Determination of Cation Mobilities in Glasses by Direct Measurement of Drift Velocities (Moving Boundary)

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A method of concentration profile measurement of luminescent ions by ion sputtering has been applied to detect the boundary between alkali ions of glass wafers, which were contacted anodically by acid solution, and succeeding hydrogen ions after the application of an electric field. The transport number of lithium ions was found to be unity. Mobilities at 25 and 50 °C agree with data obtained from conductivity measurements. From the conductivity change during transport the mobility of succeeding hydrogen ions is also evaluated.

For the determination of cation mobilities in glasses from conductivity measurements, transport numbers of the migrating ions have either to be assumed or to be determined separately, e. g., by means of radioactive isotopes, which, however, are not always available. We have applied a method[1] of measuring concentration profiles of luminescent ions in glass surface layers and leached layers by sputtering with argon ions of high energy, to directly measure drift velocities of alkali ions, hydrogen ions replacing the alkali ions in the glass network. The method is thus based on the determination of a moving boundary in thin glass layers by ion sputtering.

An electrode membrane glass containing lithium and (less) cesium, magnesium, strontium, and barium was chosen for the experiments. A wafer of uniform thickness, melted to the end of a highly resistant glass tube, was anodically contacted with dilute sulfuric acid and subjected to an electric field of 6000 V cm^{-1} at 25 and 50 °C for a certain period of time. Subsequently the anodic side was sputtered with argon ions. The boundary between the drifting alkali ions and the succeeding ions in the glass caused an increase in luminescence intensity during sputtering. From the shape of the luminescence-time curve and by the use of filters the transport number of lithium ions was found to be unity within the limits of error.

This result was confirmed by spectroscopic and, in separate experiments, by quantitative analysis of the ions transferred into cathodic mercury and simultaneous measurement of the transported electric charge. In addition, mobilities calculated from drift velocities and from conductivities of the glass using its lithium content were found to be equal.

Mean conventional mobilities obtained from drift velocity measurements are

$$u_{\mathrm{Li}^+} = 1.9\times10^{-6}\ (25\ ^\circ\mathrm{C}) \quad \text{and} \quad 1.8\times10^{-5}\ \text{Å sec}^{-1}/\text{V cm}^{-1}\ (50\ ^\circ\mathrm{C}) \quad \text{or,}$$

in absolute units,

$$\bar{u}_{\mathrm{Li}^+} = 1.2\times10^{-2}\ (25\ ^\circ\mathrm{C}) \quad \text{and} \quad 1.1\times10^{-1}\ \text{cm sec}^{-1}\ \text{dyne}^{-1}\ (50\ ^\circ\mathrm{C})$$

and agree with data calculated from conductivity measurements,

$$u_{\mathrm{Li}^+} = 1.8\times10^{-6}\ (25\ ^\circ\mathrm{C}) \quad \text{and} \quad 1.7\times10^{-5}\ \text{Å sec}^{-1}/\text{V cm}^{-1}\ (50\ ^\circ\mathrm{C}).$$

Deviations from the average were below 5%. The resulting activation energy of lithium ion mobility and of glass conductivity is 17 kcal mol^{-1}.

Combining these results with resistance changes of the glass during ion transport yielded the mean mobility of the ions replacing Li^+ in the network (H^+ more probably than $\mathrm{H_3O}^+$, because of size),

$$u_{\mathrm{H}^+} = 3.2\times10^{-7}\ \text{Å sec}^{-1}/\text{V cm}^{-1}\ (50\ ^\circ\mathrm{C}) \quad \text{or}$$
$$\bar{u}_{\mathrm{H}^+} = 2.0\times10^{-3}\ \text{cm sec}^{-1}\ \text{dyne}^{-1}\ (50\ ^\circ\mathrm{C}),$$

if a constant number of available cation sites was assumed. The mobility ratio is $u_{\mathrm{Li}^+}/u_{\mathrm{H}^+} = 56 \pm 5$. At present, the temperature dependence of the H^+-mobility is being measured in order to determine the activation energy of this process.

Extending the time between ion transport and sputtering of the specimen resulted in increasingly less sharp concentration profiles obviously caused by interdiffusion of Li^+ and H^+. This is of interest for the determination of diffusion coefficients, which, for Li^+, cannot be measured by radioactive experiments. Under consideration of the penetration depth of argon ions[2], extrapolation to zero diffusion time will be conducted to determine the very narrow mobility spectrum at the boundary $\mathrm{Li}^+/\mathrm{H}^+$.

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