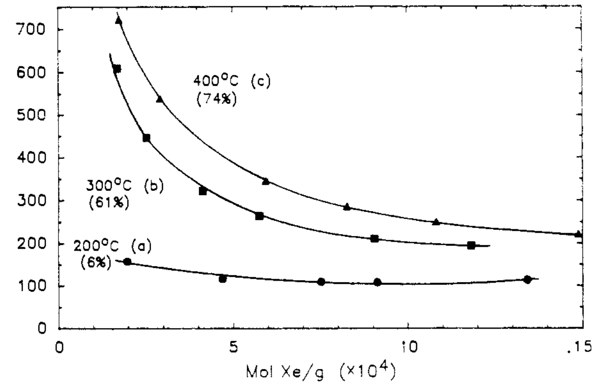

Figure 3. Variation in ^{129}Xe chemical shift with the concentration of adsorbed xenon (T = 22 °C) in reduced Pt–NaY zeolite samples previously calcined to different maximum temperatures (200, 300, and 400 °C). The percentage of surface platinum metal determined by hydrogen-chemisorption experiments is shown in parentheses for each sample.

summary, for the 400 °C reduction conditions imposed, ^{129}Xe NMR data indicate that formation of highly dispersed, NaY-supported platinum metal requires calcination at close to 400 °C and progresses through a shielded precursor species following decomposition of the metal–tetraammine salt.

These new ^{129}Xe NMR experiments represent a unique means of investigating metal–zeolite catalyst preparation and provide important insight into the chemistry of the calcination process. The sensitivity of physisorbed xenon to the influence of the metal guest makes ^{129}Xe NMR spectroscopy an important diagnostic probe of metal-clustering phenomena in zeolitic media.

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Potential Dependence of the Conductivity of Poly(3-methylthiophene) in Liquid SO_2/Electrolyte: A Finite Potential Window of High Conductivity

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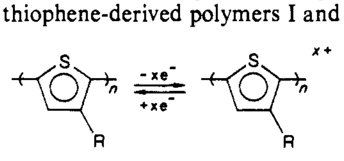
We wish to communicate the potential dependence of the conductivity of thiophene-derived polymers I and II confined to



(1)

I R = CH_3
II R = H

Pt microelectrodes. The data show a broad maximum in conductivity as suggested by theory which shows a finite width for the highest occupied electronic bands.[1] The width of the region of high conductivity and the maximum conductivity are related because the bandwidth of the highest occupied band is a measure of the degree of delocalization in the system and can be roughly correlated with carrier mobility in the band.[1] It is known that oxidation of I or II, eq 1, leads to a dramatic increase in conductivity.[2] However, electrochemical studies of I and II[2,3] failed to reveal maxima in conductivity, possibly because chemical degradation of I and II occurs at positive potentials in the media used. The medium used for our new studies is liquid SO_2/0.1 M $[(n\text{-Bu})_4N]PF_6$ at -40 °C. It has been demonstrated that liquid SO_2/electrolyte is a medium that allows observation of highly oxidized species.[4]

Previous work in this laboratory has shown that polyaniline does have a potential dependent conductivity in aqueous H_2SO_4[5] or in the solid electrolyte polyvinyl alcohol/H_3PO_4,[6] showing a well-defined maximum in conductivity at ~+0.3 V versus SCE and a region of high conductivity ~0.6 V wide. Bandwidths of polyaniline,[7] and polythiophene[1,8] have been calculated, but the results depend strongly on the structures assumed for the polymers. Such theoretical calculations should give reliable trends in bandwidth for structurally similar polymers. The calculations[1,7,8] suggest that a large fraction of the electrons in the highest occupied band might be electrochemically accessible in a number of polymers.

Arrays of eight individually addressable Pt microelectrodes (~2 μm wide, ~50 μm long, and ~0.1 μm high), separated from each other by ~1.2 μm,[3,5,9] can be coated and "connected" with I or II by anodic polymerization of the thiophene monomer in CH_3CN/0.1 M $[(n\text{-Bu})_4N]PF_6$ as described by us[3] and earlier by others.[10] Two microelectrodes connected with a redox-active polymer can be used to determine the potential dependence of the conductivity of the polymer. At a fixed potential difference (drain voltage, V_D) between the two microelectrodes, the magnitude of the drain current, I_D, between the electrodes changes as the potential of the polymer, V_G, is changed.[3,5,9] Thus, I_D–V_G curves reveal the potential dependence of the conductivity, as reflected by I_D, of the polymer.

Figure 1 shows the scan rate dependence for cyclic voltammetry of I on a Pt microelectrode array in liquid SO_2/0.1 M $[(n\text{-Bu})_4N]PF_6$ at -40 °C. Integration of the voltammogram indicates reversible removal of 9×10^{-8} mol of e⁻'s per cm² of area covered by polymer. We estimate that the oxidation process shown corresponds to removing one to two electrons per four repeat units of the polymer. At potentials negative of 0.6 V versus Ag, the features of the voltammogram correspond to those previously reported in other solvent/electrolyte systems.[2,3,10] In the region of more positive potential, new features, anodic and cathodic peaks at ~1.2 V and ~1.0 V versus Ag, respectively, are observed. The cyclic voltammetry over the entire region shown is qualitatively different than previously reported. Further work is required to establish the nature of the chemical changes accompanying the reversible removal of charge.

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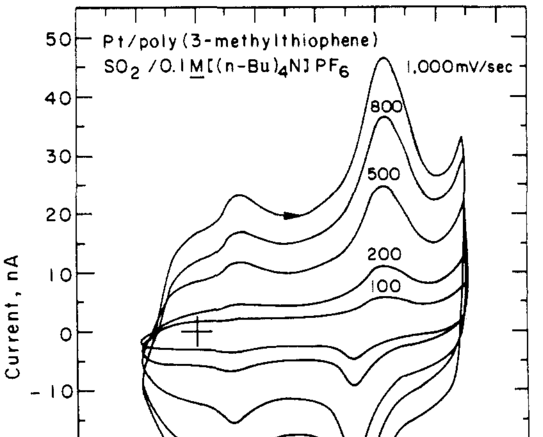

Figure 1. Top: Scan rate dependence for cyclic voltammetry of I on three adjacent Pt microelectrodes in SO_2/0.1 M $[(n\text{-Bu})_4N]PF_6$. Bottom: I_D–V_G characteristic for an adjacent pair of the microelectrodes coated with I for which cyclic voltammetry is shown. In the region of maximum I_D, the current is partially limited by the significant resistance of the microelectrode leads (~200 Ω). All data are for solutions at -40 °C.

Figure 1 also shows the I_D–V_G characteristic in liquid SO_2/0.1 M $[(n\text{-Bu})_4N]PF_6$ at -40 °C for an adjacent pair of Pt microelectrodes connected with I. Negative of 0.6 V versus Ag, the I_D–V_G characteristic corresponds to that previously observed in both liquid and solid electrolyte systems.[3,11] The new finding is that the conductivity of I significantly declines as the polymer is further oxidized, as reflected in the small values of I_D at very positive values of V_G. The polymer resistances at -0.2, +0.9, and +2.0 V versus Ag are $>10^{10}$ Ω, <100 Ω, and $\sim 10^4$ Ω, respectively. The region of high conductivity is ~1.3 V, much wider than for polyaniline.[5,6] The hysteresis evident in the I_D–V_G curve is scan rate independent in the range 10^1–10^3 mV/s and correlates with hysteresis in the cyclic voltammetry. Hysteresis in the properties of conducting polymers upon redox cycling has been explained as resulting from changes in polymer structure.[12] The behavior of II made by anodic polymerization of 2,2′-bithiophene on Pt microelectrodes is very similar to that of I, except that the region of high conductivity is more narrow (~1.0 V width), and the maximum conductivity is somewhat less.

The observation of lowered conductivity in highly oxidized polythiophenes is consistent with theoretical expectations[1,8] and is similar to observations made for polyaniline.[5,6] Considering the data for polyaniline,[5,6] I, and II, it does appear that the polymer with the greatest conductivity, I, also has the widest region of conductivity. Earlier, studies of the potential dependence of the conductivity of polypyrrole have been reported for a limited potential range.[9,13] We are currently investigating polypyrrole and its derivatives over a wider potential range to determine the width of the region of conductivity in these cases. Our findings have important practical implications relating to the use of conducting polymers I and II as electronic materials in batteries and microelectronic devices, since the polymers are shown to have a finite potential window where high conductivity occurs.

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Studies of Phosphorylated Sites in Proteins Using ^1H-^{31}P Two-Dimensional NMR: Further Evidence for a Phosphodiester Link between a Seryl and a Threonyl Residue in *Azotobacter* Flavodoxin

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Elucidation of sites of phosphorylation in proteins is important because of the significant effects of this modification on protein function. Current approaches to identify sites of phosphorylation use degradative chemical methods, which may not be satisfactory due to possible migration of the phosphate group. Direct ^{31}P NMR analysis provides little information on the identity of the amino acid residue phosphorylated since the shift value of the resonance can be influenced by a variety of factors. We report here the application of proton-detected ^1H-^{31}P multiquantum 2-dimensional NMR in the direct determination of the sites of phosphorylation in a protein. The use of these 2D techniques in proteins for ^{15}N and ^{13}C correlations (where large one-bond coupling interactions exist) is now established and has been recently reviewed.[1] Not only can this 2D technique offer sensitivity enhancement over the heteronuclear detected 2D analogue, but it also provides the greatest spectral resolution in the ^1H dimension where it is needed most. Small long-range couplings have been used to mediate 2D spectra of protons with other nuclei in metalloproteins[2-4] and oligonucleotides ($M_r \leq 10$ kDa).[5-7]

In this study we have examined *Azotobacter* flavodoxin, a protein of about 20 kDa that is an electron carrier in the bacterial nitrogen fixation system.[8,9] ^{31}P NMR studies have resolved two signals, one from a covalently bound ^{31}P and a second from the

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