

Metal/Polypyrrole Quasi-Reference Electrode for Voltammetry in Nonaqueous and Aqueous Solutions

Jalal Ghilane,[†] Philippe Hapiot,[‡] and Allen J. Bard^{*†}

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, and Sciences Chimiques de Rennes, UMR CNRS–Université de Rennes 1 N° 6226, (Equipe MACSE), Campus de Beaulieu, Bat 10C, 35042 Rennes Cedex, France

As an alternative to the usual commercial reference and quasi-reference electrodes (QREs), we propose metal (Pt, stainless steel) coated with partially oxidized polypyrrole as a QRE. The electrode is easily fabricated by cyclic voltammetry (CV) with the metal electrode in an acetonitrile or CH₂Cl₂ solution of 10 mM pyrrole containing 0.1 M Bu₄NPF₆. These QREs were more stable than the widely used metal (e.g., Ag, Pt) wire QRE as demonstrated by testing in several aqueous and organic media, with the stability checked by CV with ferrocenemethanol as the redox species. The results obtained demonstrate good stability of these QREs over a period of 1 day and relatively reproducible potential in a given solvent and supporting electrolyte. This electrode has the advantage that it does not contaminate the test solution with ions or solvent from a usual liquid electrolyte (e.g., the KCl in an Ag/AgCl). It is also simple to fabricate very small electrodes for use in nanocells, e.g., in scanning tunneling and electrochemical microscopy.

The reference electrode (RE) often causes difficulties in electrochemical measurements, especially in nonaqueous solvents such as acetonitrile (MeCN), and there is continual interest in developing alternatives to the REs currently used. It is difficult to find a stable RE that can be used for both organic and aqueous solutions. The aqueous saturated calomel electrode (SCE) is a widely used RE,¹ as are the standard hydrogen electrode (SHE) and the Ag/AgCl electrode. However, use of these electrodes in a nonaqueous solvent electrochemical cell suffers from undesirable liquid junction between the aqueous and nonaqueous phases of unknown potential, as well as the problem of diffusion of water and ions from the RE into the test solution, leading to unacceptable contamination and sometimes fouling of the RE liquid junction. In general, the formation of a liquid junction potential at the boundary between the two solutions causes an unknown, and not necessarily constant, potential drop.² Nonaqueous REs have been proposed based on metal/metal ion systems, for example, the Ag/Ag⁺ ClO₄⁻ (0.01 M) electrode in the organic solvent.³ However,

such electrodes are inconvenient to construct, involve a liquid junction between the test solution and the RE, and most importantly tend to contaminate the test solution, e.g., with Ag⁺. Moreover, the SCE, SHE, and metal/metal ion electrodes are not convenient for use in an electrochemical cell on a vacuum line or in a glovebox, which are the experimental arrangements most frequently employed for careful studies of highly purified aprotic solvents.

Because of such problems with conventional REs, quasi-reference electrodes (QREs), such as silver or platinum wires immersed directly in the test solution, are frequently employed and these largely eliminate the problems associated with a liquid junction and contamination. However, electrodes of this type usually exhibit poorly defined fixed potentials and their potential often drifts with time during a series of measurements, e.g., because of the formation of surface oxides.^{4,5} While they can be calibrated by voltammetry of a known redox couple, frequently ferrocene/ferrocenium, which is usually added to a test solution at the end of a series of experiments, this does not compensate for any drift in the QRE during a series of trials. QREs are also not useful in bulk electrolysis experiments, where the solution composition undergoes large changes during the experiment.

Another issue is the size and ruggedness of the RE. For example, in recent years, considerable progress has been achieved in the construction of potentiometric sensors in terms of miniaturization, disposability, and internal solution-free construction. However, classical REs based on Ag/AgCl or Hg/Hg₂Cl₂ still dominate. The excellent stability of these highly reliable electrodes and the firm thermodynamic basis for their potentials often outweigh the serious disadvantages of the presence of a liquid junction and the requirement of refilling and maintenance of this liquid, as well as the restriction of working position. These REs are also difficult to miniaturize and hence are inconvenient to use in very small cells, such as those for scanning electrochemical microscopy (SECM) and scanning probe microscopy (SPM).

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* To whom correspondence should be addressed. E-mail: ajbard@mail.utexas.edu.

[†] The University of Texas at Austin.

[‡] UMR CNRS–Université de Rennes.

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Therefore, there has been interest in novel REs, with an emphasis on solution- and maintenance-free arrangements, compatible with miniature, all-solid-state sensors, as reviewed recently.⁶ Generally, liquid-free REs are based on solid conducting materials and either a reversible redox buffering system or a membrane nonselective to ions, to try to maintain a constant potential, independent of changes in the sample medium. Some examples are Ag/Ag⁺ with poly(ethylene oxide)⁷ or Al₂O₃⁸ as a solid electrolyte and an Ag/AgX (sparingly soluble) system in photopolymerized hydrogels^{9,10} or screen-printed electrodes with Ag/AgCl.¹¹ An interesting concept of a one-step production of miniaturized screen-printed REs, with significant stability, was presented recently.¹² One method to obtain stable and constant potentials is the use of cation/anion- or polyion-sensitive, solvent-processible polymer (e.g., silicon rubber or polyurethane type) membranes,¹³ utilizing the potentiometric insensitivity of the membrane to common ions.¹⁴ An early report described an RE for MeCN and other nonaqueous solutions based on a film of poly(vinylferrocene) (PVFc) and the PVFc/PVFc⁺ couple. This RE was stable in MeCN for up to 21 h, but unstable in aqueous solutions.¹⁵ A quasi-reference electrode based on a Prussian blue coating on a platinum wire was also used as a RE in MeCN over a wide range of temperatures.¹⁶ In another approach a polymer, like polypyrrole (PPy), has been used to immobilize a redox species in a RE, e.g., a PPy–mercury/mercurous chloride-coated glassy carbon electrode, with mercury deposited into the PPy film.¹⁷ Similarly a PPy/Ag/AgCl system has been described.¹⁸ The open circuit potential of this electrode showed a strong dependence on the concentration of the supporting electrolyte and did not produce an RE with a constant potential. Bilayers of conducting polymers, from the point of view of application in REs, have also been studied.¹⁹ Due to mixed electronic/ionic conductivity and redox properties, conducting polymers appear to be good candidates for constituents in solution-free REs, although such electrodes have not been studied very extensively.

Conducting polymers with conjugated double bonds have attracted considerable attention in recent years as advanced materials. Among these conducting polymers, PPy is a promising material for several applications because of its good stability and simple electrochemical preparation. Pyrrole was chosen for a QRE for several reasons. First, PPy can be prepared in a one-step

process by electrochemical oxidation of pyrrole on different materials²⁰ in both aqueous²¹ and aprotic solutions.²² The electrochemical polymerization of pyrrole has been investigated intensively since Diaz et al. produced electrochemically free-standing PPy films.²³ Second, the resulting film is generally homogeneous and adheres strongly to the electrode surface. Third, it is an electrical conductor and its thickness can therefore be controlled by the electrolysis conditions. The oxidized form of the polymer is positively charged and requires the incorporation of doping anions to maintain its electroneutrality.²⁴ This last property has been widely exploited to confer new properties on the polymer and give wider applications, for instance, in electrocatalysis,²⁵ energy storage,²⁶ controlled release of chemicals,²⁷ or electroanalysis.²⁸ However, only redox polymer (not conducting polymer) modified electrodes have been used as REs.^{15,29}

In this paper, we present electrochemical solid-state electrodes, based in use of metal (Pt or stainless steel) coated with partially oxidized PPy, which can be used in both aqueous and aprotic media and does not suffer some of the disadvantages of conventional QREs, as described above, such as fragility and size limitations. Most important is the absence of any liquid system component, i.e., the inner electrolytic solution, results in low maintenance.

EXPERIMENTAL SECTION

Chemicals. All chemicals were used as received and purchased from Aldrich, unless indicated otherwise. The redox couple for cyclic voltammetry (CV) experiments was ferrocenemethanol (FcMeOH, 97%), 1 mM in 0.1 M KCl aqueous solution. Deionized water, 18 MΩ·cm, was obtained with a Milli-Q water system (Millipore). Nonaqueous solutions of FcMeOH were prepared at 1 mM concentration in 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 98%) as supporting electrolyte in different solvents: MeCN, dimethylformamide (DMF), and mixture benzene/MeCN (2:1). Pyrrole (monomer) 99% from Aldrich was used as received to prepare PPy films.

Electrochemical Measurements. Electrochemical measurements were performed with a bipotentiostat in the CHI model 660 electrochemical workstation (CH Instruments, Austin, TX). The input impedance of the reference electrode lead is 10¹² Ω. For CV experiments, a conventional three-compartment sealed glass electrochemical cell was used.

RESULTS AND DISCUSSION

Preparation of the Pt/Polypyrrole Film. Polymerization of pyrrole was carried out electrochemically in a three-electrode cell

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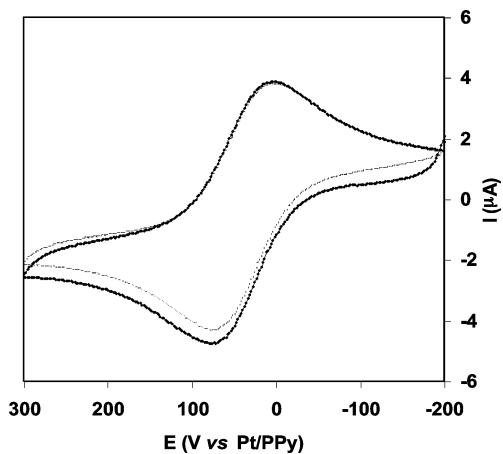


Figure 1. Cyclic voltammetry onto gold working electrode in solution containing 0.001 M FcMeOH and 0.1 M KCl in water. Solid line, first cycle; dotted line, after 12 h. Scan rate, 0.1 V/s.

with Ag/AgCl QRE, carbon counter, and platinum wire (0.5-mm diameter) working electrodes. The PPy film was electrodeposited onto Pt in a solution containing 0.1 M TBAPF₆ and 0.01 M pyrrole in MeCN or CH₂Cl₂ at room temperature. The nature of the supporting electrolyte used during the electropolymerization is important, because the anion can be exchanged and also the structure of the film depends strongly of the size of the ions incorporated during the synthesis.³⁰ The electrodeposition of PPy was carried out by sweeping the potential at 0.1 V/s over the potential range -0.6 to 1.2 V versus the Ag/AgCl for repetitive scans (50 cycles). The shape of the curve was the same as described previously.³¹ After a few cycles, the black PPy film became visible on the Pt wire. During the final scan, the working electrode was disconnected at a potential of ~0.4 V versus Ag/AgCl and the bipotentiostat was turned off. At this point, the PPy was partially oxidized to produce a film of PPy/PPy⁺PF₆⁻ on the Pt. The polymerization charge was ~360 mC/cm², corresponding to a film thickness of ~40 μm.³² The color of the PPy film depended on the thickness and varied from dark green to black in the doped state on the Pt substrate. After electropolymerization, the electrode was rinsed with water. The PPy film was checked using scanning electron microscopy, which showed homogeneous films on the Pt.

Study of Pt/PPy Film RE. To check the stability of the Pt/PPy RE, we tested it in different solutions, organic and aqueous, containing supporting electrolyte and FcMeOH as redox species using CV. The choice of FcMeOH as the redox couple is justified by its solubility at the millimolar concentration level in both aqueous and many organic solvents. In all tested solutions, the redox couple was well behaved and exhibited the typical features of a reversible CV.

(a) Aqueous Solutions. Figure 1 shows a typical voltammogram of FcMeOH in a three-electrode cell with a gold working electrode (2-mm diameter), Pt/PPy QRE, and carbon counter electrode in a solution 0.1 M KCl as supporting electrolyte and 1

Table 1. Stability of Pt/PPy QRE As Determined by CV of FcMeOH^a

solvent	time/h	$E_{1/2}/V$ vs Pt/PPy
DMF	0	0.2040
	3	0.2053
	7	0.2059
	24	0.2138
acetonitrile	0	0.0896
	3	0.0914
	7	0.0914
	24	0.0945

^a Solutions contained 0.1 M Bu₄NBF₄ and 1 mM FcMeOH; gold as working electrode; scan rate, 0.1 V/s.

mM FcMeOH. The $E_{1/2}$ of the mediator (taken as the average of the cathodic and anodic peak potentials) was 0.041 V versus Pt/PPy.

In Figure 1, we show two CV curves, the first taken at the beginning of the experiment and the other under the same conditions after the electrodes had remained in the cell for 12 h. The two curves are very close to one another, and the peak potentials were stable to within an average deviation of 2 mV over the 12-h period. Moreover, when a separate CV was carried out after one week, with the same Pt/PPy electrode after washing with water and kept in air without any protection, there was only a small shift of the peak potential of FcMeOH (~10 mV). These results clearly demonstrate the stability of Pt/PPy as a QRE in aqueous solution, with a good stability over 1 week.

From the above results, we place the potential of Pt/PPy in 0.1 M KCl as -0.189 V versus SCE or +0.052 V versus NHE.

SCE	Ag/AgCl, KCl saturated	Pt/PPy	NHE
0	-0.045	-0.189	-0.241

Potentials of QRE in aqueous 0.1 M KCl solution

(b) Nonaqueous Solvents. Again FcMeOH was used as the redox species to examine the stability of the Pt/PPy QRE with different organic solvents containing 1 mM FcMeOH with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. Carbon and gold were used as counter and working electrodes, respectively. Table 1 illustrates the change in the $E_{1/2}$ of FcMeOH as a function of the experimental time duration and solvent, DMF or MeCN. If we compare the different values of $E_{1/2}$, good stability over several hours is found. This stability was maintained for several days. The variation of $E_{1/2}$ with the time was less than 5 mV after 1 day. In addition, the results reported in Table 1 show stability of the QRE in both solvents. These results display again good stability of Pt/PPy in organic media, with no visible degradation of the film polymer or significant drift (<10 mV) over 3 days.

Stability of the Pt/PPy QRE was also observed in other organic solvents, such as a 1:2 mixture of MeCN and benzene, and tetrahydrofuran. Moreover, several redox mediators with an $E_{1/2}$ range of -1.5 to 0.3 V versus Pt/PPy were used in both oxidation and reduction CV (with the open circuit potential of the solution and CV scans starting near 0 V), and the results observed agreed with the results described with FcMeOH.

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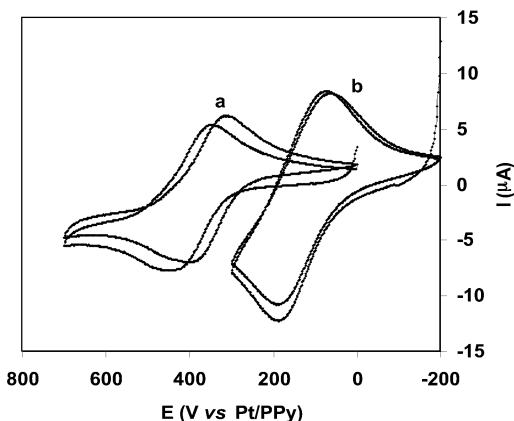
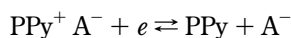


Figure 2. Cyclic voltammetry on gold electrode in solution containing 0.1 M Bu_4NBF_4 and 1 mM FcMeOH in DMF with a Ag wire as QRE (a) first scan and the 50th cycle. Similar cell with a stainless steel/PPy as QRE (b) first scan and the 1000th cycle.

Stainless Steel/PPy RE. The polymerization of PPy can be carried out with a number of metals, and we thought it of interest to see how a PPy film on a stainless steel wire behaved as a QRE. The procedure to produce the PPy film was the same as that with the Pt wire. After formation in MeCN, the stainless steel wire coated with PPy was rinsed with water and checked in both aqueous and organic media using FcMeOH CV, as before. Figure 2 compares the CV of FcMeOH on a gold working electrode in a solution containing 0.1 M Bu_4NBF_4 and 1 mM FcMeOH in DMF with a stainless steel/PPy QRE and a similar cell with a Ag wire QRE.

When CV was carried out with a Ag wire as the QRE (Figure 2a), there was a large drift in the potential (>56 mV) between the first and the 50th cycle, demonstrating that the Ag wire used as the QRE was not very stable. However, CV carried out under the same conditions, but with the stainless steel/PPy as the QRE (Figure 2b), showed a drift of the peak potential between the first and the 1000th cycle of <3 mV, demonstrating superior stability. Other metals would probably work as well in nonaqueous solvents. The low drift in potential also suggests that corrosion of the stainless steel by solvent penetrating the PPy layer does not appear to be an important factor. Even when the solvent was aqueous 1 M H_2SO_4 , we did not see any affect of corrosion after immersion for several hours, suggesting low permeability of the PPy layer on the metal surface.

Effect of Solution Anion. The Pt/PPy electrode is poised by the half-reaction



with the potential governed by the appropriate Nernst equation of the form

$$E = E^\circ + (RT/F) \ln[a_{\text{PPyA}^-}/a_{\text{PPy}^+} a_{\text{A}^-}]$$

This suggests that the potential of the electrode should depend on the nature of the anion, A^- , that can exchange into the film from the supporting electrolyte. To study this effect, the open circuit potential of a Pt/PPy electrode, formed in MeCN with PF_6^-

counterion, was studied in several aqueous solutions containing different anions. The results are given in Table 2. The Pt/PPy reference electrode was immersed for 15 min in the solution before measurements.

As expected, there is a shift in the potential of the RE with electrolyte, generally with the expected trend of tighter bonding with the anion resulting in a negative shift in potential. However, the stability should be good in all electrolytes. For example, the Pt/PPy QRE was also tested in a silver plating solution containing 1 M KCN, 0.3 M K_2CO_3 , and 0.2 M AgCN in water, noting the potentials for silver plating and stripping, and after repetitive CV scans over a 5-h period, the electrode showed stability similar to that found in KCl.

Effect of Solution Cation. In a similar way, we investigated the potential and stability of a Pt/PPy QRE with the nature of the supporting electrolyte cation by examining the potential for FcMeOH oxidation at a Pt electrode in aqueous solution. The change in the $E_{1/2}$ of FcMeOH and the open circuit potential of Pt/PPy versus SCE, as a function of the nature of the supporting electrolyte cation is given in Table 3.

If we compare the values of $E_{1/2}$ given in Table 3, we find that the supporting electrolyte cation only slightly affects the values of $E_{1/2}$, and the change of the potential observed in changing from Li^+ to K^+ is less than 6 mV. Thus, the potential of Pt/PPy is relatively independent of the nature of the supporting electrolyte alkali metal cation.

After these tests, the Pt/PPy was tested in the same solution by measuring the value of its open circuit potential versus an aqueous SCE reference electrode with similar results (Table 3). After these experiments with the Pt/PPy in LiBF_4 , the Pt/PPy was immersed again in aqueous KBF_4 solution and the open circuit value was 0.2253 V versus SCE, demonstrating an absence of history effects and the rapid equilibration of this QRE.

Effect of Solution Redox Potential. The solution redox potential, which is a function of the concentrations and formal potentials of the various redox species in the solution, can affect the potential and stability of the Pt/PPy QRE by changing the ratio of PPy and PPy^+ activities in the Nernst equation. To examine this effect, the QRE was tested in aqueous solutions with very positive ($\text{KMnO}_4/0.1$ M KCl) and very negative ($\text{V(II)}/0.1$ M KCl) potentials. Under these conditions, the measured OCP was 0.387 and -0.4 V versus SCE for KMnO_4 and V(II), respectively. Thus, total conversion of the film to either PPy in strongly reducing media or to PPy^+ in strongly oxidizing media affects the QRE potential. In a reducing medium, the color of the PPy film changed from black to blue. The PPy film also turned to blue by washing with aqueous ammonia, which is oxidized by PPy^+ , followed by final washings with water for 4 h, indicating the formation of undoped PPy. The undoped Pt/PPy QRE, obtained by washing a doped PPy film in aqueous ammonia and water, was tested in a solution containing FcMeOH. The CVs recorded show poor stability of Pt/PPy QRE, and if we compare the $E_{1/2}$ value of FcMeOH, we observe a small drift after 1 h of less than 5 mV. However, after 2 h, a large drift (~ 30 mV) of the $E_{1/2}$ value was observed. After 1 day, the drift of the potential was 120 mV compared to the first scan. These results indicate the instability of an undoped Pt/PPy QRE compared with a doped one.

Table 2. Open Circuit Potential (OCP) of Pt/PPy vs SCE as a Function of the Supporting Electrolyte Anion in Aqueous Solution

supporting electrolyte (0.1 M)	K ₂ SO ₄	KBF ₄	KPF ₆	KCl	KClO ₄	KBr	KF	K ₂ CO ₃	KCN
OCP of Pt/PPy (V vs SCE)	0.270	0.226	0.226	0.186	0.175	0.173	0.151	0.074	0.039

Table 3. Stability of Pt/PPy QRE As Determined by CV of FcMeOH and Open Circuit Potential (OCP) of Pt/PPy vs SCE as a Function of the Supporting Electrolyte Cation in Aqueous Solution

supporting electrolyte 0.1 M	$E_{1/2}/V$ vs Pt/PPy	OCP of Pt/PPy/V vs SCE
KBF ₄	0.056	0.2260
NaBF ₄	0.054	0.2345
LiBF ₄	0.060	0.2318

The Pt/PPy QRE was also tested in an aprotic solvent (1 mM naphthalene and 0.1 M TBAPF₆ in MeCN). The recorded CV showed a reversible system at -2.745 V versus Pt/PPy, with the $E_{1/2}$ remaining at the same value for continuous scanning. The Pt/PPy QRE was stable for over 4 h with a drift of the naphthalene $E_{1/2}$ of less than 3 mV. These results demonstrate good stability of the Pt/PPy QRE in an organic solvent with a mediator that generates a product with a very negative potential, as long as the solution potential where the QRE is located does not change appreciably. However, during bulk electrolysis, the QRE is not stable. For example, the OCP of the Pt/PPy QRE was 0.2 V versus SCE in the naphthalene solution. The Pt/PPy QRE was then removed and replaced by an Ag/AgCl RE and the working electrode held at a potential at -2.6 V for 1000 s to generate the radical anion of naphthalene (Np^{•-}). After this process, the color of the solution changed to green indicating the formation of Np^{•-} and a strongly reducing solution. The OCP of this solution when measured with Pt/PPy was now -0.28 V versus SCE, showing the effect of PPy⁺ reduction and in agreement with the effect

observed with V(II). Thus, the Pt/PPy QRE is less useful in strongly reducing or strongly oxidizing media and would not be useful in many bulk electrolysis experiments (as is true for most QREs).

CONCLUSION

The Pt/PPy electrode appears to be a useful RE in both aqueous and organic solvent solutions. This RE exhibits good stability over several days in different media and has several advantages compared with conventional RE, like the SCE and Ag/AgCl electrode. Pt/PPy is a solid-state liquid-free RE, eliminating problems related to the presence of liquid junction, such as contamination of test solution. The electrode is easy to fabricate, and the PPy film can be formed on different metals, such as stainless steel. The electrode can also be made very small for use in nanoscale analytical devices and in SECM and electrochemical SPM techniques. Moreover, these electrodes could be useful at higher temperatures and over a wide pressure range, as well as the measurements in a drybox and for novel solvents, such as ionic liquids.

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