Electrochemical Effect of Different Modified Glassy Carbon Electrodes on the Values of Diffusion Coefficient for Some Heavy Metal Ions

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Abstract. Glassy carbon electrode (GCE) was modified with carbon nanotubes (CNT), C₆₀ and activated carbon (AC) by mechanical attachment method and solution evaporation technique to preparation CNT/GCE, C₆₀/GCE and AC/GCE, these electrodes were modified in Li⁺ solution via cyclic voltammetry (CV) potential cycling to preparing CNT/Li⁺/GCE, C₆₀/Li⁺/GCE and AC/Li⁺/GCE. The sensing characteristics of the modified film electrodes, demonstrated in the application study for different heavy metal ions such as Hg²⁺, Cd²⁺, and Mn²⁺. Cyclic voltammetric effect by chronoamperometry (CA) technique was investigated to determination the diffusion coefficient (Df) values from Cottrell equation at these ions. Based on Cottrell equation (diffusion coefficient) of the redox current peaks of different heavy metal ions at different modified electrodes were studied to evaluate the sensing of these electrodes by the diffusion coefficient values. The modification of GCE with nano materials and Li⁺ act an enhancement for the redox current peaks to observe that the diffusion process are high at CNT/Li⁺/GCE, C₆₀/Li⁺/GCE and AC/Li⁺/GCE, but it has low values at unmodified GCE.

Keywords: Voltammetry, chronoamperometry, Cottrell equation, CNT/Li⁺/GCE, C₆₀/Li⁺/GCE, AC/Li⁺/GCE, diffusion coefficient

1. Introduction
In the electrochemistry of cyclic voltammetry for the modified electrodes have been used to determination of diffusion coefficient values by Cottrell equation [1,2] for different chemical compounds such as biochemical compounds [3-6], metal ions [7,8], blood [9,10], etc. Chronoamperometric experiments at modified electrodes are used to quantify both the concentration of [Fe(CN)₆]³⁻/⁴⁻ in the ionic liquid and the diffusion coefficient was determined [11]. The electrochemically derived of the diffusion coefficient values of several species such as Ru(bpy) in a hydrated clay. The small diffusion coefficients (typical solution value = 10⁻⁵ cm²/s) correspond well with what is known about the interaction of these species with clay surfaces. These small values indicate that the activation energy required to jump from site to site is quite large [12]. The chitosan films are permeable to both cationic [Ru(NH₃)₆]³⁺/²⁺ and anionic [Fe(CN)₆]³⁻/⁴⁻ redox couples, but anionic complexes are retained in the chitosan film. Electrochemical parameters, including apparent
diffusion coefficients for the redox probes at the electrodeposited chitosan modified electrodes are presented and are comparable to values reported for cast chitosan films [13].

Determination of the diffusion coefficient of \( \text{S}_2\text{O}_3^{2-} \) in the solution using Cottrell equations by the chronoamperometric data obtained at the short times, Because at short times, double-layer charging current and electrode surface related Faradic current are not negligible and, in fact, are often comparable in magnitude to the desired signal. For an electroactive material with a diffusion coefficient, \( D \), the current corresponding to the electrochemical reaction under diffusion control condition is described by Cottrell’s law. Chronoamperometry can also be used for the evaluation of the catalytic rate constant. At relatively short times [14]. Hydrogen diffusion coefficients in Ni, Co, Mn, and Al metal hydride electrode as a function of depth of discharge (DOD) and 3.75, 0.65, 0.4, 0.2 temperature were evaluated with modified Warburg impedance which describes more precisely the practical diffusion behavior. It was found that hydrogen diffusion coefficient in this electrode increases with the increase in DOD at ambient temperature, and for this electrode with 50% DOD, hydrogen diffusion coefficient increases with the increase of temperature and the activation energy for 21 hydrogen diffusion in it is 35 kJ mol [15].

The charge-transfer diffusion coefficient for the new electrochromic mixed-valence-compound film of vanadium hexacyano ferrate (VHF) was determined for both its oxidation and reduction processes, in H\(_2\)SO\(_4\) + M\(_2\)SO\(_4\) aqueous solutions, using short-time transient chronoamperometry (CA). It was revealed that the overall charge transfer process in a VHF film was limited by the electron diffusion rate between adjacent redox sites within the film. So \( D_{ct} \) is identified as an electron diffusion coefficient \( D_e \), which has an average value of 1.4 \( \times \) 10\(^{-9}\) cm\(^2\)/s. The calculated E-t data based on the interaction parameter theory, agree very well with the experimental curve [16]. The diffusion coefficient \( (D_1) \) of the Mn(II) ion in 0.1M KCl at lithium doped ITO electrode by using Chronoamperometry equal to 5.75 x 10\(^{-6}\) cm\(^2\)/s was determined. For diffusion control process, current versus time in accordance to Cottrell equation, a monotonic rising and current transient (current dependent of \( t^{-1/2} \)) should be observed [17].

In this work, CNT, C\(_{60}\) and activated carbon (AC) modified Mediators are fixed on the GCE surface using different methods such as CNT/Li\(^+\)/GCE, C\(_{60}\)/ Li\(^+\)/GCE and AC/Li\(^+\)/GCE to study the affect of diffusion coefficient \( D_t \) values, using Cottrell equation for different heavy metal ions Mn\(^{2+}\), Hg\(^{2+}\), and Cd\(^{2+}\).

2. Materials and Methods
2.1. Materials
CNT (Fluka, 99%), C\(_{60}\) (Fluka, 98%) and activated carbon (AC) (Fluka 98%). Other chemicals and solvents were used of annular grade and as received from the manufacturer. Deionizer water was used for the preparation of aqueous solutions. All solutions were deaerated with oxygen free nitrogen gas for 15 minutes prior to making the measurement.

2.2 Instruments
Electrochemical workstations of Bioanalytical System Inc. USA: Models BAS CV 50W with potentiostate driven by electroanalytical measuring software was connected to Personal computer to perform cyclic voltammetry (CV), chronocoulometry (CC) and chronoamperometry (CA), an Ag/AgCl (3M NaCl) and Platinum wire were used as a reference and counter electrode respectively [1].

2.3 Preparing of working electrodes
There are two methods for modification of working electrodes, mechanical attachment technique method (MA) was used by pressing of a clean GCE surface onto a few mg of CNT or AC powder placed on a filter paper. The other method is solution evaporation technique, which includes the
application of a 2 μL of saturated C₆₀ in acetonitrile solvent and subsequently dried by hot air blower before placing in voltammetric cell.

The working electrodes used in this study were GCE only and modified GCE with CNT and AC by mechanical attachment method (CNT/GCE and AC/GCE) [18, 19]. Another modified electrode with C₆₀ has evaporated solution on the GCE (C₆₀/GCE) [20-21]. CNT/Li⁺/GCE, C₆₀/Li⁺/GCE and AC/Li⁺/GCE were prepared by the doping of Li⁺ ion on to CNT/GCE, C₆₀/GCE and AC/GCE via 10 potential cycling between +600 to -600mV in presence of 0.1M LiOH during cyclic voltammetry. A platinum wire (1mm diameter) counter electrode and an Ag/AgCl (3M NaCl) reference electrode were used in CV analysis.

3. Results and Discussion

3.1. Effect of different modified electrodes

The redox current peaks of Mn²⁺, Hg²⁺ and Cd²⁺ were considerably enhanced and shifting towards the origin, when the CNT/Li⁺/GCE was used in comparison with the C₆₀/Li⁺/GCE, AC and GCE. The results confirm the electro-catalytic activity of CNT was also exerted on the redox current under the conditions of cyclic voltammetry. The degree of sensitivity/electro-catalytic response for the different electrodes increases in the order below at the Mn²⁺ and Cd²⁺.

CNT/Li⁺/GCE > C₆₀/Li⁺/GCE > AC/ Li⁺/GCE > GCE

But, it seems the modified AC/ Li⁺/GCE has a high redox current peaks comparison with CNT/Li⁺/GCE and C₆₀/Li⁺/GCE in Hg²⁺ as show in Figure 1. The activated carbon with mercury ion has a high sensitivity for redox current peaks as a good sensor with doping in Lithium ion.

![Figure 1. Cyclic voltammogram of Hg²⁺ at different modified GCE with CNT/Li⁺, C₆₀/Li⁺ and AC/ Li⁺ in 0.1M KCl as supporting electrolyte](image)

3.2. Affect the different modified electrodes on the values of diffusion coefficient (Dᵢ)

Mass Transport in Electrochemistry In order to react a species at an electrode it needs to be transported from bulk to surface. Three principal mechanisms involves are; 1) the diffusion where the movement of molecules along a concentration gradient, from an area of high concentration to an area of low concentration; 2) migration transport of a charged species
under the influence of an electric field; and 3) convection transport of species by hydrodynamic transport (e.g. natural thermal motion and/or stirring) [22].

3.3. Chronoamperometry from Cottrell equation

In Chronoamperometry (CA) the potential is stepped from an individual value \(E_i\) to \(E_e\) and the accompanying current is recorded as a function of time for an electrode in unstirred solution [1, 23-25]. The current decays as the electrolysis proceeds to deplete the solution near the electrode of electroinactive species. The current response is described by the Cottrell equation [22]:

\[
I = nFAC(D/\pi t)^{1/2}
\]

where
- \(I\) = Current
- \(n\) = Number of electron per molecule
- \(F\) = Faraday constant
- \(A\) = Electrode area
- \(D\) = Diffusion coefficient of electroactive species
- \(C\) = Concentration of electroactive species
- \(T\) = Time

![Figure 2. Chronoamperomogram or Cottrell plot obtained for the reduction of heavy metal ion in 0.1M KCl as supporting electrolyte using modified GCEs. Potential was scanned in a negative direction from -1800 to +1800mV with 250msec. pulse width versus Ag/AgCl.](image)

From the slope of a plot of \(I\) vs \(t^{1/2}\) at different concentrations of Mn(II), Hg(II) and Cd(II) in 0.1 M KCl as supporting electrolyte at different working modified GCEs (CNT/Li\(^+\)/GCE, C\(_{60}\)/Li\(^+\)/GCE and AC/Li\(^+\)/GCE), the \(D_f\) values were estimated according to the Cottrell equation [23]. The slopes of the resulting straight lines were then calculating the average values of diffusion coefficient from Cottrell equation as shown in table 1. The results show that the electron transfer is a diffusion-controlled process and the obtained diffusion coefficient value is in good agreement with reported values of diffusion coefficient.

Electrode reaction rates and most double layer parameters are extensive quantities and have to be referred to the unit area of the interface. For diffusion control process, current versus time in accordance to Cottrell equation, a monotonic rising and current transient (current dependent of \(t^{1/2}\)) should be observed. However, Figure 2 shows a non-monotonic rising current transient versus time.
dependent of power (-1/2) was observed instead indicating presence of a non diffusion controlled process. It supported the earlier finding of a complex surface process based on the scan rate study. From table 1, it seems that the values of $D_f$ of heavy metals of Mn(II), Hg(II) and Cd(II) at the modified CNT/Li$^+$ electrodes have 1.53x10^{-7}, 3.25x10^{-6}, and 4.52x10^{-7} cm$^2$/sec respectively, also for C$_{60}$/Li$^+$/GCE, 5.12x10^{-5}, 5.12x10^{-6}, 3.12x10^{-6} cm$^2$/sec and for AC/Li$^+$/GCE, 6.55x10^{-4}, 1.75x10^{-6}, 1.501x10^{-6} respectively; these values are good diffusion coefficient comparing with the values at GCE 5.19x10^{-2}, 2.23x10^{-3}, and 1.55x10^{-3} respectively.

| Electrodes     | $D_f$, Mn(II), cm$^2$/sec | $D_f$, Hg(II), cm$^2$/sec | $D_f$, Cd(II), cm$^2$/sec |
|----------------|---------------------------|----------------------------|---------------------------|
| GCE            | 5.19x10^{-2}              | 2.23x10^{-3}              | 1.55x10^{-3}              |
| CNT/Li$^+$/GCE | 1.53x10^{-7}              | 3.25x10^{-6}              | 4.52x10^{-7}              |
| C$_{60}$/Li$^+$/GCE | 5.12x10^{-5} | 5.12x10^{-6} | 3.12x10^{-6} |
| AC/Li$^+$/GCE  | 6.55x10^{-4}              | 1.75x10^{-6}              | 1.501x10^{-6}             |

3.4. Scanning Electron Microscopy (SEM)
Scanning Electron Microscopy (SEM) the fractured surfaces of the nanocomposites were studied using a JEOL attached with Oxford Inca Energy 300 EDXRF scanning electron microscope operated at 20 to 30 kV. The scanning electron photographs were recorded at a magnification of 1000X to 6000X depending on the nature of the sample. SEM analysis was carried out to investigate microcrystal. Samples were dehydrated for 45 minutes before being coated with gold particle using SEM coating unit Baltic SC030 sputter Coater. SEM was used to examine the morphology of CNT and AC microcrystal by mechanical attached on a graphite electrode surface; C$_{60}$ has evaporated on a graphite electrode surface. CNT/Li$^+$, C$_{60}$/Li$^+$ and AC/ Li$^+$ were prepared by the doping of Li$^+$ ion on the electrodes, SEM of these electrodes show in Figure 3.

![SEM images](image)

**Figure 3.** SEM of the a) CNT/Li$^+$ b) C$_{60}$/Li$^+$ and c) AC/Li$^+$ microcrystal attached to a graphite electrode surface via solvent cast on to 5 mm diameter basal plane graphite electrode and doping of Li$^+$ ion respectively. Scale bars are 2 µm.

4. Conclusion
CNT/Li$^+$/GCE, C$_{60}$/Li$^+$/GCE and AC/Li$^+$/GCE were fabricated successfully. These modified electrodes are useful in certain electrochemical applications. Diffusion coefficient ($D_f$) of electroactive species (heavy metal ions) such as Mn(II), Hg(II) and Cd(II) can be estimated from the electrochemical data
from Cottrell equation. Furthermore, an understanding of the mechanisms of charge transport, control of the pore dimensions to enhance transport properties, and complete elucidation of the role of the electrolyte in ion-exchange reactions and charge conduction are required. As these factors are mapped out, the technique will become more generally applicable in the determination diffusion coefficients for heavy metal ions chemists. The electroactive surface of the modified electrodes by determination of diffusion coefficient (Df) were calculated from cyclic voltammetric with chronoamperometric response. Under optimized conditions, good analytical performance was obtained, including suitable precision, excellent linear dynamic range and reproducibility when using the nonmaterial in working electrode to determination of diffusion coefficient.

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