RESEARCH ARTICLE

SYNTHESIS, CHARACTERIZATION OF SCHIFF BASE 4[(PHENYL IMINO)METHYL]PHENOL AND ELECTROCHEMICAL STUDY OF CADMIUM REDOX SYSTEM ON SCHIFF BASE MODIFIED WAX IMPREGNATED GRAPHITE ELECTRODE

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ABSTRACT

The schiff base ligand 4 [(phenyl imino) methyl] phenol was synthesized by reaction of aniline and p-hydroxybenzaldehyde. The ligand was characterised by elemental analysis FTIR and H^1 NMR spectroscopy. Electrochemical behaviour of cadmium ion on ligand modified WIGE was investigated on the WIGE surface by using cyclic voltammetric technique. The modification of 4[(phenylimino) methyl] phenol on WIGE was performed in 0.3V and 2.8V potential range using 100mV/s scanning rate having 10 cycles. The ligand modified Wax Impregnated Graphite Electrode was characterized by electrochemical impedance spectroscopy. The electrochemical study of cadmium ion on ligand modified electrode was studied through scan rate effect, pH effect and concentration effect. The optimum detection limit of cadmium ion on ligand modified WIGE was found to be 1 x 10^{-5}M. The interference of copper, mercury and manganese ions with cadmium ion was studied through the interference study. The diffusion coefficient values of cadmium on ligand modified WIGE was calculated by using chronoamprometry and chronocoloumetry techniques.

Key words: Cyclic Voltammetry, Chronoamperometry, Chronocoloumetry, Electrochemical impedance spectroscopy, Interference study.

INTRODUCTION

Schiff base metal complexes have been recognized as powerful catalysts in a great number of chemical reactions such as electrochemical reduction of alkyl halides in aprotic solvents, oxygenation of indols, Phenols, Flavones and others. Schiff base form an interesting class of chelating ligands that has enjoyed popular use in the coordination chemistry, inner transition and main group elements (Vigato and Tamburini 2004; Holm, Everett and Chakravorty 1966; Calligaris *et al*., 1987; Collinson and LFenton 1996; Garnovski and Vasilchenko 2002). There are many examples concerning the selective affinity of Schiff's bases toward the metal ions and, hence, their application in the construction of ISEs (Memon and Yilmaz 2002; Mashhadizadeh and Sheikhshoaie 2003; Ganjali *et al*., 2001; Ganjali, Emami and Salavati-Niasari 2002; Ganjali *et al*., 2003).

According to hard-soft acid base concept the cadmium ion is soft acid so it is suitable complex with schiff base. Cadmium is a widely known chemical pollutant and even concentration levels, its toxicity can be dangerous. Therefore, highly sensitive detection of trace cadmium content in the environment is of great importance. Spectrofluorimetry has many advantages. One of them is high sensitivity. Cadmium has been determined spectrofluorimetrically (Evcim and Reber 1954; Ryan, LPitts and Cassidy 1966; Budesinsky and West 1969; Hefley 1974; Sanchez, Navas and Santiago 1985; Aznarez *et al*., 1987; Gomis *et al*., 1989;

Huang, Yu and Pu 1986). Since the introducing of Schiff base ligands, many research groups have been interested to investigate different aspects of the chemistry of this class of ion receptors (Emadi *et al*., 2007; Rouhollahi, Zolfonoun and Salavati Niasari 2007; Shemirani *et al*., 2003; Fathi and Yaftian 2009). Chemically modified electrode (CME's) with surface designed for reacting and binding of target analyte hold great promise for chemical bonding (West, Padhye and Sonawane 1991; Haiduc and Silvestru 1990; West *et al*., 1993).

Experimental techniques

The IR spectrum of the ligand was recorded with a Perkin Elmer model 1605 FT-IR spectro photometer instrument in

KBr pellets. (Elemental analysis was performed with loco-932). H^1 NMR was recorded on a Bruker(500 MHz) Digital FT NMR spectrometer in DMSO-d^6. Electrochemical experiments were carried out using Electrochemical analyser CHI 600D instrument.

Reagent and Materials

p-hydroxy benzaldehyde (Himedia), aniline(Rankem), ethanol (spectro chem.) cadmium chloride(Universal reagent). All the solutions were prepared by using triple distilled water. Fabrication of this type electrode is easy and low cost one. The Graphite rod present in battery cell (3mm diameter) was separated out and kept in conc.HCl for 24 hours. And then the electrode was rinsed with triple distilled water and kept in ethanol for 24 hours. The porous containing graphite rod was

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obtained. This rod was warmed with paraffin wax and porous part of graphite rod was filled with wax. The graphite rod was cooled at room temperature. The paraffin wax has inert electron transfer and mass transfer. Thus bottom and top part of the rod was polished using emery sheet for electrical contact. This paraffin wax impregnated graphite rod was used as a working electrode. A platinum wire was used as a counter electrode. The Ag/AgCl (saturated KCl) was used as reference electrode.

Synthesis of 4[(phenyl imino) methyl)] phenol (Ligand)

The ligand was prepared by drop wise addition of ethanolic solution of the aniline (0.1582g, 3mM) to a ethanolic solution of p-hydroxybenzaldehyde (0.4144 g, 3mM). After the addition was completed, the mixture was stirred at room temperature for 7 hours. The yellow crystals were washed with ethanol and subsequently dried over anhydrous $CaCl_2$ in a desiccators. The schematic representation for synthesis of ligand was shown in Fig.1
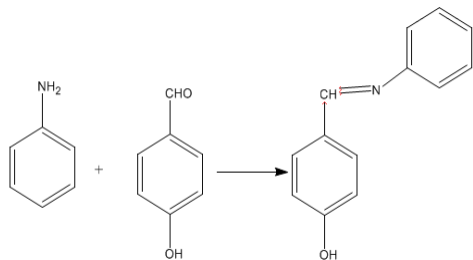

Fig. 1. Schematic representation for synthesis of ligand

Infrared spectra

Characterestic IR band (KBr, v,cm^{-1}) of Shiff base showed at 1640 (C=N)

^{1}H NMR spectra

The ^{1}H NMR spectra in DMSO-d_6 of the shiff base showed signals at Ar-OH, HC=N; Ar-H;

Preparation of 4[(phenylimino) methyl)] phenol (ligand) modified electrode

Prior to each experiment, WIGE was polished in SiC E_4 400 Emery sheet and cleaned with triple distilled water. In order to prepare a modified WIGE surface with 4[(phenylimino)methyl)] phenol, the electrode was immersed in 20ml of 0.1% 4 [(phenylimino)methyl)] phenol in alcoholic solution and the potential was cycled between +0.3 and +2.8V at different sweep rates (10, 20, 40, 80 and 100) with cycles.

RESULTS AND DISCUSSION

Electrochemical Impedance Spectroscopy

EIS experiments were carried out using different modified electrodes at the frequency range from 60KHz to 0.1Hz at the perturbation amplitude of 5mV. Fig. 2 shows that the semicircle in high frequency region was not obvious and the straight lines in low frequency region were obvious in different modified electrodes.
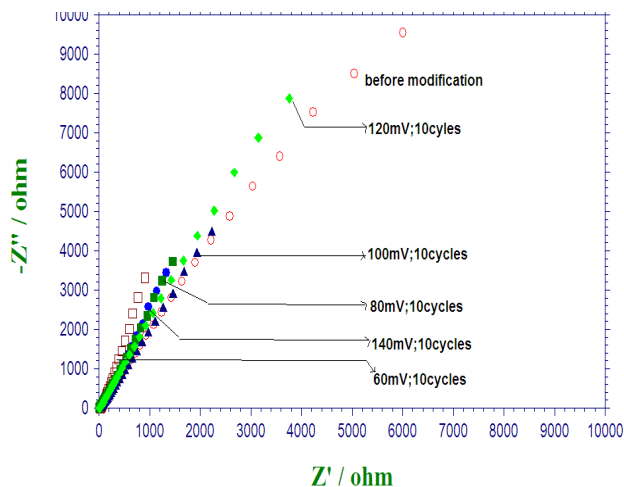

Fig. 2. Electrochemical Impedence spectroscopy for 1mM $K_4[Fe(CN)_6]$ on different modified WIGEs.

The result indicates that the electron transfer rate is fast and the process of electrode reaction is controlled mainly by adsorption and diffusion. The variety of linear slopes at different modified electrodes may be attributed to the different capacitance characteristic of electric double layer at modified electrodes, which indicated that the surfaces of different electrodes has different specific adsorptions. This results suggested that 4[(phenyl imino)methyl] phenol can effectively improve selectivity and sensitivity and achieved simultaneous determination of cadmium by the strong chelation and adsorption of 4[(phenyl imino)methyl] phenol with metal ions.

Sensing of of cadmium ion on ligand modified WIGE

Cyclic voltammogram for 0.5M NH_4F on modified electrode (a), 1mM Cd^{2+} ion on bare WIGE (b) and ligand modified electrode (c)was shown in Fig.3. The anodic as well as cathodic peak potentials were shifted to the positive side on modified electrode. The peak current for the cadmium ion was enhanced on ligand modified WIGE as compared to bare WIGE. This may be due to the increase of uptaken cadmium ion on ligand modified WIGE through complexation.
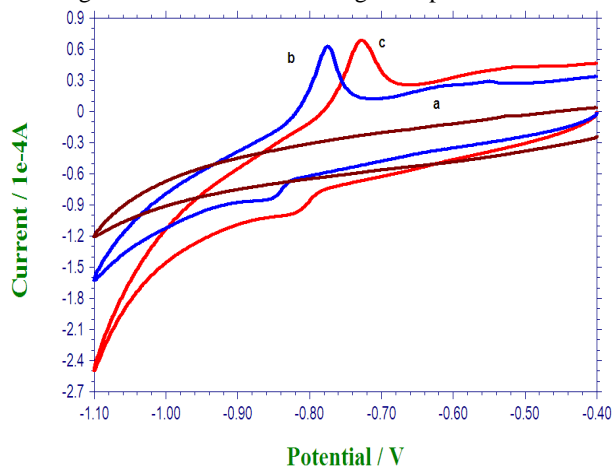

Fig. 3. Cyclic Voltammogram for a) 0.5M NH_4F electrolyte on ligand modified WIGE b) 1mM Cd(II) on bare WIGE c) on ligand modified WIGE.

Scan rate effect

Voltammogram were recorded for 1mM Cd(II) solution on ligand modified WIGE at varyng scan rates was shown in Fig.4. The peak currents for cadmium ion increased linearly with the scan rate in the range of 100 to 180 mV/s. The linear regression equation (Fig.5) expressed as which suggesting that the redox system of Cd(II)/Cd is adsorbed surface process. This is because surface adsorbed process is the rate determining step of the electrode reaction. However Ipa of cadmium ion on ligand modified WIGE was proportional to the scan rate from 100 to 180mV which demonstrating that the diffusion process of cadmium redox system is slower than the surface adsorbed process and the electrode reaction of cadmium ion is controlled by diffusion of cadmium ions from the solution of the modified electrode. From the Table I, a shift in cathodic peak potential is observed with the value of Ipa increasing with increase in scan rate. But the anodic peak potential values were almost remain constant. This suggests that complexation of Cd^{2+} ion with the ligand.
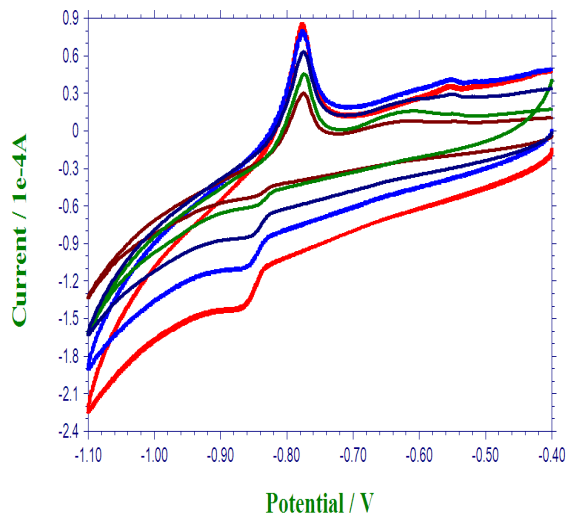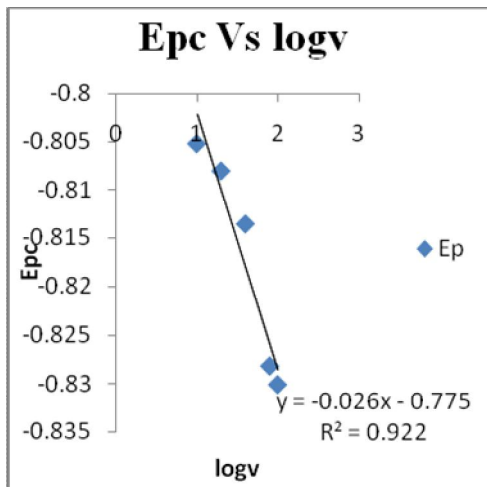
Table. I Cyclic Voltammetric parameters for 1mM Cd(II) ion on ligand modified WIGE at different sweep rates.

Scan rate mV/s	Ipc x 10^{-5} (A)	Epc (V)	Ipa x 10^{-4} (A)	Epa (V)
10mV	-6.720	-0.8053	4.280	-0.7248
20mV	-7.820	-0.8081	5.727	-0.7267
40mV	-9.677	-0.8136	6.974	-0.7276
80mV	-12.69	-0.8282	8.189	-0.7294
100mV	-13.67	-0.8301	8.350	-0.7285

Concentration effect

Fig.6 shows that the cyclic voltammogram of different concentrations of Cd(II) ion (1mM to 5mM) in 0.5 NH_4F medium. At different concentration one oxidation and reduction peaks were found. (This is due to presence of following reaction was present at higher concentrations. ($Cd^{2+} +2e^- \rightarrow Cd$ and $Cd \rightarrow Cd^{2+} +2e^-$).The cyclic voltammetric parameters were tabulated in Table. II. The linear regression equation in calibration plot (Fig.7) was represented the linearity between concentration of cadmium ions and anodic peak current. The linearity of this equation shows that the redox process diffusion controlled one.
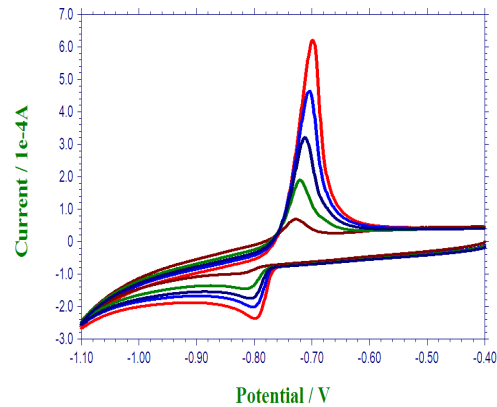

Fig. 4. Cyclic Voltammetric parameters for 1mM Cd^{2+} ion on modified WIGE at different sweep rates 10,20,40,80, 100mV NH_4F.

Fig.6. Cyclic Voltammetric Parameters for different concentrations of Cd^{2+} ion on modified WIGE at 40mV/s.
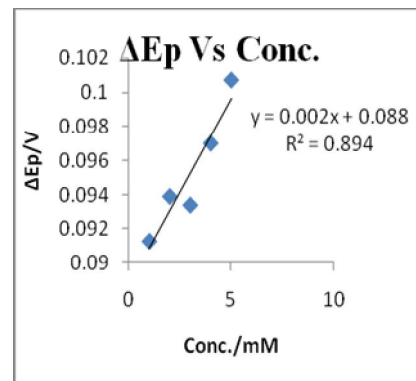

Fig. 5. A plot of Epc Vs log V.

Fig.7 A plot of ΔEp Vs Conc.

Table. II Cyclic Voltammetric parameters for different concentrations of Cd^{2+} ion on ligand modified WIGE at 40mV/s.

Conc	Ipa x10^{-5} (A)	Epa (V)	Ipc x10^{-5} (A)	Epc (V)
1mM	6.974	-0.7267	-9.974	-0.818
2mM	19.10	-0.7221	-14.50	-0.8164
3mM	32.13	-0.7129	-17.73	-0.8063
4mM	46.50	-0.7047	-20.50	-0.8017
5mM	62.29	-0.6924	-23.75	-0.7981

pH Study

Fig.8 shows that electrochemical behavior of Cd(II) on ligand modified WIGE was characterized at different pH values of the aqueous solution. In all the cases ionic strength was adjusted by adding HCl and NaOH and gradually changed by using acetate buffer. The best choice for ability to give the best shape and highest peak current was pH 2. From the Table (III), the half wave potential $E^{1/2}$ of Cd(II) was pH dependent. In our study $E^{1/2}$ value shift by less than nearly 0.0mV/pH. So there are no protons transferred in the redox system in the pH range of 2.0 – 8.0.
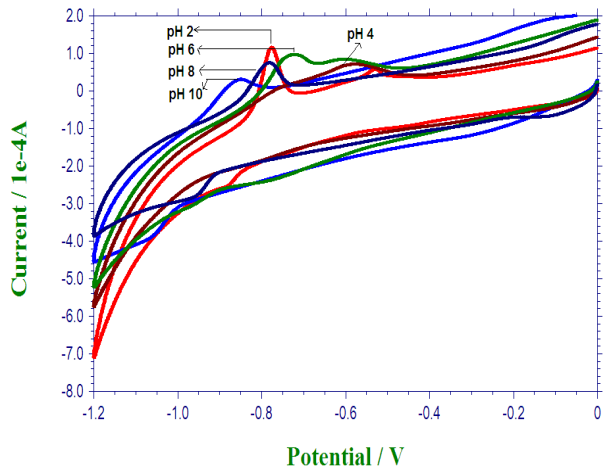

Fig. 8. Cyclic Voltammogram for 1mM Cd(II) ion on ligand modified WIGE at different pH's.

Table. III Cyclic Voltammetric parameters for 1mM Cd(II) ion on ligand modified WIGE at different pH's.

pH	Ipa x 10^{-4} (A)	Epa (V)	Ipc X 10^{-4} (A)	Epc (V)
2	1.208	-0.7781	-2.563	-0.8816
4	0.7168	-0.5803	-----	-----
6	0.8672	-0.7232	-2.460	-0.8016
8	0.7872	-0.7827	-2.850	-0.9632
10	0.3590	-0.8486	-3.906	-1.0557

Interference study

Fig.9 shows that the cyclic voltammograms of Mn(II), Cu(II), Cd(II) and Hg(II) in their mixture on ligand modified WIGE and bare WIGE. The redox peaks of three metal ions overlapped on bare WIGE (a), the peak current much lower as compared to the modified electrode(b) and the peaks appear obviously at about -0.75V(Cd), -0.5V(Mn), -0.15V(Cu) and 0.1V(Hg). This result demonstrated that the anodic peaks of Cd(II), Cu(II), Mn(II) and Hg(II) on ligand modified WIGE. The redox peaks were well separated from each other. Hence it is possible to simultaneously detect Cd(II), Cu(II), Mn(II) and Hg(II) on ligand modified WIGE. The presence of Cu and Hg are highly interfered with the other heavy metal ions even in nano molar level. The nitrogen containing ligands are more preferable to form complex with cadmium compared with mercury and copper. But in this study the presence of cadmium could not affect the oxidation peaks of the Hg on ligand modified WIGE. The nitrogen containing ligand act as a soft base. Cd^{2+} and Hg^{2+} ions were soft acids. Although

Hg^{2+} ion is highly interfered with Cd^{2+} ion which was confirmed from the appearance of sharp of Hg^{2+} ion as compared to the Cd^{2+} ion.
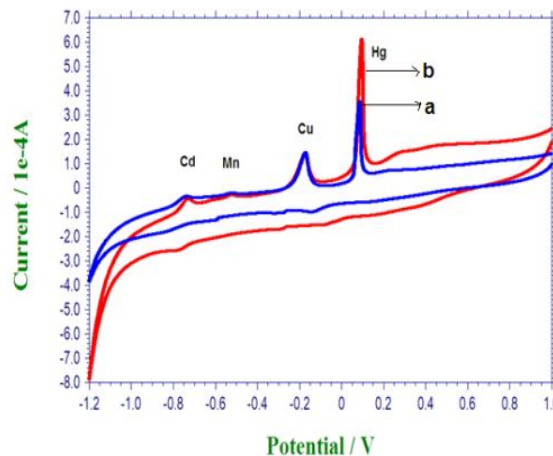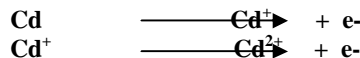

Fig. 9. Cyclic Voltammetric parameters for mixture of 1mM Cd(II), 1mM Mn(II), 1mM Cu(II) and 1mM Hg(II) ions on a) bare WIGE b) on ligand modified WIGE.

Optimum limit

The cyclic voltmmogram for different concentrations of Cd^{2+} ion in the range of 1×10^{-5} M to 5×10^{-4}M on ligand modified WIGE at constant sweep rate 40mV/s was presented in Fig.10. The cyclic voltammetric parameters were tabulated in Table. IV. At lower concentrations two anodic peaks were appeared which may be due to slow electron transfer and the following mechanism was proposed.

$$Cd \longrightarrow Cd^+ + e-$$
$$Cd^+ \longrightarrow Cd^{2+} + e-$$

From the cyclic voltammetric parameters, the optmium detection limit of Cd^{2+} ion on ligand modified WIGE was found to be 1×10^{-5}M.
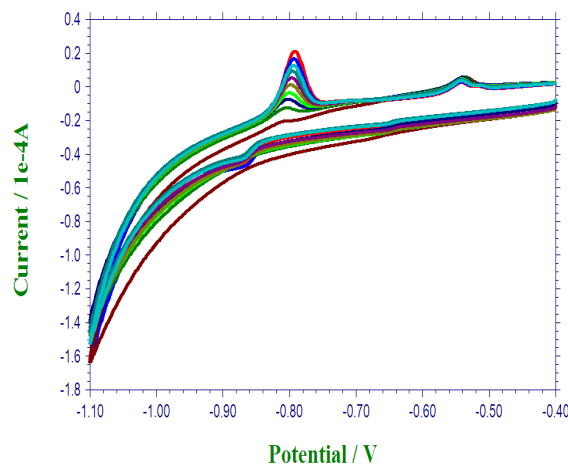

Fig.10 Cyclic voltammogram for different concentrations of Cd^{2+} ion on ligand modified WIGE at 40mV/s in the range of 1×10^{-5} M to 1×10^{-4}M.

Table. IV Cyclic voltammetric parameters for different concentrations of Cd²⁺ ion on ligand modified WIGE at 40mV/s.

Conc.	Ipa x 10⁻⁶ (A)	**Epa** (V)
1X10⁻⁵M	-----	-----
2X10⁻⁵M	-0.1187	-0.8053
3X10⁻⁵M	-0.6256	-0.8026
4X10⁻⁵M	-0.2872	-0.7998
5X10⁻⁵M	0.1616	-0.7981
6X10⁻⁵M	0.5744	-0.7971
7X10⁻⁵M	1.026	-0.7962
8X10⁻⁵M	1.362	-0.7943
9X10⁻⁵M	1.709	-0.7943
10X10⁻⁵M	2.167	-0.7926

Chrononamperometry and chronocoluometry

The chronoamperomogram and its derivative plot for different concentrations of Cd²⁺ ion in ammonium fluoride medium on ligand modified WIGE was shown in Fig.(11 and 12) respectively. The diffusion co-efficient values were tabulated in Table.V. According to the Cottrell equation, the diffusion co-efficient values were decreased with increasing concentration. This suggests that cadmium redox system is diffusion controlled one.
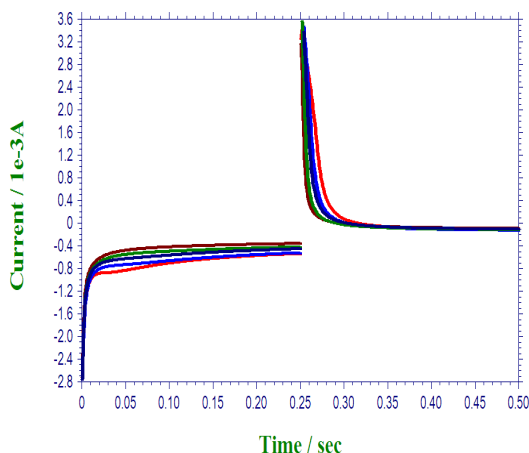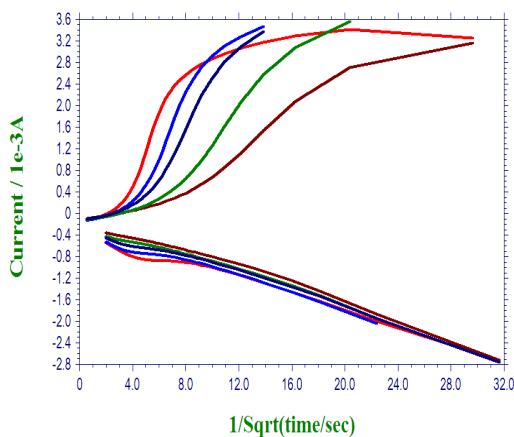

Fig,11

Fig.12

Fig.11 and 12 Chronoamperamogram and Cottrell plot for different concentrations of Cd²⁺ ion on ligand modified WIGE in fluoride medium respectively.

Table. V Diffusion co-efficient values for different concentrations of Cd²⁺ ion on ligand modified WIGE in fluoride medium.

Conc.(mM)	Forward scan (Slope)	D red/ cm²s⁻¹	Reverse Scan (Slope)	D ox/ cm²s⁻¹
1	-12.99	0.0618	8.229	0.0101
2	-5.442	0.0035	4.080	0.0026
3	-7.917	0.0034	5.218	0.0026
4	-9.580	0.0031	6.143	0.0020
5	-12.99	0.0034	8.229	0.0021

The chronocoloumogram and Anson plots for different concentrations of Cd²⁺ ion on ligand modified WIGE in fluoride medium was shown in Fig.13 and 14 respectively. The diffusion co-efficient values were tabulated in table.VI. According to the Anson equation, the diffusion co-efficient values were decreased with increasing concentration. This suggests that cadmium redox system is diffusion controlled one.
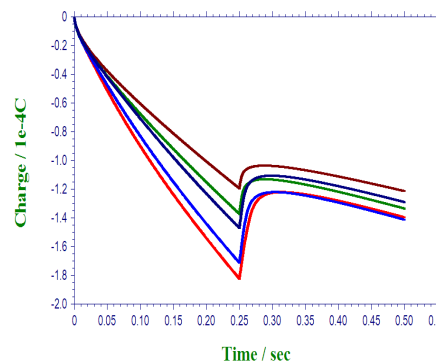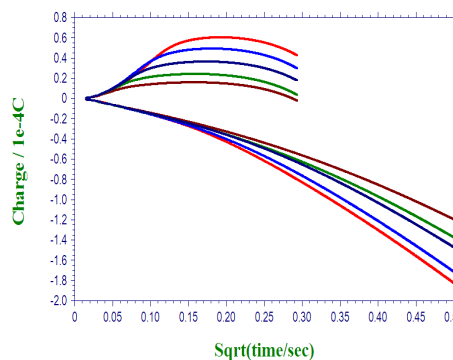

Fig.13

Fig.14

Fig.13 and 14 Chronocoloumogram and Anson plots for different concentrations of Cd²⁺ ion on ligand modified WIGE in fluoride medium.

Table. VI Diffusion co-efficient values for different concentrations of Cd²⁺ ion on ligand modified WIGE in fluoride medium.

Conc.(mM)	Forward scan (Slope)	D red/ cm²s⁻¹	Reverse Scan (Slope)	D ox/ cm²s⁻¹
1	-4.809	0.1764	-1.602	0.102
2	-3.533	0.107	-1.809	0.0574
3	-3.884	0.0916	-1.665	0.06
4	-4.555	0.086	-1.756	0.0529
5	-4.809	0.0787	-1.601	0.0458

Conclusion

The sensing of ligand on cadmium redox system was studied through the changing the peak current and peak potential values as comparad to the bare electrode. The electrochemical study of cadmium redox system was studied through scan rate effect and concentration effect. The optimum pH for analystical purpose on ligand modified WIGE was found to be 6. The optimum detection limit of cadmium ion on ligand modified WIGE was found to be 2×10^{-5}M. The simultaneous detection of heavy metal ions was inferred from the interference study. Chronoamperometry and chronocoloumetry studies were suggest that inversly proportion between concentration and diffusion coefficient.

Acknowledgements

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