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from the favorable entropy, not enthalpy, of activation. At low temperatures, $T\Delta S$ decreases, and we predict that the seven-membered ϵ-abstraction transition state will become favored at about −190 °C and below.

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Registry No. $CH_3(CH_2)_3O^{\bullet}$, 19062-98-7; $CH_3(CH_2)_4O^{\bullet}$, 26397-35-3.

Solid-State Microelectrochemistry: Electrical Characteristics of a Solid-State Microelectrochemical Transistor Based on Poly(3-methylthiophene)

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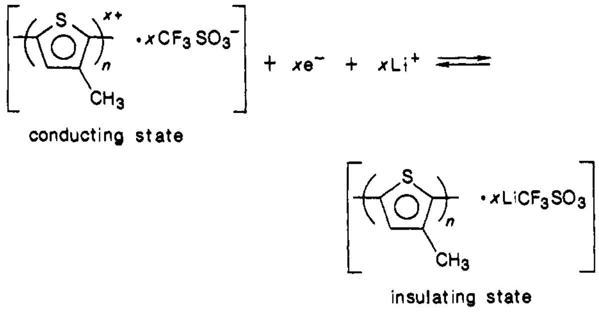
We wish to report fabrication and characterization of a "solid-state" microelectrochemical transistor on a chip with a crucial dimension (source–drain separation) of ~1 μm. The device is based on solid-state reduction and oxidation of poly(3-methylthiophene) (eq 1), connecting the source and drain of the



(1)

transistor, Scheme I. The fundamentally significant finding is that ion transport occurs across the interface between the poly(3-methylthiophene) and the solid-state electrolyte. Work from this laboratory[1] and elsewhere[2] has demonstrated microelectrochemical devices that function when immersed in fluid electrolyte solution. Our new work is inspired by availability of ionic conducting polymers[3] and recent progress in solid-state electrochemistry of molecular materials.[4–6]

The device in Scheme I has been fabricated by beginning with ~3 mm × 3 mm chips having eight, individually addressable, Pt microelectrodes (~2 μm wide, ~50 μm long, and ~0.1 μm high) separated from each other by ~1.2 μm.[1,7] Six adjacent microelectrodes, numbered 1–6, are coated with poly(3-methylthiophene) by anodic polymerization of 3-methylthiophene[7,8] using the minimum amount of poly(3-methylthiophene) necessary to connect 1–6. Two adjacent microelectrodes, 7 and 8, comprise the counter electrode, and a small spot of Ag epoxy on the chip is used as a quasi-reference. Optical microscopy shows that the poly(3-methylthiophene) is confined to microelectrodes 1–6, and cyclic voltammetry shows that each electrode allows access to the same amount (~7 × 10^{-12} mol of monomer units) of polymer, Figure 1. The solid-state device is completed by (1) removing the poly(3-methylthiophene)-coated chip from CH_3CN/0.1 M $LiCF_3SO_3$ at +0.65 V vs. SCE where the polymer is partially oxidized and contains $CF_3SO_3^-$ ions and (2) coating with poly(ethylene oxide) (PEO) containing one $LiCF_3SO_3$ for every 16 PEO units ($PEO_{16}\cdot LiCF_3SO_3$) by evaporation of solvent from 1 μM PEO (MW = 5 × 10^6), 7.1 mM $LiCF_3SO_3$ 9/1 CH_3CN/MeOH (v/v).

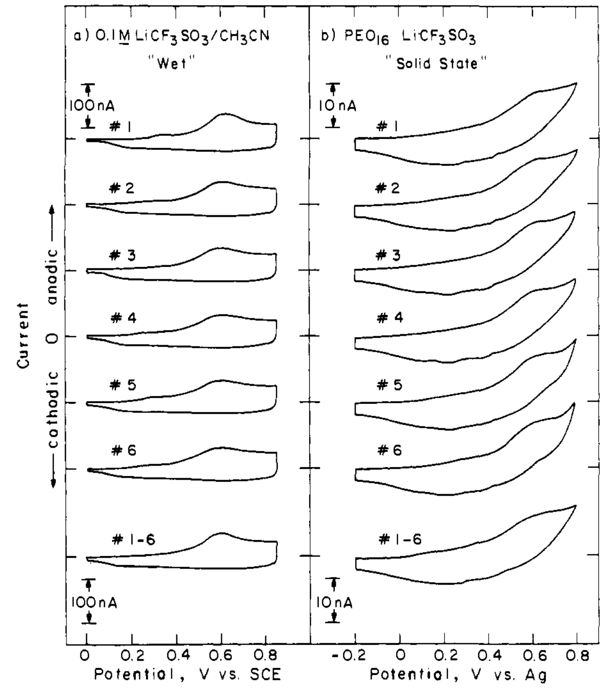


Figure 1. Comparison of cyclic voltammetry in solution (a) (100 mV/s, 25 °C, CH_3CN/0.1 M $LiCF_3SO_3$, volts vs. SCE) and solid state (b) (50 mV/s, 95 °C under N_2 $PEO_{16}\cdot LiCF_3SO_3$, volts vs. Ag) for microelectrodes 1–6 coated with poly(3-methylthiophene) scanned individually and scanned together. Note that for either solution or solid-state cyclic voltammograms the data show the same amount of polymer accessed by one electrode as with all six, but the solution scans show more electroactive polymer.

Figure 1 includes cyclic voltammetry of microelectrodes 1–6 for the solid-state device operated at 95 °C in a N_2 atmosphere. At 25 °C under N_2 the solid-state oxidation/reduction of the poly(3-methylthiophene) is not well-defined, consistent with low ionic conductivity of PEO or poly(3-methylthiophene). Data shown in Figure 1 for the solution (CH_3CN/0.1 M $LiCF_3SO_3$ at 25 °C) and the solid state (N_2, 95 °C) are for the same device. For several independently prepared devices the amount of charge associated with cyclic oxidation/reduction of poly(3-methylthiophene) is less for the solid-state measurement than for that of the solution. This suggests that not all poly(3-methylthiophene)

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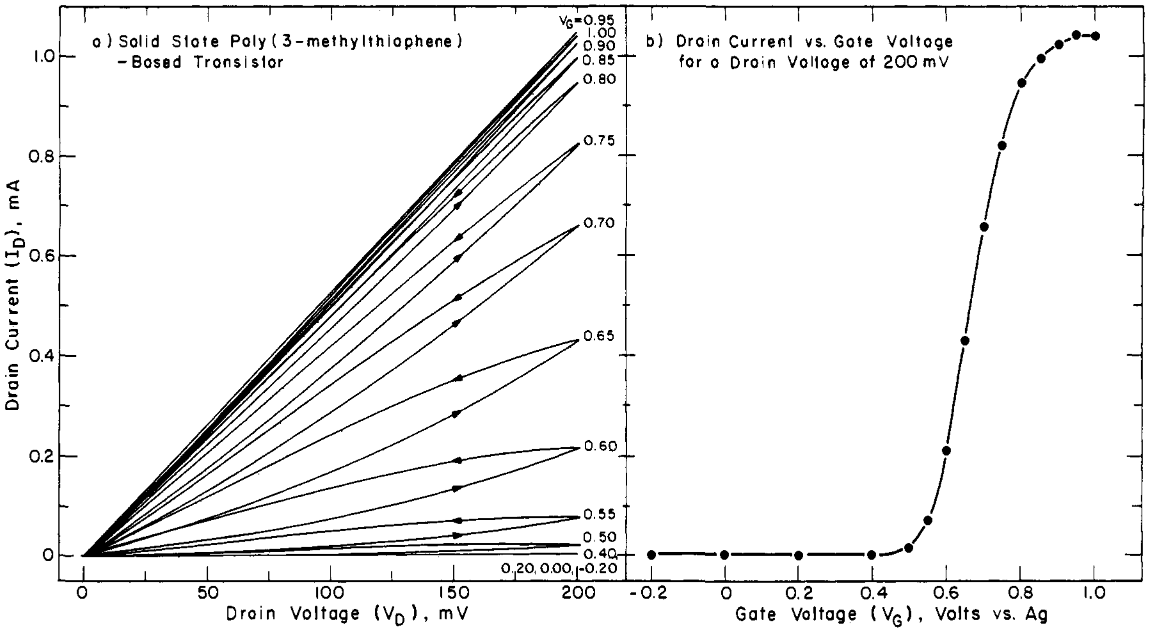
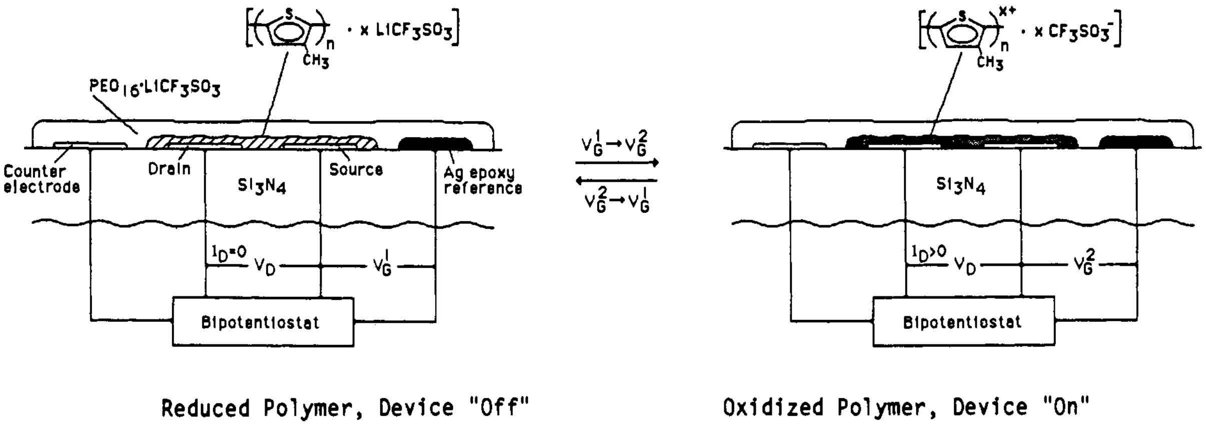


Figure 2. Characteristics of a poly(3-methylthiophene)-based, solid-state microelectrochemical transistor operated at 95 °C in a N_2 atmosphere, cf. Scheme I and text. The I_D vs. V_D data are for 5 mV/s sweeps, and the I_D vs. V_G data are steady state.

Scheme I. Solid-State Microelectrochemical Transistor



is accessible in the solid state, likely a consequence of incomplete oxidation when withdrawn from CH_3CN/0.1 M $LiCF_3SO_3$ at +0.65 V vs. SCE. It is found that driving all six microelectrodes as one electrode gives the same cyclic voltammogram as any one alone in solid state, just as for the solution device (Figure 1), showing that all of the electroactive polymer can be accessed by any one of the six microelectrodes.

Figure 2 shows characterization of the solid-state poly(3-methylthiophene)-based transistor under N_2 at 95 °C: Steady-state I_D vs. V_D (at various fixed V_G) and steady-state I_D vs. V_G (V_D = 200 mV) data are given. Hysteresis in the plots of I_D vs. V_D (V_G fixed), particularly at intermediate V_G values, is likely a consequence of large changes in the polymer structure upon oxidation. Note that at intermediate V_G values the 0–200 mV sweep in V_D causes substantial additional oxidation of the polymer toward the conductive state. The characterization data for the solid-state device are quite similar to that for the same device in CH_3CN/0.1 M $LiCF_3SO_3$ at 25 °C and to that reported previously in CH_3CN/0.1 M [n-Bu_4N]ClO_4.[7] The solid-state device turns on at ~+0.4 V vs. Ag and is on to its maximum extent at ~+0.8 V vs. Ag. The minimum resistance between source and drain for the solid-state device is ~200 Ω, about the same as that for the 25 °C solution device.[7] The maximum resistance exceeds 10^9 Ω for potentials more negative than ~+0.2 V vs. Ag. Thus, the change in conductivity with a ΔV_G of ~0.6 V is about 7 orders of magnitude. The solid-state device can be cycled on and off for many cycles but shows slow degradation in maximum I_D over a period of several hours. Degradation is much more severe for V_G more positive than +0.8 V vs. Ag. Qualitatively, the durability of the solid-state device at 95 °C is similar to that for the solution device at 25 °C, but detailed studies have not yet been made. In comparison to the solution device the solid-state device switches slowly: the turn on to >80% of the maximum I_D value requires ~5 s and the turn off to <5% of the maximum I_D requires ~1 s at 95 °C (vs. ~50 ms for turn on or turn off of the solution device at 25 °C).[7] Interestingly, it is probably slow ion transport in poly(3-methylthiophene), not $PEO_{16}\cdot LiCF_3SO_3$, that limits the switching speed.[9] Use of thicker poly(3-methylthiophene) films results in significantly slower switching. The limited ionic conductivity of poly(3-methylthiophene) implies that switching speed can be increased by preparing a "composite" polymer of poly(3-methylthiophene) and PEO as the active polymer.

Our ability to fabricate a solid-state microelectrochemical transistor based on oxidation/reduction of a polymer indicates

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that a wide range of new devices is possible. In particular, we are intrigued with the prospect of designing gas sensors using conventional redox polymers having chemically dependent $E^{0'}$ values. Since $E^{0'}$ corresponds to the value of V_G where I_D is a maximum,[10] chemically sensitive microelectrochemical transistors responsive to gases are possible. Further, small dimensions of microelectrochemical devices allow their use in very resistive media.[11] Finally, it is worth noting that the solid-state microelectrochemical device reported here is a molecule-based device having all of its components (reference, source, drain, counter electrode, switching material, and "solvent"/electrolyte) on a chip, representing the demonstration of a complete system on the chip.

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Isolation and Structure of $Os_2Cl_4[(C_6H_5)_2P(C_6H_4)]_2$. An M_2L_8 Compound with an Unprecedented Geometry and a Short Os-Os Bond

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Multiple-bond chemistry of the early-transition elements, especially Cr, Mo, W, and Re, has been the focus of intensive research efforts for the past 20 years.[1] Until quite recently, the analogous chemistry of later transition metals such as Ru and Os has been somewhat neglected. Rapid advances are being made in these areas,[2-5] but our knowledge of the bonding properties and reactivity patterns of multiply bonded diruthenium and diosmium compounds is still in a rudimentary stage.

Current efforts in this research group are aimed at expanding diosmium chemistry through the synthesis of new classes of Os_2^{6+} complexes that contain tertiary phosphine ligands. Our recent investigation[6] into the reaction between PPh_3 and $Os_2(\mu\text{-}O_2CCH_3)_2Cl_2$ led to the discovery of $Os_2(\mu\text{-}O_2CCH_3)_2(Ph_2PC_6H_4)_2Cl_2$, an unusual compound with bridging *o*-$(Ph_2P)C_6H_4^-$ groups. It is worth noting that $Rh_2(\mu\text{-}O_2CCH_3)_4$ reacts similarly with PPh_3 to give $Rh_2(\mu\text{-}O_2CCH_3)_2(Ph_2PC_6H_4)_2L_2$.[7] The X-ray structures of these products have appeared in the literature, but at the time the results were published, we had not yet investigated their reaction chemistry. We now wish to report some preliminary results from reactions of $Os_2(O_2CCH_3)_2(Ph_2PC_6H_4)_2Cl_2$ in which the acetate ligands are removed by using MeSiCl. This approach has also been used successfully in the preparation of unusual dirhodium compounds from $Rh_2(O_2CCH_3)_2(Ph_2PC_6H_4)_2L_2$[8] and $Rh_2(O_2CCH_3)_4$.[9]

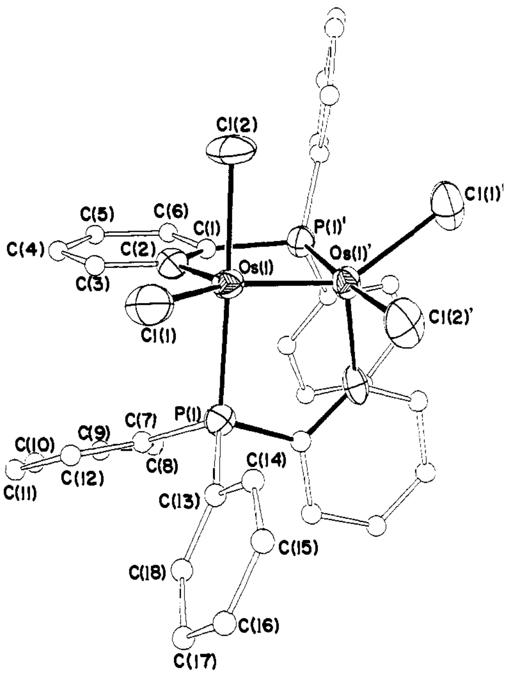

Figure 1. ORTEP drawing of the $Os_2Cl_4(Ph_2PC_6H_4)_2$ molecule with the unique atom-labeling scheme. All phenyl-group carbon atoms not in the coordination sphere are represented as small circles, for clarity. All other atoms are represented by their 50% probability ellipsoids. Some important distances (Å) and angles (deg): Os(1)-Os(1)', 2.231 (1); Os(1)-Cl(1), 2.320 (3); Os(1)-Cl(2), 2.366 (3); Os(1)-P(1), 2.385 (3); Os(1)-C(2), 2.003 (11); P(1)-C(1), 1.812 (11); Os(1)'-Os(1)-Cl(1), 143.02;Os(1)'-Os(1)-Cl(2), 92.28 (8); Os(1)'-Os(1)-P(1), 90.78 (6); Os(1)'-Os(1)-C(2), 102.2 (3); Cl(1)-Os(1)-Cl(2), 89.0 (1); Cl(1)-Os(1)-P(1), 87.0 (1); Cl(2)-Os(1)-P(1), 176.0 (1); Cl(1)-Os(1)-C(2), 114.8 (3); Cl(2)-Os(1)-C(2), 90.6 (3); P(1)-Os(1)-C(2), 91.2 (3).

Treatment of $Os_2(O_2CCH_3)_2(Ph_2PC_6H_4)_2Cl_2$ with 2 equiv of Me_3SiCl in refluxing THF for 0.5 h leads to the formation of a yellow-brown solution and the deposition of the product as a brown microcrystalline material (eq 1).[10] Additional compound crystallizes from the filtrate upon reduction of the volume; combined yield 88%. The product is air-stable and is soluble in a variety of organic solvents.

$$Os_2(O_2CCH_3)_2(Ph_2PC_6H_4)_2Cl_2 + 2Me_3SiCl \xrightarrow[\Delta]{THF} Os_2Cl_4(Ph_2PC_6H_4)_2 + 2Me_3SiOOCCH_3 \quad (1)$$

Single crystals of $Os_2Cl_4(Ph_2PC_6H_4)_2$ were grown by slow diffusion of hexane into a solution of the compound dissolved in THF. An IR spectrum of the crystals (Nujol mull) shows bands arising from vibrations of the *o*-$(Ph_2P)C_6H_4$ ligands but none that can be attributed to acetate groups.[11] In addition, the far-infrared region of the spectrum (200–300 cm^{-1}) displays several ν(Os–Cl) modes. A cyclic voltammogram of the sample in 0.2 M Bu_4NPF_6–CH_2Cl_2 reveals the presence of an accessible one-electron reduction process at $E_{1/2}$ = +0.106 V vs. Ag/AgCl.[12] This redox behavior is very similar to that reported for a variety

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(10) Anal. Calcd for $C_{36}H_{28}Cl_4P_2Os_2$: C, 41.39; H, 2.70. Found: C, 41.64; H, 3.10.

(11) Selected infrared absorption frequencies (cm^{-1}) for a Nujol mull: 1560 m, 1545 m, 1485 m, 1420 m, 1340 w, 1315 w, 1240 m, 1190 m, 1165 m, 1140 m, 1108 s, 1095 s, 1070 m, 1040 m, 1030 m, 1000 m, 910 w, 745 s, 730 s, 720 s, 695 s, 540 s, 530 s, 525 s, 480 m, 370 m, 355 m, 330 s, 315 s.

(12) $\Delta E_p = |E_{p,c} - E_{p,a}|$ = 63 mV; i_c/ia = 1 at 200 mV/s sweep rate at a Pt-disk electrode.

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