Angular distribution of ions transmitted by an anodic nanocapillary array

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Abstract. The transmission of highly collimated multicharged ions through alumina nanocapillary arrays was studied using 200 MeV and 10- to 20-keV/q ion beams. The aligned nanopores each have a diameter and length of 100 nm and 60 μm, respectively. Emergent charge-state-selected angular distributions were measured at low energy. The distributions consist of sharp two-dimensional peaks that sit on a continuum distribution. Analysis of the results from target tilting experiments indicate that the observed structure can be explained simply by multiple collisions of the projectile with nanopore walls. We discuss these results and other effects produced by applying a fine wire mesh and Au thin films to the nanocapillary array.

1. Introduction

By studying multiply charged ions transmitted through aligned nanopores, we can investigate fundamental atomic-collision processes such as charge exchange, angular scattering, and energy loss phenomena in a mesoscopic ultra-grazing ion-surface setting under a wide variety of conditions. This knowledge may help to characterize the inside of nanopores and lead to atomic physics–based diagnostics or future applications for the rapidly expanding field of nanotechnology.

In the past, the chemical and physical properties of nanoporous materials were studied using a variety of techniques [1-2]. The transmission of slow, multiply charged ions (MCIs) through nanocapillary targets is the most recent tool employed to probe the interior of nanopores [3-7]. Yamazaki et al. [3] investigated short capillaries (1-10 μm) in an Al2O3 substrate. This work was followed by other experimental [4] and theoretical [5] investigations of capillaries in thin metallic foils. Most recently, numerous systematic studies of “guided” ion transmission through low porosity (1-10%), insulating, carbonaceous capillary targets were performed by Stolterfoht and co-workers [6-7]. Their capillaries, produced by etching ion tracks in thin polyethylene terephthalate (PET) or mylar films, each had a diameter and length of 100 nm and 10 μm, respectively.

Our studies were undertaken to investigate the characteristics of anodic nanocapillary arrays, which have some physical properties different from those of PET or mylar films. Perhaps, due to these differences, our high-resolution angular scattering studies using relatively long nanopores indicate that anodic and carbonaceous targets [6-7] exhibit some different behaviors.
2. Experiment

The commercial Al₂O₃ nanocapillary array [8] is rigid and self-supporting, and has a dense distribution of nanopores (> 3x10⁹ pores/cm²) arranged in a honeycomb structure (porosity ~ 40%). The pore diameter, \(D\), and average length, \(L\), are 100 nm and 60 μm, respectively (aspect ratio, \(D/L = 1/600\)), distributed over a disk diameter of 13 mm. Application of techniques such as scanning electron microscopy, gas absorption, deuterium-based nuclear magnetic resonance and small-angle neutron scattering indicated that the pores are relatively smooth and straight [1-2]. To minimize electrical charging of the insulator target, entering low-energy ions passed through either a high-transmission (>80%) grounded grid (~100 lines/cm Mo) mounted on the entrance side, or thin Au films deposited on either the entrance side or both sides of the target array.

Incident 5- to 20-keV/q multicharged Ar and Ne ions (e.g., Ne⁺, Ne³⁺, and Ne⁷⁺) transmitted by the capillary array were then studied. An ion beam produced by the ORNL CAPRICE ECR ion source, selected by magnetic analysis, was highly collimated (\(\approx 0.02°\) measured beam divergence) before it reached the array mounted in a precision goniometer (beam current < 10 nA). Low-energy electrons could flood the upstream side of the target. Emergent ions were deflected in the vertical direction electrostatically so that final charge-state-selected angular distributions could be separated from the in-line emerging neutrals. Resultant two-dimensional angular distributions were measured using a two-dimensional position-sensitive detector (TDPSD), which could also be rotated horizontally.

3. Results

Initial investigations of ion transmission and energy loss through the porous Al₂O₃ target were performed using a 200-MeV Ti⁺¹² ion beam to assess whether the nanopores are sufficiently co-aligned to justify further investigations [9]. By measuring the transmitted intensity of ions having relatively low energy loss vs beam-target alignment in goniometer tilting experiments, we found that the 2D dispersion of nanopore longitudinal directions is about \(1.6°\) full width at half maximum (FWHM). This degree of nanopore misalignment was considered sufficiently low to warrant meaningful studies at much lower ion energy.

Angular distributions emerging from the array in different charge states were studied using a variety of low-energy ion beams. The incident beam (typically \(I < 3\) nA) illuminated at least \(2 \times 10⁶\) pores, for an incident beam diameter of 0.5 mm. For these conditions, less than one ion is inside a pore at any time (i.e., about \(0.3/q\) ions/µs/pore, where \(q\) denotes the incident charge state). As in the case of the PET film studies [6-7], the principal transmitted q-state is the incident q-state in all cases. Yields in lower q-states and neutrals formed by electron capture are typically below 3% of the entrance q-state yield. No evidence of significant energy loss is observed for the transmitted ions. Unlike PET film studies, the transmitted fraction of incident beam, \(\approx 2 \times 10⁸\), is many orders of magnitude smaller than the array’s surface porosity when wire mesh is mounted on the target.

A weak transient effect is observed initially when beam first impacts the target and after the beam-target alignment is changed [9]. After the target orientation is changed, for example in a 0.2° 1D-goniometer rotation, the transmitted ion yield immediately drops by about a factor of two and then slowly recovers with a time constant of about \(\tau = 170\) sec for a 9.5 nA incident beam current according to the relationship \(I(t)/I₀ = [1 - \exp(-t/\tau)]\), where \(I₀\) is the incident beam current measured on the target. The recovery time constant, \(\tau\), is found to be inversely proportional to \(I₀\) for beams in the 1-20 nA range. The transient response is essentially identical for the same conditions for targets prepared with wire mesh and deposited Au films.

Observed angular distributions consist of two-dimensional peaks sitting on a continuum distribution as shown in figure 1; the angular width of the narrow peaks corresponds to the nanopore aspect ratio, \(D/L\). The structure is most distinct at the highest incident projectile energy and stable in time (i.e., hours). The angular distribution and sharp peaks can be steered in the longitudinal direction of the pores within about ±0.5° without a significant loss of transmitted intensity by rotating the sample with respect to the incident beam. When the target is tilted, peaks in the angular distribution shift by \(2\mathcal{\theta}\) where \(\mathcal{\theta}\) is the tilt angle. The intense peak shown in figure 1 corresponds to incident ions.
that have been steered 0.2 ° in the X direction from the incident beam direction. Thus the transmitted ions appear to have undergone specular reflections with nanopore walls.

![Figure 1](image)

**Figure 1.** Q-state selected angular distribution for incident 140-keV Ne\(^{7+}\) ions (q' = 7+ out) transmitted by the nanocapillary array. The nanopores are tilted 0.1° with respect to the beam direction (along the X axis) to accentuate the observed structure.

Observed structure in angular distributions cannot be the consequence of wave-mechanical effects because the peak location is independent of projectile momentum. The structure is always observed for nanocapillary targets having (1) wire mesh mounted on the upstream side, (2) a thin Au film (7-15 nm) deposited on the upstream side, and (3) thin Au films (7 nm) deposited on both sides of the array. Analysis of the peak movement when the target is tilted in small steps (e.g., by 0.1° and 0.2°) has allowed the identification of single, double and triple collisions on nanopore walls and regions where ion transmission is mechanically blocked by the pore geometry [9]. Consequently, we conclude that the root cause of structure in the 2D angular distribution, which is difficult to eliminate during beam-alignment experiments, is likely due to the inherent misalignment of the nanopore longitudinal directions (1.6° FWHM) within the array. Bent nanopores could produce similar effects, but bends were not commonly found in previous studies of anodic arrays using other diagnostics [1-2].

Modified nanocapillary targets (e.g., using deposited films) affected the transmitted ion fraction significantly but not the angular distributions. Targets with wire mesh or thin Au films (7 or 15 nm thickness) deposited on the beam entrance side transmit ions without applying low-energy electrons to the film. In contrast, targets with 7-nm films deposited on entrance and exit surfaces (i.e., a Au film nanocapillary sandwich), transmit ions only when electrons impact the incident side of the array; the optimum transmission occurs when the incident ion beam current is approximately neutralized. For the sandwich, we find that transmitted ions can be gated by applying a 10-µs pulsed voltage (~10 V) to the upstream thin film (which causes electrons to be attracted to the front surface), but measurements indicate that the time correlation of transmitted pulsed ions and electrons appear as random coincidences on a µs time scale. Studies with coated targets also show that the Au-film sandwich transmits 10 to 20 times more ions than the mesh-target arrangement. Thus the nanocapillary targets
can be used as variable ion beam attenuators in the $10^{-7}$ to $10^{-8}$ regime for projectile energies in the low- to intermediate-energy range when thin Au films are applied.

4. Summary

All data suggest that the structure in the exiting ion angular distributions arises when ions bounce at ultra-low grazing angles in very large impact parameter Coulomb collisions with electrically charged nanopore walls. Some characteristics of our anodic array contrast sharply with those obtained in short (10 μm) PET film target studies using much slower incident 3-keV Ne$^{7+}$ ions, where the high-transmission “ion guidance” mechanism was identified and studied [6-7]. For example, the PET film studies found a large transmitted fraction (0.5 vs $< 2 \times 10^{-7}$ here), broad unstructured angular distributions (vs highly structured distributions here), and a strong observed transient effect (vs. a weak effect here). In addition, the PET angular distribution centroid moved differently than in present experiments when the target is tilted ($\theta$ vs 2$\theta$ here, where $\theta$ is the tilt angle). Further explanation of the present results will have to await new theoretical calculations applied to ion transmission in long Al$_2$O$_3$ pores. Thus far, contrasting theoretical approaches have been applied only in the study of the 10-μm-thick PET (insulator) films by Stolterfoht et al. [6-7] and by Burgdörfer and co-workers using a general method [10].

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