УДК 541.183; 539.1.074; 678.067

A NOVEL APPROACH TO PARTICLE TRACK ETCHING: SURFACTANT ENHANCED CONTROL OF PORE MORPHOLOGY

P.Yu.Apel[1], *S.N.Dmitriev*[1], *D.Root*[2], *V.A.Vutsadakis*[1]

Based on the understanding of the mechanism behind a long observed but thus far unexplained effect, a new method to control the geometry of nano- and micropores is described. Surfactant molecules added to an etching solution used for etching out ion tracks, create a steric-hindrance effect which is responsible for the formation of «bottleneck» or «cigar-like» pores. Filtration membranes thus obtained exhibit significantly improved flow rates without deterioration in the retention properties. New applications are made possible with these new pore geometries.

The investigation has been performed at the Flerov Laboratory of Nuclear Reactions, JINR.

Новый подход к травлению треков тяжелых частиц: управление формой пор при помощи поверхностно-активного вещества

П.Ю.Апель и др.

Предложен новый подход к формированию нано- и микропор, основанный на эффекте, который наблюдался неоднократно, но никогда ранее не был объяснен. Добавление поверхностно-активного вещества в раствор при травлении треков тяжелых ионов приводит к стерическому эффекту, обеспечивающему формирование «бутылкообразных» или «сигарообразных» пор. Фильтрационные мембраны, получаемые таким способом, характеризуются существенно более высокой производительностью при сохранении задерживающей способности. Модификация формы пор открывает возможности для новых практических приложений.

Работа выполнена в Лаборатории ядерных реакций им. Г.Н.Флерова ОИЯИ.

Chemical etching of particle tracks, also known as nuclear tracks or ion tracks, was first observed in 1958 [1]. Since 1962 [2, 3] particle tracks in solids have been the subject of intensive research. Over the years diverse applications of nuclear tracks have been developed, among which stand out the nuclear track membranes [4] and creation of micro- and nanostructures [5–8] of cylindrical or conical shapes repeating themselves in great numbers and with high uniformity. In a typical situation, an energetic heavy ion traverses a

[1] Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research, 141980, Dubna, Russia
[2] Science Products Division, Corning Incorporated, 45 Nagog Park, Acton, MA 01720, USA

solid leaving in its wake an ionization-damage track, which is subsequently etched away. The process of track etching and the geometry of the etched pores are mainly determined by two parameters — the etch rate of the highly damaged track core (V_T) and the etch rate of the bulk material (V_B) which, for simplicity, is assumed to etch isotropically (Fig. 1). If V_T
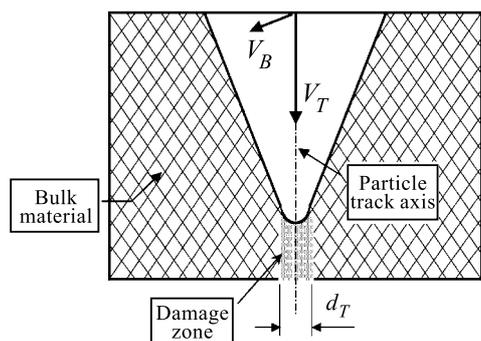

Fig. 1. Schematic model of track etching in an isotropic media. The shape of the etch pit is determined by the ratio between the etch rate along the particle trajectory, V_T, and the bulk etch rate, V_B

and V_B are of the same order of magnitude, the etch pit is a cone. The sharpness of the cone tip depends on the diameter d_T of the damaged zone around the particle track, and is typically of a nanometer scale. If $V_T \gg V_B$, the etched out pore is practically of cylindrical shape. The track core is etched out very rapidly to a cylindrical channel with diameter d_T. Further etching uniformly enlarges the channel at a rate of V_B, while maintaining its cylindrical shape.

In the present report we consider one more factor producing a dramatic effect on the evolution of the shape of the ion track pore in the process of chemical etching. When etching ion tracks, various surfactants are often added to the etching solution, with the stated intention of improving the wetting of the sample. While the influence of small molecule surfactants is restricted to a wetting function, large molecule surfactants have a much more complex effect, which is analyzed below. First, we will consider the effect of large molecule surfactants on the bulk etch rate of a solid material in an aqueous etching solution. Large molecule surfactants are composed of a hydrophobic part, normally an alkyl chain having 8–12 carbon
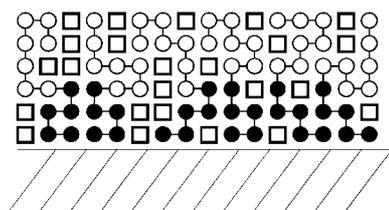

Fig. 2. A model for the adsorbed surfactant layer (9) on a hydrophobic surface. The filled (black) circles represent hydrocarbon and the open circles represent hydrophilic moieties of the surfactant chain molecules. Squares are water molecules

atoms, and a hydrophilic part, which is a polar moiety (ionic or nonionic). The surfactant molecules orient themselves with their hydrophobic part towards the surface of the bulk material and the hydrophilic part towards the aqueous solution. The surfactant layer which is formed is quasi-solid and partially protects the surface from the etching agent. However, the adsorbed layer does not consist entirely of surfactant molecules but also contains solvent (water) molecules. The structure of the adsorbed surfactant layer shown in Fig. 2 was proposed in [9]. Transport of water and ionic solutes through the barrier formed by the surfactant is probably similar to that through lipid bilayers [10]. The diffusion of H^+ and OH^- ions across such molecular layers is significantly faster than the diffusion of other ions [11]. The thickness of the adsorbed layer h is of the order of the length of a fully extended surfactant molecule. For most commonly used surfactants this quantity is 2–4 nm. The conformation of the alkyl chains in the adsorbed layer can vary depending on the nature of the solid substrate [12]. The formation of the adsorbed layer leads

to a reduction of the etch rate (V_B) of the surface of a solid that undergoes etching. The kinetics of the process in the absence and in the presence of a surfactant is illustrated by the example of a polymer treated with alkaline solutions (see the Table). The polymer-solution interface advances 2–3 times faster if there is no surfactant in the etchant. The effect of the surfactant tends to decrease at higher temperatures. Transient defects in the adsorbed layer probably arise from thermal fluctuations and promote easier diffusion of water molecules and hydroxide ions to and etch products from the polymer surface.

Table. Bulk etch rates of poly(ethylene terephthalate) in aqueous sodium hydroxide solutions with nonylphenyl deca(ethylene oxide) and in pure alkaline solutions

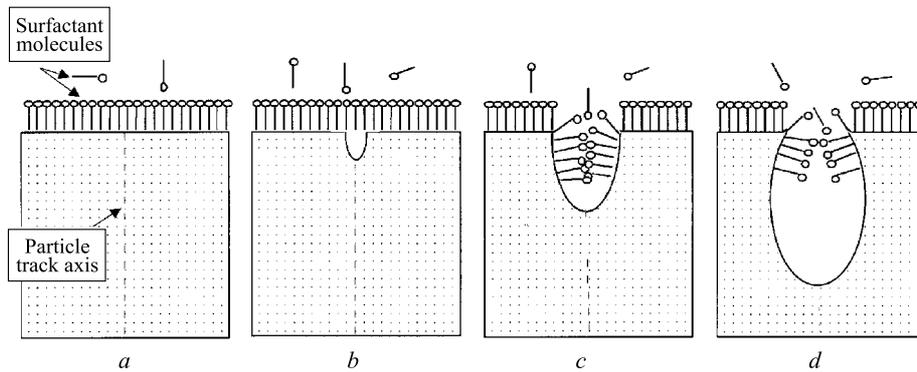| Etchant	V_B Temperature 40°	Surfactant «slowdown» ratio	V_B Temperature 80°	Surfactant «slowdown» ratio
3 M NaOH	1.3 mn/min	3.8	25 mn/min	1.8
3 M NaOH + 0.025 % surf.	0.34 mn/min		14 mn/min	
6 M NaOH	3.4 mn/min	2.1	84 mn/min	2.2
6 M NaOH + 0.025 % surf.	1.6 mn/min		38 mn/min	

Fig. 3. Evolution of a particle track in an etching solution with a surfactant. Successive phases of the changing geometry of the etched part of the track are presented as *a, b, c,* and *d*. Surfactant molecules are composed of hydrophilic «heads» and hydrophobic «tails». Etchant molecules and solvent molecules are not shown, as they are significantly smaller than the surfactant molecules

We now consider the case in which a solid material undergoing surfactant-enhanced etching contains latent (i.e., not yet etched) ion tracks. We restrict the discussion to the case of $V_T \gg V_B$, which in a surfactant-free etching solution would result in cylindrical pores. Diffusion of etchant molecules across the surfactant layer shown in Fig. 3a, initiates the formation of a small hole at the entrance of the ion track (Fig. 3b). When the hole attains a few nanometers in diameter, the surfactant molecules penetrate into the developing pore and cover its walls (Fig. 3c). Because initially $d_T \leq 2h$, further diffusion of the surfactant molecules into the growing pore is hindered. The adsorbed surfactant layer is not permeable

to large molecules. At this stage the transport of surfactant molecules into the pore can proceed only by lateral propagation on the pore internal wall surface. This process is slower than the diffusion in the bulk solution. Therefore, the volume inside the pore remains free of surfactant molecules for a certain time interval. However, the diffusion of hydroxide ions into the pore or etch products out of the pore, is not hindered due to their relatively small size. As a result, the inside diameter of what would be a cylindrical pore in the absence of surfactant molecules, grows at a higher etch rate than the pore entrance (Fig. 3d). After some time, «bottleneck» or «cigar-like» pore channels are formed. When the pore entrance diameter becomes too large for the surfactant molecules to be able to bridge the gap, the steric hindrance ceases to exist and large numbers of surfactant molecules freely diffuse into the pore and assemble on the pore walls. Starting from this moment, the etching occurs at the same (reduced) bulk rate at any point along the track axis.

This phenomenon is observed with surfactants of various types. The only requirement is that the surfactant molecules be large enough to produce the described steric-hindrance effect. Experiments have shown that anionic, cationic as well as nonionic surfactants are effective. The shape of the resulting tapering of the pore, i.e., whether concave or convex, the extend of the tapering depth and also the ratio between the small and large diameters of the tapered section, depends on the etching conditions, such as etchant and surfactant concentration and temperature, and can be varied to produce the desired result. The most significant factor is the ratio of the bulk etching rate in the absence of surfactant molecules to that in their presence (the «slowdown» ratio mentioned in the Table). However, in general, the pores are the more profoundly tapered the faster the etching of the bulk material. Vice versa, if bulk etching is very slow the bottleneck shape does not form because lateral diffusion provides transport of the surfactant molecules along the track simultaneously with the propagation of the etching front, resulting in a uniform bulk etching rate along the whole track length.

A very small amount of surfactant is enough to produce the effect. However, when the surfactant concentration is higher than the critical micellar concentration, the mechanism is more complex. The micelles may plug the pore entrance(s) providing their own steric-hindrance effect at larger pore dimensions. Experiments have shown that the effect manifests itself both in the nanometer and micrometer scales.
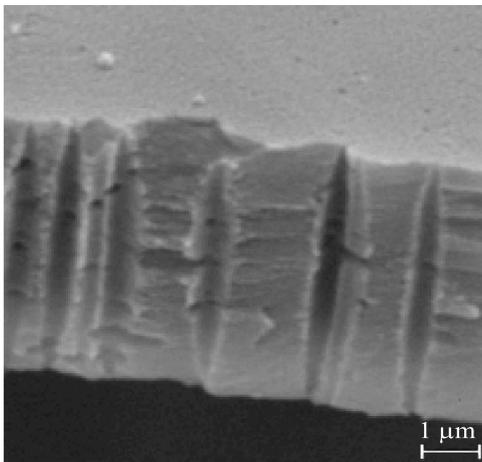

Fig. 4. SEM photo of the cross section of a PET film sample exposed to an energetic Xe ion beam and etched in a 6M NaOH solution containing a very small amount of an anionic large molecule surfactant. The film thickness is 5 μm. Surface pore density is $7 \cdot 10^7$ cm^{-2}

An example of a structure produced using surfactant-controlled etching is presented in Fig. 4. A sample of polyethylene terephthalate (PET) film was exposed to accelerated xenon ions which fully traversed the film. The film was subsequently etched in a NaOH solution with a very small amount of an anionic large molecule surfactant added, using standard conditions for the manufacturing of track mem-

branes. Since both sides of the film are subjected to the surfactant-controlled etching, the effect takes place simultaneously on each track end. The resulting etch track diameters on the film surface are ≤ 80 nm whereas the inside diameters are of about 450 nm. As a result, the volume porosity of the film is more than an order of magnitude higher than the surface porosity. A second example, illustrating the versatility of this method for geometry control, is shown in Fig. 5. Here «through» latent tracks in a PET film are partly etched in a first surfactant-free NaOH solution so that a cone of an appropriate depth and opening angle forms at each surface of the film along the ion track. Subsequent etching in a surfactant-enhanced NaOH solution, under new conditions so as to obtain $V_T \gg V_B$, results in the «bow tie» shape shown in the SEM photograph.
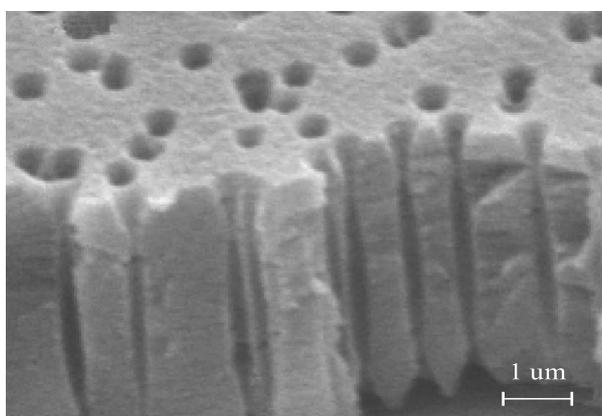

Fig. 5. SEM photo of the cross section of a PET sample exposed to an energetic Xe ion beam and partly etched in a first surfactant-free NaOH solution to obtain a small cone at each track end. Subsequent etching in a surfactant-enhanced NaOH solution, results in the «bow tie» shape shown here

While the effect was first observed during etching of latent tracks, its relative simple steric (geometric) nature easily leads to predictions of its applicability to similar situations. Thus, it was predicted that already existing pores with entrances of small enough dimensions to allow a «congestion» of surfactant molecules, would exhibit the same effect. Experiments were performed using surfactant-free etched nuclear track pores, very small in diameter and of perfectly cylindrical shape. The tracks were then etched in a surfactant-enhanced etching solution. The differential etching rates between the pore orifice and the inside of the pores resulted in the preferential enlargement of the inside pore diameter and a «cigar-like» pore shape similar to that shown in Fig. 4. Similarly, the described phenomenon is expected to appear in nonaqueous polar solvent solutions with appropriate surfactants having lyophilic and lyophobic moieties, and also in the etching of nanopores other than from particle tracks and with pore orifices other than cylindrical. Cavities connected with the surface through very small openings and subjected to the surfactant-controlled etching should behave in a similar way, irrespective of the nature or internal geometry of the cavities.

This new degree of freedom allowing the design of pore shapes, provides the most obvious benefits in membrane technology. Membranes containing an array of bottleneck nanocapillaries may serve as molecular filters with high selectivity and high permeability,

exhibiting a much higher volume porosity than surface porosity. Apart from filtration, the method can find applications in cases when porous bodies with special properties are needed. Substrates with high inner porosity can be produced and used as microcontainers for encapsulation of drugs, dyes, or other chemicals, or can be used as reaction microchambers, in which one can achieve the localization of reactants in a very small volume without their immobilization. Chromatographic or catalytic substrates could be treated in a similar fashion to enhance volume porosity.

References

1. Young D.A. — Nature, 1958, v.182, p.375.

2. Price P.B., Walker R.M. — J. Appl. Phys., 1962, v.33, p.3400.

3. Fleischer R.L., Price P.B. — Science, 1963, v.140, p.1221.

4. Fleischer R.L., Alter H.W., Furman S.C., Price P.B., Walker R.M. — Science, 1972, v.178, p.255. Also, see Flerov G.N. — Vestnik Academii Nauk, 1984, v.4, p.35 and Fischer B.E., Spohr R. — Rev. Mod. Phys., 1983, v.55, p.907.

5. Martin C.R. — Science, 1994, v.266, p.1961.

6. Blondel A., Meier J.P., Doudin B., Ansermet J.-Ph. — Appl. Phys. Lett., 1994, v.65, p.3019.

7. Schoenenberger C. et al. — J. Chem. Phys. B, 1997, v.101,p.497. In this paper the cigar-like shape of ion track pores, evidently etched with a surfactant, was erroneously explained. A number of other authors have observed the phenomenon, but have attributed it to a variety of factors not related to surfactants. See for example. Peterson D.D. — Rev. Sci. Instrum., 1970, v.41, p.1252; Guillot G., Rondelez F. — J. Appl. Phys., 1981, v.52, p.7155, and Hernandez A., Martinez-Villa F., Ibanez J.A., Arribas J.I., Tejerina A.F. — Sep. Sci. Technol., 1986, v.21, p.665.

8. Jirage K.B., Hulteen J.C., Martin C.R. — Science, 1997, v.278, p.655.

9. Kronberg B., Stenius P. — J. Coll. Interface Sci., 1984, v.102, p.410.

10. Deamer D.W., Bramhall J. — Chem. Phys. Lipids, 1986, v.40, p.167.

11. Biegel C.M., Gould J.M. — Biochemistry, 1981, v.20, p.3474.

12. Gilchrist V.A., Lu J.R., Staples E., Garrett P., Penfold J. — Langmuir, 1999, v.15, p.250.