl coatings on Ti can be used to make exceptionally stable reference electrodes. Combined with a pressurized capillary-based liquid junction, these reference electrodes reach sub-microvolt per hour level potential drift, the lowest long-term drifts reported to date for reference electrodes to the best of our knowledge. Ti rods provide a scaffold for Ag/AgCl electrodes with a high surface area and are readily compatible with continuous pressurization, offering a cost-effective alternative to Pt and other precious metals as scaffold material. Even though a very thin oxide layer forms on Ti under ambient conditions, Ti/Ag/AgCl reference electrodes are not sensitive to pH, and, unlike stainless steel/Ag/AgCl electrodes, they are not prone to corrosion in chloride containing solutions. Comparison of the performance of electrodes fabricated with methods resulting in highly porous and nonporous surfaces suggests that a microporous structure with its large surface area is a key factor in the improved reference electrode stability. These results suggest the use of Ti/Ag/AgCl reference electrodes for long-term measurement applications in which frequent recalibration is difficult. The very low volumetric flow rate of electrolyte from free-flowing capillary-based Ti/Ag/AgCl reference electrodes into samples also makes these reference electrode very suited for microfluidic systems and other system with small sample sizes,[28] providing high potential stability and preventing contamination of the reference electrode over longer time periods in spite of the small sample volumes. Further miniaturization of such electrodes may be possible by use of an internal constant pressure source, eliminating the need for a gas line connection.

ASSOCIATED CONTENT

Supplementary Information

Potentiometer contribution to potential drift and image of experimental set up, cross-section schematic of a capillary-based reference electrode, image of fully assembled capillary-based reference electrode with a polyacrylate body, and long-term stability of a capillary-based reference electrode with a polyacrylate body and an internal Ti/Ag/AgCl reference element.

AUTHOR INFORMATION

Corresponding Author

* E-mail: Buhlmann@umn.edu. Tel: +1 (612) 624-1431.

ORCID

Emily E. A. Robinson: 0009-0007-1148-3633

Blair K. Troudt: 0000-0001-6670-2855

Philippe Bühlmann: 0000-0001-9302-4674

Notes

The authors declare no competing financial interest.

Acknowledgments

This work was funded by National Science Foundation Grant CHE-2203752. Parts of this work were carried out at the Characterization Facility, University of Minnesota, which receives partial support from the NSF through the MRSEC (Award Number DMR-2011401) and the NNCI (Award Number ECCS-2025124) programs. We thank Prof. Mahesh Mahanthappa for measurement time on the potentiostat/galvanostat/EIS workstation and the UMN CSE machine shop for assistance fabricating the polyacrylate electrode bodies. E.E.A.R. acknowledges a University of Minnesota College of Science and Engineering graduate student fellowship.

References

(1) Inzelt; Lewenstam; Scholz. *Handbook of Reference Electrodes*; Inzelt, G., Lewenstam, A., Scholz, F., Eds.; Springer: Berlin ; New York, 2013.

(2) Sawyer, D. T.; Sobkowiak, A.; Roberts, J. L. *Electrochemistry for Chemists*, 2nd ed.; Wiley: New York, 1995.

(3) Troudt, B. K.; Rousseau, C. R.; Dong, X. I. N.; Anderson, E. L.; Bühlmann, P. Recent Progress in the Development of Improved Reference Electrodes for Electrochemistry. *Anal. Sci.* **2022**, *38*, 71–83.

(4) Maksimov, I.; Asakai, T.; Ohata, M. On the Optimal Use of Silver–Silver Chloride Reference Electrodes. *Accred. Qual. Assur.* **2023**, *28*, 65–68.
(5) Roscher, J.; Holze, R. Reference Electrodes. *Encyclopedia* **2023**, *3*, 478–489.
(6) Dawkins, R. C.; Wen, D.; Hart, J. N.; Vepsäläinen, M. A Screen-Printed Ag/AgCl Reference Electrode with Long-Term Stability for Electroanalytical Applications. *Electrochim. Acta* **2021**, *393*, 139043.
(7) Schmidt, B.; King, D.; Kariuki, J. Designing and Using 3D-Printed Components That Allow Students To Fabricate Low-Cost, Adaptable, Disposable, and Reliable Ag/AgCl Reference Electrodes. *J. Chem. Educ.* **2018**, *95*, 2076–2080.
(8) Brewer, P. J.; Brown, R. J. C. Effect of Silver Annealing Conditions on the Performance of Electrolytic Silver/Silver Chloride Electrodes Used in Harned Cell Measurements of pH. *Sensors* **2010**, *10*, 2202–2216.
(9) Brewer, P. J.; Brown, R. J. C. Effect of Structural Design of Silver/Silver Chloride Electrodes on Stability and Response Time and the Implications for Improved Accuracy in pH Measurement. *Sensors (Basel, Switzerland)* **2009**, *9*, 118–130.
(10) Janz, G. J.; Taniguchi, H. The Silver-Silver Halide Electrodes Preparation, Stability, Reproducibility, and Standard Potentials in Aqueous and Non-Aqueous Media. *Chem. Rev.* **1953**, *53*, 397–437.
(11) Coetzee, J. F.; Gardner, C. W. Exchange Current Densities and Other Properties of Reference Electrodes Based on the Triiodide Iodide and Silver(I) Ion-Silver Couples in Organic Solvents. *Anal. Chem.* **1982**, *54*, 2530–2532.
(12) Taniguchi, H.; Janz, G. J. Preparation and Reproducibility of the Thermal-Electrolytic Silver-Silver Chloride Electrode. *J. Electrochem. Soc.* **1957**, *104*, 123–127.
(13) Herley, P. J.; Prout, E. G. The Thermal Decomposition of Silver Oxide. *J. Am. Chem. Soc.* **1960**, *82*, 1540–1543.
(14) N. Waterhouse, G. I.; A. Bowmaker, G.; B. Metson, J. The Thermal Decomposition of Silver (I , III) Oxide : A Combined XRD , FT-IR and Raman Spectroscopic Study. *Chem. Phys. Phys. Chem.* **2001**, *3*, 3838–3845.
(15) L'vov, B. V. Kinetics and Mechanism of Thermal Decomposition of Silver Oxide. *Thermochim. Acta* **1999**, *333*, 13–19.
(16) Ritter, T.; Zosel, J.; Guth, U. Solid Electrolyte Gas Sensors Based on Mixed Potential Principle – A Review. *Sens. Actuators B Chem.* **2023**, *382*, 133508.
(17) Bindra, P.; Roldan, J. Mechanisms of Electroless Metal Plating. III. Mixed Potential Theory and the Interdependence of Partial Reactions. *J. Appl. Electrochem.* **1987**, *17*, 1254–1266.
(18) Rostami, B.; Mirzaei, S. I.; Zamani, A.; Simchi, A.; Fardmanesh, M. Development of an Enhanced Porosity AgAgCl Reference Electrode with Improved Stability. *Eng. Res. Express* **2019**, *1*, 015039.
(19) Brewer, P. J.; Leese, R. J.; Brown, R. J. C. An Improved Approach for Fabricating Ag/AgCl Reference Electrodes. *Electrochim. Acta* **2012**, *71*, 252–257.
(20) Brewer, P. J.; Stoica, D.; Brown, R. J. C. Sensitivities of Key Parameters in the Preparation of Silver/Silver Chloride Electrodes Used in Harned Cell Measurements of pH. *Sensors* **2011**, *11*, 8072–8084.
(21) Lito, M. J. G.; Camões, M. F. Meeting the Requirements of the Silver/Silver Chloride Reference Electrode. *J. Soln. Chem.* **2009**, *38*, 1471–1482.

(22) Effah, E. a. B.; Bianco, P. D.; Ducheyne, P. Crystal Structure of the Surface Oxide Layer on Titanium and Its Changes Arising from Immersion. *J. Biomed. Mater. Res.* **1995**, *29*, 73–80.

(23) Bloyce, A.; Qi, P.-Y.; Dong, H.; Bell, T. Surface Modification of Titanium Alloys for Combined Improvements in Corrosion and Wear Resistance. *Surf. Coat. Technol.* **1998**, *107*, 125–132.

(24) Głab, S.; Hulanicki, A.; Edwall, G.; Ingman, F. Metal-Metal Oxide and Metal Oxide Electrodes as pH Sensors. *Crit. Rev. Anal. Chem.* **1989**, *21*, 29–47.

(25) Emsley, J. *Nature's Building Blocks: An A-Z Guide to the Elements*, 2nd ed.; Oxford University Press: New York, 2011.

(26) Fog, A.; Buck, R. P. Electronic Semiconducting Oxides as pH Sensors. *Sens. Actuators* **1984**, *5*, 137–146.

(27) Kinoshita, K.; Madou, M. J. Electrochemical Measurements on Pt, Ir, and Ti Oxides as Ph Probes. *J. Electrochem. Soc.* **1984**, *131*, 1089.

(28) Herrero, E. J.; Troudt, B. K.; Bühlmann, P. The Effect of Paper on the Detection Limit of Paper-Based Potentiometric Chloride Sensors. *Anal. Chem.* **2022**, *94*, 14898–14905.

(29) Anderson, E. L.; Lodge, T. P.; Gopinath, T.; Veglia, G.; Bühlmann, P. More than a Liquid Junction: Effect of Stirring, Flow Rate, and Inward and Outward Electrolyte Diffusion on Reference Electrodes with Salt Bridges Contained in Nanoporous Glass. *Anal. Chem.* **2019**, *91*, 54.

(30) Diamanti, M. V.; Del Curto, B.; Pedeferri, M. Interference Colors of Thin Oxide Layers on Titanium. *Color. Res. Appl.* **2008**, *33* (3), 221–228. https://doi.org/10.1002/col.20403.

(31) Bird, J. O.; Chivers, P. J. 7 - Electrolysis. In *Newnes Engineering and Physical Science Pocket Book*; Newnes, 1993; pp 42–53.

(32) Anderson, E. L.; Troudt, B. K.; Bühlmann, P. Easy-to-Make Capillary-Based Reference Electrodes with Controlled, Pressure-Driven Electrolyte Flow. *ACS Sens.* **2021,** *6*, 2211-2217.

(33) Dohner, R. E.; Wegmann, Dorothee.; Morf, W. E.; Simon, Wilhelm. Reference Electrode with Free-Flowing Free-Diffusion Liquid Junction. *Anal. Chem.* **1986**, *58*, 2585–2589.

(34) Meier, P. C. Two-Parameter Debye-Hückel Approximation for the Evaluation of Mean Activity Coefficients of 109 Electrolytes. *Anal. Chim. Acta* **1982**, *136*, 363–368.

(35) Bard, A. J. *Electrochemical Methods : Fundamentals and Applications*; Faulkner, L. R., Ed.; Wiley: New York, 2001.

(36) Kumar, S.; Sankara Narayanan, T. S. N.; Ganesh Sundara Raman, S.; Seshadri, S. K. Thermal Oxidation of Ti_6Al_4V Alloy: Microstructural and Electrochemical Characterization. *Mater. Chem. Phys.* **2010**, *119* (1), 337–346.

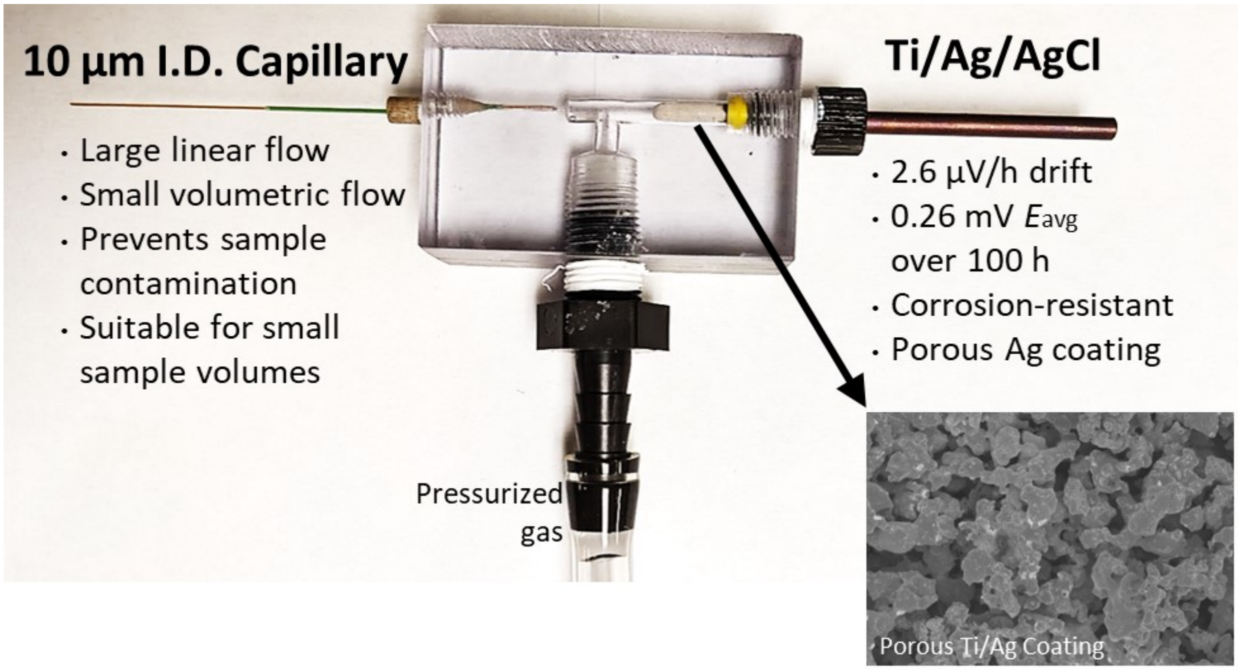
(37) Aniołek, K. The Influence of Thermal Oxidation Parameters on the Growth of Oxide Layers on Titanium. *Vacuum* **2017**, *144*, 94–100.

(38) Morf, W. E. *The Principles of Ion-Selective Electrodes and of Membrane Transport*; Akadémiai Kiadó.: Budapest, 1981.

(39) Elias, C. N.; Fernandes, D. J.; Souza, F. M. de; Monteiro, E. dos S.; Biasi, R. S. de. Mechanical and Clinical Properties of Titanium and Titanium-Based Alloys (Ti G2, Ti G4 Cold Worked Nanostructured and Ti G5) for Biomedical Applications. *J. Mater. Res. Technol.* **2019**, *8*, 1060–1069.

(40) National Archives and Records Administration. 42 CFR 493.931 Routine Chemistry. *United States Code of Federal Regulations*, last revised 2024 (accessed 2023-09-12).

TOC Figure


10 µm I.D. Capillary
• Large linear flow
• Small volumetric flow
• Prevents sample contamination
• Suitable for small sample volumes
Ti/Ag/AgCl
• 2.6 µV/h drift
• 0.26 mV E_{avg} over 100 h
• Corrosion-resistant
• Porous Ag coating
Pressurized gas
Porous Ti/Ag Coating