Critical Comparison of Reference Electrodes with Salt Bridges Contained in Nanoporous Glass with 5, 20, 50, and 100 nm Diameter Pores

Evan L. ANDERSON, Blair K. TROUDT, and Philippe BÜHLMANN[†]

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

Porous glass frits are frequently used to contain the salt bridges through which reference electrodes interface samples. Prior work with widely used glass frits with 4 – 10 nm diameter pores showed that, when samples have a low electrolyte strength, electrostatic screening of sample ions by charged sites on the glass surface occurs. This creates an ion-specific phase-boundary potential at the interface between the sample and frit, and it biases the potential of the reference half-cell. Use of frits with much larger pores eliminates this problem but results in the need for frequent replenishing of the bridge electrolyte. A methodical study to determine the optimum pore size has been missing. We show here that charge screening of sample ions occurs when the pore size of nanoporous glass frits is on the order of 1 – 50 nm and samples have a low electrolyte strength. An increase in pores size to 100 nm eliminates charge screening in samples with ionic strengths in the 1.0 M to 3.3×10^{-4} M range. However, the rates of electrolyte solution flow through frits with 1, 5, 20, 50, and 100 nm pores are still low, which makes diffusion the dominant mode of ion transport into and out of these frits. Consequently, the flow of bridge electrolyte into samples is not fast enough to prevent diffusion of ions and electrically neutral components from the sample diffusing into the salt bridge, which can result in cross contamination among samples.

Keywords Reference electrodes, nanoporous glass, salt bridges, charge screening

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Introduction

The measurement of stable and reproducible reference potentials is an area of interest for many but is not without its complications.^{1–14} Consistent and constant reference potentials are particularly difficult to measure in very dilute aqueous solutions, a problem of concern especially for accurate pH measurements of environmental importance.^{9,15–18} In many cases, salt bridges are used to provide for electrical contact between reference electrodes and samples.^{19,20} At the liquid junction formed between two mutually miscible electrolyte solutions, a junction potential develops that depends on the concentrations, mobilities, and charges of all ions involved.²¹ It is well known that electrolytes of salt bridges with matched cation and anion mobilities and a high concentration can be selected so as to minimize and dominate this liquid junction potential.²²

To reduce the cross contamination of samples and the salt bridge electrolyte by convective mixing, porous glasses with pore diameters of 4 – 10 nm have been used to contain the salt bridge.^{4,23} Unfortunately, this can introduce complications due to electrostatic screening by electrical charges on the pore walls of these frits.²³ In particular, sample-dependent phase boundary potentials were shown to develop at the interface of nanoporous glass frits with 4 – 6 nm pores due to the negatively charged

surface of glass (*e.g.*, sample cations freely enter the frit pores but anions are excluded) in all but very acidic solutions.²³ Therefore, the use of reference electrodes with frits that have such small pores is not recommended when measuring in dilute solutions, where the Debye length of the solution is larger than the size of the frit pores (Fig. 1).²³ A similar type of electrostatic screening has also been observed in electrically conducting nanoporous materials.²⁴ Reference electrodes with 500 – 1000 nm pores⁴ did not exhibit charge screening in solutions with an ionic strength from 1×10^{-1} to 1×10^{-6} M and provide for reference potentials that can be predicted very accurately after correction of the liquid junction potential as calculated, *e.g.*, with the Henderson equation.^{22,25–28} However, frits with 500 – 1000 nm pores allow for a flow rate of the bridge electrolyte into the sample that is often unacceptably large.⁴ Similarly, polymeric frits with 1 and 10 μm pores were found to exhibit no charge screening but had flow rates that quickly contaminated samples and required frequent replenishing of bridge electrolyte.⁴ Reference electrodes comprising polymeric frit materials with much smaller pore sizes are feasible but at this point require custom synthesis and are not easy to functionalize with a hydrophilic surface that does not bind certain ions specifically.⁷

To this end, we tested in the work presented here commercially available porous glass frits with pore diameters of 1, 5, 20, 50, and 100 nm. The frits were used to separate a 3.0 M KCl bridge electrolyte solution from different types of sample solutions. Because stirring of samples of low ionic strength has been shown recently to enhance the level of charge screening through

[†] To whom correspondence should be addressed.
E-mail: buhlmann@umn.edu

Fig. 1 Illustration of charge screening at the interface of a reference electrode frit and different samples. Dotted lines indicate Debye length. Panel A: Frit in contact with a sample of high ionic strength, where ions diffuse freely. Panel B: Frit in contact with a sample of low ionic strength, where negatively charged ions are screened by the negative surface charge of the glass frit.

the reduction of electrolyte strength that accompanies the convective penetration of sample into a surface layer of a few nanometers of the frit,²⁹ potentials in this work were monitored in both stirred and unstirred solutions. To determine the suitability of these electrodes for measurements of environmental waters, potentials of electrodes equipped with glass junctions with each pore size were also measured in solutions of pH 1.5 to 12.5 without background electrolyte, and, therefore, low ionic strength. Linear flow rates for each type of frit were determined and compared to the minimum flow rate required to avoid contamination to the reference electrode frits due to diffusion of sample components into the frit.

Experimental

Materials

Aqueous solutions were prepared using deionized and charcoal-treated water ($>18.2 \text{ M}\Omega \text{ cm}$ specific resistance) obtained with a Milli-Q PLUS reagent grade water system (Millipore, Bedford, MA). AgCl (98%), KCl , Na_2SO_4 , CaCl_2 , 1.0 M NaOH , and 1.0 M HCl were purchased from Sigma-Aldrich, Ag wires (0.5 mm diameter, $\geq 99.9\%$) from Alfa Aesar (Tewksbury, MA), and porous glass disks (15 mm diameter; 1.2 mm thick; 1.0 ± 0.1 , 5.0 ± 0.5 , 20 ± 2 , 50 ± 5 , and $100 \pm 10 \text{ nm}$ diameter pores) from Boraglas (Stuttgart, Germany). All chemicals were used as received.

Reference electrode fabrication

Each porous glass disk was immersed in 3.0 M KCl for at least 3 days before being mounted onto a custom-made poly(chlorotrifluoroethylene) electrode body (Fig. S1, Supporting Information), sandwiching the frit between two Viton washers. This resulted in a circular area of 8.3 mm diameter of the frit exposed to the sample solutions. Electrode bodies were filled with 3.0 M KCl saturated with AgCl , and AgCl/Ag wires (prepared as reported previously)²⁹ were inserted into this inner solution. The electrode bodies were not sealed, allowing for pressure equalization with the ambient air and,

therefore, for flow of inner filling solution out of the electrodes through the porous glass.

Potential measurements

Potentials (E) were measured at room temperature in unstirred or stirred solutions (as discussed in the Results and Discussion) with an EMF 16 potentiometer (Lawson Labs, Malvern, PA) controlled with EMF Suite 1.02 software (Fluorous Innovation, Arden Hill, MN). A Corning PC-420D stir plate was used with a 150 mL glass beaker ($55 \times 85 \text{ cm}$) and a $1.0 \times 6.4 \text{ mm}$ Teflon-coated cylindrical magnetic stir bar. The stir bar rotation rate was kept constant at 400 rotations per minute. Potentials were measured relative to a free-flowing double-junction reference electrode (DX200, Mettler Toledo, Switzerland) with 3.0 M KCl bridge electrolyte and AgCl -saturated 3.5 M KCl reference electrolyte.²⁸ Activity coefficients were calculated using a two-parameter Debye-Hückel approximation,³⁰ and potential measurements of aqueous electrolytes (excluding pH) were corrected for liquid junction potentials using the Henderson equation.²¹ The pH was monitored using a glass electrode from Hanna Instruments (Smithfield, RI) and adjusted by additions of 1.0 M HCl and 1.0 M NaOH . KCl concentrations were adjusted by serial dilution of concentrated solutions. Na_2SO_4 and CaCl_2 concentrations were adjusted by addition of concentrated stocks solutions to deionized and charcoal-treated water.

Flow rate of salt bridge electrolyte

Flow rates of the salt bridge solution through the frits into samples (5, 20, 50, and 100 nm) were measured by storing the electrodes in a sealed container with 100% humidity. The inner compartments of the reference electrodes were filled with 3.0 M KCl to a solution height of 100 mm *versus* the sample surface, and the solution height was monitored over a 30 day period (repeated three times).

Resistance measurements

Resistance was measured using a Solartron 1255B frequency response analyzer with an SI 1287 electrochemical interface (Farnborough, Hampshire, UK) controlled by ZPlot software (Scribner Associates, Southern Pines, NC). Measurements were performed at the open circuit potential with an AC amplitude of 100 mV in 3.0 M KCl . Data was collected using a Pt gauze ($50 \times 13 \text{ mm}$) counter electrode and a AgCl/Ag wire reference electrode. All data fits were performed using Mathematica 10.1 (Champaign, IL).

Results and Discussion

Reference potentials in stirred and unstirred KCl electrolyte solutions

Prior to potential measurements, the electrical resistances of reference electrodes with 1, 5, 20, 50, and 100 nm pores were determined. The thus determined electrical resistances are consistent with those previously reported for Vycor ($69 \pm 17 \Omega$) and CoralPor ($139 \pm 53 \Omega$) frits, which confirms that each frit was filled to a substantial extent with the 3.0 M KCl inner filling solution (Table 1).⁴ To simulate typical applications, the half-cell potentials of reference electrodes with glass junctions with 5, 20, 50, or 100 nm diameter pores (from here on referred to as half-cell potentials of reference electrodes with porous junctions) were measured with respect to a conventional free-flowing double-junction reference electrode in vigorously stirred (400 rotations per minute) KCl solutions (Fig. 2). The half-cell potentials of reference electrodes with porous junctions with

Table 1 Volumetric flow rate, resistance, and linear flow rates of reference electrodes with 1, 5, 20, 50, and 100 nm pore glass frits

	1 nm	5 nm	20 nm	50 nm	100 nm
Volumetric flow rate ($\mu\text{L/h}$)	$< 0.035^a$	0.035 ± 0.027	0.67 ± 0.07	3.0 ± 0.6	14.0 ± 0.5
Resistance (Ω , filled with 3 M KCl)	8000 ± 1000	240 ± 20	130 ± 10	130 ± 10	130 ± 10
Linear flow rate (mm/h)	$< 8.9 \times 10^{-4a}$	8.9×10^{-4}	1.7×10^{-2}	7.6×10^{-2}	3.6×10^{-1}

a. Not determined experimentally.

Fig. 2 Potentials of reference electrodes as a function of K^+/Cl^- activity of a KCl solution under stirred conditions. E was measured relative to a free-flowing double-junction reference electrode. All E values are corrected for liquid junction potentials at the free-flowing double junction. Error bars are 95% confidence intervals for the average of three separate experiments.

20, 50, and 100 nm pores were statistically equivalent over the entire concentration range studied ($1.0 \text{ M} - 3.3 \times 10^{-4} \text{ M KCl}$), while the half-cell potentials of the electrodes with junctions with 5 nm pores deviated significantly at intermediate and lower ionic strengths, indicating charge screening due to repulsion of sample anions by the negative charges on the glass surfaces. An independence of the half-cell potential of reference electrodes with porous junctions on the ionic strength has previously also been reported for reference electrodes with Electro-porous KT glass frits (500 – 1000 nm pores), which is consistent with their large pore size. It is worth noting that a substantial part of the experimentally observed electrode-to-electrode potential deviation for junctions with a given pore size (as indicated by the error bars in Fig. 2) can be explained by the variability of the AgCl-coated Ag wires used as the inner reference electrodes. In our experiments, the standard deviation of the EMF of AgCl coated Ag wires in 100 mM KCl *versus* a free-flowing reference electrode was measured to be $\pm 2.8 \text{ mV}$ ($n = 3$). Similar variabilities have been reported in the literature for AgCl-coated Ag wires and have been attributed, among other factors, to mechanical strains in the silver wire.³¹

For comparison to previously reported results, half-cell potentials of reference electrodes with porous junctions were also measured in stirred solutions of Na_2SO_4 and CaCl_2 (Figs. S2 and S3, Supporting Information).⁴ As for KCl sample solutions too, measurements of potentials in Na_2SO_4 and CaCl_2 solutions indicate that half-cell potentials of reference electrodes using porous glass junctions with 20, 50, and 100 nm pores do not suffer from charge screening at the sample interface of the frit.

To assess the effect of sample stirring, the half-cell potentials of reference electrodes with glass frit junctions with pore diameters of 1, 5, 20, 50, or 100 nm were measured in KCl solutions both under stirred (400 rotations per minute) and unstirred conditions (see Figs. S4, S5, and S6, Supporting Information). At high electrolyte strengths ($>0.1 \text{ M KCl}$), the half-cell potential of each electrode did not depend on whether the solutions were stirred or not. However, as the concentration of KCl was reduced ($<0.1 \text{ M KCl}$), the potentials of reference electrodes with a 1 or 5 nm pore diameter frit deviated for samples of low ionic strength significantly from those for electrodes with 20, 50, or 100 nm pore frits. This finding is consistent with observations reported previously for glass frits commercially available under the tradenames Vycor (4 – 6 nm pores) and CoralPor (4 – 10 nm pores).⁴ In addition, reference electrodes with a 1 or 5 nm pore diameter frit showed a response to solution stirring, which is consistent with an increase in charge screening as the result of the penetration of the sample a few nanometers into the frit, resulting in the dilution of the bridge electrolyte concentration with sample and, thereby, an increase in the local Debye length.²⁹

Reference potentials in stirred and unstirred solutions of pH 1.5 to 12.5

Half-cell potentials of reference electrodes with a Vycor frit (4 – 6 nm pores) have been reported to vary $\approx 40 \text{ mV}$ from $\text{pH} = 2$ to $\text{pH} = 12$ in a 0.01 M KCl background.⁴ Here we determined the half-cell potentials of reference electrodes with glass junctions with 5, 20, 50 and 100 nm pore diameters from $\text{pH} 1.5$ to 12.5 in unstirred and stirred solutions containing no background electrolyte (Figs. 3, 4, 5, and 6; see also Figs. S7 and S8, Supporting Information). This type of experiment was performed to simulate the pH measurement of rainwater,^{27,32–34} where no background electrolyte is present, and Debye lengths are large.

As Fig. 3 shows, the half-cell potentials of reference electrodes with glass junctions with 5 nm pores did not deviate significantly from that of reference electrodes with a free-flowing liquid junction in unstirred solutions until a pH greater than 9 was reached. Note that potentials in Fig. 3 were not corrected for the liquid junction potential at the free-flowing double junction electrode with respect to which the potential were determined. Therefore, the absence of deviations in the half-cell potential indicates that the half-cell potential of the free-flowing liquid junction, with contributions from the liquid junction potential at the interface of the 3 M KCl bridge electrolyte with the sample, is the same as that of the porous frit reference electrode. In contrast to the results for frits with 5 nm pores in unstirred solutions, in stirred solutions, these electrodes show significant deviations in half-cell potentials from pH 1.5 to 12.5 of up to $\approx 40 \text{ mV}$ (Fig. 3). This large deviation is consistent with what has been reported for Vycor frits (4 – 6 nm pores).⁴

Electrodes with 20 nm pore frits (Fig. 4) and, to a lesser extent, electrodes with 50 nm pore frits (Fig. 5) showed slight deviations from ideal liquid junction behavior at pH values of

Fig. 3 Potentials, E , of reference electrodes with 5 nm pores as a function of pH in unstirred and stirred solutions, measured relative to a free-flowing double-junction reference electrode. Data is not corrected for liquid junction potentials. Error bars are 95% confidence intervals for the average of three separate experiments.

Fig. 5 Potentials, E , of reference electrodes with 50 nm pores as a function of pH in unstirred and stirred solutions, measured relative to a free-flowing double-junction reference electrode. Data is not corrected for liquid junction potentials. Error bars are 95% confidence intervals for the average of three separate experiments.

Fig. 4 Potentials, E , of reference electrodes with 20 nm pores as a function of pH in unstirred and stirred solutions, measured relative to a free-flowing double-junction reference electrode. Data is not corrected for liquid junction potentials. Error bars are 95% confidence intervals for the average of three separate experiments.

Fig. 6 Potentials, E , of reference electrodes with 100 nm pores as a function of pH in unstirred and stirred solutions, measured relative to a free-flowing double-junction reference electrode. Data is not corrected for liquid junction potentials. Error bars are 95% confidence intervals for the average of three separate experiments.

10 to 12, as evident from the difference in E in the unstirred and stirred cases. This indicates that charge screening occurs in this case for the 20 and 50 nm pores too, unlike in the case of the KCl, Na₂SO₄ and CaCl₂ experiments shown in Figs. 1, S2, and S3. In addition, potential deviations increased in stirred solutions, which is consistent with an increase in charge screening as the result of the penetration of the sample solution into the frits. In contrast, the half-cell potentials of electrodes with glass junctions with 100 nm pores did not deviate significantly from those for reference electrodes with a free-flowing liquid junction, nor did their half-cell potential depend on the solution being stirred or not (Fig. 6). This shows that reference electrodes with pore diameters ≥ 100 nm can be used without charge screening contributing to the measured half-cell potential.²¹

Flow rate of the bridge electrolyte

Previously, we reported that the flow rate of reference electrodes is an important factor in determining the level of contamination that may occur from diffusion of small sample ions into the porous frit, with small ions such as K⁺, Cl⁻, and Fe³⁺ diffusing a few millimeters over 1 h.²⁹ Here we determined the volumetric flow rates of reference electrodes with nanoporous glass frits using a setup in which the bridge electrolyte level in the reference electrode was 100 mm higher than in the sample, producing a pressure of 9.8×10^{-3} bar. This resulted in volumetric flow rates for 5, 20, 50, and 100 nm pores in the range from 0.0035 to 14 $\mu\text{L/h}$ (see Table 1). These values were converted to linear flow rates with which solution passes through the nanoporous frits by dividing the volumetric flow rates by the fraction of the frit cross section not occupied by glass

($3.9 \times 10^{-5} \text{ m}^2$). This resulted in flow rates between $8.9 \times 10^{-4} \text{ mm/h}$ for the smallest and $3.6 \times 10^{-1} \text{ mm/h}$ for the largest pore frits. Flow rates for the 1 nm pore frits could not be measured with this method because of the extremely small flow rate. The comparison of these linear flow rates with the typical distance small ions diffuse in 1 h shows that diffusion dominates the transport of ions for all pore diameters studied. Therefore, the solution within the porous frits will be contaminated by sample solutions over the timescale of typical experiments. While the glass frits with pore diameters of 50 and 100 nm show no charge screening in solutions of varying pH and ionic strength, contamination of the bridge electrolyte may alter reference potentials over the time course of measurements and contribute to cross contamination between different samples. This linear flow rate could be increased by pressurizing the inner filling solution, but that would lead to increased volumetric flow rates, which is not desirable.

Conclusions

The half-cell potentials of reference electrodes comprising porous glass frits with pore diameters between 1 and 100 nm were measured in solutions of varying electrolyte concentration and pH. On one hand, half-cell potentials of electrodes with glass junctions with pore diameters of 1, 5, 20, and 50 nm were found to depend both on the sample and stirring conditions. These changes in half-cell potential result from charge screening of ions at the interface of the porous frit and the sample. This makes these pore sizes undesirable for reference electrode use in samples of intermediate or low ionic strength. On the other hand, electrodes comprising frits with pore diameters of 100 nm were found to provide half-cell potentials that only depend on the liquid junction potentials as it can be predicted with the Henderson equation, not affected by charge screening. However, while the half-cell potentials of the reference electrodes with 100 nm pore frits did not vary with the ionic strength, the flow rates of their salt bridges were found to be too low to limit diffusion of sample components into the frits when the only force driving convective flow through the frit was the pressure resulting from a bridge electrolyte level 100 mm above the sample surface. This can cause contamination of the frit and carry-over of contaminants into subsequent samples.

Having tested 1, 5, 20, 50, and 100 nm glass frits, we can recommend use of the 100 nm glass frits for applications that involve samples of low ionic strength. However, when cross contamination of samples and bridge electrolyte is a concern, liquid junctions characterized by a small volumetric but a large linear flow rate of the bridge electrolyte into the sample are preferable. In such cases, other junction types, such as capillary junctions, appear superior to junctions with porous frits.

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Supporting Information

Figures that show a schematic of the electrode body. Potentials

of reference electrodes in stirred solutions of Na_2SO_4 and CaCl_2 , and in stirred and unstirred solutions of KCl. Alternative representation of data from Figs. 3, 4, 5, and 6, facilitating comparison of data for frits with different pore sizes, for either stirred or unstirred solutions. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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