

Preliminary note

POLYMER FILMS ON ELECTRODES

PART I. THE APPLICATION OF POLY(VINYLFERROCENE)-COATED
PLATINUM ELECTRODES AS REFERENCE ELECTRODES IN
ACETONITRILE

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INTRODUCTION

It is difficult to find good reference electrodes for many nonaqueous solvents such as acetonitrile (MeCN) [1, 2]. The aqueous saturated calomel electrode (aq. SCE) is sometimes used, but this electrode suffers from the existence of an unknown, and sometimes irreproducible, liquid junction potential between the aqueous and nonaqueous solutions. Furthermore contamination of the test solution by water, K^+ , and Cl^- can occur when the aq. SCE is employed. Nonaqueous reference electrodes have been proposed based on metal/metal ion systems, for example, the Ag/Ag^+ (0.01 M) ClO_4^- electrode in MeCN [1, 3, 4]. However such electrodes are inconvenient to construct and involve a liquid junction between test solution and reference electrode. Again contamination of the test solution (e.g. by Ag^+) is a possibility. Moreover neither the aq. SCE nor the metal/metal ion electrodes are convenient to use in an electrochemical cell on a vacuum line or in a glove box, which are the experimental arrangements most frequently employed for careful studies of highly purified aprotic solvents. These difficulties have led to the frequent use of quasi-reference electrodes (QRE). These are Pt or Ag wires immersed directly in the test solution which attain a moderately stable (although often not very reproducible) potential. The exact potential of the QRE is determined at the end of a series of experiments by voltammetric measurement of an added reference redox system (such as ferrocene/ferrocenium [5]) whose potential against a true reference electrode has been established. Recent experiments in these laboratories have demonstrated the stability and the rapid and reversible redox behavior of electrodeposited poly(vinylferrocene) (PVF) films on platinum electrodes (PVF/Pt) in MeCN [6, 7]. Such films are formed by electrodeposition of the oxidized form from CH_2Cl_2 solutions on a Pt electrode. Partially oxidized films, containing both the ferrocene (Fc) and ferrocenium (Fc^+) species show a constant and reproducible potential and can be employed as a reference electrode in MeCN. Details of the preparation and behavior of such a reference electrode is described herein.

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EXPERIMENTAL

Purification of the solvents and supporting electrolyte followed previously established procedures [8, 9]. Poly(vinylferrocene) was prepared according to the procedure of Chen, Fernandez-Refojo and Cassidy [10]. Vinylferrocene (Strem Chemicals) was vacuum sublimed once and azobis(isobutyronitrile) (Pfaltz-Bauer) was recrystallized once from methanol. All nonaqueous solutions were prepared in an inert atmosphere glove box and contained 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte.

The electrochemical instrumentation, cell design, and electrode have been previously described [7]. Positive feedback was employed in all electrochemical measurements made in nonaqueous solvents to compensate for solution resistance.

Preparation of PVF/Pt reference electrodes

Poly(vinylferrocene) was electrodeposited in its oxidized form as poly(vinylferrocenium) perchlorate onto a platinum disk electrode (area: 0.035 cm²) from a stirred CH₂Cl₂ solution containing ca. 0.5 mg ml⁻¹ of PVF and 0.1 M TBAP by maintaining the potential at +0.7 (vs. a silver wire QRE) without *iR* compensation for ca. 2–3 min. The working electrode was surrounded by a cylindrical platinum foil counterelectrode to achieve more uniform film deposition. The resulting films were ca. 2 μm thick (estimated as described in ref. 7 from the total quantity of adsorbed charge and the known molecular weight of the repeating unit).

The polymer-coated electrode was removed from the CH₂Cl₂ solution, shaken to remove any adhering solution and immersed in the 0.1 M TBAP/CH₃CN test solution. The potential of the reference electrode is established by

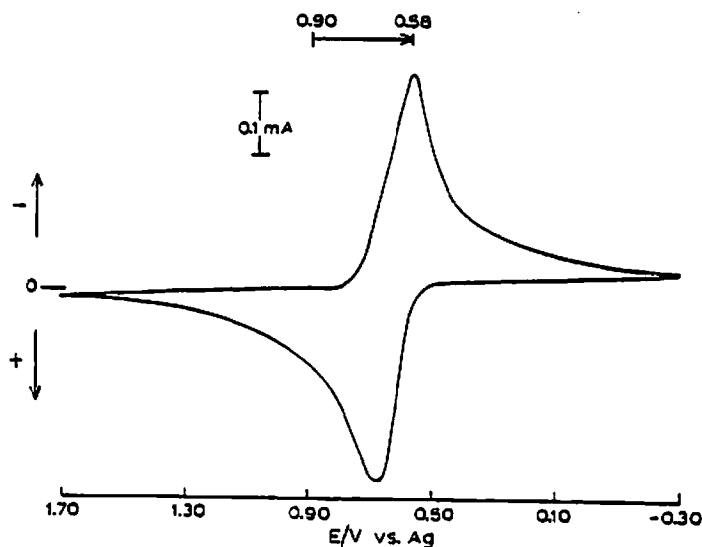


Fig. 1. Cyclic voltammogram of a 1.3 μm thick film of PVF on Pt at 0.1 V s⁻¹ vs. Ag QRE. To prepare the PVF/Pt reference electrode, the potential was stepped from +0.9 to +0.58 V.

partially reducing the film to produce an electrode in the Fc^+/Fc form. This was accomplished by first scanning the potential at the filmed electrode (vs. Ag-wire QRE) in order to locate the reduction peak (E_{pc}) (Fig. 1) (~ 0.6 V vs. QRE) and then stepping to E_{pc} (+0.58 V) and allowing the current to decay to background levels. This electrode could then be used directly in the MeCN solution as a reference electrode or removed and examined in various other solvents.

RESULTS AND DISCUSSION

MeCN solutions

The stability of the PVF/Pt reference electrode in MeCN was tested in a solution containing 0.1 M TBAP and 3.1 mM thianthrene (TH) by obtaining cyclic voltammograms for the oxidation of TH at a Pt electrode vs. this reference over a period of 21 h. The results (Table 1) demonstrate that the electrode was stable to within an average deviation of ± 2 mV over this time period. After 21 h the PVF/Pt electrode was oxidized back to the fully oxidized state; the charge required (1.03 mC) was within 5% of that originally consumed in the partial reduction (-0.98 mC). Based on previous measurements of the $HT^{\cdot+}/TH$ system [11], the potential of the PVF/Pt reference electrode in the half-oxidized state is 0.39 V vs. aq. SCE. Numerous previous experiments with PVF/Pt in MeCN solutions [7] have demonstrated the stability of both the reduced and oxidized forms of PVF and the reproducibility of the polymer reduction and oxidation waves over many cycles. Of course stability of the reference electrode requires that neither form be soluble and that the bulk test solution does not contain species which will oxidize PVF or reduce the oxidized polymer. Under the latter circumstances, the PVF/Pt wire would have to be isolated from the test solution in a separate chamber (with a porous Vycor, sintered-glass, or other similar reference electrode junction) containing only TBAP/MeCN.

TABLE 1

Stability of PVF/Pt reference electrode as determined by cyclic voltammetric studies of thianthrene^a

Solvent	Time/h	$(E_{pc} + E_{pa})/2$ /V vs. PVF/Pt
A. Acetonitrile	0	0.844
	0.2	0.838
	0.6	0.838
	1.7	0.838
	3.6	0.840
	21.0	0.838
B. Benzonitrile	0	0.922
	0.5	0.984
	1.7	0.999
	2.8	1.001
	22.7	0.942

^aSolutions contained 0.1 M TBAP and thianthrene (3.1 mM in MeCN, 3.5 mM in benzonitrile); Pt working electrode; scan rate 0.1 V s⁻¹.

Other solvents

The PVF/Pt reference electrode coated with PVF of the molecular weight employed here was less suitable for other solvents. In benzonitrile, the potential of the PVF/Pt electrode drifted over a period of 22 h (Table 1 B). This probably is caused by the gradual dissolution of the oxidized form of PVF. The reduced form of PVF was also found to be somewhat soluble in benzonitrile. Although the reduced polymer is insoluble in both methanol and DMF, the potential of the PVF/Pt electrode shifted negative with time. In DMF, a 520 mV shift in the reference potential occurred after only 15 min suggesting that poly(vinylferrocenium) perchlorate is very soluble in DMF. The change in the reference potential in methanol occurred more slowly than in DMF but after 4 h, it was still 58 mV.

In aqueous solution (1 M NaClO₄, 4.8 mM K₃Fe(CN)₆), the potential of the PVF/Pt electrode changed by +150 mV overnight even with deaeration and maintenance of a nitrogen atmosphere over the solution. When the electrode was removed from the solution and examined, it was observed that the film was green in color indicating that it had been oxidized.

In conclusion the PVF/Pt electrode appears to be a useful reference electrode in MeCN solutions. Although a ferrocene-based system is especially convenient, because the ferrocene/ferrocenium couple has been proposed as a reference redox couple in different solvents [5], other polymer electrodes, such as poly(vinylnitrobenzene) [12] or poly(vinylpyridine)-type [13] systems might also be useful. By using higher molecular weight polymer, solubility of the reduced and oxidized forms should be reduced, resulting in electrodes useful in a wider range of solvents. Similarly polymer electrodes produced by other means (e.g. dip or spin coating, covalent attachment) [12-17] might also prove to be more insoluble.

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