

## Supplementary Information for

Electrochemistry of  $\text{Fe}^{3+/2+}$  at Highly Oriented Pyrolytic Graphite (HOPG)  
Electrodes: Kinetics, Identification of Major Electroactive Sites and Time  
Effects on the Response

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## S1 | Cyclic Voltammograms for the Reduction of 0.25 mM Fe(ClO<sub>4</sub>)<sub>3</sub> in 0.1 M HClO<sub>4</sub>

Cyclic voltammetry (CV) measurements were carried out using a low concentration redox species (0.25 mM Fe(ClO<sub>4</sub>)<sub>3</sub>) in 0.1 M HClO<sub>4</sub> electrolyte. As shown in Figure S1, the behaviour is comparable to that obtained for 5 mM Fe<sup>3+</sup> (see main text).

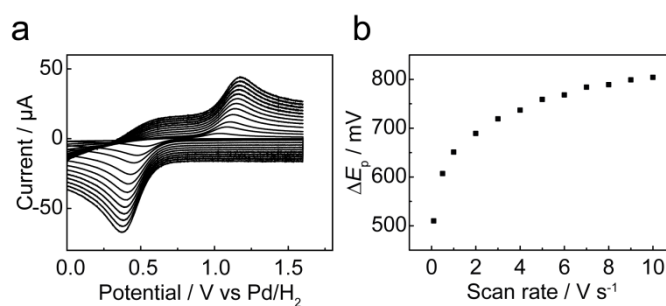


Figure S1. (a) CVs for the reduction of Fe(ClO<sub>4</sub>)<sub>3</sub> (0.25 mM in 0.1 M HClO<sub>4</sub> solution) recorded at scan rates of 0.1(smallest current), 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 (biggest current) V s<sup>-1</sup>. (b) Peak-to-peak separation for the CVs shown in (a) plotted against scan rates.

## S2 | Simulation of the CVs for the Reduction of Fe<sup>3+</sup> on AM HOPG

The finite element method was employed in COMSOL Multiphysics 5.1 (COMSOL AB, Sweden) to simulate the electrochemistry response for the reduction of Fe<sup>3+</sup> at the HOPG samples. The 2-D axisymmetric geometry employed for the droplet-cell configuration was similar to previously reported (Figure S2),<sup>1</sup> where the following diffusion equation was solved:

$$\frac{\partial c_i}{\partial t} = D_i \left( \frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial z^2} \right) \quad (\text{eq. 1})$$

where  $c_i$  (mol dm<sup>-3</sup>) and  $D_i$  (cm<sup>2</sup> s<sup>-1</sup>) are the concentration and diffusion coefficient of species  $i$  (Fe<sup>3+</sup> or Fe<sup>2+</sup>).  $D$  was assumed to be  $4.08 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> and  $5.51 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> for Fe<sup>3+</sup> and Fe<sup>2+</sup>.<sup>2</sup>

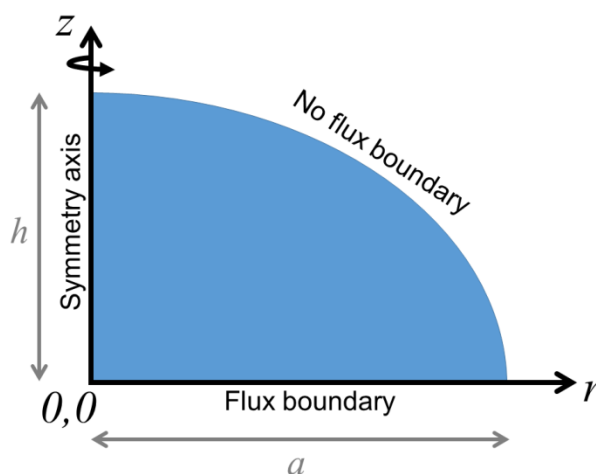
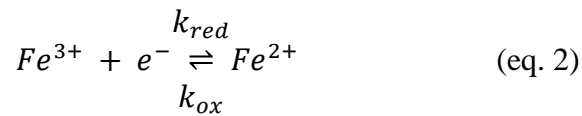


Figure S2. 2-D simulations domain for the droplet-cell configuration (not to scale).

The droplet was modelled as hemi-oblate spheroid where the height,  $h$  of the droplet is determined from the known volume,  $V$ , of solution used and the measured area,  $A = \pi a^2$ , of the droplet base determined from optical microscope measurements (allowed to vary by  $\pm 10\%$  in the modelling) and the peak current magnitudes measured during voltammetry. Typically, 75,000 triangular mesh elements were used in each simulation with the greatest density at the flux boundary.

Butler-Volmer kinetics was used to describe the potential-dependence of ET at the electrode/electrolyte interface.



where  $k_{red}$  and  $k_{ox}$  are the reduction and oxidation rate constants given by:

$$k_{red} = k_0 e^{(-\alpha f \eta)} \quad (\text{eq. 3})$$

$$k_{ox} = k_0 e^{[(1-\alpha) f \eta]} \quad (\text{eq. 4})$$

where  $\alpha$  and  $k_0$  are the transfer coefficient (assumed to be 0.5) and standard heterogeneous rate constant, respectively.  $f = \frac{F}{RT}$  is a collection of constants where  $F$  is the Faraday constant,  $R$  is the gas constant, and  $T$  is the absolute temperature (298 K).  $\eta = E(t) - E^{0'} - IR_{\Omega}$ , is the overpotential;  $E(t)$  is the potential applied to the electrode at time,  $t$  and  $E^{0'}$  is the formal potential of the redox couple.  $I$  is current and  $R_{\Omega}$  is the uncompensated resistance.

Note that the 2D model described herein gives a very similar result to an equivalent 1D model. Thus, most of the kinetic analysis simulations presented are from 1D simulations for computational efficiency.

The voltammogram taken at a scan rate,  $\nu$  of  $0.1 \text{ V s}^{-1}$  was first analysed to determine  $A$  (fitting of forward peak currents,  $I_p$ ) and  $k_0$  (fitting of the peak-to-peak separation,  $\Delta E_p$ ). Under slow  $\nu$  conditions, ohmic drop effects were negligible so as not to be considered, as shown in Figure S3a. Next, voltammograms recorded at  $\nu = 10 \text{ V s}^{-1}$  were analysed. Here, both  $k_0$  and ohmic drop,  $IR_\Omega$  may contribute to changes in  $\Delta E_p$  and can be used to determine  $R_\Omega$  as  $k_0$  is already estimated. As seen from Figure S3b, different  $R_\Omega$  values (0, 50 and  $100 \text{ }\Omega$ ) were used in the model to demonstrate the significant ohmic drop effect, based on which a reasonable value of  $30 \text{ }\Omega$  (for AM grade) or  $28 \text{ }\Omega$  (for SPI-3 grade) was adopted for simulations for CVs at fast scan rates (0.5, 1, 5, 7 and  $10 \text{ V s}^{-1}$ ). A range of  $\nu$  values were analysed to confirm the reliability of the  $k_0$  value found, as summarised in Table S1 for both AM and SPI-3 grade HOPG.

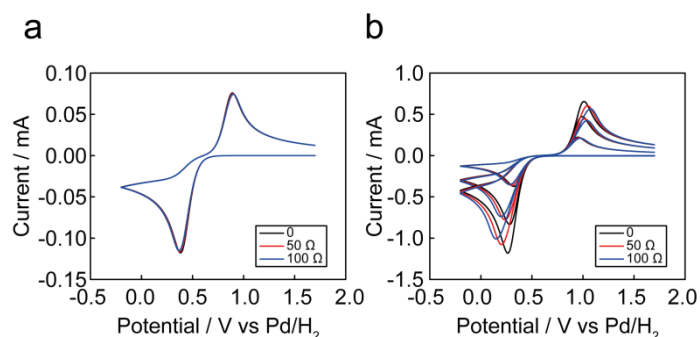


Figure S3. Simulations for the reduction of  $5 \text{ mM Fe}^{3+}$  in  $0.1 \text{ M HClO}_4$  solution, at scan rates of (a)  $0.1$ , (b)  $1$ ,  $5$  and  $10 \text{ V s}^{-1}$ , with a solution resistance of  $0$ ,  $50$  and  $100 \text{ }\Omega$  considered.

Table S1. Simulation parameters for the  $\text{Fe}^{3+/2+}$  process at AM and SPI-3 grade HOPG samples. Simulated voltammograms are shown in Figure 4 of main text.

$\nu$ ( $\text{V s}^{-1}$ )	AM				SPI-3			
	Area ( $\text{cm}^2$ )	$k_0$ ( $\text{cm s}^{-1}$ )	$R_\Omega$ ( $\Omega$ )	$\Psi$	Area ( $\text{cm}^2$ )	$k_0$ ( $\text{cm s}^{-1}$ )	$R_\Omega$ ( $\Omega$ )	$\Psi$
0.1	0.18	0.00005	0	99.0	0.178	0.00005	0	99.0
0.5	0.185	0.00005	30	99.4	0.178	0.00005	28	99.0
1	0.185	0.00005	30	99.4	0.178	0.00005	28	98.5
5	0.187	0.00005	30	99.1	0.178	0.00005	28	97.9
7	0.19	0.00005	30	98.9	0.178	0.00005	28	97.6
10	0.195	0.00005	30	98.8	0.180	0.00005	28	97.4

The least squares correlation,  $\Psi$ , between experimental and simulated data is given by the following:

$$\Psi = \left( 1 - \sqrt{\frac{\sum (x_{\text{exp}} - x_{\text{sim}})^2}{\sum x_{\text{exp}}^2}} \right) * 100 \quad (\text{eq. 5})$$

where  $x_{\text{exp}}$  and  $x_{\text{sim}}$  are the experimental and simulated functions.

### S3 | Cyclic Voltammograms for the Reduction of 0.25 mM Fe(ClO<sub>4</sub>)<sub>3</sub> in 1 M HClO<sub>4</sub>

Given that electrowetting would occur during the electrochemical transition of Fe<sup>3+/2+</sup> in HClO<sub>4</sub> solution,<sup>3</sup> an O-ring was used to confine the droplet contact with HOPG surface and CV measurements were done. As shown in Figure S4, a slightly larger peak-to-peak separation values were obtained on the CVs compared with those observed for a bare droplet, but the results are broadly similar.

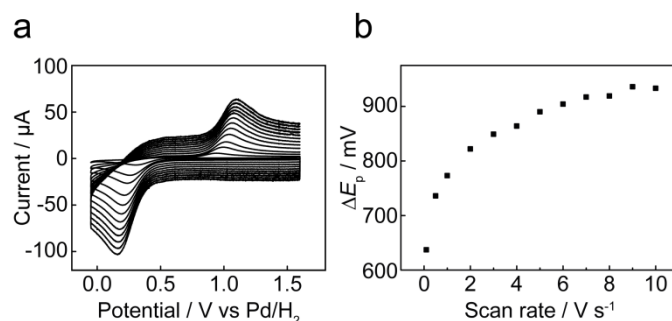


Figure S4. (a) CVs for the reduction of Fe(ClO<sub>4</sub>)<sub>3</sub> (0.25 mM in 1 M HClO<sub>4</sub> solution) recorded at scan rates of 0.1 (smallest current), 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 (biggest current) V s<sup>-1</sup>, with an O-ring (radius 3.1 mm) used to confine the working electrode area. (b) Peak-to-peak separation for the CVs shown in (a) plotted against scan rate.

#### S4 | Calculation of Standard Heterogeneous Rate Constant from SECCM CV

The standard electron transfer rate constant  $k_0$  for  $\text{Fe}^{2+/3+}$  can be estimated by considering the half-wave potential and the mass transport rate in the SECCM configuration.<sup>4</sup> The mass transport rate constant ( $k_T$ ) is dependent on the limiting current ( $I_{lim}$ ) (eq.6):

$$I_{lim} = nFAk_T C \quad (\text{eq.6})$$

where  $n$  is number of electrons transferred,  $F$  is the Faraday constant (96485 C mol<sup>-1</sup>),  $A$  is the area of the working electrode (pipet diameter 350 nm) and  $C$  is the bulk concentration of reactant ( $\text{Fe}^{2+}$ ), which is 2 mM. The limiting current was found to be 31 pA (see the CV in Figure 9a), leading to  $k_T = 0.168 \text{ cm s}^{-1}$ .

In a steady-state reaction process, the net flux of reactant species towards the electrode is balanced by the reaction rate at the electrode surface. Thus, the product of the mass transport rate constant and the concentration difference between the bulk ( $C$ ) and vicinity of the electrode surface ( $C_S$ ) equals the product of the (potential-dependent) reaction rate constant ( $k'$ ) and  $C_S$ , as shown in eq.7.

$$k_T(C - C_S) = k' C_S \quad (\text{eq.7})$$

For an irreversible electron transfer process, the  $k'$  can be defined as:

$$k' = k_0 e^{[\alpha F(E - E^{0'})/RT]} \quad (\text{eq.8})$$

where  $k_0$  is the ET rate constant,  $\alpha$  is the transfer coefficient (=0.5),  $E$  is the potential applied,  $E^{0'}$  is the formal potential of  $\text{Fe}^{2+/3+}$  (0.85 V vs Pd/H<sub>2</sub>)<sup>4</sup>,  $R$  is the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>) and  $T$  is temperature (298 K). At the half-wave potential,  $C_S$  can be regarded as half of  $C$ . Given the half-wave potential  $E_{1/2} = 1.247 \text{ V}$  (vs Pd/H<sub>2</sub>) obtained from the CV shown in Figure 9 of the main text,  $k_0$  was estimated to be  $7.4 \times 10^{-5} \text{ cm s}^{-1}$ .



## S5 | SECCM Electroactivity Mapping of AM HOPG

Ion conductance current and AC current were recorded simultaneously with the SECCM electroactivity map of HOPG (Figure 9 in the main text). As shown in Figure S5, the DC ion current is reasonably stable across the area probed, although there are some variations, which could be due to electrowetting. The AC current was relatively uniform, indicative of a stable feedback control during SECCM imaging. There is occasional slight increase in the area of step edges.

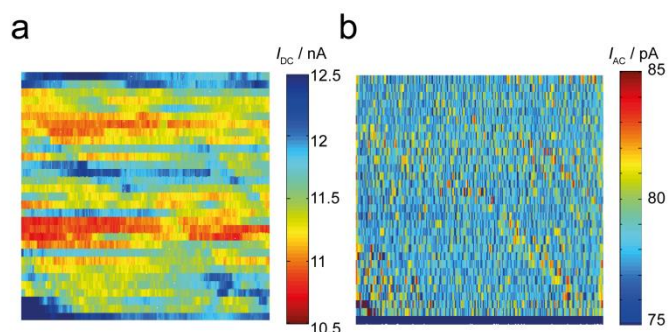


Figure S5. (a) Ion conductance current and (b) AC component maps for SECCM electroactivity imaging of an area of  $10 \mu\text{m} \times 10 \mu\text{m}$  on a freshly cleaved AM HOPG surface.

## References

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