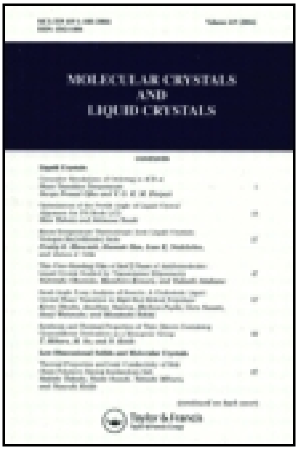

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Characteristics of Electrochemical Transistors

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Characteristics of Electrochemical Transistors

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We construct a device with transistor characteristics, taking advantage of the high ion conductivity of polymer solid electrolyte and electrochemical reversibility of conductive polymer. The device operates under a principle of operation whereby electrochemical oxidation and reduction of the conductive polymer are controlled by the gate voltage and current between the source and drain is modulated by changing the electronic state in the semiconductor layer. Poly(3-hexylthiophene) and cyanoethylpullulan are used as Polymer solid electrolyte and conductive polymer, respectively. Electric measurements show that the device has ***p****-type transistor properties and a switching speed of 50 Hz.*

Keywords: conducting polymer; polymer electrolyte; switching device

Organic field-effect transistors based on organic semiconductors have been developed in recent years [1–7]. The development has been boosted by the fact that the organic matter used in the devices is flexible and inexpensive and that the devices can be made in a printing process different from conventional semiconductor technology. These characteristics of organic field-effect transistors are expected to be an advantage for the application to paper display, electric paper, RFID tag, etc. Organic semiconductors are not in practical use yet because of their small field-effect mobility. To increase the mobility, methods such as controlling the molecular orientation in organic semiconductor layers have been attempted [8–10]. Organic transistors have thus been made based on conventional silicon device fabrication technology and their operation principle is the same as existing silicon

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semiconductors. In this situation, we developed a device principle taking advantage of organic semiconductors. In this paper, we produced a device and evaluated its properties.

The electric conductivity of conductive polymers such as polythiophene or organic semiconductors such as pentacene and copper phthalocyanine is drastically changed by chemical doping [11,12]. For example, the doping of BF_4^- to P3HT (poly-3 hexylthiophene) produces a more than 1,000-fold increase in electric conductivity than the undoped case. Organic semiconductors are electrochemically reversible in doping and dedoping if the chemical doping is performed in liquid electrolysis cells. We take advantage of these properties, that is, the increasing electric conductivity with doping and electrochemical reversibility.

The structure of electrochemical transistors is just the same, except that the insulating layer of the top-contact type organic FET is solid electrolyte [13]. The light blue part is the organic semiconductor layer and the green is the solid electrolyte (Fig. 1). A gate voltage accumulates positive or negative ions at the interface between the semiconductor and the electrolyte layers, and the doping and dedoping at the interface modulate the source-drain current. In the left figure, there is no current flowing between the source and the drain because it is not doped. However, if a gate voltage is applied to dope the semiconductor side of the interface, a doping region is formed at the interface and a

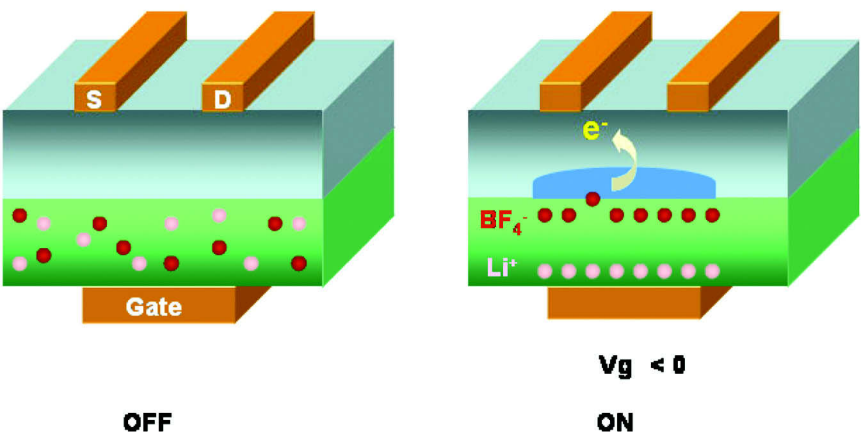

FIGURE 1 Schematic diagrams of electrochemical transistor. The green and light blue parts show the electrolyte and organic semiconductor, respectively. The blue part is the doped polymer. The S and D are the source and drain electrodes. The left and right diagrams indicate the OFF and ON condition, respectively.

current starts to flow between the source and the drain. For the example of polythiophene, the application of a negative gate voltage will accumulate BF_4^- at the interface, which dopes BF_4^- to the polythiophene and modulates the electric current.

The electrochemical transistor can be considered as a solid type of liquid electrochemical cell. So, to provide a switching function, the organic semiconductor has to be electrically reversible. Another essential point is that it requires an ion-conductive solid electrolyte. Since the doping and dedoping at the interface are chemical reactions and occur in a short period time, the switching speed of the device is determined by the diffusion velocity of the ions moving toward the boundary. Therefore, we need a solid electrolyte with high ion conduction.

To obtain high ion conduction in a solid electrolyte, we need to use a polymer with a large polar moment that promotes ionization in the solid. In other words, an insulating polymer with a high dielectric constant is required. So far, we have produced organic FETs with an insulating layer of cyanoethyl pullulan with a dielectric constant of 19, which is largest in organic materials. This time we added about 5% of $LiBF_4$ by weight to the cyanoethyl pullulan and agitated acetone in the solvent to make a thin layer. We measured the AC impedance of the layer under a vacuum of 10^{-5} Torr and observed the temperature dependence of the conductivity. As shown in this Figure 2, we found that the conductivity showed an Arrhenius-type temperature dependence and hence that the cyanoethyl pullulan with $LiBF_4$ is a solid

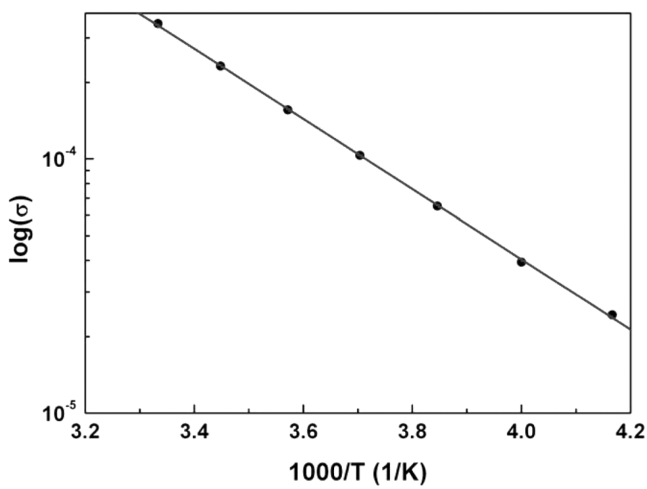

FIGURE 2 Temperature dependence of ion conductivity of $LiBF_4$/CyEPL.

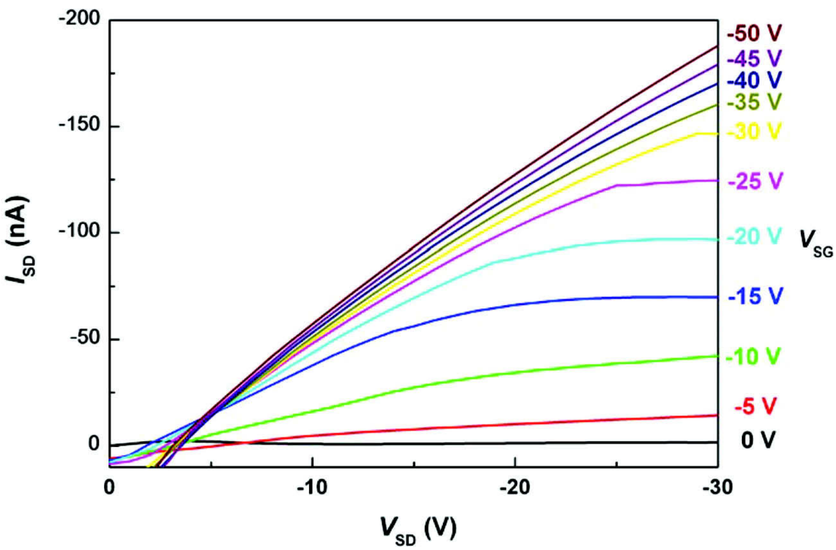

FIGURE 3 Source-drain current vs. source-drain voltage of electrochemical transistor based on P3HT and $LiBF_4$/CyEPL.

electrolyte. At room temperature, the ion conductivity was 10^{-4} Scm^{-1}, the largest in polymer electrolytes.

The experiments were performed on devices with channel length of 30 μm and channel width of 3 mm. The thicknesses of P3HT and solid electrolyte were 30 nm and 2 μm, respectively. We measured the current-voltage property between the source and the drain of the top-contact type structure shown in the figure at room temperature in a vacuum of 10^{-5} Torr. As indicated in the Figure 3, the gate voltage (V_{SG}) would enhance the source-drain current (I_{SD}), which is the same behavior observed in the enhancement type structure of the *p*-channel. The ON/OFF ratio of the source-drain current at -50 V gate voltage was 120. Although we cannot obtain the field-effect-mobility of the device, transconductance (g_m) of the transistor defined as $g_m = \delta I_{SD}/\delta V_{SG}$ is calculated to be 4.87 nS.

We measured the AC property of the device in the top-contact structure at room temperature in a vacuum, fixing the source-drain voltage (V_{SD}) at -20 V (Fig. 4). The change in the source-drain current was observed up to 300 Hz but a well-shaped sine wave was found only up to 50 Hz. When the gate voltage was changed from 0 V to -6 V, the source-drain current increased because of the doping, and when the voltage was from -6 V to 0 V, the current decreased because of the dedoping.

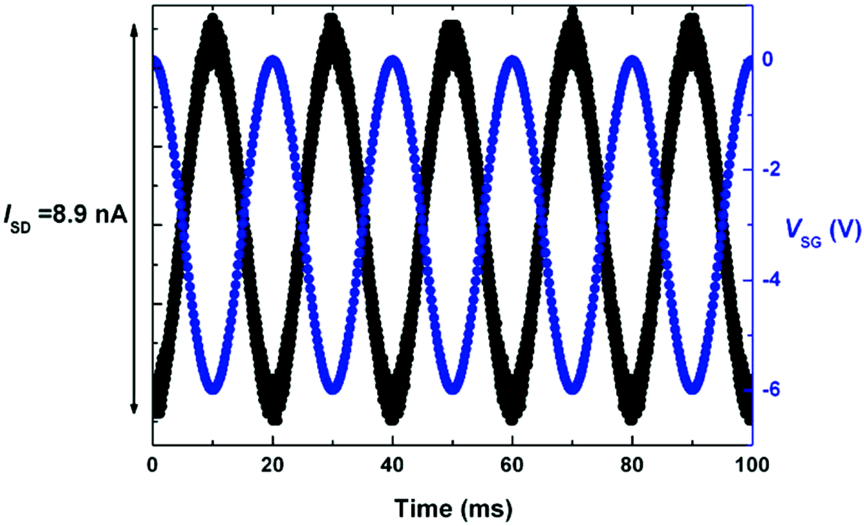

FIGURE 4 Dynamic characteristics of electrochemical transistor based on P3HT and $LiBF_4$/CyEPL.

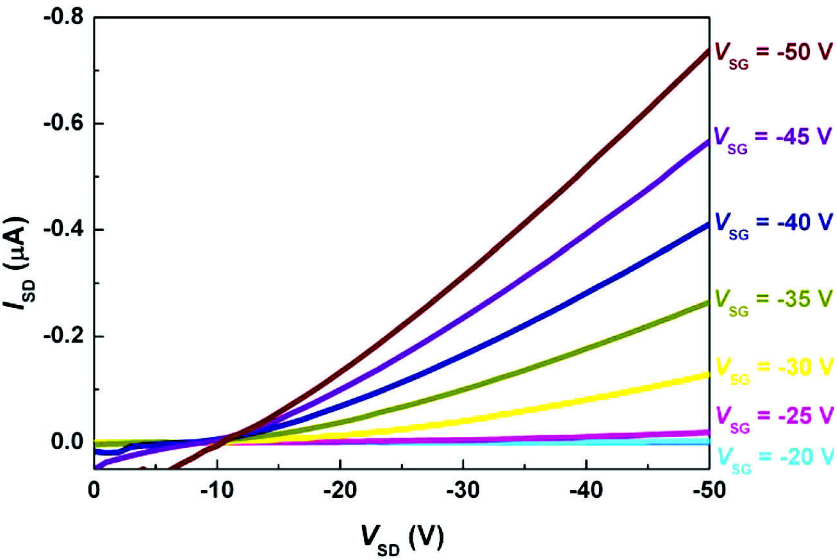

FIGURE 5 Source-drain current vs. source-drain voltage of electrochemical transistor based on CuPc and $LiBF_4$/CyEPL.

We then produced a device structure using a typical organic semiconductor, copper phthalocyanine. The copper phthalocyanine we used had a layer thickness of 30 nm. We measured the I_{SD}–V_{SD} curve in this device and observed an increase in the current at a gate voltage of more than -20 V (Fig. 5). The value of $g_m = 28.9$ nS is about six times the value obtained for the P3HT transistor. In addition to this DC property, we also measured the AC property of this device, but no meaningful data has been obtained as yet because the switching speed is estimated to be below 1 Hz. Now we are trying to produce a device by changing the thickness of the semiconductor layer and the solid electrolyte and investigate the characteristics of the device.

In summary, we fabricated a new switching device using high ion conductivity due to the polymer solid electrolyte and electrochemical reversibility of the conductive polymer. For now, the switching speed is low, however the speed will be fast by tuning up thicknesses of electrolyte and semiconductor layers and concentration of $LiBF_4$.

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