Transmission of electrons through Al$_2$O$_3$ nanocapillaries

A R Milosavljević$^{1,3}$, J J Jureta$^1$, Gy Viktor$^{1,4}$, Z D Pešić$^{1,4}$, M Mátéfi-Tempfli, S Mátéfi-Tempfli$^2$ and B P Marinković$^1$

$^1$Laboratory for Atomic Collision Processes, Institute of Physics, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia
$^2$Facultés Universitaires Notre-Dame de la Paix, Department of Physics, Rue de Bruxelles 61, B-5000 Namur, Belgium

E-mail: vraz@ipb.ac.rs

Abstract. We investigate transmission of low-energy electrons (250 eV) through insulating Al$_2$O$_3$ nanocapillaries (270 nm diameter and 15 µm length). Kinetic energy distribution of electrons transmitted through the nanocapillaries in the straightforward direction, time dependence of the transmission rate both in the straightforward direction and for tilted capillaries and angular distributions of electrons transmitted at the incident energy are presented and discussed.

1. Introduction
A great interest is devoted in recent years to studies of guiding of charged particles by nano or micro sized insulating capillaries. Particularly, the guiding of slow (3 keV) positive highly charged ions (HCI) Ne$^{7+}$ by insulating polyethylene teraphthalate (PET) nanocapillaries (100 nm diameter and 10 µm length) was first demonstrated in 2002 [1] and have been attracting a considerable attention since then. Experimental studies were performed for capillaries made in PET, polycarbonate (PC), SiO$_2$ and Al$_2$O$_3$, as well as single-glass capillaries (see e.g. [2-7] and references therein). In addition, theoretical studies gave detailed information about the guiding mechanism [8].

The process of HCI guiding is intuitively clear and has been extensively measured and described. Briefly, the highly charged particles entering the capillary deposit the charge on the insulating wall, thus forming a Coulomb mirror that deflects further stream of particles and guides them towards the exit of the capillary. It is important to point out that the Coulomb interaction is dominant in this scenario and guided particles remain “far” from the surface. Therefore, the dynamical guiding process depends on the characteristics of a used insulating surface (e.g. discharging time constants) and incident HCI current, which will then define time and angular transmission dependence. This mechanism has been well described until now analytically (see [6,7] and references therein) and also confirmed in simulations based on a detailed theoretical treatment by developing a classical trajectory transport theory that relates the microscopic charge-up with macroscopic material properties [8].

On the other hand, the first experimental investigation of electron guiding by insulating nanocapillaries, has been reported more recently [9-11]. Except possible new applications considering manipulation of electrons on the nanoscale, such as electron-controlled surface modification or

$^3$ To whom any correspondence should be addressed.
$^4$ Present address: Diamond Light Source Ltd, UK.
electron-induced processes in biomaterial, the electron guiding could be of fundamental interest. For example, the interaction of the projectile with the inner walls, the insulator charge-up and discharge processes are expected to be different, there is a secondary electron emission which may be strongly dependent on the electron energy, the ratio between the energy and the speed of a projectile is different, etc. Most recently, the investigation on electron transmission through a single glass capillary has been also reported [12-14].

The first reported results on electrons transmitted without an energy loss showed similarities with ion guiding [9,10]. The experimental results with Al₂O₃ [9] showed the existence of the guiding effect and, as found for highly charged ions, the shift of the angular distribution of transmitted electrons has been measured up to 12°. The same effect has been also seen for PET capillaries [10], at somewhat higher energies. Also, the guiding efficiency was increasing with decreasing electron incident energy, again as expected for ions. Nevertheless, there were also some new findings in electron transmission. The transmission efficiency appeared to be significantly lower than observed for highly charged ions and, moreover, the intensity of transmitted electrons significantly decreased with decreasing impact energy. Furthermore, it was found that for discharged capillaries, the measurement of the time dependence of the intensity of transmitted electrons showed a decrease, while there was no characteristic charging time needed to start HCI guiding at large tilt angles (although it was difficult to be sure since the higher used electron current could mask this effect) [9]. Finally, the transmitted electrons appeared to have very wide energy distribution, showing a significant energy loss (thus close interaction with the capillary surface). Therefore, the experiments using electrons as projectiles suggested a more complex nature of low-energy electron transport through insulating nanocapillaries than proposed for positive ions. This is also supported by the recent theoretical study [15] on electron transmission by PET capillaries, while similar joint experimental/theoretical work on electron transmission through Al₂O₃ has been reported the most recently, as well [16].

In the present paper, we report results of the experimental study on 250 eV incident electrons transmission through Al₂O₃ capillaries of 270 nm diameter and 15 μm length. Except the energy distribution of transmitted electrons, we also performed various measurements of both angular and time dependence of transmitted electron intensity for a specific energy of outgoing electrons. The present results are useful for the investigation of electron transmission through insulating capillaries and supplement our previously published data on angular distributions of elastically transmitted electrons in the energy range from 100-350 eV, dependence of transmission intensity on the incident electron energy and energy spectra for the incident energy of 100 eV [9,11].

2. Experimental set-up and capillary preparation

The experimental setup for investigation of electron transmission through insulating nanocapillary array has been described already in detail recently [9,11]. Briefly, the measurements were performed using the modified cross-beam experimental setup [17], which includes an electron gun and a double cylindrical mirror energy analyzer. This system allows measurements of transmitted current at incident electron energies from about 100 eV to 350 eV, variation of both tilt and observation angles and an energy analysis of transmitted electrons. An electron gun produces an electron beam with the energy spread of about 0.5 eV, and with a diameter and an angular divergence estimated to be approximately 1 mm and 1°, respectively. The used incident electron beam current sent to the entrance of the nanocapillary array was typically 10±1 nA. The base pressure in the experimental chamber was about 3×10⁻⁷ mbar. A sample nanocapillary array was mounted on a target holder, allowing a change of the orientation of the capillary axis with respect to the electron beam direction. The transmitted electrons, after being selected by energy are detected by a single-channel electron multiplier working in a single-counting mode.

The energy spectra of outgoing electrons were measured in the constant pass-energy mode of the energy analyzer by adjusting the retarding potential of the entrance electrode, with the overall resolution of about 1.0-1.5 eV (full width at half-maximum – FWHM). The spectra are corrected for
the transmission function which has been estimated by electron trace simulations performed in SIMION program [18].

A well ordered hexagonally close-packed Al2O3 nanochannels array (see [11,19] for more details) was produced using the self-ordering phenomenon during a two-step anodization process of a high purity (99.999%) aluminium foil. To prevent the charge-up of the target surface and its influence to the electron beam, the niobium layers of 20 nm thickness were deposited by dc-sputtering on both sides of the final membrane. The diameter of the used capillaries is about 270 nm and the inter-capillary distance about 450 nm. The length of the pores is about 15 μm, thus the aspect ratio is approximately 55. The calculated geometrical transparency is 28.5%. It should be noted that the electrochemical oxidation gives a nanocrystalline to amorphous structure with the form of Al2O3 · xH2O, therefore the composition of the capillaries cannot be exactly defined. This is also the case with the composition of the nanochannel walls, where outer parts (channel side, where the electron interactions are probably happening) are mainly hydrated alumina (Al2O3 · xH2O) but the physical properties of the alumina can be influenced by the implantation of anions from the electrolyte used for the anodization (the capillaries sample was prepared by using orthophosphoric acid solution) and possible deposited impurities. The band gap values for the hydrated and anhydrous oxides of aluminum were reported to be about 3 eV and 6.5 eV, respectively [20]. Finally, it should be noted that an angular distributions for the capillary directions (FWHM) of the present capillary array sample could be up to about 2.5°, according to recent experimental measurement by using a well collimated ions beams [21].

3. Results

3.1. Energy distribution of electrons escaping capillaries

A typical measured energy spectrum of electrons escaping the Al2O3 nanocapillary sample, for the incident energy of 250 eV and tilt (incident direction with respect to capillary axes) and observation (detection direction with respect to capillary axes) angles, respectively, \( \psi \approx \theta \approx 0^\circ \) is shown in Figure 1a. The measurement clearly shows a broad energy distribution of outgoing electrons, besides a sharp intensive peak at the incident energy (250 eV) corresponding to electrons transmitted without an energy loss. With the obtained experimental sensitivity, we did not observe any superelastic effect that would result in an energy gain of traveling electrons.

A broad energy spectrum of outgoing electrons has been also reported for PET capillaries [10], as well as for the same Al2O3 sample but with 100 eV incident electron energy [11]. We should also note that with increasing the tilt angle (\( \psi \)), the low-energy (inelastic) fraction of the spectrum becomes even more prominent [16]. These lower energy electrons are most probably due to an intensive energy loss within the capillaries, as well as secondary electron emission.

The spectrum presented in Figure 1a has been obtained for the grounded sample (note that there are metallic Nb layers on both sides of the capillary foil). It is interesting, however, to investigate the intensity of the signal from electrons escaping the capillaries with certain selected energy as a function of a positive potential of the foil with reference to the ground. When only a single incident electron energy is selected from the spectrum, the signal strongly increases with increasing the sample potential (Figure 1c). Since the higher potential of the sample foil induce additional electron acceleration, thus actually corresponds to higher incident electron energy at the capillary entrance, the presented dependence generally confirms previously reported finding about an increase of transmission with increasing the incident electron energy [9,11] (although one should mind possible effects of beam focusing). On the contrary, the intensity of electrons escaping capillaries at low energies decreases with increasing the sample potential (Figure 1b). It should be pointed out that presented results suggest a possibility of tuning the electron intensity coming from different parts of the spectrum in Figure 1a, only by tuning the potential of the capillary sample.
Figure 1. (a) Energy spectrum of electrons escaping alumina capillaries (270 nm diameter and 15 µm length, grounded sample) for projectile kinetic energy of $E_0 = 250$ eV and angles of incidence (tilt) and observation of about $0^\circ$. (b, c) Measured signal intensity of electrons escaping the capillaries with the energy of 31 eV (b) and 250 eV (c) as a function of the potential of the sample capillary foil with reference to ground.

The present measurements also show a broad energy distribution of outgoing electrons, which indicates an existence of significant electron energy loss and secondary electron emission within the capillaries thus intensive close electron-surface interaction. Therefore, a full description of electron transmission through insulating capillaries has to take into account interaction processes at and below the capillary surface (see [16] for more detailed discussion).

3.2. Time dependence of elastically transmitted electron current

Already in the first report on experimental investigation of electron transmission through insulating Al$_2$O$_3$ nanocapillaries [9], it was shown that for discharged capillaries, the transmission rate strongly decreases with time, for the straightforward beam/capillary geometry. Our further measurements have also confirmed this finding. Interestingly, a similar decrease (i.e. blocking) of transmission has been the most recently also observed for 3 keV Ne$^{7+}$ ions guiding by nanocapillaries made in PC [7], although this effect has never been observed for HCl guiding by other materials. The important results for electrons, regarding the time evolution of transmission, are the following: 1) the transmission sets-in practically immediately, i.e. no characteristic charging time, normally needed for HCl to start
deflection thus transmission at larger tilt angles, could be measured for electrons; 2) for discharged capillaries and zero tilt and observation angles (direction of the incident beam along the capillary axis), the transmission rate decreases strongly with time until some almost equilibrium conditions; 3) at larger tilt angles, the transmission rate appears to be practically constant in time. Considering the points (1) and (3), it should be noted that there is an experimental uncertainty corresponding to about 50 nC of deposited charge. The accuracy is defined by the experimental detection limit, according to the lowest measurable incident current (a few nA) and an inevitable time gap before start of acquisition (a few 10 s). Still, the present experimental results on the time dependence of the electron transmission through Al$_2$O$_3$ nanocapillaries appear to agree with the theoretical predictions obtained on the basis of a microscopic model for the electron transport within the capillary including also close interactions with the capillary wall [16].

Figure 2 shows examples of measured time dependence of the elastically transmitted electron current for the incident energy of 250 eV and the present capillary samples. Clearly, the transmitted intensity at the zero tilt angle strongly decreases with time (Figure 2a). Note that measured angular distributions (Figure 2b) also show decrease in time, preserving the FWHM of the distribution, thus confirming that the drop of intensity measured at the maximum of an angular distribution is not due to the peak broadening. Finally, note that a similar measurement of angular distributions at larger tilt angle of about 7° suggests practically constant intensity of the transmitted electron current in time (Figure 2c). It is expected that a large fraction of the measured transmitted current at about 0° (Figure 2b) corresponds to the direct electron transmission (without electron-wall scattering), while at the tilt angle of 7° (Figure 2c) the transmission is governed by either elastic electron-wall scattering or Coulomb deflection. The present measurements do not allow an accurate determination of the transmission rate; roughly, a typical proportion of electrons transmitted through the capillary array can be estimated to about $10^{-5}$. It should be also noted that measurements show a linear increase of the transmitted electron current with the increase of the incident electron flux entering the capillaries, without saturation effects in the incident current range of about 1-30 nA.

Figure 2. (a) Time dependence of the intensity of elastically transmitted electrons through the Al$_2$O$_3$ nanocapillaries (270 nm diameter and 15 μm length) for projectile kinetic energy of $E_0 = 250$ eV and angles of incidence (tilt, $\psi$) and observation ($\theta$) of about 0°. Note that acquisition starts 10-20 s after the electron beam was turned on. The experimental points are fitted by a second-order exponential decay function, with time constants of c.a. $\tau_1 = 0.2$ min and $\tau_1 = 1.3$ min. (b,c) Time dependence of angular distributions of electrons elastically transmitted through the nanocapillaries for tilt angles of about 0° (b) and 7° (c). The labels “Time” indicate the time sequence of measured experimental points (each point corresponds to the acquisition time of 5 s, with the gap of the order of 10 s between measurements needed to adjust the observation angle).
3.3. Angular distributions of electrons transmitted at the incident energy

When only electrons transmitted at incident energy are considered, the measured angular distributions are similar as seen in HCl guiding experiments. An example for the present capillary sample and the incident energy of 250 eV is given in Figure 3a. Clearly, the centroid of an angular distribution, measured over a range of the observation angle, shifts accordingly with changing the tilt angle. The guiding (i.e. measurable signal) is observed up to the tilt angle of about 11°, which is much above a geometrically allowed transmission for the present aspect ratio (about 55) convoluted with both the incident beam and capillaries angular divergence (see Section 2). The dependence of the intensity at the maximum of a distribution on the tilt angle can be fitted by a Gaussian formula (see Figure 3b) [6,9]. The latter fitting gives the so-called guiding angle (angle for which the transmission drops to 1/e fraction of its value at zero tilt angle) of about 3°. It should be noted, however, that the dependence of the maximum intensity on the tilt angle is not strictly Gaussian, which has been already discussed for the case of electron transmission through a single glass capillary [12]. Finally, it is also interesting that the FWHM of the angular distributions were found to increase practically linearly with increasing the tilt angle (Figure 3c). Similar behaviour was reported for HCl, as well (see e.g. [22]).

![Figure 3](image_url)

Figure 3. (a) Angular distributions of electrons transmitted through the Al₂O₃ nanocapillaries (270 nm diameter and 15 µm length) for different tilt angles and for projectile kinetic energy of $E_0 = 250$ eV. (b) Relative transmission (at the maximum of an angular distribution) as a function of the tilt angle. (c) Full width at half maximum (FWHM) of the angular distributions as a function of the tilt angle.

4. Conclusions

We have presented an experimental study on transmission of low-energy electrons (250 eV) through insulating alumina capillaries of 270 nm in diameter and 15 µm length. The energy distribution of electrons escaping the capillary sample, as well as the time dependence of the transmission rate are shown, which confirm a complex nature of electrons transmission through insulating nanocapillaries in comparison with the case of HCl. Interestingly, when only transmission of electrons at the incident energy is considered, the measured angular distributions show similar behaviour as for HCl.

Acknowledgment

The work was supported by the Ministry of Education and Science of Republic of Serbia (Project No. 171020). We are very grateful to Prof. N. Stolterfoht from Berlin for useful discussion.

References

[1] Stolterfoht N et al 2002 Phys. Rev. Lett. 88 133201.
[2] Skog P et al 2008 Phys. Rev. Lett. 101 223202.
[3] Kowarik G et al 2009 Nucl. Instrum. and Meth. B 267 2277.
[4] Ikeda T et al 2006 Appl. Phys. Lett. 89 163502.
[5] Nebiki T et al 2003 J. Vac. Sci. Technol. A 21 1671.
[6] Stolterfoht N et al 2010 Phys. Rev. A 82 052902.
[7] Stolterfoht N et al 2011 Phys. Rev. A 83 062901.
[8] Schiessl K et al 2007 Nucl. Instrum. Methods B 258 150 (and references therein).
[9] Milosavljević A R et al 2007 Phys. Rev. A 75 030901(R).
[10] Das S et al 2007 Phys. Rev. A 76 042716.
[11] Milosavljević A R et al 2009 Europhysics Letters 86 23001.
[12] Dassanayake et al 2010 Phys. Rev. A 81 020701(R).
[13] Dassanayake et al 2011 Phys. Rev. A 83 012707.
[14] Wang et al 2011 Phys. Scr. T144 014023
[15] Schiessl K et al 2009 Physical Review Letters 102 163201.
[16] Milosavljević A R, Schiessl K, Lemell C, Tokési K, Mátéfi-Tempfli M, Mátéfi-Tempfli S, Marinković B P, Burgdörfer J (2012) Nucl. Instr. Meth. B 279, 190.
[17] Milosavljević A R et al 2006 J. Phys. B: At. Mol. Phys. 39 609.
[18] Dahl D A 1995 SIMION 3D VERSION 6.0, User’s Manual.
[19] Mátéfi-Tempfli S et al 2006 Nanotechnology 17 3915.
[20] Özkana 惕 et al 2012 J Phys Chem C 116 1805.
[21] Juhász Z et al 2009 Nucl. Instrum. Methods B 267 321.
[22] Stolterfoht N et al 2008 Phys. Rev. A 77 032905.