A flexible all-inorganic fuel cell membrane with conductivity above Nafion, and durable operation at 150 °C

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1. Introduction

The thermodynamic advantages of converting chemical fuel energy to mechanical energy by “burning” in electrochemical cells instead of in heat engines, are as difficult to achieve as they are easy to discuss [1–3]. Central to the problem are the energy losses incurred in the reduction of oxygen to water (or hydroxide ion) at the cathode [1] and in the transport of protons from anode to cathode, together with the materials problem of dealing with the intensely reactive peroxide radical generated in the oxygen reduction process [3–5]. The latter problem seems only to be dealt
with adequately by the expensive sulfonated polytetrafluoroethylene (i.e. Nafion-type) polymers [4,5] when in the highly hydrated condition also needed to maximize the conductivity [1,6]. Unfortunately this high hydration requirement limits the cell operation to temperatures below 100°C unless operated under pressure [7], and introduces a major water management problem due to the physics of facile proton transport that requires some 9–10 water molecules to accompany each proton in the passage from anode to cathode. The consequent cathode flooding must be relieved by back-pumping (ref. [8], reviews water management). The fuel cell powered cars currently under lease-testing on Japanese, European and American roads, are miracles of engineering—and are priced accordingly.

Considering these problems and the need to use highly purified fuels to avoid catalyst poisoning when operating at temperatures below 150°C, there have been many attempts to seek alternative electrolytes capable of operating efficiently at the higher temperatures. Broadly, these divide into high temperature polymer membranes and inorganic proton conductors, though attempts to raise the operating temperature of Nafion membranes by combination with phosphoric acid and polybenzimidazole have been reported [9,10]. Also operating temperatures have been raised by incorporation of inorganic components such as silica spheres [11], and exotic structures like mordenite [12]. Although moderately successful, none of the latter escape the high cost of the Nafion component.

The most competitive of the higher temperature polymer membranes all involve some form of polybenzimidazole saturated with phosphoric acid, for which a good review has been provided by Bjerrum and coauthors [13]. These will be discussed in more detail later in this paper in relation to the results of the present paper. Some mention should be made of the attempts to use the cations of protic ionic liquids as proton carriers capable of sustaining operating temperatures above 200°C. These may be both inorganic [14] or organic in nature [15]. The incorporation of the latter into sulfonated polyimide membranes with potentially very high service temperatures has been described by Lee et al. [16].

Solid silicophosphate electrolytes produced by sol–gel processes, can have high conductivities (10−2 S/cm at 20°C) and have been seen as a viable alternative to Nafion membranes on both cost and temperature range counts [17,18]. They have the advantage that organic molecules and solid acids may be incorporated into the inorganic networks to vary the properties. However, these membranes suffer from the onset of mechanical fragility during the fabrication process, becoming laced with cracks during escape of the water that is released in the curing process [17]. Another example is that by Matsuda et al. [19]. The conductivity of their sol–gel derived glassy material reached 10−2 S/cm without the need to add highly hydrated and temperature-sensitive solid acids as in the case of ref. [17]. Unfortunately, of the many studies of such phosphate–derivatized electrolytes, favored for their stability against reduction by hydrogen, we find very few reports of the actual incorporation into, and testing of, fuel cells. In this respect, the present contribution is unusual. In the comprehensive review by Zhang and Shen [3], little attention is given to phosphate or silicophosphate membranes, though a complex sulfonate–derivatized ceramic membrane described by Peled and coworkers [20] is recognized as promising — indeed these latter workers did report fuel cell tests, in addition to favorable conductivities. Despite open circuit voltages (OCVs) that were only 0.8 V, the maximum power outputs obtained were comparable with those we will report below. Many hybrid inorganic (siloxane) – organic phosphonic acid derivatized polymer membranes have been described, e.g. the work of Kato et al. [21], but these never achieve the conductivity levels that are needed and, again, fuel cell tests are rare (perhaps because good fuel cell performance is rare). An exception is the recent work of Zeng et al. on H3PO4 imbeded in mesoporous silica [22]. Although this membrane is inflexible and of limited conductivity, the current and power densities reported (>2Acm−2 and >500 mWcm−2) for single cells are impressive.

The advantages of both the above membrane types, Nafion-like polymers and >100°C stable silicophosphate and mesoporous silica compositions, may be combined if the silicophosphate or siloxyl links are introduced in a different manner, viz., starting from the quasi-solid product of the synthetic process used to make the “SiPOH” suspension whose outstanding performance, as a liquid electrolyte, we described in a recent contribution [23]. The new material is structurally quite different from the latter suspension, not only in the absence of P–O–Si bonds (as we show in our Discussion), but also in its physical state, which is a flexible solid. By having zero peroxide radical-sensitive C–C or C–H bonds, it is also distinct from the familiar elevated temperature membranes involving H3PO4-saturated polybenzimidazoles and derivatives [13] referred to further below.

In the present contribution we provide conductivity data for this new material and, more importantly, show how the new material can serve as the membrane in simple H2/O2 fuel cells that can produce stable currents in excess of one amp/cm2 at temperatures up to at least 150°C [24].

2. Preparation and description of flexible inorganic (gel) material, and membrane

When the stable milky suspension that is the liquid electrolyte of ref. [23], is centrifuged for a long period, a thick paste, described as SiPOH, from which most of the unaltered phosphoric acid has been separated, is obtained. The exact composition of SiPOH is still unknown. It contains silicon in a six coordinated state, according to 29Si NMR spectroscopy (see below) and the X-ray diffractogram (see SI) indicates high disorder. According to ICP analysis of the material after washing with an unreactive solvent (pentafluoropropanol), it has an Si:P ratio of 1:4. When this paste is reacted with water (in which it dissolves completely), a floppy gel is formed on standing. An example would be the solution of 1.63 g of paste in 3 g of distilled water, from which the gel forms in 90 min or less. The initial gel is a mechanically frail material that shrinks away from a Teflon container and strengthens into a rubbery button (Fig. 1(b)) as water is removed by vacuum oven drying at 40°C. A modified version of the SiPOH paste preparation of ref. [23], in which the liberated HCl is collected in a novel internal chemical trap, is described in the S. I.

The weight loss vs time function for the gel formed from the initial solution of SiPOH, is shown in Fig. 1(a). It is seen to be rapid at first, but then to reach a constant mass. The low evaporation temperature was chosen to avoid the formation of any bubbles. In the process, some 90 wt% of the initial water content is lost.

This flexible material contains little or no free water because heating at 300°C is accompanied by a mass loss of only 10 wt% — and the weight of the dry (now crystalline, but hygroscopic) powder material remains almost unchanged when the temperature is raised to 600°C. As an additional measure of its stability, the gel-like material seems to be quite invariant with temperature up to 150°C (see Fig. 2 below). It has a yellowy color as seen in Fig. 1, but is colorless in other preparations. It is translucent rather than transparent, so must have some heterogeneity at the microscopic level. The calcined powder has an XRD pattern (see SI) that cannot be indexed to any known structure, and is distinct from any of the structures seen to result from calcination of the original SiPOH. The Si:P ratio must remain the same as that of the solid acid viz: 1:4 except for any excess H3PO4 retained in the unwashed SiPOH paste.
The detailed structure will be considered in the Discussion section. First we take advantage of the rubbery character to test its potential as a fuel cell membrane material.

3. Conductivity, fuel cell commissioning, and testing

The conductivity of the SiPOHgel material of Fig. 1(b) was measured on a sample cut from the anhydrous flexible button and dried 15 h in a vacuum oven at 40 °C before incorporation in the cell. The conductivity was determined using the same piston type cell with stainless steel electrodes, (mild spring compression for good electrode contact, all assembled under dry nitrogen), used in an earlier study of highly conducting rubbery polymers (protonated polydichlorophosphazenes), details of which are given in the SI. The complex impedance was determined using a Princeton Applied Research (PARSTAT 2273) potentiostat/galvanostat, modulation amplitude of 100 mV, and frequencies ranging from 1.0 Hz to 200 kHz, and analysis for dc conductivity was carried out with the usual Nyquist plots.

The results are shown in Fig. 2. Comparison is made with data from three separate reports [1,7,12] on Naion membranes measured under different conditions of hydration and pressure, with pure phosphoric acid from the melted crystal (this work), and with the most highly conducting H3PO4/PBI type membrane we could find (a PBI-Naion composite, by Li and Scott [25]). The stability of the present sample at temperatures up to 150 °C is demonstrated by the agreement of data obtained during heating with data taken during subsequent cooling (Fig. 2 caption).

The conductivity of the SiPOHgel is seen to exceed the conductivity of all other samples at any temperature above 60 °C. The most impressive comparison is that with 100% H3PO4, famous for its anomalous proton conductivity [26-28]. The closest competition by a solid material comes from a phosphoric acid-PBI-Naion composite. We note that at the highest temperature these conductors are only 1.5 decades from the theoretical (infrared) limit for ionic conductivity (10 Scm⁻¹ [29]). In consequence of the low water content and the higher operating temperature that is permitted, neither of these solid electrolytes will incur the water management problems that afflict the Naion membranes [30-37].

A second slice from the button of the pristine SiPOHgel material was tested as a membrane in a sandwich fuel cell of the type used in previous studies, for which details are here provided. The cell is illustrated, in exploded view, in Fig. 3.

Data obtained from this crude initial test exceeded our expectations for current density, but showed unsatisfactory OCV values (~0.8 V) probably due to fuel crossover effects caused by membrane imperfections. Noting the order of magnitude improvements in membrane performance obtained by Liu et al. using membrane reinforcing [38], we produced a stronger flexible membrane by incorporating a fiberglass wool filter (Cole-Palmer item QR-200 (Toyo Roshi Kaisha Ltd, Japan) ~2 mm thick initially) as
supporting matrix, as detailed in Fig. 1(b,c) and caption. The improved membrane was placed in Fig. 3 cell assembly between two standard E-Tek electrodes (LT140E-W; 0.5 mgPt/cm²) that had been lightly brushed on the contact surface with a drop of H₃PO₄ to assist with the establishment of the essential gas-catalyst-electrolyte three-phase contact. To aid this process, the assembled cell, prior to testing, was left overnight in a desiccator in the first case (Figs. 4 and 5), and in a low humidity drybox in the second case (Fig. 6).

During the testing, the cell was left 2 – 3 h at each temperature to ensure thermal equilibrium. The temperature of the cell was tracked relative to the oven atmosphere temperature during the test, for any indication of direct burning by fuel crossover. The very pleasing polarization curves obtained using the improved MEA are displayed in Fig. 4. The OCV has regained the values obtained with the previous liquid electrolyte cell [23] and, surprisingly, the maximum current now slightly exceeds the 1000 mA/cm² value reported previously for the higher temperature of 226°C, notwithstanding the thick membrane.

Membranes thinner than our >2 mm flexible discs would no doubt yield higher currents and powers. Typical polymer membranes for fuel cells are thinner by more than an order of magnitude [25]. Although the OCV for our cell is above 1 V (see Fig. 5) the oxygen electrode polarization remains unalleviated, and the current decrease restricts the maximum power output from this otherwise impressive new fuel cell to 200 mW/cm². We might hope to increase this with improved cell design to decrease the slope of Fig. 5 plot so that maximum power can be obtained at a higher potential. Refining the membrane by use of thinner supporting structures is an obvious starting point.

3.1. Durability testing

To address the question of membrane endurance under load (usually referred to as a degradation rate), we prepared a new membrane using a modified, more controlled, synthetic route than in the initial SiPOH preparation (modified route described in the S.I). The gel (designated SiPOHgel-K) appeared less robust than in the earlier preparation, perhaps as a consequence of less effective drying, but again was well supported by the same glass wool filter. Used in the same cell, Fig. 3, but with a smaller cross section active area, maximum power was reached at 187 mAcm⁻², lower than...
and at the current of maximum power at 150 °C, of phosphoric acid (85% by wt), and with the performance PA in Na
maximum power).

Fig. 2 and 6). It might be noted, parenthetically, that the cell suffered an unintended excursion to above 200 °C
previously, but quite sufficient for the purpose of endurance testing.

The cell with this membrane was submitted to constant current tests of 24 h duration (the maximum setting on our Parstat 2273 Advanced Electrochemical System) initially at a current density of 50 mACm⁻² at 120 °C in order to compare with an earlier study [39] using the same cell and the same Etek electrodes, but carried out using 85% phosphoric acid (liquid) as the electrolyte. The potential at 50 mACm⁻² in our cell (see trace 1 of Fig. 6) exceeded, by 20%, that of the earlier study (trace 2), and remained constant over the entire 24 h run. A further, and more severe, test was conducted at 151 °C at the current of maximum power, 187 mACm⁻². In this case, a noticeable downward drift was detectable after about 12 h, amounting to −0.01 mV (~2%) over the 24 h period (trace 3 in Fig. 6). This, however, is 5 times smaller than that in the corresponding Li and Scott [25] on their high performance PA in Nafion-PBI membrane under the same conditions (150 °C and maximum power).

4. Discussion

The extraordinary conductivity of this quasi-solid membrane material demands a structural interpretation. Obviously a precise structure cannot be provided for an amorphous material but some principal features can be deduced. While we will arrive at our conclusions systematically, below, we wish to stress here that there will prove to be nothing extraordinary to understand or interpret concerning the conductivity mechanisms, beyond what is abundant in the literature on phosphoric acid itself [26–28,40]. The reason will be obvious once we have reasoned our way to the conclusion that SiPOHgel is no more than a very successful sequestration of phosphoric acid in a flexible nano-permeated, defect-free but open (amorphous zeolitic) network of pure silica. The mechanical properties will be determined by the supporting fiberglass matrix – which is subject to separate optimizing development. The improvements in Nafion membrane cell performance that can be obtained by supporting matrices [38] were mentioned earlier.

The most helpful diagnostic tool in seeking understanding of the membrane performance is NMR spectroscopy because three of the four elements of our membrane have good NMR nuclei, two of them (¹H and ³¹P) in natural abundance. X-ray diffraction studies of calcined products, on the other hand, offer only puzzles at this time, because of the bewildering variety of possible Si–P–O and Si–P–O–H structures that are known [41–43] and the fact that the crystalline product of calcination of the rubbery solid of Fig. 1(b) has a powder diffraction pattern that is distinct from that of any previously recorded crystal powder pattern. All that can be said at this time is that the structure of the nearest crystal is characterized by a complex and extended medium range order of very low symmetry (see below) and is probably not relevant to the SiPOHgel structure, as we will show below.

4.1. NMR spectra

These are shown in Fig. 7(a) and (b). The sharp spectral lines for ¹H and ³¹P resonances indicate liquid-like mobility in this flexible solid material. The fact that the resonances in both the ¹H and ³¹P NMR spectra are essentially those of phosphoric acid H₃PO₄ strongly indicates that the preparation procedure has caused a total reorganization of the original “SiPOH” solid acid, (which has silicon in sixfold coordination, see Fig. 7(c)), to produce a phosphoric acid gel for which the supporting structure must be a silica or silico-phosphate net. The latter can be excluded by the solid state NMR spectra discussed below. However, the fact that the Si:P ratio must remain at the original value of 1:4, implies that the gel must be a very “tight” one. The length scales for silicate and H₃PO₄ components must remain comparable to maintain the 1:4 composition ratio.

A structure, in which the P content is realized in H₃PO₄ molecular form, would be consistent with the finding of Fig. 2 that the thermal stability limit for high conductivity is around 150 °C, the same as that attributed to phosphoric acid. That the supporting structure contains silicon in its normal 4-coordinated state (as opposed to the 6-coordinated state of ambient temperature SiPOH), is shown by the (magic angle spinning) solid state NMR spectrum
for Si (in its natural abundance) in Fig. 7(c). The resonance is found at −115 ppm referenced to the standard TMS, (but using solid tetrakis(trimethylsilyl)silane (TTSS) as external secondary reference (TTSS = 9.8 ppm)). A chemical shift of −115 ppm is at the downfield extreme of the chemical shift range for [SiO₄] groups, indeed it is some 5 ppm beyond the average for the Q₄ grouping given for silicate minerals by Magi et al. [44] and by various studies of the silica polymorphs, cristobalite, tridymite and quartz.

To find ²⁹Si spectra more downfield than the −110 ppm of the common SiO₂ polymorphs, one must turn to pure silicas of zeolitic form. For instance, the aluminum-free form of MCM-41 has three main ²⁹Si resonances at −111.3, −112.7 and −115.3 ppm [45]. Since SiPOHgel, in each of its preparations, has a broad resonance with the same average value of −115 ppm, see Fig. 8, we conclude that our material is a novel amorphous form of zeolitic silica, perhaps with even larger pores than MCM-41, occluding H₃PO₄ molecules.

Such structures are characterized by very low frequency vibrational modes that, at high temperatures (~800 °C), lead to collapse to denser more stable forms [46]. However they are indefinitely stable at moderate temperatures. Their formation was probably supported by H₃PO₄ molecules acting as templates. As established by Dove [47] and others [46,48], these open silicate structures are inherently “floppy” even though fully connected – which might account for the important flexibility that the membranes exhibit. Finally, a solid state NMR spectrum of ³¹P (not shown) produced no important new lines (a barely detectable resonance at −11 ppm is not considered significant). Thus all Si—O—P bonds have been broken in the solution—gelation process.

Since, by preparation, there are 4 P for every Si, and since the number of the H₃PO₄ molecules grows as the cube of the dimension of any nanodomain, the dispersion of H₃PO₄ in the silica network must be nanoscopic, or at least highly ramified. It is plausible that the H₃PO₄ molecules might rotate freely within the zeolitic pores to pass their protons along without actually diffusing themselves — an ideal condition. Pulsed field gradient ³¹P NMR studies of self-diffusion should help establish the extent to which such desirable behavior might characterize the new membrane.

4.2. XRD studies of calcined and amorphous structures

4.2.1. Calcined structures

The XRD patterns of the calcined SiPOH and SiPOHgel are of possible interest in relation to the complex crystalline phases in this system, but are deemed irrelevant to the discussion of SiPOHgel, so are placed in the supporting information.

4.2.2. SiPOHgel

The XRD of SiPOHgel, shown in the Si, is simple and unambiguous. The similarity to the XRD of powdered dry silica gel, taken on the same diffraction equipment, is striking (see SI.2). It is different and less complex than that of hydrated silica gel. This leaves little doubt that the material we are investigating is a fully connected amorphous silica network, with zeolite-like nanopore distributions of sufficiently floppy character to account for its flexible character. Occluded within the gel, and stabilizing its structure, there is evidently a uniform distribution of essentially pure phosphoric acid.

While this sort of structure probably does not bind the H₃PO₄ any more strongly than do the polybenzimidazolazole-based membrane materials that have been under intense study in recent years [13,25,49–51], it should not lose H₃PO₄ any more rapidly than do these post-formation-doped membranes. The very low rates of H₃PO₄ depletion recorded by Linares et al. [50] (falling rapidly to negligible under gas flow at temperatures up to 190 °C), give little cause for concern and are consistent with our own favorable constant current observations Fig. 6.

It might be asked, why not simply absorb H₃PO₄ into dry silica gel and use that material as the electrolyte? Apart from the fact that a material so prepared would have no flexibility, this has already been attempted in the work of Matsuda et al. [19] and then abandoned. These workers found that the conductivity of the aqueous H₃PO₄-soaked silica gel faded rapidly to below 10⁻¹ Scm⁻¹ on standing at 130 °C. Phosphosilicate powders compressed to disc form, with P/Si ratios near unity behaved better, retaining their 10⁻² Scm⁻¹ conductivities over longer periods of time at the same temperature [19], but this is still far below the SiPOHgel conductivity at the same temperature seen in Fig. 2. These latter studies clearly have features in common with the present study, but they evidently did not find the aqueous route to the flexible solid product that seems to have the unique properties needed for fuel cell applications, as illustrated in Figs. 4 and 5.
5. Concluding remarks

We have so far only prepared and tested SiPOHgels obtained by relatively low-temperature dehydration procedures. We surmise that a more aggressive dehydration might produce a gelled form of the >200°C-stable liquid electrolyte on which we reported recently. While the present formulation is desirable for processes operating in the range not too far above 100°C, an extension of the temperature range to the >200°C range would have advantages for some purposes and will be the subject of future investigations.

While we are not aware of other acid gels that form by self-assembly in situ via the present process, it seems quite likely that there are analogous cases, based on the hydration of other silico-noxyacids, waiting to be made. It will be interesting to determine the maximum acidity material that can be prepared in this semi-solid form by the procedure we have described. Although phosphates are preferred over sulfates for fuel cell purposes because of their stability against reduction by hydrogen, there will be other purposes for which the benign confinement of a stronger acid might be very desirable.

Acknowledgments

This work has been carried out under the auspices of the DOD-Army research office, under Grant no. W911NF-07-1-0423 for the synthesis and fuel cell work, and to W911NF-11-1-0263 for the structural analysis. We appreciate much valuable advice given by Don Gervasio during the development of our fuel cell interests. He also provided the design of the fuel cell of Fig. 3 which was used in previous joint publications [14,52].

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2015.10.034.