GLASSES AS ELECTROLYTES AND ELECTRODE MATERIALS IN LITHIUM BATTERIES (EXTENDED ABSTRACT)

J. L. SOUQUET

Laboratoire d'Ionique et d'Electrochimie du Solide (L.I.E.S., UA 1213 CNRS), E.N.S.E.E.G., Domaine Universitaire, B.P. 75, 38402 Saint-Martin-d'Hères (France)

Glasses as electrolytes

Lithium conductive glasses have reached conductivities up to 10^{-4} $(\Omega \text{ cm})^{-1}$ at room temperature [1 - 5]. The transport number of the alkali is unity and they present large Red/Ox windows. Some of them have been successfully used as solid electrolytes in electrochemical cells. The less conductive (oxide glasses) are deposited as thin films (~ 1 μm) for microgenerators [7, 8], the most conductive (sulfide glasses) are shaped in layers of about 1 mm by isostatic pressure to form button cells [6, 9].

As a guideline to new compositions, a general approach to the ionic conductivity was proposed ten years ago [10]: simply extending to glasses the electrolytic dissociation theory for liquid ionic solutions proposed one century ago by Arrhenius.

In the case of glasses, the solvent is the glass forming oxide or sulfide (*e.g.*, B_2O_3, P_2S_5 ...) and the solute is the alkali salt (Li_2O, LiI ...) which introduces the mobile alkali cations. When several salts are dissolved in the glass former, the dissociation of one salt is largely predominant. This is, for instance, the case with lithium iodide as compared with lithium oxide. In this instance, assuming constant mobility and activity coefficients for the mobile cation *versus* composition, the ionic conductivity of a glass, σ_{M^+}, is proportional to the square root of the thermodynamic activity of the more dissociated alkali salt MY (a_{MY}).

$$\sigma_{M^+} = FuK^{1/2}_{(T)}a_{MY}^{1/2} \tag{1}$$

In eqn. (1) u is the mobility and $K_{(T)}$ the salt dissociation constant. Equation (1) has been experimentally verified employing conductivity and thermodynamic measurements.

For many ionic conductive glasses, conductivity improvement may be explained by optimisation of the dissociation constant, K. For this reason, halogenated salts with the largest anions (Br^-, I^-) dissolved in a glass network of high dielectric constant such as sulfides are the most conductive. Another possibility could be the thermodynamic activity enhancement of the dissociating salt due to the metastability of the glassy state in phase separation domains.

Glasses as electrode materials

Oxide glasses have been tested as mixed conductive electrodes for electrochromic displays [11] and primary [7, 12] or secondary [13] lithium batteries. The electronic conduction mechanism is a small polaron hopping between d-orbitals of a transition metal (Fe, Cu, V ...).

The more extensively studied oxide glasses have high V_2O_5 contents due to their relatively good electronic conductivity, ease of synthesis in air, and the high oxidizing power of the V^{4+}/V^{5+} couple compared with the Li/Li^+ couple. Moreover, this oxidizing power is enhanced in glassy materials when compared with the crystalline oxidising power [12]. Discharge curves and, thus, theoretical energy density, are higher. Values for the $Li/0.95V_2O_5-0.05P_2O_5$ glass cell is 802 W h kg^{-1}, higher than for the Li/TiS_2 cell (496 W h kg^{-1}) or the Li/V_6O_{13} cell (666 W h kg^{-1}). Combined with a liquid organic electrolyte, glassy $V_2O_5-P_2O_5$ cathodes exhibit excellent reversibility while cycling at 0.5 mA cm^{-2} [13]. Due to low expansion during insertion [14] their use in thin-film-solid-state batteries has also been reported [7, 8].

Sulfide "amorphous" materials, such as MoS_2, MoS_3 [15], $MoSe_3S$ [16] and V_2S_5 [17], have been prepared by thermal decomposition [15, 16] or precipitation from aqueous solutions [15, 16]. In many aspects they may be defined as glasses. Taking into account the fact that the best lithium solid state electrolytes are sulfide glasses, we may imagine a monolithic cell with a common network former between electrolyte and electrode material providing a minimal interfacial polarization.

References

1 M. Ribes, B. Barrau and J. L. Souquet, *J. Non-Cryst. Solids, 38 - 39* (1980) 271.
2 J. P. Malugani and G. Robert, *Solid State Ionics, 2* (1980) 519.
3 M. Wada, M. Menetrier, A. Levasseur and P. Hagenmuller, *Mater. Res. Bull., 18* (1983) 189.
4 J. Akridge, *U.S. Pat. 4585714*, April, 1986.
5 J. H. Kennedy and Z. Zhang, *Solid State Ionics, 28 - 30* (1988) 726.
6 J. P. Malugani, B. Fahys, R. Mercier, G. Robert, J. P. Duchange, S. Baudry, M. Broussely and J. P. Gabano, *Solid State Ionics, 9 - 10* (1983) 659.
7 L. Jourdaine, V. Delors, J. L. Souquet and M. Ribes, *Swiss Pat. No. 4764-86-0* (1986).
8 Y. Ito, K. Miyauchi and T. Kirino, *Nippon Kagaku Kaishi, 86* (3) (1986) 445.
9 J. R. Akridge and H. Vourlis, *Solid State Ionics, 18/19* (1986) 1082 - 1087.
10 D. Ravaine and J. L. Souquet, *Phys. Chem. Glasses, 18* (2) (1977) 27 - 31.
11 T. Tatsumisago, I. Sakono, T. Minami and M. Tanaka, *J. Non-Cryst. Solids, 46* (1981) 119.
12 T. Pagnier, M. Fouletier and J. L. Souquet, *Solid State Ionics, 9/10* (1983) 649 - 654.
13 Y. Sakurai, S. Okada, H. Ohtsuka, J. Yamaki and T. Okada, *Proc. III Int. Meeting on Lithium Batteries, Kyoto, Japan, May 27 - 30, 1986, J. Power Sources, 20* (1 - 4) 1987.

14 S. Courant, M. Duclot, T. Pagnier and M. Ribes, *Solid State Ionics, 15* (1985) 147 - 153.
15 A. J. Jacobsen, R. R. Chianneli and M. S. Whittingham, *J. Electrochem. Soc., 126* (1979) 2277 - 2278.
16 D. M. Pasquariello and K. M. Abraham, *Mater. Res. Bull., 22* (1987) 37 - 44.
17 A. J. Jacobson and S. M. Rich, *J. Electrochem. Soc., 127* (4) (1980) 779 - 781.