Electrochemical Reduction of Manganese Mediated by Carbon Nanotubes/Li+ Modified Glassy Carbon Electrodes

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Glassy carbon electrodes (GCE) were modified with carbon nanotubes (CNT) with and without Li+ dopant by a mechanical attachment method. These modified working electrodes, abbreviated as CNT/Li+/GCE and CNT/GCE, produced two reduction peaks of Mn(II) at +0.8 V and +0.1 V *vs* Ag/AgCl in 0.1 M KCl, which appeared irreversible during cyclic voltammetry. The sensing characteristics of the modified film electrodes demonstrated in this study were composed of: (i) a wide working potential window ranging from +1.8 V to -1.8 V (depending on different scan rates, pH, concentration and temperature); (ii) a wide applicable pH range (from at least 2-10); (iii) a wide applicable temperature range from 5-90 ºC; (iv) a current response that is stable and fast with a satisfactory and reproducible linear voltammetric and amperometric response to various analytes; (v) a good reproducibility and recovery rate in seawater and blood; (vi) interfering metal ions such as Hg^{2+}, Cd^{2+} and Cu^{2+} appeared to pose positive interference on the reduction peaks of Mn^{2+}. The reduction current of Mn^{2+} using CNT/Li+/GCE was largely influenced by concentration, pH, temperature and scan rate. Based on the calibration curve obtained, a linear graph of up to 1 mM Mn(II), with an impressive sensitivity response of 66.7 µA/mM, was obtained. Based on chronoamperometry, a diffusion coefficient for Mn^{2+} of 1.53×10^{-7} cm^2/s was determined.

Key Words: CNT/Li+/GCE, Mn(II), Electrocatalyst, Cyclic voltammetry.

INTRODUCTION

The discovery of carbon nanotubes (CNTs) has had a profound effect on electroanalysis. The properties and applications of CNTs themselves have been studied in cyclic voltammetry. However, the modification of CNTs has recently been the focus of much research, primarily to improve their solubility in various solvents. Modified CNT electrodes also allow the electrochemist to tailor the properties of the CNT or the electrode surface, to impart any desired properties such as enhanced sensing capabilities. In the electrochemical modifications, strategies and research were carried out using modified CNT for electroanalytical and bioanalytical applications[1-4].

In analytical applications based on the effects produced upon modification of different solid electrodes, especially glassy carbon electrode (GCE) substrates with CNT, the modifications were most usually carried out by coating or preparing CNT-binder composite electrodes. Simple modified electrode designs can be obtained by incorporation of a small amount of CNT dispersion onto a GCE[5-8]. Carbon nanotubes-modified GCE are primarily used for the detection of non-metallic compounds, especially biochemical compounds[9].

Carbon nanotubes-modified electrodes like GCE may be considered as a viable alternative to mercury-based procedures in studying some heavy metals *viz.*, Cd(II) and Pb(II) by cyclic voltammetry[10,11].

The mechanism of the electrochemical reaction with lithium of the modified CNTs was studied by X-ray diffraction lithium was first intercalated in the activated multi-walled nanotubes between graphene layers, forming *n*-stages. Interlayer expansion and misfits between curved layers caused fracturing and exfoliation of the CNT with an irreversible loss of staging phenomena. The resulting solids displayed improved capacity retention on successive cycles. These results support a new strategy to improve the electrochemical performance of graphitized CNT[12-14].

Analysis of Mn(II) is usually carried out using spectroscopic methods such as ICP, AAS and less commonly voltammetric methods. Our experience shows that the voltammetric detection of Mn(II) is not easily carried out on the electrode surface of glassy carbon electrodes. However, a modified GC electrode with a lecithin film was reported to improve the redox reaction of ascorbic acid in presence of the Mn(II) ion[15].

Manganese is an interesting element for voltammetric studies as it has many oxidation states, from zero and +1 up to +7. Manganese compounds, where manganese is in an oxidation

state of +7, are powerful oxidizing agents[16,17]. Manganese is an essential trace element for human health, but where there is an excess intake, it can also cause bad effects on health. The presence of excess amounts of manganese in the natural environment can lead to the withering of leaves and cause tumor development in animals.

In this work, CNT-modified mediators were fixed on the GC electrode surface using different methods for the CNT and CNT/ Li$^+$ electrodes. Results showed the modified electrode CNT/Li$^+$ has good electrochemical behaviour in terms of stability and high sensitivity to heavy metals.

EXPERIMENTAL

Carbon nanotubes from Fluka at a purity of 98 % was used. Other chemicals and organic solvents used were of analar grade and used as received from the manufacturers (KCl, MnCl$_2$, LiOH, HCl, NaOH, NH$_4$Cl, HgCl$_2$, CdCl$_2$, CuCl$_2$ and MgCl$_2$). Distilled water was used for the preparation of aqueous solutions. All solutions had the dissolved oxygen removed with pure nitrogen gas for 15 min prior to making the voltammetric measurements.

Methods: Electrochemical workstations from BioAnalytical System Inc. USA:Models BAS CV 50W with potentiostates driven by electroanalytical measuring software was connected to a PC computer to perform cyclic voltammetry (CV), chronocoulometry (CC) and chronoamperometry (CA). An Ag/AgCl (3 M NaCl) and platinum wire were used as a reference and counter electrode, respectively. The working electrodes used in this study were a GC electrode, a modified CNT/GCE electrode that was modified by mechanical attachment and a CNT/Li$^+$/GCE electrode modified by doping with Li$^+$ ion (see below).

Preparing the CNT and CNT/Li$^+$ modified GC electrodes: A mechanical attachment technique was employed[18,19]. This technique included abrasive application of CNT microparticles at the electrode surface of the GCE, forming an array of CNT microparticles. The doping of the Li$^+$ ion onto the CNT/GCE electrode was carried out by subjecting the electrode to level-10 potential cycling in the presence of 0.1 M of LiOH between +600 to -600 mV during cyclic voltammetry.

Scanning electron microscopy: Scanning electron microscopy (SEM) of the nanocomposite CNT of 2 ± 0.2 µm size were studied using a Jeol attached to an Oxford Inca Energy 300 EDXFEL scanning electron microscope operating at 20-30 kV. The scanning electron photographs were recorded at a magnification of 1000-6000 X depending on the nature of the sample.

Samples were dehydrated for 45 min before being coated with gold particles using a Baltic SC030 Sputter Coater. SEM was used to examine the morphology of the CNT micro-crystals, which were attached mechanically on a graphite electrode surface, before and after electrolysis by cyclic voltammetry. Fig. 1a is the SEM of CNT/Li$^+$ microparticles with size (in diameter) ranging from 1-2 µm that appeared sparsely and randomly distributed on the electrode surface before electrolysis. Fig. 1b is the SEM of the CNT/Li$^+$ electrode after electrolysis of the Mn^{2+} solution. Although many of the microparticles
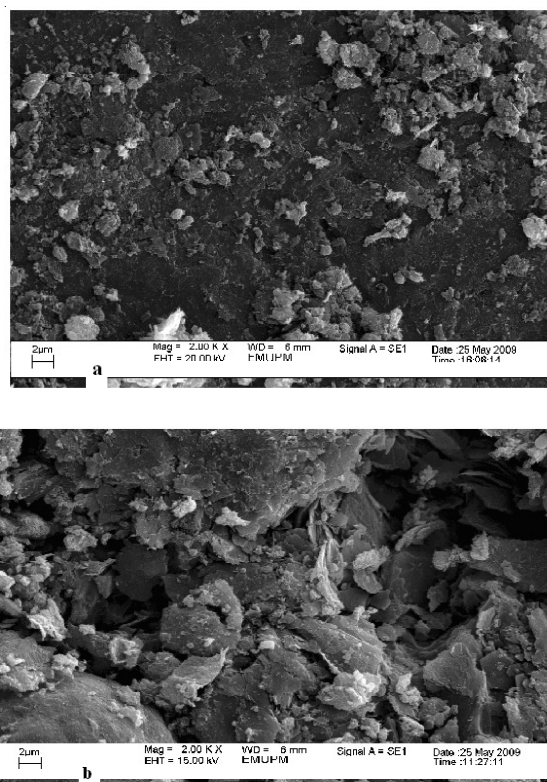

Fig. 1. Scanning electron micrographs of carbon nanotubes microparticles mechanically attached to a basal plane pyrolitic graphite electrode (a) before and (b) after electroanalysis with Mn^{2+}

still remain at about 2 µm, there are some of the CNT/Li$^+$/Mn(II) microparticles that appear to have increased slightly from 2-5 µm. The slight increase in size could be due to the presence of Mn^0.

RESULTS AND DISCUSSION

Current enhancement at modified electrodes: Fig. 2(a-b) show that the reduction peaks of Mn^{2+} were considerably enhanced by 4-5 times, with almost a 200 mV peak shifting towards the origin, when the CNT/Li$^+$/GCE electrode was used in comparison with the CNT/GCE and GCE electrode. The result confirms the electro-catalytic activity of CNT was also exerted on the reduction of Mn(II) under the conditions of cyclic voltammetry. The degree of sensitivity/electro-catalytic response for the different electrodes increases in the order of:

CNT/Li$^+$/GCE > CNT/GCE > GCE

The reduction peaks of Mn^{2+} appeared more discernable when the CNT/GC electrode was used compared to a bare GC electrode. Reduction peaks become even more pronounced and enhanced by 4-5 times at the electrode surface of the CNT/Li$^+$/GCE electrode. The reduction of Mn(II) is irreversible, since there is an absence of electro-activity on the reversal/oxidative scan during cyclic voltammetry for the GC electrode and the modified electrodes. The electro-catalytic effect appeared more enhanced since the Li$^+$ dopant would increase the conductivity of the electrode surfaces. Since the CNT/Li$^+$/GCE electrode is a more sensitive electrode, it was used for subsequent optimization studies.
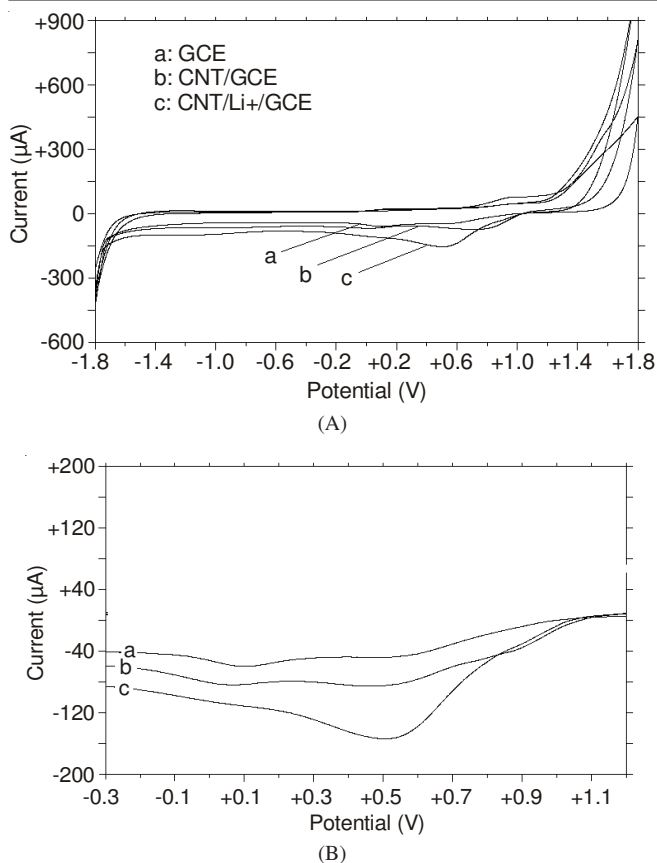
(A)

(B)

Fig. 2.   (A) Enlarged voltammogram for the reduction peak of 1 mM Mn^{2+} in 0.1 M KCl as supporting electrolyte at scanning rate 100 mv s^{-1} using (a) GCE (b) CNT/GCE and (c) CNT/Li$^+$/GCE *versus* Ag/AgCl and (B) Enlarged voltammogram for the reduction peak of 1 mM Mn^{2+} in 0.1 M KCl as supporting electrolyte at scanning rate 100 mv s^{-1} using (a) GCE (b) CNT/GCE and (c) CNT/Li$^+$/GCE *versus* Ag/AgCl

Optimization of conductive effect

Effect of varying the supporting electrolyte: The type of supporting electrolyte appears to significantly affect the reduction peak current of the Mn(II) ion. Although the electro-catalytic behaviour at the electrode surface of the CNT/Li$^+$/GCE can be observed for all the electrolytes studied, the degree of current enhancement varies in the order of: NaCl > KCl > NH$_4$Cl > Na$_2$SO$_4$, as shown in Fig. 3.
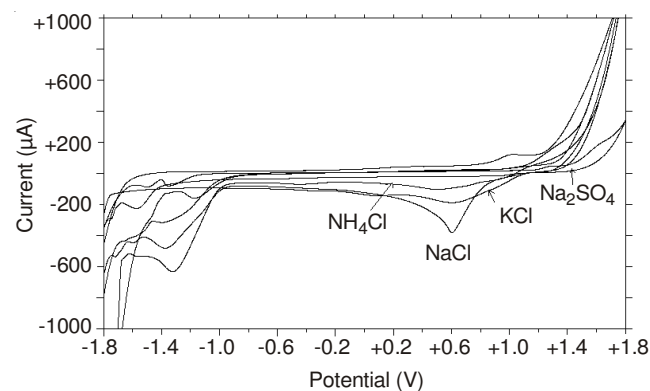

Fig. 3.   Cyclic voltammogram for the reduction peaks of 1 mM Mn^{2+} at pH 2 in 0.1 M of different supporting electrolyte NH$_4$Cl, NaCl, Na$_2$SO$_4$ and KCl at scanning rate 100 mv s^{-1} using CNT/Li$^+$/GCE *versus* Ag/AgCl

Effect of varying the pH: Based on the results of the pH studies on the reduction of Mn(II), ranging from a pH of 2 to a pH of 11, two distinct pH regions showing obvious differences in the reduction processes of Mn(II) on the CNT/Li$^+$/GC electrode surface are evident and are summarized below:

(a) Acidic media with a pH ranging from 2-6: It was observed that the reduction current of Mn^{2+} gradually and linearly increased with the lowering of pH from 6-2 accompanied by a linear shift in the reduction potential, which satisfies the linear equation of I (μA) = -48.38 pH + 354.5 with a correlation coefficient of R^2 = 0.9179 and E (mV) = -29.60 pH + 627.8 with a correlation coefficient of R^2 = 0.918, respectively. The two reduction peaks of Mn^{2+} at +800 mV and +100 mV shifted to lower potentials at +600 and -1450 mV, respectively, with an increased current for both the reduction peaks on different modified electrodes as shown in Fig. 4. The presence of stepwise (2 steps) 1-e reduction of Mn(II) to Mn(0) *via* the following is apparent:
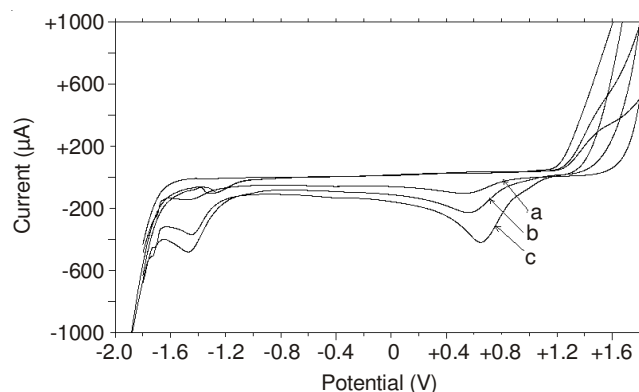

Fig. 4.   Cyclic voltammogram for effect pH 2 of 1 mM Mn^{2+} in 0.1 M KCl at scanning rate 100 mv s^{-1} using (a) GCE (b) CNT/GCE and (c) CNT/Li$^+$/GCE *versus* Ag/AgCl

$$Mn^{2+} + e \longrightarrow Mn^+ \qquad E = + 600 \text{ mV} \qquad (1)$$
$$Mn^+ + e \longrightarrow Mn \qquad E = -1450 \text{ mV} \qquad (2)$$

On the other hand, the potential of one step 2-e reduction peak of Mn^{2+} to Mn(0) at -1180 mV has been reported[17].

$$Mn^{2+} + 2e \longrightarrow Mn \qquad E = -1180 \text{ mV} \qquad (3)$$

(b) Alkaline media with a pH ranging from 7-11: In a basic media, the first reduction peak of Mn(II) shifted to a higher potential of +700 mV with the reduction current increased by almost threefold, while the second step observed in acidic media was not present, indicating the presence of a one step-2 electron reduction as shown in Fig. 5.

Effect of varying the temperature: Effect of temperature on the reduction process of Mn^{2+} was studied. The current increases gradually at a temperature range from 5-90 ºC. Fig. 6 is a plot of the log (reduction current) of Mn^{2+} *versus* the reciprocal of temperature, which was found to be fairly linear and was in agreement with the thermodynamic expectations of Arrhenius' eqns. 5 and 6[18,19].

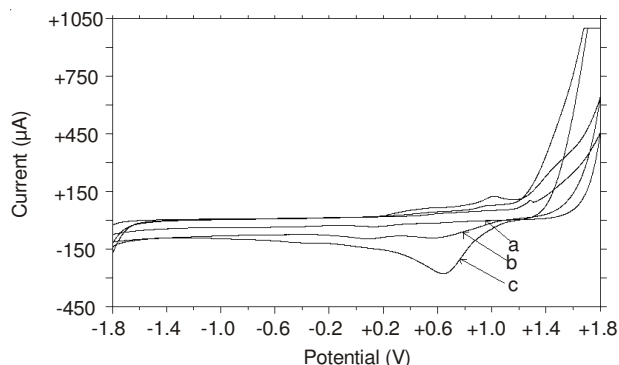$$\sigma = \sigma^0 \exp\left(-\frac{E_a}{RT}\right) \qquad (5)$$

Fig. 5. Cyclic voltammogram for effect of pH 11 on 1 mM Mn^{2+} in 0.1 M KCl at scanning rate 100 mv s^{-1} using (a) GCE (b) CNT/GCE and (c) CNT/Li^+/GCE *versus* Ag/AgCl
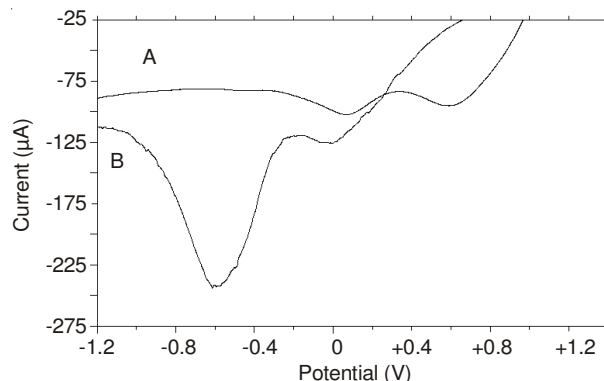

Fig. 6. Dependence of reduction current of Mn^{2+} as a function of temperature in 0.1 M KCl at scanning rate 100 mv s^{-1} using CNT/Li^+/GCE *versus* Ag/AgCl

$$D = D^0 \exp\left(-\frac{E_a}{RT}\right) \qquad (6)$$

where σ/D are conductivity/diffusibility and σ^0/D^0 are standard conductivity/the initial diffusibility.

Based on the slope of the linear graph, the value of activated energy (E_a) of Mn(II) is 17.23 KJ/mol compared with the E_a of 45.35 KJ/mol obtained from previous work[20]. The conductivity of CNT/Li^+ increases with the increasing temperature also has a significant influence on the activation energy for diffusion of the substrate of interest.

Fig. 7 shows that an increase in temperature from 25°C to 80 °C is accompanied by a sharp increase in current and also by an obvious shifting of the reduction potential towards the origin, a zero potential. Consequently, combined usage of CNT/Li^+ and the temperature increase/thermal effect would have a profound positive influence on the observed electrocatalytic effect of carbon nanotubes.

Effect of varying the scan rate: A reasonably linear dependence of Mn^{2+} reductive current on the scan rate is described by y = 0.7931X - 0.0306, R^2 = 0.97. The slope of graph log I_p (reductive current) *versus* log v (scan rate) is 0.79, which significantly differs from the theoretical value of "1/2" for diffusion-controlled processes as in Fig. 8, indicating the presence of a complex surface process.

Fig. 9 shows the linear relationship between the reductive potential and the scan rate (675 mV at a low scan rate to 715 mV at a high scan rate) and can be described by Y = 0.075x + 677.4 (R^2 = 0.9686). By extrapolating the plot to a zero

Fig. 7. Voltammogram for the two reduction peaks of 1 mM Mn^{2+} in 0.1 M KCl 100 mv s^{-1} using CNT/Li^+/GCE as a working electrode and Ag/AgCl as a reference electrode at (A) 25 °C and (B) 80 °C
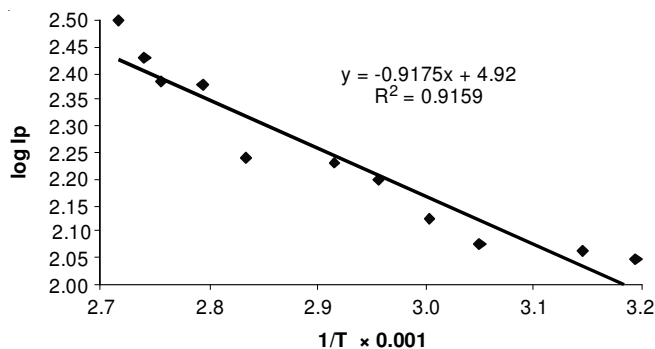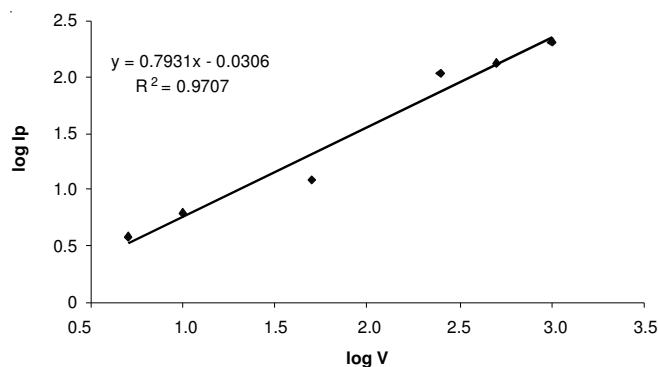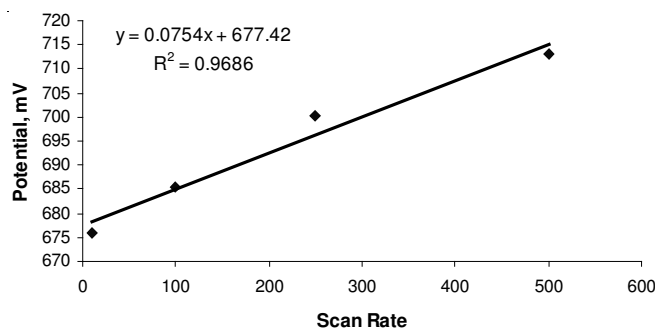

Fig. 8. Plot of log Ipc (reductive current) *versus* log V (scan rate) of 1 mM $MnCl_2$ in 0.1 M KCl as a supporting electrolyte using CNT/Li^+/GCE *versus* Ag/AgCl

Fig. 9. Plot of potential *versus* scan rate of 1 mM $MnCl_2$ in 0.1 M KCl as a supporting electrolyte at scanning rate 100 mV s^{-1} using CNT/Li^+/GCE *versus* Ag/AgCl

current, a zero current potential ($E^{0,1}$) of 677 mV for the reduction of Mn(II) ion at the CNT/Li^+/GC electrode is obtained, which should be independent of the IR effect due to the heterogeneous kinetics and morphology of the surface materials.

Calibration graph: Fig. 10 shows the calibration curve of different concentrations (0.001-1 mM) of Mn(II) in 0.1M KCl. Linearity of the plot up to a concentration of 0.1 mM of Mn^{2+} had an impressive current sensitivity of close to 64.7 μA/mM. A detection limit of 7 μM was estimated based on the formula 3σ/slope, where σ is the standard deviation of the background noise; 50 data points were taken adjacent to the reduction peaks at 100 mV/s and the slope is given by 64.7 μA/mM.
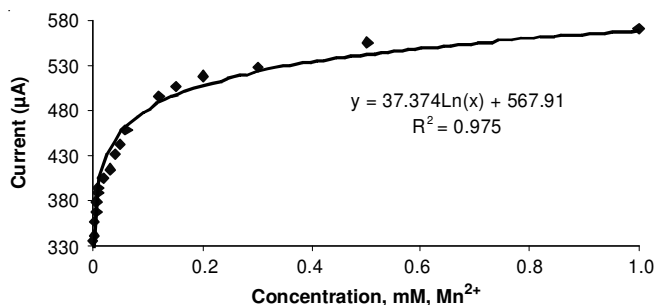
Fig. 10. Plot of reduction current *versus* different concentration (0.001-1) mM MnCl₂ in 0.1 M KCl at scanning rate 100 mv s⁻¹ using CNT/Li⁺/GCE *versus* Ag/AgCl

Chronoamperometry and chronocoulometry: Fig. 11 shows the monotonous rising and decaying transient current in accordance with the theoretical expectation of the Cottrell equation[21,22], based on the diffusion process of a planar electrode. The diffusion coefficient (D) of the Mn^{2+} ion was determined using chronoamperometry in a 0.1 M solution of KCl with CNT/Li⁺/GC as a working electrode and was equal to 1.5×10^{-7} cm²/s. Using chronocoulometry, it was found that the CNT/Li⁺/GC electrode has a total charge transfer of 10.7 μC/m² in Mn^{2+} at a pH of 2, while a lower charge transfer of 2 μC/m² in Mn^{2+} was seen at a pH of 8. This shows that the CNT/Li⁺/GC electrode in an acidic solution is more reducible than in an alkaline solution as shown in Fig. 12.
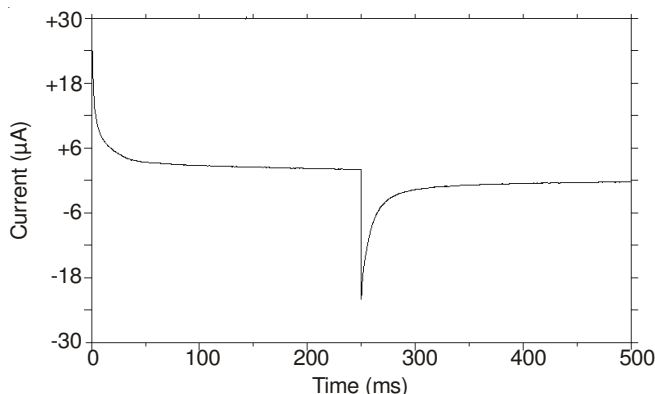

Fig. 11. Chrono-amperometry or Cottrell plot obtained for the reduction of 1 mM Mn^{2+} in 0.1 M KCl as supporting electrolyte using CNT/Li⁺/GCE *versus* Ag/AgCl. Potential was scanned in a negative direction from -1800 to +1800 mV with 250 ms pulse width
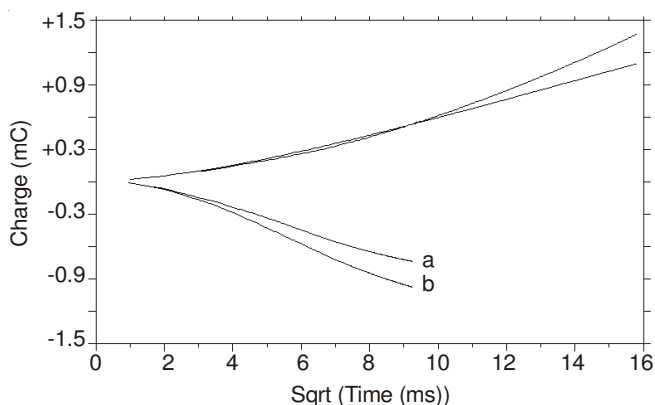

Fig. 12. Chronocoulometry or Anson plot of charge *versus* t^(1/2) obtained for the reduction of 1 mM MnCl₂ and 0.1 M KCl at (a) pH 8 and (b) pH 2 using CNT/Li⁺/GCE *versus* Ag/AgCl

Interference of heavy metals: Possible interference of some metals in the voltammetric determination of 2 mM of Mn^{2+} was studied by adding small amount of the interfering ion to a solution containing 2 mM each of Hg^{2+}, Cd^{2+} and Cu^{2+} using the optimized conditions at a pH of 2. The results in Table-1 showed positive interference by Hg^{2+}, Cd^{2+} and Cu^2 on the CV of Mn(II) by increasing the reduction current of Mn(II) by almost twofold to sevenfold and shifting its peaks to a lower potential. It appears that all the three metal (II) ions, as in the case of CNT/Li⁺, also take part in the electro-catalytic reaction by mediating the reduction of Mn^{2+}.

TABLE-1
EFFECT OF DIFFERENT HEAVY METALS
(2 mM) ON REDUCTION PEAKS OF 2 mM Mn²⁺
AT pH 2 USING CNT/Li⁺/GCE

Heavy metals	Ipc(I) (μA)	Ipc(II) (μA)	Epc(I) (mV)	Epc(II) (mV)
Mn²⁺ only	160	110	+500	-140
Mn²⁺ + Hg²⁺	307.7	238.5	0	-160
Mn²⁺ + Cd²⁺	215.4	546.2	+400.5	-1373.9
Mn²⁺ + Cu²⁺	211.5	769.2	+472.5	-1220.9

Applications of the study

Analysis of Mn(II) in seawater: CNT/Li⁺ modified glassy carbon electrode is used in the determination of the Mn^{2+} concentration in seawater. Based on the calibration graph obtained for Mn(II) standards in seawater, a known amount of previously added Mn(II) of 0.05 and 0.1 mM were determined voltammetrically with recoveries of 94.7 ± 3.3 and 98.5 ± 1.9 %, respectively (Tables 2 and 3) with excellent reproducibility as evident in the RSD of < ± 4 % .

TABLE-2
RECOVERY RATE OF 0.1 mM Mn²⁺ ADDED
IN TO SEAWATER AT SCAN RATE 100 mV/s USING
CNT/Li⁺ MODIFIED GCE

No. of sample	Conc. of Mn²⁺ (mM)	Recovery rate (%)	Mean recovery (%)	RSD (%)
1	0.097	97.0	–	–
2	0.098	98.3	–	–
3	0.102	101.5	–	–
4	0.099	99.0	–	–
5	0.099	99.0	–	–
6	0.096	96.0	98.5	1.9

TABLE-3
RECOVERY RATE OF 0.05 mM Mn²⁺ ADDED IN TO
SEAWATER SCAN RATE 100 mV/s USING CNT/Li⁺/GCE

No. of sample	Conc. of Mn²⁺ (mM)	Recovery rate (%)	Mean recovery (%)	RSD (%)
1	0.049	98.0	–	–
2	0.048	96.0	–	–
3	0.045	90.0	–	–
4	0.047	94.0	94.7	3.3

Analysis of Mn(II) in blood sample: Similarly, excellent recoveries and reproducibility of Mn(II) analysis in a complex media such as mouse blood were also obtained with the CNT/Li⁺/GC electrode. A known amount of Mn(II) (at 0.02 and 0.03 mM) that was added previously to the blood samples were determined voltammetrically with recoveries of 99.6 ± 2.1 and 99.0 ± 2.1 %, respectively (Tables 4 and 5).

TABLE-4
RECOVERY RATE OF 0.02 mM Mn²⁺ ADDED IN TO BLOOD
AT SCAN RATE 100 mV/s USING CNT/Li⁺/GCE

No. of sample	Conc. of Mn²⁺ (mM)	Recovery rate (%)	Mean recovery (%)	RSD (%)
1	0.0205	102.5	–	–
2	0.0199	99.5	–	–
3	0.0198	99.0	–	–
4	0.0195	97.5	99.6	2.09

TABLE-5
RECOVERY RATE OF 0.03 mM Mn²⁺ ADDED IN TO BLOOD
AT SCAN RATE 100 mV/s USING CNT/Li⁺/GCE

No. of sample	Conc. of Mn²⁺ (mM)	Recovery rate (%)	Mean recovery (%)	RSD (%)
1	0.0305	101.6	–	–
2	0.0290	96.6	–	–
3	0.0295	98.3	–	–
4	0.0299	99.6	99.025	2.1

Conclusion

The modified electrode of glassy carbon with CNT/Li⁺ (CNT/Li⁺/GCE) has been proven to be able to mediate effectively the reduction of Mn(II) during cyclic voltammetry. The reduction current of Mn(II) obtained at CNT/Li⁺/GCE is higher by as much as three fold to fourfold when it is compared with those obtained at the bare glassy carbon electrode. The conditions favourable for optimum sensitivity enhancement are the use of an acidic electrolyte of 0.1 M KCl and at moderately high temperatures. Excellent recoveries and reproducibility could be obtained at the CNT/Li⁺/GCE. Similar to Li(I), the presence of Hg(II), Cu(II) and Cd(II) ions exerted a positive/synergistic influence by enhancing the electro-catalytic activity of CNT.

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