Dynamics of ion guiding through nanocapillaries in insulating polymers

N. Stolterfoht, Erwin Bodewits, Rolf Hellhammer, Zoltan Juhász, Béla Sulik, Veronika Bayer, Christine Trautmann and Ronnie Hoekstra

Abstract. We review recent studies of dynamic properties concerning the ion guiding through nanocapillaries etched in polyethylene terephthalate (PET) and polycarbonate (PC). Typical lengths of the capillaries were 10 µm with diameters ranging from ~100 - 400 nm. The temporal evolution of the intensity and the angular distribution of the transmitted ions were studied by measuring transmission profiles as a function of the charge inserted into the capillaries. Tilt angles of the capillaries axis with respect to the incident beam direction were 3° and 5°. The mean emission angle of the transmission profiles exhibit pronounced oscillatory structures both for PET and PC. However, for PC nearly an order of magnitude more charge is required to induce the oscillations. In contrast to PET, with capillaries in PC we observed a strong decrease of the profile intensities with irradiation time. This observation provides evidence for blocking effects on the ion transmission. The experimental results are interpreted by simulations of the ion trajectories guided in 3 dimensions by the electrostatic field within the capillaries. This field was determined from the charge deposited at the walls of the capillaries taking into account the removal of the charges by means of a non-linear conductivity law.

1. Introduction

In the past few years the transmission of ions through nanocapillaries has received considerable attention. Capillaries in highly insulating materials keep charges deposited by the incident ions for a relatively long time on the capillary wall so that a repulsive electric field is produced. This field deflects the following ions at rather large distances so that electron capture into the projectile is inhibited. Thus, the ions are guided along the capillary axis maintaining their incident charge state during their passage even when the capillary axis is tilted with respect to the incident beam direction. The initial exploration of the ion guiding phenomenon in insulating materials have made use of capillaries in PET polymers (see [1, 2] and references therein). Thereafter, several laboratories performed theoretical and experimental work concerning charged particle guiding through capillaries in materials including PET, PC, SiO₂, and Al₂O₃ [3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. A full set of references to the studies of capillary guiding has recently been given in [13].

The outstanding property of the ion guiding is a self-organizing process, which governs the charge deposition inside the capillaries [1, 9]. As illustrated in figure 1, the incident ions produce
a significant charge patch in the entrance region which, in turn, gives rise to a deflecting electric field. When the ions are deflected, the charge deposition decreases and the charge patch reaches an equilibrium. The amount of charge in the entrance patch is rather independent on the incident ion current [14], which provides clear evidence that for PET the conductivity is governed by a non-linear (exponential) conductivity law [15].

Figure 1. Scenarios of ion guiding through capillaries in an insulating material. In (a) and (b) typical trajectories occurring in, respectively, the dynamic and the equilibrium period of the charge evolution are shown, where the black areas indicate charge patches [16].

Apart from the dominant charge patch near the entrance region, additional weaker patches are temporarily produced further inside the capillaries [9]. Recent experimental studies on the temporary charge patches [4, 16, 17, 18] have revealed oscillatory movements of the ion emission angle as a function of the deposited charge. These temporary patches play a significant role during the dynamic period of the ion guiding as indicated in figure 1(a). At equilibrium represented by figure 1(b), the secondary patches loose importance and the transmission stabilizes.

To date general agreement exists about the scope of the guiding mechanism. However, many details of the guiding properties are only partially understood. Figure 1 represents a preliminary scenario [16] proposed to explain the role of temporary charge patches in the pre-equilibrium period of the ion transmission. The temporary formation of charge patches has previously been made evident in model calculations simulating the transmission of highly charged ions through insulating capillaries [9]. However, this theoretical work has been devoted to specific cases so that more work is needed to interpret the various recent experiments revealing the dynamic properties of the ion guiding.

In the present work, we review dynamic properties of 3 keV Ne$^{7+}$ ions guided through capillaries in PET and PC. The transmitted ions show damped oscillations of the mean emission angle with increasing deposited charge. For PC nearly an order of magnitude more charge needs to be inserted into the capillaries to accomplish the oscillations. Furthermore, with PC a strong intensity decrease of the transmitted ions is observed with increasing charge insertion. The experimental results are interpreted by model calculations showing explicitly the formation of temporary charge patches and the resulting oscillations of the mean emission angle of the transmitted ions.

2. Experimental results

The reviewed experiments have been performed in an ultra-high vacuum chamber connected to the 14 GHz Electron Cyclotron Resonance (ECR) ion source of the ZERNIKE-LEIF facility at the KVI Groningen (Netherlands) [19]. The irradiation chamber was used in a high-vacuum mode, i.e., the base pressure was some 10$^{-8}$ mbar. The apparatus was set on high voltage to allow for the deceleration of the incident Ne$^{7+}$ ions from 49 keV down to 3 keV. The ion current
was varied within the range of $10 - 3000 \text{ pA}$. The beam was collimated to a diameter of $\sim 1 \text{ mm}$ with a divergence better than $0.2^\circ$ full width at half maximum (FWHM). The ions, transmitted through the capillaries, were detected using an electrostatic spectrometer.

Cylindrical capillaries in PET polymers were prepared with diameters of a few $100 \text{ nm}$ and a density of $4 \times 10^6 \text{ cm}^{-2}$ at the Ionenstrahllabor (ISL) in Berlin. Similar capillaries in PC polymers were prepared with density of $5 \times 10^7 \text{ cm}^{-2}$ in the department of Materialforschung at the GSI Helmholtzzentrum. Care was taken to optimize the parallel orientation of the capillaries. The angular spread of non-parallel capillaries was estimated to be $\lesssim 0.2^\circ$ FWHM which was significantly smaller than the angles of $\geq 1^\circ$ resulting from the capillary aspect ratios. This parallelism is a decisive condition for the experiments of dynamic guiding properties recording the time evolution of angular profiles [13, 16].

In the following, we focus our attention on Ne$^{7+}$ ions, whose incident charge state was preserved during the passage through the capillaries. The major objective of the experiments was the measurements of transmission profiles, which represent the angular distribution $dY(\theta)/d\Omega$ of Ne$^{7+}$ ions transmitted through the capillaries as a function of the observation (or emission) angle $\theta$. The transmission profiles were acquired for different angles of the capillary axis tilted with respect to the incident beam. The data for each angle were measured at a fresh spot by shifting the capillary sample to a new position. The ion current was recorded as a function of time and the deposited charge was obtained by time integration of the current. For a constant current the inserted charge is proportional to time. Thus, although we show the measured data as a function of inserted charge, we may also speak of the time evolution. More detailed information is given in previous work [13, 16, 20].

### 2.1. Intensity of the transmitted ions

To analyze the time evolution of the ion guiding we consider the total yield $Y(\psi) = \int \frac{dY}{d\Omega} d\Omega$ of transmitted Ne$^{7+}$ ions, where $\psi$ is the tilt angle of the capillary axis. Figure 2 compares the total yield for PET and PC capillaries as a function of the inserted charge. In panel (a) the results for PET capillaries with a diameter of $100 \text{ nm}$ are given. The temporal evolution exhibit an initial increase of the total yield until the equilibrium value is reached, which remains constant within the following region of inserted charges. The initial rising of the ion yield for non-zero tilt angles is a well-known feature associated with the build-up of the main charge patch in the entrance region of the capillaries (figure 1).

The initial rising of the ion yield can be approximated by the exponential charge-up function [14]

$$Y(Q_{\text{in}}) = Y_0 \left(1 - \exp \left[-Q_{\text{in}}/Q_{\text{in,c}}\right]\right)$$

(1)

The characteristic charge $Q_{\text{in,c}}$ was determined by fitting the total ion yield to eq. (1). In figure 2(a) the fit results are given as a solid line in conjunction with the characteristic value of the inserted charge $Q_{\text{in,c}}$.

In figure 2 the panels (b) and (c) show the total ion yield for capillaries in PC with diameters of 95 and $165 \text{ nm}$, respectively. The results for the two diameters exhibit a similar behavior. However, in contrast to the results for PET, the yield for PC capillaries starts to drop after the initial rise from zero to a maximum value. The total intensity for the 95 nm capillaries decreases asymptotically to zero for large charge insertion. The results for 165 nm capillaries appear to approach asymptotically a non-zero intensity value. Unfortunately, not enough data are available for larger charge deposition to be able to conclude whether the yield approaches a constant value or finally drops to zero. The decrease of the intensity is associated with the formation of a repulsive or misaligning electric field, which produce a blocking of the ion transmission within the capillaries.
Figure 2. Total ion yield $Y$ of 3-keV Ne$^{7+}$ ions transmitted through capillaries in PET and PC plotted as a function of the inserted charge [13]. The tilt angles $\psi$, the capillary diameter and length are indicated in each panel (a), (b), and (c). The experimental data are fitted by eq. (1) and the results are shown as solid lines together with the fit values $Q_{in,c}$. The dashed lines are guides to the eye.

The data for the PC capillaries were used to fit the rising part by means of eq. (1). In figure 2 the fit values for the characteristic charge $Q_{in,c}$ are shown. However, we note that the analysis of the ion yields for capillaries in PC is not as straightforward as for those in PET. Due to the blocking effect the ion yield is decreasing, which partially suppresses its initial rising. Hence, the rising curve is truncated in height and length, i.e. the equilibrium value, expected in the absence of the blocking effect, is not achieved. Thus, the fit of the PC data by eq. (1) involves uncertainties. Nevertheless, we can conclude that the $Q_{in,c}$ values for PC are significantly larger than those for PET.

2.2. Mean emission angle of the ions

Next, we analyze the mean emission angle of transmitted Ne$^{7+}$ ions. This angle was obtained by numerical integration using the well-known expression $\bar{\theta} = \int \theta (dY/d\Omega)d\theta/\int (dY/d\Omega)d\theta$.

Selected results are depicted in figure 3 where the mean ion emission angle is shown for PET capillaries of 12 $\mu$m length. With increasing charge insertion pronounced oscillations of the mean emission angle around the tilt angle are observed. The panels (a) and (b) compare the results for capillaries with a diameter of 200 nm irradiated under the tilt angles of 3° and 5°, respectively. The oscillatory structures are stretched to larger charge insertion values and their amplitudes increase with increasing tilt angle. Hence, the oscillation decreases in frequency as the tilt angle increases. Panel (c) exhibits results for ions transmitted through 400 nm capillaries tilted by an angle of 5°. The comparison of the panels (b) and (c) indicates a reduction of the oscillation frequency for the 400 nm capillaries.

When the charge deposition progresses, the oscillations become damped. After considerable damping the mean emission angles do not change any more and the mean angle approaches a constant value equal to the tilt angle. For the 200 nm capillaries the damping is weaker than...
Figure 3. Mean emission angle of the transmitted 3-keV Ne$^{7+}$ ions for capillary tilt angles of $3^\circ$ and $5^\circ$ [16]. Solid lines are guides to the eye, dashed lines indicate the tilt angle.

that for 400 nm and, hence, more oscillations are visible for the smaller diameter. Altogether, for 200 nm the mean emission angle exhibits 3 major extremes (minima and maxima) resulting from its oscillation, whereas for the 400 nm capillaries only 2 such extremes are visible. As pointed out before [7], each major extreme deviation of the mean emission angle corresponds to a charge patch so that 200 nm capillaries 3 charge patches are likely being produced (as in figure 1). Hence the capillaries of 200 nm form one more charge patch than the 400 nm capillaries.

Figure 4. Comparison of the mean emission angle of 3-keV Ne$^{7+}$ ions for different type of capillaries in PET and PC tilted by $5^\circ$ as a function of the inserted charge $Q_m$ [13].
In figure 4 the results for capillaries in PET are compared with those obtained in PC. The capillary tilt angle is 5°. For comparison the results for 200 nm PET capillaries are shown again in figure 4 (a). In figure 4 (b) and (c) data for PC are given for capillaries of the length of 10 µm and diameters of 95 and 165 nm, respectively. The curve for the 95 nm oscillates faster than that for the 165 nm capillaries. Qualitatively, the oscillations for the capillaries in PET are similar to those for PC. However, much higher inserted charge is needed to accomplish the oscillations for capillaries in PC. This result is in accordance with the finding from figure 2 that the characteristic charge $Q_{m,c}$ is significantly larger for the PC capillaries.

3. Simulations and interpretation

The reviewed experiments reveal pronounced oscillations of the mean ion emission angle, which are associated with secondary charge patches formed in addition to the dominant entrance charge patch. For PC capillaries, blocking effects on the ion transmission are observed. To gain more insight into the interpretation of the experimental observations, simulations of the ion guiding were performed. The calculation takes into account the full circular geometry of the capillaries in three dimensions.

The ions are inserted into the capillary under the tilt angle $\psi$ using random distributions for the initial x and y values, where x and y are, respectively, the horizontal and vertical coordinates perpendicular to the capillary z axis. The incident ions, that impinge on the inner capillary wall, are assumed to deposit their full charge onto the surface. Dielectric screening for the surface charges was employed [10]. The surface charges produce an electric potential that was evaluated by accumulating the individual Coulomb potentials of the point charges. Image charges of the charge patches were added to take into account the conducting Au film evaporated on the front and back side of the polymer foils. Trajectories of the ions were calculated solving the differential equations for a classical particle moving in an electric field deduced from the potential. This part represents an ab-initio calculation as it includes no adjustable parameters.

The challenging part of the calculation is the inclusion of the migration of the deposited charges. For the charge flow, that reduces the charge patches, it was assumed that the surface conductivity $\sigma_s$ is dominant within the capillary so that the bulk conductivity was neglected [9]. To evaluate the current density vector $j_s$ produced by the electric field $E$ on the surface, we used the non-linear (exponential) expression by Frenkel [15]

$$j_s = E \sigma_s \exp \left( \frac{|E|}{E_c} \right)$$

which was revised with respect to the present capillary geometry [13]. The parameter $E_c$ is a characteristic field governing the exponential increase of the surface current. The formula implies two regions where for $|E| \ll E_c$ the current follows a linear dependence of the field (as in Ohm’s law) and for $|E| \gtrsim E_c$ the current is determined by an exponential field dependence. Hence, the non-linear conductivity law implies two adjustable parameters $\sigma_s$ and $E_c$. These parameters were chosen in accordance with the results of previous experimental studies [14] showing that the current flow takes place in the non-linear region.

The ion insertion and the charge flow were treated sequentially in iterations. After a small number of ions (typically 20 out of several thousands) were inserted into the capillary, the deposited charges were displaced in proportion to the ion insertion time. The distance and direction of the charge displacement were determined using eq. (2) with the electric field vector evaluated at the location of the charge under consideration. Thus, the charges were moved along the capillary wall parallel and perpendicular to the capillary z axis. Remarkably, it was found that the charge patches are more weakened by the charge flow along the capillary wall in x-y direction than by the flow in the z direction.
In figure 5 the calculated trajectories of 3-keV Ne\(^{7+}\) ions are shown for different charges \(Q_{in}\) inserted into the capillaries. The lowest panels depict the deposited charges and potentials present after the insertion of the maximum value of \(Q_{in}\). The potentials, shown in the lowest panel, are in accordance with the position of the charge patches. We point out strong focusing effects on the ion beam by the entrance potential that are expected to enhance the ion transmission. In the charge distribution one can clearly distinguish the dominant charge patch in the entrance region from two additional charge patches in the center and the exit of the capillary (compare also figure 1). The secondary charge patches are formed during the dynamic period of the ion guiding process as can be seen from the ion trajectories in the panels above. The entrance charge patch reveals the migration of the charges along the wall perpendicular to the capillary axis. A significant amount of charges are visible in the upper half of the capillary, which cannot directly be reached by the incident ions.

![Figure 5](image.png)

**Figure 5.** Trajectories of 3-keV Ne\(^{7+}\) ions transmitted through a capillary of 200 nm diameter and 10 \(\mu\)m length. The capillary tilt angle is 5\(^\circ\). Each panel shows 20 trajectories evaluated after the charge \(Q_{in}\) was inserted into the capillary. The lowest two panels show the charge distribution and the potential created after the maximum charge insertion of \(Q_{in} = 6\) fC. The 3 potential curves correspond to equidistant positions on the y axis directed upwards.

From the simulations of the ion trajectories we could interpret several features of the ion guiding. The oscillation of the mean emission angle is faster for smaller tilt angles. The charge deposition length increases for decreasing tilt angle so that less charge is needed to achieve the ion deflection to the capillary exit. Moreover, the oscillation frequency decreases with the capillary diameter in agreement with the experimental observation (figure 3). The large differences between PET and PC in the charge insertions needed to accomplish the oscillations are not fully understood. The model calculations suggest that more charge is needed for a polymer of higher conductivity, i.e., for the PC polymer.
The main features of the PC capillaries is the blocking of the ion intensity. The observed ion blocking appears to be inconsistent with the above provisional conclusion that PC has a higher conductivity. However, from figure 5 we note that the potential in a single capillary is relatively low so that it cannot be responsible for the ion blocking. It is likely that the charge in neighboring capillaries enhance the repelling center potential [13]. Moreover, for non-zero tilt angles the present calculations provide evidence that blocking is caused by an ion misalignment at less loaded charge patches so that the ions start to miss the exit. Similar effects for ion blocking by overloaded charge patches have been observed in previous simulations [9].

In summary, novel aspects of ion guiding were observed from the simulations. The oscillations of the ion emission angle are conclusively understood in terms of forming transient charge patches governed by a non-linear discharge law. Remarkably, the entrance potential focus the ion beam which is likely be responsible for the large amount of ion transmission. The migration of the charges along the wall perpendicular to the capillary axis is an important phenomenon to understand the weakening of the deflection field at the charge patches. However, we expect that future effort is needed to gain more information about the blocking of the ion guiding.

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