tration, the number of cations in the solution is too much, and the negative charge of the inner surface of the nanopores wall can be effectively shielded whether or not there is voltage. ΔV decreases, and the γ becomes smaller (shown in Fig. 4).



Fig. 4 (color online) Schematic diagram of the potential variation of a single conical nanopores in different concentration solutions (a) low concentration (b) optimum concentration (c) high concentration.

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4 - 73 Current Hysteresis and Potential Energy Barrier Breakdown in Nanopores

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Asymmetric conically shaped nanochannels fabricated by ion-track-etching have been proved to be a versatile platform for biosensor and single molecule analysis^[1-4]. Just as biological nanochannels, single conical nanopores possess some special physicochemical functions, such as ion selectivity, current rectification and current switch^[5,6]. This work presents the recent characteristic study of the polymer nanopores prepared by single ion hits.

PET (polyethylene terephthalate) membranes (diameter=25 mm, thickness=13 μ m) were irradiated with a heavy ⁸⁶Kr²⁶⁺ions of 25 MeV/u energy at the Lanzhou Interdisciplinary Heavy Ion Microbeam (LIHIM) to create a single damage track through the membrane. Then, the single conical nanopore has been successfully prepared in every PET membrane by chemical etching. The transport properties of the nanochannels, were studied by measuring the current-voltage (I-V) curve of these single conical nanopores in different electrolyte solutions.

In order to study the properties of conical nanopore in detail, we used a measurement method which can give two sets of I-V curves in a form of hysteresis. Here, we firstly measured the current under the positive voltage and then measured it applying the negtive voltage. After a ferric chloride solution or chromium chloride solution immersion, nanochannel adsorbs the corresponding trivalent ions, and hence it is hardly cleaned by ultra pure water. The inner wall of the channel has a positive charge due to the excessive adsorption of trivalent cations. Therefore, in the low concentration of potassium chloride solution, there is reverse rectification and cation selectivity.

As shown in Fig. 1, the conical nanopore has was soaked by the ferric chloride solution when concentration of the potassium chloride solution increases gradually, providing an interesting phenomenon. When the positive voltage was applied increasuring to about 1.5 V, the current decreased suddenly. This phenomenon occursred only once at the measurement with appropriate concentration of the potassium chloride solution in a group of different concentrations of the potassium chloride solutions. We believe that the reason for this phenomenon is that the ferric ions attracted by the nanochannels were expelled from this nanopore by electric field force. When the solution concentration increases, the electric double layer became thinner, and interaction between the anions in the double layer and the ferric ions on the nanopore wall increased. In the case of increasing the applied voltage, the sum of the other forces of some ferric ions exceeded the threshold of the pore wall adsorption force, and then leaved the nanopore under the action of electric field force. Due to the decrease of the positive charge, the potential well in the nanochannel decreased abruptly in a short time, leadsing to the sudden decrease of the current.



Fig. 1 Current-voltage curve of the single conical nanopore in 0.01 mol/L KCl with a scan range from -2 V to 2 V (0 V-2 V-(-2 V)-0 V). The single conical nanopore has been modified by ferric ions.

A similar phenomenon could occur in the low concentration of magnesium chloride solution when the conical nanopore without modification had the tip with smaller pore size. As shown in Fig. 2, this phenomenon occurred in the case of negative voltage when the positive voltage was applied at first. This phenomenon can be repeated in a set of measurements, which is different from the ferric ions modified conical nanopore. However, it is more surprising that this phenomenon disappeared when the negative voltage was applied at first providing normal rectification of *I-V* curve (Fig. 3). It is clearly that voltage played a vital role in this phenomenon. When the positive voltage was applied at first, cations were accumulated at the double layers, and potential well was very shallow. When the positive voltage decreased to zero, the potential well was still very shallow because it didn't return to the state without voltage in time. At the same time, for a small number

of anions in the double layer, the potential energy barrier was relatively low. Therefore, when the negative voltage gradually increased to about -1.5 V, some of the anions in the double layer passed through the potential energy barrier. The potential well in the nanochannel rapidly became shallow, therefore the current reduced in a short period of time.



Fig. 2 (color online) Current-voltage curve of the single conical nanopore in 0.001 mol/L KCl with a scan range from -2 V to 2 V (0 V-2 V-(-2 V)-0 V).



Fig. 3 (color online) Current-voltage curve of the single conical nanopore in 0.001 mol/L KCl with a scan range from -2 V to 2 V (0 V-(-2 V)-2 V-0 V).

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