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Electro-responsive asymmetric nanopores in polyimide with stable ion-current signal

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ABSTRACT For the preparation of a single asymmetrically shaped nanopore in a polyimide membrane, Kapton foils were irradiated with single heavy ions and subsequently etched from one side in sodium hypochlorite (NaOCl). The other side of the membrane was protected from etching by a stopping medium containing a reducing agent for hypochlorite ions (OCl^-). The resulting conical nanopore rectified ion current and exhibited a stable ion-current flow.

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1 Introduction

Track etching is a widely used method for producing membranes with pores having diameters from tens of nanometers to the micrometer range, offering high aspect ratio and homogeneity of the pores [1]. More recently, an increased interest in the production of narrower pores with openings down to a few nanometers has developed [2]. In particular, novel biotechnological filtration and sensing processes require extremely small pores with diameters similar to those of biochannels [2, 3]. Achieving this goal is much easier with conical pore geometry than with the commonly used cylindrical shape. Moreover, such asymmetric pores allow higher fluxes of transported media because their flow and electrical resistance are defined by the narrow tip aperture. To meet these needs, the technique of producing conical nanopores in polyethylene terephthalate (PET) has recently been developed [4]. However, the application of membranes with pores having diameters in the nanometer range is highly limited due to their unfavorable transport properties; namely the fact that ion currents through the PET nanopores are not stable, but fluctuate strongly in time. The amplitude of such fluctuations may even reach 100% of the signal [5–8], and pores of diameter approximately 2 nm tend to close completely. These properties result from the chemical structure of the polymer as well as from the radiation damage and the etching process. Polymeric chains are broken and subsequently modified chemically during etching, forming so-called "dangling ends". According to the existing concepts of polymers

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in solution, they move continuously in a more or less random fashion [9, 10]. The broken chains also seem to contribute to the formation of a gel layer, which makes the transport through the pores even less defined [11]. Another drawback of pores in PET is the very small opening angle of only several degrees, which does not provide a sufficiently large ion flow. Here, we report on the production of asymmetric nanopores in polyimide – a material known for its excellent mechanical and electrical resistance in a wide range of temperatures. Even with an opening diameter in the nanometer range, the polyimide pore produces a stable ion-current signal [12]. We also show that a single asymmetric nanopore in a polyimide foil, similar to the situation in PET, acts as an ion-current rectifier.

## 2 Experimental methods

2.1 Materials and irradiation

Stacks of six polyimide foils (12.5-µm thick, Kapton 50 HN, DuPont) were irradiated under normal incidence with single uranium ions of energy 2640 MeV at the linear accelerator UNILAC (GSI, Darmstadt) [13]. Under these conditions, the range of the ions in polyimide was larger than the thickness of the foil stack, and the energy loss of the ions was well above the threshold required for homogeneous track etching [14]. For single-ion irradiation, a metal mask with a 0.1-mm diameter aperture was placed in front of each stack. The strongly defocused ion beam was blocked promptly as soon as one ion passed through the foil stack and was registered by a particle detector behind the samples.

2.2 Chemical etching of single-ion irradiated polyimide membranes and ion-current measurements

Track etching of the polyimide foil was performed in sodium hypochlorite (NaOCl) at 50 °C [15, 16]. The selection of this temperature represented a compromise between efficient track etching and preventing NaOCl from rapid decomposition. Earlier studies on polyimide foils have shown that a strongly basic pH value of the etchant, as well as high content of active chlorine, ensure the formation of conical pores with large opening angles [15]. We therefore used a NaOCl solution of initially high pH value (12.6) with an active chlorine content of 13%. The irradiated polyimide foil was placed between two chambers of a conductivity cell and etched from one side [4, 17, 18]. The other half of the cell

was filled with 1 M potassium iodide (KI) solution as a stopping medium for the OCl$^-$ ions of the etchant. As soon as the etchant completely penetrated the foil, iodide ions reduced OCl$^-$ to Cl$^-$ ions:

$$OCl^- + 2H^+ + 2I^- \rightarrow I_2 + Cl^- + H_2O$$
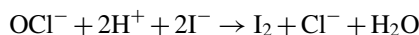
Via this reaction, the etching process stopped immediately after the breakthrough, allowing the preparation of extremely narrow pores. Due to the presence of I$_2$, the solution became yellow, indicating colorimetrically the etching breakthrough of the track. The cell was connected to a home-built electronic feedback circuit with a current/voltage converter of pA sensitivity, controlled by software written in LabView 5.0 (National Instruments). During etching, a voltage of 1 V was applied across the cell, monitoring the electric current with inert Pt electrodes. This allowed fast determination of the breakthrough moment, indicating that the etching of the membrane was completed. Moreover, when the potential on the etchant side was positive, the OCl$^-$ ions were pulled out from the pore, providing additional protection from etching to the other side of the membrane [4]. Application of the chemical and electrical stopping procedures ensured a slow increase of the opening diameter of the conical pore after the breakthrough. We typically observed a rather constant current for several minutes, which indicated that the opening diameter did not change. To obtain nanopores, the etching was interrupted shortly after the breakthrough moment by washing out the etchant with water and KI. Longer etching led to a gradual increase of the pore opening, monitored by an increase in the current.

In order to examine transport properties of the pores produced in this way, both chambers of the cell were filled with 0.1 M KCl. The pH value was adjusted with a commercial buffer (Merck Tritisol). Ion-current measurements were performed with Ag/AgCl electrodes. We determined current–voltage characteristics (I–V) and ion-current transients at constant voltage. I–V curves were recorded using voltage-ramping of frequency 0.005 Hz.

3   Results and discussion

Figure 1 presents a current-vs-time plot recorded during the etching process – the last 30 min, including the breakthrough moment, are shown. The breakthrough is characterized by a sudden increase in the current from zero to a value of typically several pA when the two chambers of the cell become connected. Using the stopping medium and a positive voltage on the etchant side indeed ensured that after the breakthrough the current did not increase significantly for approximately 8 minutes (Fig. 1a). Right after the breakthrough, the current typically exhibits some instability, most probably due to the redox reaction occurring at the tip of the conical pore, which influences the current recorded by the electrode. In the course of time, the concentration of the I$^-$ ions close to the membrane diminishes as the diffusion delivering them from the bulk does not replace the ions used in the reaction with OCl$^-$ quickly enough. The chemical stopping then loses its effectiveness, indicated by the increase in the current and the pore diameter (Fig. 1b).
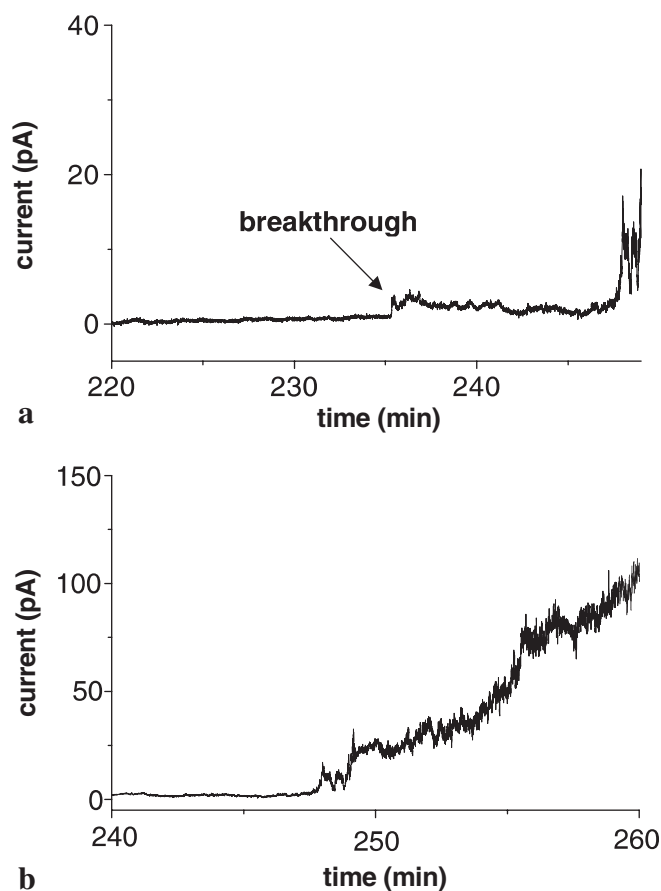

FIGURE 1   Ion current recorded during etching of a single-ion irradiated Kapton foil, performed in NaOCl, at 50 °C. **a** The last 30 min of etching are shown. The moment of breakthrough is indicated by an increase in the current. **b** The etching process was extended to observe the current increase during pore growth

The geometry of the resulting pore is determined by two etching processes occurring simultaneously: (i) preferential dissolution of the track region along the ion trajectory with the rate v_t, and (ii) general chemical attack of the material by the so-called bulk etch rate v_b. The half-opening angle β of the etched pore is given by the formula $\beta = \arcsin(v_b/v_t)$ [1, 15].

The bulk etch rate was determined by thickness measurements of a Kapton foil subjected to 3 h of symmetric etching at 50 °C. The foil thickness (measured at 30-min intervals) decreased linearly with time, giving the value $v_b = 0.42 \pm 0.04\ \mu m/h$. The track etch rate was calculated from the moment of breakthrough and the foil thickness to be $v_t = 3.12 \pm 0.65\ \mu m/h$ (the large uncertainty results from rather strong fluctuations in the etching time required for reaching the breakthrough for different samples). The corresponding pore opening angle reached therefore $\beta = 8 \pm 3°$. The diameter of the large opening D was calculated by the product of the bulk etch rate and the time of etching multiplied by two. Taking into account the thickness decrease of the polymer after typically 4 h of etching, the large opening was approximately 2.4 μm in diameter. This value was confirmed by scanning-electron-microscopy studies of the polyimide sample irradiated with higher fluences (e.g. 10^6 ions/cm^2), and etched under identical conditions (see Fig. 2).

The diameter of the narrow opening d has been estimated on the basis of ion-current measurements using the standard KCl solution. Assuming an ideal conical shape, the narrow opening of the resulting pore is given by the following equation [4]:

$$d = 4LI/\pi D\kappa U ,$$

where L is length of the pore, κ stands for the specific conductivity of the electrolyte, U denotes the voltage applied across the membrane and I is the ion-current measured. The etching process described here gives the possibility of producing pores with an effective diameter d as small as 2 nm.

Figure 3 shows the I–V curves for a single asymmetric pore, measured in 0.1 M KCl at pH 7 and pH 2. Similar to PET [4], the conical Kapton pore rectifies the ion current at neutral pH. Lowering of the pH value diminishes the rectification effect, and at pH 2 the pore exhibits a linear I–V characteristic. The rectification is also electrolyte concentration dependent. It decreases with an increase in the concentration but it is still non-linear at 3 M KCl.

The inset of Fig. 3 shows a stability test of the ion current vs. time performed at 180 mV. Despite its very small value, the ion current does not fluctuate. This behavior differs significantly from that of a single conical pore in a PET membrane [4]. Moreover, a polyimide foil with a single pore stored in distilled water for several weeks does not change its ion-current properties.

An important question to discuss is why the polyimide pore is stable and differs so significantly from the pore in PET. We would like to point out that the chemical structure of the polymers, the radiation damage induced by heavy ions as well as the etching procedure collectively influence the final transport properties of the pores. In the case of PET, the broken chains are hydrolyzed during etching by NaOH, which leads to the formation of carboxylate end groups [19]. Due to the presence of the aliphatic (ethyl) part, the dangling bonds
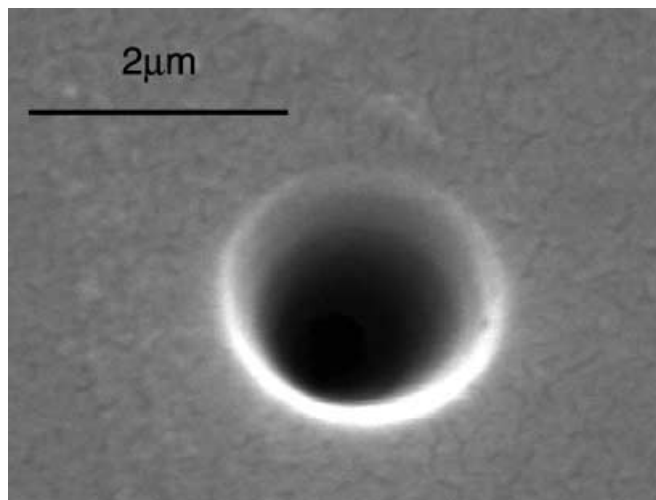

FIGURE 2   Scanning electron microscopy (SEM) image of the wide opening of a single conical pore on the etched side of a polyimide foil. The sample was irradiated with Bi ions at a fluence of 10^6 ions/cm^2 and subsequently etched at 50 °C, for 4 h. The narrow opening of the pore is below the SEM resolution
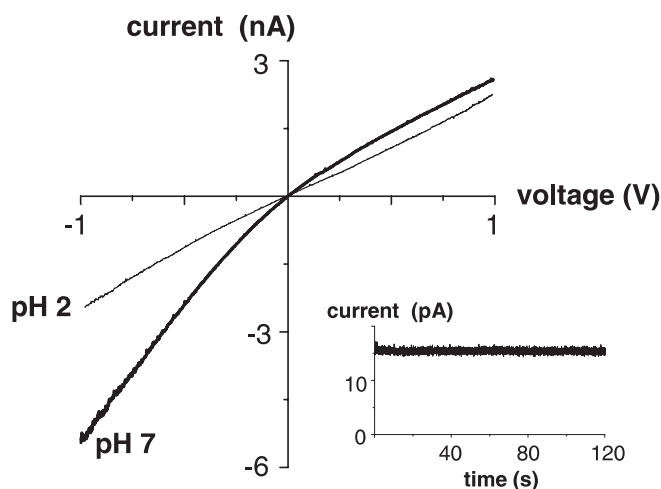

FIGURE 3   Current–voltage characteristic of a single asymmetric pore in a polyimide foil with symmetric electrolyte conditions on both sides of the membrane (0.1 M KCl) for two pH values. The *inset* shows the ion current-vs-time behavior recorded at a voltage 180 mV. The diameter of the small opening of this pore, calculated on the basis of the conductivities for positive and negative voltages, is equal to approximately 2 nm

can perform random rotational, and also partly translational, movements [9, 10]. In the pores with openings in the nanometer range, the bond movement may strongly influence the ion flow.

The chemical structure of Kapton, in contrast, is based on aromatic rings, which render a strong rigidity to the material. Similar to the situation in PET, scission of the polyimide chains and subsequent etching also lead to the formation of carboxylate groups. In this case, however, the groups are attached to the polymeric chains consisting of rigid aromatic rings, which prevent them from any significant movement. As a result, the etched surface is also expected to be smoother on the micrometer scale. We also would like to point out that the macroscopic smoothness of the membrane is basically influenced by the structure of the polymer, including the amorphous, semi-crystalline, and crystalline properties of different domains. To test this possibility, an etched Kapton foil was imaged by scanning force microscopy under water. Figure 4 shows that the surface is indeed extremely smooth, with roughness smaller than 20 nm.

We would also like to discuss the possible origin of the ion-current rectification observed for the rigid pore in a Kapton membrane. The strong pH dependence indicates that the rectification is governed by the surface charge of the pore. At pH 7, the carboxylate groups are not protonized, and the pore wall is negatively charged. Due to the conical shape of the pore, the electric potential inside the pore is more negative close to the narrow entrance than at the wide opening of the pore [20, 21]. An asymmetric potential implies that a stronger electric force is acting on the ions entering the pore at the narrow opening compared to those ions moving in the opposite direction. Superposition of the asymmetric electric field inside the pore and the external voltage leads to the asymmetry of the ion flow in both directions. The rectification effect becomes stronger for higher voltages [21]. Ion-current rectification governed by this mechanism can occur only when the pore diameter is comparable to the thickness of the Debye
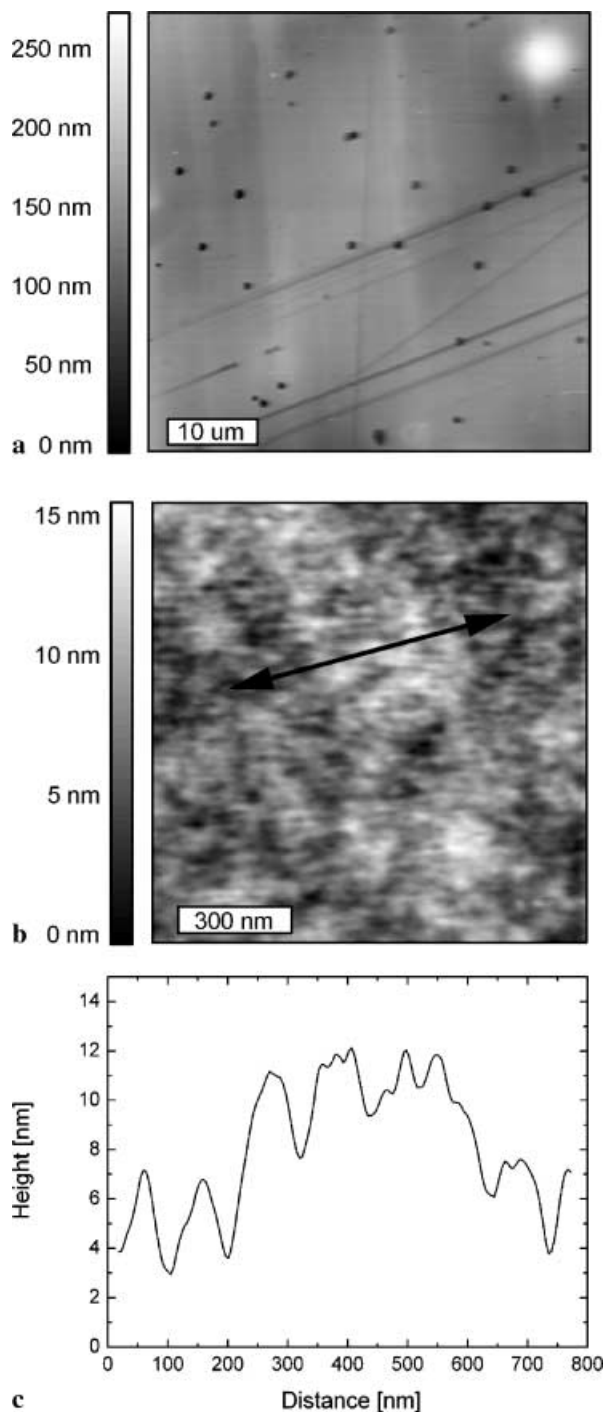
FIGURE 4 **a** Overview image of a Kapton foil in water, recorded by scanning force microscopy. The gray scale indicates the height axis. The sample was irradiated with Bi ions at a fluence of 10^6 ions/cm^2 and was etched from one side in NaOCl at 50 °C for 2 hours. The etched ion tracks are clearly visible. The long scratches are caused by the production process of the polymer. **b** High-resolution scanning force micrograph of an irradiated and etched Kapton foil imaged in contact mode under water. A part of the sample without pores is shown. **c** The topography of the line scan (see the *arrow* in **b**) indicates the overall smoothness of the etched Kapton foil within several nm

4   Conclusions

The preparation of a single asymmetric pore in a polyimide foil has been presented. One-side etching with a strongly oxidizing etchant containing OCl$^-$ was applied together with a stopping medium, which reduced the OCl$^-$ ions to Cl$^-$. The etching process was therefore stopped immediately after the breakthrough. This enabled us to obtain conical pores with extremely narrow apertures at the cone tip. According to conductivity measurements, the effective diameters can be as small as 2 nm. The rectification behavior observed for the Kapton pore was an additional indication of the nanometer size of the pore opening. In order to further examine our indirect size determination of the narrow cone aperture, direct imaging by SFM is highly desirable. However, such measurements are very difficult, because they require an extremely sharp force tip and must be performed under liquid.

We have shown that the effect of ion-current rectification strongly depends on the surface charge of the pore, which has been modified by the pH of the electrolyte. At low pH, the pore is neutral and loses its rectifying properties. Ion currents through single nanometer-sized pores in polyimide create a stable signal which, compared to nanopores produced in other polymers so far, is an exceptional feature. We assume that the smoothness and the rigidity of the etched pore, as a result of the aromatic polymer structure, play an important role. Finally, it should be noted that the narrow conical pores in the polyimide foil keep their current characteristic over several weeks.

The membrane with a single nanopore is especially interesting in the light of recent studies of translocation of bio-oligomers through an engineered asymmetric channel formed by the staphylococcus aureus α-hemolysin [3, 22, 23]. The synthetic pore presented here, producing a stable ion-current signal, could serve as a model system for those studies.

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