AcceptedImpacts Reveal and Quantify Monolayer Adsorption on Single Alumina Particles

Qianqi Lin and Richard G. Compton*

Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South
Parks Road, Oxford OX1 3QZ, UK

*To whom correspondence should be addressed

Email: richard.compton@chem.ox.ac.uk

Phone: +44 (0) 1865 275957

Fax: +44 (0) 1865 275410

Abstract

A particle impact method is used to quantify adsorption of redox active species on single insulating particles by simulation of individual spike transient, circumventing the complexity of measurements with ensembles of particles. For catechol, anthraquinone and chloranil molecules and the ferrocene moiety of poly(vinylferrocene) adsorbed on alumina, the surface coverages are found to be (3.0 ± 0.9) , (1.5 ± 1.4) , (2.7 ± 1.7) and $(2.1 \pm 0.7) \times 10^{-10} \text{ mol cm}^{-2}$, and the charge diffusion coefficients are found as (2.5 ± 0.5) , (7.9 ± 4.0) , (0.4 ± 0.2) and $(2.4 \pm 0.8) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively.

Keywords

Particle Impacts, Chronoamperometry, Adsorption, Monolayer, Coverage, Charge diffusion

INTRODUCTION

The particle impact technique provides a simple but efficient and reliable way to characterise particles and especially nanoparticles electrochemically. Impact events can be measured by immersing a microelectrode into a solution containing a suspension of particles. By virtue of the particles' Brownian motion, a single nanoparticle may diffusively collide with the electrode and a redox reaction is triggered if a certain potential is applied to the electrode. A current-time "spike" is then observed in chronoamperometry. Importantly, individual impact chronoamperometry ensures the single particle is in direct contact with the electrode, allowing assessment of its behaviour and the associated electrochemical processes. Conversely, ensemble voltammetry is often distorted due to the particles agglomerating correspond to the oxidation or reduction of nanoparticles,[1-4] 'indirect' impacts are mediated processes. The latter was introduced by Bard's group as a form of 'electrocatalytic amplification',[5-10] and further developed by Pumera's group, amongst others, in the electrocatalysis of the hydrogen evolution reaction by layered transition metal dichalcogenides nanoparticles,[11] as well as in Pt/Fe- or Fe nanoparticles labelled graphene nanosheets mediated oxygen reduction.[12] More recently, indirect particle impacts have been employed for quantitative mechanistic analysis, such as measurement of the catalytic rate constant for ferrocene mediated L-cysteine oxidation by using poly(vinylferrocene) modified graphene nanoplatelets.[13] Zhao *et al.* also found catalytic efficiency for catechol mediated NADH oxidation by using catechol modified gold nanoparticles.[14]

We recently provided proof of concept of the method to quantify adsorption and charge diffusion of electroactive species on the surface of individual insulating particles (Scheme 1).[15] In this method, particles are modified with electroactive species and suspended in aqueous solution for impact experiments. The impact spike transient is then simulated, based on the theory for Fickian charge diffusion from one molecule to another over the surface of a

full sphere.[16] The electron diffusion over the surface of the particle is assumed to be faster than for example rotation of the sphere. The modelling is achieved by introducing two parameters, the dimensionless time (τ) and the dimensionless current (Nu), defined as the following:[15, 16]

$$\tau = tD/r^2 \quad (1)$$

$$Nu = \frac{I}{2\pi nF\Gamma D} \quad (2)^\dagger$$

where t and I is time and current in particle impact chronoamperometry, n is the number of electrons transferred per modifier molecule, F is the Faraday constant ($96\,485\text{ C mol}^{-1}$), Γ is surface coverage of modifier, and D is diffusion coefficient of charge transferred over the surface of the sphere. The theoretically generated log-log plot of Nu versus τ ('working curve') is shown in Fig. 1.

Scheme 1. Charge Diffusion Model: Reactant (R) Reduced to Product (P)

[†] Expression for Nu in eq 2 corrects the equation given in reference 15.

Fig. 1. Theoretical log-log plot for dimensionless current versus time for a full sphere in point contact with the electrode surface. Inlay: corresponding dimensionless current-time.

In the present work, adsorption and charge diffusion of catechol, anthraquinone, chloranil and poly(vinylferrocene) on the surface of alumina particle are studied via impacts by modelling the individual spike transients. The surface coverages of redox active species on the surfaces of insulating alumina particles derived from this method will be shown to be consistent with the charge passed per impact spike, and revealed to be correlated with a full monolayer coverage as estimated from the molecular size for the molecules lying flat on the surface.

Scheme 2. Redox Reactions of Catechol (H₂C), Anthraquinone (AQ), Chloranil (TCBQ) and Poly(vinylferrocene) (PVFc).

EXPERIMENTAL

Chemical Reagents and Solutions

The alumina particles (Al_2O_3 , sold as '1 μm ') were purchased from Buehler (Lake Bluff, IL, U.S.A.), which was designed to be deagglomerated.[17] The actual size of alumina was examined by scanning electron microscopy as $0.58 \pm 0.40 \mu\text{m}$ in diameter.[15] Poly(vinylferrocene) (PVFc, molecular weight of ca. 50 000) was purchased from Polyscience Inc. (Warrington, PA, U.S.A). All other chemicals were purchased from Sigma-Aldrich (St Louis, MO, U.S.A). They were of analytical grade and were used as received. The structure of catechol (H_2C), anthraquinone (AQ), chloranil (tetrachloro-*p*-benzoquinone, TCBQ) and poly(vinylferrocene) (PVFc) is shown in Scheme 2. pH 3 buffer solution was freshly prepared from 0.1 M citric acid/sodium citrate, with 0.1 M KCl supporting electrolyte, using a Hanna pH213 pH meter. pH 3 was chosen because catechol is more stable in acidic conditions.[18] All aqueous solutions were prepared using deionised water with resistivity not less than 18.2 $\text{M}\Omega \text{ cm}$ at 298 K (Merck Millipore, Billerica, MA, U.S.A).

Preparation of Modified Alumina Particles

Catechol, anthraquinone, chloranil and poly(vinylferrocene) modified alumina particles (abbreviated as $\text{H}_2\text{C-Al}_2\text{O}_3$, $\text{AQ-Al}_2\text{O}_3$, $\text{TCBQ-Al}_2\text{O}_3$ and $\text{PVFc-Al}_2\text{O}_3$, respectively) were prepared as follows. 0.159g of alumina particles were first mixed with 50 mL of solutions containing modifiers (concentrations and solvents are listed in Table 1). The mixture was then sonicated (FB15050, 50/60 Hz, 80W, Fisher Scientific, Germany) for 15 min to allow the full adsorption of modifiers onto alumina particles. For $\text{H}_2\text{C-Al}$, the mixture was centrifuged for 15 min and the excess catechol was washed using pH 3 aqueous buffer. The settled particles were transferred for further experiments. For the rest, the mixture was divided into several 5 mL portions, with each added to a sample vial and left in a desiccator under vacuum to evaporate the solvent. The excess

anthraquinone and chloranil were washed using acetonitrile, while the excess poly(vinylferrocene) was washed using dichloromethane. The difference in preparation is due to that water evaporates very slowly under vacuum.

Table 1. Concentrations and solvents used in preparation of modified alumina particles

Modifiers	Concentration of modifier in preparation / mM	Solvent used in preparation
Catechol	20	pH 3 buffer
Anthraquinone	5	Acetonitrile
Chloranil	20	Acetonitrile
Ferrocene moiety of poly(vinylferrocene)	2	Dichloromethane

Electrochemical Apparatus

A standard three-electrode cell was used to conduct all the electrochemical experiments. Either a glassy carbon electrode (GCE, diameter 3.0 mm, ALS distributed by BASi, Tokyo, Japan) or a carbon fibre microdisc electrode (μ -CE, diameter 33 μ m, ALS distributed by BASi, Tokyo, Japan) was used as the working electrode. The former was used for preliminary cyclic voltammetry, and the latter was used for impact chronoamperometry. Both electrodes were cleaned by polishing in an alumina slurry of decreasing particle size (1.0-0.05 μ m, Buehler, Lake Bluff, IL, U.S.A.). A saturated calomel electrode (SCE, ALS distributed by BASi, Tokyo, Japan) and a platinum wire (99.99%, Good Fellow, Cambridge, U.K.) were used respectively as the reference and counter electrode. All experiments were conducted in a thermostated Faraday cage at 25 ± 1 °C. Voltammetric measurements were realised using a μ Autolab III potentiostat (Autolab, Utrecht, Netherlands) and impact chronoamperograms were recorded using an in-house-built low-noise potentiostat.[19] Measurement of the latter was achieved with a low current-amplifier LCA-4K-1G (FEMTO, Messtechnik GmbH, Germany), with its output bandwidth limited using a 250 Hz 4-pole Bessel filter (Linear Technology DC338A-B, Farnell, Leeds, UK). The generated analogue signal was oversampled and digitised using

LabJack U6 (LabJack Corporation, Lakewood, CO, US) at a stream rate of 4 kHz. A highly stabilised (1 kHz bandwidth) classic adder potentiostat was used for potentiostat control.[20]

Experimental Procedures

For cyclic voltammetry, unmodified '1 μm ' alumina particles were abrasively modified onto the GCE surface for 200 figure of "8" cycles of mechanical adhesion / polishing. Voltammograms were recorded in the blank solution, to confirm the cleanliness of the electrode. After the GCE was rinsed and N_2 blown dried, the modified alumina particles were either abrasively modified or drop-casted onto the GCE surface. Voltammetric measurements were run at the same scan rate in the same electrolytic solution.

For impact chronoamperometry, the modified alumina particles were suspended in 5 mL of N_2 saturated pH 3 aqueous solution supported with 0.1 M KCl (referred as a "blank solution" in the following section). Chronoamperograms were recorded for 20 s. Before each measurement, the solution was bubbled with N_2 to evenly disperse the particles and remove oxygen. In addition, the $\mu\text{-CE}$ was rinsed or polished prior to N_2 blown drying to remove possible surface blockage.

RESULTS AND DISCUSSION

We first report the cyclic voltammetry of the four types of modified alumina particles immobilised on a glassy carbon electrode. The particles are catechol-alumina, anthraquinone-alumina, chloranil-alumina and poly(vinylferrocene)-alumina. Second, the particles were dispersed in the electrolytic aqueous solution. Collisions between the particles and a carbon fibre microdisc electrode were studied via particle impact chronoamperometry. Finally, the experimental spike transients were simulated using the charge diffusion theory, allowing the derivation of surface coverage and charge diffusion coefficient of modifiers over the surface of the sphere, leading to the insight that the coverage is approximately monolayer.

Fig. 2. Voltammograms in a nitrogen-degassed pH 3 aqueous solution supported with 0.1 M KCl at a glassy carbon electrode immobilised with modified (lines) and unmodified (dashed line) alumina particles. (a) Catechol-alumina, (b) anthraquinone-alumina, (c) chloranil-alumina,

and (d) poly(vinylferrocene)-alumina. Scan rate = 100 mV s⁻¹. Current density is obtained from dividing the current by the electrode area.

The cyclic voltammetry of modified alumina particles immobilised onto a GCE surface was conducted to confirm the adsorption of modifiers on the surface of alumina. Following the synthesis of modified alumina particles as described in the Experimental Section, catechol-alumina (H₂C-Al₂O₃) was first abrasively modified onto the GCE. The electrode was transferred to the blank solution. Cyclic voltammetry was run from -0.30 to +0.90 V (*vs.* SCE) and reversed to -0.30 V at a scan rate of 100 mV s⁻¹ (Fig. 2a, line). For comparison, a blank voltammogram was recorded in the same electrolytic solution using a GCE immobilised with unmodified alumina (Fig. 2a, dashed line). An oxidative response can be observed at ca. +0.42 V, corresponding to the oxidation of the adsorbed catechol to *o*-benzoquinone (Scheme 2a). The oxidative peak occurs at the same potential as recently reported elsewhere.[15]

Second, anthraquinone-alumina (AQ-Al₂O₃) was abrasively modified onto the GCE. The electrode was transferred to the electrolytic solution to scan the voltammetry from -0.10 to +0.50 V (*vs.* SCE) and back to -0.10 V (Fig. 2b, line). The dashed line in Fig. 2b shows the blank voltammogram recorded in the same range using a GCE immobilised with unmodified alumina. A reductive response commencing at ca. -0.34 V corresponds to the reduction of the adsorbed anthraquinone to anthrahydroquinone (Scheme 2b). The reduction potential is in a good agreement with the literature reported value as -0.36 V for anthraquinone modified carbon powder immobilised at a basal plane pyrolytic graphite electrode, after recalculating the literature value of the potential to pH 3 with the use of Nernst equation.[21] Third, chloranil-alumina (TCBQ-Al₂O₃) was abrasively modified onto the GCE and the electrode was transferred to electrolytic solution. A voltammogram was recorded in the potential window between +0.60 and 0 V (*vs.* SCE, Fig. 2c, line), in comparison with another blank voltammogram at a GCE immobilised with unmodified alumina (Fig. 2b, dashed line). A reductive peak at ca. +0.28 V can be ascribed to the reduction of chloranil to tetrachloro-*p*-

hydroquinone (Scheme 2c). The observed mid-point potential, +0.29 V, is close to the value reported for chloranil derivatised carbon paste electrode in pH 3 buffer, as +0.20 V after corrected the reference electrode to SCE.[22]

Fourth, poly(vinylferrocene)-alumina (PVFc- Al_2O_3) was drop-casted onto the GCE prior to its voltammetric measurement between 0 and +0.70 V (vs. SCE) in the electrolytic solution (Fig. 2d, line). The dashed line in Fig. 2d depicts the blank voltammogram obtained using a GCE immobilised with unmodified alumina. The oxidative signal at ca. +0.45 V can be described by the one-electron oxidation of the ferrocene moiety to the ferrocenium cation (Scheme 2d). This is close to the value, +0.52 V, reported for poly(vinylferrocene) modified graphene nanoplatelets immobilised onto the edge-plane pyrolytic graphite electrode.[13] The back peak is broader and smaller than the forward peak, which can be rationalised to the ion-pairing between the ferrocenium cation and the chloride anion from the supporting electrolyte. The ferrocenium cation is hence stabilised, and its reduction becomes thermodynamically less favourable.[23] However, for consistency, KCl was still chosen to be the supporting electrolyte so that parameters of PVFc- Al_2O_3 can be comparable to the other three types of modified particles. Note the reason of drop-casting PVFc- Al_2O_3 instead of abrasive modification is that the former gives significantly better oxidative signal. This may originate from variability of electrical contact between the modified alumina particles and glassy carbon electrode surface in terms of surface preparation.

It is inferred from the voltammetric signals that catechol, anthraquinone, chloranil and poly(vinylferrocene) are all adsorbed on the surface of alumina particles. However, the voltammetry cannot be employed to determine the surface coverage of redox active species on the particles. The modification of ensemble particles on the macroelectrode often leads to agglomeration and/or aggregation,[24-26] complicating possible simulation and quantitative analysis. In contrast, impact chronoamperometry ensures the individual particle being

measured is directly in contact with the microelectrode.^[26] Therefore, in order to genuinely quantify adsorption of the molecules on the particles, the study of impacts of individual particles is essential.[13, 27]

Particle Impact Chronoamperometry

Table 2. Parameters for the four modified alumina particles

Modifier	(a)	(b)	(c)	(d) (e) (f)			(g)
	Number of impact spikes	Average charge passed per impact spike, 10^{-13} C	Molecular area of modifiers, 10^{-15} cm ²	Surface coverage of modifiers on single alumina particles, 10^{-10} mol cm ⁻²			Diffusion coefficient of charge, 10^{-6} cm ² s ⁻¹
				From (b)	From (c)	From spike transient simulation	
Catechol	246	6.0 ± 0.7	5.5	2.9 ± 0.3	3.0 ± 2.5	3.0 ± 0.9	2.5 ± 0.5
Anthraquinone	375	4.3 ± 3.4	10	2.1 ± 1.7	1.6 ± 1.6	1.5 ± 1.4	7.9 ± 4.0
Chloranil	172	5.1 ± 1.0	8.4	2.5 ± 0.5	2.0 ± 1.9	2.7 ± 1.7	0.4 ± 0.2
Ferrocene moiety of poly(vinylferrocene)	156	2.1 ± 0.8	5.6	2.1 ± 0.8	2.9 ± 2.8	2.1 ± 0.7	2.4 ± 0.8

With the aim of quantifying the adsorption of different molecules on single alumina particles, impact chronoamperometry was conducted. The cyclic voltammetry in the preceding section allows estimations of the minimum potentials required for impacts of individual modified alumina particle at a μ -CE to be seen although a large overpotential was typically applied to fully drive the exhaustive redox of the surface bound molecules.[15, 27, 28] The oxidation of H₂C-Al₂O₃ and PVFc-Al₂O₃ should take place when the applied potential is more positive than +0.42 and +0.45 V, and the reduction of AQ-Al₂O₃ and TCBQ-Al₂O₃ should occur when the applied potential is more negative than -0.34 and +0.28 V, respectively.

Fig. 3. Particle impact chronoamperograms of 0.0159 g modified alumina particles at a carbon fibre microdisc electrode, in a nitrogen-degassed pH 3 aqueous solution supported with 0.1 M KCl. Various potentials were applied to the electrode for different particles: (a) Catechol-alumina at +0.90 V, (b) anthraquinone-alumina at -0.80 V, (c) chloranil-alumina at -0.50 V, and (d) poly(vinylferrocene)-alumina at +1.00V. Baselines are corrected for modelling individual spike transients in the following discussion.

The modified alumina particles were suspended in the blank solution. The electrode was potentiostatted at +0.90, -0.80, -0.50 and +1.00 V for $\text{H}_2\text{C-Al}_2\text{O}_3$, $\text{AQ-Al}_2\text{O}_3$, $\text{TCBQ-Al}_2\text{O}_3$ and $\text{PVFc-Al}_2\text{O}_3$ respectively for 20 s to run the chronoamperometry. Fig. 3 shows impact spikes can be observed for the four different modified alumina particles, with the number of spikes recorded in Table 2a. The charge passed during the collision between a modified alumina particle and μ -CE can be derived by integrating the area under the individual spikes. The histograms in Fig. 4 shows the distribution of the charge passed per impact spike (Q), with the average value of (6.0 ± 0.7) , (4.3 ± 3.4) , (5.1 ± 1.0) and $(2.1 \pm 0.8) \times 10^{-13}$ C for $\text{H}_2\text{C-Al}_2\text{O}_3$, $\text{AQ-Al}_2\text{O}_3$, $\text{TCBQ-Al}_2\text{O}_3$ and $\text{PVFc-Al}_2\text{O}_3$, respectively (Table 2b). Q can be correlated with the surface coverage (Γ) of the modifier on the alumina particle via[15, 28]

$$\Gamma = \frac{Q}{neN_{\text{A}}S_{\text{alumina}}} \quad (3)$$

Fig. 4. Histograms of charge passed per impact spike, with log-normal distribution plotted in the curve. (a) Catechol-alumina, (b) anthraquinone-alumina, (c) chloranil-alumina, and (d) poly(vinylferrocene)-alumina.

where e is the electronic charge, N_A is the Avogadro constant and S_{alumina} is the surface area of alumina. According to Scheme 2, the value of n is 2 for catechol, anthraquinone and chloranil, but 1 for poly(vinylferrocene). As the radius of alumina (r) is ca. $0.29 \mu\text{m}$,^[15] S_{alumina} is ca. $1.06 \times 10^{-8} \text{ cm}^2$ according to $S_{\text{alumina}} = 4\pi r^2$. With the measured Q , Γ can be estimated as (2.9 ± 0.3) , (2.1 ± 1.7) , (2.5 ± 0.5) , and $(2.1 \pm 0.8) \times 10^{-10} \text{ mol cm}^{-2}$ for $\text{H}_2\text{C-Al}_2\text{O}_3$, $\text{AQ-Al}_2\text{O}_3$, $\text{TCBQ-Al}_2\text{O}_3$ and $\text{PVFc-Al}_2\text{O}_3$, respectively (Table 2d). These values are consistent with monolayer coverage of modifiers with the assumption that molecules are close-packed parallel to the surface of the single alumina particle, according to $\Gamma = S_{\text{alumina}} / S_{\text{molecule}}$ where S_{molecule} is the molecular area of modifiers calculated as follows using the catechol molecule as an example in Scheme 3. By assuming each molecule is a rectangle, both side lengths can be estimated by using trigonometry for bond lengths, bond angles and Van der Waals radii of terminating atoms. S_{molecule} can hence be predicted, as listed in Table 2c. Note that S_{molecule} for

ferrocene moiety in poly(vinylferrocene) is estimated by considering the planar five-membered ring with a two-membered alkyl chain (Scheme 2d) in a rectangle parallel to the surface of alumina. The corresponding Γ is (3.0 ± 2.5) , (1.6 ± 1.6) , (2.0 ± 1.9) and $(2.9 \pm 2.8) \times 10^{-10}$ mol cm^{-2} for $\text{H}_2\text{C-Al}_2\text{O}_3$, $\text{AQ-Al}_2\text{O}_3$, $\text{TCBQ-Al}_2\text{O}_3$ and $\text{PVFc-Al}_2\text{O}_3$, respectively (Table 2e).

Scheme 3. Catechol Molecular Area Model

Modelling Individual Impact Spike Transients

Following the model developed from the theory of charge diffusion from one molecule to another over the surface of a full sphere,[15, 16] the work turns to model individual impact spike transients. As shown in the inlay of Fig. 5, an individual spike was first chosen from particle impact chronoamperometry. After baseline subtraction, the decaying part of the transient (Fig. 5 inlay, highlight) was analysed. The logarithm of corresponding current versus time was then plotted, as shown as circles in Fig. 5. The theoretical $\log Nu$ versus $\log \tau$ was also plotted, as shown as curves in Fig. 5. Since the scale of theoretical $\log \tau$ and $\log Nu$ is 3.5 and 3.0 respectively, the experimental $\log t$ and $\log I$ should be adjusted to be the same scale. In order for experimental circles to fit theoretical curves, differences in horizontal and vertical

axes will be observed. According to the relation between t and τ (eq 1) as well as I and Nu (eq 2), the differences can be used to derive the coverage (Γ) and charge diffusion coefficient (D) of the modifier on the surface of individual alumina particles. The modelling was repeated for five individual spikes to obtain the average value of Γ and D .

Fig. 5. Comparison of theoretical (curves, bottom and left axes) and experimental (circles, top and right axes) log-log plot. The scale of both horizontal axes and both vertical axes is 3.5 and 3.0, respectively. Inlay: chronoamperometry of the experimental individual impact spikes, with baseline subtracted for the modelling. The transients highlighted are used for analysis, the logarithm of which correspond to the circles. (a) Catechol-alumina, (b) anthraquinone-alumina, (c) chloranil-alumina, and (d) poly(vinylferrocene)-alumina.

For $H_2C-Al_2O_3$, $AQ-Al_2O_3$, $TCBQ-Al_2O_3$ and $PVFc-Al_2O_3$, the coverages were found to be (3.0 ± 0.9) , (1.5 ± 1.4) , (2.7 ± 1.7) , and $(2.1 \pm 0.7) \times 10^{-10}$ mol cm^{-2} respectively (Table 2e), and diffusion coefficients were found to be (2.5 ± 0.5) , (7.9 ± 4.0) , (0.4 ± 0.2) , and $(2.4 \pm 0.8) \times 10^{-6}$ $cm^2 s^{-1}$ respectively (Table 2g). Table 2 shows the value of coverages are reasonable, comparing well to the average charge passed per impact spike, as well as monolayer estimation

from alumina surface area as demonstrated in the preceding section. Note that the values reported are of ferrocene moiety of poly(vinylferrocene), but not of the polymer. The surface coverage for $\text{H}_2\text{C-Al}_2\text{O}_3$ is slightly different from the value reported[15] since eq 2 has been corrected by taking n into consideration. However, the updated value is even closer to estimations from the other two methods. The diffusion coefficient for $\text{TCBQ-Al}_2\text{O}_3$ is about one magnitude smaller compared to the other three modified alumina particles. This can be noted from the inlay of Fig. 5c that the impact spike transient of $\text{TCBQ-Al}_2\text{O}_3$ is much less steep than the other three. The low diffusion coefficient reflects slow intrinsic charge diffusion among adsorbed chloranil molecules.

CONCLUSIONS

This work has successfully simulated individual impact spike transients to determine the charge diffusion coefficients among the molecules over the surface of alumina, as (2.5 ± 0.5) , (7.9 ± 4.0) , (0.4 ± 0.2) , and $(2.4 \pm 0.8) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ respectively for catechol, anthraquinone and chloranil molecules, and ferrocene moiety of poly(vinylferrocene). The surface coverages were found to be (3.0 ± 0.9) , (1.5 ± 1.4) , (2.7 ± 1.7) , and $(2.1 \pm 0.7) \times 10^{-10} \text{ mol cm}^{-2}$ accordingly. The new electrochemical method of modelling impacts reveals monolayer adsorption of diverse species on single insulating particles by comparison of theoretical and experimental log-log plot for the spike current-time transient. Note however that curve must be taken to ensure the transient timescale is sufficiently long to avoid distortion by the measuring electronics.[29, 30]

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