

A three-electrode-system to control the flow of ions and charged particles through synthetic nanopores

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In many systems, controlling the flow of ions, rather than of electrons, is a crucial problem. For electrons, diodes and transistors are the basic elements that control, switch on/off and amplify the signals. For the ionic current, there exist very limited possibilities to tune the ion flow.

Recently, an electrochemical device able to rectify ion current on the basis of the charged surface of an asymmetric single pore in a polymer film has been developed [1]. One mode of operation entails applying a constant voltage across the membrane; however, changing the current would require changing the concentration and/or pH of the electrolyte. Because this is time consuming and disturbs the conditions of operation, this option may not be applicable for a given system. It is, therefore, necessary to introduce an independent “switch”, which would be able to modulate the ion current through the pore with a minimum disturbance of the operation conditions. Such a device would be very valuable for the controlled release or separation of charged biomolecules in biological or medical applications.

A prototype of such a device has been produced recently. It consists of a porous polyethylene terephthalate (PET) membrane (10^7 - 10^8 pores/cm², diameter of the pores 100-300 nm) fabricated by the track-etching technique. One membrane side was covered with a thin gold layer. This layer is used as an additional electrode, whose potential influences the flow of charged molecules through the pores.

The operation of the system was tested by spectroscopic measurements of the amount of a cationic dye – methylen blue, which passed through the membrane under given combinations of U_I and U_{gate} (see Fig. 1).

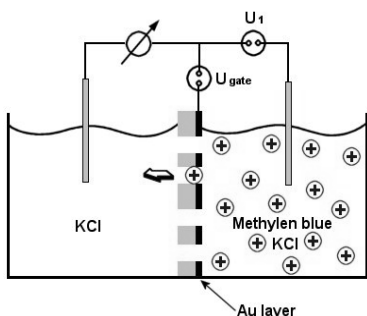


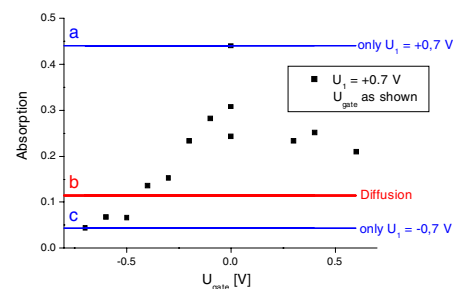
Fig. 1: Three-electrode set-up to control the flow of charged dye molecules through a porous polymer foil (10^7 - 10^8 pores/cm², diameter about 100-300 nm, foil thickness 10 μ m) covered with a thin layer of gold.

The following combinations of U_I and U_{gate} were used (see Fig. 2)

- Reference measurement with no voltage applied in order to estimate the transport due to diffusion (line b)
- $U_I = +0.7$ V, gold electrode not connected (line a)
- $U_I = +0.7$ V, U_{gate} different values from -0.7 to $+0.6$ V (data points)
- $U_I = -0.7$ V, gold electrode not connected (line c)

It was shown that at constant U_I , applying different voltages to the gate electrode changed the transport of the dye. Negative U_{gate} at positive U_I clearly decreased the dyes transport even below the diffusion level while positive values had almost no influence on the transport. This presumably results from adsorption of Cl⁻ ions to the gold layer, which hinders charging the layer positively.

Fig. 2: Amount of dye (expressed as absorption measured spectroscopically) transported through pores in PET after 3 h as a function of U_{gate} . $U_I = +0.7$ V was kept constant.



Similar measurements were performed with PET membranes containing single cylindrical pores with diameter of about 60 nm. One membrane side was covered by a thin gold layer. We measured ion current through the pore, which in this case is a sum of currents between the two outer electrodes and between the gold electrode and the electrode on the side without gold layer. Various combinations of U_I and U_{gate} were tested, $U_I = 0$ V being displayed in Fig. 3. For the single-pore membranes we observed also a much stronger change of ion current for negative gate voltages than for positive U_{gate} .

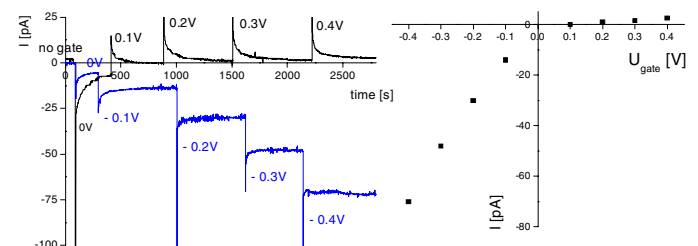


Fig. 3: Ion current through a single pore of diameter 66 nm for different gate voltages, while keeping U_I at 0 V. *Left:* Current approaching equilibrium values after applying various voltages U_{gate} . *Right:* $I(U_{gate})$ equilibrium values.

In order to prevent adsorption of halide ions to the gold surface we insulated it with 1-Hexadecanethiol. It is known that the thiol group binds very strongly to the gold surface. We indeed observed that the system with thiols could also regulate the dyes flow for positive gate voltages.

Further studies are planned with smaller pores, and will focus on improving the gold layer insulation and on testing the device application for various charged particles.

References

- [1] Z. Siwy and A. Fulinski, Phys. Rev. Lett. **89**, 198103 (2002)