Electrodiffusion processes with the conversion of polarization direction of electric field in the formation of planar waveguide structures using ion exchange technique in glass

Roman Rogoziński

Silesian Technical University, Institute of Physics, ul. Bolesława Krzywoustego 2, 44−100 Gliwice, Poland.

The paper presents the results of investigation involving electrodiffusion processes with the changes of the direction of electric field polarization. The ion exchange model has been described, which allows for the dependence of diffusion constants on their normalized concentrations. Experimental results have been compared with the predicted theoretical ones for the assumed ion exchange model.

1. Introduction

Ion exchange technique is a commonly used method for the formation of gradient waveguide structures in glass bases. The technologically simplest form of this technique makes use of thermal activation of admixture ions introduced to the glass base from liquid source. Concentration gradients of the exchanged ions occurring near the glass surface cause this process to assume a purely diffusive character. The shape of refractive profiles of the waveguides obtained in such a way is determined by the ratio between the mobility of admixture ions and the mobility of glass ions subject to exchange. With the predetermined temperature of the process, the time of its duration is a parameter which determines the depth of the refractive profile. In order to obtain deep refractive profiles, such processes must be carried out for a comparatively long time. Apart from ion exchange technique, which is based on purely thermal diffusion of admixture ions, the process can also be carried out in the presence of the external electric field [1]−[4]. It is shortly referred to as electrodiffusion process. A characteristic feature of the process is the phenomenon of directed migration of ions introduced to the glass, affected by the presence of electric field. It can be used as a tool to form deep waveguide structures in a comparatively short time. There is an additional parameter occurring in the process, *i.e.*, intensity of electric field. By changing the value and direction of the applied electric field during the process, there is another possibility of exerting influence on the final form of the refractive profiles. First attempts to apply time-based changes of electric field in electrodiffusion processes can be found in paper [5]. Refractive profiles of planar

waveguide structures obtained in such a way are not possible to obtain in processes based on purely thermal ion exchange in a given glass-admixture system. Therefore, the application of electrodiffusion processes with electric field, whereof the value and direction can be changed in time, creates new potentials to form their refractive profiles with modal properties focused on particular applications, *e.g.*, in sensor related applications [6].

2. Electrodiffusion process description

The model describing electrodiffusion processes accepted in papers [1]−[5] is based on the assumption that diffusion constants and mobilities of both kinds of exchanged ions are independent of their concentration. With the application of such assumptions, there occur considerable differences between theoretical predictions and measurement results involving the refractive profiles obtained. Better conformity with theoretical predictions can be obtained by introducing the dependence of diffusion constants of both types of exchanged ions on their normalized concentrations [7], or the dependence of mobility of admixture ions introduced to glass on the normalized concentration of admixture [8].

In further considerations involving the modelling of ion exchange process, it was assumed [9] that two fluxes of exchanged ions occur within the glass volume. Ions of type A constitute the admixture introduced to glass, and ions of type B are viewed as a component of glass subject to exchange (ions of the modifier having the lowest activation energy):

$$
\begin{aligned}
\vec{\Phi}_A &= -D_A \nabla c_A + \mu_A c_A \vec{E}_0 \ [\text{m}^{-2}\text{s}^{-1}], \\
\vec{\Phi}_B &= -D_B \nabla c_B + \mu_B c_B \vec{E}_0 \ [\text{m}^{-2}\text{s}^{-1}]
\end{aligned}
\tag{1}
$$

where: c_A, c_B — absolute concentrations of ions A and B $[\text{m}^{-3}]$,

μ_A, μ_B — electric mobility values of ions A and B $[\text{m}^2\text{V}^{-1}\text{s}^{-1}]$,

D_A, D_B — diffusion constants of ions A and B $[\text{m}^2\text{s}^{-1}]$,

$\vec{E}_0 = \vec{E}_e + \vec{E}_d$,

$\vec{E}_0$ — local electric field $[\text{Vm}^{-1}]$,

$\vec{E}_e$ — external electric field $[\text{Vm}^{-1}]$,

$\vec{E}_d$ — diffusive electric field effected by the difference in mobility between the exchanged ions $[\text{Vm}^{-1}]$.

We assume the dependence between μ_i and D_i ($i = \text{A, B}$) has the form of Nernst−Einstein formula [10]

$$
\mu_i = \frac{e}{HkT} D_i \ [\text{m}^2\text{V}^{-1}\text{s}^{-1}]
\tag{2}
$$

k — Boltzmann's constant $[\text{JK}^{-1}]$,

T — temperature $[\text{K}]$,

H — correlation factor $(0 < H \leqslant 1)$.

The equilibrium concentration $c_0 = c_A + c_B$ ($c_0 = c_B$ — in glass before exchange), as well as normalized concentrations of ions $u = c_A/c_0$ and $w = c_B/c_0$ satisfying the condition $u + w = 1$ were introduced. The dependence on normalized concentrations has been assumed for diffusion constants of both ion types in the form given in [7]

$$D_A(u) = D_{0A} \exp(Au),$$

$$D_B(w) = D_{0B} \exp(Bw),$$

$$D_{0i} = D_{0i}^* \exp\left(-\frac{\Delta Q_i}{RT}\right), \quad (i = A, \ B). \tag{3}$$

In the above equation, ΔQ_i stands for activation energy of the i-th component [Jmol^{-1}], R stands for universal gas constant [JK^{-1}mol^{-1}].

Making use of the normalized concentrations u and w, Eq. (1) can be written in the following form:

$$\vec{\Phi}_u = \frac{\vec{\Phi}_A}{c_0} = -D_A \nabla u + \mu_A u \vec{E}_0, \quad [\text{ms}^{-1}],$$

$$\vec{\Phi}_w = \frac{\vec{\Phi}_B}{c_0} = -D_B \nabla w + \mu_B w \vec{E}_0, \quad [\text{ms}^{-1}]. \tag{4}$$

Both normalized ion beams expressed by Eqs. (4) satisfy the following condition within the glass volume:

$$\vec{\Phi}_u + \vec{\Phi}_w = \mu_B \vec{E}_e. \tag{5}$$

It has been assumed in the above equation that within the glass area devoid of admixture ions ($u = 0$), local electric field is equal to external field ($\vec{E}_0 = \vec{E}_e$). Inserting Eqs. (4) to (5), and introducing the denotation $\alpha = 1 - D_A/D_B$, the local electric field in glass is calculated

$$\vec{E}_0 = \frac{\vec{E}_e}{1 - \alpha u} - \frac{HkT}{e} \frac{\alpha \nabla u}{1 - \alpha u}. \tag{6}$$

In Equation (6), the first component is connected with external electric field, and the second one stands for diffusive field.

The following continuity equation is obligatory within glass volume for vector $\vec{\Phi}_u$

$$\frac{\partial u}{\partial t} + \nabla \cdot \vec{\Phi}_u = 0. \tag{7}$$

Taking into consideration (4) in the above equation, we obtain

$$\frac{\partial u}{\partial t} = \nabla \cdot (D_A \nabla u - \mu_A u \vec{E}_0). \tag{8}$$

By calculating $\nabla \cdot \vec{E}_0$ on the basis of (6), taking into account that $\nabla \cdot \vec{E}_e = 0$, we derive from (8) the equation describing time-space related changes of normalized

concentration of admixture introduced to glass

$$\frac{\partial u}{\partial t} = \frac{D_A}{1-\alpha u}\left[\Delta u + \frac{\alpha}{1-\alpha u}(\nabla u)^2 - \frac{e}{HkT}\frac{1}{1-\alpha u}\nabla u \cdot \vec{E}_e\right]$$
$$+\frac{1-u}{(1-\alpha u)^2}\left[\nabla u - \frac{e}{HkT}u\vec{E}_e\right]\cdot\nabla D_A + \frac{u(1-\alpha)^2}{(1-\alpha u)^2}\left[\nabla u - \frac{e}{HkT}u\vec{E}_e\right]\cdot\nabla D_B. \qquad (9)$$

3. Initial and boundary conditions

For the modelling of fabrication processes of planar waveguide structures, Eq. (9) is solvable for 1-dimensional conditions, assuming the geometry of the system as indicated in Fig. 1. For primary processes [9] (preliminary diffusion, preliminary
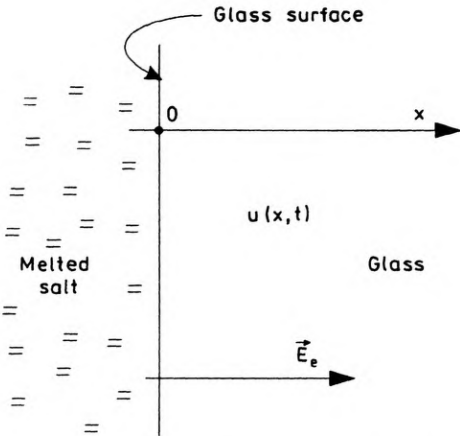

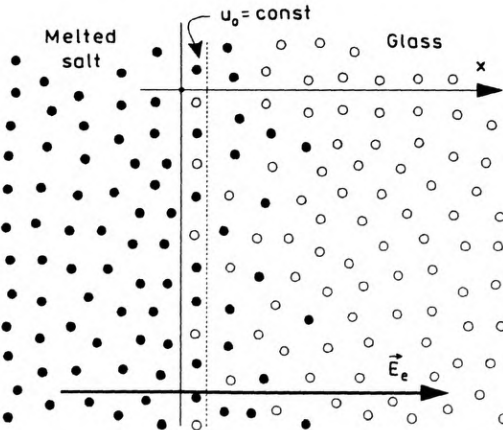Fig. 1. Geometry of the system for the solution of Eq. (9)

Fig. 2. Boundary condition on the melted salt-glass interface allowing for the stability of normalized concentration of admixture under glass surface (acc. to Eq. (11))

electrodiffusion), the initial condition for normalized concentration of admixture ions introduced to glass has the following form:

$$u(x, 0) = 0 \quad \text{for} \quad x \geqslant 0. \tag{10}$$

Boundary conditions for Eq. (9) in the case of electrodiffusion processes can be determined in a few ways. In paper [5] it was assumed that the normalized concentration of admixture introduced to glass within the area under glass surface is constant (Fig. 2)

$$u(0, t) = u_0 \quad \text{for} \quad t \geqslant 0. \tag{11}$$

The assumption is true when the kinetics of the ion exchange process through the surface is much higher than the processes of electrodiffusive ion migration within the glass volume. The assumption makes no distinction as to the polarization direction of the external electric field.

According to another approach [6], which allows for electrical neutrality of glass, it is assumed for the polarization being in conformity with the positive direction of x-axis that the normalized beam of admixture ions passing through the glass surface from liquid phase is equal to the beam of mobile ions of the modifier in the glass volume, in the area where $u = 0$ (Fig. 3)

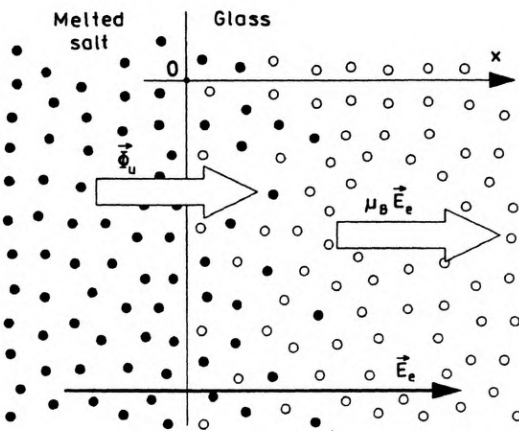$$\vec{\Phi}_u|_{x=0} = \mu_B \vec{E}_e. \tag{12}$$

Fig. 3. Boundary condition on the melted salt-glass interface for positive polarization of electric field (acc. to Eq. (12))

With the polarization direction of electric field being changed, both types of ions can pass through glass surface to the liquid phase (Fig. 4). In that case, the condition of electrical neutrality of glass must satisfy the following equation

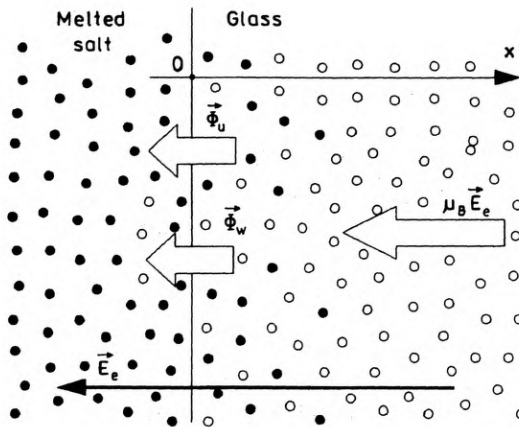$$\vec{\Phi}_u|_{x=0} + \vec{\Phi}_w|_{x=0} = \mu_B \vec{E}_e. \tag{13}$$

Fig. 4. Boundary condition on the melted salt-glass interface for negative polarization of electric field (acc. to Eq. (13))

4. Technological processes

In order that the electrodiffusion process with the use of liquid admixture source (nitrates) could be performed, physical contact of at least one surface of glass base with melted salt must be ensured, while effecting simultaneously potential difference between both glass surfaces. Hence, it is necessary that these surfaces be electrically isolated. Technical proposals to solve the problem provided in literature [5] suggest that a suitably shaped vessel filled with melted salt should be made and immersed in a crucible which is also filled with melted salt (Fig. 5). Electric field is effected by placing respective electrodes into both vessels. Then the electrodiffusion processes are running through all walls of the vessel. That kind of solution ensures that both surfaces of glass sample are effectively electrically isolated. Yet the solution has many weak points. Appropriate glass forms with suitably finished surfaces and respective glass homogeneity must be prepared. The salt filling the vessel (form) melts, with suitable melting temperature being reached after a definite time period. The thermal
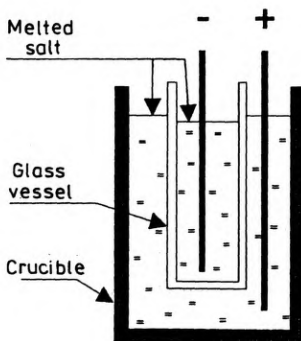

Fig. 5. Glass vessel which enables total electric isolation of both electrodes in electrodiffusion processes

diffusion processes taking place simultaneously result in the creation of preliminary distribution of admixture in glass which is difficult to define.

The attempts to apply glass bases formed as easy to prepare optical flats, with appropriately constructed crucible ensuring that the beginning of the contact of melted salt with glass surface [11] and the initiation time of the process can be precisely defined, have indicated that electrodiffusion processes with the application of one liquid electrode are possible to perform (Fig. 6). The second electrode is made
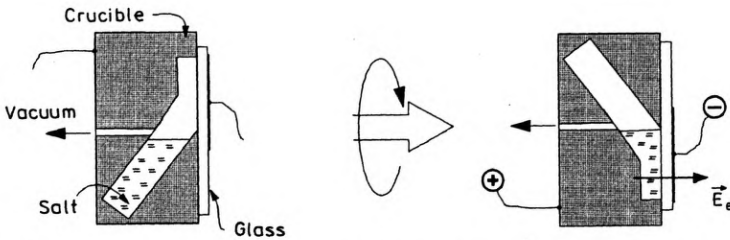

Fig. 6. Axial section of the system for the realization of electrodiffusion process with one liquid electrode

up by a layer of electroconductive glue resistant to high temperatures. In such a system, the modifier ions (Na^+) leaving the glass are neutralized to metallic sodium under the surface of negative electrode, and in effect the electrode adhesion to glass is getting worse with the time. The waveguide structure is created here under the glass surface which gets into contact with the melted salt (Fig. 7). In this solution, it is not possible to effect the flow of admixture ions beam in glass in the opposite direction, after changing the direction of electric field polarization.
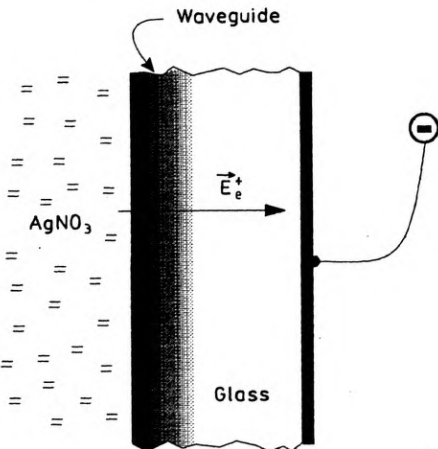

Fig. 7. Formation of waveguide structure in the electrodiffusion process with one liquid electrode

According to the solution proposed [12] which suggests the application of two symmetrical crucibles (Fig. 8) it is possible to use two liquid electrodes on both sides of glass plate. With the advantages of system from Fig. 6 being preserved, it allows
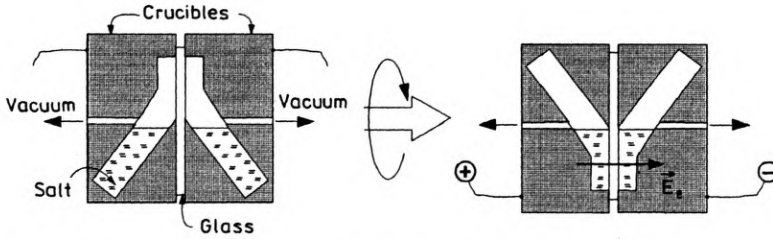
Fig. 8. Axial section of the system for the realization of electrodiffusion processes with two liquid electrodes
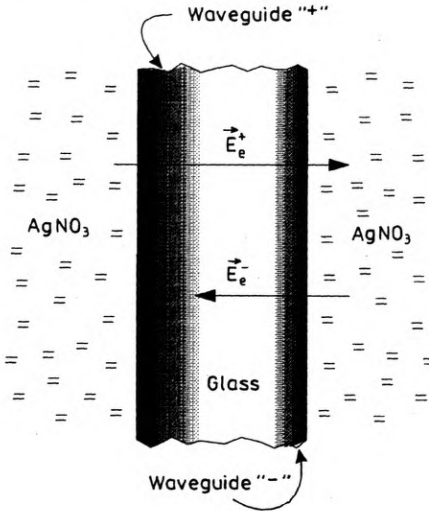

Fig. 9. Formation of two waveguide structures in the electrodiffusion process with the change of electric field polarization (two liquid electrodes)

the electrodiffusion processes to be carried out with the change of electric field polarization. By applying the same type of melted salt in both crucibles we can simultaneously obtain — during the process with the change of electric field polarization — two waveguide structures on both sides of base glass (Fig. 9).

5. Results

Sodium-calcium glass of the chemical composition presented in Table 1 [13] was used as the base for waveguide formation in the electrodiffusion processes carried out. The glass contains a considerable amount of Na^+ ions, which, due to the fact that they have low activation energy [9], can be changed into ions of the admixture introduced in the diffusion and electrodiffusion processes. Ions Ag^+ were applied as admixture introduced to glass, with pure melted $AgNO_3$ used as their source. All refractive profiles of the created planar waveguide structures were determined with the use of IWKB procedure, based on the measurements of effective refractive

T a b l e 1. Chemical composition of soda-lime glass

Component	[% by weight]
SiO_2	75
Na_2O	12.2
CaO	7.4
MgO	3.9
Al_2O_3	0.6
K_2O	0.2
Others	0.7

indexes of guided modes. Figure 10 presents the measured refractive profiles of waveguides made in electrodiffusion processes in the system with one liquid electrode (Fig. 6), for different values of the electric field applied. For the purpose of comparison, a purely diffusive profile was also presented. It can be seen here that electric field has considerable influence on the waveguide refractive profiles obtained in this type of glass. In order to predict the influence of electric field with changing polarization direction on the form of the refractive profiles, using the exchange model described by Eq. (9), the parameters D_{0A}, D_{0B}, A, B and H were determined from Eqs. (3). The values of these parameters were obtained by iterative fitting of the numerical solution of Eq. (9) to the measured refractive profile of the waveguide made in the system from Fig. 8, with pointed direction of electric field polarization. Figure 11 presents the solution of Eq. (9) matched to the measured refractive profile as well as parameters of diffusion constants determined in this way. The said parameters were then inserted to Eq. (9), with all the processes being subjected to theoretical modelling with the change of electric field polarization.

soda-lime glass
1 - diffusion: t = 1 [h], T = 300 [°C]
2 - electrodiffusion: t = 0.75 [h],
                  E = 7.5 [V/mm],
                  T = 299 [°C];
3 - electrodiffusion: t = 0.75 [h],
                  E = 15.6 [V/mm],
                  T = 302 [°C];
4 - electrodiffusion: t = 0.75 [h],
                  E = 46.2 [V/mm],
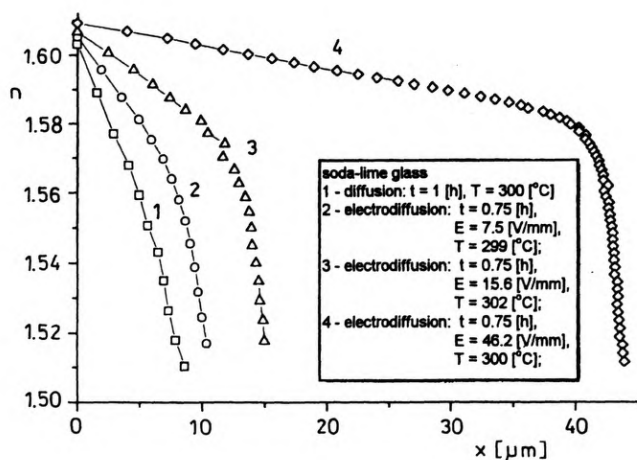   T = 300 [°C];

Fig. 10. Refractive profiles (obtained from measurements of effective indices with IWKB procedure application) of planar waveguides formed in sodium-calcium glass using ion exchange technique $Ag^+ \leftrightarrow Na^+$ (source − $AgNO_3$) in diffusion and electrodiffusion processes with one liquid electrode (in the system from Fig. 6)
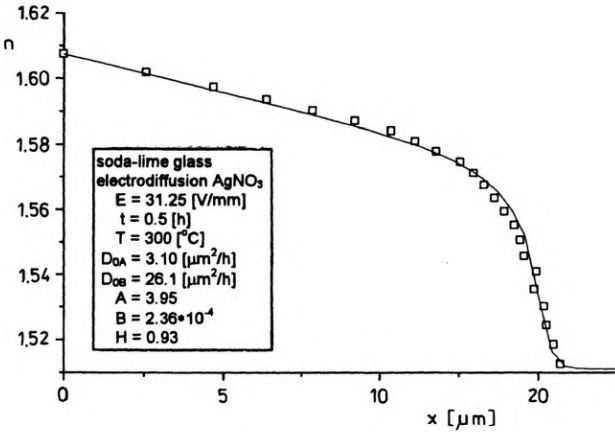
Fig. 11. Determined parameters D_{0A}, D_{0B}, A, B and H for the solution of Eq. (9) (solid line) fitted to the waveguide profile formed in sodium-calcium glass in electrodiffusion process, in the system with two liquid electrodes (Fig. 8)

Making use of the system with two liquid electrodes (melted $AgNO_3$), the processes were carried out over different time periods with respect to positive or negative polarization (Fig. 9), but the overall duration time of the process was preserved. The parameters involved in these processes are presented in Tab. 2. As can be seen from Fig. 9, due to the application of the same admixture source on both sides of glass, a second waveguide structure is formed on the opposite side of base plate when converting the direction of electric field polarization. Assuming for our purposes that the waveguides created on both sides of glass have symbols "+" and "−", it must be emphasized that upon applying one changing cycle of electric field polarization, the waveguide of "−" type is created only when the negative polarization of the field is taking place. The formation of the waveguide of "+" type involves the participation of both polarization directions. Figure 12 presents the measured refractive profiles of the waveguides of "+" type created in processes whose parameters are presented in Table 2. Starting with profile 1 obtained with the defined polarization direc-

T a b l e 2. The parameters of selected electrodiffusion processes with the conversion of polarization direction of electric field

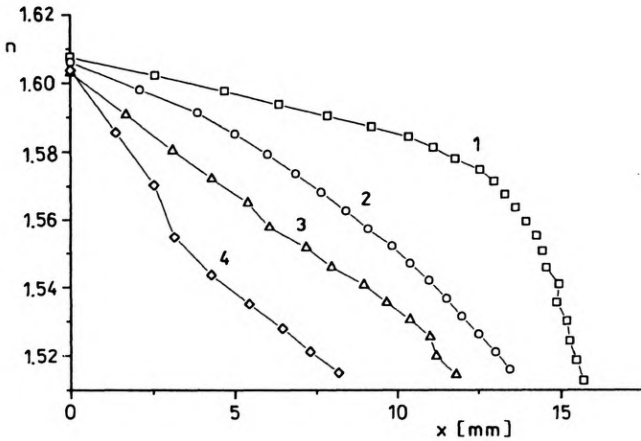| Electric field intensity [V/mm]	Total duration of process [h]	Duration of applying the field [h]	Temperature of process [°C]
+31.25	0.5	0.5	300.8
+32.30 −16.10	0.5	0.33 0.16	305.0
+31.30 −15.60	0.5	0.25 0.25	303.2
+31.30 −15.60	0.5	0.16 0.33	305.8

Fig. 12. Measured refractive profiles of planar waveguides formed in sodium-calcium glass using ion exchange technique $Ag^+ \leftrightarrow Na^+$ in electrodiffusion processes with the polarization change of the applied electric field ($1 - E = +31.25$ V/mm, $t = 0.50$; $2 - E = +32.30$ V/mm, $t = 0.33$ h, $E = -16.10$ V/mm, $t = 0.16$ h; $3 - E = +31.30$ V/mm, $t = 0.25$ h, $E = -15.60$ V/mm, $t = 0.25$ h; $4 - E = +31.30$ V/mm, $t = 0.16$ t, $E = -15.60$ V/mm, $t = 0.33$ h)

tion, a progressive tendency can be observed (profiles 2, 3 and 4) effected by "extraction" of the introduced Ag^+ ions out of glass by the converted electric field. Figure 13 shows how these processes can be predicted as a numerical solution of Eq. (9) based on diffusion parameters obtained before. A good qualitative conformity can be seen here between measurement results and the assumed model describing the ion exchange process. The measured refractive profiles of respective waveguides
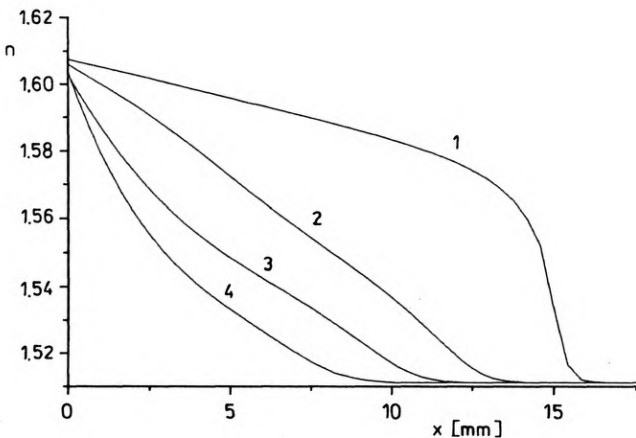

Fig. 13. Equivalents of refractive profiles of waveguides from Fig. 12 obtained as the solution of Eq. (9) with parameters D_{0A}, D_{0B}, A, B and H determined as a result of fitting (Fig. 11). ($1 - E = +31.25$ V/mm, $t = 0.50$; $2 - E = +32.30$ V/mm, $t = 0.33$ h, $E = -16.10$ V/mm, $t = 0.16$ h; $3 - E = +31.30$ V/mm, $t = 0.25$ h, $E = -15.60$ V/mm, $t = 0.25$ h; $4 - E = +31.30$ V/mm, $t = 0.16$ t, $E = -15.60$ V/mm, $t = 0.33$ h)
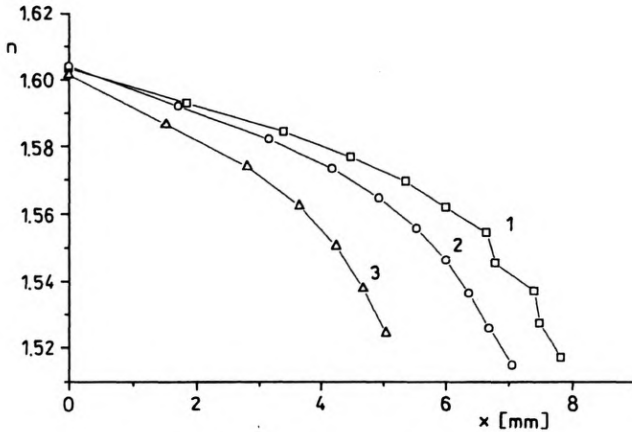
Fig. 14. Measured refractive profiles of planar waveguides formed in sodium-calcium glass using ion exchange technique $Ag^+ \leftrightarrow Na^+$ in electrodiffusion processes with the polarization change of the applied electric field. Waveguide of "−" type (Fig. 9) formed in glass bases in which the structures from Fig. 12 were formed. (1 − $E = -31.30$ V/mm, $t = 0.16$ h, $E = +15.60$ V/mm, $t = 0.33$ h; 2 − $E = -31.30$ V/mm, $t = 0.25$ h, $E = +15.60$ V/mm, $t = 0.25$ h; 3 − $E = -32.30$ V/mm, $t = 0.33$ h, $E = +16.10$ V/mm, $t = 0.16$ h
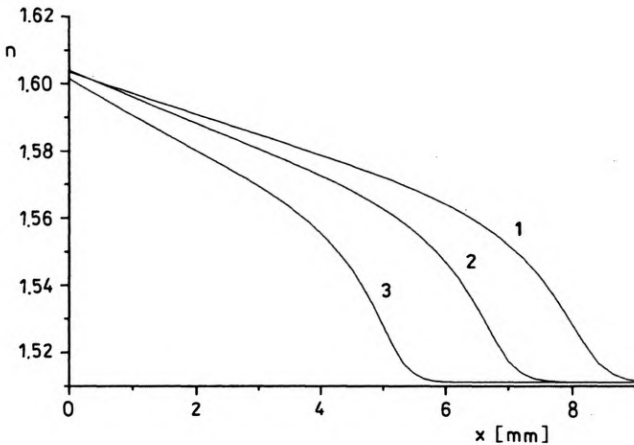

Fig. 15. Equivalents of refractive profiles of waveguides from Fig. 14 obtained as the solution of Eq. (9) with parameters D_{0A}, D_{0B}, A, B and H determined as a result of fitting (Fig. 11). (1 − $E = -31.30$ V/mm, $t = 0.16$ h, $E = +15.60$ V/mm, $t = 0.33$ h; 2 − $E = -31.30$ V/mm, $t = 0.25$ h, $E = +15.60$ V/mm, $t = 0.25$ h; 3 − $E = -32.30$ V/mm, $t = 0.33$ h, $E = +16.10$ V/mm, $t = 0.16$ h)

of "−" type obtained in the processes carried out are presented in Fig. 14. As mentioned above, for these waveguides, the introduction of Ag^+ ions was initiated after converting the direction of electrical field polarization. The measured refractive profiles show in this case only the change in structure depth effected by changing the time of its formation. Theoretical prediction of these waveguide profiles is presented in Fig. 15.

6. Conclusions

The investigative studies demonstrated the possibility of carrying out electrodiffusion processes in flat base plates, with the application of liquid electrodes on both sides of glass. As a result, it was possible to carry out processes of that type with the conversion of the direction of electric field polarization. Refractive profiles of planar waveguides obtained in that way have different character from the ones obtained in purely diffusive or electrodiffusive processes with defined direction of field polarization. This creates new possibilities for the formation of refractive profiles. It should also be emphasized that there was a comparatively good prediction involving refractive profiles obtained in such technological processes with the use of ion exchange model which allows for the dependence of diffusion cnstants of the exchanged ions on polarization of the field. In further investigative studies to be carried out in this field, it appears possible to apply multiple cyclic changes of the direction of field polarization. Due to the fact that the application of the said model of ion exchange yielded good results with respect to theoretical prediction, such processes could be used for the formation of refractive profiles of a given character. It is believed that such technological processes will soon be applied for the creation of strip waveguide structures.

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