

Nano-impacts Reveal the Electron Transfer Kinetics of the Ferrocene/Ferrocenium Couple Immobilised on Graphene Nanoplatelets

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Abstract: The kinetics of the ferrocene/ferrocenium ($\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$) redox couple immobilised on graphene nanoplatelets (GNPs) in aqueous solution are evaluated using the nano-impacts method. Single GNPs modified with poly(vinylferrocene) [PVFc] are allowed to impact a microelectrode. For the duration ($\sim 10 - 100$ ms) of the impacts the GNP adopts the potential of the electrode and acts as a 'chemically modified nanoelectrode'. The study of individual impacts facilitates the resolution of fast electron transfer kinetics which for the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ couple is shown to be at least $3 \pm 1 \text{ s}^{-1}$.

1. Introduction

The ferrocene/ferrocenium redox couple is one of the most important electrochemical systems finding widespread usage as a paradigmatic outer-sphere electron transfer redox reaction:



The fundamental importance of this couple is probably best highlighted by Chidsey who used a surface bound ferrocene species to evidence the validity of the Marcus-Hush electron transfer model.^[1] Significant work in the literature has focused on the measurement of electron transfer kinetics of the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ couple using metallic electrodes.^[1-2] Recently there is an increasing demand on the production of new carbon nano-materials and characterization of the electron-transfer properties of these solids. Measurement of the response of $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ at these materials^[3] is one route by which the influence of the carbonaceous electronic structure upon the influence the electron-transfer process can be probed. However, such studies involving large ensembles of particles are commonly complicated by the measurement of non-ideal voltammetry.^[4] Such non-idealities are possibly the result of multi-layer formation and/or associated capacitive effects serving to alter or distort the voltammetric response.

The method of nano-impacts^[5] detects random collisions between the nanoparticles and the electrode based on the Brownian motion of the particles in solution. Charge is transferred between nanoparticles and a potentiostatted electrode, giving rise to current "spikes" in chronoamperometry.

electroactive species modified on the surface of nanoparticles.^[7] The latter not only provides a non-destructive method to detect nanoparticles, but also opens the study for conductive and insulating nanoparticles. As compared to modification with single ferrocene molecules,^[7c] modification with polymers such as poly(vinylferrocene) [PVFc] introduces a higher number of electroactive centres in the nanoparticles, leading to greater nano-impacts signals and facilitating the electron transfer kinetic studies. Nano-impacts can be used to study the size,^[6a, 6b] concentration^[6c] and catalytic properties^[8] of nanoparticles, as well as surface coverage of redox moieties^[7b, 7c] on the nanoparticulate surface. However, quantitative measurement of electron transfer kinetics at individual nanoparticles are very limited.^[9]

In this work, we demonstrate the use of nano-impacts to access the kinetics of the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ redox couple. Graphene nanoplatelets are chemically modified with PVFc and studied using the nano-impacts method. Upon impact each individual GNP acts as a single nanoelectrode and hence can be used to probe the electron transfer to the modifying layer. Conventionally, macro- or micro-electrodes are used to study the kinetics of a redox process, but such experiments often exhibit distorted voltammetry. The study of *individual* GNPs significantly minimises capacitive effects and ensures the particle being measured is directly contacting the electrode;^[10] thus facilitating the measurement of fast electron transfer.^[11] A strategy is thus demonstrated to allow study of electron transfer at new nanomaterials, such as the GNPs or alternatively carbon nanotubes and nanodots, among others. The key abbreviations frequently used in this article are listed in Table 1.

Table 1. Key abbreviations frequently used in this article.

Abbreviations	Full terms
$\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$	The ferrocene/ferrocenium couple
PVFc	Poly(vinylferrocene)
GNPs	Graphene Nanoplatelets
PVFc-GNPs	Poly(vinylferrocene) modified graphene nanoplatelets
DCM	Dichloromethane
EPPG	Edge-plane pyrolytic graphite
SCE	Saturated calomel electrode

Experimental Section

Chemical Reagents

All chemicals were provided by Sigma-Aldrich (St Louis, MO, USA) at reagent level unless stated below. The graphene nanoplatelets (GNPs, width of $15 \mu\text{m}$, thickness of 7 nm , estimated from scanning electron microscopy^[12]) were purchased from Strem Chemicals (Newburyport, MA, USA). Poly(vinylferrocene) [PVFc] was purchased from Polyscience Inc.

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While 'direct' impacts correspond to the redox process of nanoparticles themselves,^[6] 'indirect' impacts relate to the

(Warrington, PA, USA). Dichloromethane (DCM) was purchased from Fisher Scientific (Loughborough, UK). All reagents were used with no further purification. All aqueous solution was prepared using deionised water of resistivity not less than 18.2 MΩ cm at 298 K (Millipore, Billerica, MA).

Preparation of GNPs Suspension and PVFc Modified GNPs

The preparation of GNP suspensions follows the method reported earlier.^[7c] For the unmodified GNPs suspension, 5.6 mg of the GNPs were mixed with 100 mL aqueous solution supported with 0.1 M NaClO₄. The mixture was sonicated (FB15050, Fisher Scientific, 50/60 Hz, 80 W, Germany) for 10 min to generate an evenly distributed suspension, 5 mL of which was used for individual experiments. The suspension was prepared fresh every day. The bulk density of the loose GNPs powders is $1 \times 10^5 \text{ g m}^{-3}$ as reported by Strem Chemicals Inc.^[13] To estimate the weight of a single GNP, its density is assumed to be the same as graphite, $2.26 \times 10^6 \text{ g m}^{-3}$.^[14] Taking the volume of the single GNP, the weight of the GNPs can be determined as $1.68 \times 10^{12} \text{ g mol}^{-1}$, and the concentration of the GNPs in use can be determined as *ca.* $3 \times 10^{-14} \text{ M}$.^[7c]

To prepare the PVFc modified GNPs (PVFc-GNPs) suspension, two stock solutions were prepared fresh daily. 2.1 mg of PVFc was dissolved in 5 mL of DCM. 7.0 mg of GNPs was mixed in another 25 mL of DCM and sonicated. 1 mL of each mixture were mixed together in a sample vial. The resulting mixture was left in a desiccator for 30 min to evaporate the solvent. For cyclic voltammetry, only PVFc-GNPs at the bottom of the vial was used to modify the surface of the electrode, while the excess PVFc remained in the vial walls during evaporation of the solvent. For nano-impacts chronoamperometry, 5 mL of aqueous solution with 0.1 M NaClO₄ was added to the vial. Such a supporting electrolyte was chosen in order to minimise the ion-pairing between the ferrocenium and the anion,^[7c, 15] which will be elaborated in the following section. The mixture was shaken vigorously and sonicated to ensure the PVFc-GNPs are well suspended in the solution.

Carbon Fibre Micro Wire Electrode Fabrication

Carbon fibre micro wire electrodes were fabricated following the method developed by Ellison *et al.*^[16] A carbon fibre (diameter 7.0 μm, Goodfellow, Cambridge, UK) was connected to a metal wire using silver epoxy (RS Components, Corby, UK) conductive adhesive. To set the adhesive, the fibre-wire was placed in an oven at 60 °C for 20 min. After cooling down, it was threaded through a plastic micro pipette tip, leaving only the carbon fibre protruding out of the tip end. The gap between the wire and the tip was sealed with cyanoacrylate adhesive. It was left overnight to set the adhesive. The carbon fibre outside the tip was cut to leave 1 mm in length.

Electrochemical Procedures

All the electrochemical measurements were achieved by using a μAutolab II potentiostat (Autolab, Utrecht, Netherlands). The cell was set up in a standard three electrode configuration. Either an edge-plane pyrolytic graphite (EPPG) electrode (radius 2.0 mm) or a carbon fibre micro wire electrode performed as the working electrode. A saturated calomel electrode (SCE, ALS distributed

by BASi, Tokyo, Japan) was used as the reference electrode and a graphite rod was used as the counter electrode. The in-house EPPG was fabricated using highly ordered pyrolytic graphite (HOPG) (Le Carbone, Sussex, UK) of SP13 (ZYH) grade. The edge plane was realised by adjusting the disc surface perpendicular to the graphite crystal surface. Both voltammetric and chronoamperometric experiments were completed in a Faraday cage and thermostated at $25 \pm 1^\circ \text{C}$.

Cyclic Voltammetry at EPPG Electrodes

An EPPG electrode was polished on the alumina slurry of decreasing particle size (1.0–0.05 μm, Buehler, IL, UK). Prior to any modifications, a cyclic voltammogram was to confirm the electrode was clean. All cyclic voltammetric measurements were performed in an aqueous solution with 0.1 M NaClO₄ as supporting electrolyte. In “drop-casting experiments”, 5 μL of 0.5 mM PVFc in DCM was drop-casted on the EPPG electrode. The electrode was left still until to evaporate the organic solvent. In “abrasive modification experiment”, PVFc-GNPs were transferred to a piece of filter paper (70 mm, Fisherbrand, Loughborough, UK). The particles were abrasively modified onto the EPPG electrode for at least 100 cycles of figure of eight. After both electrode modifications, a cyclic voltammogram was recorded in the blank solution at a scan rate of 50 mV s⁻¹.

Nano-impact Chronoamperometry at Carbon Fibre Micro Wire Electrodes

A carbon fibre micro wire electrode was used to conduct nano-impacts. 5 mL of modified/unmodified GNPs suspension was bubbled with nitrogen for 5 min in order to remove the dissolved oxygen. Chronoamperograms were recorded at different potentials from + 0.3 to 1.2 V for 20 s. Before each scan, an even suspension was obtained by further bubbling of 10 s. After 10 scans, the sample was re-sonicated to prevent the aggregation of GNPs. Each sample was used for no more than 40 scans.

2. Results and Discussion

First, the cyclic voltammetry of an ensemble of PVFc-GNPs immobilised on a macro edge-plane pyrolytic graphite (EPPG) electrode is established, confirming the adsorption of PVFc onto the GNPs surface. Second, nano-impacts of individual PVFc-GNPs at a carbon fibre micro wire electrode are investigated. The charge transferred per nano-impacts spike is then studied as a function of the applied potential. In particular, the overall charge transferred is conserved during an impact event,^[17] using the electronics employed allowing measurement *via* the integration of individual spikes. Finally, the electron transfer rate is inferred by modelling of this response.

2.1 Cyclic Voltammetry

The cyclic voltammetry of PVFc (molecular weight of *ca.* 50,000) was first studied by modification of an EPPG electrode *via* drop-casting experiments. The electrode was drop-casted, dried and transferred to a 25 mL supporting electrolyte. Cyclic voltammetry was run from 0 V to +0.70 V (vs. SCE) and swept back to 0 V at a scan rate of 50 mV s⁻¹ (Figure 1, black line). For comparison,

an unmodified EPPG electrode was used to record the voltammetry in the same electrolytic solution (Figure 1, blue line). A well-defined oxidative response is observed at ca. +0.42 V (vs. SCE). This is in a good agreement with a literature report, as +0.41 V (vs. SCE) for PVFc coated multiwalled carbon nanotubes modified glassy carbon electrode in pH 7.4 phosphate solution.^[18] The redox response can be ascribed to the oxidation of the ferrocene moiety to ferrocenium, as shown in Equation (1).

Following the procedure described in the Experimental section (see Supporting Information), PVFc-GNPs were prepared. In order to demonstrate the adsorption of PVFc onto GNPs, an EPPG electrode was modified by abrading it on PVFc-GNPs powders. The electrode was transferred to 25 mL aqueous supporting electrolyte. Cyclic voltammetry was recorded between 0 V and +0.70 V (vs. SCE) at a scan rate of 50 mV s⁻¹ (Figure 1, red line). An oxidative peak occurs at +0.39 V, which is close to the oxidation potential in drop-casting PVFc on the electrode surface (Figure 1, black line). Therefore, PVFc was confirmed to be modified onto the GNPs.

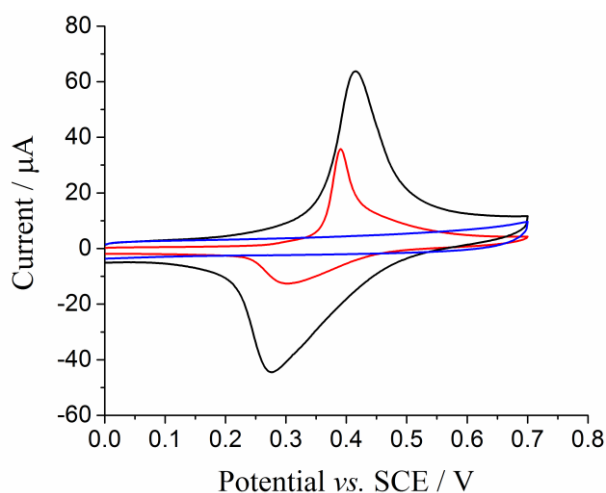


Figure 1. Voltammograms in a N₂ degassed aqueous solution supported with 0.1 M NaClO₄. Blue line: at unmodified EPPG electrode. Black line: at PVFc modified EPPG electrode via drop-casting. Red line: at PVFc-GNPs modified EPPG electrode via abrasive modification. Scan rate = 50 mV s⁻¹.

Figure 1 shows the reductive back peak is less defined than the oxidative forward peak at both PVFc (black line) and PVFc-GNPs (red line) modified EPPG electrodes. This could be due to the co-ordination^[7c, 15] of the ferrocenium and the anion from supporting electrolyte, which stabilises the former sufficiently that its reduction becomes thermodynamically unfavourable. However, this influence of ion-pairing has been minimised by the choice of NaClO₄ as compared say to KCl (see Supporting Information, choice of supporting electrolyte). Furthermore, modification with PVFc via drop-casting (Figure 1, black line) shows a higher peak current and a larger peak-to-peak separation as compared to modification with PVFc-GNPs via abrading (Figure 1, red line). While the higher peak current originates from the greater concentration of PVFc adsorbed on the electrode surface, the resulting larger peak-to-peak separation implies the non-ideality of voltammetry. With the increasing concentration of the electroactive species, the capacitive effect enhances, leading to a more distorted

voltammetric response. To bypass this issue towards the study for electrode kinetics of Cp₂Fe/Cp₂Fe⁺, 'nano-impacts' method can be introduced as an effective alternative.

2.2 Nano-impacts Chronoamperometry

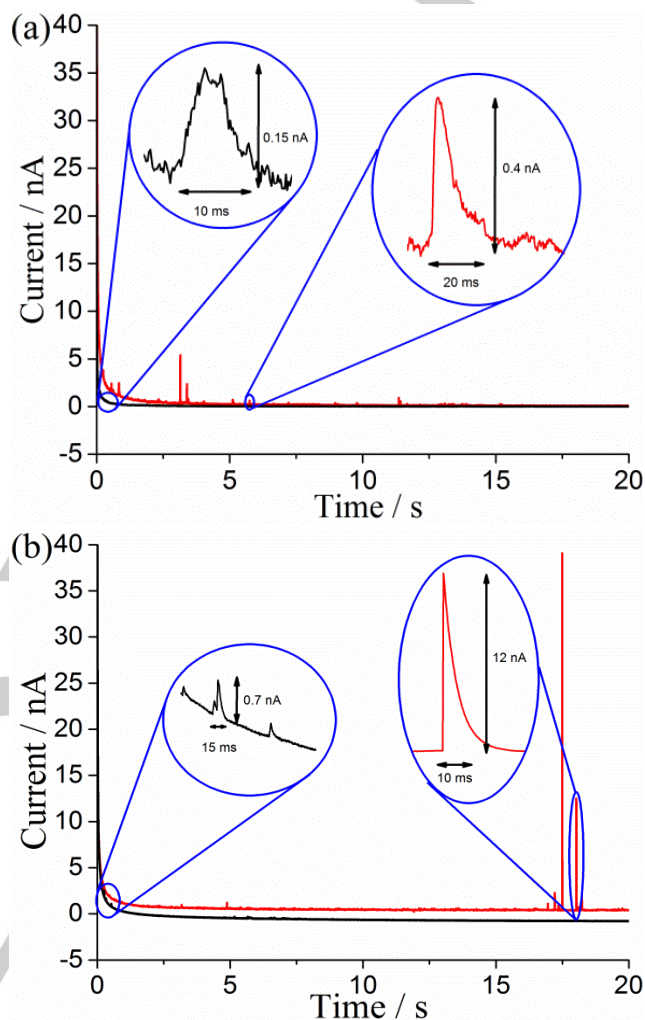


Figure 2. Chronoamperograms of 3×10^{-14} M GNPs suspension measured using a carbon fibre micro wire electrode in a N₂ degassed aqueous solution supported with 0.1 M NaClO₄. (a) +0.30 V and (b) +1.00 V. Black lines: suspension of unmodified GNPs. Red lines: suspension of PVFc-GNPs. For clarity, the red line in (b) is shifted downward by 2 nA.

Having evidenced the adsorption of PVFc on the GNPs, we next studied individual modified GNP particles *via* 'nano-impacts'. Chronoamperometry was used to detect and characterise nano-impacts of PVFc-GNPs at a carbon fibre micro wire electrode^[16] (radius 3.5 μm). According to the cyclic voltammetry studies in the preceding section, oxidation of PVFc might be expected to occur when the potential applied to the electrode is ca. +0.39 V or more (Figure 1, blue line). A carbon fibre micro wire electrode was immersed into a 5 mL PVFc-GNPs suspension and potentiostatted for 20 s at +0.30 V and +1.00 V, respectively. As a control experiment, chronoamperograms were also recorded in the presence of unmodified GNPs in the same solution the same electrode.^[16] As shown in Figure 2, impact spikes can be observed in the presence of both PVFc-GNPs (red lines) and unmodified GNPs (black lines). The average charge passed per spike (*Q*) can be quantified by taking the average of the

individual spike areas.^[17] At +0.30 V (Figure 2a), Q for PVFc-GNPs is (3.6 ± 0.7) pC, which is comparable in size as that for unmodified GNPs being (1.8 ± 0.2) pC. When the applied potential increases to +1.00 V (Figure 2b), the charge passed for the PVFc-GNPs becomes very much higher at (60.6 ± 8.7) pC. In contrast, Q for the unmodified GNPs remains at (3.3 ± 0.4) pC. As shown in the Surface Coverage section (see Supporting Information), the average charge passed per spike at +1.00 V is consistent with a monolayer coverage of PVFc on the surface of a GNP. This is achieved likely by interaction between the Cp rings in PVFc and the aromatic rings in GNPs. Due to monolayer insertion of counter ions into PVFc, transfer of ClO_4^- from water into the PVFc layer is unlikely to be the rate-determining step.

Upon collisions between a GNP particle and the electrode, two possible types of charge transfer take place resulting in impact spikes, namely capacitive and Faradaic. The physical origin of the two types of processes has been elaborated in earlier work.^[7c, 12] The black lines in Figure 2 show that Q for unmodified GNPs increases slightly for only ca. 1.5 pC upon elevation of the applied potential from +0.30 to +1.00 V, indicating it follows capacitive^[7c, 12] behaviour. In contrast, the red lines in Figure 2 demonstrates a sharp increase of ca. 57 pC in Q for PVFc-GNPs between +0.30 and +1.00 V. This likely corresponds to Faradaic^[7c] impacts arising from the oxidation of PVFc adsorbed on the GNPs. Note that at +0.30 V (Figure 2a) Q for PVFc-GNPs (red line) is marginally higher (\sim ca. 1.8 pC) than that for unmodified GNPs (black line), this discrepancy arises due to the onset of the oxidation of PVFc which commences at +0.25V (Figure 1, red line).

2.3 Analysis of Nano-impacts: Electron Transfer Kinetics

A potential dependent study was then conducted to investigate the electrode kinetics involved in the Faradaic process. Chronoamperometry was repeated with the applied potential varied from +0.30 to +1.20 V, for 0.28 mg of PVFc-GNPs suspended in 5 mL of N_2 degassed aqueous solution with 0.1 M NaClO_4 using a carbon fibre wire electrode. The average charge passed per spike (Q) was plotted against the electrode potential (Figure 3, blue squares). For comparative purposes, the potential variation of the capacitive impact spikes for the unmodified GNPs was recorded (Figure 3, black squares). The blue squares in Figure 3 shows the onset of PVFc-GNPs oxidation at ca. +0.70 V. The complete oxidation of PVFc-GNPs occurs when the applied potential is above +0.90 V, reaching the maximum charge passed per spike (Q_{max}) at (66.0 ± 5.2) pC. These data again suggest Faradaic charge transfer from PVFc-GNPs to the electrode during the collisions.

Having established the oxidation of PVFc-GNPs at both EPPG macro electrodes and carbon fibre micro wire electrodes, it can be revealed that the "switch on" threshold potential increases from ca. +0.39 V in the "ensemble" voltammetry (Figure 3, red line) to ca. +0.70 V in the individual impact chronoamperometry (Figure 3, blue squares). The origin of this potential shift of ca. 300 mV reflects the finite electron transfer kinetics of the PVFc/PVFc⁺ couple revealed by the short timescale of the nano-impacts, which has been elaborated in earlier work.^[7c] To scrutinise the cause of onset potential shift, Tafel analysis was performed with the individual nano-impact data to derive the transfer coefficient (β for oxidation) for the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ couple.^[19] Utilising the relationship between the

average charge passed per impact spike and the applied potential (Figure 3), Tafel analysis can be realised by taking the lower potential data (green line), where the electron transfer is hypothesised to be under pure kinetic-control. Note that in comparison with the signal from the drop-cast layer significant overpotential is present so that any cathodic reaction can be neglected. As shown in Figure 3 inlay, $\ln|Q|$ was plotted versus potential, giving a straight line of gradient $\beta F/RT$. The transfer coefficient, β , can hence be estimated as 0.18 ± 0.02 .

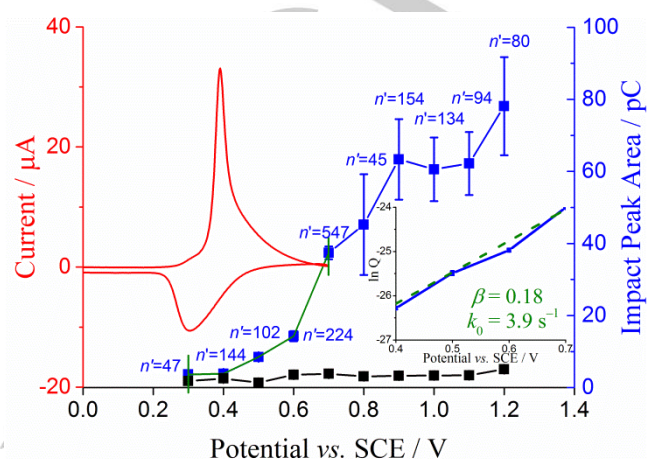
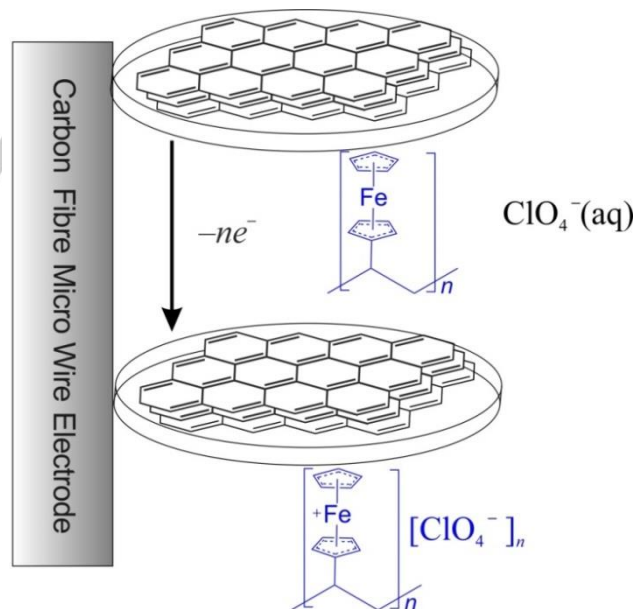


Figure 3. Analysis for PVFc-GNPs in a N_2 degassed aqueous solution supported with 0.1 M NaClO_4 . Red line: voltammogram of PVFc-GNPs modified EPPG electrode. Scan rate = 50 mV s^{-1} . Squares: the average charge transferred per nano-impacts spike of PVFc-GNPs (blue) and unmodified GNPs (black) at a carbon fibre wire electrode. The error bars are



derived from $\text{SD}/(n')^{1/2}$, where SD is the standard deviation and n' is the number of spikes. Green line: Tafel analysis region. Inlay: Tafel plot.

Scheme 1. Model for the nano-impacts between the PVFc-GNPs and the carbon fibre micro wire electrode. n is the number of monomer units.

A simple physical model is next developed for the nano-impacts between the PVFc-GNPs and carbon fibre micro wire electrodes (Scheme 1). During a nano-impact, charge is transferred to the electrode from ferrocene units in the PVFc

layer on the individual GNP. The electron transfer undergoes first order kinetics with a rate of k_{Fc} (s^{-1}), which can be related to the surface coverage of ferrocene units, Γ ($mol\ cm^{-2}$), via

$$\frac{d\Gamma}{dt} = -k_{Fc}\Gamma \quad (2)$$

where t is time. Hence, assuming Butler-Volmer kinetics, accurately describe the rate of electron transfer

$$k_{Fc} = k_0 \exp\left(\frac{\beta F \eta}{RT}\right) \quad (3)$$

where k_0 is the standard electrochemical rate constant (s^{-1}), F is the Faraday constant ($96,485\ C\ mol^{-1}$), η is the overpotential corresponding to $E - E_f^0$ with E_f^0 the formal potential, R is the ideal gas constant ($8.314\ J\ K^{-1}\ mol^{-1}$) and T is the absolute temperature (K). After substituting Equation (3) in (2), the solution for Equation (2) becomes

$$\ln \Gamma_{\text{final}}^{\text{initial}} = -k_0 t_{\text{impact}} \exp\left(\frac{\beta F \eta}{RT}\right) \quad (4)$$

where t_{impact} is the duration of the impacts event. The value of t_{impact} used is 18 ms, derived from the average duration of all the Faradaic impact spikes. By setting the limit of the integral $\Gamma_{\text{final}} = 0.5\ \Gamma_{\text{initial}}$, the overpotential at which 50% of the material is oxidised ($\eta_{1/2}$) can be defined from Equation (4) and can thus be simplified and rearranged to give;

$$k_0 = -\frac{\ln 0.5}{t_{\text{impact}} \exp\left(\frac{\beta F \eta_{1/2}}{RT}\right)} \quad (5)$$

Measurement of the 'half-wave' potential ($E_{1/2} = +0.70\ V$) and formal potential ($E_f^0 = +0.35\ V$) from Figure 3 yields the value for $\eta_{1/2}$ as $0.35\ V$. Substitution of all the known parameters gives $k_0 = 3 \pm 1\ s^{-1}$, which is consistent with prior literature estimations which range from 0.35 to $44\ s^{-1}$ either for direct charge transfer from ferrocene derivatives to carbon electrodes^[3b-e], or indirect charge transfer via multiwalled carbon nanotubes^[3a]. The value for k_0 is determined assuming the absence of contact resistance between the particles and the electrode, hence possible interference from contact resistance cannot be completely ruled out during the nano-impacts so that the value of $3 \pm 1\ s^{-1}$ should be considered to be a lower limit for k_0 . Although the use of current decay curves in the impact spikes is feasible for extraction of k_{Fc} by taking log (current) vs. time, the kinetic information is complicated by the impulse response of the potentiostat.^[17] However, the individual impact spike area remains undisturbed,^[17] so the method employed in this work is effective for electron transfer kinetic studies.

3. Conclusions

In this work we have successfully demonstrated the measurement of electron transfer kinetics for individual poly(vinylferrocene) modified graphene nanoplatelets via nano-impacts. Graphene nanoplatelets, acting as temporary nanoelectrodes for the short duration of their contact with the electrode, allows the resolution of fast electron transfer kinetics which for Cp_2Fe/Cp_2Fe^+ in $0.1\ M\ NaClO_4$ is $3 \pm 1\ s^{-1}$ or faster. This strategy provides a promising tool to obtain kinetic information relating to a wide range of applications in energy storage, drug delivery, bioimaging, sensors and composites.

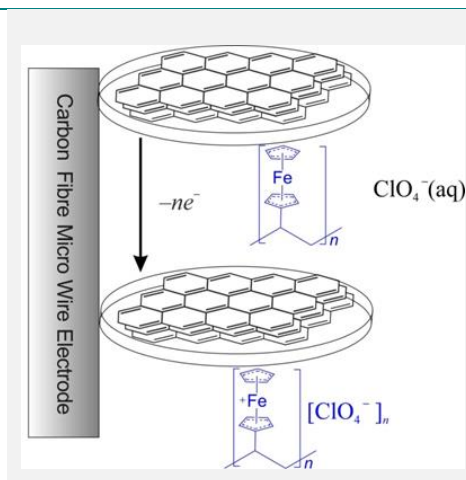
Keywords: Electron transfer • Kinetics • Redox chemistry • Graphene • Nanoparticles

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ARTICLE

The kinetics of the ferrocene/ferrocenium ($\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$) redox couple in aqueous solution are evaluated using the nano-impacts method. Single graphene nanoplatelets (GNPs) modified with poly(vinylferrocene) [PVFc] are allowed to impact a microelectrode. For the duration ($\sim 10 - 100$ ms) of the impacts the GNP adopts the potential of the electrode and acts as a 'chemically modified nanoelectrode'. The study of individual impacts facilitates the resolution of fast electron transfer kinetics which for the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ couple is shown to be at least $3 \pm 1 \text{ s}^{-1}$.



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