

On the analysis of field-assisted ion diffusion into glass

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 4089

(<http://iopscience.iop.org/0953-8984/4/16/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 11:50

Please note that [terms and conditions apply](#).

On the analysis of field-assisted ion diffusion into glass

R Oven, D G Ashworth and M C Page

The Electronic Engineering Laboratories, The University of Kent, Canterbury, Kent CT2 7NT, UK

Received 6 December 1991

Abstract. The process of field-assisted diffusion of ions into glass is analysed theoretically without the introduction of a conventionally used quasi-neutral space-charge approximation. The analysis shows that the quasi-neutral approximation is valid over a wide range of injection rates and processing temperatures. This result, which is of relevance to the manufacture of glass-based optical waveguides by the field-assisted injection of silver or potassium ions, is achieved by analysing the stationary state solution of a model drift-diffusion equation.

1. Introduction

Recently, much research effort has been put into the manufacture of integrated optic waveguides in glass substrates by the process of ion diffusion (Ramaswamy and Srivastava 1988a, b, Honkanen and Tervonen 1988, Yip *et al* 1990, Page *et al* 1991). A number of processes (Honkanen and Tervonen 1988, Yip *et al* 1990) use an externally applied electric field, either to assist the diffusion process or to alter the concentration profile. The mathematical model used to describe this process (Abou-el-Leil and Cooper 1979) is based on the coupled drift and diffusion of two ion species: the invasive ion, for example silver or potassium, and the indigenous sodium ions present within the glass. In the model the coupling of the motion of the two species of ions is due to electrostatic interactions only. The invasive and indigenous ions, which are both positively charged and mobile, are assumed to move with respect to a fixed negative background charge associated with non-bridging oxygen ions (Ramaswamy and Srivastava 1988a, b). Hence, any local deficiency of invasive or indigenous ions will cause a negative space charge, which may attract other invasive or indigenous ions. It is important, however, to distinguish between a number of possible ways in which a space charge might occur within the glass during the field-assisted diffusion process. A space charge can occur near the ion-injecting anode if the injection rate of invasive ions is somehow limited and not equal to the rate at which the indigenous ions move away from the anode. It is well known (Carlson 1974) that when the injection rate is zero, i.e. when there is a blocking electrode, a high-field region builds up rapidly. Under these extreme conditions the field becomes so large that the non-bridging oxygen ions begin to move towards the anode (Carlson 1974). Presumably, if the ion source is intermediate between fully injecting and blocking, a form of high-field region will arise. Alternatively, a positive space charge region may occur at the cathode if this electrode cannot remove or

neutralize the indigenous ions at the required rate. The formation of these types of space charge region will not be considered here.

It is known (Ramaswamy and Srivastava 1988a, b) that another form of space charge region may occur within the bulk of the glass when the invasive ions have a much lower mobility than the indigenous ions. In this case a local space charge within the glass occurs at the boundary between the low- and high-ion-mobility regions. This has the effect of speeding up the motion of the low-mobility ions and slowing down the motion of the high-mobility ions. It is the analysis of this type of space charge that will be considered in this paper.

2. Quasi-neutral analysis

The field-assisted transport of ions in glass is usually modelled (Abou-el-Leil and Cooper 1979), in one dimension, via the following model. Firstly, the fluxes j_A and j_B of the invasive and indigenous ions respectively are assumed to have drift and diffusion components such that

$$j_A = C_A \mu_A E - D_A \partial C_A / \partial x \quad (1)$$

and

$$j_B = C_B \mu_B E - D_B \partial C_B / \partial x \quad (2)$$

where C_A and C_B are the concentrations of the invasive and indigenous ions, μ_A and μ_B are the ion mobilities, D_A and D_B are the self-diffusion coefficients and x is a spatial variable. The electric field, E , includes the externally applied electric field as well as any component arising from the local space charge near the diffusion boundary. Strictly speaking, the electric field and ion concentrations should be related via Poisson's equation

$$C_A + C_B - C_0 = (\epsilon/q) \partial E / \partial x \quad (3)$$

where C_0 is equal to the mobile sodium ion concentration in the original glass, ϵ is the dielectric constant, which has been assumed to be independent of x , and q is the ion charge. However, in the conventional analysis (Abou-el-Leil and Cooper 1979, Ramaswamy and Srivastava 1988a, b, Honkanen and Tervonen 1988) it is assumed that the local space charge is small, and equation (3) can be replaced by the space charge neutrality condition

$$C_A + C_B = C_0 \quad (4)$$

for the purpose of calculating the ion concentrations. This, which will be termed the quasi-neutral approximation, was originally applied to the analysis of the ion exchange process by Doremus (1964). In this process the invasive ions from a molten salt exchange places with the indigenous ions in the glass through a single interface. No externally applied field is present during the process. The validity of the quasi-neutral approximation has been investigated in a numerical analysis of a silver-sodium ion exchange process by Walker *et al* (1983). In this analysis an estimation was made of the magnitude of the internal space charge by calculating concentration profiles

utilizing the quasi-neutral approximation. It was concluded that the internal space charge was negligible, hence showing the calculations to be self-consistent. However, this was for a process during which no external electric field was applied.

Consistent with the approximation of equation (4) is the condition for the continuity of the ion fluxes

$$j_A + j_B = j_0 \quad (5)$$

where j_0 is the total ion flux which is a spatial constant. The concentration C_A and ion flux j_A are also related by the continuity equation

$$\partial C_A / \partial t = -\partial j_A / \partial x \quad (6)$$

where t is time. The continuity equation for the indigenous ions is implied in equations (4) to (6).

By assuming the self-diffusion coefficients to be independent of the concentration and assuming that the Einstein relation links the ion mobilities and self-diffusion coefficients, Abou-el-Leil and Cooper (1979) made use of the quasi-neutral approximation by deriving from equations (1), (2) and (4) to (6) the following diffusion equation:

$$\frac{\partial C^*}{\partial t^*} = \frac{-M}{[C^*(M-1)+1]^2} \frac{\partial C^*}{\partial x^*} + \frac{\partial}{\partial x^*} \left(\frac{1}{[C^*(M-1)+1]} \frac{\partial C^*}{\partial x^*} \right) \quad (7)$$

where C^* , x^* and t^* are dimensionless concentration, distance and time variables defined by

$$C^* = C_A / C_0 \quad x^* = j_0 x / C_0 D_A \quad t^* = j_0^2 t / C_0^2 D_A \quad (8)$$

and $M = D_A / D_B$ is the diffusion ratio.

If j_0 is maintained constant with time and if $M < 1$ then Abou-el-Leil and Cooper (1979) argued that the concentration profile C^* evolves with time into a *stationary state*. This forms as a result of the balance between the diffusional forces trying to reduce the concentration gradient between the low- and high-mobility regions and the force due to the electric field which attempts to increase the concentration gradient. Using the boundary conditions $C^* \rightarrow 1$ as $x \rightarrow -\infty$ and $C^* \rightarrow 0$ as $x \rightarrow +\infty$, which imply the complete replacement of the indigenous ions by the invasive ions in the region near the glass surface, an analytical solution to equation (7) was obtained, of the form

$$C^*(x^*, t^*) = 1 / \{1 + \exp [(1 - M)(x^* - t^*)]\}. \quad (9)$$

It has been confirmed, using numerical integration of (7), that the profile does indeed evolve into this stationary state (Honkanen *et al* 1987).

The procedure used by Walker *et al* (1983) for estimating the space charge may, in principle, be applied to the quasi-neutral solution for field-assisted diffusion, i.e. equation (9). However, this approach is not rigorous. Instead, if a space charge does exist, then the set of equations (1) to (3) and (6) should be solved simultaneously with the equation

$$j_A + j_B + (\epsilon/q) \partial E / \partial t = j_0 \quad (10)$$

replacing equation (5). It is not necessary to include a continuity equation for C_B in the modified set since this is implied in equations (3), (6) and (10).

In the next section we solve the modified set of equations, again seeking a stationary state solution in order to make the problem analytically tractable. Any differences between the new solution and the previous stationary state solution, equation (9), will indicate the relative importance of making the quasi-neutral approximation.

For simplicity, we also use concentration-independent self-diffusion coefficients and assume that the Einstein relation is valid in our analysis. These approximations are known not to be valid for ion motion in many glasses (Day 1976, Ramaswamy and Srivastava 1988a, b, Honkanen and Tervonen 1988). However, it is expected that our general conclusions concerning the internal space charge will not be affected by these assumptions.

3. Analysis

It is possible to manipulate equations (1), (2), (3), (6), (8) and (10) to derive the partial differential equation for C^* , but with E as an unknown function:

$$\frac{\partial C^*}{\partial t^*} = \frac{-MG^2}{[C^*(M-1) + G]^2} \frac{\partial}{\partial x^*} \left(\frac{C^*}{G} \right) + \frac{\partial}{\partial x^*} \left(\frac{G^2}{[C^*(M-1) + G]} \frac{\partial}{\partial x^*} \left(\frac{C^*}{G} \right) \right) + M \frac{\partial}{\partial x^*} \left(\frac{C^* \lambda}{[C^*(M-1) + G]} \frac{\partial E}{\partial t^*} \right) \quad (11)$$

in which

$$G(x^*, t^*) = 1 + \lambda \partial E / \partial x^* \quad (12)$$

and

$$\lambda = \epsilon j_0 / q C_0^2 D_A. \quad (13)$$

If we assume $M < 1$ and that the profile C^* and electric field E have reached their stationary states, then following Abou-el-Leil and Cooper (1979), we can introduce the variable $\eta = x^* - v^* t^*$, where v^* is a velocity. Hence,

$$\partial / \partial t^* = -v^* d/d\eta \quad \partial / \partial x^* = d/d\eta \quad (14)$$

thus enabling equations (11) and (12) to be combined in order to eliminate the variable E . The resulting equation can be written, after integrating once with respect to η , in the form

$$-v^* C^* + k = [MG/(M-1) + G^2(d/d\eta)(C^*/G)] + v^* M C^* (1-G) [C^*(M-1) + G]^{-1} \quad (15)$$

where k is an integration constant.

We now apply the boundary conditions $C^* \rightarrow 1$, $G \rightarrow 1$ as $\eta \rightarrow -\infty$ and $C^* \rightarrow 0$, $G \rightarrow 1$ as $\eta \rightarrow +\infty$. Also, $(d/d\eta)(C^*/G) \rightarrow 0$ as $\eta \rightarrow \pm\infty$. Therefore,

$$k = M/(M-1) \quad v^* = 1. \quad (16)$$

These constants have assumed the same values as in the quasi-neutral analysis of Abou-el-Leil and Cooper (1979) for the above boundary conditions.

Defining $g = C^*/G$ enables (15) to be written as

$$dg/d\eta = (M - 1)g(1 - g) \quad (17)$$

which integrates to give

$$g = 1/\{1 + \exp[(1 - M)\eta]\} \quad (18)$$

where we have set the integration constant to zero, following Abou-el-Leil and Cooper (1979).

From equations (6), (8) and (14) we obtain

$$j_0 dC^*/d\eta = dj_A/d\eta \quad (19)$$

which integrates to give

$$j_0 C^* = j_A + k_1 \quad (20)$$

where k_1 is a constant of integration. Since $j_A \rightarrow 0$ and $C^* \rightarrow 0$ as $\eta \rightarrow \infty$, then $k_1 = 0$. Substituting for j_A , from equation (20) into (1), and using (8) and (14), gives

$$E = (j_0/C_0\mu_A)[1 + (d/d\eta) \ln C^*]. \quad (21)$$

Substituting the derivative of equation (21) into equation (12) and using equation (14) gives

$$C^*/g = 1 + B(d^2/d\eta^2) \ln C^* \quad (22)$$

in which

$$B = j_0\lambda/C_0\mu_A. \quad (23)$$

Since g is known from equation (18), C^* may be calculated by solving equation (22).

4. Discussion and conclusions

If typical values of parameters are substituted into equation (23) it can be seen that the coefficient B is small. For example, the material parameters from Page *et al* (1991) for silver-ion injection into a soda-lime glass at 283°C are: $C_0 = 5.2 \times 10^{+27} \text{m}^{-3}$, $\mu_B = 2.1 \times 10^{-13} \text{m}^2 \text{V}^{-1} \text{s}^{-1}$, $M \simeq 1/3$ and $J (= j_0q) = 5 \text{A m}^{-2}$. Then, assuming $\epsilon = 10\epsilon_0$, equation (23) gives $B = 1.6 \times 10^{-8}$. This shows that the term in B may be neglected in equation (22) and we have, to first order, $C^* = g$ which is the quasi-neutral approximation, equation (9). If g is substituted for C^* in the second term on the right-hand side of equation (22) then, by using equation (17), a higher-order approximation for C^* is obtained:

$$C^* = g \left[1 - B(1 - M)^2 g(1 - g) \right]. \quad (24)$$

The maximum of the function $g(1-g)$ is equal to $1/4$, and occurs at $\eta = 0$. Hence, it can be seen from equation (24) that even if $M \ll 1$ the small size of B means that $C^* = g$ is still a good approximation.

Recently, Yip *et al* (1990) have reported on the manufacture of optical guides in glass using the field-assisted diffusion of potassium ions at 385 °C. These guides were manufactured with a constant potential applied across the glass, rather than a constant current, so direct comparison with the above model is not possible. However, the order of magnitude of current density may be estimated from the conductivity of soda-lime glass at the processing temperature. From a sodium-ion mobility of $2.1 \times 10^{-13} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 283 °C and an activation energy of 0.9 eV, the sodium-ion mobility $\mu_B \simeq 3.3 \times 10^{-12} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 385 °C. Assuming $C_0 \simeq 5.2 \times 10^{+27} \text{ m}^{-3}$ gives an initial glass conductivity $\sigma = q\mu_B C_0 \simeq 2.7 \times 10^{-3} \Omega^{-1} \text{ m}^{-1}$. Yip *et al* (1990) used fields up to $5 \times 10^4 \text{ V m}^{-1}$; hence, $J \simeq 135 \text{ A m}^{-2}$. The same authors reported a potassium diffusion coefficient $\simeq 10^{-15} \text{ m}^2 \text{ s}^{-1}$; thus, from equation (23), $B \simeq 1.6 \times 10^{-4}$. Hence, even under these high current densities, the approximation $C^* = g$ appears valid.

In conclusion, we have shown that the quasi-neutral approximation is valid without the use of any *a priori* assumptions concerning the nature of the space charge.

Acknowledgments

The authors thank the University of Kent Research Committee for financial support of this work.

References

- Abou-el-Leil M and Cooper A R 1979 *J. Am. Ceram. Soc.* **63** 390
- Carlson D E 1974 *J. Am. Ceram. Soc.* **57** 291
- Day E D 1976 *J. Non-Cryst. Solids* **21** 343
- Doremus R H 1964 *J. Phys. Chem.* **68** 2212
- Honkanen S and Tervonen A 1988 *J. Appl. Phys.* **63** 634
- Honkanen S, Tervonen A, Von Bagh H and Leppihalme M 1987 *J. Appl. Phys.* **61** 52
- Page M C, Oven R and Ashworth D G 1991 *Electron. Lett.* **27** 2073 (errata **27** 2300)
- Ramaswamy R V and Srivastava R 1988a *J. Mod. Opt.* **35** 1049
- 1988b *IEEE J. Lightwave Technol.* **LT-6** 984
- Walker R G, Wilkinson C D W and Wilkinson J A H 1983 *Appl. Opt.* **22** 1923
- Yip G L, Noutsios P C and Kishioka K 1990 *Opt. Lett.* **15** 789