A Polyaniline-Deposited Nonplatinum Metal as a Potentiometric Sensor—An Inexpensive Alternate to Conventional Platinum for Some Potentiometric Redox Reactions

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Abstract: For the purpose of employing an inexpensive alternative to conventional platinum for use by upper-division as well as graduate students, polyaniline (PANI)-deposited stainless steel (SS) and mild steel (MS) electrodes are described as indicator electrodes for potentiometry and potentiometric titrations of some redox reactions. PANI is deposited on the nonplatinum metal by electrochemical polymerization of aniline using cyclic voltammetric technique. Alternate methods to produce the PANI electrodes are also suggested. The electrodes respond to concentration changes of hydroquinone (H_2Q), Fe^{2+}/Fe^{3+}, and $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ in HCl electrolytes, and the potential variation with concentration follows the Nernst relationship. Under identical experimental conditions, the response time of the PANI/SS, PANI/MS, and Pt electrodes for a change in concentration of Fe^{3+} in a mixed electrolyte of Fe^{2+} and Fe^{3+} is found to be about 20 s. Neutralization reaction of HCl versus NaOH, redox reaction of Fe^{2+} and Ce^{4+}, and redox reaction of Fe^{2+} and $KMnO_4$ in several concentrations in the range from 1 mM to 100 mM are carried out using the PANI/SS, PANI/MS, and Pt indicator electrodes. The performance of the PANI/SS and PANI/MS electrodes is as good as that of the Pt at all concentration levels of the titrations. The electrodes can be reused for several titrations by storing them in an acid electrolyte for a long period of time. Thus, the conventional inert Pt or Au can be substituted for by using a PANI-deposited nonplatinum reactive metal as a potentiometric sensor for redox titrations.

Introduction

Potentiometric analysis is one of the important experimental techniques that upper-division as well as graduate students often learn and practice in the chemical laboratory [1, 2]. For the purpose of potentiometric titrations, students are generally instructed to use Pt or Au as the indicator electrode and to measure the potential (*E*) during the course of the titration [3, 4]. A sharp deflection of *E* is the indication of the end point of a titration. These metals are used because they are chemically inert and fairly free from passivating surface film in commonly used electrolytes. On the other hand, a common metal or alloy, for example, Cu or mild steel (MS) cannot sense the redox reactions, as it undergoes corrosion, which is accompanied by formation of surface film. As a consequence, a common metal is unsuitable as an indicator electrode for potentiometric analysis. Nevertheless, it is interesting and advantageous to employ an inexpensive common metal, by using a suitable surface modification, as a potentiometric indicator electrode. Because a large number of students are generally trained in a chemistry laboratory class, substantial cost savings are expected by using a nonplatinum metal instead of a platinum metal. Furthermore, it may be more interesting for the students, if they prepare the electrodes themselves rather than using commercially available Pt electrodes.

Among the electronically conducting polymers, polyaniline (PANI) is simple, stable and can easily be synthesized [5–7]. The PANI undergoes intrinsic redox processes in acidic electrolytes that are accompanied by insertion and deinsertion of solution species into/from the polymer in the potential range between 0 and 1.2 V [8]. In brief, PANI is in a reduced state, known as leucoemeraldine (LE), at potential values below 0.2 V. At about 0.2 V, LE undergoes partial oxidation resulting in emeraldine (EM). EM undergoes further oxidation to pernigraniline (PE) at about 0.85 V. Owing to these properties, the PANI is anticipated to be suitable for a variety of applications [9]. Electrochemical deposition of PANI from acidic electrolytes is generally studied on a noble metal or a carbon electrode [5]. The common nonplatinum metals have only been scarcely studied for this purpose as the anodic oxidation of aniline to PANI competes with surface oxidation of the metal [10–12]. Nevertheless, potentiodynamic deposition of the PANI on several nonplatinum metal electrodes is studied in various electrolytes of different concentrations. The success of deposition depends on the metal and the electrolyte as well as its concentration [13]. In the present investigation, SS and MS are deposited with the PANI, and studied as potentiometric indicator electrodes for redox titrations. The results suggest that the performance of PANI/SS and PANI/MS electrodes is as good as that of a Pt electrode. It is thus anticipated that students can conveniently replace the conventional Pt or Au inert electrode by a common metal deposited with PANI. It is interesting for the students to know that the Nobel Prize in Chemistry for the year 2000 was awarded to Professors A. J. Heeger, A. G. MacDiarmid and H. Shirakawa for their innovative research on conducting polymers. PANI belongs to this class of polymers.

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Experimental Procedure

AR grade chemicals, vacuum-distilled aniline and double-distilled water were used for all experiments. Grade 304 SS and commercially pure MS sheets of about 0.5 mm in thickness were sectioned into strips of about 10-cm length and 1-cm width, and a 1-cm^2 area at an end of the strip was used as the electrode area. Students may prefer to use commercial aniline without distillation if it is not partly oxidized (which may be assessed by intensity of the pink color aniline displays due to oxidation), deionized water, and a scrap SS or MS. The electrodes were polished to a uniform and mildly rough finish with successive grades of emery papers, washed free of emery particles, rinsed with double-distilled water and used for electrodeposition of PANI. There are several methods of polymerization of aniline to PANI. Potentiodynamic, potentiostatic, and galvanoststic methods are electrochemical in nature with the PANI being formed as an adherent deposit on the electrode. On the other hand, PANI can also be prepared as a powder by chemical oxidation [6]. Two different methods of making the electrode are described below:

Electrochemical Method

A glass electrochemical cell of about 50-mL capacity is used. The experimental setup is schematically shown in Figure 1. The working electrode (SS or MS) is placed symmetrically between two Pt-foil auxiliary electrodes. Students may use even MS as auxiliary electrodes in place of Pt electrodes. A saturated calomel electrode (SCE) is used as the reference electrode and the potential values against SCE are reported. The PANI deposition is carried out by cycling the electrode potential between –0.2 and 1.2 V in either 0.5 M H_2SO_4 electrolyte containing 0.5 M aniline for SS, or 0.5 M oxalic acid electrolyte containing 0.5 M aniline for MS. An EG&G PARC potentiostat model Versastat is employed for this purpose. The electrode is cycled several times at a scan rate of 10 mV s^{-1} for the purpose of growing the PANI layer to a thick film of about 30 μm. Cyclic voltammograms recorded during deposition of the PANI on SS at a scan rate of 10 mV s^{-1} in 0.5 M H_2SO_4 containing 0.5 M aniline are shown in Figure 2a. During the forward sweep of the initial cycle, the surface oxidation of SS takes place at about 0.3 V followed by oxidation of aniline to nucleate the initial layer of PANI at about 1.1 V. During the reverse sweep, the reduction peak of the PANI to leucoemaraldine (LE) state is clearly noticed. From the second cycle onwards, the initial layer of PANI, which is deposited during the first cycle, inhibits the oxidation of SS. As a result, the current peak at 0.3 V corresponding to surface oxidation of SS is absent. On the other hand, the redox peaks of the PANI corresponding to LE to emeraldine (EM) at 0.2 V and EM to pernigraniline (PE) at 1.0 V are present. There is an increase in size of the cyclic voltammograms, indicating growth in the PANI thickness, with an increase in cycle number. Subsequent to termination of the growth after ten cycles, the thickness of the PANI is estimated from the charge of the voltammogram following the procedure given in the literature [14], and it is about 30 μm.

When the MS is cycled in 0.5 M H_2SO_4 + 0.5 M aniline electrolyte, the open-circuit-corrosion rate and surface-oxidation rate of the electrode are dominant, and the oxidation of aniline to PANI does not take place. Consequently, the electrolyte medium is changed to oxalic acid (OA), which is a milder acidic medium than H_2SO_4. On repeated cycling of the MS electrode at a scan rate of 10 mV s^{-1} in 0.5 M OA + 0.5 M aniline, there is nucleation and growth of the PANI; however, the shape of the voltammograms is different and the growth rate of PANI is lower in OA medium than with the SS in H_2SO_4 electrolyte. The current peaks of the votammograms are not sharp and they are overlapping. The thickness of the PANI layer on MS is about 10 μm after 10 cycles of deposition.

After deposition, the PANI/SS and PANI/MS electrodes are washed in 0.5 M H_2SO_4 that is free of aniline, and then they are subjected to cyclic voltammetry in 0.5 M H_2SO_4. Voltammograms recorded for the PANI/SS electrode are shown in Figure 2b. Current peaks corresponding to LM/EM and EM/PE are present suggesting that the PANI is conducting and electrochemically active akin to the PANI deposited on Pt [6]. Students may learn basic principles, theory, and typical experiments of cyclic voltammetry from the published literature [15–17]. Instead of cyclic voltammetry, students may deposit PANI by fixing the working electrode potential at about 1.2 V using a potentiostatic method for about 10 min duration. On the other hand, a constant anodic current of about 5 mA cm^{2-} is passed through the electrode for about 10 min. For the later technique a dc power source or a battery will be sufficient. These electrochemical techniques produce PANI as a deposit on the electrode.

Chemical Method

In a nonelectrochemical route, PANI powder can be synthesized by oxidizing aniline with $K_2S_2O_8$ or KIO_3 in an acidic medium. In a typical experiment, 50 mL of 0.5 M HCl containing 0.5 M aniline is used, and 50 mL of 0.5 M KIO_3 is added at about 0 ^{o}C. A precipitate of PANI is obtained, which is filtered, washed repeatedly with distilled water, and dried. A dry sample of PANI powder (90 wt %) is mixed with a PTFE (Teflon) suspension as binder (10 wt %) and a thick slurry is made. The slurry is applied on a cleaned stainless steel (SS) mesh and heated at about 120 ^{o}C in an oven to evaporate the solvent. The electrode is compacted under mild pressure, and dipped in 0.5 M H_2SO_4 for about 20 min. Soaking in dilute acid facilitates doping of anions into the polymer, which makes PANI electronically conducting. The electrodes prepared by all the above methods perform alike for the potentiometric titrations.

Potentiometric response of the PANI/SS and PANI/MS electrodes was assessed by measuring the potential of the electrodes in redox electrolytes of several concentrations. Potentiometric titrations were repeated three to five times to ensure reproducibility. A digital voltmeter of high input impedance (> 10^9 Ω) was used for potential measurements.

Results and Discussion

Potentiometric Response of PANI/SS and PANI/MS Electrodes. Potentials (E) of the PANI/SS, PANI/MS and also Pt (for comparison) electrodes were measured in 0.5 M HCl electrolytes consisting of hydroquinone (H_2Q), Fe^{2+}/Fe^{3+}, and $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ of several concentrations. The data for a few experiments are presented in Figure 3, and the data of the other experiments are similar.

The concentration dependence of E for a schematic redox process [3, 4], Ox + ne$^-$ = Red, is given by the Nernst equation:

$$E = E^0 + (2.303RT/n\,F)\log(C_{\mathrm{Ox}}/C_{\mathrm{Red}}) \tag{1}$$

where E^o is the standard electrode potential of the reaction, n is the number of electrons, C represents the concentration of the reduced species (Red) or the oxidized species (Ox), and the other symbols have their usual meanings. Thus a value of ($59/n$) mV is expected for the slope of a plot of E versus $\log(C_{\mathrm{Ox}}/C_{\mathrm{Red}})$ at 25 ^{o}C. The data in Figure 3 are linear and slopes of the plots are close to $59/n$ mV (Table 1). This suggests that the PANI/SS and PANI/MS electrodes as well as the Pt electrodes behave alike towards potential sensing of the redox reactions. The above concentration-dependent potential measurements were attempted with SS and MS electrodes in the absence of PANI. The potential values measured were corrosion potentials instead of the reversible potentials of the redox species in 0.5 M HCl, and the response to variation in concentration was absent; thus, the surface modification of SS

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Table 1. The Nernstian Slopes Measured from the Concentration Dependence of Redox Reactions

Redox Couple	No. of electrons (n)	Electrode	Slope in mV $dE/d\log(C_{Ox}/C_{Red})$
Fe^{3+}/Fe^{2+}	1	PANI/SS	54
		PANI/MS	54
		Pt	54
$[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$	1	PANI/SS	53
		PANI/MS	54
		Pt	54
H_2Q	2	PANI/SS	25
		PANI/MS	24
		Pt	24
HCl	1	PANI/SS	55
		PANI/MS	55
		Pt	55

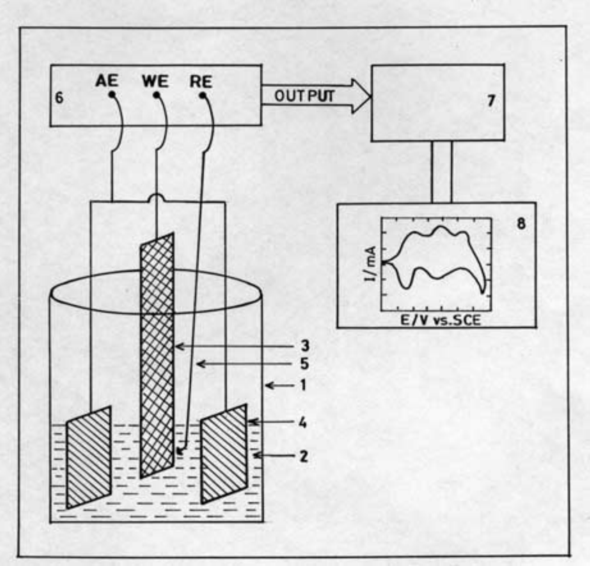

Figure 1. Experimental setup for potentiodynamic deposition of PANI on SS or MS: 1: electrochemical cell, 2. electrolyte, 3. working electrode (WE) of SS or MS, 4. auxiliary electrodes (AE), 5. reference electrode (RE), 6. potentiostat, 7. personal computer, 8. monitor.

and MS by the PANI is responsible for the Nernstian behavior of reversible potentials of the redox species.

Potentiometric response-time of the electrodes was measured by recording the shift in E on changing concentrationof the redox species. Figure 4 shows the data for the PANI/SS and Pt electrodes for a concentration change of Fe^{2+}/Fe^{3+} under identical experimental conditions. Subsequent to addition of a concentrated solution of Fe^{3+} to the electrolyte, there is a shift in E and it reaches a steady value within 20 s in the case of both the electrodes. These results suggest that the PANI/SS and PANI/MS electrodes are useful as potentiometric sensors, and the potentiometric response behavior of these electrodes is as good as that of the conventional Pt.

Potentiometric Titration of a Neutralization Reaction. Potentiometric titrations of HCl saturated with quinhydrone versus NaOH were carried out using the PANI/SS, PANI/MS and Pt as indicator electrodes in several concentrations. In the vicinity of the inflection point, the variation of E of the PANI/SS electrode with volume (Vol) of NaOH titrant, the first differential ($\Delta E/\Delta Vol$) versus volume curve, and the second differential ($\Delta^2 E/\Delta Vol^2$) versus volume curve are shown in Figure 5 for a titration of 0.1 M HCl against 0.1 M NaOH. At the end point, the potential jump is about 400 mV (Figure 5a), the end point is very sharp (Figure 5b), and the volume corresponding to the end point is read out easily (Figure 5c).

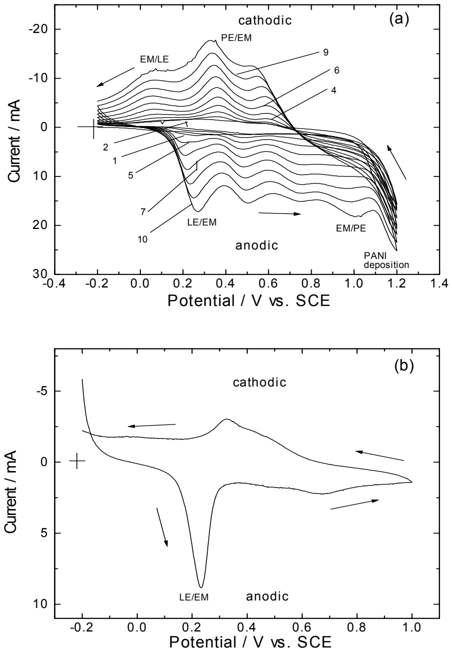

Figure 2. (a) Cyclic voltammograms (10 cycles) at a scan rate of 10 mV s^{1-} during deposition of PANI on SS in 0.5 M H_2SO_4 containing 0.5 M aniline; the size of the voltammogram increases with the scan number. (b) Cyclic voltammogram of PANI/SS electrode in 0.5 M H_2SO_4 at a scan rate of 2 mV s^{1-}. The area of the electrode is 1.0 cm^2.

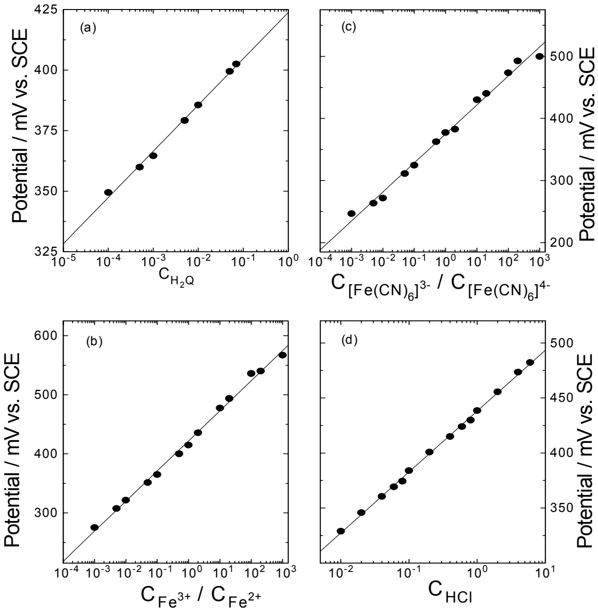

Figure 3. Nernstian behavior of the potential of the PANI/SS (a and b) and PANI/MS (c and d) electrodes for (a) hydroquinone (H_2Q) in 0.5 M HCl, (b) Fe^{3+}/Fe^{2+}, (c) $[Fe(CN)_6]^{3-}/Fe(CN)_6]^{4-}$, and (d) HCl at ambient temperature. C refers to concentration.

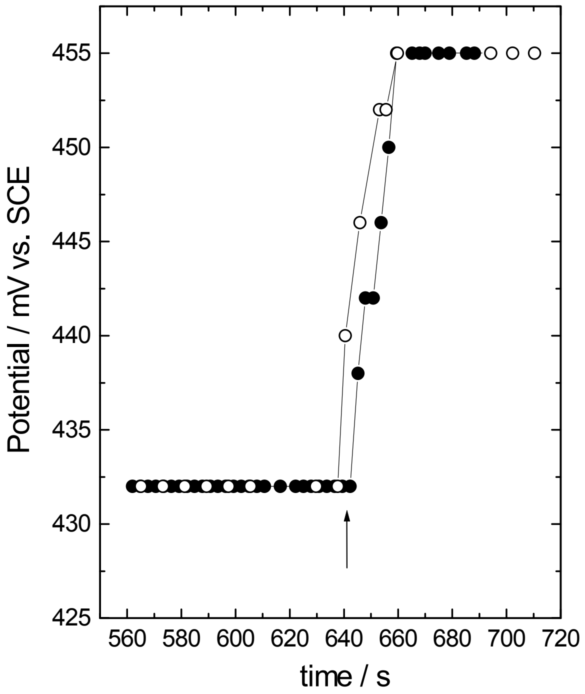

Figure 4. Potential (*E*) of PANI/SS (●) and Pt (O) electrodes as a function of time during a change in concentration of 50 mL of Fe^{2+} (0.01 M) and Fe^{3+} (0.01 M) mixed electrolyte. Shift in *E* from 432 to 455 mV versus. SCE starts on addition of 5 mL of 0.2 M Fe^{3+} solution to the electrolyte to make the concentration of Fe^{3+} (0.028 M) and Fe^{2+} (0.009 M). The arrow indicates the time of addition.

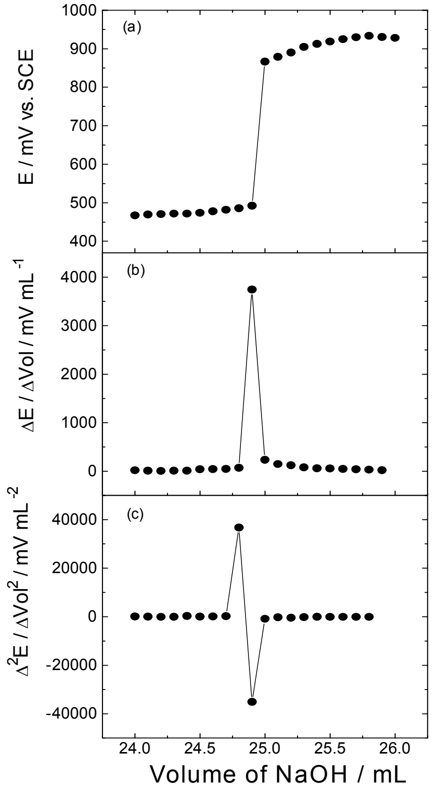

Figure 5. (a) Potential (*E*), (b) the first derivative ($\Delta E/\Delta Vol$), and (c) the second derivative ($\Delta^2E/\Delta Vol^2$) of the PANI/SS electrode against the volume (*Vol*) of 0.1 M NaOH added to 25.0 mL of 0.1 M HCl in the vicinity of the inflection point.

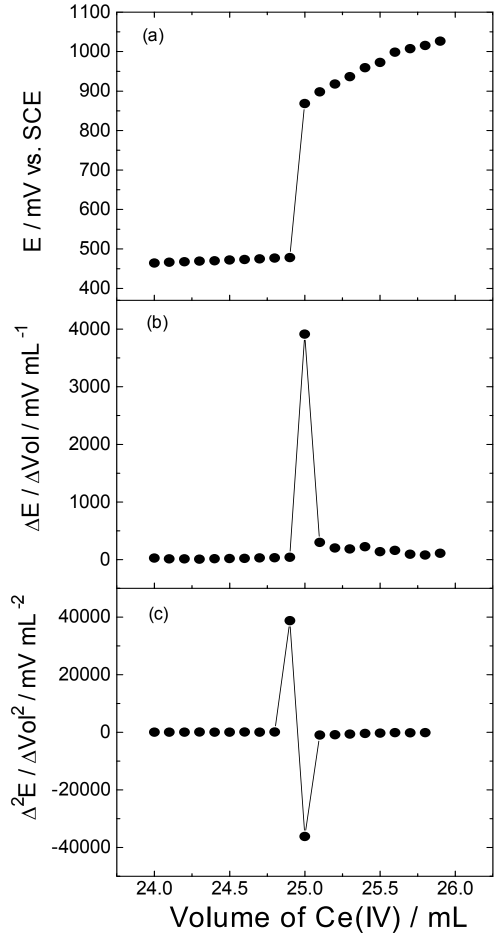

Figure 6. (a) Potential (*E*), (b) the first derivative ($\Delta E/\Delta Vol$), and (c) the second derivative ($\Delta^2E/\Delta Vol^2$) of the PANI/SS electrode against the volume (*Vol*) of 0.02 M Ce(IV) added to 25.0 mL of 0.02 M Fe^{2+} in the vicinity of the inflection point.

Carrying out multiple titrations ensured the reproducibility of the titrations. The results of the analysis of HCl of several concentrations obtained from titrations using the PANI/SS, PANI/MS, and Pt electrodes are summarized in Table 1 of Supporting Material. The results obtained with the PANI/SS and PANI/MS electrodes are as reliable as those of the Pt electrode.

Potentiometric titration of Fe^{2+} versus Ce^{4+}. The potentiometric titration curve of 0.02 M Fe^{2+} versus 0.02 M Ce^{4+}, the first differential curve, and the second differential curve are shown in Figure 6. Akin to the neutralization reaction, *E* of the PANI/SS indicator electrode shows a sharp and substantial shift (about 400 mV) at the end point. The results of analysis of Fe^{2+} of several concentrations obtained from titrations using the PANI/SS, PANI/MS, and Pt electrodes are given in Table 2 of the Supporting Material. The results obtained using the three electrodes are similar.

Potentiometric Titration of Fe^{2+} with $KMnO_4$. The titration curve of 0.001 M Fe^{2+} against 0.0005 M $KMnO_4$, the first differential curve, and the second differential curve are shown in Figure 7. The results of the analysis are given in Table 3 of the Supporting Material. Even in low concentrations, the end point of the titration using the PANI/SS and PANI/MS electrodes is measured with good accuracy. The results are comparable with those obtained using the Pt electrode. For the purpose of cross-examination, titrations were carried out using SS and MS electrodes in the absence of PANI. Similar to the discussion given previously, the electrode potential did not respond to the concentration changes during the titration and the end point could not be identified.

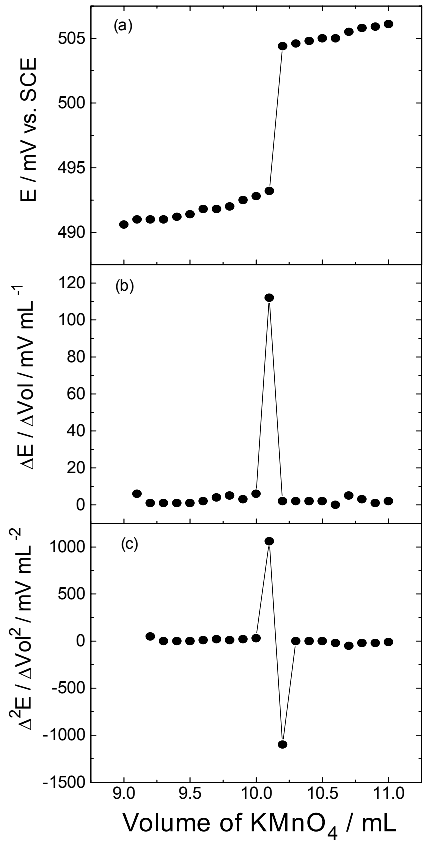

Figure 7. (a) Potential (*E*), (b) the first derivative ($\Delta E/\Delta Vol$), and (c) the second derivative ($\Delta^2 E/\Delta Vol^2$) of the PANI/SS electrode against the volume (*Vol*) of 0.0005 M KMnO$_4$ added to 25.0 mL of 0.001 M Fe^{2+} in the vicinity of the inflection point.

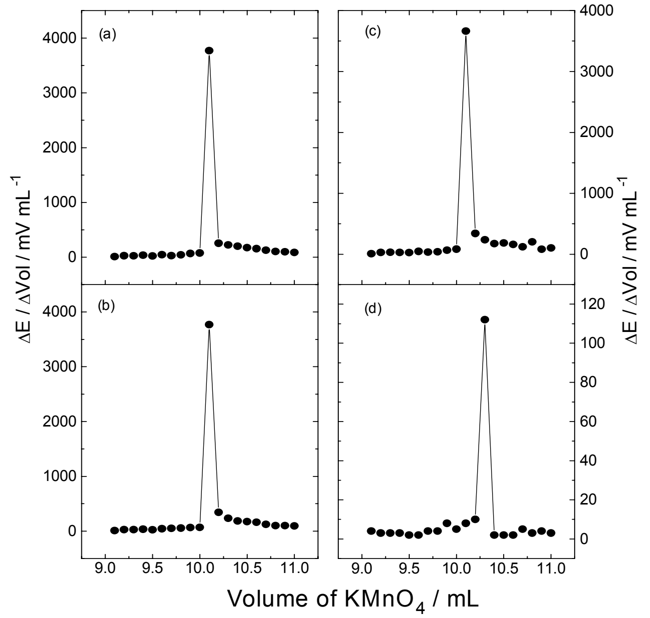

Figure 8. The first differential ($\Delta E/\Delta Vol$) of the titration curve obtained using the PANI/MS electrode for titrations - (a) 0.1 M Fe^{2+} versus 0.05 M KMnO$_4$, (b) 0.05 M Fe^{2+} versus 0.025 M KMnO$_4$, (c) 0.01 M Fe^{2+} versus 0.005 M KMnO$_4$ and (d) 0.001 M Fe^{2+} versus 0005 M KMnO$_4$. In all titrations the volume of Fe^{2+} in 0.5 M HCl supporting electrolyte is 25 mL.

Sensitivity of thePotentiometric Titrations

In all the titrations described above, the concentration of the titrating species was varied from 0.001 to 0.1 M. The magnitude of the potential jump at the end point for the PANI/SS, PANI/MS, and Pt electrodes was low in solutions of 0.001 M concentration, whereas it was typically, for Fe^{2+} versus KMnO$_4$ titration at the PANI/MS electrode, very high at higher concentrations as shown in Figure 8. For concentrations of 0.02 M and above, the magnitude of the shift in *E* is about 400 mV against 100 mV for a concentration of 0.001 M. A comparison of the data for PANI/SS, PANI/MS, and Pt electrodes suggests that at the Pt electrode as well, the shift in *E* at the end point in 0.001 M electrolyte is smaller in magnitude and similar to the data for the PANI/SS and PANI/MS electrodes. As the potentiometric titrations are considered sensitive only down to 0.001 M concentrations of the reacting species [3, 4], it is clear that the PANI/SS and PANI/MS electrodes are as sensitive as the Pt electrode for redox potentiometric titrations.

Durability of PANI/SS and PANI/MS Electrodes. Durability is examined by repeatedly using the electrodes over a long period of time. A PANI/SS electrode is prepared and used for the neutralization titration of HCl versus NaOH. After completing a titration, the electrode is washed free of alkali using 0.5 M HCl, stored in 0.5 M HCl, and used for the neutralization titration again after one day or two days. Likewise, the electrode is stored for about a month with intermittent titrations. The electrode is found to be stable and the titrations are reproducible. The sensitivity of the aged PANI/SS electrode is as good as that of a freshly prepared electrode.

Hazards and Safety Measures

All the chemicals used for the given experiments, namely, H$_2$SO$_4$ (CAS: 7664-93-9), HCl (CAS: 7647-01-0), aniline (CAS: 62-53-3), iron salts, hydroquinone (CAS: 123-31-9), and NaOH (CAS: 1310-73-2) are hazardous. HCl, H$_2$SO$_4$, and NaOH are corrosive in nature. The metal (SS and MS) strips may have sharp edges. Students are advised to take general care while handling chemicals and metals by wearing gloves, goggles, face shields, etc.

Conclusions

The PANI/SS and PANI/MS indicator electrodes behave alike and these electrodes are as good as the Pt for potentiometric analysis. The conventional Pt indicator electrode can be replaced by the PANI deposited on a commonly available nonplatinum metal electrode, not necessarily on SS and MS alone as used in the present study. Although conducting polymers other than PANI can also be used, the use of PANI is advantageous due to its stability and ease of synthesis.

Supporting Material. Data for potentiometric titrations.are available as a PDF file (http://dx.doi.org/10.1007/s00897020540b).

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