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### **Preliminary note**

## **Use of Nafion coatings on glassy carbon electrodes as localized sources of protons for electrogenerated radical-anions in acetonitrile**

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### **INTRODUCTION**

Since the first paper [1] dealing with the use of Nafion® \*\* to modify the surface of an electrode, the results of dozens of studies involving Nafion-coated electrodes have been reported. Most of these investigations have centered on the mechanisms of charge and mass transport within Nafion films [2–6] and on the catalytic properties of films loaded with various electroactive transition-metal species [7–13] and other electron-transfer agents [14,15]. To the best of our knowledge, no previous publication has appeared in which a Nafion film, in its hydrogen ion form, on an electrode surface serves as a localized proton source for radical-anions or carbanions generated via reduction of organic compounds in a non-aqueous solvent. Accordingly, we wish to present the findings of preliminary studies of the cyclic voltammetric behavior of anthracene and naphthalene at bare and Nafion-coated glassy carbon cathodes in acetonitrile. In addition, using such electrodes, we have begun to examine the electrochemistry of 1,1,4,4-tetraphenyl-1,3-butadiene, a species whose reduction leads to a distribution of products that depends on the availability and strength of added proton donors.

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\*\* Nafion is a perfluorinated polysulfonated polymer produced by E.I. DuPont de Nemours and Co.

## EXPERIMENTAL

*Reagents*

Acetonitrile employed as solvent was purchased from American Burdick & Jackson Laboratories, Inc., and tetra-*n*-butylammonium perchlorate utilized as supporting electrolyte was obtained from the G. Frederick Smith Chemical Co.; neither reagent was subjected to further purification.

Nafion, in its hydrogen ion form, was supplied by the Aldrich Chemical Company, Inc., as a 5% solution of the ion-exchange powder in a mixture of lower aliphatic alcohols and 10% water. Anthracene, naphthalene, and 1,1,4,4-tetraphenyl-1,3-butadiene were used as received.

*Electrodes, instrumentation, and procedure*

Cyclic voltammetric experiments were performed in a three-electrode cell of conventional design [16]; the working electrode consisted of a glassy carbon rod (Tokai Electrode Manufacturing Co., Tokyo, Japan) press fitted into a shroud of Teflon to provide an exposed disk with an area of 0.077 cm<sup>2</sup>, and additional information about the fabrication, polishing, and cleaning of the electrode is available in a previous publication [17]. As a reference electrode, we employed a saturated cadmium amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride [17], but all potentials in this paper are quoted with respect to the aqueous saturated calomel electrode (SCE).

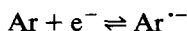
We prepared a Nafion-coated glassy carbon disk by placing one or two drops of the aforementioned Nafion solution onto the surface of the inverted working electrode with the aid of a micropipet; the alcoholic solvent was allowed to evaporate for approximately 1 h, and the surface of the coated electrode was rinsed with acetonitrile before a series of experiments. It is noteworthy that the Nafion coatings are readily soluble in dimethylformamide, but are insoluble in acetonitrile; in fact, a Nafion-coated electrode can be soaked in acetonitrile for at least several hours without having its electrochemical properties affected.

Other details about the equipment used to perform the cyclic voltammetric experiments can be found in an earlier publication [16].

## RESULTS AND DISCUSSION

*Cyclic voltammetric behavior of anthracene*

As has been observed with other electrodes in several different non-aqueous solvent systems [18], the cyclic voltammogram of a 2 mM solution of anthracene in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate recorded at a scan rate of 50 mV s<sup>-1</sup> with a bare glassy carbon electrode exhibits two cathodic waves with peak potentials of -2.00 and -2.55 V that correspond, respectively, to formation of the radical-anion



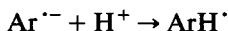
and dianion of the starting material (symbolized by Ar in this paper):



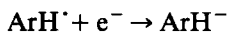
Whereas the first step of the reduction is reversible, because the comparatively stable radical-anion does not readily accept a proton, the second electron-transfer process is nominally irreversible due to the fact that the dianion is protonated rapidly to yield dihydroanthracene.

Figure 1, which focuses on just the first electron-transfer process, displays four sets of cyclic voltammograms recorded at several different scan rates for a 2 mM solution of anthracene containing 0.1 M tetra-*n*-butylammonium perchlorate. As shown in Fig. 1A, in the presence of just the supporting electrolyte-solvent system (which typically contains 15–25 mM water), the electrogenerated radical-anion of anthracene is not protonated rapidly, so that the first-electron transfer is reversible at a scan rate as low as 20 mV s<sup>-1</sup>.

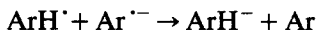
However, if a sufficiently potent proton donor is purposely added, the radical-anion (Ar<sup>·-</sup>) is converted into a radical (ArH<sup>·</sup>),



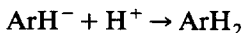
and the result of this protonation is that the voltammetric peak corresponding to oxidation of the radical-anion will be smaller than before. Once formed, the radical is reducible at a potential more positive than that of the starting material



or, alternatively, the radical can undergo a solution-electron-transfer reaction with the radical-anion



after which the monoanion (ArH<sup>-</sup>) is protonated:



Depicted in Fig. 1B are cyclic voltammograms showing the first electron-transfer process for anthracene in a solution containing 20 mM diethyl malonate, which serves as a source of protons for the radical-anions. Quite obviously, the proton donor diminishes the degree of reversibility of the reaction; and, at a scan rate of 20 mV s<sup>-1</sup>, a wave signaling oxidation of the radical-anion is no longer visible because protonation of the radical-anion is so efficient. We have discovered that a Nafion film, in its protonated form, can do what diethyl malonate does, namely serve as a proton donor for electrogenerated radical-anions. Figure 1C shows the reduction of anthracene at a glassy carbon electrode coated with a layer of Nafion; at a scan rate of 200 mV s<sup>-1</sup>, the wave for oxidation of the radical-anion is diminished, whereas the anodic peak is not evident at a scan rate of 20 mV s<sup>-1</sup>.

Figure 1D depicts cyclic voltammograms for anthracene in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate recorded with a glassy carbon electrode coated with Nafion that, prior to the experiments, was pre-treated for 30 min with an aqueous 0.1 M solution of tetramethylammonium hydroxide. In accordance with our expectations, removal of hydrogen ions from the Nafion film

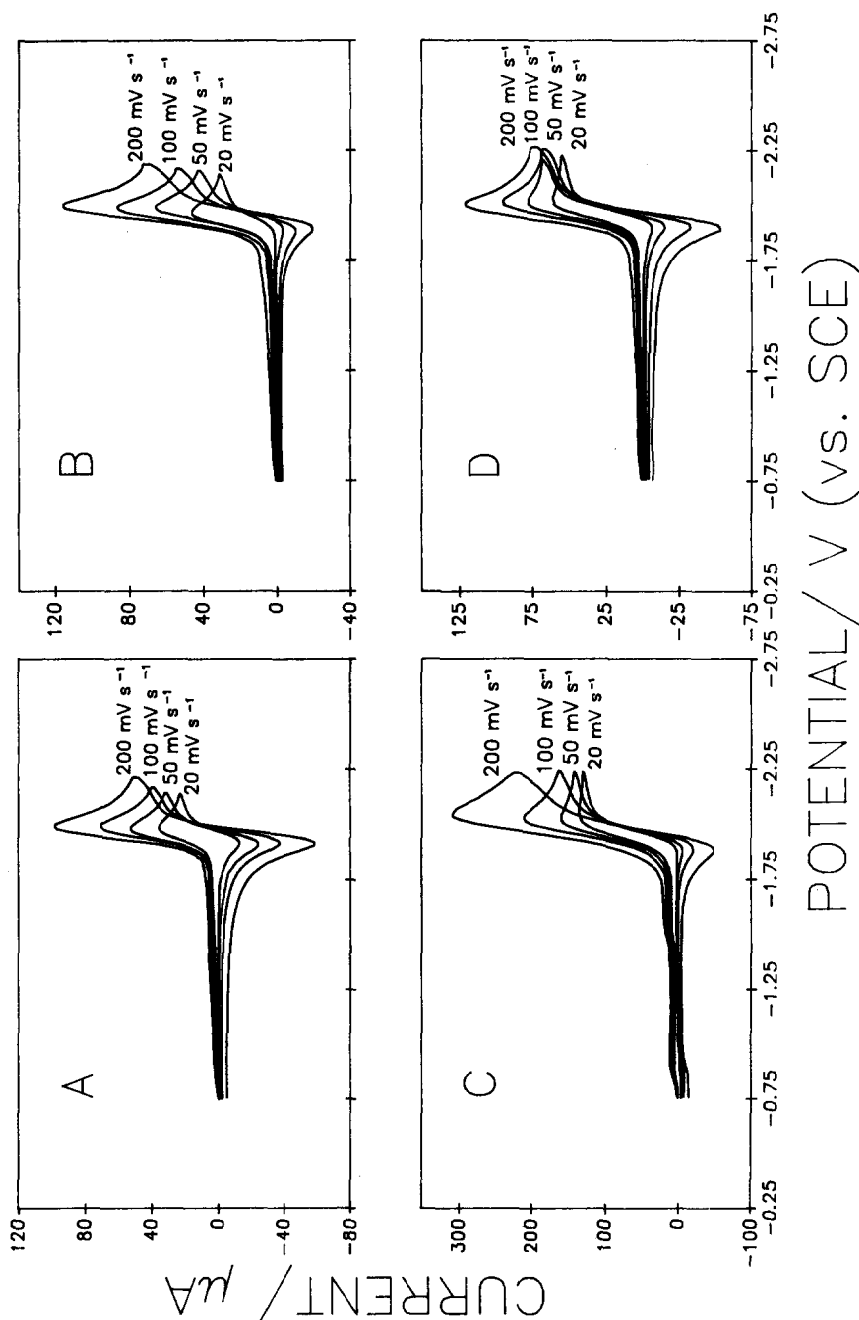


Fig. 1. Cyclic voltammograms for the potential region corresponding to the first electron-transfer process for a 2.0 mM solution of anthracene in acetonitrile containing 0.1 M tetra-n-butylammonium perchlorate. (A) Bare glassy carbon electrode. (B) Bare glassy carbon electrode in the presence of 20 mM diethyl malonate. (C) Glassy carbon electrode coated with Nafion in its protonated form. (D) Glassy carbon electrode coated with Nafion pre-treated to remove protons.

by neutralization (and, presumably, their replacement by tetramethylammonium cations) prevents protonation of the radical-anion of anthracene and restores the reversibility of the first electron-transfer process.

Close inspection of the various sets of cyclic voltammograms shown in Fig. 1 raises some intriguing issues. Notice that the cathodic peak currents obtained in the presence (Fig. 1B) of diethyl malonate are only slightly larger than those measured in a nominally proton-free environment (Fig. 1A). As pointed out by Jezorek and Mark [19], among others, the addition of a viable proton donor should transform the reduction of anthracene from a one- to a two-electron process; for strictly reversible reactions, this change should cause the cathodic peak currents in Fig. 1B to be approximately 2.8 times larger than those in Fig. 1A. Jezorek and Mark performed controlled-potential electrolyses of anthracene in both anhydrous dimethyl sulfoxide and dimethyl sulfoxide + water media; they confirmed that the coulometric  $n$  values are 1 and 2, respectively, but electrolysis products were not identified. Wawzonek and Wearing [20] demonstrated that 9,9',10,10'-tetrahydro-9,9'-biphenanthrene is formed when phenanthrene is electrolyzed in dimethylformamide containing tetra-*n*-butylammonium iodide. Although a satisfactory explanation of the results seen in Figs. 1A and 1B requires further research, it is conceivable that the electrogenerated radical-anion ( $\text{Ar}^{\cdot-}$ ) of anthracene is protonated by diethyl malonate to yield the radical ( $\text{ArH}^{\cdot}$ ), which undergoes dimerization to afford a bianthracene.

In comparison with Figs. 1A and 1B, the cathodic peak currents in Fig. 1C are much larger. On the basis of our preliminary experiments, it is not yet possible to assess the relative importance of two opposing effects: (i) the ability of the protonated Nafion film to convert radical-anions ( $\text{Ar}^{\cdot-}$ ) into more easily reducible neutral radicals ( $\text{ArH}^{\cdot}$ ), which should increase the cathodic current — *if the radicals do not dimerize inside the Nafion layer* — and (ii) the probability of diminished mass transport of anthracene within the Nafion film, which should decrease the cathodic current.

#### *Cyclic voltammetric behavior of naphthalene*

Figure 2 reveals the cyclic voltammetric behavior of a 2 mM solution of naphthalene in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate at a glassy carbon electrode in the absence and presence of diethyl malonate as well as at a Nafion-coated electrode. In the absence of a proton donor, one-electron reduction of naphthalene to its radical-anion is a reversible process, even at a scan rate as low as  $20 \text{ mV s}^{-1}$  (Fig. 2A). However, when diethyl malonate is present (Fig. 2B), reduction of naphthalene is highly irreversible because its radical-anion is more basic and more completely protonated than the radical-anion of anthracene. Shown in Fig. 2C are cyclic voltammograms for naphthalene obtained with a Nafion-coated carbon electrode. At a scan rate of  $100 \text{ mV s}^{-1}$ , a small wave is seen for oxidation of the radical-anion; however, at slower scan rates ( $< 50 \text{ mV s}^{-1}$ ), the electrogenerated radical-anion is so effectively protonated in the Nafion film that the electron-transfer process is rendered irreversible. As discussed above in connection with the

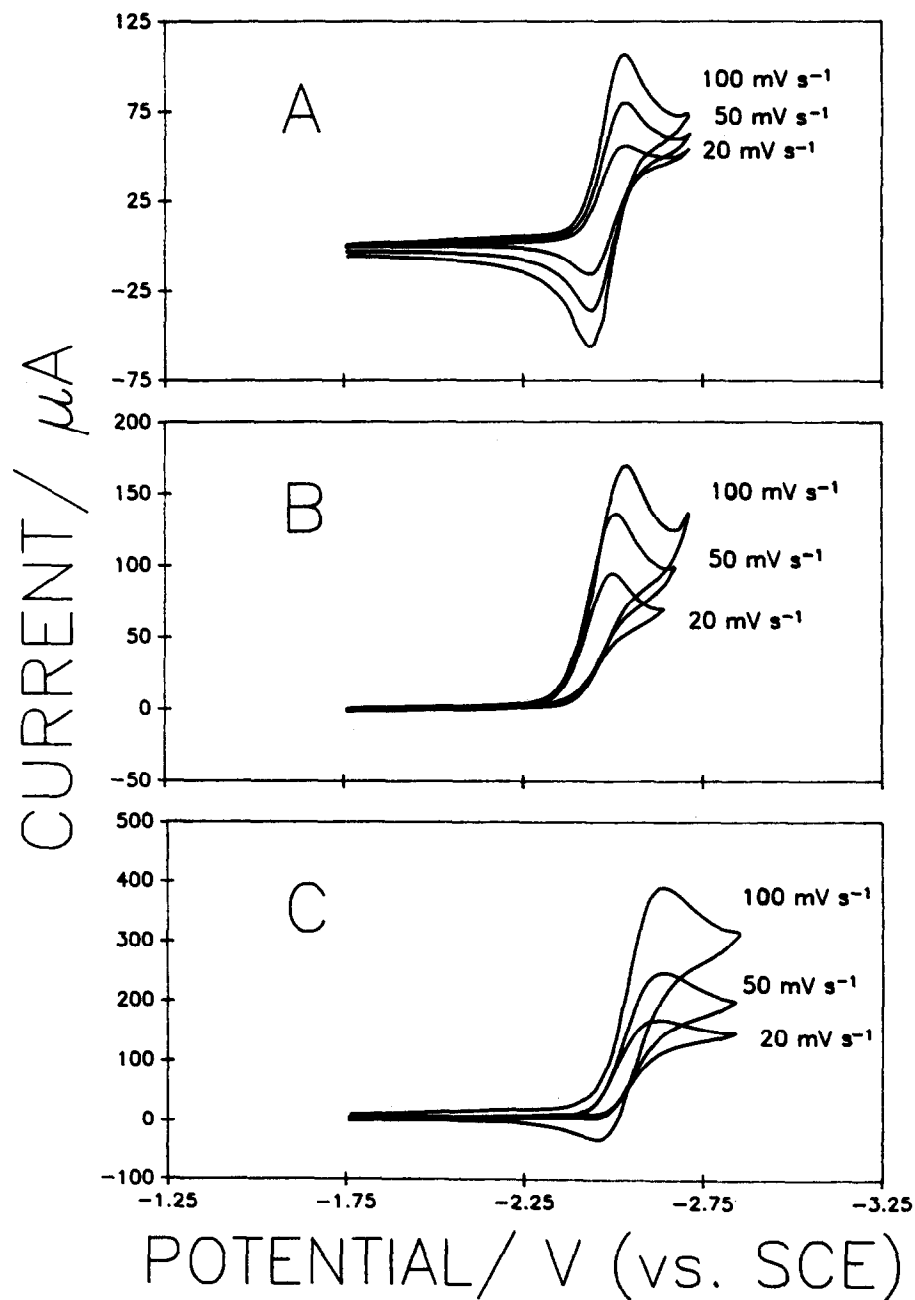


Fig. 2. Cyclic voltammograms for a 2.0 mM solution of naphthalene in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate. (A) Bare glassy carbon electrode. (B) Bare glassy carbon electrode in the presence of 20 mM diethyl malonate. (C) Glassy carbon electrode coated with Nafion in its protonated form.

electrochemical behavior of anthracene, the cathodic peak currents for naphthalene in Fig. 2C are unexpectedly high in comparison with those measured in Fig. 2B.

#### *Cyclic voltammetric behavior of 1,1,4,4-tetraphenyl-1,3-butadiene*

In an earlier investigation [21], we observed that a cyclic voltammogram for 1,1,4,4-tetraphenyl-1,3-butadiene at a hanging mercury drop in dimethylformamide containing tetra-*n*-butylammonium perchlorate exhibits three cathodic waves with peak potentials of  $-1.93$ ,  $-2.17$ , and  $-2.61$  V as well as an anodic peak at  $-1.85$  V; the first two reduction waves are attributable to formation of the radical-anion and dianion of the starting material, the third cathodic wave corresponds to reduction of 1,1,4,4-tetraphenyl-1-butene (an electrolysis product), and the lone anodic wave is caused by oxidation of the initially formed radical-anion.

Figure 3 illustrates cyclic voltammograms obtained with a glassy carbon electrode at a scan rate of  $200 \text{ mV s}^{-1}$  in a solution of 1,1,4,4-tetraphenyl-1,3-butadiene in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate. An experiment with a bare carbon electrode (Fig. 3A) provided a cyclic voltammogram showing three cathodic waves with peak potentials ( $-2.00$ ,  $-2.09$ , and  $-2.57$  V) similar to those reported previously [21]; there are tiny anodic waves at  $-2.02$ ,  $-1.86$ , and  $-1.52$  V, the first two of which are probably due, respectively, to oxidation of the dianion and radical-anion of the parent compound. In the presence of excess diethyl malonate (Fig. 3B), the first two cathodic waves merge, undoubtedly because the electrogenerated radical-anion is protonated to form the more easily reducible neutral radical, and no anodic waves are seen; furthermore, the peak at  $-2.51$  V is smaller with respect to the peak at  $-1.97$  V — compare Figs. 3A and 3B — because, in accord with earlier work, the yield of 1,1,4,4-tetraphenyl-1-butene formed from the starting material is lower (whereas the yield of non-electroactive 1,1,4,4-tetraphenyl-2-butene is higher) when a proton donor is present. Figure 3C reveals that, in contrast to the cyclic voltammogram depicted in Fig. 3A, reduction of 1,1,4,4-tetraphenyl-1,3-butadiene at a Nafion-coated glassy carbon electrode gives rise to a greatly diminished second wave for production of the dianion of the starting material; in addition, the third cathodic wave appears to be decreased slightly. It would be interesting to examine the results of preparative-scale electrolyses of 1,1,4,4-tetraphenyl-1,3-butadiene at large Nafion-coated electrodes to learn to what extent the distribution of products will differ from that obtained without a proton donor [21].

#### *Possible advantages and other applications of Nafion-coated electrodes*

Although we hope to characterize in quantitative detail the voltammetric response of Nafion-coated electrodes, when they are used as a source of protons for electrogenerated bases, we are especially interested in applications of such electrodes in organic electrosynthesis.

One advantage of the Nafion-coated electrode is that the source of protons is localized at the interface where reactive intermediates are generated. When diethyl malonate is used as a proton donor, its conjugate base can engage in undesired side

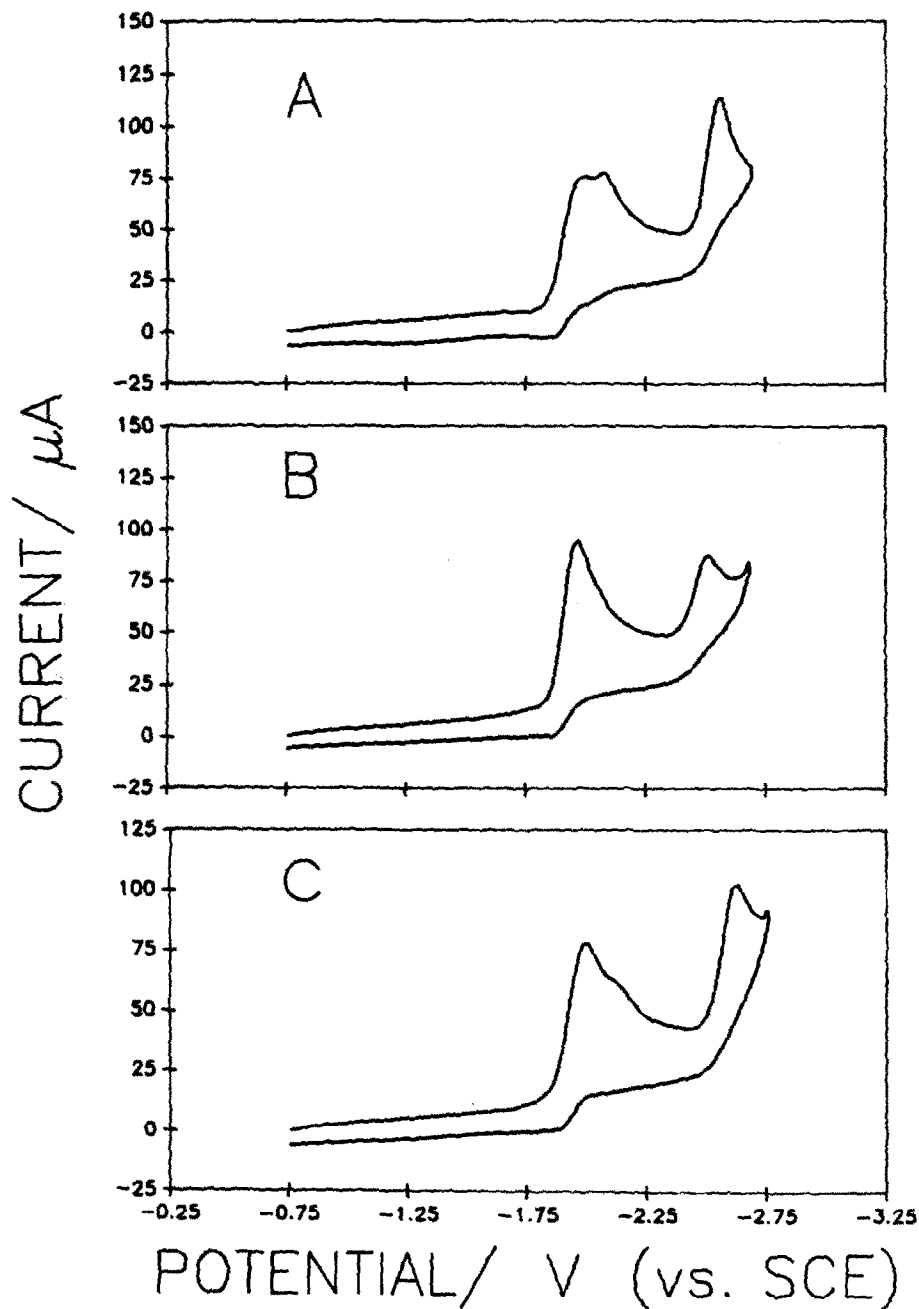


Fig. 3. Cyclic voltammograms recorded at a scan rate of  $200 \text{ mV s}^{-1}$  for a  $1.0 \text{ mM}$  solution of 1,1,4,4-tetraphenyl-1,3-butadiene in acetonitrile containing  $0.1 \text{ M}$  tetra-*n*-butylammonium perchlorate. (A) Bare glassy carbon electrode. (B) Bare glassy carbon electrode in the presence of  $20 \text{ mM}$  diethyl malonate. (C) Glassy carbon electrode coated with Nafion in its protonated form.



reactions in the bulk of the solution; for example, we have observed the formation of alkylated diethyl malonate species during the reductions of alkyl monohalides [17,22], acetylenic halides [23,24], and 1,10-dihalodecanes [25]. If one employs an electrode that is coated with Nafion in its deuterated form, it should be feasible to electrosynthesize a variety of deuterium-containing materials.

In recent years, we have investigated the electrochemical reduction of a number of phenyl-conjugated, unsaturated hydrocarbons, including 1,1,4,4-tetraphenyl-1,2-butadiene [21], 1,1,4,4-tetraphenylbutatriene [26], phenylpropadiene [27], 1-phenyl-1-hexyne [28–30], and 1-phenyl-1,2-hexadiene [29]. For these systems, pathways for reduction are inevitably complicated, and product distributions are profoundly influenced, by proton-transfer reactions in which the parent compound usually participates; such self-protonation reactions involving the parent molecule often promote isomerization of the starting material. It is worthwhile to consider the possibility that electrodes coated with Nafion in its protonated form can permit one to exercise additional control over the course of an electroorganic process in which proton transfer plays an important role.

We believe that the preceding kinds of applications, as well as the search for other non-aqueous solvent systems in which proton-bearing Nafion films on electrodes are stable, merit further attention.

## REFERENCES

- 1 I. Rubinstein and A.J. Bard, *J. Am. Chem. Soc.*, 102 (1980) 6641.
- 2 H.L. Yeager and A. Steck, *J. Electrochem. Soc.*, 128 (1981) 1880.
- 3 H.S. White, J. Leddy and A.J. Bard, *J. Am. Chem. Soc.*, 104 (1982) 4811.
- 4 C.R. Martin, I. Rubinstein and A.J. Bard, *J. Am. Chem. Soc.*, 104 (1982) 4817.
- 5 D.A. Buttry and F.C. Anson, *J. Am. Chem. Soc.*, 105 (1983) 685.
- 6 C.R. Martin and K.A. Dollard, *J. Electroanal. Chem.*, 159 (1983) 127.
- 7 D.A. Buttry and F.C. Anson, *J. Am. Chem. Soc.*, 106 (1984) 59.
- 8 M. Krishnan, X. Zhang and A.J. Bard, *J. Am. Chem. Soc.*, 106 (1984) 7371.
- 9 I. Rubinstein, *J. Electroanal. Chem.*, 176 (1984) 359.
- 10 F.C. Anson, Y.-M. Tsou and J.-M. Savéant, *J. Electroanal. Chem.*, 178 (1984) 113.
- 11 F.C. Anson, C.-L. Ni and J.-M. Savéant, *J. Am. Chem. Soc.*, 107 (1985) 3442.
- 12 K.-Y. Wong and F.C. Anson, *J. Electroanal. Chem.*, 237 (1987) 69.
- 13 W.J. Vining and T.J. Meyer, *J. Electroanal. Chem.*, 237 (1987) 191.
- 14 T.P. Henning, H.S. White and A.J. Bard, *J. Am. Chem. Soc.*, 104 (1982) 5862.
- 15 K. Shigehara, E. Tsuchida and F.C. Anson, *J. Electroanal. Chem.*, 175 (1984) 291.
- 16 K.L. Vieira and D.G. Peters, *J. Electroanal. Chem.*, 196 (1985) 93.
- 17 J.A. Cleary, M.S. Mubarak, K.L. Vieira, M.R. Anderson and D.G. Peters, *J. Electroanal. Chem.*, 198 (1986) 107.
- 18 J. Perichon in A.J. Bard and H. Lund (Eds.), *Encyclopedia of Electrochemistry of the Elements*, Vol. 11, Dekker, New York, 1978, pp. 71–161.
- 19 J.R. Jezorek and H.B. Mark, Jr., *J. Phys. Chem.*, 74 (1970) 1627.
- 20 S. Wawzonek and D. Warring, *J. Am. Chem. Soc.*, 81 (1959) 2067.
- 21 T.-Y.R. Chen, M.R. Anderson and D.G. Peters, *J. Electroanal. Chem.*, 197 (1986) 341.
- 22 D.M. La Perriere, W.F. Carroll, Jr., B.C. Willett, E.C. Torp and D.G. Peters, *J. Am. Chem. Soc.*, 101 (1979) 7561.
- 23 R.-L. Shao, J.A. Cleary, D.M. La Perriere and D.G. Peters, *J. Org. Chem.*, 48 (1983) 3289.

- 24 R.-L. Shao and D.G. Peters, *J. Org. Chem.*, 52 (1987) 652.
- 25 J.C. Bart and D.G. Peters, *J. Electroanal. Chem.*, in press.
- 26 T.-Y.R. Chen, M.R. Anderson and D.G. Peters, *J. Electroanal. Chem.*, 222 (1987) 257.
- 27 T.-Y.R. Chen, M.R. Anderson, S. Grossman and D.G. Peters, *J. Org. Chem.*, 52 (1987) 1231.
- 28 W.M. Moore and D.G. Peters, *J. Am. Chem. Soc.*, 97 (1975) 139.
- 29 J.Z. Stemple and D.G. Peters, *J. Org. Chem.*, in press.
- 30 J.Z. Stemple and D.G. Peters, *J. Electroanal. Chem.*, submitted.