

Investigations of the feasibility of constructing a polypyrrole-mercury/mercury chloride reference electrode

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A polypyrrole-mercury/mercury chloride reference electrode was initially constructed by *in situ* electropolymerization of pyrrole on a mercury pool anode in a 0.5 M sodium *para*-toluene sulfonate and 1.0 M sodium chloride mixture solution. However, in this procedure, insufficient amount of mercury was incorporated in the polypyrrole film for reaction with chloride ions to yield a mercury/mercury chloride half cell. Alternatively, a polypyrrole film was galvanostatically deposited on a glassy carbon electrode in the presence of sodium *para*-toluene sulfonate. Mercury was electrochemically deposited from mercury(I) nitrate at the polypyrrole-coated electrode. The resulting film was deprotonated in 5 M NaOH. Cyclic voltammetry was then carried out in 10 M HCl in order to exchange the *para*-toluene sulfonate ions with chloride ions and to oxidize mercury for the formation of mercury chloride within the film. A reproducible null potential difference was obtained when the polypyrrole-mercury/mercury chloride electrode was employed as an indicator electrode against a saturated calomel reference electrode in saturated potassium chloride solution. © 1997 Elsevier Science Ltd.

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Introduction

Polypyrrole is one of the most frequently researched polymers. This stems partly from the ease of its synthesis in a doped form by electropolymerization as a free standing film, its relatively stable conductivity compared to other conducting polymers, and the ready commercial availability of many of its derivatives. Many applications of polypyrrole-modified electrodes in electroanalysis have now been reported^{1–13}. Ge and Lin¹⁴ constructed a polypyrrole-coated carbon electrode, the electrical resistance of which was found to vary as a function of hydronium ion. This electrode was then shown to act as a pH indicator electrode. In other investigations, polypyrrole often acts as a transduction matrix support enabling the desired chemical reactions to take place on the electrode surface prior to electrode reactions. For example, based on specific metal ion–ligand interactions, a ligand is being incorporated into the polypyrrole backbone, followed by exposure of the resultant electrode assembly to the targeted metal ion analytes. Hence, by *in situ* electropolymerization of pyrrole on a glassy carbon electrode in the presence of the anionic complexing ligand dihydroxyanthraquinone sulfonate¹, the polypyrrole-coated electrode was shown to exhibit better sensitivity for Cu²⁺ relative to Cu⁺. Alternatively, by functionalizing pyrrole itself before electropolymerization, 3-substituted polypyrroles with aza crown ethers of variable cage size² were shown to exhibit electrochemical selectivity towards Li⁺, Na⁺ and K⁺.

In the parallel work aimed at developing enzyme-based biosensors, by *in situ* electropolymerization, Adejolu *et al.* incorporated the enzyme urease³ and

sulfite oxidase⁴ into a polypyrrole film to construct a potentiometric biosensor for urea and an amperometric biosensor for sulfite determination, respectively. On the other hand, Yon-Hin and Lowe⁵ employed a carbodiimide coupling reaction to modify glucose oxidase with 3-carboxymethyl pyrrole, which was then copolymerized with pyrrole monomers on a platinum electrode to develop a biosensor for glucose. Such a biosensor was shown to exhibit a high immobilized enzyme activity. In addition, polypyrrole also provided a suitable matrix support for antibody–antigen interactions on an electrode surface. By incorporating anti-thaumatins into a polypyrrole film, Sadik *et al.*⁶ reported the construction of an immunosensor for the detection of thaumatins. In some work, counter ions are often found to be easily incorporated or removed from polypyrrole films when the films are doped and dedoped during voltammetric scans in an electrolyte solution containing the counter ions. Such a characteristic has been exploited to construct polypyrrole-based sensors for several anions, including nitrate^{7,8}, nitrite⁷ and perchlorate ions^{9,10}. By a similar approach, some metal complexes¹¹ (e.g. Mo(CN)₈⁴⁻) and biomolecules¹² (e.g. adenosine 5'-triphosphate) were also incorporated into polypyrrole films during electropolymerization. Subsequent anodic voltammetric scans expelled the incorporated molecules from the film, giving rise to a controlled release of molecules from the polypyrrole-modified electrodes. More recently, Aoki *et al.*¹³ demonstrated the possibility of constructing a biocompatible electrode by culturing mammalian cells on polypyrrole-coated indium-tin oxide electrode. Interestingly, upon an acetylcholine stimulation, a higher catecholamine secretory rate was observed from cells cultured on a polypyrrole-poly(styrene sulfonate)-coated electrode than that on a bare

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indium-tin oxide electrode. Notably, work exemplified here clearly showed that tremendous efforts have so far been concentrated on the development of polypyrrole-modified electrodes as a working or an indicator electrode.

Many of the polypyrrole-coated electrodes described above were constructed by electropolymerization of pyrrole on a solid metal electrode. In contrast, Bradner and Shapiro¹⁵ have previously demonstrated the deposition of doped polypyrrole films on a mercury drop anode in aqueous media. This resulted in flexible, free-standing films with conductivity values ranging from 40 to 90 S cm⁻¹. These workers have later discovered that the electropolymerization of pyrrole on a liquid mercury anode in the presence of halide ions promoted the formation of insoluble mercury halide salts entrapped in the films¹⁶. By adopting a similar methodology, in this work we describe our attempts in constructing a polypyrrole-mercury/mercury chloride electrode and the characterization of this electrode as a polymeric reference electrode. Contrary to work described in the preceding paragraph, in our laboratory, polypyrrole modified electrodes are developed as novel polymeric reference electrodes.

Experimental

Chemicals. Pyrrole (Aldrich, Sydney, Australia) was doubly distilled and stored under nitrogen at 0°C. Sodium *para*-toluene sulfonate (NapTS) and mercury (II) nitrate, purchased from Aldrich, were used as received. Analytical reagent (AR) grade mercuric nitrate (Aldrich), nitric acid (Rhône-Poulenc, France), potassium chloride (BDH, Sydney, Australia) and acetonitrile (BDH) were used as received. Analytical reagent (AR) grade sodium hydroxide and acetic acid (Fisons) were used in the preparation of pH 4.7 buffer solutions. All aqueous solutions were prepared with deionized water purified by a Milli-Q water system. Mercury was purified by passing through 1.0 M nitric acid, followed by distilled water and absolute alcohol and was finally dried under reduced pressure.

Apparatus. A Model 66 TS-10 Wenking potentiostat provided the constant current required for the galvanostatic polymerization of pyrrole. All other electrochemical experiments were performed with a MacLab/4e potentiostat driven by a version 1.3 EChem software (ADInstruments Pty Ltd, Sydney, Australia). Potential difference was recorded relative to an Activon Ref. 401 saturated calomel reference electrode (Activon Scientific Products Company Pty Ltd, Sydney, Australia) and was displayed on a PHM 82 Standard pH/mV meter (Radiometer, Copenhagen).

Experimental procedure

Electropolymerization on a mercury pool anode. Pyrrole was initially polymerized in a cell equipped with mercury pool acting as an anode (27 cm² area) and a stainless steel mesh cathode (5 cm diameter) positioned 2 cm above the mercury surface. The apparatus was suspended by a thin wire from a firm metal plate to minimize vibrations due to the surroundings. The cell was kept at 0°C and was continuously purged by nitrogen gas during polymerization. In a typical experiment, a well-mixed solution containing 0.5 M NapTS, 0.3 M pyrrole and 1.0 M NaCl in pH 4.5 sodium acetate buffer was used. The apparatus

was allowed to equilibrate for 15 min, and was not disturbed once the reaction had begun. Polymerization was conducted galvanostatically at 20 mA for 3.5 h. The black polypyrrole film was then peeled off of the anode surface. The film was washed by Soxhlet extraction in acetonitrile for 12 h before drying. Films of approximately 0.5 cm² in area were then cut by a scalpel for use in subsequent characterization experiments.

Electropolymerization on a glassy carbon electrode. In a second set of experiments, polypyrrole films were galvanostatically deposited onto a 3 mm diameter glassy carbon electrode (Bioanalytical Systems, Inc., West Lafayette, IN, USA) by applying a constant current of 5 mA and a total charge of 750 mC. The solution used for electropolymerization consisted of 0.1 M pyrrole and 0.1 M NapTS in a 0.5 M acetate buffer (pH 4.90). Reduction of mercury at a potential of -0.50 V vs Ag/AgCl was carried out at the resulting polypyrrole-coated electrode in a stirred solution of 0.5 M Hg(NO₃)₂ in 1% HNO₃ for 20 min. A platinum electrode was used as an auxiliary electrode in these experiments. The extended reduction time ensured a saturation of mercury at the polypyrrole-coated electrode. The Hg/polypyrrole/glassy carbon electrode was subsequently exposed to 5 M NaOH and 10 M HCl, respectively, for a desired duration, to encourage an exchange of the *para*-toluene sulfonate counter ions in the film with chloride ions¹⁷⁻¹⁹. Cyclic voltammetry (between -2 V and 1 V at 100 mV s⁻¹) was simultaneously carried out while the electrode was being treated in 10 M HCl to encourage oxidation of mercury within the polypyrrole film.

The potential difference between the polypyrrole-mercury/mercury chloride reference electrode and a commercial saturated calomel reference electrode was measured in the presence of KCl solutions of various concentrations. All potential difference readings were obtained after 15 min of equilibration in the KCl solution. Conductivity of all polypyrrole films was measured using a locally constructed modified four-probe device.

Results and discussion

Polypyrrole-mercury/mercury chloride film deposited on a mercury anode. In this work, we are interested in the fabrication of a polypyrrole-mercury/mercury chloride electrode. Initially, the procedure reported by Bradner and Shapiro^{15,16} was adopted to carry out *in situ* electropolymerization of pyrrole on a mercury pool electrode in the presence of NapTS and NaCl. According to these workers, as much as 3.3% (by weight) of mercury was incorporated in polypyrrole films prepared on the mercury pool anode. The pTS⁻ ions were deliberately chosen as the counter ions in these experiments to fabricate films with appreciable conductivity^{20,21}, while Cl⁻ ions were needed for reaction with mercury to yield mercury chloride in the polypyrrole film. Indeed, conductivity of films obtained was found to lie in the range of 48-90 S cm⁻¹. These values compare favourably with those reported previously²¹. The Nernstian behaviour of such films was then examined. By using polypyrrole-mercury/mercury chloride films as an indicator electrode, a plot of the potential difference, measured against a commercial saturated calomel reference electrode ($E_{\text{sat.calomel}} = 240$ mV) vs the logarithm of chloride ion concentration was constructed, as

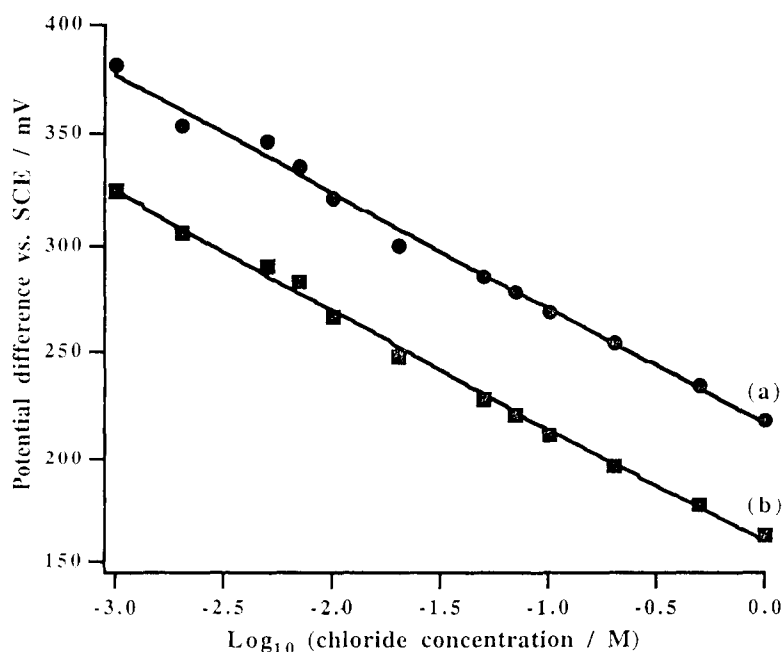


Figure 1 A plot of potentiometric response (measured against a saturated calomel reference electrode) as a function of \log_{10} (chloride concentration). A polypyrrole-mercury chloride film prepared on a mercury pool anode (a) or a polypyrrole film prepared on a stainless steel plate (b) was used as indicator electrode

shown in *Figure 1a*. The plot displays a linear relationship (correlation coefficient is 0.996, $N = 12$) with a slope of $-54.3 \pm 3.5 \text{ mV decade}^{-1}$ (the errors represent a 95% confidence interval of the slope). For comparison, a separate polypyrrole film deposited on a stainless steel electrode (i.e. no mercury was entrapped in the film) was used in the experiment. *Figure 1b* shows that a linear plot (correlation coefficient is 0.994, $N = 12$) with a slope of $-55.0 \pm 4.3 \text{ mV decade}^{-1}$ was also obtained owing to the doping and dedoping of chloride ions in the polypyrrole film. These results indicated very similar behaviour between the two films and it is likely that negligible amount of mercury was entrapped in the polypyrrole film while being deposited on the mercury pool anode. An uneven distribution of mercury across the film was visually observable and the average amount of mercury was determined by stripping voltammetry to be approximately 1%. Further, the polypyrrole-mercury/mercury chloride electrode exhibited a stable null potential difference for only approximately 60 min. Following these experiments, we have decided to investigate an alternative approach of electrochemical deposition of mercury at a polypyrrole-coated electrode to ensure a larger amount of mercury in the film.

Polypyrrole-mercury chloride coated glassy carbon electrodes. In these experiments, electropolymerization of pyrrole was carried out galvanostatically on a glassy carbon electrode in the presence of 0.1 M pyrrole and 0.1 M NapTS. Hg_2^{2+} was then reduced electrochemically onto the polypyrrole-coated electrode. At this point, some dendritic features were visible on the resulting polypyrrole-mercury surface. In addition, mercury deposition in these films was visible through a grey discolouration of the black polypyrrole surface.

It has previously been reported¹⁷⁻¹⁹ that treatment of a polypyrrole film with acids and bases results in protonation and deprotonation of the polymer, respectively.

Further, the base treatment was found to decrease the conductivity of the film by several orders of magnitude, while the acid treatment would restore the conductivity. More recently, Forsyth and Truong¹⁹ investigated the structures of electrodeposited polypyrrole films prepared with pTS^- and other anions by ^{13}C solid state n.m.r. spectroscopy. These workers demonstrated that pTS^- was completely removed from the film in both acidic and basic solutions. We have adopted this treatment to dedope polypyrrole-mercury films prepared above in order to exchange the pTS^- ions incorporated during electropolymerization with Cl^- ions. Therefore, immediately after exposing the film in a 5 M NaOH bath for 15 min, the film was treated in 10 M HCl for 3 min. In addition, cyclic voltammetry was carried out while the film was being treated in 10 M HCl to oxidize the deposited mercury. This was to promote the chemical formation of mercury chloride within the polypyrrole film. To investigate the effects of the acid and base treatments in this work, the conductivity value was determined to be approximately 22 S cm^{-1} for a free standing polypyrrole film polymerized on a stainless steel plate, and this was reduced to 0.2 S cm^{-1} after it was being treated with NaOH but increased to 24 S cm^{-1} upon subsequent exposure to 10 M HCl. More encouragingly, such base-acid and voltammetrically treated polypyrrole films were found to show a reproducible ($N = 20$) null potential difference against a commercial saturated calomel reference electrode in saturated KCl solution.

Voltammetric studies of polypyrrole-mercury/mercury chloride-coated electrodes. Polypyrrole-mercury/mercury chloride coated electrodes fabricated above were also characterized by cyclic voltammetry in a 1.0 M KNO_3 supporting electrolyte. *Figure 2a* shows the cyclic voltammogram obtained at a polypyrrole coated glassy carbon electrode, where the peaks at +1.50 V and -1.00 V

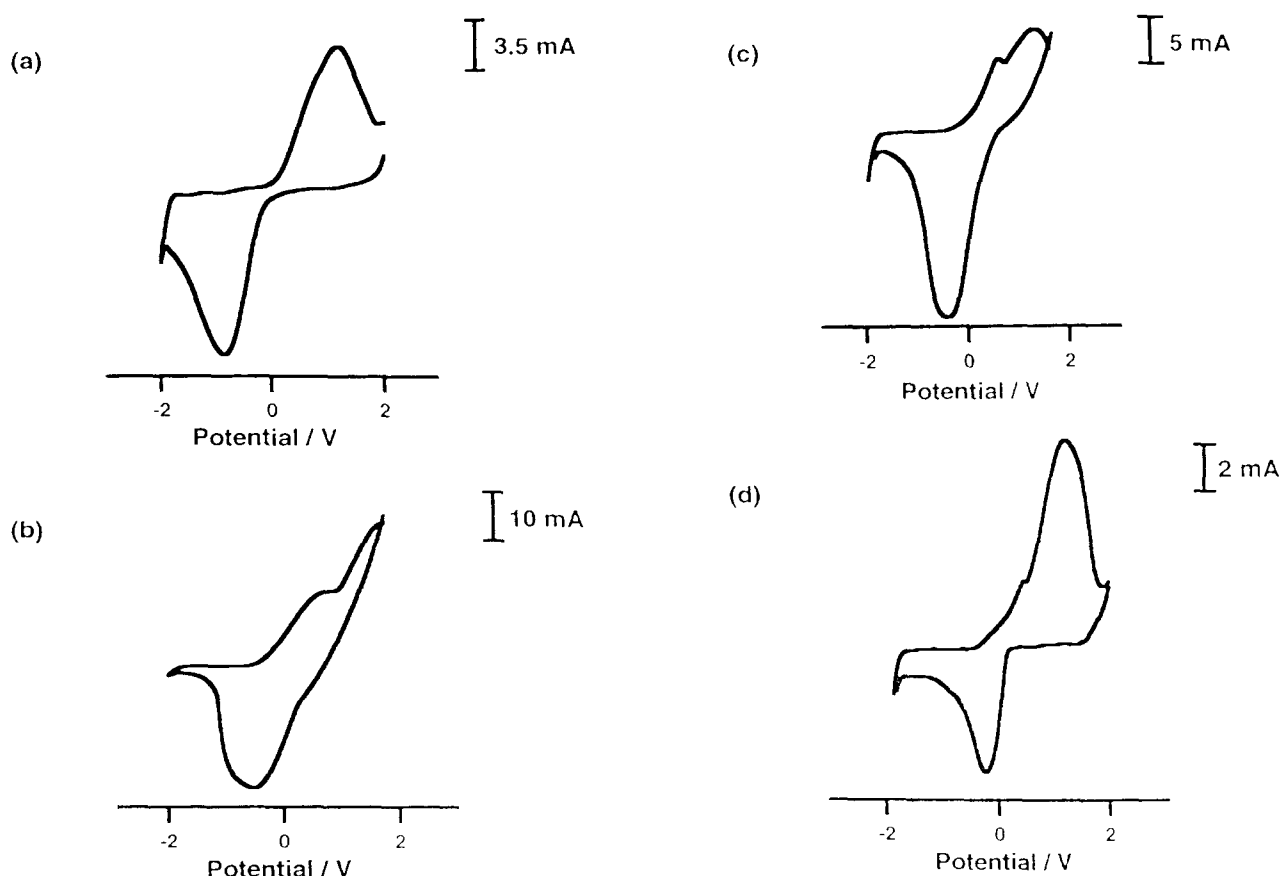


Figure 2 Cyclic voltammograms obtained, in 0.1 M KNO_3 supporting electrolyte, after each step in the preparation of a polypyrrole-mercury chloride coated glassy carbon electrode. The working electrode was a polypyrrole-coated glassy carbon electrode (a). Mercury was then electrochemically reduced at the electrode (b). The resultant electrode was treated in 5 M NaOH (c), followed by 10 M HCl (d)

correspond to the oxidation and reduction of polypyrrole, respectively. Following this, mercury was electrochemically deposited on the polypyrrole-coated glassy carbon electrode and the cyclic voltammogram obtained at this electrode in 1.0 M KNO_3 is displayed in *Figure 2b*. A new peak due to the oxidation of mercury was now observed at +0.56 V. Interestingly, the polypyrrole reduction peak has shifted to a more positive value of -0.40 V and its peak current has increased. The grey discoloration of the film was observed to have decreased significantly after this particular scan. The cyclic voltammogram obtained at the polypyrrole-mercury coated electrode after being treated in NaOH is shown in *Figure 2c*, where both the oxidation and reduction peaks of polypyrrole have been reduced in height compared to *Figure 2b*. Further, the mercury peak current was observed to have reduced after treating the electrode in 10 M HCl, as shown in *Figure 2d*. This decrease in peak current is consistent with the removal of free mercury caused by reaction with chloride ions. The small mercury peak observed in *Figure 2d* indicated an incomplete reaction, resulting in a mercury/mercury chloride equilibrium. This then enables the establishment of a half cell system similar to that in conventional calomel reference electrodes.

Potentiometric studies of polypyrrole-mercury/mercury chloride electrodes. In a series of optimization experiments, we have initially varied the exposure time of the polypyrrole-mercury/mercury chloride coated electrode in 5 M NaOH from 2 min to 30 min while maintaining a

3 min treatment in 10 M HCl. By using the null potential difference in saturated KCl solution as a criterion, we found that a large potential difference ($\geq +30$ mV) was obtained when the exposure duration was shorter than 15 min. Presumably, in these experiments, insufficient chloride ions were exchanged into the polypyrrole film for the formation of mercury chloride salt. On the other hand, with exposure durations longer than 15 min, we have been unsuccessful in obtaining potential difference readings smaller than -40 mV. Hence, an optimum exposure duration of 15 min in 5 M NaOH was used in subsequent work. In investigating the optimum exposure duration in 10 M HCl, following the treatment in 5 M NaOH for 15 min, the polypyrrole-mercury coated electrode was placed in the acid bath for increasing periods of time starting from 2 min. Cyclic voltammetry was conducted simultaneously while the electrode was treated in 10 M HCl. It was found that a minimum duration of 3 min was needed to yield a null potential difference against a saturated calomel reference electrode in saturated KCl solution. It is likely that insufficient mercury ions were produced voltammetrically when the exposure duration was shorter than 3 min for reaction with exchanged Cl^- in the polypyrrole films. On the other hand, under the present conditions, after longer exposure times, it was likely that an unfavourably large mercury chloride-to-mercury concentration ratio for an equilibrium system was established within the polypyrrole films.

Potentiometric experiments in a series of Cl^- solutions ranging from 10^{-6} M to 1 M were also carried out.

Potential difference readings varying from -25 mV to -60 mV , against a commercial saturated calomel reference electrode, were obtained. Note that a commercial saturated calomel reference electrode is generally regarded as functional when a potential difference smaller than 40 mV relative to a second saturated calomel reference electrode was measured²². In the present work, the deviation from the expected null potential difference would be partly due to a leakage of mercury and/or mercury chloride from the polypyrrole-coated electrode in chloride solutions less concentrated than the saturated KCl solution. In addition, the chloride counter ions in the polypyrrole films would still be doped and dedoped during these potentiometric experiments, contributing to the non-zero potential difference readings obtained. In fact, according to a recent model developed by Lewenstam *et al.*²³, apart from the counter ions, the co-ions (e.g. Na^+ in our work) can also be exchanged at the interface. Further, there would also be contributions from the junction potential at the polypyrrole-chloride solution interface.

All polypyrrole-mercury/mercury chloride coated glassy carbon electrodes fabricated were stored in saturated potassium chloride solution. From our investigations, we have yet to maintain a stable potential of these electrodes longer than three days. This is again likely to be due to a leakage of mercury and/or mercury chloride from the polypyrrole films. In a different investigation, Kinlen *et al.*²⁴ reported that after annealing, a film of Nafion formed a cation-selective membrane which effectively blocked the diffusion of chloride ions to the surrounding solution. In their work, high temperatures were used to anneal the Nafion. Based on a similar attempt, we have coated polypyrrole-mercury chloride electrodes with a Nafion film but care was taken not to thermally degrade the conductivity of the polypyrrole coating. In these experiments, large negative potential difference readings were obtained, indicating contributions from junction potentials arising from the interfaces between the sandwiched layers. Nonetheless, our results indicated that the Nafion coating did not seem to have aided sufficiently in stabilizing the potential difference. Attempts in coating the polypyrrole mercury chloride modified electrodes with other polymers are currently being investigated in our laboratory in order to prevent leakage of mercury and/or mercury chloride and stabilizing the potential of the electrodes.

In summary, this study has demonstrated the feasibility of constructing polypyrrole-mercury/mercury chloride electrodes which show a reproducible null potential difference against a saturated calomel reference electrode in saturated KCl solution. Further work is still needed in improving the stability of the potential of these

electrodes and their performance in solutions less concentrated than the saturated solution. Polypyrrole films are robust, lightweight, economical, maintenance-free and environmentally friendly. Based on the developments in microelectrodes, attempts described here may open up the possibility of developing very small polypyrrole-mercury/mercury chloride electrodes containing less mercury compared to conventional saturated calomel reference electrode. Such a development is deemed to be environmentally friendly.

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