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A bidirection-adjustable ionic current rectification system based on biconical micro-channel

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We developed a simple, cheap and bidirectional ionic current rectification system based on the integration of biconical micron-channel, working electrode and reference electrode. This system maybe have potential, realistic and future values for studying two-way ionic transport in the cell membrane.

Rectification exists in biological system diffusely and relates closely to the selective transport of ions and molecules. A typical example is the inwardly rectifying current-voltage relation of K^+ ion channels¹. Ion channels spanning cell membranes open and close in response to stimuli² with ions being blocked or passing through the pores. And that is exactly the current-rectification function of an ion channel. Here ionic current rectification (ICR) is a phenomenon of asymmetric ionic current-voltage curves which has been investigated because of its potential application in electromechanically-gate control³, biomolecules detection⁴, and drugs delivery⁵. The degree of ICR can be evaluated with rectification ratio defined as the ratio of currents measured at the same absolute voltage amplitudes⁶.

The key for ICR is the asymmetry in the shape of a nano- or micropore and / or inhomogeneous charge distribution on the inner surface⁷. Therefore, it is of great importance to construct an asymmetrical environment in a nano- or micropore to generate ICR. In order to change the surface charge distribution of the pore wall, many kinds of materials are immobilized onto the inner surface, such as small molecules⁸, biological macromolecules⁴, and polyelectrolytes⁶, etc. A special kind of modification material is surfactant molecule. For example, the rectification degree of the nanopore could be adjusted by varying the modified region and the concentration of a cationic surfactant hexadecyl trimethylammonium bromide (CTAB) when CTAB was added into the working electrolyte of KCl⁷. Differing from the materials mentioned above, CTAB was not immobilized on the inner wall but existed

in the solution dynamically. This work proved that surfactant molecules can be used to tune the rectification of a nanopore. In 1997, the first systematic study on ICR using a quartz nanopipette electrode with diameter 40 nm was reported⁹. Since then, ICR has been observed in nanometer systems based on nanopipette^{6, 10}, silicon-based nanochannel¹¹, and track-etched polymer nanopores^{12, 13}. Along with discovering ICR phenomenon, theoretical study on ICR was also developed^{2, 9, 14-16}, but all of them were focused on elaborating the mechanism of rectification of nanometer system. Although the explicit mechanism of ICR is still debatable, one thing is consistent: the sizes of the systems are nanometer scale. According to Bard's study⁹, asymmetric current-voltage curves can be obtained when the diffuse double layer (DDL) thickness is comparable to the diameter of the nanochannel (or nanopore). However, Mayer' paper¹⁷ in 2010 introduced a strategy for generating ICR through micropore. This method generates ICR by electroosmotic flow (EOF) of liquids of varying conductance into or out of the narrowest section of a pore. Rectification ratios vary using pores with diameters ranging from 10 nm to 2.2 μm . Unlike previous methods in which ICR only occurs when the diameter of a nanopore is comparable to the thickness of DDL, this work presents ICR in micropore with diameter much larger than the thickness of DDL, thus extending the phenomenon of ICR to the micrometer range. When the ICR phenomenon based on quartz nanopipette was discovered⁹, Bard proposed a model for asymmetric currents. They tried explaining the asymmetric behaviour with the permselectivity at the tip terminus of the pipette along with the geometry at the terminus. The simplified model for the tip consists of two conical regions linked by a connecting pore. Interestingly, when a nanopore in the similar shape with the model was prepared in a poly (ethylene terephthalate) (PET) foil with the track-etching technique¹⁸, in contrast to single conical nanopore, the biconical nanopore did not rectify ionic current because of the lack of asymmetry. However, after the formation of positive charges near one of the two openings of the pore and leaving the rest part of the pore with negative charges, the device showed significant ICR phenomenon. In

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another case, the inner surface of the symmetric biconical PET nanochannel was modified using asymmetric ion sputtering of Au and Pt¹⁹. As a result, the metal-polymer composite and asymmetric metal-metal composite could rectify ionic current instead of the symmetric metal-metal composite. So it can be concluded that the asymmetry of the two cones of a biconical nanopore is the essential factor for ICR.

Herein, we developed a new ICR system based on the integration of biconical micro-channel, working electrode and reference electrode. The biconical microchannel was fabricated with a CO₂-laser-based pipette puller using quartz capillaries. The laser puller is usually used to pull a capillary into two almost identical pipettes⁶. In our experiment, the laser puller was stopped before the capillary broke into two sections. The "stop" button was pressed at the moment when the program ran for two cycles. Thus, a biconical microchannel comprising two conical regions was made. This method of preparing a biconical pore is much easier and uncomplicated compared with track-etching technique. The outside diameter of the narrowest point of the biconical channel ranges from 60 to 120 μm (Fig. 1A). After two self-made Ag/AgCl electrodes acted as the working electrode and reference electrode, respectively, and were inserted into the two conical regions separately, a simple ICR device was set up.

We used two kinds of modification materials for the biconical channel which were respectively modified to the inner surface statically and dynamically. A positively charged polyelectrolyte, polyethyleneimines (PEIs) was used to modify the inner surface of one conical region aiming at constructing the asymmetry of the two cones of the biconical channel. The modification procedure was as follows. H₂O was injected into the right cone followed by PEIs aqueous solution (1 g L⁻¹) being injected into the left cone. The following modification procedure was the same as Liu's work⁶. The other kind of material is surfactant. Cationic surfactant hexadecyl trimethylammonium chloride (CTAC) and anionic surfactant sodium dodecyl sulfate (SDS) were separately added into the working electrolyte of KCl. The mixed solution was sucked into the channels from the left orifice with an auralave and the modification procedure was completed without other operation. What's more, recycling the modified biconical channel is also quite simple. After electrochemical scanning, the modification layer of surfactant on the inner surface can be removed easily by washing with water. As for removing PEIs layer, H₂SO₄ solution was injected into the channel, followed by the channel being baked at 80 °C for 14 h. Obviously, reusing the channel can support both rapid cost reduction and the improvement of reproducibility.

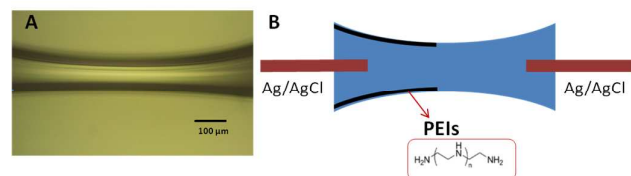


Fig. 1 (A) Microscope image of the central section of a biconical micro-channel. (B) Scheme of the integration of PEIs asymmetrically modified biconical micron-channel, working electrode and reference electrode.

Another advantage of as-prepared biconical channel is that it can act as an electrochemical cell with working electrolyte placed in it and no other container is needed for electrochemical scanning. Linear sweep voltammetry (LSV) was implemented on the integration of PEIs modified biconical micron-channel, working electrode and reference electrode (Fig. 1B). Since the charged states of the two conical regions were different, the two Ag/AgCl electrodes acted as the working electrode separately in two LSVs. So, just by one condition of a biconical channel, we can get two current-voltage curves simultaneously. This device never being reported by other researchers¹⁸⁻²⁰ maybe have potential, realistic and future values for studying two-way ionic transport in the cell membrane.

To confirm that only the asymmetrically modified biconical channel can rectify ion current, the symmetrically modified channels and bare channels were also tested with LSV. The results (Figs. 2A,B) exhibit that the current-voltage curves obtained with bare channel and the symmetrically modified channel are nearly straight lines showing no signs of rectification. A few differences for two curves in Fig. 2A should be due to the slight geometric asymmetry of biconical micro-channel, which has been offset by the symmetrically modified in a way (Fig. 2B). However, the asymmetrically modified biconical channel rectifies ionic current obviously (Fig. 2C). And the rectification directions are opposite when the two Ag/AgCl electrodes inserted in the different conical regions of the channel act as working electrode separately.

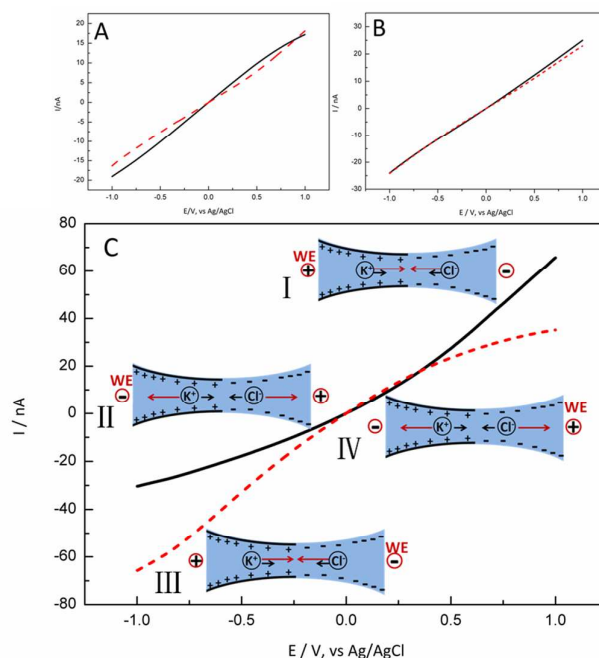


Fig. 2 Linear sweep voltammograms (LSVs) measured as working electrode situated in the two cones of the channel separately. The biconical channels: (A) bare, (B) symmetrically modified, (C) asymmetrically modified, solid curve: working electrode in PEIs modified cone, dash curve: working electrode in bare cone. The insert: schematic illustration of the ICR phenomenon (Red arrows represent the effect of electric field and black arrows represent the effect of surface charge). The concentration of KCl: 1 mM. Scan rate: 10 mV s⁻¹.

The current-voltage curve bends upwards showing positive rectification when the electrode situated in the PEIs modified conical region acts as working electrode. On the contrary, when the working electrode is located in the other conical region, the rectification direction is reversed showing negative rectification.

To explain the mechanism of the ICR occurring in the biconical micro-channel, we proposed a speculation. In particular, the positive charge density on the inner surface decreases from the modified (left) region to the bare (right) region and the right region bears negative surface charge. In addition, both electrophoresis and EOF have effect on ICR, but the EOF directions of the left and right region are opposite, so the effect of EOF can be ignored. On the other hand, positive charges on the surface of left cone tend to exclude K^+ and attract Cl^- while negative charges on the right cone tend to attract K^+ and exclude Cl^- . In brief, the distribution of surface charge is likely to accelerate the motion of K^+ to the right and the motion of Cl^- to the left and accordingly obstruct their motion in the opposite directions. When the working electrode is located in the left conical region and negative voltage is applied (Fig. 2C, II), electric field will drive K^+ moving to the left and Cl^- moving to the right. Since the procedure was obstructed as mentioned above, the ionic current is lower. On the contrary, when positive voltage is applied (Fig. 2C, I), the effect of electric field and surface charges are coincident, so the ionic current is higher. Synthetically, ionic current is higher at positive voltage than at negative voltage. So the current-voltage curve bends upward. For another case in which the working electrode is inserted in the bare conical region (Fig. 2C, III, IV), the direction of ICR is opposite since the effect of electric field is reversed. So with one biconical channel, we can observe ICR phenomenon in two opposite directions.

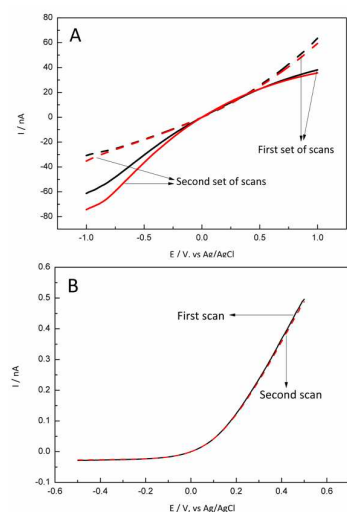


Fig. 3 LSVs for the biconical channel with solution containing 0.1 mM CTAC and 1 mM KCl. (A) Successive two set of scans with working electrode in the two cones, respectively. (B) Successive scans with an interval of 3 min. Scan rate: 10 mV s^{-1} .

Based on the simplicity and availability of this biconical channel system, we have reason to believe that such a simple device could be applied in studying two-way ionic transport in the cell membrane.

To check whether the dynamic modification is still valid, cationic surfactant CTAC was used to alter the surface charge property of the biconical channel. As CTAC solution is sucked into a channel, a positively charged layer would form on the inner surface of the channel *via* electrostatic interaction. Surprisingly, the results of LSVs (Fig. 3 A) demonstrate that ICR can also occur in the biconical channels with CTAC in the solution. In addition, the directions of rectification are opposite when the working electrodes lie in the two conical regions separately. Furthermore, all of the negative ICRs occurred in the left cones from which the solutions were sucked in. Based on these facts, we speculated that CTAC molecules do not exist in the channel evenly but form a decreasing concentration gradient from left to right due to the sucking procedure. So there is discrepancy of charge density between the central section and the two conical regions of the channel that attributes to the bi-directional ICR. After two curves were recorded with working electrodes situated in two cones separately, the scan was repeated again (Fig. 3A). Besides, the same scan was repeated after an interval of 3 min. The curves coincide with the first scan (Fig. 3B). Actually even if with 5 continuous cycles of scans, the rectification curves still coincide with the first scans very well, which declares that the potential applied in the first scan won't affect the following scan and that the surfactant modified system is stable. SDS is an anionic surfactant that would not alter the polarity of the negatively charged inner surface of the quartz channel. But when pH is lower than 3, the dissociation of silanol would be inhibited severely and SDS may affect the property of the inner surface. As expected, the ionic current was rectified with SDS in the solution when pH being around 2 instead of neutral condition (Fig. 4B).

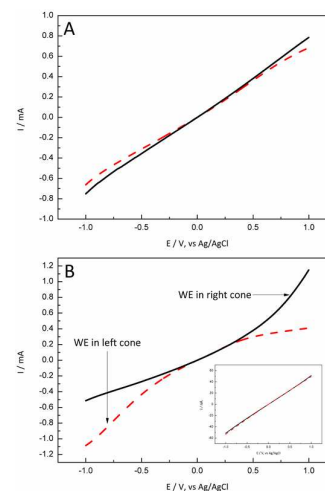


Fig. 4 LSVs for the biconical channel with solution (pH 2.02) containing (A) 1 mM KCl, (B) 1 mM SDS and 1 mM KCl. Scan rate: 10 mV s^{-1} . The insert: LSVs for the channel with neutral solution containing 1 mM SDS and 1 mM KCl.

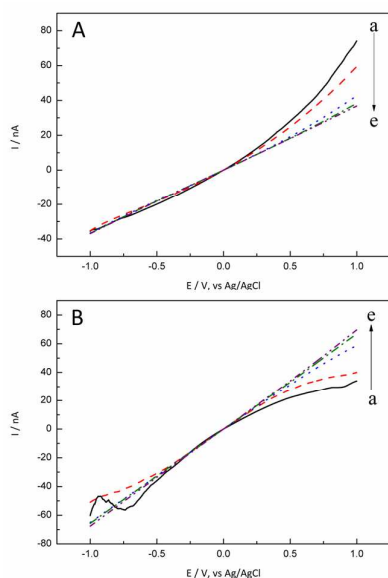


Fig. 5 Scan rate dependent current-voltage responses of a biconical micro-channel with solution containing 0.1 mM CTAC and 1 mM KCl. (A) Working electrode in left cone; (B) Working electrode in right cone. Scan rate (mV s^{-1}): (a) 2, (b) 10, (c) 50, (d) 100, (e) 200.

For comparison, LSV was also implemented when the solution contains no SDS with the same pH condition (Fig. 4A). The nearly linear curves prove that the ICR is owing to SDS. And the opposite directions of rectification also declare that the asymmetry may generate in the same way as CTAC system.

For charged conical nanopores, potential scan rate in LSV plays an important role in ICR as the degree of rectification has been found to be strongly dependent on it^{21, 22}. Theoretical and experimental study shows that the degree of ICR decreases with scan rate increasing. Then for the biconical micro-channel, how scan rate act on the ICR was also concerned. The results (Fig. 5) exhibit that the degree of ICR is lower at high scan rates no matter which conical region the working electrode lies in. And the trend is consistent regardless the channel is modified with PEIs or CTAC. The influence of scan rate may be explained by the result of theoretical study that the mass transport of ionic species occurred inadequately on the time scale of the high scan rate.

In summary, a simple, convenient and cheap method to get a biconical micro-channel was developed. On this basis, we constructed an easily-controlled and bi-directional ICR systems composed of the integration of biconical micron-channel, working electrode and reference electrode. The modified biconical channels generate ICR with outside diameter ranging from 60 to 120 μm which extends ICR to more extensive range. Furthermore, the direction of rectification can be reversed easily by changing the connection between electrodes and electrochemical work station. Anionic surfactant SDS was firstly used to modify the quartz channels and the acidic solution made the modification possible. The dependence of ICR in biconical micro-channels on scan rate is also studied which supplements the research on scan-rate-dependent ICR.

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