IONIC CURRENT RECTIFICATION THROUGH pH-REGULATED NANOPORES

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This research article reports the pH dependent ionic current rectification (charge transport) in track-etched cylindrical nanopores of polycarbonate (PC). For preparation of cylindrical nanopores, irradiated PC foil was chemically etched with 6M NaOH solution on both sides in electrochemical cell. The behavior of ionic transportation was recorded with stepping voltage at different ionic concentrations and the pH of electrolytic solution under symmetric and asymmetric condition in an electrolytic cell. The results revealed that bulk concentration and pH of electrolytic solution significantly influence the ionic conductance. Under highly asymmetric pH condition, the nanopores behaves like solid state p-n junction diode and rectification through the nanopores was observed. The functional carboxylic group (-COOH) and movable ions of electrolytic solution inside the nanopores wall are found responsible for ionic current transportation (ICT) but for ionic current rectification (ICR), asymmetric combination of pH of potassium halides electrolyte in electrolytic cell was responsible.

1. Introduction

Due to their potential application in wide areas such as sample pre-concentration in micro/nano- fluidic devices, contribution to physiological process/mechanism in living organism and development in sensing devices and much more, nanopores/nanochannels have attracted great attention of scientific community in recent years [1-4]. The ion concentration polarization (ICP) phenomena of nanopores have been used successfully to detect biological entities such as DNA [5, 6], proteins [7] etc. The configuration of nano- fluidic system is based upon the highly sensitive ionic current depression near the nano junction [1, 8-10]. The ion current depression is similar to that of diode like current voltage behavior [11-13]. In cylindrical nanopores, the ionic current transportation (ICT) behavior at negative applied voltage is found to be differ from that of positive applied voltage and suggesting a preferential direction for ICT [14]. When voltage is applied across the membrane, the ion concentration decreases from anodic side for cation selective membrane and vice versa [15, 16]. In the present investigation, ionic current rectification through track etched cylindrical nanopores of PC membrane using potassium halides electrolytic solutions with different molar concentrations and pH have been studied. Ionic current rectification (ICR) means the asymmetric current density at negative/positive voltages. In this report, the ionic current rectification mainly depends on the size of anions, molar concentrations and pH values of the electrolytic solutions [17-20].

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2. Experimental details

2.1 Sample preparation

The pristine samples of polycarbonate (PC) in the form of foils having thickness 12μm with composition $C_{16}H_{14}O_3$ were procured from ICI, Hartfordshine, England. As procured samples were irradiated with 14.2 MeV/n ^{238}U ions of fluence 10^6 ions/cm^2 using heavy ion accelerator UNILAC in Linear Accelerator (LINAC) department at GSI, Darmstadt, Germany. The irradiated PC foil then exposed for 30 min in the presence of UV light on both sides, used to enhance the sensitivity of texture/tracks in the sample [21]. Further, the PC foil with as prepared latent tracks were tailored using chemical etching[22], in an electrolytic cell having two separated chambers with electrodes connected to suitable DC power supply, in order to obtain nanopores. The cylindrical nanopores can be feasible using symmetric track etched process for 45 min. at 40^0 C having etching solution 6M NaOH. Firstly, the etching ions created cones with variable length from both surfaces of PC foil (Fig.1). The as growing cones would met each other as time passes and a sharp depreciation in the resistance of membrane has been recorded i.e. current rate through the membrane increases. The reduction in the resistance of the membrane to the current flow solely depends upon etching time duration. The time duration approx. 45 min. for etching was sufficient in order to obtain the smooth cylindrical nanopores. The neutralization of etchant was carried out with stopping solution and removal of residual salts was done with deionized water. The cylindrical nanopores in PC foil were observed by SEM micrograph shown in Fig. 2 and the pore diameter was found to be ~90nm.
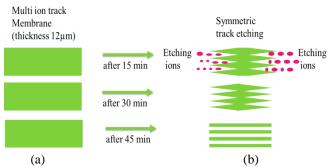

Fig. 1. *Scheme representing a symmetrical track etching process of the un-etched part of ion track using 6N NaOH at 40^0 C to get cylindrical segment (not on scale). (a) Irradiated polycarbonate membrane. (b) Shape of pores by etching ions in polycarbonate membrane after different times.*
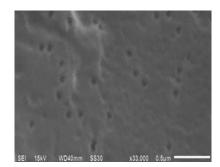

Fig. 2 *SEM micrograph of cylindrical nanopores of PC foil.*

2.2 Ion current rectification

The as prepared multi-ion tracked PC membrane [23] with cylindrical nanopores was fitted in between the two chambers of electrolytic cell and the ionic transport properties have been studied under ambient conditions. The schematic diagram of the apparatus used for measurements

is shown in Fig.3. The electrodes made up of Ag/AgCl were attached at both ends of this cell and were used for ionic conduction through PC membrane [24]. The ion current rectification measurements have been precisely recorded in the voltage range from -2V to 2V [7-9, 24, 25]. The electric current was measured by programmable picoammeter with voltage source (Keithley, 6487). The conduction measurements were regulated either by varying molar concentration of electrolytic solution (KCl, KBr and KI) or by changing pH (acidic/basic character) of electrolytic solution. The controlled process was employed to enable the cations/anions selection for ionic transportation current (ITC) through the PC membrane as similar to the typical behavior observed in various biological channels [1].
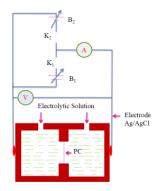

Fig. 3   Schematic diagram of an electrochemical cell.

Moreover, the pH switching and tuning (acidic/basic character) can stimulate the transition between swollen and collapsed state of pH responsive molecules/ions which vary the degree of current rectification [26, 27]. The pH value of electrolyte is higher/lower than the isoelectric point as the surface is deprotonating/protonating respectively [28].This pH switching and tuning is adjusted with 1M HCl or 1M KOH solution [29]. All the chemicals used were of analytical research (AR) grade.

3. Results and discussion

The cylindrical shape of the nanopores in PC has been confirmed by imaging cross-sections of the membranes with SEM. The track-etching technique allows very easy control over the shape of the pores. Details of chemical etching procedures, which lead to cylindrical nanopores are given in the experimental section.
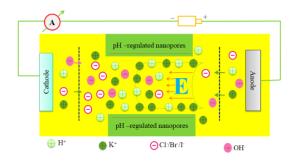

Fig. 4   Schematic representation of ionic transportation through pH-regulated nanopores containing multiple ionic species. Cations and anions are enriched (depleted) at the cathode (anode) side of the nanopores when ICP occurs at the nanofluidic interfaces.

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We observed that I-V behavior of cylindrical nanopores with change in concentration and change in pH of potassium halides electrolyte, there was no significant changes due to change in electrolyte concentration as well as pH of potassium halides i.e. KCl, KBr and KI as shown in figs. 5 - 8, Both (Forward/reverse) side of nanopores the ICT behavior is same i.e. no rectification observed. This is due to both side of chamber is filled with same electrolyte, same concentration of electrolyte also the diameter of nanopores is same on both side of membrane. The motion of the ions is toward each other as well as toward junction under the influence of the applied electric field. The ions cross the junction, which allows smooth flow of the ions from the bulk solutions, and steady flow of the current. The similar behavior was observed, if we change the pH of electrolyte but both side of chamber filled with the same pH value electrolyte. A slightly change has been seen in I-V behavior this is due to change in radius of negative ions i.e. Cl^-, Br^- and I^-. Pores are cylindrical in nature therefor forward and reverse I-V characteristics are nearly same. In Figs. 5 & 6 shows forward/reverse ions current at voltage upto ±2V as a function of bulk electrolyte concentration. A higher number of ions can flow the chamber through nanopores under the influence of increase in voltage form -2V to 0V and 0V to +2V. With increase in electrolyte concentration which leads to increase in concentration of ions in the nanopores and increase current density
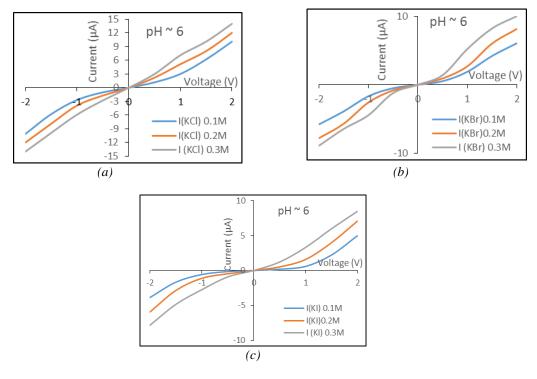

(a)

(b)

(c)

Fig. 5 I-V characteristics for conduction through cylindrical nanopores of polycarbonate membrane at different molar concentrations 0.1, 0.2 and 0.3M of (a) KCl, (b) KBr, and (c) KI.
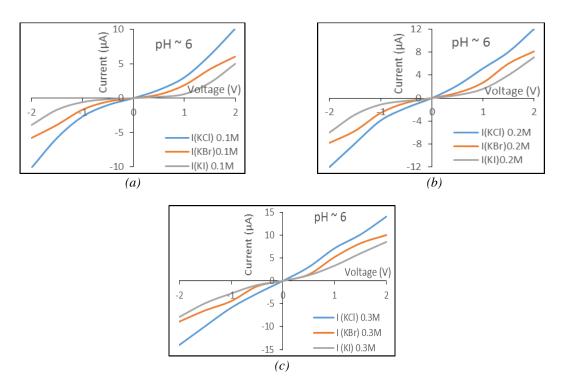
(a)

(b)

(c)

Fig. 6. I-V characteristics for conduction of KCl, KBr and KI electrolytes through cylindrical nanopores of polycarbonate membrane at pH~6 of different concentrations (a) 0.1M, (b) 0.2M and (c) 0.3M.

A scheme of nanopores that connect two chambers of electrolytic cell with identical composition of electrolyte is shown in Fig 3. As ions move across the nanopores due to applied potential, they collide with the solvent molecules and transfer the momenta. At applied positive voltage bias, anions are majority charge carriers and they haul the solvent molecules toward positive electrode. As potential is increased, the concentration of ions in steady state deviate from that in equilibrium. It results in the concentration enhancement in the nanopores and the magnitude of potential varies accordingly such that a constant current of anions i.e. Cl⁻, Br⁻ and I⁻ is maintained. From Figs. 5 & 6, the concentration of anions inside the nanopores is larger than that of chambers. Therefore, anions inside the pores can sustain large current than those at the entrance and the exit of pores. As a result, anions depleted near the entrance of the pores in the left chamber and accumulate at the exit of pores in right chamber. Due to this, the current voltage curve deviate from linearity i.e. non-ohmic behavior show in figures 5 & 6. The existence of depletion and accumulation regions at the entrance of nanopores due to applied potential is known as polarization concentration and exhibit evidence of the coupling that exist between nano structure and transport in nanopores [30]. At higher concentration of potassium halides, the effect of surface charge is small due to high bulk ionic concentration. The surface charge effect is negligible for KCl, KBr and KI upto 1M concentration as reported in ref. [7].

Chemical etching of PC membrane results in the formation of carboxylate groups on the pore walls and on the surface of the membranes. A direct consequence of the presence of carboxylate groups is the possibility of regulating the surface charge by immersing the membranes in electrolyte solutions at different concentration and different pH values [31]. By increasing the pH from 3 to 11, a change in ionic current was observed under applied potential [32] as shown in figure 7 & 8. Firstly, here we observed I-V curve of PC cylindrical nanopores recorded under symmetric conditions of different electrolyte this means that both chamber of electrolytic cell was filled with same pH of electrolyte. In this situation we only observed change in current w.r.t. change in applied electric field in other words we can say that we observed symmetric curve in forward and reverse biasing case no rectification seen as shown in figure 7 & 8, this is due to the fixed charges are compensated by mobile counter ions under electric current flow across the

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nanopores. The electrical conductivity in the region of pores depends on the direction of flow of electric current and polarity of applied potential [33]. A schematic representation of ionic transportation through pH-regulated cylindrical nanopores containing multiple ionic species shown in fig. 4.
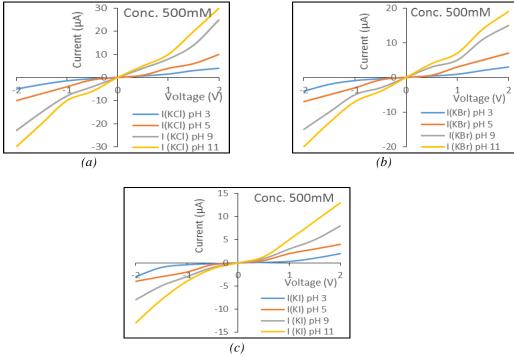

(a)

(b)

(c)

Fig. 7. I-V characteristics for conduction through cylindrical nanopores of polycarbonate membrane at different pH values 3, 5, 9 and 11 of (a) KCl, (b) KBr and (c) KI at molar concentration of 500mM.
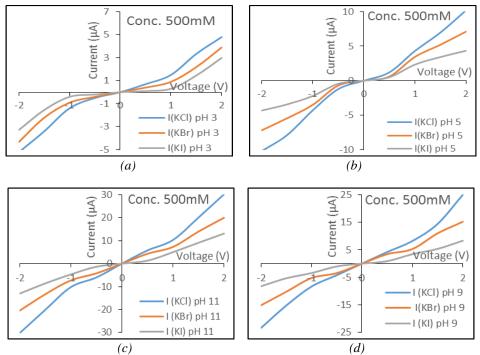

(a)

(b)

(c)

(d)

Fig. 8 I-V characteristics for conduction through cylindrical nanopores of polycarbonate membrane at different electrolytes KCl, KBr and KI of pH (a) 3, (b) 5 (c) 9 and (d) 11 at molar concentration of 500mM.
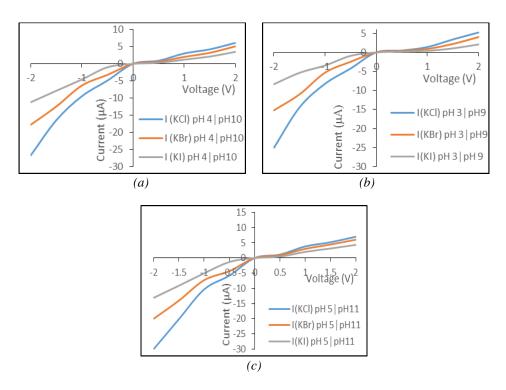
Fig. 9 I-V characteristics for conduction through cylindrical nanopores of polycarbonate membrane at asymmetric pH values (a) KCl, (b) KBr and (c) KI.
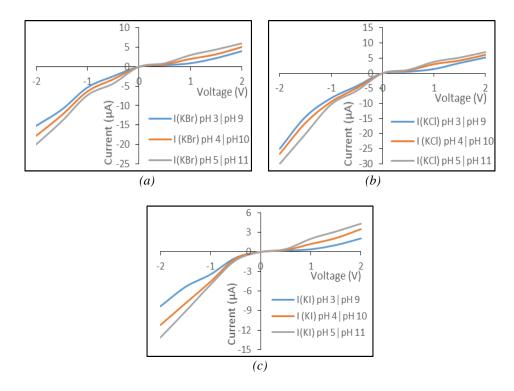

Fig. 10 I-V characteristics for conduction through cylindrical nanopores of polycarbonate membrane at different electrolytes KCl, KBr and KI of asymmetric pH (a) pH 3│pH 9, (b) pH 4│pH 10 and (c) pH 5│pH 11

Secondly, we manipulated the ionization state of the nanopores residues in asymmetric way. For this ionic current rectification in PC cylindrical nanopores the one chamber is filled with acidic and another one is filled with basic electrolyte of potassium halide for making pH

responsive nanopores. There was a remarkable difference in that case observed under asymmetric pH condition shown in figure 9 & 10. This enables the cation/anion selection between rectifying ionic current by changing pH under asymmetric conditions. We reports here (figure 9 & 10) the results for three different asymmetric combinations: (a) pH 3 │ pH 9; (b) pH 4 │ pH 10; and (c) pH 5│pH 11. Here the measurement results a typical diode I-V curve. A increase in resistance in positive voltage applied and a decrease in negative applied voltage. This type of behavior is typical of solid state p-n junctions, polymer ion exchange membrane and molecular rectifier[34, 35, 36]. This is due to the nanopores leads to a bipolar-type charge system, with a positive net charge in one side and negative net charge in another side. This effect of opposite sign of fixed charge on either side of the nanopores is seen in figure 9 & 10. Furthermore, the pH regulation in asymmetric way can significantly tune the ionic current rectification through the cylindrical nanopores and ICR characteristics in case of different potassium halides are quite similar.

4. Conclusions

Ionic current rectification (ICR) through cylindrical nanopores functionalized with pH-regulation has been investigated. The obtained results exhibit that the charge of polyelectrolyte layer highly depends on pH and concentration of electrolytic solution. When the electrolytic solution become more acidic/basic character, the polyelectrolyte become more positively/negatively charged.

The cations/anions charge magnitude changes as pH changes. The ICR is attributed to the depletion and enrichment of ions inside the nanopores subjected to opposite potential biases as well as asymmetric pH combination of filled electrolyte. This flow of charged species will likely to be strong parameter for use in the operating system of implantable chemical/biological nanofluidic analyzers or sensors. In addition, ions or molecules transport and translate the signal into voltage or current compatible with solid state electronics.

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