Reference Electrodes with Salt Bridges Contained in Nanoporous Glass: An Underappreciated Source of Error

Maral P. S. Mousavi and Philippe Bühlmann*

Department of Chemistry, University of Minnesota, 207 Pleasant Street South East, Minneapolis, Minnesota 55455, United States

Supporting Information

ABSTRACT: In electroanalytical measurements, nanoporous glass plugs are widely used to contain the electrolyte solution that forms a salt bridge between the sample and the reference electrode. Even though reference electrodes with plugs made of nanoporous glass (such as Vycor or CoralPor glass) are commercially available and are frequently used, the limits of their use have not been explored thoroughly. It is shown here that at ionic strengths lower than 100 mM, the half-cell potentials of reference electrodes with nanoporous glass plugs are not sample independent, as it would be desirable, but they depend on the ionic sample composition. Sample dependent shifts of more than 50 mV in the half-cell potential were encountered. Reference potentials were found to be affected in aqueous solutions by HCl, NaCl, KCl, and CaCl2 and in acetonitrile by CF3COOH and the supporting electrolyte tetrabutylammonium perchlorate. These observations cannot be explained by the liquid junction potential between two mutually miscible electrolyte solutions, as commonly described with the Henderson equation. Instead, they result from the surface charge density on the glass surface and the resulting electrostatic screening of ion transfer into the glass pores when the latter have dimensions comparable to or smaller than the Debye length. Users of reference electrodes with nanoporous glass plugs need to be aware of these limitations to avoid substantial measurement errors.

Reference electrodes are an inevitable part of almost every electrochemical measurement, be it potentiometry, amperometry, voltammetry, impedance spectroscopy, or another electroanalytical method. Most reference electrodes contact the reference solution and the sample through a salt bridge filled with an electrolyte solution. Limiting factors for the use of these salt bridges are the loss of electrolyte into the sample and contamination of the salt bridge by sample components. To minimize these effects and to obtain low and stable junction potentials, porous plugs filled with electrolyte solution are often used, separating the reference from the sample solution while maintaining electrical contact between the two. These porous plugs must have a low electrical resistance while avoiding excessive transfer of electrolyte and sample components through the junction. In order to provide these characteristics, several materials with a high porosity and relatively small pores have been used both by academic researchers and commercial suppliers. Many studies investigated the properties of reference electrodes with microporous ceramic plugs, which were reported to have pore diameters in the 0.1–3 μm range. Nanoporous glass plugs commercially available under the brand names Vycor and CoralPor have also been very popular for the fabrication of reference electrodes and offer the advantage of further restricting liquid flow. The preparation of these glasses is based on the observation that ternary mixtures of silicon dioxide, boric acid, and alkali oxides may phase-separate on proper heat treatment, resulting in a porous skeleton rich in silica and surrounded by alkali and boric oxide. The latter can be leached out with acids, leaving back a nanoporous and strongly hydrophilic glass, sometimes referred to as “thirsty glass”. The pore diameter can be controlled to some extent and has been reported to lie in the range of 4–20 nm.

Reference electrodes with nanoporous glass junctions are used widely for electrochemical measurements in both aqueous and organic media. In the brief period from January 2012 to May 2013 alone, more than 70 publications in various journals explicitly reported using reference electrodes equipped with Vycor glass plugs (see the Supporting Information for a list of these references). Since many publications from the same time period described the use of reference electrodes of an unspecified nature, the actual number of studies for which reference electrodes with nanoporous glass plugs were used is likely much larger. However, even though the use of reference electrodes with nanoporous glass plugs was first proposed already in 1955, the effect of nanoporous glass junctions on the performance of reference electrodes in water has to our knowledge not been reported in the literature and limitations of their performance in organic solvents have been only associated with insolubility effects and mobility differences.

Received: July 16, 2013
Accepted: September 4, 2013
Published: September 4, 2013

Editors’ Highlight

dx.doi.org/10.1021/ac402170u1 Anal. Chem. 2013, 85, 8895–8901
This study critically probes the weaknesses of reference electrodes with nanoporous glass plugs and discusses the conditions that can lead to large measurement errors introduced by shifts in the reference potential. Even though limited variations in the potential of reference electrodes may not be a concern in some electrochemical measurements, many others require a highly reproducible reference electrode potential. For example, an error of 5 mV in the measurement of a monovalent ion with an ion-selective electrode results in an error of 18% in the determined ion activity. In this study, we encountered discrepancies in reference potentials from reference electrodes with nanoporous glass plugs of more than 50 mV and found a substantial dependence of reference potentials on the composition of the sample solutions.

Importantly, the largest errors that we observed cannot be explained by the well-known liquid junction potentials as they occur at the interface of two miscible electrolyte solutions. Instead, large errors were caused by electrostatic screening of ion transport through the nanopores of the porous glass plugs and the concomitant formation of a phase boundary potential at the interface of sample and plug. This phenomenon is not only analogous to the formation of a phase boundary potential at the interface of sample and plug. This phenomenon is not only analogous to the formation of a phase boundary potential at the interface of sample and plug. This phenomenon is not

**EXPERIMENTAL SECTION**

Cylindrical nanoporous glass plugs (porous Vycor tips, MF-2064; 3 mm diameter, 3 mm length) were purchased from Bioanalytical Systems (Mount Vernon, IN). A Vycor plug and a glass tube (5 cm long, 3 mm diameter) were placed in a Teflon heat shrink tube, followed by heating with a heat gun for 3 min to attach the plug to the glass tube. Aqueous reference electrodes with nanoporous glass plugs were then prepared by inserting an AgCl/Ag electrode into the glass tube equipped with the Vycor glass plug at one end and filling of the tube from the other end with a solution that contained 1.0 mM KCl and 1.0 M lithium acetate (LiOAc). Note that KCl and LiOAc are both equitranferrent salts, i.e., salts composed of a cation and an anion with equal mobility. In order to completely fill the nanoporous glass plugs with 1.0 M LiOAc, the electrodes were then stored in stirred 1.0 M LiOAc solutions for at least 1 week. Calibration curves were measured by successive dilution or addition of aliquots of concentrated solutions of NaCl, KCl, CaCl₂, or HCl.

**Measurements in Aqueous Media.** All potential measurements were performed in stirred aqueous solution at room temperature (25 °C) with an EMF 16 channel potentiometer (Lawson Laboratories, Malvern, PA) controlled with EMF Suite 1.02 software (Lawson Laboratories). For comparison, external reference electrodes (DX-200; Mettler Toledo, Columbus, OH) with a free flow double-junction AgCl/Ag electrode, a 1.0 M lithium acetate (LiOAc) bridge electrolyte (movable ground glass sleeve junction) and a 3.0 M KCl reference electrolyte were used. All the solutions were prepared with deionized purified water (18.2 MΩ cm specific resistance, EMD Millipore, Philadelphia, PA), and all measurements were performed in triplicate. The pH measurements were performed with a pH half-cell electrode from Mettler Toledo.

**Measurements in Organic Solutions.** Reference electrodes with nanoporous glass plugs for use in organic solutions were prepared by inserting an Ag wire into a glass tube equipped with a Vycor glass plug at one end, filling of the tube from the other end with an acetonitrile solution that contained 10.0 mM AgNO₃ and 100 mM tetrabutylammonium perchlorate (NBu₄ClO₄), and inserting the thus-prepared electrodes into a stirred solution of identical composition at least for 1 week prior to measurements. Cyclic voltammograms of bis(pentamethylcyclopentadienyl)iron, Me₅FeC₆ (97%; Aldrich, Milwaukee, WI) were measured with a CHI600C potentiostat (CH Instruments, Austin, TX). All electrochemical measurements were carried out with a scan rate of 100 mV/s, using a three electrode setup with a 3.0 mm-diameter gold disk as the working electrode (BAS, West Lafayette, IN), a 0.25 mm Pt wire coil (99.998%, Alfa Aesar, Ward Hill, MA) as the auxiliary electrode (total surface area ≈ 0.5 cm²), and the reference electrodes with nanoporous glass plugs prepared in house. The working electrode was polished on Microcloth polishing pads using 5.0 μm Micropolish II deagglomerated alumina, both from Buehler (Lake Bluff, IL). After polishing, the working electrode was rinsed thoroughly with deionized water and then ethanol, followed by drying under a stream of argon. Prior to measurements, all solutions were purged with argon for 15 min while stirring vigorously to remove dissolved oxygen. All potentials are reported with respect to 10 mM Ag⁺/Ag reference electrodes with nanoporous glass plugs.

All electromotive force (emf) values for measurements with a free-flow liquid-junction were corrected for liquid junction potentials using the mobility of the ion,₂¹,₂² and the Henderson equation, except for the measurements with trifluoroacetic acid, CF₃COOH (Figure 7). Ionic activities were calculated using a two-parameter Debye–Hückel approximation.₂⁴ To obtain free flow salt bridge junctions, glass pipettes were pulled in a flame to give tip diameters of ≈20 μm and filled with either aqueous LiOAc solutions (1.0 M) or acetontinrile solutions of NBu₄ClO₄ (100 mM). In all free flow experiments, reference electrodes with nanoporous glass plugs were placed into these pipets filled with electrolyte solution and a small flow of solution out of the pipet into the sample was confirmed. These measurements were then repeated in the same sample solutions but without the electrolyte solution filled pipet, i.e., with direct contact of the nanoporous glass plugs and the sample solution. A 125SB frequency response analyzer and a SI 1287 electrochemical interface from Solartron (Farnborough, Hampshire, U.K.) with a three-electrode system were used to...
determine the electrical resistance of the nanoporous glass plugs. A Pt wire and a free flow double-junction AgCl/Ag electrode with a 1.0 M lithium acetate (LiOAc) bridge electrolyte were used as counter and reference electrodes, respectively. Resistances were obtained by fitting of impedance spectra with ZPlot software (Scribner Associates, Southern Pines, NC) in the 10^4 to 10^5 Hz range.

RESULTS AND DISCUSSION

In an ideal electroanalytical measurement, the salt bridge that connects the sample and reference half cells does not contribute to the measured cell potential. To achieve near ideality, salt bridges typically contain an equimolar salt in high concentration, minimizing the liquid junction potential at the interface of the salt bridge and the sample. This work shows that, when used in samples of moderate or low ionic strength, reference electrodes with nanoporous glass plugs exhibit far from ideal behavior. Quite to the contrary, these reference electrodes exhibited near Nernstian responses to several ions, both in aqueous media and organic solvents.

As shown in Figure 1, reference electrodes with nanoporous glass plugs and aqueous 1.0 M LiOAc/1.0 mM KCl inner electrolyte solutions respond potentiometrically to aqueous HCl solutions. To investigate whether the measured emf responses were due to entrapment of previously measured samples in the plug pores, as well-known for reference electrodes with conventional porous ceramic plugs when there is small or negligible flow of salt bridge electrolyte into the sample, the response to HCl was measured in four sequential steps. At first, the HCl solution was diluted to raise the pH, then HCl was added into the diluted solution to lower the pH again, then a second dilution was performed, and finally HCl was added a second time. If indeed occurring, low diffusive or convective mass transfer into and out of the porous plug would be expected to result in a substantial memory effect. However, Figure 1 shows only a very small hysteresis effect. The four pH responses curves from the two dilutions and two HCl additions deviate from one another by only a few millivolts, i.e., much less than the nearly 100 mV of emf response between pH 2 and 5. This clearly shows that sample entrapment in the porous plug and ensuing hysteresis have only a minor effect on the observed potentiometric response. Interestingly, the pH response is not limited to the region of lowest ionic strength but is largest from pH 4 all the way down to pH 2, where the ionic strength is 10 mM. Indeed, in this region the pH response has a slope of approximately 30 mV/decade, which is roughly half of the Nernstian response slope of 58 mV/decade as exhibited by a pH glass electrode.

Figure 2 illustrates how the potentiometric response of the reference electrode with the nanoporous plug depends on the ionic strength of the sample. In HCl solutions with a background of high ionic strength (50 mM CaCl2), the observed emf changes less than 2 mV upon a thousandfold change in the concentration of HCl (filled triangles), whereas similar measurements without the CaCl2 background yielded emf changes of more than 100 mV (filled circles). Note that the difference in the potentiometric responses cannot be explained by liquid junction potentials between the sample and the adjacent bridge electrolyte solution, as illustrated by the lack of a potentiometric response to HCl in solutions without the CaCl2 background when a free-flow double-junction reference electrode was used (open circles).

These potentiometric responses are all consistent with electrostatic screening of ion access into the pores of the nanoporous glass plugs, as is similarly known, e.g., for ion exchange resins, nanoporous opal films, nanopores, and nanotubes. Access of ions into and diffusive transport of ions through porous materials may be affected by electrostatic forces if the surface of these materials exhibit a surface charge due to electrically charged surface functional groups or adsorbed ions. If the sum of the Debye screening length of the electric field within the pores and the ion radius is much smaller than the pore size, ionic diffusion through the porous material is not significantly affected by electrostatic forces. However, when the pore size approaches the nanometer range, electrostatic interactions with the surface charge start to affect the presence of cations and anions with opposite effects. This results in
partial or even complete exclusion of ions of one sign from the porous material, an effect that is referred to as permselectivity. Since the electrochemical potential of any type of ion in the pores has to equal its electrochemical potential in the bulk of a solution in equilibrium with this porous material, it can be shown readily that an electrical phase boundary potential must develop at the interface between the bulk solution and the porous material.14

A lower pH reduces the surface charge and weakens electrostatic screening, while at higher pH, the negative surface charge on the glass surface due to deprotonation of silanol groups27,28 results in partial exclusion of anions from the glass nanopores. This is consistent with the effect of the ionic strength on the potentiometric response. Since the Debye screening length decreases with the ionic strength,29,30 the permselectivity of nanoporous materials is lost at high ionic strengths.15,16,20,26,31,32 This explains the different potentiometric pH responses in absence and presence of a CaCl2 background, as shown in Figure 2.

To further test the consistency of this model with experimental observations, the potentiometric responses of reference electrodes with nanoporous glass plugs to solutions of different metal chlorides were determined. Figure 3 shows that the KCl and NaCl responses are identical within error, giving no evidence for specific interactions of the monovalent cations K+ and Na+ with the glass surface. In an intermediate range from 1.0 mM to 30 mM, the KCl and NaCl responses are close to the theoretical (Nernstian) response that is expected for the permselective population of the nanopores with monocations. Also, as expected for an increasingly shorter Debye screening length at high ionic strength, the measured emf reaches a plateau at high KCl and NaCl concentrations. Similar observations were made for the CaCl2, but the response slope in the 1.0 mM to 30 mM range was only half as large as for NaCl and KCl. This is indeed expected in the case of permselective cation transfer into the glass nanopores considering the inverse relationship of the phase boundary potential change and the charge number of the cation.

As for the HCl response shown in Figure 2 too, the high ionic strength provided by a 1.0 M LiOAc background eliminated the responses to NaCl, KCl, and CaCl2 (Figure 4A), which is again consistent with the electrostatic screening model. Use of a more dilute ionic background of 1.0 mM LiOAc to provide a well-defined phase boundary potential restores the response to NaCl, KCl, and CaCl2 but again confirms the overall low level of ion selectivity (Figure 4B).

However, the H+ response stands apart from the responses to the two monovalent cations Na+ and K+, which is not surprising given the specific interaction of H+ with deprotonated surface groups on glass.

Electrostatic screening effects at the interface between sample solutions and the nanoporous salt bridge plugs are consistent with the dimensions of the nanopores. The Debye lengths in 0.001 and 1.0 M LiOAc are 9.6 and 0.30 nm,29,30 respectively. The former is much larger than the ionic radii of H+, Na+, K+, Ca2+, and Cl−, which are all less than 1.0 nm.33 Moreover, the Debye length in the 0.001 M LiOAc solutions is also substantially larger than the average pore size of the porous glass plugs used in this study, which was 4.0 nm.11 Consequently, electrostatic screening effects are to be expected.

Further insight into the effect of electrostatic screening on the ion transport through the nanoporous glass plugs was gained from electrical resistance measurements. For this purpose, a reference electrode with a nanoporous glass plug filled with 1.0 M LiOAc/1.0 mM LiCl and an inner filling solution of the same composition was inserted into a stirred solution with a much lower ionic concentration (1.0 mM LiOAc/1.0 mM LiCl). As Figure 5 shows, the electrical resistance of the nanoporous glass plug remained steady over 24 h at 5.8 ± 0.8 kΩ. Note that if free ion transport from the plug into the 1.0 mM LiOAc solution had gradually depleted the LiOAc in the nanoporous plug, the electrical resistance should have gradually increased over the time frame of several hours that is necessary for diffusion through a plug of 3 mm thickness. Moreover, the measured value of the electrical resistance in this experiment is much closer to the 2.1 ± 0.1 kΩ resistance of a nanoporous glass plug filled with 1.0 M LiOAc/1.0 mM LiCl solution when in contact on both sides with 1.0 M LiOAc/1.0 mM LiCl than to the 166 ± 6 kΩ resistance of a nanoporous glass plug filled with 1.0 mM LiOAc/1.0 mM LiCl in contact on both sides with 1.0 mM LiOAc/1.0 mM LiCl. This suggests that even after 24 h of exposure on one side to 1.0 mM LiOAc/1.0 mM LiCl, the plug which was filled originally 1.0 M LiOAc/1.0 mM LiCl, is still filled.

Figure 3. Effect of CaCl2, NaCl, and KCl on the potentiometric response of reference electrodes with nanoporous glass plugs as a function of the ionic strength.

Figure 4. Ion selectivity of the HCl, CaCl2, KCl, and NaCl responses of reference electrodes with a nanoporous glass plug in a background of (A) 1.0 M LiOAc and (B) 1.0 mM LiOAc.
predominantly with this solution of much higher concentration. This is consistent with an interfacial layer at the water/porous glass interface that inhibits anion transfer to a large extent by electrostatic screening.

A look at the recently published literature shows that reference electrodes with nanoporous glass plugs are not only used frequently for measurements with aqueous samples but are also very popular for measurements in organic solvents such as acetonitrile,34 propylenecarbonate,35 methanol,36 dichloromethane,37 and ionic liquids.38 This prompted us to investigate the performance of reference electrodes with nanoporous glass plugs also with acetonitrile as a representative organic solvent. To assess the potential contribution of the nanoporous glass plugs, the peak potential in the oxidation of decamethylferrocene, Me10Fc, in a cyclic voltammogram (CV) was measured with respect to a reference electrode with a nanoporous plug and an inner filling solution containing 10.0 mM AgNO3 and 100.0 mM tetraethylammonium perchlorate (NBu4ClO4) in acetonitrile. The Me10Fc+/Me10Fc couple was chosen because it is known to be minimally affected by the sample composition.39,40 For comparison and to look at the aqueous experiments performed for Figure 2, the peak potential of the Me10Fc oxidation was also determined with respect to a free-flow double junction electrode, for which only a conventional liquid junction potential is expected at the interface to the sample. For the latter purpose, a reference electrode with a nanoporous plug was placed into a pipet filled with an acetonitrile solution containing 100 mM NBu4ClO4 as the electrolyte solution. When the thus prepared double junction electrode was placed into samples, it was ensured that a very small flow of the 100 mM NBu4ClO4 into the sample occurred.

As expected, in the free flow setup, the potential of the reference electrode was only minimally affected by the concentration of the supporting electrolyte (Figure 6, empty circles). However, when the nanoporous plugs were directly in contact with the sample, a change in the peak potential of the Me10Fc oxidation of 20 mV was observed upon stepwise dilution of the supporting electrolyte from 100 to 6.25 mM. This finding confirms electrostatic screening also in acetonitrile solution, despite the fact that the pK values are well-known to be much higher in acetonitrile than in water,41 making it harder to ionize the glass surface in this solvent.

The effect of CF3COOH, on the potential of reference electrodes was investigated as well. CF3COOH is commonly used to change the pH of organic solutions in order to probe the pH dependence of redox potentials and elucidate the mechanism of electron transfer reactions.42–44 Such studies would be seriously compromised if the potential contribution of the reference electrode were affected by addition of CF3COOH but changes observed in the CVs were mistakenly interpreted as changes in the redox potentials of an electroactive species caused by the involvement of protons in the electron transfer step.

As can be seen from Figure 7, the reference electrodes with nanoporous glass plugs show permselectivity for CF3COOH at low ionic strength. Addition of CF3COOH to a solution that does not have a sufficiently high concentration of supporting electrolyte (6.25 mM) causes significant undesirable changes in the reference potential (Figure 7A). However, by increasing the concentration of supporting electrolyte or avoiding direct contact between the porous plug and the sample, the changes in the reference potential during the measurement can be minimized (Figure 7B). As in the case of the experiments with aqueous solutions, the potential changes at low ionic strengths can be explained by anion exclusion and formation of a charge separation layer at the interface of the sample and the nanoporous glass plug.

CONCLUSIONS

In this work, we demonstrated that the porous glass plugs frequently used to provide an interface between reference electrodes and samples can cause unwanted variations in reference potentials. Repulsion forces between freely dissolved anions and the negative charges of the nanopore surfaces have been recognized as the source of error. Not only at low but even at moderately high ionic strengths, the Debye length exceeds the radius of the pores, resulting in anion exclusion from the porous plugs and formation of a charge separation layer at the interface of the porous glass and the sample. This effect occurs both with aqueous and organic solutions. The potential of the reference electrodes with nanoporous glass plugs is sample independent only in solutions with comparatively high ionic strength, and the use of a highly concentrated salt bridge electrolyte alone does not prevent...
measurement errors. In situations where modifying the sample composition to achieve a high ionic strength is not possible, the free-flow double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.

While we emphasize here the problems that can arise when using reference electrodes with nanoporous glass plugs, it is evident that reference electrodes with nanoporous plugs prepared from other materials may also be affected by the same problem if they have surfaces with ionizable groups. For example, some of the problems observed by Illingworth with a double-junction setup is preferable. Electrostatic theory suggests that, alternatively, micro- rather than nanoporous plugs may be used to avoid unwanted sample dependencies of the reference potential.


Supporting Information

Reference Electrodes with Salt Bridges Contained in Nanoporous Glass:
An Underappreciated Source of Error

Maral P.S. Mousavi and Philippe Bühlmann*

Department of Chemistry, University of Minnesota, 207 Pleasant Street South East, Minneapolis, Minnesota 55455, United States
In this study, we demonstrated that using nanoporous glass plugs in reference electrodes can result in unwanted variations in the reference potential. Reference electrodes with nanoporous glass plugs, either obtained commercially or prepared in house, are very common. In the brief period from January 2012 to May 2013 alone, more than 70 publications in various journals, listed below, explicitly reported using reference electrodes equipped with Vycor glass plugs.\textsuperscript{1-70} Since many publications from the same time period described the use of reference electrodes of an unspecified nature, the actual number of studies for which reference electrodes with nanoporous glass plugs were used is likely much larger.