

Electro-analytical characterization of carbon paste electrode for detection of heavy metal ion

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Carbon paste electrodes (CPE) as an electrochemical sensor has been fabricated using graphite powder and paraffin oil. The basic electrochemical parameters of the CPE electrode are characterized by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). Potassium ferricyanide $K_3[Fe(CN)_6]$ solutions as benchmark media to check redox reactions. Results illustrated that electron transfer to the electrode surface was diffusion controlled by both the techniques. The detection limits are 8×10^{-5} M for $K_3Fe(CN)_6$ and 0.019 M for lead ion. The diffusion coefficient (D), no. of electron transfer, and charge transfer coefficient were also investigated.

Keywords: Carbon paste electrodes, Cyclic voltammetry, Electrochemical impedance spectroscopy

Rapid industrialization has brought in major challenges in environmental field, water discharged from industry as well as the ground water, are contaminated by heavy metals. Heavy metal(s) are non-degradable and wide spread pollutants thus persistent in to the environment. There is a permissible limit of each metal, above this limit all metals are generally toxic and some are even hazardous. Industrial waste water contains several metal ions, such as lead, nickel, copper, aluminum and zinc. These are some common toxic ions because their metals are used in a large number of industries such as batteries manufacture, electroplating, metal finishing, mine, brewery, pharmaceutical and so on^{1,2}. Moreover, lead is omnipresent in the environment and is very hazardous for all the living organisms. The recognized potential for human safety hazards presented by lead in the environment necessitates monitoring of its concentration in industrial effluents as well as domestic waste water sources³.

The basic step to develop a process for removal of this heavy metal depends on the concentration. The qualitative and quantitative techniques such as inductively coupled plasma atomic emission spectrometry (ICPAES), atomic absorption spectroscopy (AAS), and inductively coupled plasma mass spectrometry (ICPMS) for detecting these heavy metals are sometimes complex. Chemical sensors can play an important, effective and efficient role in the

detection of this heavy metals⁴⁻⁷. And electrochemical sensors are the very popular sub class of chemical sensor which has the wide spread application for heavy metal ion determination. Electrochemical methods are very superior with some qualities, such as simple and rapid procedure, low cost equipment's and in situ experimentation⁸.

Different Electrochemical sensors can be made depending on the nature of the pollutant. To obtain a good and reliable electrochemical sensor, selection of electrode material becomes essential which constitutes the detection platform⁹.

In this regard, carbon paste electrodes (CPEs) have lots of benefits such as low cost, fixed response, renewability, low Ohmic resistance, and no necessity for internal solution. For this purpose conductive graphite powder usually becomes a good choice. To make the electrode it was dispersed in a non-conductive mineral oil as a binder, to make carbon paste. CPEs have been modified to lift the selectivity, sensitiveness, detection limit and other features of the electrodes¹⁰. Recent reports on heavy metal ion suggested that lots of attention is going-on a modification of electrode by numerous materials such as metal oxide nanomaterials, carbon based naomaterials and so on. But these all materials are very costly comparatively with graphite. So in our work, we present a low cost graphite material to fabricate an unmodified CPE for the detecton of lead heavy metal

ion in aqueous solution. This fabricated electrode has the capability to detect lead from the water samples. Two different electrochemical techniques, namely cyclic voltammetry (CV) and Electrochemical impedance spectroscopy (EIS), were applied for analysis of the sensor. Potassium hexacyanoferrate $K_3Fe(CN)_6$ solution was used to check the competence of the sensor. Further it shows its application in heavy metal ion detection such lead.

Experimental Section

Reagents, apparatus and analytical procedure

Graphite powder, (size $40\mu m$), paraffin liquid, and Alumina powder 98% were purchased from Loba chemicals. Potassium hexacyanoferrate (III) ($K_3Fe(CN)_6$) was purchased from Sigma-Aldrich. Lead (II) nitrate ($Pb(NO_3)_2$), Potassium nitrate 98% (KNO_3) and NaOH chemicals are obtained from Merck. Double distilled water was used for all experiments. Analytical measurements were performed on a PARSTAT MC 1000 electrochemical workstation (AMETEK, USA). The electrochemical cell was a three-electrode system: A platinum wire counter electrode, an Ag/AgCl (saturated KCl) reference electrode, and the carbon paste as a working electrodes. To characterize the conductive activities of the prepared electrodes cyclic voltammetry is a common and convenient method in voltammetry.

Electrode preparation

A clearer approach for making a carbon electrode is carbon paste method which is used by several researchers. In this method firstly 0.70 gm of carbon

source i.e; graphite is mixed with 0.3 gm suitable binder like paraffin oil in mortar. After that the paste is left for self-homogenization period of 24 h. Then prepared paste was packed into the electrode body (insulin syringe) and smoothed on a clean A_4 paper until it had a shiny appearance. A thin copper wire was inserted through the opposite end of the electrode body for electrical contact. The schematic preparation of this electrode is shown in Fig. 1.

Results and Discussion

Cyclic voltammetry (CV) experiment was applied to CPE using $K_3Fe(CN)_6$ with 1 M KNO_3 as an electrolyte. The CV curves Fig. 2(a) of CPE at different scan rates (10 mV/s-50 mV/s) shows that the redox peak potential of the electrode was not appreciably different for ferricyanide system. The unmodified CPE shows the well furnished oxidation and reduction peak currents. The oxidation and reduction peak currents from CV measurements can be described by Randles-Sevcik equation. Given as below¹¹:

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} V^{1/2} \quad \dots (1)$$

where, I_p is the peak current (A), A is the surface area of the working electrode (cm^2), n is the number

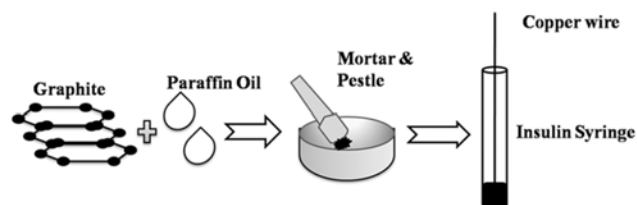


Fig. 1 — Preparation procedure of working electrode by carbon paste method

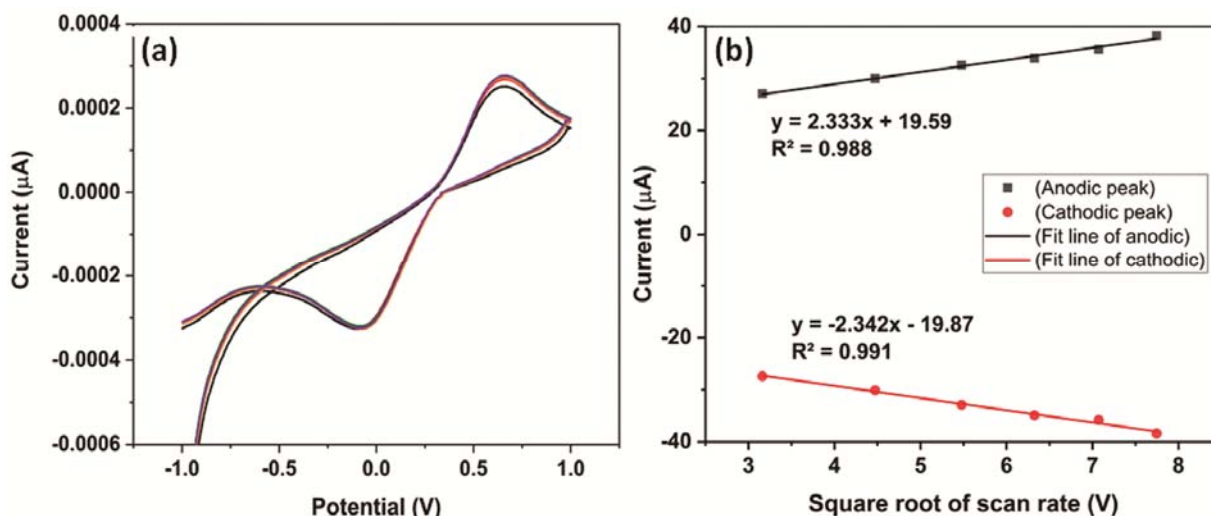


Fig. 2 — Cyclic voltammetry of 1mM $K_3Fe(CN)_6$ in 1 M KNO_3 with carbon paste electrode (a) current vs potential at different scan rates and (b) current vs square root of scan rates

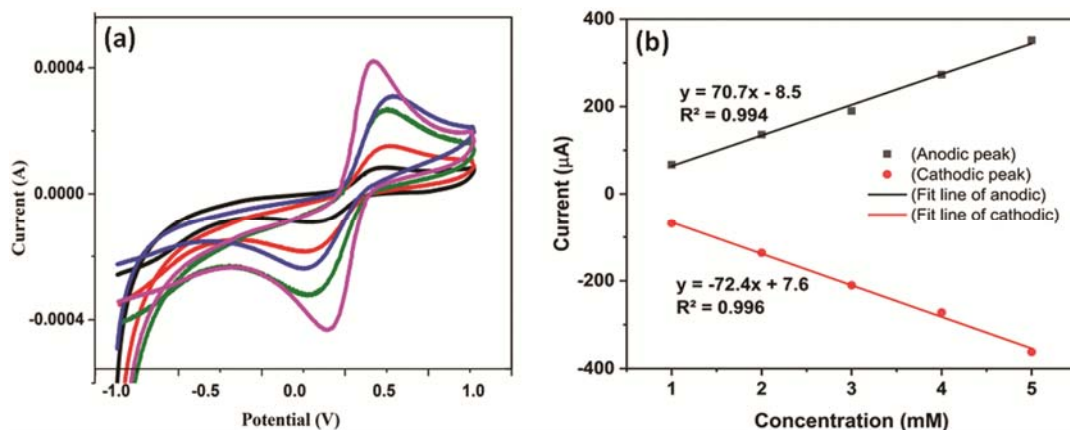


Fig. 3 — Cyclic voltammetry (a) peak current vs potential at varying concentrations of $K_3Fe(CN)_6$ of 30 mV/S scan rate and (b) Concentration versus anodic and cathodic peak current

of electrons involved in the reaction, D is the diffusion coefficient, (cm^2/s), V is the scan rate (V/s) and C is the initial concentration (mol/L). By the above equation, calculated area of electrode and diffusion coefficient was $0.45cm^2$ and $6.80 \times 10^{-3} cm^2/s$ respectively.

The CPE (a) shows a small current response with well-defined oxidation peak at around $-0.35 V$ and reduction peak at around $-0.29 V$. In the scan rate study Figure 2b illustrates that the kinetics of the reaction is diffusion controlled because the peak current is proportional to the square root of scan rate¹². Diffusion controlled kinetics suggest that the concentration of target ion can be deduced from the change in current of the system¹³. Figure 3(a) and (b) shows the peak height at varying concentrations of $K_3Fe(CN)_6$ of 30 mV/S scan rate and its calibration curve. The limit of detection (LOD's) for ferricyanide may also be calculated based on the standard deviation of the response (σ) of the curve and the slope of the calibration curve by using the formula: $-LOD = 3.3 \times (\sigma/b)$. Limit of Detection (LOD's) is $8 \times 10^{-5} M$ for $K_3Fe(CN)_6$ at CPE.

Electrochemical impedance spectroscopy (EIS)

The EIS is an effective method for correlating the electrocatalytic activity and charge transfer resistance of the electrode¹⁴. In this work it is often used to study the electrochemical processes at the electrode–electrolyte interface, reaction mechanisms and kinetics. The impedance experiment was performed in the presence of $1.0 mM K_3Fe(CN)_6$ in $1 M KNO_3$ at a scanning frequency from 0.1 to $100,000 Hz$ with initial potential $0.48V$. The absence of the semicircle in the Nyquist plot for CPE at high frequency depicted an enhanced ionic conductivity at the

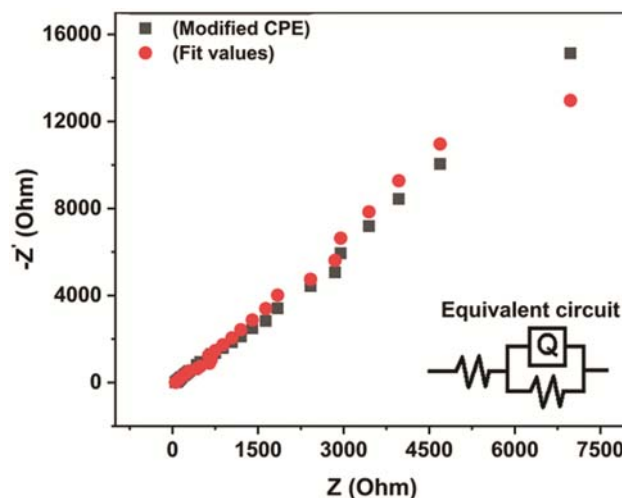


Fig. 4 — Nyquist plots for CPE in $1mM K_3Fe(CN)_6$ with $1 M KNO_3$ solution (inset model of an $R(QR)$ electrical circuit)

electrode–electrolyte interface (Fig. 4). The linear portion in the graph at lower frequencies corresponds that the electron transfer rate is fast and the process of electrode reaction is controlled mainly by diffusion and adsorption. This implies that the redox process occurred was dependent on mass transfer¹⁵. Similar result was come¹⁶. Based on the equivalent circuit fittings, the R_{ct} values and no. of electrons were found to be $5.206 \times 10^5 \Omega$ and 0.8 respectively.

Application in heavy metal ion detection

The prepared electrode was further applied for the detection and quantification of lead heavy metal ion in the aqueous solutions. CV behavior of the lead $Pb(NO_3)_2$ was investigated in $1 M KNO_3$ as an electrolyte for different concentrations of $1-5 mM$. A well-defined sharp oxidation peak at $-0.25 V$ and small reduction peak at about $-0.65 V$ was observed.

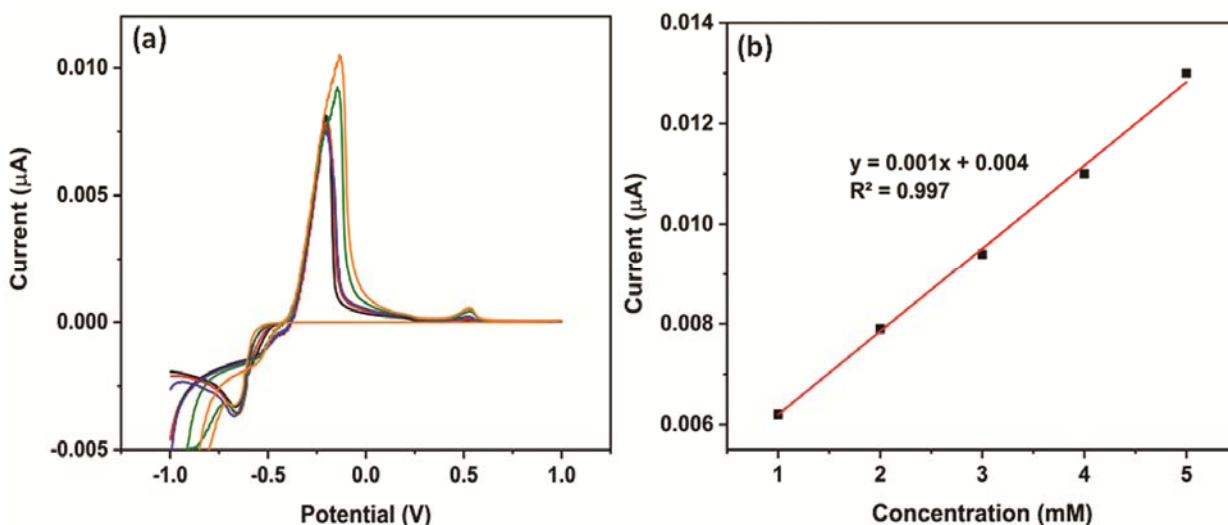


Fig. 5 — Cyclic voltammetry of 1-5mM Pb(NO₃)₂ in 1 M KNO₃ at different concentrations (a) current vs. potential (b) Calibration curve

As we can see in graph the oxidation peak was slightly shifted towards a positive potential at higher concentration. The calibration curve Figure 5(b) gives a linear equation at different concentration range with a good R^2 value of 0.997. We have found that the fabricated electrode holds a great potential to detect a lead ion and the detection limit was calculated to be 0.019 M. The quantification limit for heavy metal ion was calculated according to the formula¹⁷: $LOQ = 10(S/b)$ where, b is the slope of calibration curve and S is the std. deviation of the intercept. And the calculated value is 0.63 M for lead ion by unmodified CPE.

Conclusion

In summary, we have investigated the electrochemical performance of a CPE prepared from graphite, and characterized the redox properties of this unmodified electrode by K₃Fe(CN)₆. Cyclic voltammetry results suggest that the anlyte reaction is diffusion controlled and the EIS results verify this phenomenon. In addition, the constructed sensor was successfully applicable for the determination of lead heavy metal ion in aqueous solution. The developed electrode can be easily prepared and the detection limits were 8×10^{-5} M for K₃Fe(CN)₆ and 0.019 M for lead ion. This method can be a good approach for monitoring of lead in environmental samples. Its environmentally friendly material, simple operation and low cost make it suitable for *in-situ* measurement of heavy metal ions. In addition, this work is currently underway in order to investigate optimization the

parameters for the determination of other metal species of environmental interest.

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