

## Proton-conducting gel electrolyte

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### Abstract

Proton conduction in solid state xerogels and polymeric gels are reported. Xerogels, doped with known proton conductors, were prepared by “sol–gel” method starting either from inorganic precursor sodium metasilicate (termed as hydrogel) or organic precursor tetraethyl orthosilicate (termed as silica or SiO<sub>2</sub> alcogel). The dopants chosen for the former were NH<sub>4</sub>BF<sub>4</sub>, NH<sub>4</sub>Cl, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and N<sub>2</sub>H<sub>6</sub>SO<sub>4</sub>, while for the latter, the dopants used were H<sub>3</sub>PO<sub>4</sub>, NH<sub>4</sub>BF<sub>4</sub>, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub>. The SiO<sub>2</sub>:H<sub>3</sub>PO<sub>4</sub> alcogel gave the highest room temperature conductivity ( $\sim 10^{-3}$  S cm<sup>-1</sup>). Some of the xerogels studied by us were stable even up to 300 °C. Another interesting group of proton-conducting materials discussed in this paper is polymeric gel which was prepared by dispersing PMMA in the liquid electrolyte obtained by dissolving *o*-, *m*-, *p*-hydroxybenzoic acid; *o*-, *m*-, *p*-nitrobenzoic acid and three dicarboxylic acids, viz., oxalic, malonic and succinic acid, in a high-dielectric constant organic solvent. The role of the dissociation constants of the dissolved acids and the interaction of the polymer were discussed. The addition of polymer, inspite of the increasing viscosity, was found to sometimes lead to an increase in the conductivity of liquid electrolyte, which was explained on the basis of a breathing polymer chain model.

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### 1. Introduction

Gel electrolytes are emerging as useful materials for technological applications because of the ease with which gels can be easily designed into thin film as well as bulk forms. They can be prepared in desired shapes and large areas can be deposited by dip, spin or spray coating methods. These advantages, coupled with the fact that many gels have been found to possess a good ionic conductivity and ionic exchange property [1–3], has led to interesting applications in

many electrochemical solid state ionic devices like (i) high-energy density batteries, (ii) fuel cells, (iii) sensors and (iv) electrochemical display devices. The subject of the study of materials and devices based on gel electrolytes has recently been termed as “sol–gel ionics” [4] or “gel ionics” [5]. “Gel” can essentially be thought of as a substance that contains a solid skeleton (polymers or long chain molecules cross-linked to create a tangled network) enclosing a continuous liquid phase. The properties of gel depend strongly on the interaction of these two components. The liquid prevents the polymer network from collapsing into a compact mass while the network prevents the liquid from flowing away. Depending upon the chemical composition and other factors, gels

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vary in chemistry from viscous fluid to fairly rigid solids, but typically they are soft and resilient or “jelly-like.”

In brief, most gel materials are macroscopically like solid, but exhibit liquid-like characteristics microscopically due to the presence of a large number of liquid-filled micropores. The ultraporous structure of gels is likely to provide channels for ion migration. This offers the possibility of synthesizing good ion conducting gel materials. On the basis of the method of preparation, the gel electrolytes can be classified as follows.

(a) *Xerogel/aerogel electrolyte*. These gels are obtained by a “sol–gel” process involving polymerization through hydrolysis-related chain linking. Such gels behave as “gel electrolytes” if they contain mobile ions arising from either its own generating groups (like  $H^+$  or  $OH^-$  from the hydrolysed bonds) or from the dissociated dopant salt cations like  $Li^+$ ,  $Na^+$ ,  $H^+$ , ( $H_3O^+$ ) or  $OH^-$ , etc.

(b) *Polymeric gel electrolyte*. These are either obtained by adding substantial amount of plasticiser (like PC, EC, PEG) in a solid polymer electrolyte (plasticiser breaks the solid polymer skeleton and allows greater mobility to the charge carriers for ionic transport) [6] or by immobilizing liquid electrolyte and making it highly viscous with the addition of an inert polymer-like PAN, PMMA, etc. The ion transport mechanism in these gel materials appears to be dominated by the liquid electrolyte while the addition of polymer increases the viscosity and changes the dielectric constant and, hence, degree of dissociation [7–11].

Many gel electrolytes of both the above types (i.e., xerogel and polymeric gel) are reported in the literature for  $Li^+$  and  $Na^+$  but not many studies are reported on proton-conducting gel electrolytes. This paper first gives a brief overview and then reports some of the recent results on proton-conducting gel electrolytes developed in our laboratory. The specific proton-conducting systems studied by us are as follows.

(i)  $Na_2SiO_3$ -based “xerogels” (termed as hydrogel) doped with proton-conducting materials like  $KH_2PO_4$ ,  $N_2H_6SO_4$ ,  $NH_4Cl$  and  $NH_4BF_4$ .

(ii) Tetraethyl orthosilicate (TEOS)-based  $SiO_2$  alcogels, a class of xerogel, doped with  $NH_4BF_4$ ,  $KH_2PO_4$ ,  $NH_4H_2PO_4$  and  $H_3PO_4$ .

(iii) “Polymeric gel” as a result of dispersal of PMMA (polymethyl methacrylate) in liquid electrolytes obtained by dissolving different amounts of acids (viz. *o*-, *m*- and *p*-hydroxybenzoic acids; *o*-, *m*- and *p*-nitrobenzoic acids; three dicarboxylic acids, i.e., oxalic, malonic and succinic). The role of relative dissociation constants of the acids and amount of PMMA in the gel is particularly discussed. The addition of PMMA is found to ‘sometimes’ enhance the conductivity inspite of higher viscosity. These results are discussed in the light of the “breathing polymer chain model” recently proposed by us [12].

## 2. Proton-conducting xerogels

### 2.1. Xerogels: some basics

A schematic representation of method of obtaining xerogel/aerogel electrolytes by the “sol–gel” process is shown in Fig. 1 in which the precursor to “gel” formation is obtaining “sol” [13–15]. A “sol” represents a suspension or dispersion of discrete colloidal particles in a liquid phase. All the “sols” cannot be converted into gel. For sol–gel transition, there must be a strong “particle–solvent interaction” so that at least part of the solvent gets bound. At the transition, the solution or sol becomes a rigid, porous mass

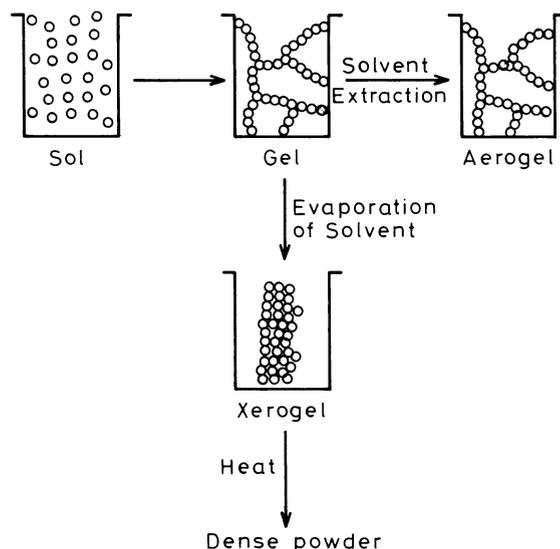


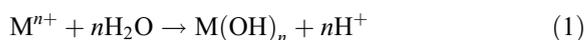
Fig. 1. Schematic representation of “sol–gel” process.

through destabilization, precipitation or supersaturation [16,17]. Once through the sol–gel transition, the solvent phase is removed with ordinary evaporation to create xerogels, or with hypercritical evacuation to form aerogels [18,19] as shown in Fig. 1. At this point, the dried gel is microporous. Oxides of early transition metals (Ti, V, Zr), group IIIA metals (B, Al, etc.) and silicon easily form “gel” through the simple process of hydrolysis. Based on the “precursor” materials, the xerogels are classified as:

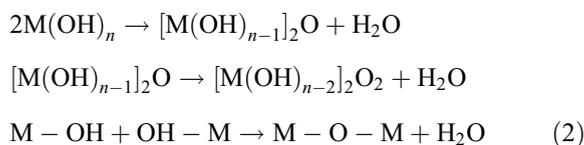
- (i) Hydrogel: prepared by aqueous-based sol–gel process and starts with “inorganic” metal salt precursor like sodium metasilicate.
- (ii) Alcogel: prepared by alcohol-based sol–gel process and starts with organic metal alkoxide precursor like tetraethyl orthosilicate.

The processes involved in the formation of hydrogels and alcogels are described below.

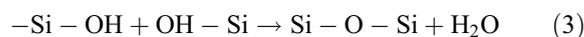
For hydrogel, the first step of the “sol formation” is accomplished by the hydrolysis of metal cations,  $M^{n+}$ , which are solvated by the water molecules according to the reaction:



Hydrolysis is followed by “internal condensation,” a process in each step where  $H_2O$  gets removed and a number of M–OH linkages give way to the formation of M–O–M linkages. This happens in sequence as under:



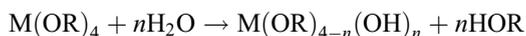
For the case of silicate gels, silicic acid is the predominant mono nuclear solution species introduced on hydrolysis of the inorganic salt. The formation of silicic acid in aqueous solution is followed by polymerization of monomers. The polymerization reaction is based on the condensation of silanol (Si–OH) groups:



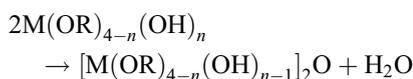
The above process of two or more monomers joining (or condensing) can, respectively, lead either

to the growth of molecular size or polymerisation depending upon the linear or planar mode of joining as discussed by Iler [17].

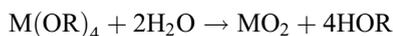
Steps involved in the sol–gel process for “alcogel system” is almost similar but the alcogels are made almost exclusively from metal alkoxides  $M(OR)_4$  like tetraethyl orthosilicate (TEOS). The reactions involved are hydrolysis,



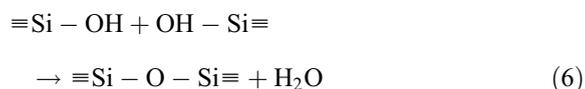
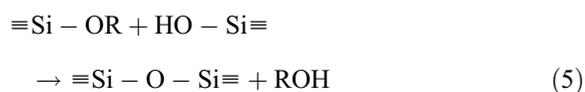
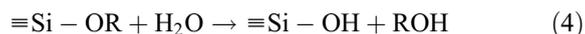
and condensation



with overall reaction given by



where R is an alkyl group  $C_xH_{2x+1}$ . At the functional group level, the above general reactions may be written for the special case of silicon alkoxide as sequencing hydrolysis, alcohol condensation and water condensation steps given below [13]:



The hydrolysis reaction replaces alkoxide group (OR) with hydroxyl group (OH). Subsequent condensation reactions involving silanol groups produce siloxane bonds (Si–O–Si) plus the by-product alcohol (ROH) (Eq. 5) or water (Eq. 6). Because water and alkoxisilanes are immiscible, a mutual solvent such as alcohol is used as a homogenizing agent. The xerogel prepared by the above-described sol–gel processes have unique amorphous structure with a high degree of porosity. The porous structure of gels can be easily modified by chemical or physical methods.

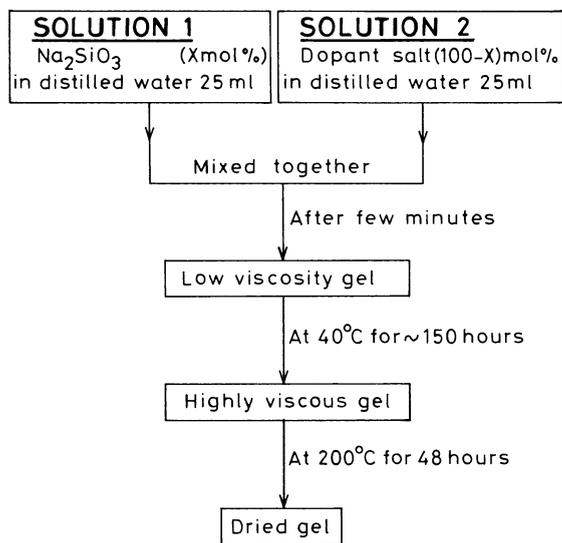
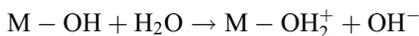


Fig. 2. Schematic representation of different steps involved in the gel preparation.

## 2.2. Proton-conducting “hydrogels”

In proton conductors, the charge transport is primarily due to  $\text{H}_3\text{O}^+$ ,  $\text{H}^+$  or  $\text{OH}^-$ . Early proton-conducting gels studied are oxide gels which, from a chemical point of view, may be considered to be hydrous oxides  $\text{MO}_x \cdot n\text{H}_2\text{O}$ , where  $\text{M} = \text{Ti}, \text{Zr}, \text{V}, \text{Si}$ , etc.; colloidal oxide particles have fully hydrated surfaces. The hydration mechanism involves the dissociation of adsorbed water molecules at the surface of the oxide. The  $\text{H}^+$  and  $\text{OH}^-$  ions, respectively, bond to the oxygen and metal sites, leading to the formation of two surface hydroxyl groups  $\text{M}-\text{OH}$  [1]. The  $\text{M}-\text{OH}$  groups at the surface undergo acid and base dissociations as given below [4,20]:



The room temperature conductivity of proton-conducting hydrous oxides is  $\sim 10^{-5} \text{ S cm}^{-1}$  [21]. It depends to a small extent on the oxidation state of the metal cation  $\text{M}^{n+}$ , but strongly depends on the amount of water in the gel. Another interesting gel system is the silicate system in which more proton conduction is promoted, since the synthesis process involves acid-catalyst providing additional source of protons. Dunn

et al. [22] have studied the transport properties of acid catalyzed silica gel during the sol–gel transition. Many organically modified silica gel systems (ORMOSIL) have been developed. Recently, Charbouillot et al. [23] used alkylamines as network modifiers to prepare “aminosils” as a new class of “ormosils.” These “aminosils” were obtained via the hydrolysis of a mixture of aminated organosiloxanes  $\text{R}'\text{Si}(\text{OR})_3$  ( $\text{R}'$ -amino group;  $\text{R} = \text{CH}_3$  or  $\text{C}_2\text{H}_5$ ) and an acid. The silica backbone provides mechanical strength while the organic amino groups offer solvating properties with respect to the guest ionic species. Films of the material were transparent and exhibited proton conductivity ( $\sigma = 10^{-5} \text{ S cm}^{-1}$ ) at room temperature.

In our laboratory, we have directed our effort to developing  $\text{Na}_2\text{SiO}_3$ -based “hydrogels” doped with known proton-conducting salts like  $\text{N}_2\text{H}_6\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{KH}_2\text{PO}_4$  and  $\text{NH}_4\text{BF}_4$ . A schematic representation of method of preparation of hydrogel is shown in Fig. 2. To obtain hydrogel, aqueous solution of sodium melasilicate was used as inorganic precursor to which solution of dopant salts like  $\text{NH}_4\text{BF}_4$  or  $\text{NH}_4\text{H}_2\text{PO}_4$  or  $\text{KH}_2\text{PO}_4 \cdot \text{NH}_4\text{Cl}$  or  $\text{N}_2\text{H}_6\text{SO}_4$ , etc. were added and left for gelling at  $40^\circ\text{C}$  for  $\sim 3\text{--}4$  days. The highly viscous gel so obtained was dried at  $200^\circ\text{C}$  for 48 h. The dried gel was ground to fine powder which was used for experimental studies either as such or as

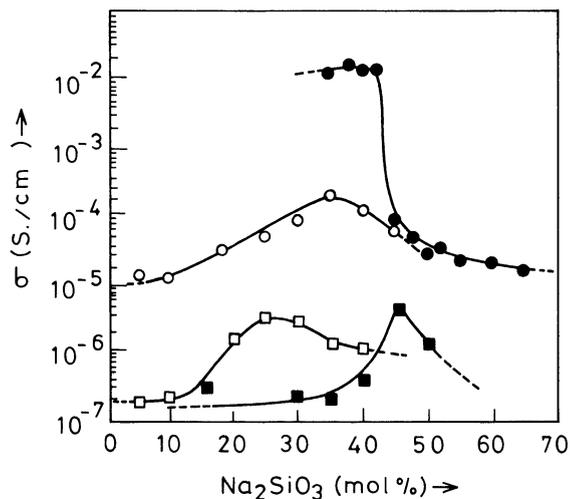


Fig. 3. Composition dependence of electrical conductivity for different hydrogels: (□-□)  $x\text{Na}_2\text{SiO}_3+(100-x)\text{NH}_4\text{Cl}$ ; (■-■)  $x\text{Na}_2\text{SiO}_3+(100-x)\text{NH}_4\text{BF}_4$ ; (○-○)  $x\text{Na}_2\text{SiO}_3+(100-x)\text{KH}_2\text{PO}_4$ ; (●-●)  $x\text{Na}_2\text{SiO}_3+(100-x)\text{N}_2\text{H}_6\text{SO}_4$ .

pellets prepared at  $\sim 6 \text{ ton cm}^{-2}$  pressure. Detailed structural characterisation (IR, XRD, DTA) and ion transport measurements have been carried out [24,25]. Here, we only describe briefly some of the results on the ion transport behaviour.

The electrical conductivity evaluated by impedance spectroscopy as a function of the dopant concentration in the gel is given in Fig. 3. It is obvious that doping the  $\text{Na}_2\text{SiO}_3$  hydrogels with proton-conducting salts has helped in augmenting the conductivity. Further, it may be noted that the gellification takes place only in

a limited compositional range. The dashed (.....) line indicates that in this range, it was not possible to obtain dried solid state xerogel. Fig. 4a and b, respectively, gives the temperature dependence of ionic transference number and electrical conductivity. The significant conclusions which can be drawn from these results are as follows.

(a) Pure  $\text{Na}_2\text{SiO}_3$  gel at higher temperature is partially electronic. Our DTA/TGA results have shown that at temperatures more than  $300^\circ\text{C}$ , many H–O–H bonds are broken and dehydration of the gel

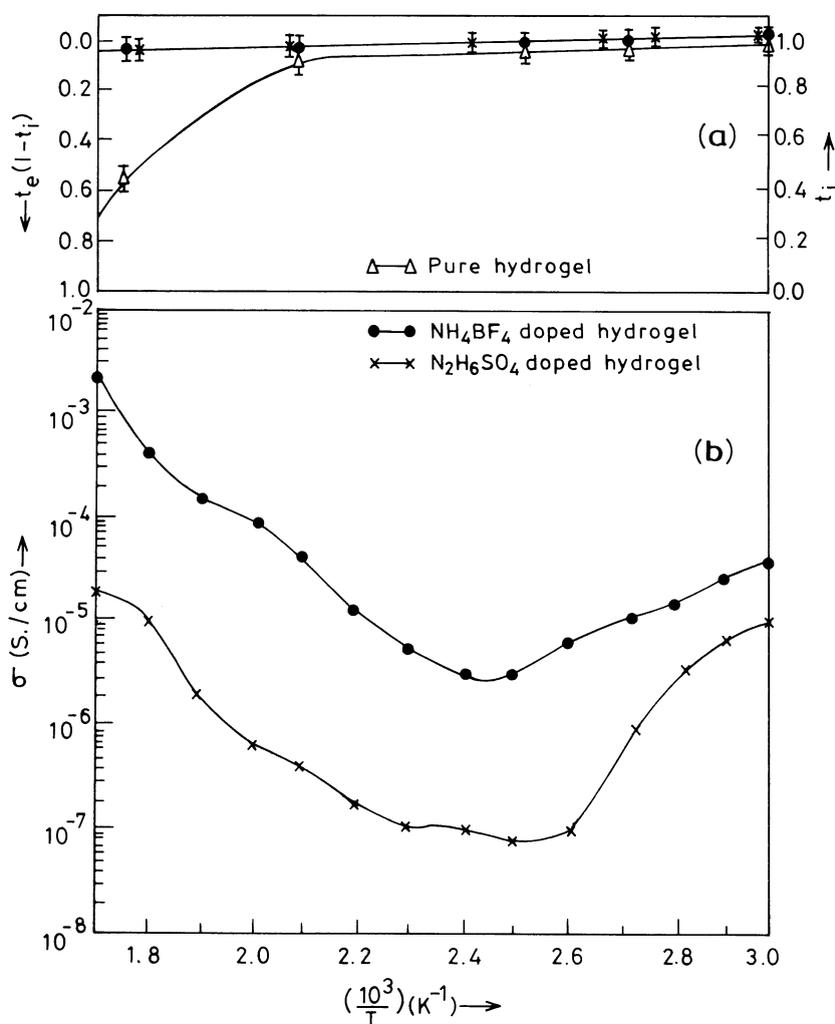


Fig. 4. Temperature dependence of (a) ionic transference number for ( $\Delta$ – $\Delta$ ) pure hydrogel, ( $\bullet$ – $\bullet$ )  $x\text{Na}_2\text{SiO}_3+(100-x)\text{NH}_4\text{BF}_4$  ( $x=45$  mol%) and ( $\times$ – $\times$ )  $x\text{Na}_2\text{SiO}_3+(100-x)\text{N}_2\text{H}_6\text{SO}_4$  ( $x=40$  mol%). (b) Electrical conductivity for ( $\bullet$ – $\bullet$ )  $x\text{Na}_2\text{SiO}_3+(100-x)\text{NH}_4\text{BF}_4$  ( $x=45$  mol%) and ( $\times$ – $\times$ )  $x\text{Na}_2\text{SiO}_3+(100-x)\text{N}_2\text{H}_6\text{SO}_4$  ( $x=40$  mol%).

occurs. Hence, ionic (protonic) conductivity contribution decreases. On the other hand, the doped gels continue to remain “ionic” even up to 300 °C.

(b) The conductivity initially decreases with temperature due to the desorption of surface physisorbed water but then increases. The increase in conductivity at higher temperature is also linked with a possible phase transition as evidenced by our DTA studies. The conductivity in the 300–400 °C range is very high ( $\approx 10^{-3} \text{ S cm}^{-1}$ ). This high value of conductivity, coupled with the fact given in (a) that  $t_{\text{ion}}$  is approximately one even at such high temperatures, makes these materials as potential candidates for good intermediate temperature proton conductor.

(c) However, the “not so favourable” point for these materials is the fact that some  $\text{Na}^+$  mobility has been noted by Rai and Chandra [26] from the ionic mobility measurement by transient ionic current technique and NMR line narrowing for  $\text{Na}^{23}$  nuclei. Therefore, the high ionic conductivity at high temperature may not be purely protonic but partially due to  $\text{Na}^+$ .

These results (particularly (c)) prompted us to switch over to a gel matrix which does not contain  $\text{Na}^+$ . We switched over to  $\text{SiO}_2$  gels derived from an organic precursor TEOS (termed earlier as “alcogel”) doped with different proton-conducting dopant salts. The results are discussed below.

### 2.3. Proton-conducting “alcogels”

Many studies are reported by several workers to prepare xerogel by using organic precursor (i.e., tetraethyl orthosilicate). Tatsumisago and Minami [27] have prepared silica gel films containing dodecamolybdophosphoric acid,  $\text{H}_3\text{PMO}_{12}\text{O}_{40}\cdot 29\text{H}_2\text{O}$  (MPA) by sol–gel method. The film containing 42 wt.% MPA exhibits the highest room temperature proton conductivity value,  $3 \times 10^{-3} \text{ S cm}^{-1}$  at 90% R.H. In a similar work, Minami et al. [28] have prepared proton-conducting bulk silica gels and silica gel films containing perchloric acid,  $\text{HClO}_4$ , dodecatungstophosphoric acid  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 29\text{H}_2\text{O}$  (WPA), or tetra-*n*-butylammonium perchlorate (*n*-Bu) $_4\text{NClO}_4$  by sol–gel method.  $\text{HClO}_4$  or WPA-doped dried bulk gels and gel films exhibited higher conductivities ( $2 \times 10^{-2}$  and  $6 \times 10^{-3} \text{ S cm}^{-1}$ , respectively) than the dried gel doped with (*n*-Bu) $_4\text{NClO}_4$  ( $\sim 10^{-7} \text{ S cm}^{-1}$ ).

We have prepared “alcogels” starting from organic precursor TEOS. Dopants used are  $\text{H}_3\text{PO}_4$  acid and salts  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{KH}_2\text{PO}_4$  and  $\text{NH}_4\text{BF}_4$ . Hydrolysis and condensation are the necessary steps involved in the gellification as discussed earlier. To prepare the above alcogels, ethanolic solution of TEOS was used as organic precursor to which dopant

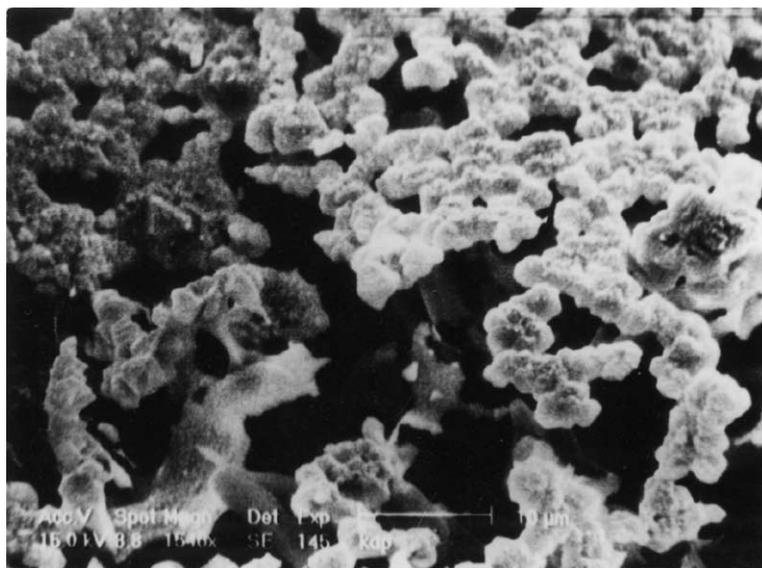


Fig. 5. SEM micrograph of pure  $\text{SiO}_2$  gel.

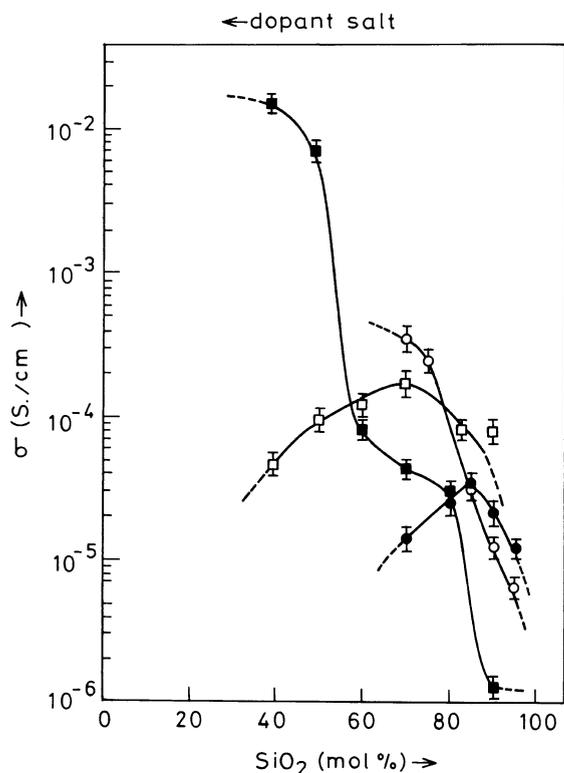


Fig. 6. Composition dependence for different alcogels: (O–O)  $x\text{SiO}_2+(100-x)\text{NH}_4\text{H}_2\text{PO}_4$ ; (■–■)  $x\text{SiO}_2+(100-x)\text{H}_3\text{PO}_4$ ; (●–●)  $x\text{SiO}_2+(100-x)\text{KH}_2\text{PO}_4$ ; (□–□)  $x\text{SiO}_2+(100-x)\text{NH}_4\text{BF}_4$ .

electrolytic solution of  $\text{H}_3\text{PO}_4$  or ADP or  $\text{NH}_4\text{BF}_4$  or KDP was added. Also, one to two drops of HCl was added as catalyst. The mole ratio of TEOS/EtOH/ $\text{H}_2\text{O}$ /HCl was kept constant, i.e., 1:8:30:0.05. The transparent solution so obtained is kept for gelling at  $40^\circ\text{C}$  for 3–4 days followed by drying at  $\sim 200^\circ\text{C}$  for  $\sim 48$  h. The dried gel ingot which, for further measurements, was used either as such or as a pellet obtained from its well ground powder at a pressure of  $\sim 4$  tons  $\text{cm}^{-2}$ .

All the prepared gels were transparent. Porosity of a typical gel was  $\sim 80\%$  as measured by gas adsorption method. The SEM photograph showing the porous surface morphology of our typical “alcogel” is shown in Fig. 5. These pores may entrap the dopant electrolyte solution. First, hint in this direction was taken by us when we were cutting gel ingots and a liquidus material was seen oozing out. Therefore, these doped alcogels

can be modelled as “solid–liquid electrolyte” composite. Detailed confirmatory evidence in this regard using IR, XRD and DSC results will be published elsewhere [29]. A necessary consequence of the hypothesized “solid–liquid electrolyte” composite will be liquid-like conductivity. The composition dependence of conductivity of different alcogels is given in Fig. 6. It is to be noted that the gellification is in a limited compositional range. The best conductivity was for  $\text{SiO}_2\text{--H}_3\text{PO}_4$  alcogel ( $\sim 10^{-2}$  S  $\text{cm}^{-1}$ ) while the  $\text{SiO}_2\text{--NH}_4\text{BF}_4$ ,  $\text{SiO}_2\text{--NH}_4\text{H}_2\text{PO}_4$  and  $\text{SiO}_2\text{--KH}_2\text{PO}_4$  gels gave conductivity of  $\sim 10^{-4}$  S  $\text{cm}^{-1}$ .

The temperature dependence of conductivity is shown in Fig. 7. For discussion purposes, the  $\sigma$  vs.  $1/T$  plot can be divided into three distinctive regions. In Region 1, the conductivity after a small increase

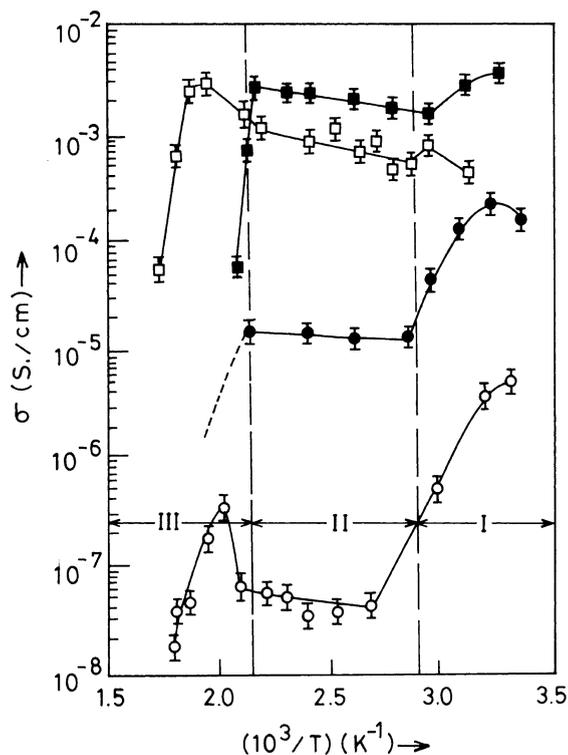


Fig. 7. Temperature dependence of electrical conductivity for different alcogels. (□–□)  $x\text{SiO}_2+(100-x)\text{NH}_4\text{H}_2\text{PO}_4$  ( $x=70$  mol%); (■–■)  $x\text{SiO}_2+(100-x)\text{H}_3\text{PO}_4$  ( $x=50$  mol%); (●–●)  $x\text{SiO}_2+(100-x)\text{NH}_4\text{BF}_4$  ( $x=70$  mol%); (O–O)  $x\text{SiO}_2+(100-x)\text{KH}_2\text{PO}_4$  ( $x=85$  mol%). Note that the plotted values (for  $\text{KH}_2\text{PO}_4$  doped gels) are 1/10th of the actual experimental values.

decreases with temperature. In Region 2, the conductivity varies negligibly or very slowly with temperature, while at the higher temperature end of Region 3, the conductivity drops sharply with increasing temperature. Region 1, can be assigned to be due to the desorption of physisorbed water. The conductivity in Region 2 can be attributed to the liquid electrolyte entrapped in the pores of porous SiO<sub>2</sub> alcogel, which is typical of “liquid-like conductivity.” The drop in conductivity in Region 3 ( $T > 150$  °C) is due to the loss of electrolyte as a result of evaporation.

### 3. Proton-conducting polymer gel electrolytes

As discussed earlier, the term polymer gel electrolytes refer to system, which is obtained first by dissolving dissociable salts/acids in a suitable solvent and then the electrolyte is immobilised with the addition of polymer. Since the first report of high conductivity in polymer gel electrolytes [30], most of the work on these materials has been mainly with various lithium salts like LiClO<sub>4</sub>, Li(CF<sub>3</sub>SO<sub>3</sub>), LiBF<sub>4</sub>, LiPF<sub>6</sub>, etc. because of their use in lithium batteries. Not much work has been done on proton-conducting polymeric gel electrolytes. Initial work was with strong acids like H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl, [31,32], salicylic acid [33], hydroxybenzoic acids and aliphatic dicarboxylic acid [12]. The use of organic carboxylic acids for developing proton-conducting gel electrolyte is a promising proposition since the carboxylic groups are proton donors while the ring to which these are attached are generally nonpolar. In the following paragraphs, we give some results obtained by us in our programme of developing such polymeric gels.

The organic acids used by us as the liquid electrolytes for polymeric gellification in order to develop proton-conducting polymer gels are given in Table 1 along with their dissociation constants  $k$  (or acidity constant). Organic solvent to be used should have high dielectric constant to help the dissociation of the organic acids. The solvent used was the ternary mixture of EC+PC+DMF which has been earlier found by us [34] as giving the best results. So long as one uses high-dielectric constant solvent, the role of solvent is only marginal. Liquid electrolytes of each acid with different concentrations were prepared and their conductivity was measured using WTW

Table 1  
Dissociation constants of the organic acids used by us in preparing polymeric gel electrolytes

Hydroxybenzoic acid			Nitrobenzoic acid			Dicarboxylic acid (COOH-(CH <sub>2</sub> ) <sub>n</sub> -COOH)		
<i>o</i> -	<i>m</i> -	<i>p</i> -	<i>o</i> -	<i>m</i> -	<i>p</i> -	Oxalic ( <i>n</i> =0)	Malonic ( <i>n</i> =1)	Succinic
105	8.3	2.6	670	32	36	5400	140	6.4

conductivity meter LF-330 and HP4284 A precision LCR meter operating from 20 Hz to 1 MHz. The conductivity meter was calibrated by using standard KCl solution. The measured values of electrical conductivity of the liquid electrolytes (without any added polymer) of the three systems listed in Table 1 are given in Fig. 8. The following general observations can be made.

(i) The conductivity, as expected, depends upon the dissociation constants listed in Table 1. For example, the dissociation constants of *o*->*m*->*p*-hydroxybenzoic or nitrobenzoic acid and the same is true for the conductivities given in Fig. 8a and c. Similarly for dicarboxylic acids, both the dissociation constants and the conductivity for oxalic acid>malonic acid>succinic acid as given in Fig. 8b.

(ii) The conductivity initially increases linearly with the acid concentration in the electrolyte but at higher concentrations, the rate of increase is slow and tends towards saturation. This is due to ion association.

The result of adding polymer PMMA on the conductivity of best of each series of the above liquid electrolytes is shown in Fig. 9. We investigated different molarity solution (which are likely to have different degrees of ion association) in order to see whether the conductivity changes induced by PMMA is in any way related with the degree of ion association of the starting electrolyte. The significant conclusions which can be drawn from Fig. 9 are as follows.

(i) The conductivity initially increases with the amount of added PMMA peaks and then decreases at high concentration. This is an unexpected result. A preliminary result was earlier reported by us [12] for some 1-M electrolytes.

(ii) It is obvious that the extent of peak conductivity enhancement due to the addition of polymer does depend upon the molarity. In general, high molarity electrolytes were more effected by the addition of

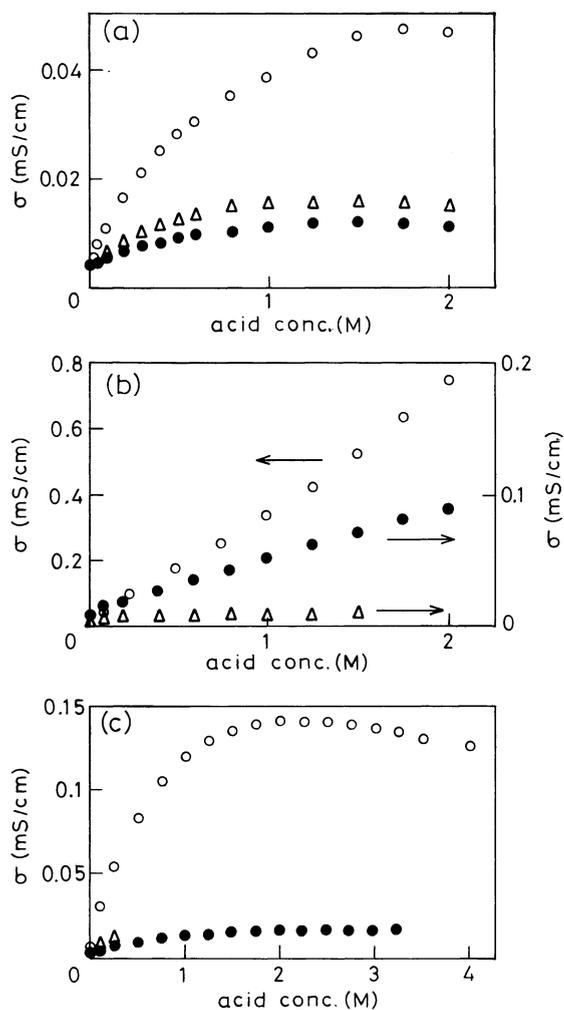


Fig. 8. Variation of conductivity with acid concentration in mole per liter (M) for (a) *o* (○)-, *m* (●)- and *p* (△)-hydroxybenzoic acid. (b) Oxalic (○), malonic (●) and succinic (△) acid. (c) *o* (○)-, *m* (●)- and *p* (△)-nitrobenzoic acid. Because of limited solubility of *p*-nitrobenzoic acid, the data was limited to low acid concentration regime only.

PMMA. However, in some cases (like that of ortho-nitrobenzoic acid) the conductivity enhancement is barely perceptible.

The above two conclusions are somewhat unexpected if we take a simplistic explanation. The addition of PMMA obviously do two things: (a) increases viscosity and (b) decreases dielectric constant since dielectric constant of PMMA is much lower than the solvent EC+PC+DMF. The former may lead to

decrease in the ionic mobility while the latter would decrease the number of dissociated charge carriers. Both would predict a decrease in the conductivity as has been found in many lithium gel electrolytes. In all our results, we have consistently noted an enhancement in the conductivity. For salicylic acid, Grillone et al.

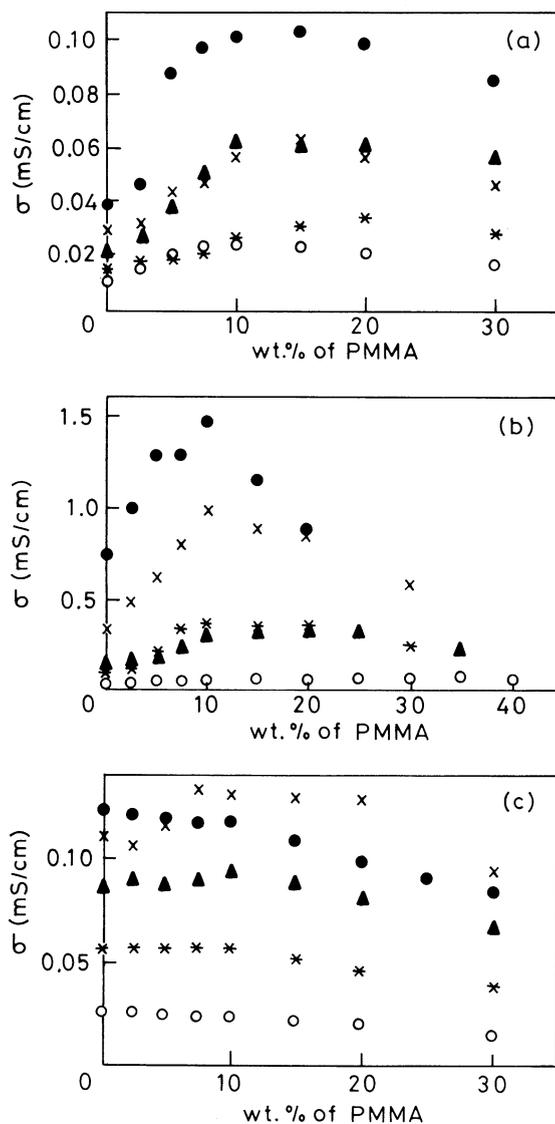


Fig. 9. Variation of conductivity with the addition of PMMA to the 0.1 M (○), 0.25 M (\*), 0.50 M (▲), 1.0 M (×) and 2 M (●) solution of (a) *o*-hydroxybenzoic acid, (b) oxalic acid and (c) *o*-nitrobenzoic acid in EC+PC+DMF.

[33] have also observed an increase in the conductivity on gellification. Therefore, we have to evolve or model some additional manner other than the above in which the added polymer is interacting with the liquid electrolyte. Chandra et al. [12] recently have suggested a “breathing polymer chain model.” The polymer chain is assumed to breathe while it opens or folds occupying different volume in the process. This leads to localized pressure fluctuations assisting either in breaking the neutral ion-associated pairs or “unblocking” of the viscosity controlled mobility or both resulting in a conductivity enhancement. Let us reexamine the nature and the process of the formation of our polymer gel electrolyte. Most of the regions of a polymeric gel can be considered as a polymer network swollen with the liquid electrolyte. Thus, polymeric gels are unique (liquid + polymer) hybrid network which are able to

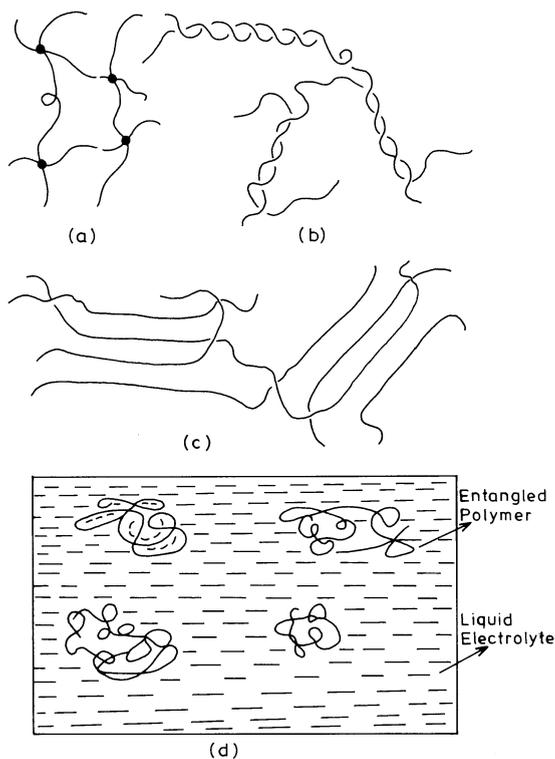


Fig. 10. Entangled polymer gel network under different situations. (a) Chemical gel network with junction points [35]. (b) Physical gel network having junction zones [35]. (c) Physical gel network having fringed micelles [35]. (d) Entangled polymer networks filled up with liquid electrolyte dispersed in electrolyte solution (present gel model).

sustain the diffusive liquid-like ion transport. Polymeric gels can be obtained as a result of chemical or physical cross-linking as shown in Fig. 10 a–c [35]. The former is associated with the covalent bonding of polymer chain by means of a chemical reaction to form a certain number of tie or “junction points” as shown in Fig. 10a. The formation of polymeric gel as a result of physical cross-linking is associated with the formation of entanglement network of “junction zones” (Fig. 10b) or “Fringe micelles” (Fig. 10c). Either of these three cases would give our “gel” a structure in which there are regions with polymer hosts functioning as containers of liquid electrolytes distributed all over the liquid electrolyte as shown in Fig. 10d. Given the situation of Fig. 10d, the “breathing polymer” mechanism hypothesized by Chandra et al. [12], as mentioned earlier, can lead to the conductivity enhancement. Of course, at very high concentrations of adding polymer (PMMA), the high viscosity effect would dominate resulting in a decrease in conductivity.

#### 4. Conclusions

Good proton-conducting materials such as solid xerogels (hydrogel and alcogel) and viscous polymeric gel have been developed by following simple methods of synthesis. Hydrogels studied are  $\text{Na}_2\text{SiO}_3$ -based gels doped with  $\text{NH}_4\text{BF}_4$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{N}_2\text{H}_6\text{SO}_4$ , and alcogels studied are TEOS derived giving  $\text{SiO}_2$ -alcogels doped with  $\text{H}_3\text{PO}_4$ ,  $\text{NH}_4\text{BF}_4$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{KH}_2\text{PO}_4$ . The polymeric gels were obtained by immobilising as gels the aprotic solution electrolytes of *o*-, *m*-, *p*-hydroxybenzoic acid; *o*-, *m*-, *p*-nitrobenzoic acid and three dicarboxylic acids, viz., oxalic, malonic and succinic acid. It has been found that the polymer has a role to play in the modification of conductivity of polymeric gels for which a “breathing chain model” is discussed.

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