Short communication

Voltammetry in electrolyte-free liquids using a three-electrode probe with a sol–gel matrix

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1. Introduction

Electrochemical measurements in resistive media (e.g., in electrolyte-free liquids with low dielectric constants and in many solids) have become more common since the development of methodology and theory related to electrodes with surface areas below the 10^{-6} cm^2 level [1]. Interrogations of solids and of electroactive polymers by cyclic voltammetry are examples of areas of study that have utilized this methodology; reviews of these topics, [2, 3], are available. The commensurately low currents result in iR (ohmic) losses that do not obviate interpretation of the data. Bond and Lay [4] investigated the cyclic voltammetry of the ferrocene/ferricinium couple in acetonitrile in the absence of deliberately added supporting electrolyte using Pt and Au working electrodes with diameters in the 0.5–25 μm range. The expected sigmoidal current/voltage curves that result from hemispherical diffusion were observed, and Nernstian behaviour was suggested from E against log $(i_{limiting} - i)/i$ plots on the rising portion of the voltammogram. However, the oxidation and reduction curves did not coincide even at scan rates of 5 mV s^{-1}, which was attributed to influence of migration on the reduction of the charged ferricinium species.

A complementary approach is to use a cell design that does not require current flow through the sample matrix. In the early studies the working electrode was imbedded in an anion or cation exchange membrane that was used to separate the electrolyte-free sample liquid from an internal chamber that housed the reference and/or counter electrode in contact with an electrolyte-containing liquid [5, 6 and citations therein]. For example, Kaaret and Evans used a Nafion® membrane as a separator between an electrolyte and a sample phase comprising electrolyte-free water, hexane or acetonitrile [6]. Either Pt mesh imbedded in the Nafion® or Pt chemically deposited on Nafion comprised the working electrode. Experiments with perchloric acid as the internal electrolyte and a pH 10 solution of hydrazine in water as the sample demonstrated that the state of the membrane, which was highly acidic due to the cation-exchange nature of Nafion®, controlled the pH of the

working electrode. The assembly was used for the flow injection amperometric determination of various amines, phenols and quinones [6]. The signal was generated by oxidation under controlled potential conditions. Schiavon et al. [7] used a porous composite as a separator and working electrode to prepare a sensor for analytes in both gases and highly resistive liquids. The composite was a Teflon-reinforced Nafion® disc coated with a porous electrode material on the side facing the sample. The voltammetry of *p*-benzoquinone in hexane (with perchloric acid as the isolated electrolyte) resembled that for the analyte in an acidified nonaqueous solvent.

In the above barrier-type cell designs, the current path is partially through an aqueous electrolyte, which limits their robustness and range of applicability. An important extension was to use the same medium as the separator and the electrolyte, thereby allowing the elimination of a contacting liquid. Initial analytical tests of this concept used electrodes imbedded in Nafion® as the cell. Amperometric gas sensors, the designs of which are summarized in a recent review [8], for dioxygen [9], hydrogen [10], carbon monoxide [11] and an *N*-nitrosamine [12] are representative applications. A limitation was that the amperometric response was a function of humidity [13].

Solids prepared by sol–gel chemistry, which were first reported as solid electrolytes for voltammetric studies in 1990 [14], are alternatives to organic ionomers such as Nafion® as supports for electroanalytical measurements. Three-electrode cells prepared with silica sol–gels as the supporting electrolyte were employed for the voltammetric determination of gas-phase carbon monoxide [14], hydrogen peroxide [15], and monomethyl hydrazine [16]. In contrast to sensors with Nafion® as the solid phase electrolyte, a response that was independent of humidity over a wide range was observed with a sol–gel electrolyte [14]. Ionic bridges among the electrodes were provided by the electrolyte in the pore structure of the silica.

The present study was initiated to determine whether the three-electrode cell with a silica sol–gel as the electrolyte was suited to the voltammetric determination of analytes in liquids that did not contain added

electrolyte. The hypothesis was that the negative sites on the silica backbone will minimize the leaching of electrolyte from the pore volume of the solid into the contacting sample phase, thereby retaining ionic conductivity of the probe matrix. The investigation was a step toward a goal of making a robust probe for the voltammetric determination of redox-active components in aprotic solvents, an example of which is the determination of antioxidants (e.g., 2,6-di-*t*-butyl-4-methylphenol) in surrogate jet fuel (e.g., dodecane).

2. Experimental details

2.1. *Reagents*

The precursor to the silica sol–gel was tetraethyl orthosilicate (TEOS), 98% purity, obtained from Aldrich Chemical Company (Milwaukee, WI). House-distilled water, which was deionized with a Barnstead NANOpure II system, and Spectrophotometric Grade ethanol (Aldrich) were used as cosolvents in the preparation of the silica. The surfactant used in the preparation of the silica was Triton X-114 (Sigma Chemical Co., St Louis, MO). Ammonium hexafluorophosphate, >95% purity (Aldrich), was doped as an electrolyte into the silica during gelation. The analytes were ferrocene, which was purchased at 98% purity (Aldrich) and 2,6-di-*t*-butyl-4-methylphenol (i.e., butylated hydroxytoluene, BHT), a 99% pure reagent (Alfa Aesar Ward Hill, MA). The sample solvents were acetonitrile (anhydrous) and dodecane, (Aldrich) with respective purities of 99.8% and >99%. The electrode materials were purchased from Alfa Aesar at a minimum purity of 99.9%.

2.2. *Probe fabrication and application*

Figure 1 shows the cell design. Platinum wires (0.4 mm dia.) comprised the working and counter electrodes. The quasi-reference electrode was a 0.25 mm Ag wire. The electrodes were supported in a 3.5 mm plastic tube filled with an epoxy resin made by mixing 301A resin and 301B hardener (Epoxy Technology, Billerica, MA) in a 4:1 ratio by weight. The epoxy was cured for 24 h at room temperature, after which the surface was smoothed using 100 and 400 grit sandpaper (3M, St. Paul, MN) sequentially. The counter and reference electrodes were coplanar with the surface of the epoxy, whereas the working electrode protruded above this plane. The plane was coated with a silica sol–gel film, which was cast from 7 μL of sol. The silica sol consisted of 0.1 mL of TEOS, 9.0 mL of ethanol, 1.0 mL of water, 0.6 mL of water saturated with NH_4PF_6, and 1 mL of Triton X-114. The sol was magnetically stirred for 15 min prior to use for film formation. The gelation time was at least 1 h but not more than five days under ambient laboratory conditions. With longer exposures to air, cracking was an occasional problem (they can be stored indefinitely in water once the gelation is com-
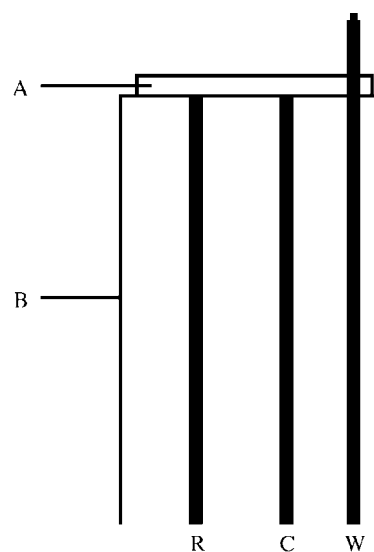

Fig. 1. Design of probe based on a silica sol–gel matrix. A, sol–gel film; B, plastic mold with epoxy filler; R, Ag quasi-reference electrode; C, Pt auxiliary electrode; W, Pt working electrode.

plete). A portion of the working electrode and the entire areas of the reference and counter electrodes were coated with silica by this procedure.

All electrochemical measurements were made with a model 630 electrochemical workstation from CH Instruments (Austin, TX). All potentials were measured and reported vs a Ag quasi-reference electrode.

3. Results and discussion

Cyclic voltammetry of $K_4Fe(CN)_6$ in water was performed using the probe in Figure 1. The voltammogram (Figure 2) suggested that the $Fe^{II,III}$ couple was reversible. The peak potential difference, 80 mV, was greater than the theoretical range, 57–60 mV (depending on the difference between the formal potential and the switching potential), which is consistent with some uncom-
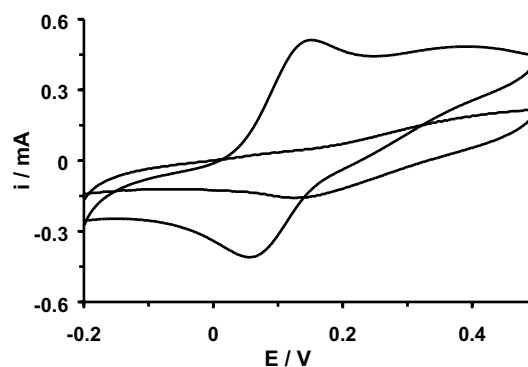

Fig. 2. Cyclic voltammetry of 1.0 mmol dm^{-3} $K_4Fe(CN)_6$ in water using the probe in Figure 1 as the cell. Background voltammogram (lower currents) obtained in water alone. Conditions: scan rate 100 mV s^{-1}; supporting electrolyte NH_4PF_6 entrapped in the pores of the silica matrix; initial potentials −0.20 V.

pensated iR loss in the cell. Also shown is the background voltammogram (probe inserted into water); the source of the anodic process near 0.4 V was not identified. The nature of the electrolyte in the silica had a profound influence on whether redox occurred. When the experiment was repeated with $MgCl_2$ rather than NH_4PF_6 as the electrolyte in the probe, a voltammogram was not observed. Apparently, the former salt leached from the silica, which made it nonconductive. This behaviour is strong evidence that the current path is primarily through the sol–gel matrix rather than the water, even though 1 mmol dm^{-3} $K_4Fe(CN)_6$ has a significant ionic strength. Further evidence for this model was the dependence of anodic peak current, i_{pa} on scan rate, v. A plot of i_{pa} vs $v^{1/2}$ was linear over the range 10 to 200 mV s^{-1}, which is indicative of a diffusion-limited current. A linear least squares fit of the data (five points) had $r^2 = 0.996$ and an ordinate intercept of 40 nA (i_{pa} ranged from about 0.5 to 2.5 μA). That the current was diffusion-limited supported the view that the path through the sample phase was not significant in that a contribution from migration would have been expected.

A more stringent test of the probe is to use a liquid phase with a dielectric constant lower than that of water in conjunction with a non-ionic analyte. With ferrocene, $Fe^{II}(Cp)_2$, as the analyte and acetonitrile as the solvent, cyclic voltammograms were obtained that were indicative of reversible charge transfer but with uncompensated iR loss perturbing the shape (Figure 3). Regarding the latter point, the difference in peak potential, ΔE_p, at a given v was a function of $Fe^{II}(Cp)_2$ concentration. At 100 mV s^{-1}, ΔE_p was 40, 80, 130 and 160 for 0.12, 0.25, 0.50 and 1.0 mmol dm^{-3} $Fe^{II}(Cp)_2$, respectively. The influence of v on ΔE_p followed the trend expected for this model; at 10, 220, 50, and 100 mV s^{-1} the peak potential differences were 160, 200, 260 and 320 mV when the concentration was 10 mmol dm^{-3} $Fe^{II}(Cp)_2$. However, the formal potential, which was taken as the average peak potential, was nearly constant; with the same sequence of v, the respective values were 0.25, 0.26,

0.26 and 0.28 V. The use of working electrodes with dimensions of micron level can alleviate the uncompensated iR loss problem; however, a three-phase boundary probe with these electrodes is difficult to fabricate.

Cyclic voltammetry at 100 mV s^{-1} was used to quantify $Fe^{II}(Cp)_2$ in acetonitrile with the sol–gel probe. A linear least squares fit of the anodic peak current to concentration over the range 0.05–1.0 mmol dm^{-3} (five points) yielded the following: slope, 2.5 nA (μ mol dm^{-3})$^{-1}$; standard deviation of the fit, ± 0.1 nA (μ mol dm^{-3})$^{-1}$; and r, 0.995. A detection limit of 10 μmol dm^{-3} was calculated as the concentration that yielded a signal of three times the standard deviation of the blank.

The sol–gel probe was used to determine BHT in acetonitrile on the basis of its oxidation by square wave voltammetry. Voltammograms for 0.5 mmol dm^{-3} BHT were obtained at an amplitude of 50 mV and a frequency of 1.0 Hz. A peak at 1.45 V was developed for the oxidation of BHT. Overlap of the background process with BHT oxidation compromised the linearity of the method. A linear least squares fit of the current at 1.45 V against concentration over the range 0.12–2.0 mmol dm^{-3} BHT (five points) yielded the following: slope, 0.84 nA (μmol dm^{-3})$^{-1}$; standard deviation of the fit, ± 0.1 nA (μmol dm^{-3})$^{-1}$; and r, 0.982. The background process also influenced the detection limit; a value of 40 μmol dm^{-3} was calculated using the previously stated criterion.

Preliminary experiments were performed in dodecane, which was selected because it is a jet fuel surrogate. The test compound was $Fe^{II}(Cp)_2$. At a scan rate of 5 mV s^{-1}, oxidation and reduction peaks were developed at 0.65 and 0.55 V, respectively, with 10 mmol dm^{-3} $Fe^{II}(Cp)_2$ (Figure 4). The formal potential taken as the average peak potential, 0.60 V, is near the value reported for the $Fe^{II,III}(Cp)_2$ couple in nonaqueous solution in the presence of supporting electrolyte, 0.45 V vs SCE [17]. The ratio of the anodic to cathodic peak currents, 0.89, was near the theoretical value of 1.0 for reversible, diffusion-limited charge transfer. The departure from
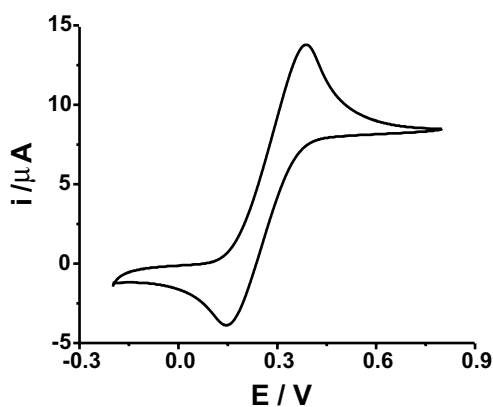

Fig. 3. Cyclic voltammetry of ferrocene, $Fe^{II}(Cp)_2$, in acetonitrile with the probe in Figure 1 as the cell. Conditions: 10 mmol dm^{-3} $Fe^{II}(Cp)_2$; scan rate 50 mV s^{-1} (scan initiated at −0.25 V).
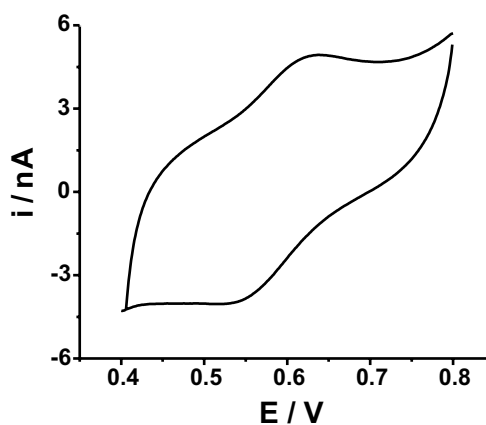

Fig. 4. Cyclic voltammetry of ferrocene, $Fe^{II}(Cp)_2$, in dodecane with the probe in Figure 1 as the cell. Conditions: 10 mmol dm^{-3} $Fe^{II}(Cp)_2$; scan rate 5 mV s^{-1} (scan initiated at −0.40 V).

idelity was probably due to measurement problems related to the background current, which was about twice the peak current under these conditions.

4. Conclusion

The study demonstrates that a solid-state, three-electrode probe based on a silica sol–gel matrix is suited to the voltammetric interrogation of liquids in the absence of added supporting electrolyte. The oxidation of $Fe^{II}(Cp)_2$ by cyclic voltammetry in acetonitrile and dodecane was apparently reversible; however, uncompensated iR loss caused the peak potentials to differ by more than the theoretical value. The oxidation of BHT in acetonitrile was demonstrated. Square wave voltammetry permitted the determination of this analyte down to 40 μmol dm^{-3}. The application of the probe to determination of BHT and related antioxidants in low dielectric constant solvents such as dodecane is the long term goal of this study. Presently, we are investigating modified probe designs that will give lower background currents in such solvents, thereby facilitating electroanalytical applications.

Acknowledgements

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