CHAPTER 3

*In-situ* Ion-Exchanging of Ferricyanide on Aromatic Unit Bearing Poly Ionic Liquid – Graphite Nanopowder (PIL-GNP) Composite Chemically Modified Electrode and its Selective Electrocatalytic Oxidation and Sensing of Ascorbic Acid

3.1 Introduction

By virtue of their appealing physicochemical properties like favourable ionic conductivity, high polarity, non-volatility and high thermal stability, ionic liquids (IL’s; room temperature molten salts) have found enormous applications in various research fields like fuel cells, super capacitors, greener chemical transformations and electrochemical sensors (Ueki and Watanabe, 2008; Opalloa and Lesniewski, 2011; Yu et al., 2005; 2008). Poly ionic liquids (PIL’s), which have properties of both ionic liquids and polymers, has been emerged as an important electrode material, especially as a powerful conducting system, dispersant, stabilizer and absorbent for carbon materials etc (Yuan et al., 2013; Ye et al., 2013). For instance, alkyl imidazolium based PIL’s have been used as a stabilizer to stabilize graphene materials (Kim et al., 2011) and as a wrapping agent to single walled carbon nanotubes (SWNT’s) via electrostatic and π-π interactions (Li et al., 2012). Although, extensive material based research work on PIL-nano carbon based composites have been reported in the literature, studies on PIL bearing metal complex based redox active units such as ferricyanide and ferrocene suitable for electrochemical applications are very limited (Mao et al., 2015; Chang et al., 2013). Although, IL and PIL have ion-exchangeable ions, due to its stable structure, physical characteristic and unfavourable ion-exchanging feature, they have been rarely used as an ion-exchanger in electrochemistry. In fact, to achieve the ion-exchange behaviour, ILs or PILs have to be subjected for drastic chemical conditions for pre-longed timings (Yu et al., 2005; 2008; Chang et al., 2013). Here in, we show an efficient and facile ion-exchanging behaviour of PIL with ferricyanide ion after being adsorbed with graphite.
nanopowder as GNP-PIL nanocomposite and used as a modified electrode for electrochemical applications.

Among various redox mediators used in the electrochemistry, undeniably ferricyanide (Fe(CN)$_6^{3-}$) is a most striking electron mediator due to its well studied electrochemical properties (Lawrence et al., 2002). In aim to access the electrochemical feature of their underlying surface, extensive electrochemical studies have been carried out with various unmodified and modified electrodes like GCE (Yu et al., 2005), Au (Vogt et al., 2005), multiwalled carbon nanotube (MWCNT)-modified GCE (Yu et al., 2008), nanoporous carbon modified GCE (Poh and Pumera, 2012) etc., using ferricyanide as a redox system in aqueous solution. In fact, technique like scanning electrochemical microscope has been often used ferricyanide as a solution phase probe to image the electroactive sites of the underlying surface (Bard et al., 1990). Indeed, only limited reports were available in the literature for Fe(CN)$_6^{3-}$ confined electrodes for electrochemical applications. For instance, ferricyanide doped polyvinyl pyridine and Tosflex modified electrodes (Zen et al., 2000b), ferricyanide confined poly(allylamine hydrochloride) and anionic polysaccharides (Noguchi and Anzai, 2006), ferrocyanide doped poly-l-lysine film (Wu et al., 2009), ferricyanide incorporated polyelectrolyte-calcium carbonate microsphere (Li et al., 2000) and ferricyanide confined methyl imidazolium tethered multiwalled carbon nanotube modified electrode (Xiang et al., 2000). In the above cases, an ionic interaction between anionic ferricyanide and cationic functional sites of the polymer electrodes is tuned for the ferricyanide surface-confined electrode preparations. Indeed, PIL bearing ion-exchange system is rarely worked out for ferricyanide surface confinement in spite of its ionic-character. It is likely that condition such as hydrophobic interaction, structure and geometric factors (active site buried inside the core) of PILs are responsible for the unfavourable ion-exchanging behaviour of the Fe(CN)$_6^{3-}$. Recently, Zen group reported a ferricyanide ion-exchanged hydrophobic PIL of 1-butyl-3-vinylimidazolium hexafluorophosphate and 1,9-di(3-vinylimidazolium)nonane hexafluorophosphates on screen printed carbon electrode surface, which was prepared by an in-situ chemical polymerization technique at 70°C for 40 min in air, for electrocatalytic oxidation of sulfide ion in neutral pH solution (Chang et al., 2013). Here in, we report a highly redox active ferricyanide confined PIL, made up of
block co-polymer of 3-pentyl-N-vinyl-imidazolium chloride and styrene, having hydrophilic, hydrophobic and aromatic characteristics, modified graphite nano system, designated as GCE/GNP-PIL@Fe(CN)$_6^{3-}$ for electrochemical and electro analytical applications. The PIL-GNP modified electrode (i.e., GCE/GNP-PIL@Fe(CN)$_6^{3-}$) prepared by simple blending procedure showed a facile ion-exchange of ferricyanide ion within few (15±5) min and displayed highly redox active and stable electrochemical response for ascorbic acid oxidation in pH 7 phosphate buffer solution (PBS). As prepared ferricyanide confined PIL-GNP composite electrode was characterized by field emission scanning electron microscopy (FE-SEM), Raman and Fourier transform infrared spectroscopy (FT-IR) techniques. As a proof of concept, selective and sensitive detection of AA in couple of real samples were successfully demonstrated with recovery values about 100%.

3.2 Experimental Section

3.2.1 Materials and Reagents

Graphite nano powder, 400 nm, ~ 98% purity (SRL, India), potassium ferricyanide (Merck, India), ascorbic acid (AA) (Rankem, India) and N-pentyl chloride, styrene, 2,2-azobis-isobutyronitrile (AIBN) (Sigma Aldrich, India) were used without further purification. The gold and carbon screen-printed electrode (AuSPE/SPCE) (0.0707 cm$^2$) were gifted by Prof. Jyh-Myng Zen, Taiwan. Aqueous solutions were prepared using deionized and alkaline potassium permanganate distilled water (DD water). The supporting electrolyte pH 7 phosphate buffer solution (PBS) of ionic strength, I = 0.1 mol L$^{-1}$ was used throughout this work.

3.2.2 Instrumentation

All the electrochemical measurements were performed on a CHI Model 660C electrochemical workstation (USA). A conventional three electrode system which consists of a modified glassy carbon electrode (GCE) of 0.0707 cm$^2$ geometrical surface area as working electrode, a platinum wire as counter electrode, and an Ag/AgCl (3M KCl) electrode as reference electrode was used. A JEOL, JSM-6700F (Japan) instrument was used for scanning electron microscopy (SEM) analysis. FTIR analysis was carried
out using Shimadzu IR Affinity-1 spectrometer (Japan) instrument by KBr method. Agiltron Raman Spectrometer (USA) with 532 nm laser probe instrument was used for Raman spectroscopic analysis.

3.2.3 Procedure for GCE/GNP-PIL@Fe(CN)$_6^{3-}$ Preparation

In first, ionic monomers of 1-vinyl-3-pentyl imidazolium bromide were prepared as per the literature procedure (Zhang et al., 2009; Mecerreyes, 2011). Shortly, 5g of 1-vinyl-imidazole and 13.1 g of n-pentyl chloride were taken in dry crew type Schlenk flask and kept for heating around 70 °C about 3 hrs, followed by addition of styrene and radical initiator 2,2'-Azobisisobutyronitrile (AIBN) then heated to 70 °C, which leads to formation of polymerized block copolymer (PIL). The product obtained was dissolved in methanol and re-precipitated in ethylactate. Then, 10 mg of dried PIL powder was mixed with 2 mg of graphite nanopowder (GNP) suspended in 1ml ethanol and ultra sonicated for 30 min to obtain a homogeneous black suspension. In next, 5 μl of GNP-PIL ethanolic suspension was drop casted on a cleaned GCE surface and air dried at room temperature for 10±5 min. In a similar way, other carbon material modified GCE surfaces were also prepared. The ferricyanide ion-exchanged chemically modified electrode (CME) was prepared by twenty continuous potential cycling of GCE/GNP-PIL modified electrode in 2 mM potassium ferricyanide dissolved in pH 7 PBS at a potential window of -0.3 to 0.6 V versus Ag/AgCl at $v = 50 \text{ mV s}^{-1}$ (Scheme 3.1 A-C). As prepared modified electrode is medium transferred to a blank pH 7 PBS and pre-treated at the same potential window for ten continuous potential cycles. Such electrochemical procedure resulted to stable surface confined ferricyanide modified electrode (i.e., GCE/GNP-PIL@Fe(CN)$_6^{3-}$). For the Raman and FTIR physicochemical characterizations, a gold screen printed electrode (Au-SPE) and for SEM analysis, carbon based screen printed electrode (SPCE) were used. For FTIR studies, as prepared Au-SPE/GNP-PIL@Fe(CN)$_6^{3-}$ electrode dried in a desiccator for overnight then the modified film peeled off carefully using a doctor’s needle (0.5 mm × 3.5 cm) was subjected for examination.
3.3 Results and Discussion

3.3.1 Electrochemical Behaviour of GCE/GNP-PIL@Fe(CN)$_6^{3-}$

Initial cyclic voltammetry experiment was carried with a block co-polymer of 3-pentyl-N-vinyl-imidazolium chloride bearing styrene modified glassy carbon bare electrode surface (GCE/PIL; without GNP) for immobilization of ferricyanide ion by potential cycling method (Scheme 3.1, control-1). Fig. 3.1 A, curve a is a twenty continuous CV response of the GCE/PIL in 2 mM potassium ferricyanide containing pH 7 PBS at a $v = 50$ mV s$^{-1}$. As can be seen, a poor and unaltered redox peak response at equilibrium potential, $E_{1/2}$ ($E_{1/2} = E_{pa}+E_{pc}/2$; where $E_{pa}$ and $E_{pc}$ corresponding to the anodic and cathodic peak potentials) and peak-to-peak separation ($\Delta E_p = E_{pa}-E_{pc}$) of 160±5 mV vs Ag/AgCl and 145 mV were observed. After the experiment, the modified electrode was gently washed with distilled water and was medium transferred to a blank pH 7 PBS and CV cycled again. It is expected that, since PIL contains cationic sites, anionic Fe(CN)$_6^{3-}$ will be ion-exchanged and show well defined surface confined ferricyanide redox peak in blank solution. Unexpectedly, as can be seen in Fig. 3.1 A, curve b, the modified electrode failed to show any ferricyanide redox peak. This observation ascribes inability of the bare cationic PIL to hold Fe(CN)$_6^{3-}$. It is likely that hydrophobic nature and un factorable structural forms are responsible for failure of Fe(CN)$_6^{3-}$ loading on the PIL. Interestingly, when the same experiment was repeated with GNP-PIL nanocomposite modified GCE electrode (GCE/GNP-PIL), a sharp and continuous growing redox peak response at equilibrium potential, $E_{1/2}$ and $\Delta E_p$ values of 90±5 mV vs Ag/AgCl and 110±5 mV were observed (Fig. 3.1 B, curve a). After twenty continuous CV cycles, the working electrode was gently washed with distilled water then transferred to a blank pH 7 PBS and CV was performed again (Scheme 3.1, A-C). Unlike to the previous case, a well defined redox peak without any alteration in the peak potentials $E_{1/2}$ and $\Delta E_p$ (100±5 mV vs Ag/AgCl and 105±5 mV) was noticed (Fig. 3.1 B, curve b). The surface concentration, $\Gamma_{FeCN}$ of the electro active ferricyanide species was calculated using the following equation (Bard and Faulkner, 2009):

$$\Gamma_{FeCN} = \frac{Q}{nA_{geo}F}$$  \hspace{1cm} (3.1)
Where $Q_t$ is the charge consumed (20.6 μC), obtained from integrating the anodic peak area in CV under the background correction recorded at slow scan rate (10 mV s$^{-1}$) in a blank pH 7 PBS, $n$ is the number of electron consumed (1) and $A_{geo}$ the electrode geometric area (0.0707 cm$^2$). Calculated $\Gamma_{(FeCN)}$ value is 3.0×10$^{-9}$ mol cm$^{-2}$, which indicate existing of multiple monolayers of the electro-active species on the modified electrode surface. The value obtained in this work is relatively higher than that of the values obtained with the other ferricyanide modified electrodes like Tosflex-Fe(CN)$_6^{3-}$ (0.09×10$^{-9}$ moles/cm$^2$) (Zen et al., 2000b) and Fe(CN)$_6^{3-}$-PIL-SPCE (0.85×10$^{-9}$ moles/cm$^2$) (Chan et al., 2013). This observation attributes unique feature of PIL-GNP for favourable loading of Fe(CN)$_6^{3-}$ ion.

**Fig. 3.1** Twenty Continuous CV Responses of (A) GCE@PIL and (B) GCE/GNP-PIL in 2 mM K$_3$Fe(CN)$_6^{3-}$ Solution (curve a) and Their Stability (curve b) in pH 7 PBS, (C) Effect of Scan rate (10-500 mV s$^{-1}$) on the CV Response of GCE/GNP-PIL@Fe(CN)$_6^{3-}$ in pH 7 PBS. Plots of (D) log $i_p$ vs logv, (E) $E_p$ vs logv and (F) Effect of pH Solutions on the CV Response of GCE/GNP-PIL@Fe(CN)$_6^{3-}$ at a Scan rate 50 mV s$^{-1}$. 

40
Effect of scan rate on the redox behaviour of the GCE/GNP-PIL@Fe(CN)$_6^{3-}$ in pH 7 PBS was investigated (Fig. 3.1 C). A systematic increase in the redox peak currents against increase in scan rate was noticed. The ratio of anodic-to-cathodic peak currents, $i_{pa}/i_{pc}$ at various scan rates was almost unity. Fig. 3.1 D is a double logarithmic plot of $i_p$ vs $v$ for the redox peak. Calculated slope value ($\partial \log (i_{pa})$ and $(i_{pc})/\partial \log v$) of the double logarithmic plots was 0.6, indicating that the electron-transfer processes in the film is due to the semi-infinite diffusion controlled behaviour (Li et al., 2010b). Fig. 3.1 E is a plot of $E_{pc}$ and $E_{pa}$ vs scan rate. The peak potential values increase regularly with increase in scan rate. Calculated peak-to-peak separation potential, $\Delta E_p$ at $v = 50$ and 200 mV s$^{-1}$ are 104 and 180 mV respectively. Applying Laviron theory (Laviron, 1979), the charge transfer coefficient ($\alpha$) and apparent electron transfer rate constant ($k_s$) can be calculated for a surface controlled process using following equations:

$$\frac{S_a}{S_c} = \alpha/1-\alpha \quad (3.2)$$

$$\log k_s = \alpha \log (1-\alpha) + (1-\alpha) \log \alpha - \log \left[\frac{RT}{nF\nu}\right] - \alpha (1-\alpha) \frac{nF\Delta E_p}{2.3RT} \quad (3.3)$$

Where, $S_a$ and $S_c$ are the slopes of the linear plots of $E_{pa}$ vs log ($\nu$) (70 mV decade$^{-1}$) and $E_{pc}$ vs log ($\nu$) (74 mV decade$^{-1}$), $\nu$ is applied scan rate (500 mV s$^{-1}$) and $\Delta E_p$ is peak separation (225 mV), from which $\alpha$ and $k_s$ are calculated to be 0.51 and 1.04 s$^{-1}$ respectively. The obtained $k_s$ value of 1.04 s$^{-1}$ for the GCE/GNP-PIL@Fe(CN)$_6^{3-}$ modified electrode is found to be quite comparable with MWCNT@Hb/Nf modified GCE (0.98 s$^{-1}$) (Kumar et al., 2012b) and iron hexacyanoferrate modified GCE (1.4 s$^{-1}$) (Kumar and Pillai, 2006) electrodes indicating good redox activity of the Fe(CN)$_6^{3-}$ redox film. Fig. 3.1 F is CV response of the GCE/GNP-PIL@Fe(CN)$_6^{3-}$ at different solution pHs. The peak potentials were independent with solution pH indicating absence of any proton involvement in the electrochemical reaction.

Other carbons such as functionalized-multiwalled carbon nanotube (f-MWCNT), pristine-multiwalled carbon nanotube (i-MWCNT), purified-multiwalled carbon
nanotube (p-MWCNT), single walled carbon nanotube (SWCNT) and activated charcoal (AC) were also combined with the PIL and subjected to the electrochemical treatment for doping of Fe(CN)_6^{3-} as explained above in Fig. 3.1 B. Fig. 3.2 is a typical CV responses of various carbon-PIL@Fe(CN)_6^{3-} modified glassy carbon electrode in pH 7 PBS. Calculated Γ_{FeCN} and ΔE_p values were displayed as insets in the respective Fig. 3.2. Amongst all, f-MWCNT showed the highest value of Γ_{FeCN} (36.67 n mol cm^{-2}), but with the poorest ΔE_p value (139 mV). Similarly activated charcoal and SWCNT modified electrodes showed the best ΔE_p values (70 mV and 74 mV) but with lowest Γ_{FeCN} value (1.12 n mol cm^{-2} and 1.36 n mol cm^{-2}). On the other hand GNP-PIL based electrode showed a moderate Γ_{FeCN} (3.01 n mol cm^{-2}) and ΔE_p (104 mV) values. Following conclusions can be drawn from the observation; (i) multilayer arrangement of graphitic structure is important for efficient PIL loading, (ii) functional group such as hydroxyl, carbonyl and phenolic in carbon favours PIL stabilization, possibly via hydrophilic interactions, (iii) pi-pi interaction between aromatic pi electrons and sp^2 carbon in graphitic structure is a key factor for the strong interaction, (iv) impurities such as Fe, Co and Ni and carbonaceous present in MWCNT doesn’t have any influence on the PIL loading and in turn Fe(CN)_6^{3-} immobilization.

Fig. 3.2 (A-F) CV Response of Ferricyanide Surface Confined Various Carbon Nanomaterials - PIL Modified Electrodes in pH 7 PBS at a v = 50 mV s^{-1}. Insets are its ΔE and Γ_{FeCN} Values.
In order to access the role of poly ionic liquid in Fe(CN)$_6^{3-}$ doping, six different block copolymers of poly(1-vinyl-3-alkyl imidazolium anion)-co-polystyrene (PIL-Co-PSt; (structure is given in scheme 3.1) having varied counter anion species (Cl-, SO$_3$CF$_3^-$, BF$_4^-$ and PF$_6^-$; Fig. 3.3 A-D), length of alkyl side chains (butyl and pentyl; Fig. 3.3 E and Fig. 3.3 A) and aromatic unit position (Fig. 3.3 F) were subjected to modification on the GCE/GNP and further to the Fe(CN)$_6^{3-}$ loading (Scheme 3.1, controls-2, 3 and 4).

![Fig. 3.3](image)

**Fig. 3.3** (A-F) CV Responses of Ferricyanide Confined Various Poly Ionic Liquids/GNP Modified Electrodes in pH 7 PBS at a $v = 50$ mV s$^{-1}$.

Fig. 3.3 A-F are the CV responses of various GCE/GNP-PIL@Fe(CN)$_6^{3-}$ modified electrode systems in pH 7 PBS. As can be seen, except chloride ion based PIL (PIL$_1$-Co-PSt; Fig. 3.3 A), other counter ions such as SO$_3$CF$_3^-$ (PIL$_2$-Co-PSt; Fig. 3.3 B), BF$_4^-$ (PIL$_3$-Co-PSt; Fig. 3.3 C) and PF$_6^-$ (PIL$_4$-Co-PSt; Fig. 3.3 D) showed either poor or unstable CV response of the ferricyanide doped composite film. A moderate length of alkyl side chains such as butyl and pentyl attached in imidazonium group of the PIL favoured for immobilization of PIL on GNP and further to higher Fe(CN)$_6^{3-}$ loading,
stability and surface coverage (PIL$_5$-Co-PSt; Fig. 3.3 E and PIL$_1$-Co-PSt; Fig. 3.3 A). Similarly, when the aromatic unit position in PIL is replaced, wherein, the benzene ring is removed from the PIL network and added in the imidazonium site, as in inset plot of Fig. 3.3 F, an unfavourable ferricyanide attachment was noticed with that system. From the above observations following conclusions can be drawn: (i) An optimal ratio of hydrophilic (from chloride anion) and hydrophobic (from lengthy alkyl chain) sites is necessary for successful ion-exchange of ferricyanide on PIL-GNP composite. (ii) Hydrophobic interactions of butyl and pentyl chain within PIL network makes significant structural changes and intern favours the ferricyanide ion-exchange. In fact, there may be an unfavourable structural condition when the imidazolium active site bearing benzyl group adsorbed on graphitic sites of GNP by pi-pi interactions. It is expected that sterric factor with the imidazolium site may be occurred that avoids doping of ferricyanide ion on the sterric region. (iii) Counter ion, which has less ionic size such as chloride ion is favourable for ferricyanide ion-exchange with PIL-GNP nanocomposite. (iv) PIL active site attached on the surface of the GNP, which has relatively higher hydrophilic than hydrophobic region favours the ferricyanide ion-exchange; where as, PIL active site attached on the interior region of the GNP, wherein, PIL active site is associated with larger hydrophobic regions than that of hydrophilic sites, unfavours the ion-exchange of ferricyanide ion. Thus, the GNP-PIL nanocomposite film prepared with 3-pentyl-N-vinyl-imidazolium chloride and styrene (PIL$_1$-Co-PSt) is found to be optimal and suitable for electrochemical application like AA electro-catalytic oxidation reaction.

3.3.2 Physicochemical Characterization of GCE/GNP-PIL@Fe(CN)$_6$$^{3-}$

The ferricyanide confined chemically modified electrode (GCE/GNP-PIL@Fe(CN)$_6$$^{3-}$) was characterized by using various physicochemical techniques and the results were summarized below. Fig. 3.4 is the comparative SEM images of GNP, GNP-PIL and GNP-PIL@Fe(CN)$_6$$^{3-}$ hybrid at different magnifications. Unmodified GNP showed sheets like arrangement with smooth surface feature (Fig. 3.4 A and B). On blending GNP with PIL, polymer wrapping like structure on graphite sheets with rough surface was noticed (Fig. 3.4 C and D). Indeed, there is no characteristic surface morphological change on loading Fe(CN)$_6$$^{3-}$ into GNP-PIL nanocomposite (Fig. 3.4 E and F). Elemental analysis of GCE/GNP-PIL@Fe(CN)$_6$$^{3-}$ showed presence of 1.32 wt.% of Fe on the surface of the
modified electrode (Table 3.1).

![Fig. 3.4 SEM Images](image)

**Fig. 3.4** SEM Images of (A-B) SPCE/GNP, (C-D) SPCE/GNP-PIL and (E-F) SPCE/GNP-PIL@Fe(CN)$_6^{3-}$ at Different Magnifications.

| Table 3.1 FE-SEM EDAX Data of GCE/GNP@PIL-Fe(CN)$_6^{3-}$ |
|-----------------|-----------------|-----------------|
| **Element** | **Wt.$\%$** | **Atomic$\%$** |
| 1. C K | 89.31 | 92.67 |
| 2. N K | 05.54 | 04.93 |
| 3. O K | 01.77 | 01.38 |
| 4. Cl K | 02.06 | 00.72 |
| 5. Fe K | 01.32 | 00.29 |

Fig. 3.5 A is a typical comparative raman spectroscopic response of various modified systems showing specific peaks at 1333 cm$^{-1}$ and 1570 cm$^{-1}$, associated with Raman-active D band, arises from sp$^3$ hybridized carbon and G band, presenting the vibration of sp$^2$ hybridized carbon, respectively. The relative intensities of the D and G bands ($I_D/I_G$ ratio) can be taken as a measure for the disorder-ness in the graphitic structure. The
measured \( I_D/I_G \) ratio values for GNP (Fig. 3.5 A, curve a), GNP-PIL (Fig. 3.5 A, curve b) and GNP-PIL@Fe(CN)\(_6^{3-}\) hybrid (Fig. 3.5 A, curve c) are 0.54, 0.82 and 0.79 respectively. The observation of marked increase in the ratio of GNP-PIL over to GNP is due to the existence of additional aromatic unit of PIL on GNP. A nearly unaltered Raman response of GNP-PIL before and after ferricyanide loading indicates absence of graphitic influence with ferricyanide immobilization. FT-IR/KBr response of GNP-PIL@Fe(CN)\(_6^{3-}\) showed a characteristic peaks at 2104.34 cm\(^{-1}\) and 2025.26 cm\(^{-1}\) (Fig. 3.5 B, curve c) corresponding to the stretching vibration of \( \text{–CN} \) group in the Fe(CN)\(_6^{3-}\) hybrid (Vishnu and kumar, 2017).

Fig. 3.5 Comparative (A) Raman and (B) FT-IR patterns of GNP (curve a) and GNP-PIL (curve b) and GCE/GNP-PIL@Fe(CN)\(_6^{3-}\) (curve c) Samples.

3.3.3 Electrocatalytic Behaviour of GCE/GNP-PIL@Fe(CN)\(_6^{3-}\)

In next, electrocatalytic feature of the modified electrode (GNP-PIL@Fe(CN)\(_6^{3-}\)) towards ascorbic acid (AA) oxidation in pH 7 PBS was studied. Comparative CV responses of GCE/GNP-PIL@Fe(CN)\(_6^{3-}\) and GCE/GNP without and with 1 mM of AA and its electrokinetics are given in Fig. 3.6. As can be seen, the highest electro oxidation peak current along with reduced over potential by >100 mV was noticed with GCE/GNP-
PIL@Fe(CN)$_6^{3-}$ (Fig. 3.6 A, curve b) over the unmodified electrode (Fig. 3.6 A, curve c) indicating efficient electro-catalytic activity of the GCE/GNP-PIL@Fe(CN)$_6^{3-}$ towards AA oxidation reaction in this work.

**Fig. 3.6** (A) CV of GCE/GNP-PIL@Fe(CN)$_6^{3-}$ without (curve a) and with 1mM AA (curve b) Respectively in 0.1 M PBS at a $v = 10$ mV s$^{-1}$. Curve c is the Response of GCE/GNP with 1mM AA. (B) Effect of Scan rate on CV Response of GCE/GNP-PIL@Fe(CN)$_6^{3-}$ in Presence of 2 mM Ascorbic Acid in pH 7 PBS. Plots of (C) $i_{pa}$ vs $v^{1/2}$, (D) $i_{pa}/v^{1/2}$ vs $v$ and (E) $E_{pa}$ vs log$v$. (F) Comparative Bar Diagram Depicting Electrocatalytic AA (1 mM) Oxidation Current Against Various Carbons – PIL Modified Electrodes Ion-Exchanged with Ferricyanide in pH 7 PBS.

Effect of scan rate on the AA oxidation response of GCE/GNP-PIL@Fe(CN)$_6^{3-}$ modified electrode was investigated (Fig. 3.6 B-E). It can be noticed that the anodic peak current of modified electrode increase with increase in scan rate (Fig. 3.6 B) and found to be linear starting from zero with square root of the scan rate (Fig. 3.6 C). Calculated slope for the plot of $i_{pa}$ vs $v^{1/2}$ is 4.1 $\mu$A (mV s$^{-1}$)$^{1/2}$ or 129 $\mu$A (V s$^{-1}$)$^{1/2}$. These observations suggest diffusion controlled electro-transfer reaction mechanism for the AA
oxidation reaction on the modified electrode (Wu et al., 2009). The current function \(i_{\text{pa}}/v^{1/2}\) for the catalytic oxidation of ascorbic acid was calculated and plotted against scan rate as in Fig. 3.6 D. Highest current function value at low scan rate and scan rate at >70 mV s\(^{-1}\) with low current function value were noticed. This response is typical indication for the electrochemical-chemical (EC) coupled reaction of AA oxidation in this work (Margel and Anson, 1978). Fig. 3.6 E is a plot of AA oxidation peak potentials \(E_{\text{pa}}\) measured at different scan rate against \(\log v\). As can be seen, catalytic oxidation peak \(E_{\text{pa}}\) of AA shifted to more positive potentials and a plot of \(E_{\text{pa}}\) vs \(\log v\) yielded a slope \(\partial E_{\text{pa}}/\log v\) = 58.9±2 mV decade\(^{-1}\), suggesting a kinetic limitation in the reaction between electro-active sites of the Fe(CN)\(_6\)\(^{3-}\) film and AA.

Fig. 3.6 F, displays the electrocatalytic AA oxidation peak currents of various carbon-PIL@Fe(CN)\(_6\)\(^{3-}\) modified glassy carbon electrodes as a bar diagram. The GCE/GNP-PIL@Fe(CN)\(_6\)\(^{3-}\) has the highest oxidation peak current over the other modified electrodes suitable for electrochemical AA sensor application. It is noteworthy that although f-MWCNT showed about 5 times higher \(\Gamma_{\text{FeCN}}\) value over GNP for Fe(CN)\(_6\)\(^{3-}\) (as shown in Fig. 3.2); GNP-PIL@Fe(CN)\(_6\)\(^{3-}\) is found to show the highest electrocatalytic feature over other carbon based electrodes (Fig. 3.6 F). Presumably, surface active sites in GNP-PIL@Fe(CN)\(_6\)\(^{3-}\) exist near the edges of GNP rather than interior which can’t be accessed by the Fe(CN)\(_6\)\(^{3-}\) due to hydrophobic interactions, and hence showed facile electrocatalysis towards AA.

The number of electrons involved in the rate determining step \(n_a'\) and the total number of electrons involved in the ascorbic acid oxidation \(n'\) are important kinetic parameters to elucidate the mechanism of the electrochemical oxidation reaction. The \(n_a'\) and \(\alpha'\) values were estimated from the following Tafel equation for the totally irreversible electron transfer reaction under conditions (i.e. in a potential range) of diffusion controlled reaction (Bard and Faulkner, 2009; Bockris and Reddy, 1997; Nicholoson, 1964).

\[ E_{\text{pa}} = k + (b_a/2) \log v \]  \hspace{1cm} (3.4)

\[ \text{Tafel slope, } b_a = 2.303RT/(1-\alpha')n_a'F \]  \hspace{1cm} (3.5)
Where $k$ is a constant related to $R$, $T$, $F$, $D_{AA}$ ($D_{AA}$ is the diffusion coefficient of AA), with the slope $(\partial E_{pa}/\partial \log (v)) = 58.9$ mV decade$^{-1}$, $b_a$ can be calculated as 116 mV decade$^{-1}$. From the equation (5), $(1-\alpha') n_a'$ value was calculated as 0.5; if $n_a' = 1$, then estimated $\alpha' = 0.5$ (Xi et al., 2013).

To evaluate $n'$ value, we resorted the following Randle’s Sevick equation relating $i_{pa}$ and $v^{1/2}$ for the totally irreversible diffusion-controlled electrode processes:

$$i_{pa} = 2.99 \times 10^5 n'[1-(1-\alpha)\ n_a']^{1/2} A_{geo} C_{AA} D_{AA}^{1/2} v^{1/2}$$  \hspace{1cm} (3.6)

Where $C_{AA}$ is the substrate bulk concentration, $[(1-\alpha') n_a'] = 0.5$, $A_{geo} = 0.0707$ cm$^2$, $C_{AA} = 2 \times 10^{-6}$ mol cm$^{-3}$ and $D_{AA} = 5.8 \times 10^{-6}$ cm$^2$s$^{-1}$ (Robinson and Anderson, 1990; Roy et al., 2006), with the slope $(i_{pa}/v^{1/2}) = 129$ µA (Vs$^{-1}$)$^{1/2}$ from Fig. 3.7 C, $n'$ was calculated to be 1.89. Overall, the catalytic oxidation of ascorbic acid on GCE/GNP-PIL@Fe(CN)$_6^{3-}$ modified electrode occurs as a two electron process ($n' = 2$). Based on the kinetic parameters obtained, electro-catalytic oxidation mechanism (EC) of Fe(CN)$_6^{3-}$ towards AA oxidation is then deduced as following electrochemical pathway (Li et al., 2010b).

$$\text{Fe(CN)}_6^{4-} \leftrightarrow \text{Fe(CN)}_6^{3-} + e^-$$  \hspace{1cm} (3.7)

$$\text{Ascorbic acid} + 2\text{Fe(CN)}_6^{3-} \rightarrow \text{Dehydroascorbic acid} + 2\text{Fe(CN)}_6^{4-}$$  \hspace{1cm} (3.8)

Under a hydrodynamic condition, the GCE/GNP-PIL@Fe(CN)$_6^{3-}$ is subjected to amperometry i-t for quantification of ascorbic acid (AA) at applied potential ($E_{app}$) 150 mV vs Ag/AgCl in pH 7 PBS. Successive spikes of 25 µM AA results to a systematic increase in current signal up to 300 µM of AA with a current sensitivity of 0.08 µA µM$^{-1}$ (Fig. 3.7 A, curve a). Control experiment with GCE/GNP-PIL (Fig. 3.7 A, curve b) and GCE/GNP (Fig. 3.7 A, curve c) showed about ten times lower current signals towards AA sensing. An RSD for detection of ten successive spikes of 25 µM AA is 1.8%. Calculated detection limit (DL = $3\sigma_{sb}/m$, where, 3 is signal-to noise ratio, $\sigma_{sb}$ is the standard deviation of a signal obtained from six measurements and $m$ is the sensitivity calculated from the slope of the calibration plot) value is 1.4 µM (Fig. 3.7 A, inset). The sensitivity value noticed in this work is relatively higher than that of the sensitivity values of AA.
oxidation obtained with other PIL and Fe(CN)$_6^{3-}$ modified electrodes with different strategies (Table 3.2). Interestingly, the AA sensing behaviour is found to be highly selective and not interfered with other co-existing biochemicals such as nitrite, glucose, cysteine, uric acid, hydrogen peroxide and catechol (Fig. 3.7 B). The present system showed good performance for real sample assay towards AA content present in two different kinds of commercial available fruit juice samples (Fig. 3.7 C and D) with good recovery values given in Table 3.3.

![Graphs showing comparative amperometric I-T responses](image)

**Fig. 3.7** Comparative Amperometric *I*-/*T* Responses of (A) GCE/GNP-PIL@Fe(CN)$_6^{3-}$ (Curve a), GCE/GNP-PIL (curve b) and GCE/GNP (curve c) for Detection of 25 μM AA with Calibration Plot of GCE/GNP-PIL@Fe(CN)$_6^{3-}$ as Inset; (B) Interference Study of GCE/GNP-PIL@Fe(CN)$_6^{3-}$ Towards AA with Coexisting Biochemicals; (C and D) Real Sample Analysis of AA in Commercial Juice Samples Using GCE/GNP-PIL@Fe(CN)$_6^{3-}$ by Standard Addition Approach at *E*$_{app}$ = 0.15 V vs Ag/AgCl in pH 7 PBS.
Table 3.2 Comparison of the Analytical Performance of GCE/GNP@PIL-Fe(CN)$_6^{3-}$ for the Electrochemical Determination of Ascorbic Acid by Various Chemically Modified Electrodes.

<table>
<thead>
<tr>
<th>Modified electrode</th>
<th>$E_{app}$/V</th>
<th>Detection limit /μM</th>
<th>Linearity/μM</th>
<th>Sensitivity μA/μM</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. [Fe(CN)$_6$]$^{3-}$/PDMA/BDD</td>
<td>0.4</td>
<td>-</td>
<td>1-28</td>
<td>0.233</td>
<td>[Roy et al., 2006]</td>
</tr>
<tr>
<td>2. IL-CPE</td>
<td>-</td>
<td>8.0</td>
<td>10-3000</td>
<td>0.0252</td>
<td>[Sun et al., 2007]</td>
</tr>
<tr>
<td>3. FDTME/GCE</td>
<td>0.3</td>
<td>-</td>
<td>1-50</td>
<td>0.026</td>
<td>[Zen et al., 2000b]</td>
</tr>
<tr>
<td>4. [BMIM]$<em>6$P$<em>2$Mo$</em>{18}$O$</em>{62}$/GC</td>
<td>0.07</td>
<td>0.1</td>
<td>10-80</td>
<td>0.063</td>
<td>[Ammam et al., 2011]</td>
</tr>
<tr>
<td>5. GCE/GNP@PIL-Fe(CN)$_6^{3-}$</td>
<td>0.15</td>
<td>1.4</td>
<td>25-300</td>
<td>0.08</td>
<td>This work</td>
</tr>
</tbody>
</table>

PDMA = N, N dimethylaniline, BDD = boron doped diamond; IL = N-butylpyridinium hexafluorophosphate; PAH = poly(allylamine) hydrochloride, PSS = poly(sodium 4-styrenesulfonate), CaCO$_3$ = calcium carbonate; FDTME = ferricyanide-doped Tosflex-modified electrode; [BMIM]$_6$ = 1-butyl-3-methylimidazolium tetrafluoroborate, P$_2$Mo$_{18}$O$_{62}$ = Molybdenum-containing polyoxometalates.

Table 3.3 Results of the Ascorbic Acid (AA) Real Sample Analysis Obtained with GCE/GNP@PIL-Fe(CN)$_6^{3-}$ by Amperometric $I-T$ Method at an $E_{app}$ = 0.15 V Vs Ag/Agcl in PH 7 PBS.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample #1 Tropicana grape juice</th>
<th>Sample #2 Tropicana grape juice</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Linear equation</td>
<td>$y = 5.67 \times 10^{-2} x + 2.002$</td>
<td>$y = 5.68 \times 10^{-2} x + 2.811$</td>
</tr>
<tr>
<td>2. Regression</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>3. Dilution factor</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>4. Original/ Detected (μM)</td>
<td>50.35</td>
<td>93.6</td>
</tr>
<tr>
<td>5. Spiked</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>6. Detected</td>
<td>49.01</td>
<td>49.63</td>
</tr>
<tr>
<td>7. Recovery</td>
<td>98.02%</td>
<td>99.26%</td>
</tr>
<tr>
<td>8. Net [AA]</td>
<td>0.050 mM/ml</td>
<td>0.093 mM/ml</td>
</tr>
</tbody>
</table>
3.4 Conclusion

A highly stable ferricyanide confined GCE/GNP-PIL modified electrode, GCE/GNP-PIL@Fe(CN)$_6^{3-}$ was successfully fabricated by ion-exchanging ferricyanide ion with PIL (a block co-polymer of 3-pentyl-N-vinyl-imidazolium chloride and styrene). Physicochemical characterizations with SEM, Raman and FT-IR revealed strong immobilization of PIL on GNP. It was found that hydrophilic, hydrophobic and sp$^2$ carbon sites of PIL-GNP influences the immobilization of ferricyanide ion. The ferricyanide ion immobilized electrode showed a specific surface-confined redox peak at an equilibrium potential, $E_{1/2} = 100 \pm 5$ mV vs Ag/AgCl. The GCE/GNP-PIL@Fe(CN)$_6^{3-}$ modified electrode facilitates efficient ascorbic acid oxidation and showed an excellent electro-catalytic activity and amperometric $i-t$ sensing of ascorbic acid at considerably low potential, 150 mV (Ag/AgCl) without any interference from co-existing biochemical’s in physiological solution. The proposed electrode was validated by analysing couple of ascorbic acid containing commercial fruit juice samples with 100% recovery.

In our next work, we would like to prepare some more metal complexes-surface confined carbon nanomaterial modified electrodes by new strategies and would like to extend for selective electroanalytical applications.