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V. R. Oganessian, V. V. Trofimov, M. Danziger[1],
D. Hermsdorf[2], O. L. Orelovich

PROTON TRACKS AND FORMATION OF PORES IN POLY[DIETHYLENE GLYCOL BIS-(ALLYL CARBONATE)]

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[1]IST GmbH, Vor dem Gröperntor 20, 06484 Quedlinburg, Germany
[2]Institut für Kern- und Teilchenphysik, TU Dresden, Mommsenstr. 13, 01062 Dresden, Germany

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Треки протонов и образование пор
в поли[диэтиленгликоле бис-(аллилкарбонате)]

Современная дозиметрия нуждается в эффективных детекторах для регистрации легких ионов, особенно имеющих энергии до 10 МэВ/нуклон. Поэтому данное исследование посвящено развитию материалов для этой задачи. В работе проводилось облучение наиболее эффективного детектора CR-39 низкоэнергетическими протонами. С помощью чувствительного электролитического травления и электронной сканирующей микроскопии был осуществлен полный анализ от открытия до конечного образования поры. Наблюдался последовательный процесс сквозного пробоя треков. Форма поры и соответствующие параметры ее образования обеспечили моделирование процесса. Были определены скорости травления и коэффициент селективности. Отмечено влияние потерь энергии на геометрию.

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Oganessian V. R. et al. E18-2004-27
Proton Tracks and Formation of Pores
in Poly[Diethylene Glycol Bis-(Allyl Carbonate)]

Modern dosimetry needs effective detectors to register light ions, especially those having energies down to 10 MeV/a.m.u. That is why in the research in hand we pay attention to development of materials for such a task. In this work the most effective detector CR-39 irradiated with low-energy protons was applied. A full analysis from opening to final formation of a pore was made with the help of sensitive electrolytic ething and electron scanning microscopy. Successive process of track breakthroughs was observed. The shape of the pore and corresponding parameters of its formation provide simulation of the process. Etching rates and factor of selectivity were determined. The influence of energy losses on geometry was noted.

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

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INTRODUCTION

Among modern detectors for neutron dosimetry and registration of light particles the favourable and the most effective is CR-39 which is known in chemistry as poly[diethylene glycol bis-(allyl carbonate)] or PADC. For the first time, application of CR-39 for this purpose was proposed by Cartwright and Shirk (Cartwright, 1978). Its characteristics are unique in the case of low energies down to 10 MeV/a. m. u. Nuclear reactions between incident neutron and atom of media generates protons. Registration of these particles is possible through the chemical etching. There are two methods which are used in investigations: etching in alkali solutions with and without electric field. The second one means electrochemical treatment and is known for many years (Al-Najjar et al., 1979). Groups of researchers presented different results on kinetics of etching process and dependences of important parameters such as track etching rate v_T and mechanisms of pore growth (Tommasino et al., 1985; Fromm et al., 1991). One should note that analysis in these methods is based on data obtained from geometrical results and has restrictions. Up to now it is still an important task to find a universal dependence on energetic factor. Most of expressions for calculation deal with indirect value of track etching rate (Fleischer et al., 1975; Somogyi, 1980; Fuji, 1986; Oda et al., 1993) which is presented as a function of bulk etching rate v_B and radial size of pore on the surface. In contrast, a method of electrolytic etching is an effective and relatively simple tool which allows one to analyse parameters of the track during direct observation. It was succesfully used in case of swift heavy ions in polymers (Schulz et al., 1997; Oganessian et al., 2003). First of all, such a method can be useful to determine the size of the track and the moment of opening. This combined with data from post-etching microscopy makes it possible to construct a model of the pore.

1. EXPERIMENT

Because of application of the electrolytic etching, it is necessary to get through tracks in material. The principle of this method is simple. Track becomes a source of electrical conductivity beginning from its opening. Being etched from both sizes, the channel grows together with voltage on electrodes. In the case of low-energy particles a sample must be thin enough if needed to get through tracks. Such requirements are not important for chemical and electrochemical methods,

and most of the samples being used up to now by researchers are 0.5–1 mm in thickness. That is why first of all samples must be produced.

In our case it was CR-39 type TASTRAK (Track Analysis Systems Ltd., UK). Plates of thickness 500 μm were divided into squares of 50x50 mm. Then each of them was subjected to mechanical treatment with a boring lathe and precise tools. Thus, in the center of the sample an eroded area of diameter 7 mm and thickness 250 and 400 μm was made. This value depends on the type of the used tool. Finally, we have a sample with a cavity in the center on one side, the other side being smooth. Such a geometry is safe for treating the area before and after chemical action and it is guaranteed that only this area will be under etching.

Irradiation was done at the tandem accelerator in the Forschungszentrum Rossendorf (Rossendorf, Germany). Protons with energies from 5.5 to 7 MeV were directed perpendicularly to the surface of the samples. Fluence was in the range from 14 to $16{\cdot}10^4$ tracks/cm^2. Such a difference is because of the requirements of two methods of the analysis: conductometric etching and electron scanning microscopy. The first method is necessary for direct observation of pore openings (low fluence) and the second one is for post-etching analysis of geometrical characteristics (high fluence).

The set-up of electrolytic etching together with measuring circuit is the same as presented in the previous work (Oganessian et al., 2003). A highly sensitive voltmeter having a resolution of 1 μV at an internal resistance of 10 GΩ was used. Reference resistance is $R_{\rm ref} = 30$ kΩ. Direct current with the voltage on electrodes $U_0 = 2$ V was applied. Concentration of sodium hydroxide is 7.25 n and temperature is 60 °C. These conditions were chosen after test experiments. It should be noted that such a concentration corresponds to that typically used for CR-39, but temperature is somewhat lower because of optimization between the task and the etching rates. Primary measured parameter is voltage through $R_{\rm ref}$. Then it is possible to get value of the voltage through the sample and corresponding resistance. It was realized with the following basic relation:

$$R(t) = R_{\rm ref}\left(\frac{U_0}{U_v(t)} - 1\right), \tag{1}$$

where $R(t)$ is the resistance of the sample, and U_v is the voltage through the reference resistance.

2. RESULTS AND DISCUSSION

Data collected from computer program were processed and presented as a function $U_v(t)$ and of sample resistance with etching time (see Figs. 1 and 2) obtained from Eq. (1).

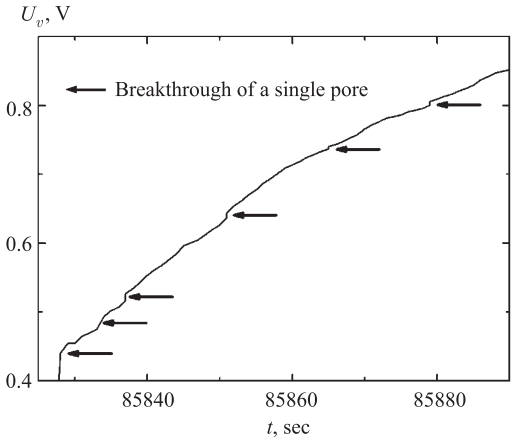

Fig. 1. Voltage through the reference resistance

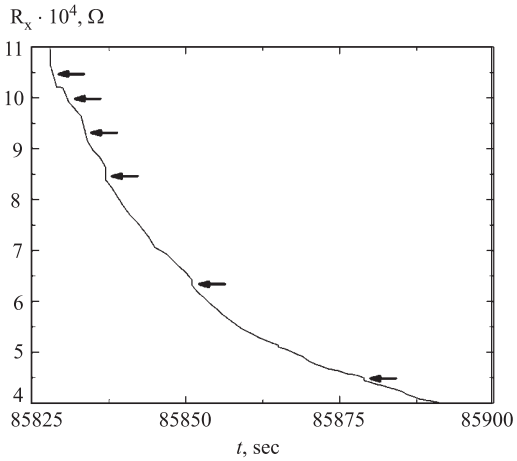

Fig. 2. Resistance of the sample as a function of etching time

«Steps» on this curve correspond to the pore openings. An obvious fact is that the values of the steps become smaller with time. It means that the process of opening is sequential. The first step corresponds to a bigger track size and the last one to a smaller track size. Moreover, results can be presented as total effective conductive diameter (see Fig. 3) for all the open pores using the formula

$$D(t) = \sqrt{\frac{4l}{\pi k R(t)}}. \tag{2}$$

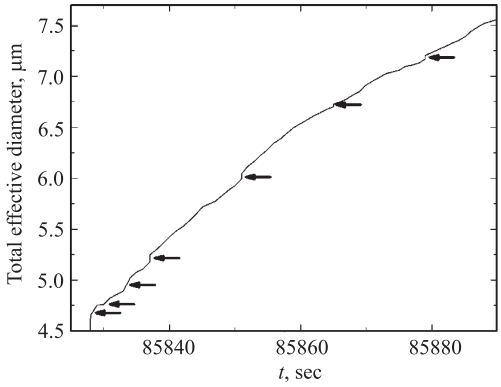

Fig. 3. Total effective conductive diameter of open pores

The corresponding height of steps for individual openings is from 0.05 to 0.1 μm and indicates effective value of a channel. One should note that in the case of light low-energy ions the effective value is determined as an average between inner and outer diameters because of the formation of a cone. It is schematically shown in Fig. 4 and determined by the expression for a single pore:

$$d_{\text{eff}} = \sqrt{d_{\text{out}} \cdot d_{\text{in}}}. \tag{3}$$

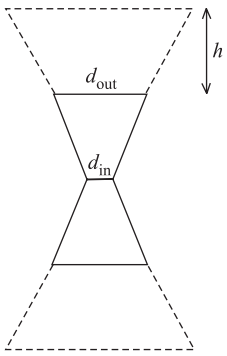

Fig. 4. Principal scheme of a conical pore etched from both sides. h is the removed layer. Dotted lines demonstrate the removed part of the pore

This significantly differs from the case of heavy ions, which are usually characterized by cylindrical pores.

At the same time, information about etching rates was obtained. The bulk etching rate v_B was measured as the removed thickness. In most of the samples

this parameter corresponds to (2.9±0.2) μm/h. It is more than that for chemical etching and can be explained by the influence of electric field which accelerates the process.

Data on pore geometry and track etching rate v_T require an additional analysis at scanning electron microscope. Model JSM-840 (JEOL, Japan) was used. Track etching rate was obtained from microphotographs as a visible length of pore along the path of projectile. Removed layer was taken into account. Using both parameters, the factor of selectivity is $v = v_T/v_B$ and in these experiments equals 1.02±0.01. It proves that the pore is a typical cone. In Fig. 5 one can see a cleavage of the sample.

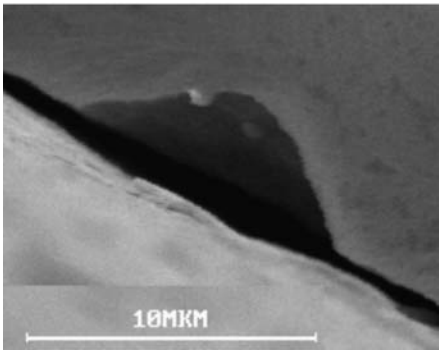

Fig. 5. Etched pore at a cleavage of the sample

With microscopy and etching rates, a model of the pore was constructed. There are assumptions, which were taken into account. The thickness reduction is the same for both sides of the sample and the cone angle is constant from the initial surface down to the visible edge of the pore. This model uses data of energy losses depending on the range calculated using the computer program SRIM (Ziegler et al., 1985). Figure 6 simulates the process.

The transition zone between the cones is invisible from microscopy but corresponds to conductivity as displayed by voltmeter.

Comparison of Figs. 5 and 6 reveals a contradiction. Figure 5 describes the situation as two separate cones from both sides and Fig. 6 corresponds to the "hour-glass"-like pore. The difference comes from different methods of v_T determination. Previous works on light ions used this parameter from microscopy directly or indirectly. The most reliable of the methods uses the expression for dependence of v_T on actual energy W in time t at the corresponding depth (Dörschel et al., 1996):

$$v_T(W,t) = \frac{dL(W,t)}{dt} + v_B. \tag{4}$$

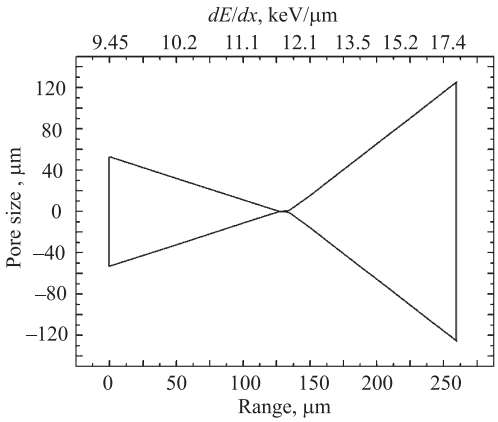

Fig. 6. Reconstructed model of a pore after 40 hours of etching. Dependence of depth and energy losses on the pore size

Here L denotes the length of etched pore and is a function of energy and etching time. In this approach, the assumption of constant angle during the above modeling is restricted for application and should be taken into account. For understanding of this influence, the curve of energy losses is presented (see Fig. 7).

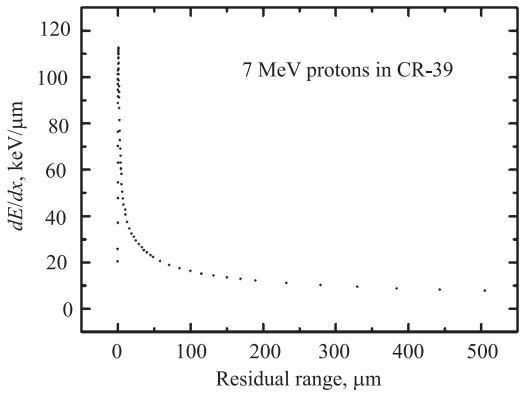

Fig. 7. Energy losses of 7 MeV protons in CR-39 versus the depth

It can be seen that for the case of a 250-μm-thick sample the energy loss, i.e., the track etching rate, differs relatively little along the trajectory of ion in the sample and mostly is important at a point of leaving the target material and for energies smaller than 7 MeV.

Moreover, the diameters on the surface of both sides are not the same and this fact is explained by the difference between energy losses. Degree of material radiation damage is greater at the end of projectile range. It can be called $D_{\rm out}/D_{\rm in}$ ratio, and it varies from 1.8 to 2.3 depending on ion energy. It is obvious that such a factor will be bigger with an increase of difference of energy losses at edges of the sample.

Combining conductometric curves, Eq. (3) and the above model, we obtained the inner diameter of the cone. Its average value is 5 Å. This parameter can be considered as track core size for a given energy interval of protons in CR-39. The given diameter is significantly less than that for other heavier ions. In comparison with carbon, neon, and xenon this difference is 10–16 times (Yamauchi et al., 2003) and for iron this coefficient is 34 (Yasuda et al., 2001). Compared with fission fragments, proton tracks are 50 times smaller (Bohus, 1989). This fact leads to the assumption that tracks of the ^1H ions should be considered as special particles from radiation damages point of view.

The time of breakthrough and correspondingly track etching rate were also determined by the curves. This rate differs from that obtained by microscopy and equals (3.49$\pm$0.2) μm/h if the same track etching rate from both sides of the sample is assumed. Such a divergence corresponds to the existence of zones with different conductivity (Schulz, 1997) and gradient of v_T. Therefore, the visible edge of the cone indicates that a conductive channel of a smaller size follows next. It characterizes low-energy particles, which create a narrow zone of weak radiation damages in depth of material. Besides, it gives information about the real structure of the pore. This situation can be presented schematically as hour-glass profile, and neck-like part is explained by the forestalling of etching along the track in comparison with conical part growth.

CONCLUSIONS

The method of electrolytic etching was applied to CR-39 detector as not typical for this material. For this purpose thin samples down to 250 μm were made from industrially manufactured plates. Using sensitive method, pore openings were observed directly. With these data, effective diameter was determined and equation for the case of a conical pore gave value of the assumed zone within a track core. Electron scanning microscopy proved calculations of selectivity factor and reconstructed model of the pore was proposed. Due to direct observation of the process, time of breakthrough and corresponding track etching rate were determined. With these data, the corrected profile of the pore was described. However, it is still a question on function v_T of depth, and can be obtained from other methods such as observation of the pore growth evolution with time along the path of ion while there is no conductivity. Improvements for detailed

observation of about 10 and more pores with better conditions of the experiment should be made. Also it could be used for lower energies after production of thinner samples (100 μm and less). It looks interesting to apply this method to other particles such as alpha particles, ions of lithium, carbon, etc.

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Издательский отдел Объединенного института ядерных исследований
141980, г. Дубна, Московская обл., ул. Жолио-Кюри, 6.
E-mail: publish@pds.jinr.ru
www.jinr.ru/publish/