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Fast ion conducting lithium glasses—Review

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Abstract. For the last few years fast ion conducting lithium glasses are being studied due to their potential use in advanced electrochemical devices. A number of glass systems containing oxides, sulphides and other lithium compounds prepared by both conventional cooling and rapid quenching techniques have been reported. In this paper we review the transport properties of lithium ion conducting glasses. The special features of the ionic conduction process have been highlighted and some experimental techniques to study transport properties have been described. Some of the common observations of the properties have been discussed and finally some important problems for future development have been pointed out.

Keywords. Glassy electrolytes; electrical conductivity; transport number; glass structure; solid state batteries.

1. Introduction

Electrochemical cells using lithium ion conducting electrolytes develop high voltages (> 2 V) and high specific energy density (~ 1000 Wh/kg) due to the light weight and highly electropositive character of the lithium metal. Therefore, many research groups have focussed their attention on lithium-based battery systems. Many of these lithium batteries are primary non-rechargeable batteries with liquid electrolytes and suffer from the fact that the organic solvents usually used are highly reactive and toxic. Solid electrolytes which conduct lithium ions, are expected to play an important role as materials for advanced batteries. In addition, these electrolytes have other applications such as in timers, coulometers, solid state display devices, sensors etc. The crystalline Li-conductors, which have been investigated in greater detail are suspected for large scale production, due to stringent structural requirements for the desired properties. Thus non-crystalline solids, which can be easily produced on larger scales, are receiving recent attention. Glassy lithium-solid electrolytes have been studied extensively and are found to have definite advantages over crystalline conductors like isotropic properties, ease of thin film formation, flexibility of size and shape (at satisfactory cost) etc. One of the important features of glass as solid electrolyte is the possibility of continuously changing composition over a wide limit. Although some of the lithium ion conducting glasses find application as positive electrodes, only those which would be useful as electrolytes are discussed here. This review includes a brief discussion about the general theory of ionic conduction as applied to glasses and the results obtained on some of the promising glass systems. Finally some of the problems for the future development of the glassy solid electrolytes and their applications are discussed.

2. General features of ionic conduction in glasses

The mobile ionic species in a solid conductor move rapidly through a framework which is formed by other atoms of the lattice. This ability of a material to allow the movement of ions through it can be estimated by the measurement of a range of transport properties like conductivity, diffusion, motional narrowing of NMR lines etc. The ionic conductivity of a solid, σ, usually follow an equation of the form

$$\sigma = \sigma_0 \exp(-E/kT), \tag{1}$$

where σ_0 = pre-exponential factor, E = activation energy of conduction, k = Boltzman's constant and T = absolute temperature. Accordingly, the activation energy can be estimated from the slope of the plot of log σ vs reciprocal temperature.

For simple ionic conductors, (1) may be derived phenomenologically from the general definition of conductivity, in terms of density of charge carriers (n) of charge q, having a mobility μ given as

$$\sigma = nq\mu. \tag{2}$$

The Einstein expression for the drift mobility of a diffusing species is

$$\mu = qD/kT, \tag{3}$$

where kT is the Boltzman's factor, and the diffusion coefficient (D), is expressed as

$$D = D_0 \exp(-\Delta G_m/kT), \tag{4}$$

contains the Gibb's free energy term given by

$$\Delta G_m = \Delta H_m - T\Delta S_m, \tag{5}$$

for the ion jump from one atomic site to a neighbouring vacant site. It follows from (2) to (5) that E in (1) contains the migration enthalpy (ΔH_m) in addition to any energy E_d that might be required to create mobile point defects

$$E = \Delta H_m + E_d. \tag{6}$$

Oxide glasses are by far the most widely studied systems. The ionic character of the conductivity in oxide glasses has been established by Warburg (1884). These glasses are formed by network forming oxides (SiO_2, B_2O_3, P_2O_5, GeO_2 etc) giving rise to a random corner-linked tetrahedron arrangement broken in some places by the network modifier alkali oxides. The structure has large holes which facilitate ionic migration. These holes are surrounded by non-bridging oxygens (NBO) which act as host for alkali ions. A two-dimensional schematic diagram is shown in figure 1.

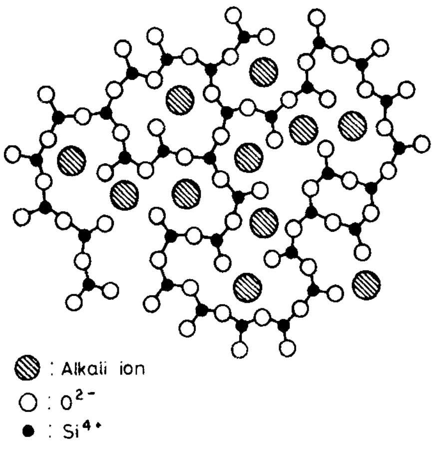

Figure 1. Two dimensional schematic representation of a silica glass with modifier alkali cations.

The conductivity of a glass shows a behaviour typical of a thermally-activated process as discussed above and the current carriers are predominantly alkali ions. The appropriate model consists of a alkali metal ion in a potential well undergoing thermal vibration and having finite and equal probability of surmounting the barriers and moving to any adjacent potential well. The quantitative treatment of such a model was provided by Stevels (1957) which was later modified by Taylor (1959). The model considers a distribution in the magnitude of the energy barrier and is consistent with the random network of the glasses. Such a model, therefore, gives an average value of activation energy of DC conduction, since the ion encounters potential energy barriers of various heights during the long range motion.

Although a number of different other transport models (Nakajima 1972; Charles 1961; Tomozawa 1977) are available to explain the Arrehenius-like temperature dependence of ionic conductivity in glasses, the models similar to that described above, have been widely accepted (Hughes and Isard 1972).

The ionic conductivity of alkali-containing oxide glasses increases and the activation enthalpy decreases, as the alkali oxide concentration is increased. However, the conductivity is not a linear function of the alkali metal ion concentration. This has led to the concept that some of the alkali metal ions are mobile, while others are "trapped" in the structure and can undergo local, but no long-range motion. The work carried out in recent years has provided more insight into this phenomenon and predicts glass formation in new systems with exceptionally high values of conductivity. One important observation is that the conductivity is proportional to the square root of the alkali oxide activity in the alkali silicates (Ravaine and Souquet 1973, 1977, 1978). This leads to the concept that the alkali metal ions exist in the structure in such a way that one can think in terms of an association-dissociation equilibrium of the alkali oxide in the glass solvent, with the charge carried only by the dissociated cations. This approach is analogous to that used in liquid electrolyte solutions.

The extension of these ideas is to attempt for increasing the oxide activity (concentration) to enhance the conductivity. There are limits as to how far one can go in this direction, before devitrification becomes a problem due to the reduction in the size of the anionic group in the structure. This problem can be overcome and the concentration of undissociated alkali metal ions increased by the addition of alkali halides. In such cases one can assume that neither the alkali metal ion nor the halide ion becomes bound into the macromolecular anionic structure, which consists primarily of shared tetrahedral groups. Quite large concentrations of alkali halides and other simple salts can be incorporated in these glasses and since the cationic and anionic species are highly dissociated, the conductivity can be increased substantially about two orders of magnitude for lithium glasses. As in analogous liquid solutions, the degree of dissociation and thus the contribution to the conductivity is greater, the larger the ion with which the mobile cation is associated. It has also been found that sulphide analogs of the oxide glasses have ionic conductivities about an order of magnitude higher.

3. Techniques for electrical characterization

3.1 *Conductivity measurement*

The most useful parameter of a solid electrolyte is its ionic conductivity as a function of temperature. The parameter determines the mass transport rate through the solid and thus influences the power production of an electrochemical device, of which solid electrolyte forms a part. It can be measured using both AC and DC techniques with ionically blocking or conducting electrodes at two, three or four points of contact. DC measurements present polarisation problems when performed with blocking electrodes whereas use of reversible electrodes may involve appreciable charge transfer resistances due to Faradiac processes at the electrode-electrolyte interface. The single frequency AC measurement provides only an approximate information about the conductivity of a material. The situation in a solid cell, however, is much more complicated since there are various factors which contribute towards ultimate electrical impedance. The contribution due to movement of ions through the bulk of the electrolyte, electrode-electrolyte interface impedance, charge transfer across the interface and the resulting double layer are all summed up in single frequency measurements. All these electrical and electrochemical parameters are functions of applied frequency and their responses are quite different in the different frequency ranges due to their widely different relaxation times. With recent advances in electrochemistry, rigorous analysis of the AC response of an electrolyte or electrochemical cell is possible. Complex impedance (Z^*), admittance (Y^*), permittivity (ε^*) and modulus (M^*) are the four basic functions for analysis of AC data (Hodge *et al* 1976). Baurale (1969) first applied this technique for zirconia solid electrolytes and in subsequent years a large number of materials have been analysed including glasses (Armstrong *et al* 1974; Ravaine and Souquet 1974). The details of the techniques have been comprehensively reviewed (Bottelberghs 1978; McDonald 1976a; Britzs 1980; Johnscher 1978; Shlesing 1980; Grant *et al* 1977; McDonald and Jacobs 1976b). In principle, the various forms of the AC data provide separately the detailed information about various physical processes in an electrochemical cell. This is done by comparing the experimental plots with those that would have been generated by model systems called equivalent circuits which consist of resistances and capacitances combined either in series or parallel.

3.2 *Transport number measurement*

Some of the materials show conductivity due to more than one ion and sometimes also due to electrons. The value of this electronic conductivity largely decides the ultimate device application of the material. For example, an electrolyte for pacemaker application, where low currents and long shelf life is a basic requirement which must not exihibit any electronic leakage current. Hence, the electronic transport number t_{el} (fraction of the total charge carried by electrons) should not exceed 10^{-6}. On the other hand, for load levelling where the system would be cycled daily, it can be as high as few percent if high ionic conductivity is otherwise obtained. Tubandt's (1932) method which is widely used, gives the measure of ionic transport number but does not give an exact idea about the low level electronic conductivity. Wagner's (1956) asymmetric polarisation cell method which employs one electrode reversible to ions and other completely blocking the ion, gives accurate values of electronic conductivity of the electrolytes. The combination of the electronic conductivity, so determined, with total conductivity yields transport number of electrons and ions. Estimation of the electrochemical decomposition potential of the electrolytes is an advantage of this technique. In recent years, pulse technique has also been designed for transport number measurements (Yakoto 1955). The results are generally supplemented by open circuit potential measurements which show near thermodynamic values if the transport number of mobile species is near unity (Wagner 1957).

4. Glass systems

Otto (1966) was the first to report glasses with high Li^+ conductivities at relatively low temperatures. Nearly 100 different compositions in the M_2O-B_2O_2-SiO_2 (M = Li, Na, K) reported by him are still being investigated for possible applications. He observed that high Li^+-conductivities could be obtained in borate glasses if more than 40 m/o lithium compounds could be incorporated in the glass without devitrification. The value of 10^{-1} (ohm-cm)$^{-1}$ at 350°C, reported by him for one of the compositions is still the highest conductivity reported so far, for Li^+-conducting borate glasses. The knowledge about the advanced applications of glasses and their large scale production potential, stimulated the interest of many investigators and the results on a large number of glassy systems have been reported.

4.1 *Alkali borates*

Activation energy of electrical conduction increases linearly with increasing M_2O content (M = alkali metal) in M_2O-SiO_2-B_2O_3 glasses containing less than 25 m/o M_2O (Otto 1966). Replacement up to 50 m/o of B_2O_3 by SiO_2 showed small change in the value of activation energy for a given alkali content. The pre-exponential factor was almost independent of M_2O content. Lithium content of the glasses was further increased by incorporating lithium salts like Li_2SO_4, LiCl or LiF and this helped in obtaining enhanced conductivities than in those containing Li_2O alone. All the conductivity measurements were initially carried out at single frequency (1 kHz). Tuller *et al* (1980) later verified the conductivity values by application of complex impedance analysis.

These results on the borate system promoted interest of many investigators to obtain the crystalline fast ion conducting compositions [$Li_4B_7O_{12}X$ (X = Cl, Br, I)], with boracite structure (Jeitschko 1972a, b; Jeischko *et al* 1977) even in the glassy form. For example the glass system B_2O_3-Li_2O-LiX has shown promising results (Levasseur *et al* 1978, 1979). Ionic conductivity is a strong function of polarizability of the anion or in other words the conductivity is a function of ionic radius of the anion. A glass containing LiI shows a maximum conductivity of $3{\cdot}4 \times 10^{-2}$ (ohm-cm)$^{-1}$ at 350°C with an activation energy of 0·46 eV. As expected the increase in the concentration of Li^+ lead to an increase in the ionic conductivity. Based on this observation various authors have studied multicomponent systems. One such system, Li_2O-LiF-Li_2SO_3-Li_2SO_4-B_2O_3, has been studied (Smedly and Angell 1978) where total Li_2X content is varied between 43 and 84 m/o. A glass with 70 m/o LiX shows a maximum conductivity [$2{\cdot}26 \times 10^{-3}$ (ohm-cm)$^{-1}$] at 200°C. The high conductivity of this glass has been suggested to be due to the salt-like structure of the glass at the higher Li_2X levels. The influence of F/O ratio on conductivity has also been investigated. Glass transition temperature shows dependence on heating and cooling rate (q) during its measurement and also on the F/O ratio. Dependence of heating and cooling rate on T_g leads to the following relationship.

$$\frac{d\ln|q|}{d(1/T_g)} = -\frac{\Delta H^*}{R}, \tag{7}$$

where ΔH^* represents the activation energy for structural relaxation. An increase of ΔH^* with increase of LiF content is correlated with increased packing density. Even then, the glass with higher LiF content is reported to exhibit higher conductivity. While attempting to elaborate the conduction mechanism of fluoroborate glasses, an isothermal drift in the conductivity at temperatures below T_g, is observed (Boehm and Angell 1979). Differential scanning calorimetry and conductivity measurement on quenched and annealed glasses, in the temperature range 150–200°C, yield an activation energy which is less by one order of magnitude, than the characteristic activation energy for primary structural relaxation. The discrepancy is explained in terms of secondary structural relaxation, frequently observed in polymeric glasses. The complete AC response of fluoroborate and sulphoborate glasses is studied by combining conductance studies in the frequency range 0·1 Hz to 10^6 Hz with Fourier transform interferrometric spectral measurements, in the range 10^{12}–10^{13} Hz (Angell 1981). The total AC response, is shown in figure 2. It may be noted from the figure that it covers 7 orders of magnitude of frequency-dependent conductivity and the far IR spectrum with the conversion from conductivity to optical absorption coefficient α. These results are interpreted with the help of computer simulation of the observed high fictive temperatures of Li and Na silicate glasses using the principle of motional ion dynamics.

In order to explain the exceptionally high values of conductivities from structural aspects, which would help in predicting new systems, attempts have been made to correlate conductivity results with those obtained from various spectroscopic techniques. Based on some such analysis ionic conductivities in B_2O_3-Li_2O-Li_nX system ($n = 1, X = Cl, Br, I; n = 2, X = SO_4; n = 3, X = PO_4$) have been explained (Levasseur *et al* 1979a,b, 1980, 1981a,b,c; Hagenmuller *et al* 1979; Irion *et al* 1980). The maximum conductivity attained in this system is approximately 10^{-2} (ohm-cm)$^{-1}$ at 300°C and is dependent on Li_2O and Li_nX contents. Raman spectroscopic studies on B_2O_3-xLi_2O and B_2O_3-xLi_2O-$yLiCl$ have been carried out and the results are shown in figure 3a, b. Pure boron oxide glasses are characterised by a strong Raman peak at 806 cm^{-1} (figure 3a). The addition of Li_2O to B_2O_3 brings about a progressive disappearance of

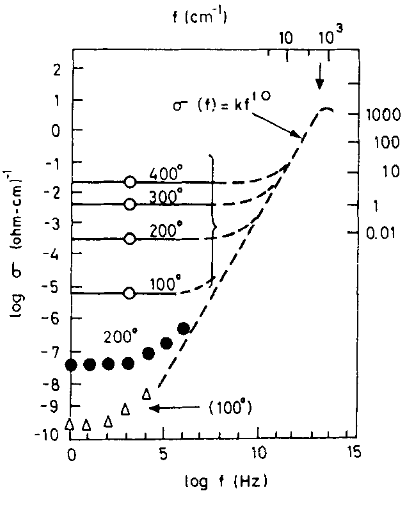

Figure 2. Frequency dependent conductivity of sulphoborate glass. Conductivity at higher frequencies determined from optical absorption coefficient (Angell 1981).

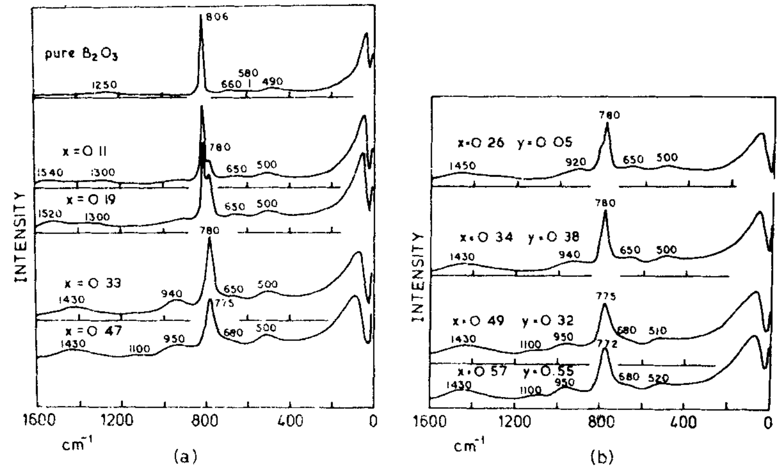

Figure 3. Raman spectra of glasses. **a.** B_2O_3-$x$$Li_2O$ and **b.** B_2O_3-$x$$Li_2O$-$y$LiCl (Levasseur *et al* 1980).

this peak and a quick intensity increase of a new strong peak at 780 cm^{-1}. At $0{\cdot}05 \leqslant x \leqslant 0{\cdot}25$ both the peaks are simultaneously present in the spectra of the B_2O_3-$x$$Li_2O$ glasses, but at $x = 0{\cdot}33$ the 806 cm^{-1} peak has completely vanished. This modification of the spectra is attributed to the progressive substitution of boroxal rings (boron only in III coordination) by triborate and tetraborate groups (boron simultaneously in III and IV coordinations). Comparing the Raman spectra of B_2O_3-$x$$Li_2O$-$y$LiCl glasses, of various compositions, (figure 3b), with that of B_2O_3-$x$$Li_2O$ (figure 3a), it is clear that there are no modifications in the structure. For a given x the spectra for binary and ternary systems are identical and it may be concluded that the addition of LiCl does not induce any modification in the vitreous boron-oxygen lattice and the interpretation of the vibrational spectra of simple borate glasses may be extended to the spectra corresponding to ternary composition. Raman scattering studies of glasses belonging to B_2O_3-$x$$Li_2O$-$y$$Li_2SO_4$ shows no modifications and the spectrum of SO_4^{2-} anions in the glass is analogous to that observed for SO_4^{2-} in aqueous solutions (Walraffen 1965). Therefore it seems that there is no apparent interaction between boron-oxygen lattice and diluted salt solutions. Investigations have also been performed on glasses containing Li_3PO_4 and its behaviour with respect to boron-oxygen network has been studied. The Raman spectra shows that PO_4 units are bound to boron-atoms. The conductivity rise has been attributed to dissociation of lithium salts. Basu *et al* (1983) have reported high values of conductivity nearly 10^{-4} (ohm-cm)$^{-1}$ at 250°C for Li borate glasses containing Li_3PO_4. They have predicted that ($Li_2O + B_2O_3$) and Li_3PO_4 mix almost ideally without any major structural change. An EPR study of fast Li^+ conducting glasses in B_2O_3-Li_2O-LiCl has been carried out, after x-ray irradiation at room temperature (Levasseur 1979b). Two types of paramagnetic centres have been reported to be present. The first is a Cl_2^- species (V_k centre) present in vitreous domain where low concentration of LiCl prevailed whereas the second is of BOHC (boron oxygen hole centre) type which is reported to be generally present in glasses. Studies on glass-forming ability in Li_2O-LiCl-Al_2O_3-B_2O_3 have been pursued for increasing Li^+ concentration (Takahashi and Yamamoto 1979). A glass with nominal composition of

29 Li_2O-24Li_2O-3Li_2O-44B_2O_3 (in mole %) shows maximum conductivity (7 × 10^{-3} (ohm-cm)$^{-1}$ at 300°C) with an activation energy of 0·43 eV. Near ideal open circuit voltages of the cells and motional narrowing of ^{7}Li NMR spectra supports Li^+ motion in these glasses. High Li^+ conductivity has been reported in lithium chloroborate glasses, nearly 10^{-2} (ohm-cm)$^{-1}$ at 300°C (Button *et al* 1980). It has been demonstrated that substitutions of Cl for O (not-site-for site) in chloroborate glasses with composition 36·4 m/o Li_2Z (Z = O, Cl_2) – 63·6 m/o B_2O_3 results in systematic increase in Li-ion conductivity and decrease in T_g and density. Total B and Li contents have been maintained constant to facilitate changes in O/B ratio. Glasses with same O/B ratio are compared. Most NMR studies predict that the relative numbers of BO_3 and BO_4 units are characteristic of a given O/B ratio and represent overall glass structure (Geissberger *et al* 1982a; Irion *et al* 1980; Bray and O'Keefe 1963). Button *et al* (1982) have, however, contradicted this view and visualized a systematically weakened and expanded network to accommodate the excess of LiCl and accordingly the structure must show compositional variation from binary to ternary. The inability of spectroscopic technique leads the authors (Button *et al* 1982) to question the validity of such technique to verify structural hypothesis such as Krogh-Moe model. The tentative model proposed by them is based entirely on the results of T_g and density. They have argued that the large (r_{Cl^-} = 1·8 Å) negatively charged Cl cannot be accommodated in the structure without significant reorganization.

Figure 4 shows the schematic two-dimensional mode of the structure of a glass at relatively (a) low (b) high alkali contents and (c) a proposed structure for chloroborate glasses. It has been suggested that the Cl^- substitution induces bias for polyborate unit formation with connected BO_4 tetrahedra (*eg* diborate groups) at the expense of units with unconnected tetrahedra (*eg* tetraborate).

The ^{11}B NMR data for the lithium chloroborate and lithium fluoroborate glasses shows that no observable amounts of new covalently bonded boron microstructures (MS) are present in the network of the ternary systems and the types of units present depend on the O/B ratio of the glass (Geissberger *et al* 1982). This implies that the

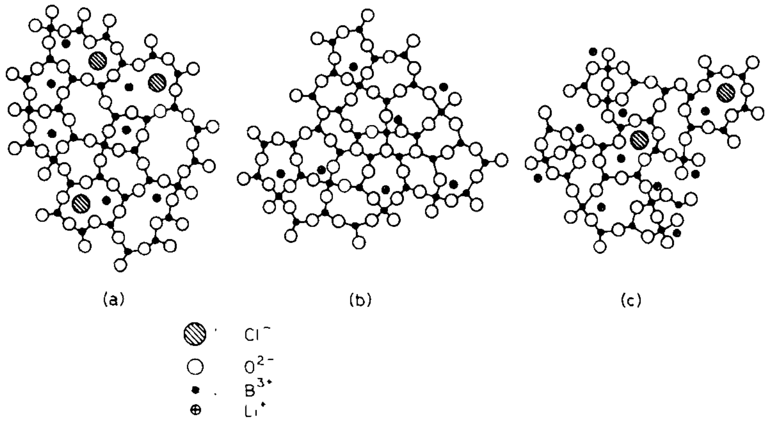

Figure 4. Two dimensional schematic representation of a lithium chloroborate glass. **a**. ternary glass with low lithium content; **b**. binary glass with high alkali content; **c**. proposed weakened and expanded structure for a ternary glass (Button *et al* 1982).

lithium halide enters the borate network interstitially, as dissociated ions and therefore does not contribute to network formation. Motional narrowing studies of the ^{7}Li NMR spectra for one of the glasses indicates that ^{7}Li ion is mobile with a characteristic activation energy of 0·2 eV. Similar studies of the ^{19}F spectra indicate either fluorine ion mobility or a very strong dependence of the ^{19}F spectrum on the lithium ion motion. Bray *et al* (1980), earlier, studied ^{10}B NMR spectra of B_2O_3 and Na_2O-B_2O_3 glasses and extended it to explain the behaviour of Li- borate containing 65 m/o Li_2O. The glasses have been thought to be composed of various structural groupings (tetraborate, metaborate, diaborate etc.) found in crystalline compounds. ^{10}B NMR spectra gives the exact number of each grouping present in the glass and facilitates formulation of specific structural units. Computer simulation techniques, to investigate the second moment and the quadrupolar structure of satellites in borate glasses with low lithia content, have explained the results in terms of BO_3 and BO_4 units (Tabby and Hendrickson 1980).

In the continued efforts to explore the possibility of highly conducting glasses, some of the investigators have studied mixed isotopic conductivity in lithium borate system. The conductivity with various ^{6}Li/^{7}Li ratios has been determined as a function of temperature using impedance analysis (Downing *et al* 1982). The conductivity decreases continuously with slight increase of activation energy as ^{7}Li is substituted for ^{6}Li and the conductivity does not follow the classical diffusion theory. The data are interpreted in terms of an absolute reaction rate theory incorporating quantum partition function. AC and DC conductivities of borate glasses containing a total of 0·2 mole fraction of $^6Li_2O$ and $^7Li_2O$ are measured (Peterson 1982; Abou *et al* 1978) and the observed mixed alkali behaviour is thought to originate from the mass difference of alkali ions.

For application as solid electrolytes, the material with required high ionic conductivity, has also to be compatible with the metal anodes. Conductivities have been optimised for borate glasses but there are no reports about their durability with molten Li or water. Durability of glasses with molten Li and water is the extension of earlier work on borate glasses where durability in molten Li was studied with and without applied field (Barsoum *et al* 1981). The lithium chloroborate glasses, investigated recently, have been studied in the temperature range 180–250°C against Li (Velez *et al* 1982). The formation of reaction layers was observed. The diffusion-controlled chemical attack predicted for corrosion was supported by parabolic increase of layer thickness with time. The rate of corrosion shows dependence on Li_2O content in the Li_2O-B_2O_3 and Li_2X/B_2O_3 $(X = Cl, O)$ ratio in the B_2O_3-Li_2O-$(LiCl)_2$ system. For higher B_2O_3 contents (> 70 m/o) durability decreases with increasing chlorine content. While for lower B_2O_3 concentrations (< 50 m/o), LiCl additions help to increase durability. The activation energy of corrosion varies from 0·5 eV for pure B_2O_3 to 2 eV for high $(LiCl)_2/B_2O_3$ contents. It is suggested that a glass with minimum B_2O_3 content, consistent with glass formability, would show optimum resistance to molten Li attack. Some glasses are also studied for durability in water and buffered solution (pH = 7) at 30 and 40°C. The dissolution takes place by a reaction controlled mechanism. A minimum dissolution rate is obtained for 25–30 m/o Li_2O in the binary Li_2O-B_2O_3 system. This is found to agree well with the maximum structure connectivity for this range. The increased dissolution rate with increased LiCl contents implies a open and weakened structure with LiCl additions proposed earlier (Button *et al* 1982).

4.2 *Alkali silicate glasses*

Glasses in various alkali silicate systems show sharp decrease in resistivity and activation energies with increasing alkali content up to 20–25 m/o M_2O (M = Na, K, Li) followed by much smaller changes at larger M_2O contents (Charles 1966; Otto and Milburg 1968; Hakim and Uhlman 1971). Highest conductivities of 7×10^{-6}, 1×10^{-6} and 1×10^{-6} (ohm-cm)$^{-1}$ at 100°C are observed for glasses with 45 m/o Na_2O, 40 m/o K_2O and 40 m/o Li_2O respectively with activation energies ranging from 0·54–0·60 eV. Comparison of conductivities of glasses and glass ceramics with compositions related to that of β-eucryptite, ($LiAlSiO_4$) shows better electrical properties for glasses than the glass ceramics (Johnson *et al* 1975, 1976). Single crystals, however, yield (Biefeld *et al* 1978) higher conductivity along *c* axis than the glass but the activation energy is higher (nearly 0·82 eV against 0·62 eV for glass). Attempts have been made to increase the conductivity of the Li_2O-Al_2O_3-$2SiO_2$ glass by substituting Ga for Al, Ge for Si and B for Si. However, it does not show any major effect on conductivity. Examination of the effect of replacing Si by S in the system $Li_2Si_2O_5$-Li_2SO_4 shows linear increase in conductivity with Li_2SO_4 content (Kone *et al* 1979). High ionic conductivities are observed for a glass at the boundary of glass formation region. The activation energy (0·66 eV) does not change with composition and the increase of conductivity is attributed to the increase of σ_0. Electrical conductivity, derived from complex impedance analysis, in Li_2O-SiO_2-Li_2SO_4 system shows slightly higher values [10^{-5} (ohm-cm)$^{-1}$ at 100°C] compared to those obtained with single frequency measurement (Souquet *et al* 1980; Kone *et al* 1982). The Raman spectra indicate the presence of glassy-disilicates and sulphates. From a structural point of view SO_4 tetrahedra seems to be incorporated in the micromolecular skeleton of the silicate groups. This insertion is thought to inhibit recrystallization by destroying the regularity of the SiO_4 chains and allows glass formation with high lithium content (Li/Si = 2·2). The redox stability, studied by cyclic voltametry, shows extensive stability domain. Prasad *et al* (1980) have reported glasses in $LiNbO_3$-SiO_2 system with 35 m/o SiO_2 which show conductivity of the order of 10^{-4} (ohm-cm)$^{-1}$ at 200°C. However, a similar glass doped with 0·1 m/o Fe_2O_3 exhibits higher conductivity of nearly 10^{-3} (ohm-cm)$^{-1}$. Higher addition of Fe_2O_3 causes a decrease in conductivity which the authors have associated with the onset of nucleation of crystallites within the glass matrix. A number of observations are consistent with predominantly ionic conduction; however, no direct verification like fabrication of concentration cell, has been attempted. Raman spectra of Fe_2O_3 containing SiO_2-Li_2O glasses indicate that a significant fraction of trivalent iron deforms the local glass structure to form a range of structurally distinct sites as in crystalline solids. The trivalent Fe^{3+} exists in its distinct local environment in the glass structure. It has been concluded that the impurities are unable to enhance the electronic conductivity of these glasses.

4.3 *Alkali phosphate glasses*

Exceptionally high values of ionic conductivity in the unusual glass forming system M_2O-MF-$Al(PO_3)_3$ (M = Li, Na, K, Cs) which does not contain any conventional glass former, have been reported by Evastrop'eV *et al* (1974). A glass with nominal composition $50\,LiF:30Li_2O:20Al(PO_3)_3$ shows the highest conductivity of the order of 10^{-2} (ohm-cm)$^{-1}$ at 300°C. The corresponding activation energy is 0·52 eV. The transport number of lithium ion is greater than 0·999 and does not change appreciably with temperature. Fluorine ion does not contribute towards conductivity. Some of these results have been later confirmed by Jagla and Isard (1980) who have prepared a number of glasses with different LiF contents. They have also determined the transport number to be around unity by Tubandt's (1932) method. The conductivity has been determined from a frequency-independent conductance plateau. The mixed alkali effect has been observed in $Al(PO_3)_3$-NaF-LiF system and is supported by electrical measurements, IR spectra, density, refractive index, average dispersion and molecular refraction studies (Pronkin 1978).

A more detailed investigation on the LiF-Li_2O-$Al(PO_3)_3$ has been carried out (Kulkarni *et al* 1981). Glass formation region in this system has been studied in both conventional and rapid quenching technique (Kulkarni 1984). The latter technique gives an extended glass formation region incorporating 40 m/o Li_2O against only 25 m/o in the former technique. DC electrical conductivity of the glasses has been derived from impedance/admittance analysis. Complex impedance has been measured over a wide range of frequency (5 Hz–13 MHz) at various temperatures using silver paste electrodes. A representative impedance plot is shown in figure 5. It may be observed that at each temperature the high frequency data are represented by nearly perfect circular arcs all of which pass through the origin and have their centres on a straightline also passing through origin and making a very small angle of three 3° with the real axis. Therefore, the circular arcs may be considered as nearly perfect semicircles. These semicircular arcs originate from the ionic migration in the bulk of the electrolyte and the intercept on real axis represents true DC value of the resistance excluding electrode polarisation effects which appear at lower frequencies. The observed phenomenon has been accurately modelled by proposed equivalent circuit. A glass with nominal composition 70LiF-15Li_2O-15$Al(PO_3)_3$ shows the highest value of conductivity [$1·3 \times 10^{-3}$ $(\text{ohm-cm})^{-1}$] at 230°C. The electronic conductivity of these glasses has been obtained from Wagner's asymmetric cell and very low values for electronic currents have been recorded ($8·57 \times 10^{-7}$ A/cm^2). The transport number of Li^+

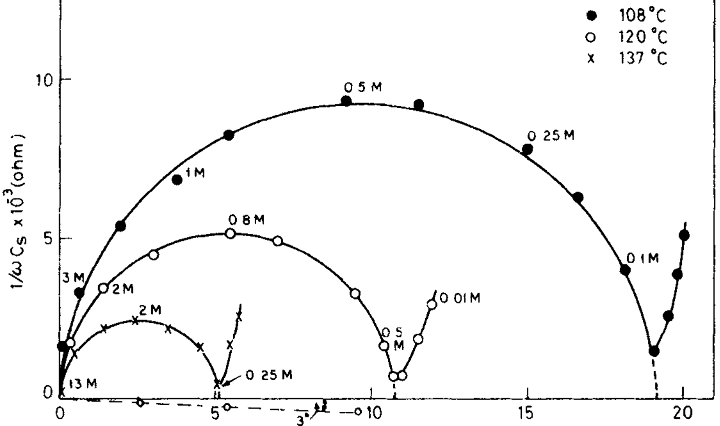

Figure 5. Complex impedance plots of LiF-Li_2O-$Al(PO_3)_3$ glass at various temperatures with silver electrodes (number on top indicate frequency in MHz).

exceeds 0·999. Near thermodynamic values of open circuit potentials supported the unit value for t_{Li^+}. From the long term stability of the cells fabricated (over a month) it has been concluded that the glasses are compatible with lithium anodes (Maiti *et al* 1983).

The electrical conductivity of the LiF-Li_2O-Al$(PO_3)_3$ glasses increases almost linearly with increasing Li-ion concentration as shown in figure 6. It may be pointed out that the extrapolation of the straight line plots at each temperature to the concentration axis leads to a fixed value of Li^+ ion concentration which does not participate in the conduction process. Thus the number of effective charge carriers in the glass is very low. The calculated mobilities are almost 4 orders of magnitude higher than that in the lithium conducting glass electrodes (Bauck 1975). The exceptionally high mobility explains the high conductivity of these glasses (Kulkarni 1984a).

Glass transition temperature, electrical conductivity and the Raman spectra for $AgPO_3$-Ag_2SO_4 and $LiPO_3$-Li_2SO_4 system have been determined and compared (Malugani *et al* 1978). The highest conductivity of the order of 10^{-7} (ohm-cm)$^{-1}$ at 25°C is reported for the Li glasses. The conductivity increases with increasing Li_2SO_4 content while the T_g and the activation energy decrease continuously. The Raman spectra does not show any significant modification above 200 cm^{-1} for $LiPO_3$ glass. It has been suggested that the sulphate additions form relatively independent substructures in the glass which are responsible for the improved ionic conductivity. The glasses in the system $LiPO_3$-LiX (X = Cl, Br, I) investigated by Malugani and Robert (1979) show linear increase in electrical conductivity, decrease in activation energy and glass transition temperature, with increasing LiX content. For a given LiX/$LiPO_3$ ratio the conductivity increases with halogen radius. There is a close agreement between the transference number obtained from Wagner's polarisation technique and emf method. The conductivity is essentially due to Li^+ ions. Analysis of Raman spectra of these glasses indicates almost no change in the vibrational modes of the P-O bonds implying that the halogens are not incorporated in the polyphosphate chains. It is suggested that

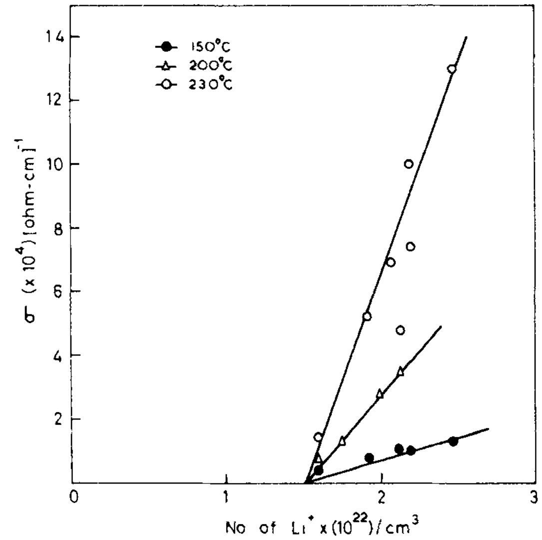

Figure 6. Ionic conductivity as a function of lithium ion concentration at three different temperatures for LiF-Li_2O-Al$(PO_3)_3$ glasses.

a relatively independent alkali halide substructure is formed which contributes to the enhanced alkali ion transport. Structural details of the vitreous state due to changing composition in Li_2O-LiCl-P_2O_5 system have been explained from Raman spectroscopic results. (Doreau *et al* 1980). The maximum conductivity of the order of $5 \cdot 10^{-7}$ at 25°C is reported. Glasses in $LiPO_3$-$ZnCl_2$ and $LiPO_3$-$AlCl_3$ mixed systems have also shown good ionic conductivity (Doreau and Robert 1980). A mechanism of exchange of ions has been proposed to explain the properties of these glasses. It was observed that the structural hypothesis developed for $AgPO_3$-MI (M = Na, K) does not hold for $LiPO_3$-$ZnCl_2$ but explains the properties of $LiPO_3$-$AlCl_3$ glasses.

4.4 *Sulphide glasses*

In an attempt to improve the ionic conductivity of lithium glasses, several possibilities concerning either the addition of lithium salt or the change of support glass have been considered. Substitution of halides by sulphate (Malugani and Robert 1979) and changes in oxide modifier/oxide former ratio to modify lithium metaphosphate glasses have also been attempted (Abou 1979), but it does not show appreciable increase in conductivity. Based on this work, oxide-based (Li_2O-P_2O_5) vitreous support has been replaced by its sulphured homologue (Li_2S-P_2S_5). This choice has been considered from the fact that sulphur compounds often show higher ionic conductivities than those of their oxide analogues (Ribes *et al* 1980). Glass formation has been reported in LiI-Li_2S-P_2S_5 system (Malugani and Robert 1980). The conductivity of a glass with nominal composition 0·37 Li_2S-0·18 P_2S_5-0·45 LiI glass at 20°C is nearly 10^{-3} $(\text{ohm-cm})^{-1}$ with an activation energy of 0·31 eV (Mercier *et al* 1981). Electronic conductivity obtained by Wagner's method is reported to be less than 10^{-7} $(\text{ohm-cm})^{-1}$ at 25°C. The redox stability of the glasses has been determined by cyclic voltametry and by Wagner polarization method. A typical voltagram obtained for the glass is shown in figure 7. The cathodic and anodic limits are characterized respectively by a reversible peak at $e_0 = -1 \cdot 9$ V and by a non apparent reversible peak at $e_0 = +1$ V. The cathodic peak is thought to be due to reduction of Li^+ while on the return cycle the oxidation peak corresponds to the dissolution of 80 % of the deposited metal. In the anodic range, the electrochemical reaction relative to the oxidation wave is

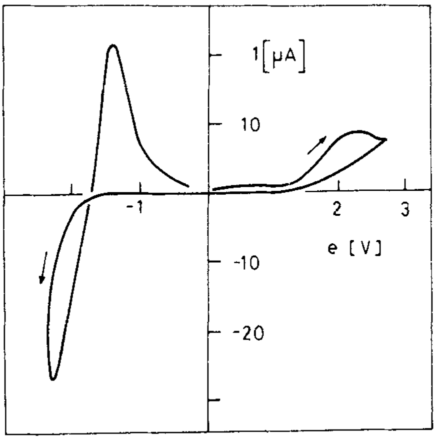

Figure 7. Cyclic voltametry curve for a LiI-Li_2S-P_2S_5 glass (Mercier *et al* 1981).

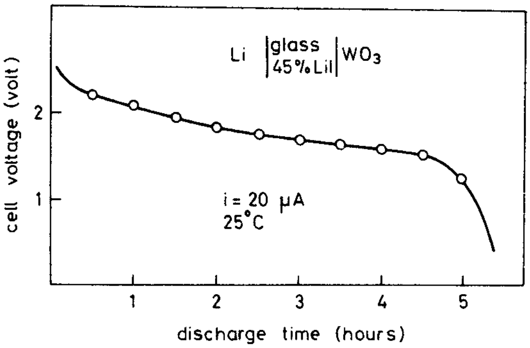

Figure 8. Discharge characteristics of a LiI-Li_2S-P_2S_5 glass in Li/Glass/WO_3 cell (Mercier *et al* 1981).

attributed to the sulphides strongly bonded to the glassy network. The electroactivity range thus determined is about 2·9 V. The discharge characteristics of a cell using LiI-P_2S_5-Li_2S glass has been studied at room temperature. An output curve obtained for the cell Li/glass/WO_3 is shown in figure 8. It may be noted that the discharge at 25°C at a current density of 20 μA shows the cell stability for nearly 4 hr.

Souquet *et al* (1980) and Mercier *et al* (1981) have investigated M_2S-GeS_2 system (M = Li, Na, Ag). GeS_2 formed stable glasses with alkali sulphides in the range 1–0·5 molar ratio of GeS_2/M_2S. The electrical conductivity of these glasses has been measured over a range of temperature for different compositions. At 50 m/o Li_2S, the conductivity is maximum [4×10^{-5} (ohm-cm)$^{-1}$] with an activation energy of 0·51 eV. The structure investigated by Raman spectroscopy shows that it consists of GeS_4 tetrahedral units. Peaks for Ge-S-Ge and stretching modes of Ge-S bond with non-bridging sulphur atoms are detected. At lower frequencies translational and vibrational motions of the network fragments and also of Li^+ vibrations are observed. Electrochemical stability of these glasses is tested by three-electrode voltametry. The stability range of 4 volts observed is slightly greater than that expected from thermodynamic data corresponding to the formation of pure sulphide (2·3 volts for Li_2S). This is assigned to the lower thermodynamic activity of sulphide in glass and to the slow kinetics of electrochemical reaction involving sulphur ions.

4.5 *Quenched glasses*

High Li^+ ion conductivities have also been reported in a number of specially prepared glass systems in which one normally does not expect glass formation. Glasses have been prepared by rapid quenching techniques in Li_2O-Nb_2O_5 (Glass *et al* 1978), Li_2O-Ta_2O_5 (Nassau *et al* 1979a, b, 1981a), Li_2O with Al_2O_3, Ga_2O_3 and Bi_2O_3 (Glass and Nassau 1980), WO_3 (Nassau *et al* 1980), MoO_3, Li_2SO_4 with SrMg $(SO_4)_2$ and $La_2(SO_4)_3$ (Nassau and Glass 1981b). The conductivity values are reported to be greatly enhanced compared to those normally observed in the corresponding crystals. These enhanced conductivities [$\sigma_{250°C} \sim 10^{-3}$ (ohm-cm)$^{-1}$] are almost 10^{20} times greater at room temperature than in single crystal $LiNbO_3$ and are attributed to increased Li^+ ion mobilities. A $LiNbO_3$ glass with octahedrally coordinated niobium has been visualised. A schematic two-dimensional representation is shown in figure 9.

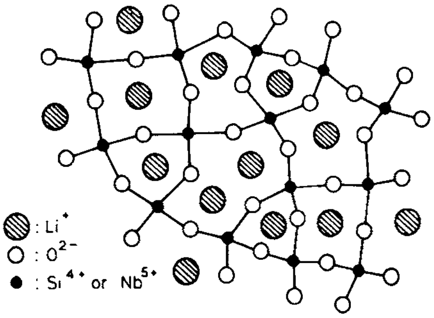

Figure 9. Schematic two dimensional representation of a lithium niobate glass with octahedrally coordinated niobium (Glass *et al* 1979).

This $LiNbO_3$ glass has been compared with silicate glasses containing tetrahedrally coordinated silicon (figure 1). Following are the important differences between these two systems. As mentioned earlier the addition of Li_2O to SiO_2 glass results in non-bridging oxygen ions in the structure which acts as hosts for alkali ions. However, in $LiNbO_3$ the Li^+ is necessary for charge neutrality but not in the structure. The conductivity of all the glasses, when plotted against the lithium atomic fraction, increases and shows a maximum of about 10^{-3} (ohm-cm)$^{-1}$ at 500°K for all the systems. However, the maxima occurred at different values of Li^+ fractions. No single explanation is appropriate for these unusual results. It is thought that the atomic substitutions attempted might have resulted in vacant interstitial sites which depend partly on the degree of short range order and partly on the distance over which the concept of local charge neutrality can be extended. It has been proposed that these glasses be viewed as quenched liquids rather than defected solids. The structure of rapidly quenched $Li\,(Nb_{0\cdot8}P_{0\cdot2})O_3$ glass is studied by x-ray diffraction and the co-ordination number of Nb is six (Yasui *et al* 1982). By constructing NbO_6 octahedral model the radial distribution function has been calculated. From the density and the radial distribution function a mixed model of ilmenite and pyrochlore is proposed to be most suitable for $Li\,(Nb_{0\cdot8}P_{0\cdot2})O_3$ glass. Electrical conductivity is around 6×10^{-4} (ohm-cm)$^{-1}$ at 450°K with an activation energy of 0·49 eV.

5. Concluding remarks

Recent studies on conducting glasses reveal some essential features of the research trends of new lithium glasses in connection with the improvement of ionic conductivity.

For some of the systems the results can be compared with the corresponding crystalline form whereas, for others they cannot. In general, the lack of structural knowledge of these glasses has slowed down the process of determining an exact transport mechanism. The distribution and number of charge carriers and their contribution to overall conductivity are not very clearly understood. Nevertheless, large data are available for discussion.

One of the interesting observations is the relative insensitivity of σ_0 to composition. For many orders of change in the magnitude of conductivity, σ_0 changes insignificantly as observed for Li-borate glasses (Angell 1981). In classical ionic conductors $\log \sigma_0$ is expected to vary linearly with composition. The observed fact in highly conducting glasses thus contradicts the classical diffusion theory (Tuller *et al* 1980).

Inorganic glasses containing alkali halides show dependence of conductivity on concentration and are therefore expected to give information regarding structural

Table 1. Ionic conductivities at different temperature and activation energy for number of lithium conducting glasses.

Glass composition	σ(25°C) (ohm-cm)$^{-1}$	σ(T°C) (ohm-cm)$^{-1}$	Activation energy (eV)	Reference
Li_2O-B_2O_3 (42·5–57·5 m/o)	7·1 × 10^{-8}	6·1 × 10^{-3} (350)	0·60	Otto (1966)
Li_2O-B_2O_3 (63–37 m/o)	6·3 × 10^{-11}	—	0·73	Levasseur *et al* (1979)
Li_2O-Li_2Cl_2-Li_2SO_4-SiO_2-B_2O_3 (35–10–30–12·5–12·5 m/o)	3·3 × 10^{-6}	9·7 × 10^{-2} (350)	0·53	Otto (1966)
Li_2O-LiCl-B_2O_3 (31·8–12·3–59·9 m/o)	3·2 × 10^{-6}	1·7 × 10^{-2} (300)	0·50	Levasseur *et al* (1979)
Li_2O-LiCl-Al_2O_3-B_2O_3 (29–24–3–44 m/o)	1·3 × 10^{-6}	1·5 × 10^{-2} (350)	0·49	Takahashi and Yamamoto (1979)
Li_2O-LiF-Li_2SO_4-Li_2SO_3-B_2O_3 (22·1–12–6–15·8–20·5–28·5 m/o)	6·2 × 10^{-7}	2·3 × 10^{-3} (200)	0·57	Smedly and Angell (1978)
Li_2O-Li_3PO_4-B_2O_3 (25–10–65 m/o)	7·44 × 10^{-9}	1·0 × 10^{-3} (330)	0·62	Basu *et al* (1983)
Li_2O-LiI-B_2O_3				
Li_2O-LiF-B_2O_3 (20–36–44 m/o)		3·14 × 10^{-4} (200)	0·58	Smedly and Angell (1978)
Li_2O-Li_2SO_4-B_2O_3 (0·71–1·1–1·0 mole ratio)	—	2·10 × 10^{-2} (300)	0·58	Levasseur *et al* (1979)
Li_2O-SiO_2 (40–60 m/o)	9·20 × 10^{-9}	1 × 10^{-6} (100)	0·63	Otto and Milbert (1968)
Li_2O-Al_2O_3-SiO_2 (25–25–50 m/o)	6·20 × 10^{-10}	6·1 × 10^{-4} (350)	0·72	
Li_2O-Al_2O_3-SiO_2 (25–25–50 m/o)	6·20 × 10^{-10}	6·1 × 10^{-4} (250)	0·72	
Li_2O-B_2O_3-SiO_2 (39–13–48 m/o)	4·30 × 10^{-9}	1·5 × 10^{-3} (350)	0·67	Biefeld *et al* (1978)
Li_2O-SiO_2 (33·3–66·7 m/o) ($Li_2Si_2O_5$)	2·8 × 10^{-9}	1·9 × 10^{-3} (350)	0·70	
$Li_2Si_2O_5$-Li_2SO_4 (71·5–28·5 m/o)	1·3 × 10^{-8}	8·7 × 10^{-3} (350)	0·66	Kone *et al* (1979)

Li_2O-Li_2SO_4-SiO_2	—	1×10^{-5} (100)	0·56–0·65	Souquet *et al* (1980, 1982)
$LiNbO_3$-SiO_2 (65–35 m/o)	—	1×10^{-4} (200)		Prasad *et al* (1980)
$LiPO_3$-LiF (60–40 m/o)	$6{\cdot}7 \times 10^{-9}$	—	0·63	Malugani and Robert (1979)
$LiPO_3$-LiCl (70–30 m/o)	$1{\cdot}0 \times 10^{-7}$	$1{\cdot}0 \times 10^{-3}$ (220)	0·63	
$LiPO_3$-LiI (67–33 m/o)	$1{\cdot}0 \times 10^{-6}$	$1{\cdot}0 \times 10^{-3}$ (194)	0·56	
$LiPO_3$-LiBr (67–33 m/o)	$3{\cdot}2 \times 10^{-7}$	$1{\cdot}3 \times 10^{-3}$ (220)	0·57	
$LiPO_3$-Li_2SO_4 (67–33 m/o)	$1{\cdot}0 \times 10^{-7}$	$3{\cdot}5 \times 10^{-3}$ (250)	0·66	Malugani *et al* (1978)
Li_2O-LiF-$Al(PO_3)_3$ (30–50–20 m/o)	$5{\cdot}8 \times 10^{-7}$	$1{\cdot}0 \times 10^{-2}$ (300)	0·56	Evastrop'eV *et al* (1974), Jagla and Isard (1980)
Li_2O-LiF-Al $(PO_3)_3$ (15–70–15 m/o)		$1{\cdot}3 \times 10^{-3}$ (220)	0·53	Maiti *et al* (1983)
Li_2S-P_2S_5 (33–66 m/o)	$1{\cdot}1 \times 10^{-4}$			Ribes *et al* (1979)
Li_2S-LiI-P_2S_5 (37–45–18 m/o)	$1{\cdot}0 \times 10^{-3}$		0·31	Malugani and Robert (1980), Mercier *et al* (1981)
Li_2S-GeS_2 (50–50 m/o)	$4{\cdot}0 \times 10^{-5}$		0·51	Souquet *et al* (1981), Ribes *et al* (1980)
Li_2O-Nb_2O_5 (50–50 m/o)	$1{\cdot}6 \times 10^{-6}$	$5{\cdot}3 \times 10^{-3}$(350)	0·44	Glass *et al* (1978)
Li_2O-Ta_2O_5 (50–50 m/o)	$5{\cdot}0 \times 10^{-6}$	$6{\cdot}4 \times 10^{-3}$(350)	0·39	Nassau *et al* (1979a, b; 1981)

changes. The conductivity tends to increase with a drop in corresponding activation energy. A linear decrease has been observed by Malugani *et al* (1978). Though its origin is not known, it is expected to result from a structural breakdown since the glass transition temperature also repeats this observation. It is assumed that the anion is not inserted into the micromolecular chain and the chain preserves the characteristics of the original glass. This structural hypothesis has been confirmed by Raman spectroscopy with borate glasses as well as phosphate glasses. The Raman spectrum does not show any modification, corresponding to P-O vibrational mode upon addition of large quantities of halides. Tuller *et al* (1980) have interpreted this model as a form of phase separation which may occur on a scale difficult to identify by most conventional means. Phase separation would, however, be expected to show discontinuous change in activation energy as the highly conducting phase changes from isolated pockets to a continuous phase throughout the material.

Conductivities of glasses containing alkali salts also show almost linear increase with radius of halide ion. Two factors have been suggested to explain the observed behaviour. The first concerns the polarizability of anions the larger the anion, the greater is the polarizability, and thus the ease with which its electron cloud may be deformed. The second approach considers dilation of structure due to larger radius of anions thereby decreasing the packing density which eases the squeezing of the ion through the opening. This model also supports the decrease in activation energy, since the activation energy for motion is inversely proportional to the size of the opening. Although these models are reasonable and agree qualitatively with experimental results, the universal acceptance might require data analysis in much greater detail.

Quenching techniques show the ability to produce wide variety of new oxide glasses. Though the glasses so prepared give thin films or flakes (2 μm thick) the area is too low (few mm^2) to permit any large scale application. It is therefore necessary to explore techniques which will give films with larger surface area. Structural aspects of these

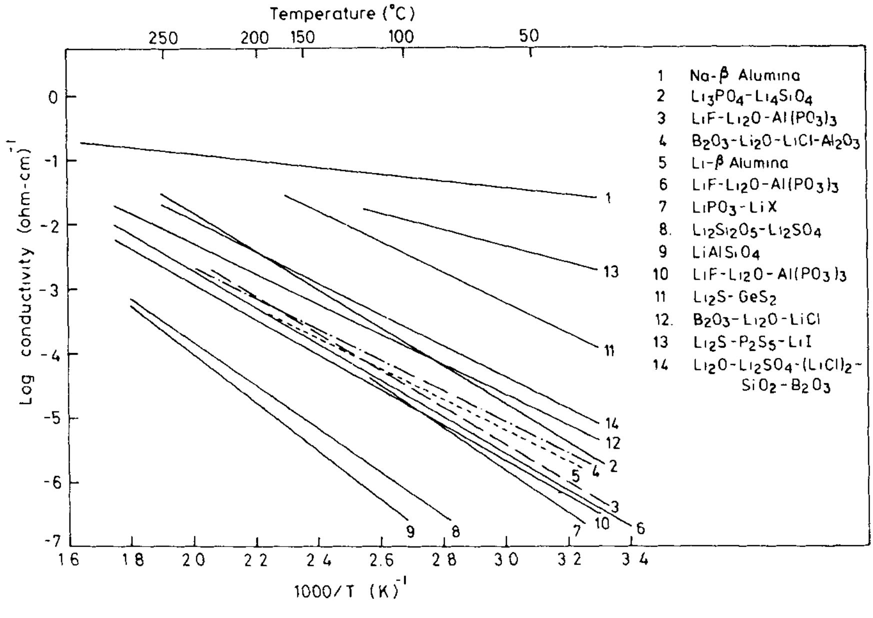

Figure 10. Electrical conductivity of some of the lithium ion conducting glasses.

glasses are not yet very clear as compared to conduction mechanism and it becomes difficult to predict new systems.

To conclude this review on the present knowledge of the electrical properties of glassy electrolytes, we have shown in table 1 a comparison of the performance of different lithium conducting glassy electrolytes. Composition, conductivity and activation energies are included. A plot of log σ *vs* reciprocal of temperature, for different glassy solid electrolytes along with some of the well-known crystalline solid electrolytes like β-alumina, Li_4SiO_4-Li_3PO_4 etc is given in figure 10. It may be noted that the electrical properties of these electrolytes compare quite well with the traditional crystalline electrolytes.

Finally, it may also be noted that most of the conductivity measurements have been inadequately performed without information on possible electronic and anionic transport numbers. Applicability of glasses, characterised for electrochemical applications such as batteries, coulometers, potential memory cells and display devices remain to be tested for many systems. Electrochemical stability range (redox-stability) and charge transfer kinetics are to be optimised to get the most suitable electrolyte. The knowledge about electrochemical performance is, however, not the only essential aspect for future development in this class of materials, but the structural studies will also play an important role to predict new glassy systems, which would be useful for practical applications in future advanced devices.

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