

Spontaneous Mesoporosity-Driven Sequestration of Ionic Liquids from Silicone-Based Reference Electrode Membranes

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ABSTRACT

Nanopore-driven sequestration of ionic liquids from a silicone membrane is presented, a phenomenon that has not been reported previously. Reference electrodes with ionic liquid doped polydimethylsiloxane (PDMS) reference membranes and colloid-imprinted mesoporous carbon (CIM) as solid contact are not functional unless special attention is paid to the porosity of the solid contact. In the fabrication of such reference electrodes, a solution of a hydroxyl-terminated silicone oligomer, ionic liquid, crosslinking reagent and polymerization catalyst is deposited on top of the carbon layer, rapidly filling the pores of the CIM carbon. The catalyzed polymerization curing of the silicone quickly results in crosslinking of the hydroxyl-terminated polydimethylsiloxane oligomers, forming structures that are too large to penetrate the CIM carbon pores. Therefore, as solvent evaporation from the top of freshly prepared membranes drives the diffusional transport of solvent towards that membrane surface, the solvent molecules that leave the CIM carbon pores can only be replaced by the ionic liquid. This depletes the ionic liquid in the reference membrane that overlies the CIM carbon solid contact and increases the membrane resistance by up to three orders of magnitude, rendering the devices dysfunctional. This problem can be avoided by pre-saturating the CIM carbon with ionic liquid prior to the deposition of the solution that contains the silicone oligomers and ionic liquid. Alternatively, a high amount of ionic liquid can be added into the membrane solution to account for the size-selective sequestration of ionic liquid into the carbon pores. Either way, a wide variety of ionic liquids can be used to prepare PDMS-based reference electrodes with CIM carbon as a solid contact. A similar depletion of the K^+ ionophore BME-44 from ion-selective silicone membranes was observed too, highlighting that the depletion of active ingredients from polymeric ion-selective and reference membranes due to interactions with high surface area solid contacts may be a more common phenomenon that so far has been overlooked.

Conventional reference electrodes such as the well-known Ag/AgCl electrode typically contact the sample through a salt bridge that contains concentrated aqueous KCl solution to minimize the liquid junction potential at the interface to the sample and provide a sample-independent reference potential.¹⁻⁵ A salt bridge, however, has some drawbacks, such as the need for refilling and the risk of cross contamination of the electrolyte of the bridge and the sample solution.⁶⁻¹⁰ To address this problem, solid-contact reference electrodes have been developed that comprise a polymeric membrane doped with a hydrophilic or moderately hydrophobic salt or an ionic liquid that slowly dissolves into the sample.¹¹⁻¹⁵ Mechanistically, there is a difference between the hydrophilic salts that have very low solubilities in the polymeric membrane, and more hydrophobic salts and ionic liquids.¹⁶⁻²² The latter partition between the reference membrane and the aqueous sample, thereby controlling the phase boundary potential at the interface between the reference membrane and the aqueous phase as long as samples do not contain high concentrations of hydrophobic ions.

Ionic liquid doped reference membranes are prepared by blending an ionic liquid with the same type of polymeric matrixes as are commonly used for ion-selective electrodes.²³⁻³⁰ In particular, the popular poly(vinyl chloride) (PVC) has been used repeatedly for this purpose.^{26-28, 31-35} To meet the requirement of ion mobility, a significant fraction of the weight of these membranes is made up of plasticizer. However, plasticizers may gradually leach out from the membrane to the sample, which is not suitable for many applications, such as for implantation into living tissue.³⁶⁻⁴⁰ To address this concern and because a range of biocompatible silicones are commercially available,⁴¹⁻⁴³ we previously developed ionic liquid reference electrodes prepared with silicone matrixes.^{24, 44}

We found that from among seven commercially available silicone materials, only poly(3,3,3-trifluoropropylmethoxysiloxane) doped with the ionic liquid 1-methyl-3-alkylimidazolium bis(trifluoromethylsulfonyl)imide worked well as a membrane matrix for reference electrodes. The other six silicones were suspected to work poorly, mainly because of the limited miscibility between the ionic liquid and the polymer matrix, as shown by differential scanning calorimetry.²⁴ This explanation was consistent with the minimal reduction of the electrical resistance caused by addition of ionic liquid into the silicone matrixes that performed poorly. Notwithstanding, the similarity of the polymer backbones of the tested silicone matrixes made the results surprising and left a suspicion that there might be other factors at play too.

In this work, we report on reference membranes prepared from a well-characterized hydroxyl-terminated polydimethylsiloxane (PDMS-OH) oligomer. Unlike the commercial self-curing silicones used in prior work, this silicone does not contain any inorganic fillers that might affect the performance of reference membranes. Moreover, while the exact composition of commercial silicone caulks and sealants is not known and can only be inferred from materials safety data sheets, we had a precise knowledge of the concentration and nature of the crosslinker reagent and the catalyst used to prepare the reference membranes.

As in the earlier work, reference electrodes were prepared with ionic-liquid-doped silicone membranes and colloid-imprinted mesoporous carbon (CIM) as a solid contact, which provides a large double layer capacitance and, thereby, very small long-term emf drifts.^{13, 31, 45-48} Only reference membranes that contained more than 20 wt % ionic liquid with respect to the amount of PDMS-OH provided good potential stability and the desired independence of the half-cell potential from the sample concentration. We show here that the poor performance of reference membranes with insufficient amounts of ionic liquids is caused by selective ionic liquid sequestration into the

pores of the CIM carbon. This is the first documented example in which contact with a high surface area solid contact material has resulted in the depletion of an active ingredient from a polymeric membrane used in potentiometric measurements. However, we also have data that show similar depletion of an ionophore by adsorption onto a high surface carbon.

EXPERIMENTAL SECTION

Materials. Hydroxyl-terminated poly(dimethylsiloxane) (PDMS-OH, $M_n \sim 110,000$), KCl, trifluoroacetic acid, and vinyltriacetoxysilane were purchased from Sigma-Aldrich (St. Louis, MO, USA) and the ionic liquids 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_{10}mim^+][NTf_2^-]$), 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_{12}mim^+][NTf_2^-]$), 1-methyl-3-octadecylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_{18}mim^+][NTf_2^-]$), trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ($[P_{6,6,6,14}^+][NTf_2^-]$) from Iolitec (Tuscaloosa, AL, USA). 1-Dodecyl-3-methylimidazolium bis(pentafluoroethanesulfonyl)amide $[C_{12}mim^+][C_2N_2^-]$ was prepared by metathesis from 1-dodecyl-3-methylimidazolium bromide and lithium bis(pentafluoroethanesulfonyl)imide.^{49, 50} All ionic liquids were washed 10 times for purification before use (see Supporting Information for details). Graphite rods were purchased from GraphiteStore (Northbrook, IL, USA). Aqueous solutions were prepared with deionized and charcoal-treated water ($>18\text{ M}\Omega/\text{cm}$ specific resistance) obtained with a Milli-Q Plus reagent-grade water system (Millipore, Bedford, MA, USA). The CIM carbon was synthesized as reported previously.³¹

Electrode Fabrication. To prepare reference electrode membranes, 250 mg of the PDMS-OH (250 mg), ionic liquid (multiples of 12.5 mg), trifluoroacetic acid (125 mg) and vinyltriacetoxysilane (30 mg) were dissolved in 1 mL of toluene and stirred with a magnetic stir bar for 30 minutes. Note that throughout this work weight percentages of ionic liquid are reported

relative to the amount of PDMS-OH and not the total weight of the cured membranes. Electrodes were prepared by insertion of a graphite rod (outer diameter 0.235 mm) into a glass tube (inner diameter 0.235 mm) and filling of the gap between the graphite and the tube with aqueous 60 wt % Teflon dispersion (purchased from Sigma-Aldrich, St. Louis, MO, USA), followed by drying at room temperature overnight. The graphite surface exposed at the end of the tube was then polished with sandpaper (starting with 300 grit and finishing with 1500 grit) and rinsed first with water and then ethanol, followed by drying with a stream of argon. CIM carbon films were made by mixing 100 mg of CIM carbon powder with 0.1 mL of the 5 wt % Teflon dispersion, followed by roller pressing this blend until a thickness of 120 μm was obtained. A hole punch was then used to cut out circular pieces of the CIM carbon films (diameter of 5.6 mm, ≈ 5 mg). A CIM carbon film was placed on top of the graphite rod, and 50 μL of toluene was added onto the CIM carbon film and the exposed end of the glass tube to avoid bubble formation on the CIM carbon in the subsequent step. Then, a total of 200 μL of the reference membrane solution was added onto the CIM carbon film. The ionic liquid doped membranes of the thus prepared reference electrodes were then cured in an oven (semi-closed environment) at 55 $^{\circ}\text{C}$ for 24 h in the presence of a beaker with aqueous saturated NaBr solution to maintain a humidity of 50%.⁵¹

In some cases, the CIM carbon layer was presaturated with an ionic liquid. In those cases, a solution of 7.3 mg ionic liquid in toluene was applied onto the CIM carbon film and the toluene was allowed to evaporate prior to the application of the reference membrane solution,

For comparison, PDMS-OH membranes doped with ionic liquids were also mounted into Philips electrode bodies⁵² (Glasbläserei Möller, Zürich, Switzerland) with an inner filling solution. For this purpose, 1 mL of toluene solutions of the reference membrane components were poured into circular Teflon Petri dishes of 25 mm diameter and cured as described above for the solid

contact electrodes. A hole punch was used to cut circular pieces from these master membranes for mounting into the electrode bodies.

All electrodes were conditioned for 24 h in 1 mM KCl saturated with the respective ionic liquid.

Potentiometric Measurements. Potentiometric measurements were performed with an EMF 16-channel potentiometer (Lawson Labs, Malvern, PA, USA) controlled by 1.03 EMF Suite software (Fluorous Innovation, Arden Hills, MN, USA). A double-junction reference electrode (DX200, Mettler Toledo, Switzerland; AgCl-saturated 3.0 M KCl as inner reference electrolyte and 1.0 M LiOAc as bridge electrolyte) was used as a conventional external reference electrode. All emf values were corrected for the liquid junction potential at the double-junction reference electrode by using the Henderson equation.⁵³ Activity coefficients were calculated based on a two-parameter Debye-Hückel approximation.⁵⁴

IR Spectroscopy. Attenuated Total Reflection Infrared (ATR IR) spectroscopy measurements were performed on a Bruker Alpha Platinum ATR spectrometer with a built-in diamond attenuated total reflection set up.

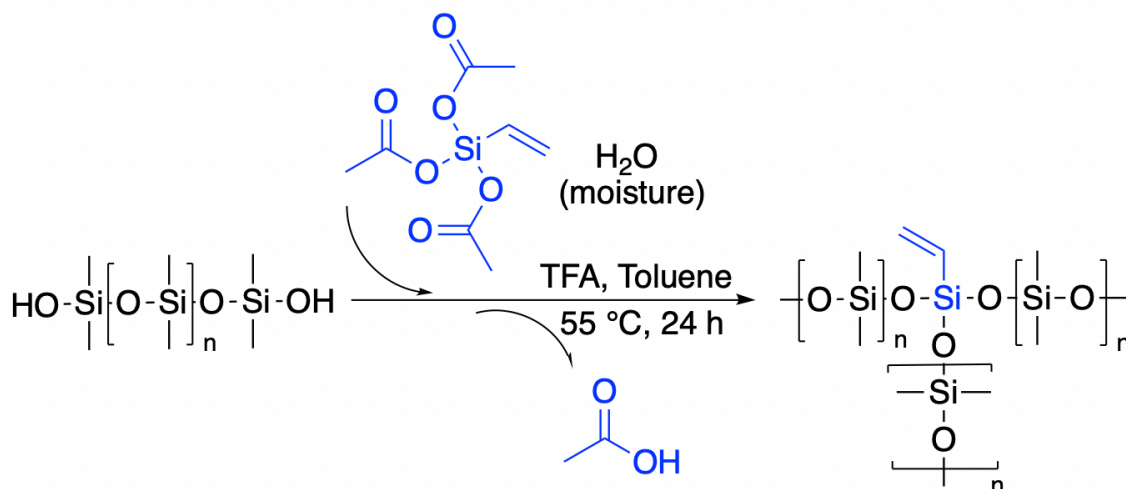
DSC: A TA Instruments Q1000 DSC (New Castle, DE) differential scanning calorimeter with a liquid nitrogen cooling system was used for all DSC measurements. The capped sample pans were thermally equilibrated at 40 °C for 1 min. Then samples were scanned to –150 °C and back to 40 °C, with a consistent 1 °C/min heating and cooling rate. Midpoints of transition zones were used to determine glass transition temperatures.

RESULTS AND DISCUSSION

Silicone Materials and Reference Membrane Fabrication. The PDMS-OH oligomer used in this work is a large molecular weight silicone with terminal hydroxyl groups. It was crosslinked with the acetate-evolving crosslinker vinyltriacetoxysilane, a process catalyzed by trifluoroacetic acid (see Scheme I), which was chosen because of its high volatility. While other catalysts for this reaction would remain in the reference membrane and could affect its performance, trifluoroacetic acid evaporates readily, and remaining traces may leave the membrane upon contact with water by preferential distribution into the aqueous phase.

The curing of this silicone depends on the temperature, membrane thickness, and ambient humidity. With 50 mg of the custom PDMS-OH applied to the CIM carbon and the surrounding exposed end of the glass tube forming the electrode body (resulting in a thickness of the reference membrane of approximately 250 μm), the membranes were stored for curing at 55 °C and an ambient humidity of 50% for 24 h. We found these conditions to result in faster curing for membranes of this thickness than curing at room temperature or ambient humidity. In order to further improve the removal of catalyst and any byproducts of the crosslinking process, the membranes were equilibrated prior to use for 24 h with 1 mL KCl solution saturated with the respective ionic liquid. Note that a glass tube was chosen as the electrode body because the in-situ curing of the silicone not only crosslinks the polymer but also covalently attaches the reference membrane to the tube by reaction with hydroxyl groups on the surface of the glass. This provides a strong mechanical seal and prevents electrical leakage currents.

Scheme 1. Curing chemistry of PDMS-OH as performed in this work.



High Electrical Resistance of Reference Electrode Membranes Doped with 5 wt % of Ionic Liquids. To verify whether reference electrodes with CIM carbon solid contacts and ionic liquid doped custom PDMS-OH membranes exhibit the desired independence of the half-cell potential on the sample composition, membranes were doped with 5 wt % of the ionic liquids $[\text{C}_{12}\text{mim}^+][\text{NTf}_2^-]$, $[\text{C}_{18}\text{mim}^+][\text{NTf}_2^-]$, or $([\text{P}_{6,6,6,14}^+][\text{NTf}_2^-])$ with respect to the amount of PDMS-OH. However, none of these membranes were found to be suitable for use in reference electrodes. All electrodes exhibited unexpectedly high resistances of the same magnitude as PDMS-OH membranes that were not doped with an ionic liquid (see Table 1). In theory, perfectly pure silicone membranes contain no ionic species and should, therefore, exhibit an infinitely high electrical resistance to direct current. Therefore, the finite resistance of the undoped PDMS-OH membranes clearly indicates the presence of ionic impurities, although the very high resistance of $7.5 \pm 4.6 \text{ G}\Omega$ suggests that the concentration of impurities in these reference membranes is very low. The high resistance of the reference membranes doped with 5 wt % ionic liquid implies that only a very

small fraction of the ionic liquid used for the preparation of these reference membranes is freely dissolved in the silicone matrix.

Table 1. Electrical resistances of reference electrode membranes doped with different amounts of ionic liquids ($n=3$), as measured with solid contact electrodes and CIM carbon contacts. For comparison, the resistance (Ω) of membranes free of ionic liquid was $10^{9.5 \pm 0.4}$.

ionic liquid/ logarithm of resistance (Ω)	[C ₁₀ mim ⁺] [NTf ₂ ⁻]	[C ₁₂ mim ⁺] [NTf ₂ ⁻]	[C ₁₈ mim ⁺] [NTf ₂ ⁻]	[P _{6,6,6,14} ⁺] [NTf ₂ ⁻]	[C ₁₂ mim ⁺] [C ₂ N ₂ ⁻]
5 wt % ^a	–	9.0 ± 0.0	10.0 ± 0.1	9.2 ± 0.0	-
20 wt % ^a	6.4 ± 0.2	6.8 ± 0.1	7.5 ± 0.4	6.5 ± 0.4	7.7 ± 0.2
5 wt % ^{a,b}	6.6 ± 0.3	6.7 ± 0.3	7.4 ± 0.4	6.8 ± 0.3	7.3 ± 0.4

^a With respect to PDMS-OH. ^b CIM carbon presaturated with ionic liquid.

The electrical resistance of reference membranes doped with three different ionic liquids decreased by more than two orders of magnitude when the amount of ionic liquid used for the preparation was increased by a factor of four from 5 to 20 wt % (see Table 1). Clearly, this cannot be explained by a proportional increase in electrolyte concentration in the reference membrane.

Notably, very different results were obtained when PDMS-OH membranes were doped with 5 to 25 wt % [C₁₂mim⁺][NTf₂⁻] and mounted into electrode bodies with an inner filling solution (see Table S1). In that case, the electrical resistances of the reference membranes did not vary with the ionic liquid content and were of the same order of magnitude as for the corresponding solid contact electrodes with the PDMS-OH membranes doped with 20 wt % [C₁₂mim⁺][NTf₂⁻]. The small difference in resistance between the two cases was the result of slightly different membrane cross sections and thicknesses.

As shown in the following, all these findings can be explained by size-selective partitioning of the ionic liquids into the pores of the CIM carbon.

Size-Exclusive Separation of Ionic Liquid into CIM Carbon Pores. The average molecular weight, M_w , of the PDMS-OH used in this work was 110,000 g/mol, which corresponds to 1410 monomer units per molecule. Light scattering measurements of PDMS solutions in toluene (the same solvent as used for the preparation of reference membranes in this work) have shown that the z-mean-square radius of gyration (R_g) of the PDMS molecules in nanometers can be calculated from the empirical expression $0.0808 M_w^{0.45}$, where M_w is the molecular weight.⁵⁵ Using this expression, an R_g value of 15 nm is obtained for the PDMS-OH used in this work. This shows that the size a PDMS-OH molecule in a random coil conformation is smaller than the size of the CIM carbon pores, which is 22–32 nm, as detected by N₂ gas sorption analysis (see Figure S1). However, in the membrane curing process, silicone chains crosslink quickly, resulting in polymer aggregates that are too large to enter the pores of the CIM carbon (see Figure S2). Indeed, even when only three PDMS-OH molecules are crosslinked to one another, the resulting aggregate has an R_g of 25 nm, which is already larger than some of the smaller pores of the CIM carbon used in this work, and an aggregate of six PDMS-OH molecules has an R_g of 34 nm, which is larger than the majority of pores.

In contrast, ionic liquid molecules are small enough to penetrate CIM carbon pores. Because in the fabrication process 67 wt % of the PDMS-OH/ionic liquid solution applied to the CIM carbon is the solvent toluene itself, the pores of the CIM carbon are filled in the initial phase of fabrication with a large amount of toluene. However, as toluene evaporates in the curing process from the system, the ionic liquid enters the CIM carbon pores, replacing the toluene molecules, while the PDMS-OH aggregates are getting larger and larger and due to size exclusion cannot

enter those pores. During the membrane curing process, this results in ionic liquid depletion in the reference membrane that overlies the CIM carbon, explaining the high observed device resistances.

To confirm this explanation, different amounts of ionic liquid (0 to 25 wt % with respect to the amount of PDMS-OH) were added into the toluene solution used to prepare reference membranes, and reference membranes were prepared on electrodes with and without a CIM carbon film. ATR IR spectrometry was used approximately one day after the completion of the silicone curing to determine the ionic liquid content in the near-surface region of these reference membranes. In the membranes that had never contacted CIM carbon, the combined absorbance of the two peaks at 1330 and 1350 cm^{-1} (the out-of-phase and in-phase SO_2 stretching vibrations, respectively)⁵⁶ is proportional to the amount of the ionic liquid $[\text{C}_{12}\text{mim}^+][\text{NTf}_2^-]$ (see Figure 1). On the other hand, membranes that were prepared on top of a CIM carbon solid contact contained significantly less ionic liquid. In particular, preparation of reference electrodes with small total amounts of ionic liquid led to only very small concentrations of the ionic liquid in the membrane overlying the CIM carbon, consistent with nearly quantitative ionic liquid sequestration into the CIM carbon pores. For reference membranes prepared with higher total amounts of ionic liquid, the absorbance at 1350 cm^{-1} increased with a slope nearly identical to that for the electrodes without CIM carbon, suggesting that for each of the membranes in contact with the CIM carbon a constant amount of ionic liquid was removed from the reference membranes by sequestration into the CIM carbon pores.

The intersection of the black and red curves in Figure 2 shows that the amount of ionic liquid absorbed by 5.0 mg CIM carbon reaches an upper limit when the silicone membrane was prepared using 12 mg of ionic liquid (corresponding to approximately 18 wt % of ionic liquid with respect to the amount of PDMS-OH). The red curve of this figure shows that the electrical

resistance of the reference membranes decreases rapidly by three orders of magnitude when the CIM carbon pores are filled with the ionic liquid and the excess ionic liquid quickly increases the ionic liquid concentration in the reference membrane, a transition that looks like the endpoint in a titration curve.

Further evidence for the filling of the CIM carbon pores by the ionic liquid is also obtained from a quantitative comparison of the amount of ionic liquid sequestered into the pores, as determined from Figure 2, and the pore volume independently determined by N₂ gas sorption analysis of CIM carbon (see Figure S1). We found that the ionic liquid completely fills the CIM carbon pores, as opposed to only adsorbing onto the pore walls. A maximum of 7.2 mg ionic liquid was absorbed by 5.0 mg of CIM carbon (Figure 2), which matches quite well the maximum uptake of 9.1 mg of ionic liquid into 5.0 mg of CIM carbon as predicted from the total pore volume of CIM carbon and the density of the ionic liquid (see the Supporting Information). The slightly smaller than predicted uptake of the ionic liquid into the CIM carbon may be related to the presence of pores too small for [C₁₂mim⁺][NTf₂⁻] to enter. Notably, the mass of a hypothetical monolayer on the mesoporous CIM carbon walls would be only 2.2×10^{-3} mg (see the Supporting Information).

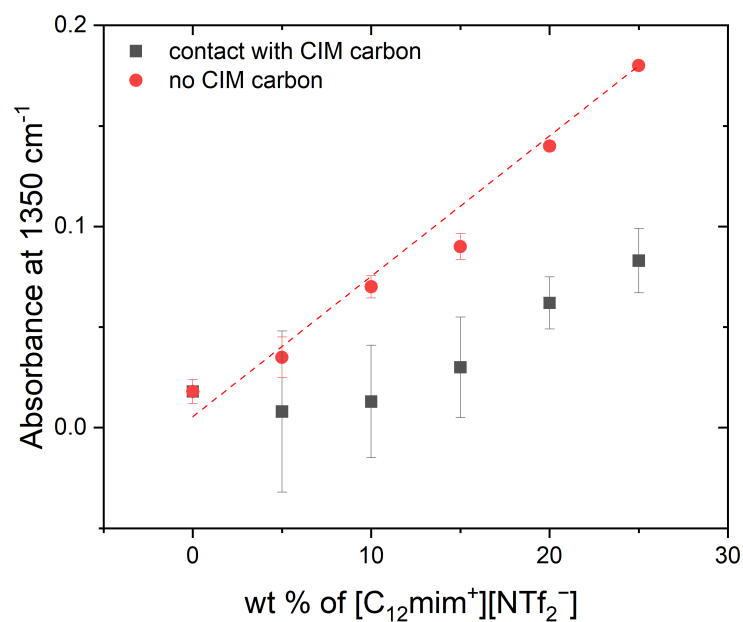


Figure 1. Combined ATR IR absorbance at 1330 and 1350 cm^{-1} of reference membranes that never had contact with CIM carbon (●) and membranes prepared in contact with CIM carbon (■), for varying weight percentages of $[C_{12}mim^+][NTf_2^-]$ with respect to the amount of PDMS-OH in the reference membrane solutions that were applied to electrodes with and without CIM carbon solid contacts. For full spectra, see Figure S3 of the Supporting Information.

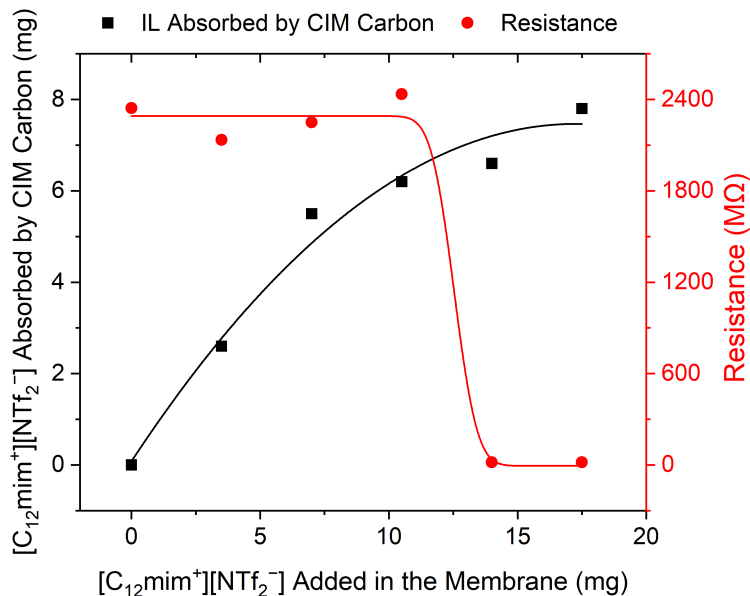


Figure 2. Amount of $[\text{C}_{12}\text{mim}^+][\text{NTf}_2^-]$ absorbed from solid contacted reference membranes into the 5.0 mg CIM carbon of one solid contact electrode, along with the electrical resistance of reference electrodes with a CIM carbon solid contact and membranes prepared with varying total amounts of $[\text{C}_{12}\text{mim}^+][\text{NTf}_2^-]$.

As discussed above, reference electrodes with membranes in which the ionic liquid is *not* depleted can be prepared by depositing onto the CIM carbon a toluene solution containing a high content of ionic liquid besides the PDMS-OH, crosslinker, and catalyst. An alternative method to prepare functional reference electrodes is to presaturate the CIM carbon pores with ionic liquid before application of the toluene solution. As shown in Table 1, devices were prepared by presaturating 5.0 mg of CIM carbon with 7.3 mg of any of the five ionic liquids used in this study, followed by application of a toluene solution containing the PDMS-OH, crosslinker, catalyst, and only 5 wt % of the respective ionic liquid. Upon membrane curing, these devices exhibited resistances very similar to those prepared with CIM carbon with empty pores and toluene solutions containing 20 wt % ionic liquid. We have not observed any differences in the performance of reference electrodes prepared with or without presaturation. However, presaturation of the CIM

carbon with an ionic liquid may reduce the time required for device fabrication as the need for toluene diffusion out of and ionic liquid diffusion into the CIM carbon pores after application of the toluene solution is eliminated.

Dependence of the Half-Cell Potential of Optimized Reference Electrodes with Different Ionic Liquids. The performances of reference electrodes based on the ionic liquids used in this work have previously been reported for devices without a porous solid contact and have been found satisfactory for electrolyte concentrations as they are typical in biological samples.²⁴ Therefore, we focused in this work on the response of our reference electrodes to KCl. This minimized any contributions from the liquid–liquid junction potential at the conventional free-flowing double-junction reference electrode with respect to which the emf of the solid-contact reference electrodes were measured.¹ Moreover, K^+ is the least hydrophilic inorganic cation common in clinical chemistry samples, and, therefore, the most likely one to interfere with an improperly working ionic liquid based reference electrode. For this work, emf responses were tested for K^+ activities that are an order of magnitude higher than what is found in human blood.

Table 2 and Figure S4 of the Supporting Information show that when the CIM carbon pores are filled with the ionic liquid, either by pre-saturating the CIM carbon film with ionic liquid or by incorporating a large amount of ionic liquid to the reference membrane, the KCl concentration of samples has no significant effect on the potential of the reference electrodes ionic liquid doped membranes. There are only minimal differences between the results for the five different ionic liquids, although $[C_{12}mim^+][NTf_2^-]$ and $[C_{18}mim^+][NTf_2^-]$ stand out as giving particularly good reproducibilities and small responses to KCl. Most importantly, this data confirms that a sufficient amount of ionic liquid overcomes the problem caused by sequestration of the ionic liquid into the mesoporous CIM carbon.

Table 2. Effect of KCl on the potential and resistance of ionic liquid based reference electrodes with a CIM carbon solid contact ($n=3$). All percentages of ionic liquid are given with respect to the amount of PDMS-OH.

ionic liquid ($n=3$)	20 wt % of ionic liquid		5 wt % of ionic liquid (CIM carbon presaturated)	
	slope K^+ (mV/dec) ^a	logarithm of resistance (Ω)	slope K^+ (mV/dec) ^a	logarithm of resistance (Ω)
[C ₁₀ mim ⁺][NTf ₂ ⁻]	1.4 ± 1.3	6.4 ± 0.2	0.3 ± 0.2	6.6 ± 0.3
[C ₁₂ mim ⁺][NTf ₂ ⁻]	0.6 ± 0.3	6.8 ± 0.1	0.7 ± 0.4	6.7 ± 0.3
[C ₁₈ mim ⁺][NTf ₂ ⁻]	0.4 ± 0.4	7.5 ± 0.4	0.4 ± 0.3	7.4 ± 0.4
[P _{6,6,6,14} ⁺][NTf ₂ ⁻]	2.2 ± 2.4	6.5 ± 0.4	-1.2 ± 0.9	6.8 ± 0.3
[C ₁₂ mim ⁺][C ₂ N ₂ ⁻]	1.5 ± 0.6	7.7 ± 0.2	-0.7 ± 0.5	7.3 ± 0.4

^a In the K^+ concentration range from 0.05 to 100 mM.

Phase Separation in Reference Electrode Membranes Doped with Ionic Liquid. Phase separation in ionic liquid doped reference membranes was previously implied as a potentially critical factor in determining the suitability of ionic liquid doped polymers in reference electrodes.²⁴ Moreover, we noted that when ionic liquid doped PDMS-OH membranes were cured at different temperatures, this affected the size of ionic liquid droplets seen by visible light microscopy and Raman imaging (see Figures S5–S7). Higher curing temperatures resulted in smaller ionic liquid droplets, presumably because faster crosslinking of the PDMS-OH hindered the formation of larger ionic liquid droplets. To further study this effect, we performed differential scanning calorimetry (DSC) on reference membranes prepared in contact with CIM carbon. For

the DSC analysis, pieces of these PDMS-OH membranes were removed from the underlying CIM carbon film.

For membranes doped with $[\text{C}_{12}\text{mim}^+][\text{NTf}_2^-]$ (5 wt %), the DSC result showed no phase separation, consistent with the high electrical resistance (see Table 3) and, therefore, depletion of ionic liquid due to contact with the CIM carbon. For the membranes with 20 wt % $[\text{C}_{12}\text{mim}^+][\text{NTf}_2^-]$ with respect to PDMS-OH, phase separation was observed by DSC (see Figures S8–S10); the glass transition temperature, T_g , of $[\text{C}_{12}\text{mim}^+][\text{NTf}_2^-]$ at 20 °C is a clear sign for phase separation of $[\text{C}_{12}\text{mim}^+][\text{NTf}_2^-]$ from the PDMS-OH.

This data demonstrates that phase separation in itself is not a sufficient criterion to predict whether an ionic liquid doped reference membrane can function properly in a reference electrode. As long as the solubility of the ionic liquid in the polymer is sufficiently high and, therefore, the electrical resistance is low, a reference membrane can perform satisfactorily even if it contains phase-separated ionic liquid droplets. Phase separation of the ionic liquid in the polymer is not necessarily undesirable. Indeed, phase-separated ionic liquids may help to increase the lifetime of such a reference membrane, as the phase-separated droplets may replenish the ionic liquid that is dissolved in the polymer as it is continuously leaching out of the reference membrane in its normal working mode. However, the observation of phase separation by either DSC or microscopy can

still be useful to explain why reference membranes with a particular ionic liquid perform poorly if that phase separation is an indication of a poor solubility of the ionic liquid in the polymer.

Table 3. Electrical resistances and phase separation of reference electrode membranes doped with different amounts of $[\text{C}_{12}\text{mim}^+][\text{NTf}_2^-]$ ($n=3$). Ionic liquid doped PDMS-OH membranes were fabricated on top of a CIM carbon film but then removed for DSC analysis.

ionic liquid amount ^a	logarithm of resistance (Ω)	phase separation
5 wt %	9.3 ($\pm$ 0.2)	no
20 wt %	7.2 ($\pm$ 0.1)	yes

^a With respect to PDMS-OH.

Notably, the depletion of active components from the polymeric membrane as a result of a solid contact material with high porosity and a large surface area is not limited to ionic liquid reference electrodes only. Indeed, this can also be a complication in the fabrication of ionophore-doped ISEs. For example, ISEs comprising ion-selective membranes in direct contact with gold solid contacts with 10 mmol/kg BME-44 as K^+ ionophore,⁵⁷ potassium tetrakis(4-chlorophenyl)borate as ionic sites (50 mol % with respect to the ionophore), and a PDMS-OH matrix (prepared with trifluoroacetic acid as catalyst and vinyltriisopropenoxysilane as crosslinker) showed a close to Nernstian response (62.7 mV/decade), a detection limit of approximately 0.001 mM and a good selectivity ($\log K_{\text{K,Na}}^{\text{pot}} \approx -3.0$). On the other hand, when sensing membranes of the same type were prepared with a CIM carbon solid contact, the detection limit for K^+ worsened to ≈ 0.1 mM, K^+ response slopes were only approximately half of the expected Nernstian value, and reliable selectivity coefficients could, therefore, not be determined. The very different behavior of these ISEs can be explained by adsorption of BME-44 onto the CIM carbon (for details, see the Supporting Information). While measuring adsorption of BME-44 from the a PDMS-OH

matrix onto CIM carbon cannot be easily observed directly, we equilibrated diethyl ether solutions of BME-44 with CIM carbon and observed a decrease of the ionophore concentration by UV-vis spectrometry due to adsorption onto the CIM carbon (Figure S11). Assuming Langmuir adsorption, the equilibrium constant for adsorption of BME-44 to CIM carbon was estimated from this data to be $6.2 \times 10^4 \text{ M}^{-1}$, which is of a similar order of magnitude as, for example, for the adsorption of pyrene derivatives from similar solvents onto graphene.⁵⁸ Notably, assuming a footprint of $4.5 \times 10^{-18} \text{ m}^2/\text{molecule}$, formation of a full monolayer of BME-44 onto 1.0 mg of CIM carbon would require 0.14 mg of BME-44. However, each solid contact ISE had been prepared with 1.0 mg CIM carbon and 0.1 mg BME-44, showing that the total surface area of the CIM carbon is sufficiently high to lead to ionophore depletion that affects the potentiometric performance. This problem may be correctable by using a larger amount of ionophore, but that evidently requires the producers of ISEs to be aware of the possibility for ionophore depletion due to interaction with the high surface area solid contact material.

CONCLUSIONS

Reference electrodes comprising silicone membranes doped with an ionic liquid are promising as miniaturized and biocompatible reference electrodes. This work demonstrates that when a mesoporous carbon is used as a solid contact for reference electrodes with in-situ cured ionic liquid silicone membranes, an unusual size-exclusive phase separation occurs. When the silicone precursor and ionic liquid are applied as a solvent solution onto the CIM carbon, the silicone rapidly crosslinks, forming much larger molecules, thus allowing only ionic liquid molecules to enter CIM pores as the solvent evaporates from the pores. Therefore, the reference membrane overlying the CIM carbon is depleted of ionic liquid, resulting in a high device resistance.

The high electrical resistance of the reference membrane can be overcome by pre-

saturating the CIM carbon with ionic liquid prior to silicone polymerization or by adding additional ionic liquid to the reference membrane. Either way, it is possible to prepare PDMS-OH-based reference electrodes using a wide range of ionic liquids, avoiding device deterioration during long term measurements. In view of wearable and implantable sensors, future work will have to confirm that this is still true in biological system, taking also into account possible effects of the released ionic liquids.

This is the first example for the sequestration of an active ingredient from a reference or ion-selective membrane into the solid contact material, but it appears very likely that this phenomenon may occur also in a variety of other circumstances. While we have only used CIM carbon for this work, it seems reasonable to expect similar effects also for other high surface carbon and non-carbon solid contact materials. Also, while this type of sequestration appears less likely for plasticized poly(vinyl chloride) membranes, it may also occur for other polymeric matrixes that are either applied in an already polymerized form or are prepared by in-situ polymerization, such as self-plasticizing polyurethanes, polyacrylates, and polymethacrylates. Finally, while the cause for sequestration in the PDMS-OH/ionic liquid case is size selectivity, another reason for sequestration can also be surface adsorption onto high surface solid contact materials. In particular, we have observed the loss of the K^+ ionophore from silicone sensing membranes due to adsorption onto CIM carbon solid contacts. As high surface area solid contact materials are gaining rapidly in popularity, consideration of such effects will be crucial to the optimization of device fabrication.

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NOTES

The authors declare the following competing financial interests: A.S., P.B., and the University of Minnesota (UMN) have a patent and a patent application (U.S. patent no. 9,874,539; US2020/059979) relating to the use of CIM carbon in ion-selective and reference electrodes. The UMN and the inventors are entitled to standard royalties should licensing revenue be generated from these inventions.

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SUPPLEMENTARY INFORMATION

CIM carbon synthesis, procedure for washing of ionic liquids, calculations for prediction of maximum amount of ionic liquid entering CIM carbon pores, assessment of the extent of adsorption of BME-44 to CIM carbon, sample dependence of the emf for PDMS-OH reference electrode membranes doped with different ionic liquids, N₂ gas sorption analysis of CIM carbon, DSC results, and visible and Raman images of PDMS-OH membranes comprising 5 wt % [C₁₂mim⁺][NTf₂⁻].

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TOC graphic

