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Ion Gel Gated Polymer Thin-Film Transistors

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A major goal of organic electronics is the development of compatible materials sets, including conductors, semiconductors, and insulators, that enable the fabrication of electronic circuitry on flexible substrates at low cost. In this regard, there has been significant interest in developing new kinds of solution processible organic dielectric materials that can serve as gate insulators in organic thin-film transistors (OTFTs).[1] An important figure of merit for prospective gate dielectrics is the specific capacitance, which determines how much charge can be induced in the semiconductor channel of an OTFT for a given applied gate voltage; higher capacitance translates into higher induced charge densities and therefore both higher ON currents and lower switching voltages. Large specific capacitances have been achieved using solution processible ferroelectric polymers[1c] and ultrathin self-assembled multilayers[1d,e] as gate insulator films in OTFTs. The capacitances of these systems approach 1 μF/cm^2, which compares favorably with typical ceramic dielectrics; for example, a 150 nm thick layer of SiO_2 has a capacitance of 20 nF/cm^2.

Several groups have also demonstrated that solution processible solid polymer electrolytes, such as polyethylene oxide (PEO) with dissolved Li salts, can be used as gate insulator materials in transistors.[2] These systems have even larger specific capacitances, on the order of 10 μF/cm^2. PEO/$LiClO_4$ films, for example, have been used to gate organic single crystals,[2a−c] organic semiconductor thin films,[2d,e] and carbon nanotubes.[2f] High ON currents and low voltage operation are achieved using PEO/$LiClO_4$, but a significant disadvantage is the relatively slow polarization time of this solid electrolyte. The polarization is limited by ionic conductivities, typically on the order of 10^{-4}−10^{-5} S/cm.[3a] For polymer electrolyte gated transistors, the slow polarization time results in low transistor switching frequencies (a few hertz), greatly limiting potential applications.

In this communication, we demonstrate that a gel electrolyte (a so-called "ion gel") based on a mixture of an ionic liquid and a block copolymer[3b,e] can provide both large specific capacitance (>10 μF/cm^2) *and* greatly improved polarization response times (∼1 ms) when used as the gate dielectric in a polymer TFT. The improved properties allow transistor operation at frequencies greater than 100 Hz, significantly faster than what has been demonstrated previously and opening the door to a broader range of applications. Furthermore, the ion gel material is solution processible, making it potentially compatible with high throughput patterning methods (e.g., ink jet printing).

Unlike traditional solid polymer electrolytes, which are obtained by the dissolution of salts by ion-coordinating polymers,[3a] the ion gel electrolyte is formed by gelation of poly(styrene-*block*-ethylene oxide-*block*-styrene) (SOS) triblock copolymer in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), a room temperature ionic liquid; the structures of these materials are shown in Figure 1. From a materials design standpoint, high ionic conductivity is desirable in the gel electrolyte because it will favor both high capacitance and short polarization response times.[3c−e] The ionic liquids of the imidazolium family have been widely studied and are known for their high ionic conductivity which is typically on the order of ∼10^{-3} S/cm or above.[3e] In particular, [BMIM][PF_6] is a commonly used ionic liquid and is relatively hydrophobic (although HF can be produced over time). [BMIM][PF_6] is also selective for poly(ethylene oxide) (PEO) blocks. Considering that the ionic motion is coupled to the segmental dynamics of the solvated polymer in these ion gels, PEO is a suitable polymer for the solvated block due to its low T_g (∼220 K) and rapid segmental dynamics.[3e] For our experiments, SOS and [BMIM][PF_6] (1:9 by wt) were dissolved in methylene chloride (CH_2Cl_2). The solution was mixed for 12 h with continuous stirring in order to obtain a homogeneous solution then poured into a Petri dish at ambient temperature. After the complete evaporation of the solvent, transparent ion gels were formed.

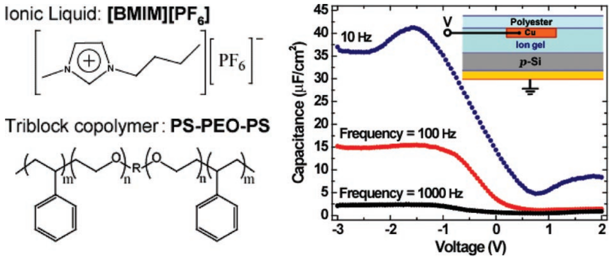

Figure 1. Structure of the ionic liquid and triblock copolymer ion gel components (left) and *C*−*V* characteristics of a *p*-Si/ion gel/Cu test structure (see inset) at three frequencies (right). The *C*−*V* curves indicate large frequency-dependent hole accumulation in the Si at negative bias on the top contact.

The capacitance−voltage (*C*−*V*) characteristics of the ion gel were measured using a metal−insulator−semiconductor (MIS) test structure consisting of a 120 μm thick ion gel layer sandwiched between *p*-type silicon (<100> orientation, 25 Ω·cm) and a laminated top copper contact (∼4 × 10^{-3} cm^2). *C*−*V* measurements were made using an HP 4192A LF impedance analyzer as a function of frequency. The right panel of Figure 1 shows that the specific capacitance C_i of the MIS structure increases upon sweeping the bias applied to the top metal contact from positive to negative voltages. This is expected because *p*-type carriers in the *p*-Si should be depleted at the gel−Si interface at positive bias and should accumulate for negative bias. Importantly, the capacitance of the MIS structure reaches a maximum of 41 μF/cm^2 at 10 Hz, a value that is far greater value than is achievable with typical inorganic or organic dielectric layers. Figure 1 also shows that the specific capacitance decreases as frequency increases, but even at 1 kHz, the capacitance value of 2.4 μF/cm^2 remains higher than other dielectric material candidates.

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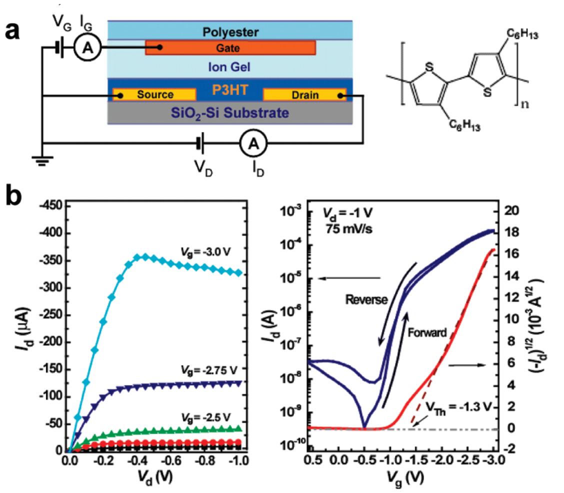

Figure 2. (a) Schematic illustration of the bottom contacted (BC)-TFT structure (left). The device has a channel length of 20 μm and channel width of 200 μm. The right side shows the structure of the polymer semiconductor (P3HT) used in the device. (b) Output characteristics (left) and transfer characteristics (right) obtained from the device. The TFT has a threshold voltage of -1.3 V and a subthreshold slope of 0.11 V/dec.

Top-gated polymer TFTs (Figure 2a) were fabricated using the ion gel gate dielectric and regioregular poly-3-hexylthiophene (P3HT) as the semiconductor layer. 35 nm thick Au source and drain contacts were vapor deposited onto an SiO$_2$$-$Si substrate through a silicon stencil mask to define a 20 μm $\times$ 200 μm channel (length $\times$ width). The P3HT was spin-coated onto the source and drain patterned SiO$_2$$-$Si substrate from a 3 g$\cdot$L^{-1} P3HT/1,2-dichlorobenzene solution. The ion gel was pasted by hand over the P3HT semiconductor layer, and then the gate contact was prepared by pressing a polyester-supported 400 μm wide copper strip to the top of the gel overlapping the source and drain electrodes. All electrical measurements were performed in vacuum at $\sim 10^{-6}$ Torr. Figure 2b shows the output ($I_D$$-$$V_D$) and transfer ($I_D$$-$$V_G$) characteristics of the device. The output characteristics display reasonable saturation behavior, and importantly, the output current, I_D, is greater than -300 μA at a gate bias (V_G) of -3 V and drain voltage (V_D) of -1 V. For comparison, a typical p-channel P3HT transistor with identical channel dimensions and a 300 nm SiO$_2$ gate dielectric produces output currents no greater than 10 μA at $V_G = -50$ V and $V_D = -100$ V.[4a] Thus, a much larger maximum output current is achieved with the ion gel gated transistor at significantly reduced drive voltages. Further, the current ON-to-OFF off ratio is reasonably good at $\sim 10^5$, and from the slope of the $V_G - \sqrt{|I_D|}$ curve in Figure 2b, the saturation mobility is calculated to be $\sim$0.6 cm^2/V$\cdot$s. The mobility value is exceptionally high (typical field effect mobility for P3HT is 0.1 cm^2/V$\cdot$s),[4] which may be due to the filling of a large fraction of carrier traps in P3HT at high gate-induced hole densities.

The typical transient response of an ion gel gated transistor to a 100 Hz square-wave gate voltage input is shown in Figure 3. It is evident that when $V_D = -1$ V, the output voltage V_{OUT} of the TFT tracks the trace of the input gate signal, though there is some distortion of the output waveform due to short-lived capacitive displacement. When $V_D = 0$ V, no steady output voltage is produced; only the transient response is observed, as expected. Inspection of the inset to Figure 3 reveals that response time of the device is on the order of 1 ms when switching from OFF to ON (i.e., stable output is obtained in 1 ms) and is approximately 0.5 ms when switching from ON to OFF. Collectively, the transient response of the ion gel gated transistor suggests that operation at frequencies of a few hundred hertz should be possible.

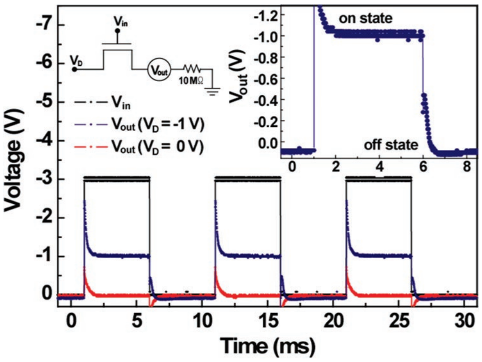

Figure 3. The transient response of an ion gel gated P3HT TFT. The plot shows the output voltage response at constant drain bias when the gate voltage is pulsed at 100 Hz. The left inset shows the measurement setup. The right inset shows an expanded view of the output response.

In summary, we have fabricated polymer semiconductor thin-film transistors using an ion gel as the gate dielectric layer. The gate capacitance of the ion gel can be as large as 40 μF/cm^2 at 10 Hz and 2 μF/cm^2 at 1 kHz. Moreover, the polarization response time of the ion gel is much faster than previously tested solid polymer electrolytes, allowing the ion gel gated transistors to operate at higher frequencies and establishing ion gels as an attractive new class of solution processible gate dielectric materials for organic electronics. There is also considerable scope for further optimization of performance, for example, in terms of choice of ionic liquid, polymer molecular weight, and concentration.

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