On the transport of potassium ions through borosilicate glass
A combined experimental and theoretical study

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The transport of potassium ions through potassium borosilicate glass has been investigated experimentally by measuring the back side current induced by ion bombardment of the front side. The experimental data are compared to calculations employing the Nernst-Planck-Poisson model. The analysis allows deriving the bulk ion conductivity respectively diffusion coefficient of the material. The role of interface transport is discussed.

I. INTRODUCTION

The ion conductivity of glassy material is the basis for several technical applications in the field of energy conversion and storage. The generally accepted model for ion transport in ion conducting glasses implies the thermally activated hopping of ions between different sites separated by an activation barrier [1]. Currently established techniques for determining ion conductivities include the impedance spectroscopy [2],[3],[4], the radioactive tracer technique [5] and pulsed field gradient NMR [6]. Here, we describe an alternative approach based on measuring the macroscopic transport of ions through the material of interest.

II. EXPERIMENTAL APPROACH

The experimental setup constructed for this investigation consists of an ion source for production of a c.w. potassium ion beam, an electrostatic ion guide and a sample holder connected to an electrometer amplifier. The entire setup shown in Fig. 1 is housed in a high vacuum chamber operated at a pressure of about 10⁻⁶ mbar. The ion source employed is based on a homemade thermionic emitter consisting of a mixture of potassium aluminosilicate (synthetic Leucite) with molybdenum [7]. This source provides a continuous ion current of up to 20 nA. The ion beam is guided towards the sample, which is mounted in an electrically insulating holder. The back side of the sample is mechanically pressed onto a stainless steel electrode. The front side of the sample is covered by a ring electrode with central opening of 2 cm diameter. The actual area A bombarded by the ion beam is also circular with a diameter of 1 cm, enforced by apertures mounted directly in front of the sample. In the experiment ions are either adsorbed to the surface and then transported into and through the bulk material or implanted into the sample and then transported through the bulk material. The back side electrode is connected to an electrical high vacuum feed through and fed into a home-made electrometer amplifier. The current detected at this backside electrode is subsequently A/D converted and processed in a personal computer. The kinetic energy of the ion beam in the laboratory frame is given by the repeller potential \( U_R \) applied to \( L_1 \) which can be adjusted between about 50 Volt and 3000 Volt. \( L_2 \) is always set to -1500 Volt, \( L_3 \) is used for refocusing the ion beam, \( L_4 \) (defining two apertures spaced by 26 mm) and \( L_5 \) (ring electrode) are set to ground potential, the distance between the \( L_4 \) and \( L_5 \) is 2 mm. In general the setup provides the possibility to investigate the time evolution of the current. That means switching either the intensity or the kinetic energy of the ion beam leads to a material characteristic response of the back side current. However, all measurements reported in this work have been performed under stationary equilibrium conditions. The effective input current impinging onto the sample is measured by replacing the sample by a blank metal plate.

The glass sample investigated (K₂O * SiO₂ * 2 B₂O₃) has been prepared by heating a stoichiometric mixture of K₂CO₃, B₂O₃ und SiO₂ for 2 h to about 1100 °C. The molten mixture is cooled by pouring the material into a cylindrical steel pot with 2 cm diameter. It is annealed at 433 °C for five hours and then cooled at a rate of 0.5 °C per minute to room temperature. Afterwards the sample is cut into slices of approximately 800 \( \mu \)m thickness. Finally the surface of the disk is thoroughly polished using SiC to the desired thickness of 100 \( \mu \)m to 250 \( \mu \)m. The thickness \( d \) of the sample used was 175 \( \mu \)m, the temperature 50°C.

![Figure 1. Scheme of the experimental setup.](image-url)
III. THEORETICAL MODEL

In order to gain deeper insight into the transport processes leading to the experimentally observed ion current at the backside electrode, we have performed numerical simulations of the ion transport. More specifically, we have setup a model based on the Nernst-Planck-Poisson (NPP) equations. According to the Nernst-Planck (NP) theory, the flux $J$ of ions transported per unit time through an area of interest is given by

$$J = -D \left( \nabla n + n \nabla \phi \right) = -D \left( \nabla n + n \nabla \phi \right) \frac{Z e}{k_B T} , \quad (1)$$

where $D$ is the diffusion coefficient. The first term describes the diffusion of the ions due to the ion-density gradient $\nabla n$ while the second term introduces the migration of the ions under the influence of a potential gradient $\nabla \phi$. The ion density $n$ contains the potassium ions injected as well as the background potassium ions, $n_{bg}$, present in the sample prior to ion bombardment. The combination of the two contributions to transport is termed electrodiffusion throughout the rest of this work. The ion charge is given by $Ze$, $k_B$ is Boltzmann’s constant and $T$ the temperature. The time dependence of the ion distribution enters via Fick’s second law

$$\frac{\partial n}{\partial t} = -\nabla \cdot J . \quad (2)$$

As the ions themselves give rise to an electric potential, the ion distribution inside the glass and the potential must be calculated in a self consistent manner. Ultimately, the electric potential has to fulfill the Poisson equation

$$\varepsilon_0 \nabla \cdot \left( \varepsilon \nabla \phi \right) = -e Z (n - n_{bg}) , \quad (3)$$

where $\varepsilon_0$ is the vacuum permittivity and $\varepsilon$ is the dielectric function of the borosilicate glass.

We assume the ion beam shines homogenously on a circular region of the glass sample. The sample is shaped like a disk with diameter much larger than the sample thickness. Hence, only transport perpendicular to the sample surface has to be taken into account, transport in radial direction may be neglected. Since the emission of ions other than potassium ($K^+$) by the emitter is negligible [7] and the electronic conductivity of the borosilicate glass is much smaller than the ion conductivity, we may exclusively concentrate on the transport of potassium ions, consequently $Z = +1$. Additionally, we assume isotropic material properties such that the dielectric function can be expressed by a dielectric constant $\varepsilon \equiv \varepsilon_i = 10$.

As a consequence of these approximations, the NPP equations simplify to the expressions

$$\bar{J} = -D \left( \frac{\partial n}{\partial z} + n \frac{\partial \phi}{\partial z} \right) \frac{Ze}{k_B T} , \quad (4)$$

$$\varepsilon_0 \varepsilon_i \left[ \frac{\partial^2 \phi(z)}{\partial z^2} \right] = -e \left( n(z) - n_{bg} \right) , \quad (5)$$

A. Discretization

In order to solve Eqs. (4)-(6), the z-axis of the sample is discretized into $n_z$ increments and an ion density $n_i$ as well as a potential $\phi_i$ is assigned to each of the increments. The ion flux between the two adjacent increments $i$ and $i+1$ is given by $J_{i,i+1}$. The discrete NPP equation are thus given by

$$J_{i,i+1} = -D \left( \frac{n_{i+1} - n_i}{\Delta z_{i,i+1}} + \frac{n_i \Delta z_{i,i+1} + n_{i+1} \Delta z_{i+1,i} \phi_{i+1} - \phi_i}{2 \Delta z_{i,i+1}} \right) \frac{e}{k_B T}$$

$$\phi_i = \left( e \left( n_i - n_{bg} \right) \Delta z_i \Delta z_{i,i+1} + e_0 \varepsilon_i \left( \phi_{i+1} \Delta z_{i+1,i} + \phi_{i-1} \Delta z_{i,i-1} \right) \right) / e_0 \varepsilon_i \left( \Delta z_{i,i+1} + \Delta z_{i,i-1} \right) \quad (8)$$

$$\frac{d}{dt} n_i(t) = \left( J_{i,i+1} - J_{i,i-1} \right) / \Delta z_i \quad (9)$$

where $\Delta z_i$ is the size of increment $i$ and $\Delta z_{i,i+1} = 0.5 \left( \Delta z_i + \Delta z_{i+1} \right)$. In general we do not restrict all $\Delta z_i$ being identical. The diffusion coefficient $D_i$ is assumed to be the same in the entire bulk sample, $D_{bulk}$. In general, the first increment on the grid is assigned a different diffusion coefficient reflecting the transport through the interface layer. Under the conditions relevant to the current work this effect is negligible. See section V for further discussion.

As shown by Eq. (8), the potential in increment $i$ depends on the ion current in the increment itself as well as on the potentials in the neighboring increments $i+1$ and $i-1$. This feature leads to the self-consistency problem that was already mentioned above. If we assume the sample initially is electron-neutral, the potential is zero everywhere. Subsequently, the implantation of ions for example in the first increment leads to a modification of the potential there. At the same time, the modification of the potential in the first increment implies that the potential in the second increment has to be calculated again (since the potential in the second increment depends on the potential of the first increment). A recalculation of the potential in the second increment implies that the potential in the first increment has to be calculated again and so on. We solve this self-consistency problem by subsequently calculating the potential (8) for increments 1 to $n_z$ several times until the potential converges to values that are self-consistent with the ion distribution in the glass. Convergence can be enhanced if we keep the time step small such that the ion distributions changes only marginally between two subsequent time steps and take the converged potential of the previous time step as starting point for the calculation in the actual time step.

B. Boundary conditions

To consistently calculate Eq. (8), we need to define how the potential behaves at the boundary of the glass sample. The backside of the glass sample is in contact with a metal electrode which is put to ground level. Neglecting contact
potentials, we may assume that the potential at the rear end of the sample is \( \phi_{\text{rear}} = 0 \). The potential at the front end of the sample is the surface potential which is ultimately defined by the ion distribution at the surface and inside the bulk material. As the ions in the first increment define the ion density at the surface and electrodes in front of the sample are far away and thus should hardly influence the potential just in front of the sample, we may set \( \phi_{\text{front}} = \phi_1 \).

C. Backside current

We assume that the ions are neutralized as soon as they reach the backside of the sample. Therefore, the current detected at the backside electrode is given by

\[
I_b = e A J_{\text{neut}} ,
\]

with the electron charge \( e \) and the sample area \( A \).

D. Ion source

When the potassium ions leave the emitter, they are accelerated toward the sample via the repeller voltage \( U_R \). As a consequence, the ions reaching the sample surface charge the surface and lead to a surface potential that is self consistently calculated by Eq. (8) such that the effective kinetic energy of the ions reaching the surface is reduced corresponding to

\[
E_{\text{kin}} = e (U_R - \phi) .
\]

Thus, the ion current reaching the sample surface is given by

\[
I_n = \frac{(U_R - \phi_1)}{U_R} I_0 ,
\]

where \( I_0 \) is the experimentally measured blind current. This leads to an additional source term in the Nernst-Planck equation

\[
\frac{\partial n}{\partial t} = \frac{(U_R - \phi_1)}{A \Delta z e U_R} I_0 .
\]

The continuous transport of ions from the emitter to the glass together with the electrodiffusion of ions through the glass leads to a dynamic equilibrium of the ion distribution and, thus, to an equilibrium backside current after some seconds. In the following, we compare such steady state currents to the experimental data. A more elaborate description of the theoretical approach will be presented elsewhere [8].

IV. RESULTS

The current induced by the transport of potassium ions through borosilicate glass has been measured for three different blind current functions (see inlay of Fig. 1) corresponding to average input currents of about 1.5 nA (\( I_{0,A} \)), 3 nA (\( I_{0,B} \)) and 6 nA (\( I_{0,C} \)). As shown in Fig. 2, for all three input currents the backside current increases with increasing repeller voltage.

Evidently, the slope of the current – voltage curve is small between 50 and about 200 Volt but increases significantly beyond this voltage. In order to get a first picture of the transport characteristics, we assume that the ions are adsorbed to the surface of the dielectric material such that the surface potential, \( U_{\text{surf}} \), is identical to the repeller voltage. This situation would apply, if there are enough surface sites available and no decay process of surface charges is operative. Note, that this assumption places an upper limit to \( U_{\text{surf}} \). In this situation, the voltage drop across the sample would also be given by \( U_R \), since the backside is basically operated at ground potential. By assuming the transported current is simply field driven, i.e. assuming Ohm’s law, the slope of the current – voltage curve can be translated to a conductivity \( \sigma \). In Table 1 we present the effective conductivity \( \sigma_{\text{eff,exp}} = \sigma \cdot d/A \) derived for the region between 600 and 800 Volt. For comparison, the specific conductivity measured by impedance spectroscopy is \( 4 \cdot 10^{-14} \) S/cm, compatible with the data in Table 1.

In the following, we present the results of a NPP analysis as outlined in section III. The following information has been used as input to the calculation. The blind current is directly taken from the experimental measurement assuming it is homogenously distributed over the relevant bombardment area. The background ion density of the material is \( n_{\text{bg}} = 7 \cdot 10^{21} \) ions per cubic centimeter as given by the glass composition. The only adjustable parameter is the effective bulk diffusion coefficient.

One of the first results of the theoretical analysis pertains to the surface potential. The actual surface potential is in general smaller than the repeller potential due to two physical effects. First, the transport of ions through the interface and consequently through the bulk reduces the surface ion density.

<table>
<thead>
<tr>
<th>Repeller voltage [V]</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Backside current [nA]</td>
<td>( I_{\text{back}}(I_{0,A}) )</td>
</tr>
<tr>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>200</td>
<td>2.0</td>
</tr>
<tr>
<td>400</td>
<td>3.2</td>
</tr>
<tr>
<td>600</td>
<td>4.6</td>
</tr>
<tr>
<td>800</td>
<td>6.0</td>
</tr>
</tbody>
</table>

TABLE I. EFFECTIVE CONDUCTIVITY OF THE BOROSILICATE GLASS

| Effective conductivities in S/cm |
|-------------------------------|----------------|----------------|
| \( I_{0,A} \) | \( I_{0,B} \) | \( I_{0,C} \) |
| \( \sigma_{\text{eff,exp}} \) | \( 1.65 \cdot 10^{-14} \) | \( 3.67 \cdot 10^{-14} \) | \( 8.02 \cdot 10^{-14} \) |
| \( \sigma_{\text{eff,exp}} \) | \( 1.78 \cdot 10^{-14} \) | \( 3.45 \cdot 10^{-14} \) | \( 5.30 \cdot 10^{-14} \) |
This originates from the linear increase in both types of analysis. Diffusion contribute similarly to the transport. There are rewarding to search for a situation where migration and transport is dominated by migration. For the future, it might fall on top of each other. Ultimately, this implies that the surface potential leads to a situation where all curves basically increases almost linearly with \((\text{Table 1})\). We further showed that the effective conductivity which exhibit very good agreement with the theoretical model based on the Nernst-Planck-Poisson equations. The experimental and theoretical analysis yields effective specific conductivities from the theoretical current - voltage curves. The numbers derived are given in Table 1. Evidently, there is good agreement between the experimental and theoretical analysis of conductivities.

VI. REFERENCES