Bombardment Induced Ion Transport Through an
Ion-conducting Ca30 glass

P.V. Menezes, J. Martin, M. Schäfer and K.-M. Weitzel
Philipps-Universität Marburg, Fachbereich Chemie, Hans Meerwein Strasse, 35032 Marburg, Germany.
Email: weitzel@chemie.uni-marburg.de

I. INTRODUCTION

The transport of alkali ions through solid electrolytes is a key process in the field of energy storage and energy conversion [1,2]. Typically the transport is characterized via the diffusion coefficient or the conductivity. Conventional approaches to ion conductivity include e.g. impedance spectroscopy (IS), pulsed field gradient NMR and tracer diffusion techniques [1]. These techniques typically include either two or more electrodes or no electrode. Recently, we have introduced an alternative approach to ion transport through solid electrolytes, which involves only one electrode and consequently only one electrolyte / electrode interface [3,4]. This approach is advantageous in situations where the sample is too thin to connect two electrodes or where contact potentials are an important issue.

This work describes the application of the recently developed bombardment induced ion transport (BIIT) approach to measure the sodium ion conductivity.

II. EXPERIMENTAL APPROACH

The ionic conductivity of a glass sample has been investigated by the bombardment induced ion transport (BIIT) technique. A continuous $K^+$ ion beam is generated by thermionic emission from heated potassium aluminosilicate [4,5]. The ion beam is accelerated to a well defined kinetic energy in the laboratory frame by applying the appropriate repeller voltage, $U_R$, to the ion emitter. Subsequently, the ions are guided to the surface of a glass sample. Ions attach to the front side of the sample, which generates a surface potential. Since the back side of the glass sample is directly connected to a metal electrode the ion bombardment causes a potential gradient and a concentration gradient in the glass. This induces ion transport in the glass due to the laws of electrodiffusion, which can be detected as the current at the backside electrode, hence the name BIIT. For more experimental details we refer to [4,5,6].

The glass sample was prepared by heating a stoichiometric mixture of Na$_2$CO$_3$, CaCO$_3$ and (NH$_4$)$_2$HPO$_4$ to 1150°C for 1h. The molten mixture has been poured into a steel cylinder with inner diameter of 20mm. The glass has been annealed at 400°C for 10h before cooling to room temperature. The actual sample is obtained by cutting thin discs from the glass cylinder and polishing down to the desired thickness, in the current case 1.45mm. The final composition of the glass is 25% Na$_2$O – 30% CaO – 45% P$_2$O$_5$. Its ionic conductivity is known to originate from the mobility of Na$^+$ ions.

III. RESULTS

A. Current - Voltage Curves

We first concentrate on the overview measurement. For this purpose the repeller potential of the ion source is ramped stepwise from zero to 500 Volt. At each kinetic energy the corresponding equilibrium back side current is measured. As shown in Fig. 1 for small repeller voltages the current increases linearly with the kinetic energy of the ion beam. Above a repeller voltage of about 200 Volt the current saturates. The linearly increasing regime originates from an Ohm’s law like behavior. The slope directly gives the conductivity of the sample. The saturation above 200 Volt is due to a limitation of the back side current, which in the current setup does not exceed about 2/3 of the blind current. Note that the blind current which is measured in a separate experiment, where the ion beam directly impinges onto a metal electrode, has been kept constant for the entire measurement as indicated in Fig. 1.

B. Temperature dependence of current - voltage curves

In order to determine ionic conductivities more specifically we have measured the current - voltage relation discussed above for four different temperatures. The experimental data are shown in Fig. 2 as symbols. In this case we restrict the data acquisition to the low voltage regime. Evidently the linear regression to the data indicates straight lines, the slope of which directly reflect the conductivity of the actual sample. The slope increases with increasing temperature as expected for thermally activated ion transport. The results from this conductivity analysis are discussed in the next section.
C. **Temperature dependence of ion conductivity**

The temperature dependence of the ionic conductivity is given by the Nernst-Einstein relation

$$\sigma_{\text{spec}} = \frac{\sigma_0}{T} = \frac{\Delta n_i}{kT}. \quad (1)$$

Thus, a plot of ln (σ-T) versus 1/T is expected to yield a straight line, with the slope containing the information on the activation energy. The data are presented in Fig. 3. From the analysis we derive an activation energy of 1.02 eV ± 0.06 eV. This number can be compared to e.g. information from IS, which yields a number of 0.99 eV ± 0.02 eV \(^8\) in perfect agreement with the current BIIT data. This agreement is noteworthy since the conceptual approach of BIIT is significantly different from IS. The IS data clearly correspond to the mobility of Na\(^+\) in the Ca30 glass. The agreement between the activation energies derived from BIIT and IS suggests that Na\(^+\) mobility in the bulk of the glass also determines the activation energy in the BIIT experiment. Yet, we have to emphasize that the ion transport in the current experiment is induced by K\(^+\) bombardment. This raises the question, whether characteristics of K\(^+\) transport through the glass play an important role. In order to shed further light on this question we have also compared the absolute conductivities determined in the IS experiment to the BIIT data. As it turns out the BIIT data are about a factor of 2 smaller than expected based on the extrapolation of the IS data to our temperatures. We speculate that this lowering of the absolute conductivity is due to an alteration in the interface region caused by the diffusion of K\(^+\) into the material. This is also supported by a more recent experiment where for a fresh Ca30 sample a conductivity has been observed in BIIT, which matches the extrapolation of the IS data \(^9\). Note, that the conductivity data presented in Fig. 2 have been obtained after bombarding the glass sample for about 4 weeks at an input current of about 2 to 3 nA.

More recently we have also analyzed the sample after the BIIT experiment by means of TOF-SIMS \(^9\). Here, a pronounced diffusion profile extending several hundred nm into the sample has been observed for the K\(^+\). Most interestingly a complementary reduction of Na\(^+\) as well as Ca\(^+\) is obtained on the same depth scale.

Fig. 2. Current - voltage curves for different temperatures as indicated.

IV. **SUMMARY AND OUTLOOK**

The ionic conductivity of a sodium containing glass has been investigated by means of the recently developed BIIT technique. This BIIT approach is based on K\(^+\) bombardment of the sample. From the temperature dependence of the ionic conductivity we derive an activation energy of 1.02 eV in agreement with IS. The absolute ionic conductivities, however, are a factor of 2.5 smaller than that of the pure Ca30 glass. This discrepancy originates from the introduction of K\(^+\) ions into the Na\(^+\) conducting glass. The conceptual approach demonstrated is believed to open access to mixed alkali ion effects in the region of interfaces.

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**REFERENCES**


