Phase Diagram and Conductivity of the Polymer Electrolyte: PEO\textsubscript{R}LiCF\textsubscript{3}SO\textsubscript{3}

Poul Ravn Sørensen\textsuperscript{1} and Torben Jacobsen\textsuperscript{2}

\textsuperscript{1} Chemistry Department, RISØ National Laboratories, DK-4000 Roskilde, Denmark and
\textsuperscript{2} Fysisk Kemisk Institut, The Technical University of Denmark, DK-2800 Lyngby, Denmark

SUMMARY

A simple model for the concentration dependence of the electrical conductivity of the polymer electrolyte: poly(ethyleneoxide) - LiCF\textsubscript{3}SO\textsubscript{3} is presented. It is assumed that the crystals with stoichiometry: 4 polymer oxygens to 1 lithium ion are insulating and the surrounding conducting solution is saturated in the 4:1 crystals. Correcting the space available for conduction with a volume correction factor accounts qualitatively for the concentration dependence of the conductivity.

Recent results (WESTON and STEELE 1981, OWEN 1982, PAPKE et al. 1981) on polymer electrolytes of the type poly(ethyleneoxide) - alkali salts have shown that the conductivity depends strongly on the concentration, which is usually given as the ratio between the oxygens from the polymer and the cations added. When this ratio, \( R \), approaches 4, the conductivity drops off rather sharply whereas at lower salt concentration, (higher \( R \)'s), a diffuse maximum is observed in the conductivity.

WESTON and STEELE (1981, 1982) investigated both the PEO\textsubscript{R}LiCF\textsubscript{3}SO\textsubscript{3}, (\( R = 6, 8, 10 \)) and the PEO\textsubscript{R}LiClO\textsubscript{4} electrolytes and resolved a long standing discrepancy between the results of ARMAND (1978, 1979) and those obtained by most other workers. They showed that the use of high purity acetonitrile for the solvent casting, produces films (called 'high purity' films) without any signs of crystallinity whereas lower grade of acetonitrile give films ('low purity' films) containing crystalline regions embedded in an amorphous matrix.

The aim of the present paper is to present a simple model that accounts qualitatively for the concentration dependence of the conductivity of the 'low purity' type electrolytes.

These substances in general contain two phases (amorphous and crystalline) and two components (salt and polymer). Thus the composition in both phases must be fixed when the phases are in equilibrium. As to the composition of the crystalline phase it is now fairly well established (SHRIVER 1981) that four oxygens (from the polymer) coordinate one cation in a regular helical structure corresponding to \( R = 4 \) in the crystals. In the amorphous phase the composition denoted \( R_{\text{SAT}} \) is unknown.
Consider a mixture of $S$ mol salt and $P$ mol polymer (on a monomer basis). Let $x_S$ and $y_P$ be the amounts of salt and polymer forming the crystalline phase. The mass balances determining $x$ and $y$ are:

$$y_P = 4 \times x_S$$

and

$$(1-y)P = R_{\text{SAT}}(1-x)S$$

giving:

$$x = \frac{R_{\text{SAT}} - R}{R_{\text{SAT}} - 4} \quad \text{and} \quad y = \frac{R_{\text{SAT}}/R - 1}{R_{\text{SAT}} - 4}$$

where $R = P/S$.

If the crystals are insulating their presence will reduce the effective space available for conduction. In the following very crude calculation we assume that both saturated solution and crystals have the same density: $\rho$. $M_S$ and $M_P$ are the molecular weights of the salt and the polymer repeat unit. Assuming the conductivity of the mixture of salt and polymer to be proportional to the volume fraction of the conducting saturated solution the apparent conductivity, $\sigma_{AP}$ is given by:

$$\sigma_{AP} = \sigma_{\text{SAT}} \frac{(1-x)M_S S + (1-y)M_P P}{M_S S + M_P P}$$

$$= \sigma_{\text{SAT}} \frac{M_S + M_P R_{\text{SAT}}}{R_{\text{SAT}} - 4} \frac{R - 4}{M_S + M_P R}$$

This expression gives the conductivity as a function of $R$ for saturated solutions containing crystals of 4:1 stoichiometry. For solutions below the saturation concentration the conductivity can be related to the sum of the diffusion coefficients of the individual ions, $D_1 + D_2$, through:

$$\sigma = \frac{(D_1 + D_2) F^2 C}{RT}$$

where $F$, $R$ and $T$ have their usual meaning and $C$ is the volume concentration of the salt.

If the diffusion coefficients are assumed to be concentration independent we obtain:

$$\sigma = \sigma_{\text{SAT}} \frac{C}{C_{\text{SAT}}}$$

where $C_{\text{SAT}}$ is the saturation concentration.

As an example consider the results for the polymer electrolyte PEO$_R$LiCF$_3$SO$_3$ given by SØRENSEN and JACOBSEN (1982). If 1.39 is