presence of the derivative of natural Asa was demonstrated by electron-impact GC–mass spectrometry at 70 eV. The retention time and mass spectrum of the natural Asa derivative were consistent with those of the synthetic material in all respects. The retention times of the derivatives of synthetic Asa and natural Asa and a mixture of the derivatives of synthetic and natural Asa were all 5.7 min. The major fragment ions in the mass spectrum of the derivative of the natural Asa and their relative intensities were *m/e* 202 (45), 171 (23), 160 (100), 128 (17), 101 (10), 88 (11), and 70 (30). The intensities of the major fragment ions are the same as the intensities of the major fragment ions in the mass spectrum of the derivative of synthetic Asa, as reported in ref 16, within the experimental error of the background corrections. GC–mass spectral data were obtained by using an SE-52 coated fused silica capillary column (0.3-mm i.d. × 30 m) in a Hewlett Packard 5982A GC/mass spec/data system modified for direct connection of the fused silica column to the mass spectrometer ion source.

The distribution and biological significance of this new amino acid remain to be determined and are subjects of current investigation in our laboratories. In view of the divalent cation chelation effects associated with the malonic acid moiety of Gla,[1,2] a systematic study of proteins known to bind divalent metals may detect the presence of Asa in other biological systems.

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Polymer Films on Electrodes. 6. Biconductive Polymers Produced by Incorporation of Tetrathiafulvalenium in a Polyelectrolyte (Nafion) Matrix

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We describe the preparation of a polymer layer on an electrode [based on the perfluorinated ion exchange polymer, Nafion[1] and tetrathiafulvalene (TTF)] which exhibits both ionic and electronic conductivity. Most "polymer electrodes"[2] involve charge transport by electron exchange between incorporated electroactive centers and ionic migration; the overall redox process in such polymers is diffusional in nature.[3] Other purely electronically conductive polymer layers, e.g., polypyrrole, have also been described.[4] We have found that when TTF^+ is incorporated into Nafion, the behavior approaches that of an "organic or one-dimensional conductor"[5] and allows significantly more rapid redox processes of solution species compared to the same matrix with other cations.

The electrodes were prepared, as previously described,[6] by covering a Pt disk with a drop of an EtOH solution of Nafion (equiv wt ~970) and allowing the EtOH to evaporate. The dry thickness of the resulting film determined with a Sloan Dektak surface profile measuring system was 0.7 μm. TTF^+ was incorporated into the film by immersing the electrode in an aqueous solution of ~1 mM TTFCl for 20 min. The behavior of this electrode, denoted Pt/Nafion,TTF^+, will be contrasted with others incorporating other ions, e.g., $Ru(bpy)_3^{2+}$[6] or Cp_2FeTMA^+ ([(trimethylammonio)methyl]ferrocene). The cyclic voltammogram (CV) of the Pt/Nafion,TTF^+ electrode (Figure 1a) in an aqueous 1 M KBr solution is remarkably similar to the CV of a film of TTF alone (prepared by evaporation of a benzene solution of TTF on a Pt electrode) (Figure 1b). The anodic peak corresponds to TTF^+ formation and the sharp cathodic peak to reduction to TTF. The nature and shape of the CV's suggest major structural changes, e.g., as described for TTF–TCNQ electrodes.[7] The redox processes in the electrode are clearly indicated by the accompanying color changes (colorless in the TTF form and purple in the TTF^+ form). At scan rates (v) up to 50 mV/s, the peak currents (i_p) vary directly with v, and even at v = 20 V/s little diffusional tailing is observed on the CV waves. Contrast this to the Pt/Nafion,Cp_2FeTMA^+ electrode (Figure 1c) where the waves resemble diffusion controlled reactions and for $v > 25$ mV/s i_p varies as $v^{1/2}$.[8] For this latter electrode the effective diffusion coefficient (D) determined from electrochemical measurements[3] is ~8.5×10^{-11} cm^2/s; similarly D for $Ru(bpy)_3^{2+}$ in Nafion is ~10^{-10} cm^2/s.[6b] Note that the "effective diffusion coefficient" actually represents the rate of charge transfer through the film through electron hopping, counter ion movement, and actual diffusion.[3] The effective diffusion coefficient determined from electrochemical measurements for Pt/Nafion,TTF^+ electrodes is about 1000 times higher.

The mediated oxidation of solution species, such as FeY^{2-} (Y^{4-} is the tetraanion of ethylenediaminetetraacetic acid), is also very different with Nafion,TTF electrodes. The CV of a Pt/Nafion,TTF^+ electrode prepared as above and cycled several times in 1 M KBr, when immersed in a 0.08 M FeY^{2-} solution (Figure 1d) shows redox processes for the FeY^{2-}/FeY^- system which occur at essentially the same potentials as on Pt (Figure 1e) (i.e., oxidation of FeY^{2-} occurs *before* the TTF/TTF^+ wave), with the currents about one-third those of a bare Pt electrode of the same area. The redox waves for the Nafion,TTF^+ itself are essentially unchanged. With the Pt/Nafion,Cp_2FeTMA^+ electrode in an identical experiment (Figure 1f), the mediated current is much smaller and is found only where the polymer oxidation occurs. Similar contrasting behavior between the Nafion,TTF^+ and Nafion,Cp_2FeTMA^+ is found with the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couple as the solution species. The highly conductive nature of the Pt/Nafion,TTF^+ electrode is also illustrated by the following experiment. If the CV sweep is stopped at a potential where the polymer is in the oxidized (TTF^+) form (0.0 V in Figure 1d), the current for FeY^{2-} oxidation remains steady. If the electrode is now disconnected, the purple TTF^+ is immediately reduced by FeY^{2-} to the colorless TTF form, and on a new CV scan the peak for TTF^+ reduction has disappeared.

The following experiments demonstrate that the described effects cannot be attributed to TTF^+-enhanced transport of solution species through the polymer layer or porosity of the layer. If, after the experiments with the Pt/Nafion,TTF^+ electrode in FeY^{2-} or $Fe(CN)_6^{3-}$ solutions, the electrode was immersed in a supporting electrolyte solution not containing electroactive species and cyclic voltammetry carried out immediately, no waves for the Fe species were observed. Thus the film does not absorb appreciable amounts of these. Moreover CV at a Pt electrode

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(1) (a) Produced by E. I. duPont de Nemours and Co., Wilmington, DE. (b) Grot, W. *Chem.*-Ing.-Tech. **1978**, *50*, 299.

(2) (a) Peerce, P. J.; Bard, A. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *112*, 97. (b) Merz, A.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 3222. (c) Itaya, K.; Bard, A. J. *Anal. Chem.* **1978**, *50*, 1487. (d) Van de Mark, M. R.; Miller L. L. *J. Am. Chem. Soc.* **1978**, *100*, 639, 3223. (e) Daum, P.; Murray, R. W. *J. Electroanal. Chem. Interfacial. Electrochem.* **1979**, *103*, 289. (f) Kaufman, F. B.; Engler, E. M. *J. Am. Chem. Soc.* **1979**, *101*, 547. (g) Brown, A. P.; Anson, F. C. *Anal. Chem.* **1977**, *49*, 1589. (h) Oyama, N.; Anson, F. C. *J. Electrochem. Soc.* **1980**, *127*, 640. (i) *Ibid.* **1980**, *127*, 247 and references therein.

(3) (a) Peerce, P. J.; Bard, A. J. *J. Electroanal. Chem.* **1980**, *114*, 89. (b) Laviron, E. *Ibid.* **1980**, *112*, 1. (c) Andrieux, C. P.; Saveant, J. M. *Ibid.* **1980**, *111*, 377.

(4) (a) Diaz, A. F.; Kanazawa, K. K.; Gardin, G. P. *J. Chem. Soc., Chem. Commun.* **1979**, 635. (b) Noufi, R.; Tench, D.; Warren, L. F. *J. Electrochem. Soc.* **1980**, *127*, 2310.

(5) See, e.g.: (a) Engler, E. *Chem. Tech.* **1976**, 274. (b) Perlstein, J. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 519 and references therein.

(6) (a) Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 6641. (b) *Ibid.*, submitted for publication.

(7) (a) Jaeger, C. D.; Bard, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1690. (b) *Ibid.* **1980**, *102*, 5435.

(8) At very low scan rates (~1 mV/s), however, the Nafion,Cp_2FeTMA^+ electrode shows i_p proportional to v.

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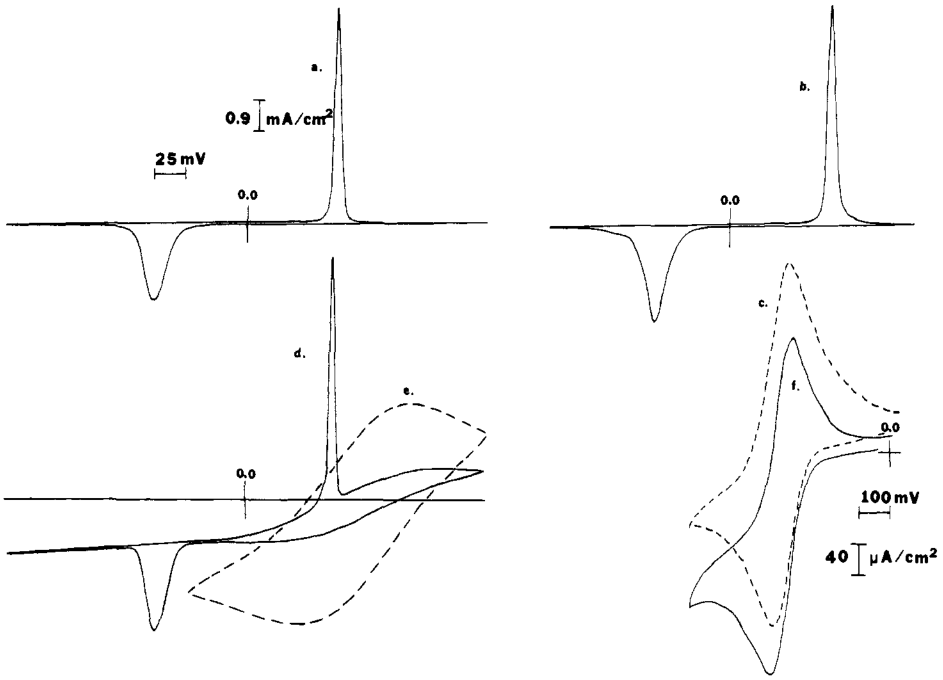

Figure 1. Cyclic voltammograms (10 mV/s) of (a) Pt/Nafion,TTF^+ electrode in 1 M KBr; (b) Pt/TFF (~800-Å thickness) electrode in 1 M KBr; (c) Pt/Nafion,Cp_2FeTMA^+ in 0.2 M Na_2SO_4; (d) Pt/Nafion,TFF^+ electrode in 0.08 M FeY^{2-}, 1 M KBr; (e) Pt electrode in same solution as (d); (f) Pt/Nafion,Cp_2FeTMA^+ electrode in 0.1 M FeY^{2-}, 0.2 M Na_2SO_4. All electrode potentials are given vs. SCE. Current and potentials scales given for (a) also supply to (b), (d), and (e). Potentials are negative to the right and cathodic currents are drawn upward.

covered with Nafion shows currents for FeY^{2-} and $Fe(CN)_6^{3-}$ at least 50 times smaller than that of a bare Pt electrode of the same area, so that transport of species through the film itself or via pin holes[2a] makes only a small contribution.

At this time the effect observed can best be explained as the formation of an internal TTF structure in the polymer film analogous to that found in TTF^+ salts,[5,7] especially after the polymer electrode has been taken through several cycles. Indeed after repetitive electrochemical cycling, observation of the electrode surface by scanning electron microscopy shows the formation of small (<1-μm diameter) needles of crystalline TTF Br on the surface of the polymer exposed to the solution, with some of these embedded into the Nafion surface. The behavior and formation of these crystals is currently under investigation. However, the enhanced conductive properties and color changes in the Nafion,TTF^+ electrodes are found even after a few cycles before large domains of crystalline TTF Br are apparent. One can also contrast the Nafion,TTF^+ electrodes with TTF films prepared by evaporation in terms of stability. The TTF Br film electrodes[7] are stable under cycling for only ~30 min, while the polymer electrodes can be cycled without change for at least several hours.

Moreover, incorporation of TTF^+ decreases the "dry" resistance of the Nafion film. The Nafion,TTF^+ layer on Pt was cycled in 1 M KBr, removed from solution, blotted dry, and allowed to dry in air for 10 min. A drop of Hg was placed on the polymer layer as an electrical contact. The i–V curve across the TTF-containing polymer between the Pt and Hg contacts was typically ohmic and independent of v and showed a resistance of ~3 kΩ. A Nafion,TTF electrode which had not been cycled showed a resistance of ~4 MΩ. A "dry" Pt/Nafion electode which does not contain TTF and was subjected to cycling in 1 M KBr shows purely capacitive behavior (i proportional to v and essentially independent of V). While the actual resistivity of the film cannot be computed from these measurements because of uncertainties in the nature of the Hg contact, the results clearly show the dramatic effect of incorporation of TTF^+ into the film.

These Nafion,TTF^+ films may find several applications, e.g., as electrochromic devices and in stabilization of semiconductor electrodes. Experiments with covalently attached polymer layers[9] or electrodeposited polypyrrole[4b] have shown that irradiated semiconductor electrodes (e.g., n-Si) in photoelectrochemical cells can often be stabilized by such layers. A critical factor in the design of such layers is the rate at which photogenerated charge in the semiconductor can be transported through them to solution species. The Nafion,TTF^+ layers look especially attractive for such an application and preliminary experiments have shown similar enhanced charge transport with these layers on semiconductors.[10]

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[9] See, e.g.: Fischer, A. B.; Wrighton, M. S.; Umana, M.; Murray, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 3442 and references therein.

[10] The support of this research by the National Science Foundation (CHE 8000682) and the Solar Energy Research Institute is gratefully acknowledged.

Kijanimicin. 1. Structures of the Individual Sugar Components

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Kijanimicin,[1] the major component of a complex of antibiotics produced by *Actinomadura kijaniata* nov. sp.,[2] contains five sugars. Acidic hydrolysis of kijanimicin using 0.5 N methanolic hydrogen chloride at 25 °C for 16.5 h afforded methyl 2,6-dideoxy-4-*O*-methyl-β-L-*ribo*-hexopyranoside (**1**)[3] (Chart), mp 76.0 °C, $[\alpha]_D$ −12.4° (CH_3OH) and the α anomer (**2**) as a gum $[\alpha]_D$ −209.2°. The ^1H NMR (Table I), ^{13}C NMR (Table II) and mass

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[1] Isolated from a culture of a soil sample collected in Kenya and named after the Swahili word "kijani" for green, which is the color of the fermentation broth. Kijanimicin is also referred to as SCH 25663.

[2] J. A. Waitz, A. C. Horan, M. Kalyanpur, B. K. Lee, D. Loebenberg, J. A. Marquez, G. Miller, and M. G. Patel, *J. Antibiotics*, in press.

[3] Unless otherwise stated in this and the following paper, all specific rotations were recorded in chloroform at 26 °C (*c* 0.3); IR and NMR spectra were recorded in $CDCl_3$ (reference Me_4Si). All compounds gave either satisfactory microanalyses or high-resolution mass spectral data.

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