

## STUDY OF LITHIUM ENCAPSULATION IN POROUS MEMBRANE USING ION AND NEUTRON BEAMS

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### Abstract

Ion track-etched membranes are porous systems obtained by etching of the latent ion tracks using a suitable etchant solution. In this work, control of the pores' spatial profiles and dimensions in PET polymers was achieved by varying etching temperature and etching time. For determination of the pores' shape, Ion Transmission Spectroscopy technique was employed. In this method, alterations of the energy loss spectra of the transmitted ions reflect alterations in the material density of the porous foils, as well as alterations of their thickness. Simulation code, developed by the team, allowed the tomographic study of the ion track 3D geometry and its evolution during chemical etching. From the doping of porous membranes with lithium-based solution and its analysis by Thermal Neutron Depth Profiling method, the ability of porous PET membranes to encapsulate nano-sized material was also inspected. The study is important for various applications, e.g., for catalysis, active agents, biosensors, etc.

**Keywords:** Latent ion tracks, etching, doping, Ion Transmission Spectroscopy, Thermal Neutron Depth Profiling

### 1. INTRODUCTION

The energetic ions, passing through polymers, may induce latent ion tracks with supposedly cylindrical shape. The transformation of the latent ion tracks into pores via the process of the chemical etching [1] provokes a high interest because by changing the etching conditions a different shape of the pores can be obtained [2]. A promising approach to obtain information about the micro-channels (pores) in a non-destructive way is to measure the energy loss of the mono-energetic charged particles passing through the thin foil of the analyzed material [3]. With this method, the alteration of the energy loss reflects the change in the density and thickness of the thin film. If the non-etched film is uniform with no pores, it is possible to observe the Full Energy Peak (FEP). By etching the material, it is possible to observe the change in the position of the FEP. If there are also passing-through channels, in addition to the REP will also be present in the energy spectrum the Reduced Energy Peak (REP). The shape of the spectra between the REP and FEP gives information about the shape of the micro-channels.

Obviously, the formed porous membranes can be used to store the nano(micro)-particles. To clarify this possibility, one-side etched membranes were doped with the lithium solution. The solution was analyzed by Thermal Neutron Depth Profiling (TNDP), nondestructive nuclear analytical technique [4,5]. The possibility to use membranes as storage of the micro-particles or nano-particles can found application in many fields of research and technology, spanning the micro-electronics to biological studies [6].

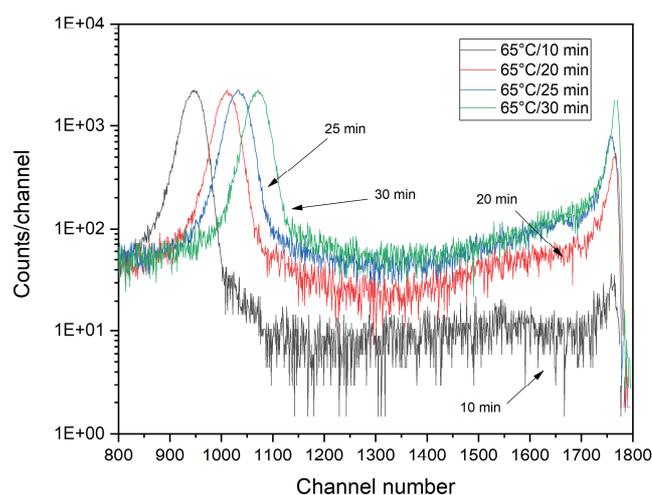
### 2. EXPERIMENTAL SETUP

Polyethylene terephthalate (PET) thin film, 18  $\mu\text{m}$  in thickness, was irradiated with the Xe ions with energy 1.2 MeV/n (157 MeV) and fluence of  $10^6$  Xe/cm<sup>2</sup>. These ions passing through the PET create latent tracks that can be visualized after chemical etching. The chemical etching was performed using the NaOH solution of 9 M

concentration. Important parameters for the chemical etching are the temperature and the time of etching. We performed both double-side and one-side etching at different temperatures for the fixed time, or at the fixed temperature (50 °C, 65 °C or 75 °C) for different time (ranging from 5 to 60 minutes). The one-side and double-side etched membranes were analyzed using the Ion Transmission Spectroscopy (ITS) thermal Neutron Depth Profiling (TNDP). To perform the ITS study, a thin  $^{241}\text{Am}$   $\alpha$ -source was employed to provide quasi-mono-energetic ions. The transmitted spectra were analyzed by the Monte Carlo tomography codes developed at the NPI Rez for the laboratory purposes. The codes calculate the energy loss spectra of the  $\alpha$ -particles by numerical integration. The resulting spectrum is obtained as a sum of all particular spectra, taking into account the density of the pores as an input parameter. The one-side etched PET samples were doped using the 5 M LiCl water solution for 3 hours and dry in air for 48 hours in the controlled environment (at RT and lower relative humidity). To analyze the encapsulation of lithium inside the sample, a series of the TNDP measurements was performed and examined. The TNDP analysis was carried out at the CANAM infrastructure, on the LWR15 research reactor (operated by the Research Center Rez). The samples were irradiated with a thermal neutron beam of the  $10^7 \text{ n}_{\text{th}} \text{ cm}^{-2}\text{s}^{-1}$  intensity, provided by a short mirror neutron guide system. Thermal neutrons induced an intensive, isotropic nuclear reaction  ${}^6\text{Li}(n,\alpha)\text{T}$ , producing two reaction products,  $\alpha$ (2.051 MeV) and T(2.734 MeV), emitted in the opposite directions. Even though the natural abundance of the  ${}^6\text{Li}$  isotope is only about 7.59 %, the high cross section (940 barns) assures (under the intense neutron beam bombardment) a fast data collection. The Li depth profiling was evaluated from the energy spectra using the LIBOR code developed by our team [7]. By this way, it is possible to get an estimation of encapsulation of Li in the pores and the size (length) of the (incomplete) pores (dips).

### 3. RESULTS

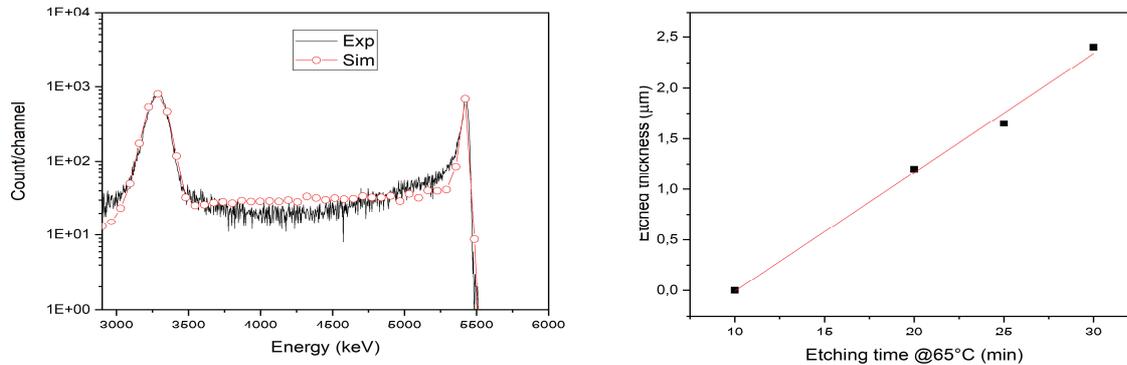
Successive energy spectra of the 5.486 MeV alpha-particles, transmitted through the PET foil etched gradually at the fixed temperature of 65°C for different (increasing) time, are shown in **Figure 1**. Before etching the spectrum consists of only one peak, the full energy loss peak (FEP).



**Figure 1** Series of the ITS spectra of alpha particle transmitted through the PET foil etched in the 9 M NaOH solution for the indicated times at 65°C

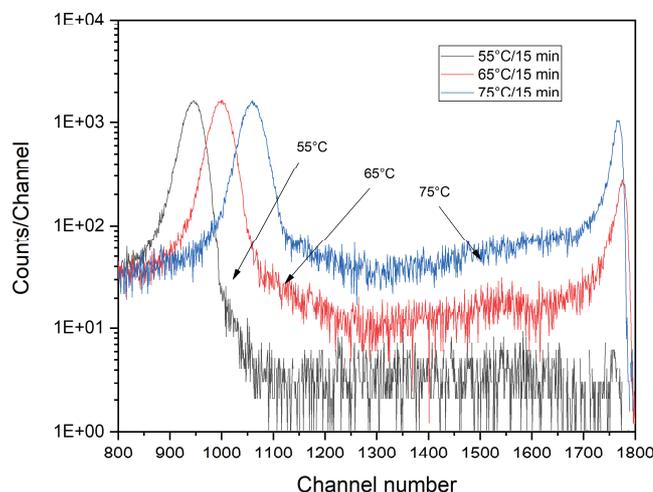
With the etching, additional counts begin to grow at the higher energy side, gradually up to the FEP. Consequently, by increasing the etching time, also the ratio between the FEP and REP counts is growing. An interesting feature of the spectra, seen in **Figure 1**, is a gradual shift of the REP towards the higher energy. This is due to the step-like bulk etching (i.e., lowering of the film's thickness). Using the Monte Carlo simulation, the shape of the emerging pore and the etched-out thickness of the foil can be calculated for all etching times.

A typical result of the simulation (with the overlapping ITS experimental spectrum) is shown in **Figure 2a**. From the given simulation follows that the shape of the pores is cylindrical with a diameter of 5  $\mu\text{m}$ . Concerning the etching of the foil bulk in the 9 M LiCl solution, for etching temperature of 65 °C an etching rate of 117 nm per minute was determined, see **Figure 2b**.



**Figure 2** (left-a) Comparison of the ITS spectrum (measured on the PET foil etched for 30 minutes at 65 °C) with a Monte-Carlo simulation; (right-b) bulk etched-out thickness calculated by the Monte-Carlo simulation considering the REP position

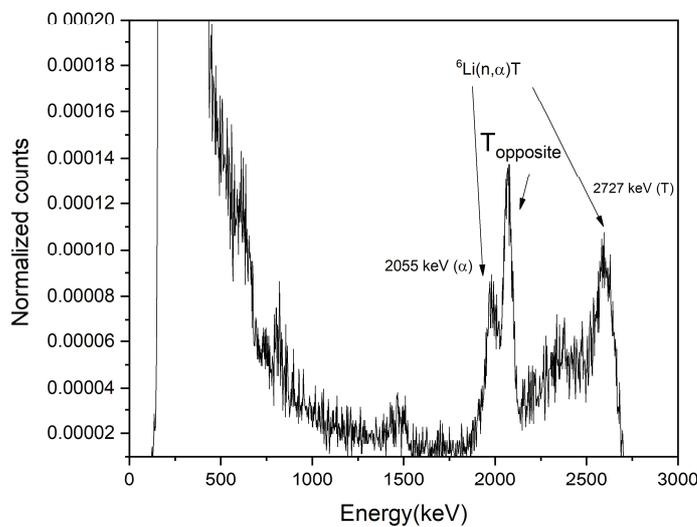
Similar results can be seen in **Figure 3**, where successive energy spectra for the PET foils etched for the fixed etching time and at different temperatures, are shown. From the **Figure 3** it is clear that the condition of the 55°C/15 minutes etching step is close to the threshold for the creation of the pass-through pores.



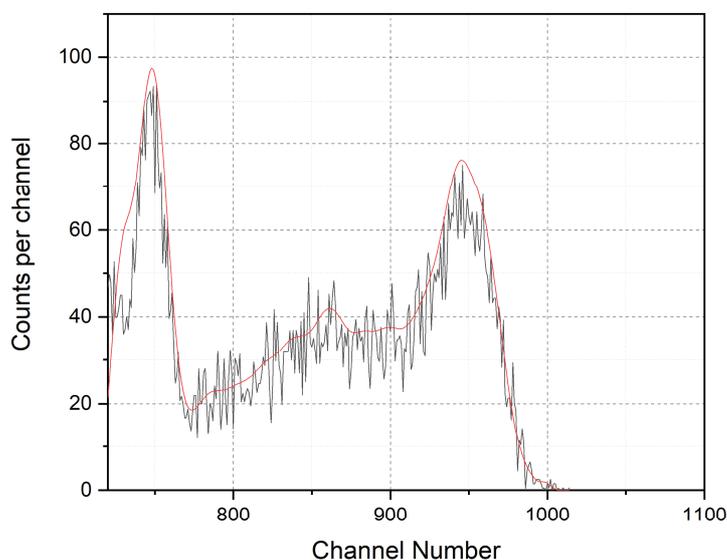
**Figure 3** Series of the ITS spectra for  $\alpha$ -particles transmitted through the PET foils etched isochronally for the fixed time of 15 minutes and at different temperatures

Using these data, a set of foils with incomplete pores (dips) was produced. This was achieved by one-side etching in the 9 M NaOH water solution with the fixed temperature of 50 °C and different times between 15 and 60 minutes. These foils were then doped only on the etched side with the 5 M LiCl water solutions for 3 hours, and then left to dry in controlled environment (at RT and lower relative humidity) for 48 hours. After the preparation, the samples were analyzed using the TNDP technique. The measurement was performed with the non-etched side of the foil faced towards the solid-state detector (Canberra PIPS). The **Figure 4** shows the TNDP spectrum obtained for the sample etched time 45 minutes. In the spectrum, both alpha ( $\alpha_{2051}$ ) and

triton ( $T_{2734}$ ) peaks are depicted, together with an additional ( $T_{\text{opposite}}$ ) peak that corresponds to tritons from the opposite (i.e., etched) side of the sample. This part is dominant, indicating that most of Li (43 %) was attached to the etched surface zone, a part of it in-diffused towards the surface zone of the non-etched side (37 %) and a smaller part was gathered inside the pores (20 %). Using the LIBOR code, the distribution of the Li atoms in the one-side etched foil was evaluated (**Figure 5**). One can see that Li was concentrated mainly on both (etched and non-etched) sides (or near both surfaces) of the foil with a certain amount resisting also inside the pores. Surprisingly, in the center part of the foil in the pores a certain elevation in the Li concentration is indicated. This is not clear, it can be related to the effect of free radicals created in the pores during etching, where the Li ions are trapped and reside there.

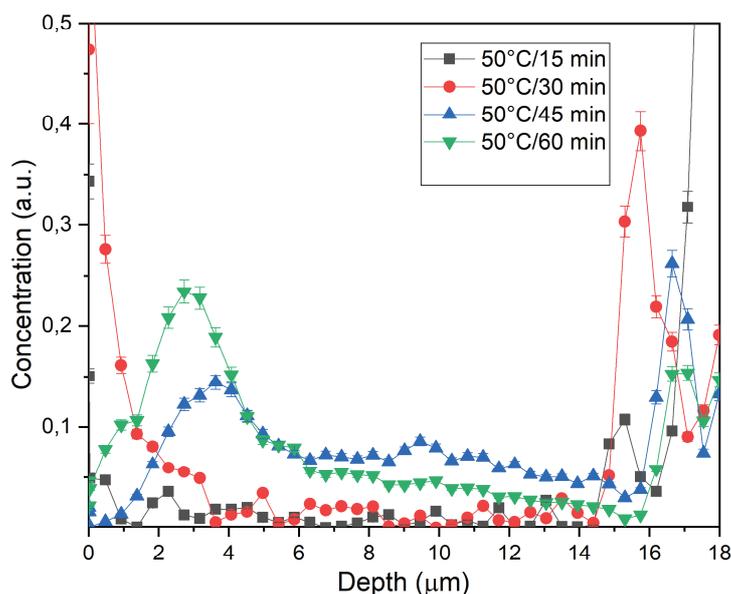


**Figure 4** The TNDP spectrum measured for the PET foil etched at 50°C for 45 minutes and doped with the 9 M LiCl water solution



**Figure 5** Simulation fitting performed by the LIBOR code on the TNDP spectrum shown in Figure 4

The **Figure 6** reports on the distribution of Li in the samples, etched on both-sides isothermally at 50 °C for different time, and analyzed by TNDP. One can see that the concentration of Li in PET, etched for 15 and 30 minutes, is the highest on both surfaces (and negligible in the pores). This can be assigned to the role of just emerging (incomplete) pores (dips), where Li can gather and reside. Surprisingly, however, the concentration on both sides is not even, and also the Li depth distribution is different. This fact is not clear, but it might be assigned to unequal etching process proceeding on both sides due to creation of slightly different radiation defects caused by slowing down Xe ions penetrating through the foil. The foils etched for longer time (45 - 60 minutes) show the higher incorporation of Li inside the pores, and, to a certain surprise, a decline (loss) of Li on the surface. This effect can lead to a desirable process of the Li encapsulation in the pores.



**Figure 6** Depth profiles of Li in the PET foil, etched in 9 M NaOH obtained by the LIBOR code

#### 4. CONCLUSIONS

The PET foils irradiated with swift heavy ions (157 MeV Xe,  $10^6$  Xe/cm<sup>2</sup>) were isochronally or isothermally etched in the 9 M NaOH water solution under a control regime (at 50 - 75°C for 5 - 60 minutes) and inspected by the Ion Transmission Spectroscopy (ITS). Partially, they were also doped with Li (in 5 M LiCl water solution for 3 hours, subsequently dried for 48 hours) and analyzed by noninvasive Thermal Neutron Depth Profiling (TNDP).

The ion transmission study showed how the pores' shape can be evolved (from the initially incomplete to the finally fully opened 3D form of a certain parameters) during the gradually etching process. In the present experiment, the pores could be developed into a cylindrical form with a large diameter of 5 μm within the high etching rate procedure. The study of the Li distribution in the PET porous foils pointed out on an interesting behavior of the Li incorporation into pores in their different developing stage. One could see that Li resides mainly on the surface of the foils after etching for the first several tens of minutes (for the etching temperature 50°C), for longer etching time, however, Li penetrates into the pores massively and forms there a stock of Li-based matter (obviously micro- and nano-particles). Surprisingly, on the surface of the etched foils a negligible amount of Li remains only. This process is interesting for a possible, desirable encapsulation of Li in the pores of thin polymers. An important result is that there exists the possibility to manipulate the quantity and the position of the incorporated Li by changing of the etching parameters.

Further information on study of etching process, control of the pore shape and filling of the pores with different materials (including Li-based nanoparticles) for possible future applications will be collected in next experiments.

## ACKNOWLEDGEMENTS

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