Supporting Information

Structure-Function Correlations in Graphene Screen-Printed Electrodes: Capacitive and Faradaic Behaviour

Tharinda Kasemphong,[1] Monchai Jitvisate,[2] Chanida Jakkrawhad,[1] Wichayaporn Kamsong,[3] Chanpen Karuwan,[3] Pachanuporn Sunon,[4] Supinya Nijpannich,[5] Phanawan Whangdee,[6] Theeranun Siritanon,[1] Kamonwad Ngamchuea*[1]

[1] School of Chemistry, Institute of Science, Suranaree University of Technology, 111 University Avenue, Suranaree, Muang, Nakhon Ratchasima 30000, Thailand

[2] School of Physics, Institute of Science, Suranaree University of Technology, 111 University Avenue, Suranaree, Muang, Nakhon Ratchasima 30000, Thailand

[3] National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Pathum Thani 12120, Thailand

[4] Institute of Research and Development, Suranaree University of Technology, 111 University Avenue, Suranaree, Muang, Nakhon Ratchasima, 30000, Thailand

[5] Synchrotron Light Research Institute, 111 University Avenue, Suranaree, Muang, Nakhon Ratchasima, 30000, Thailand

[6] Department of Applied Physics, Faculty of Sciences and Liberal Arts, Rajamangala University of Technology Isan, Nakhon Ratchasima, 30000, Thailand

*Corresponding author: Kamonwad Ngamchuea, School of Chemistry, Institute of Science, Suranaree University of Technology, 111 University Avenue, Suranaree, Muang, Nakhon Ratchasima, 30000, Thailand. Email: kamonwad@g.sut.ac.th; Tel: +66 (0) 44 224 637

Simulation vs. Experiment: Faradaic Behaviour

Cyclic voltammograms of the $[Fe(CN)_6]^{4-/3-}$ couple were simulated using a 1D diffusion model to a planar electrode under excess supporting electrolyte (i.e. negligible migration). Concentration profiles of the reduced and oxidized species, $C_O(x,t)$ and $C_R(x,t)$, were obtained by solving Fick's law of diffusion:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} (i = O,R) \qquad \text{(S1)}$$

over $0 \le x \le L$, with L chosen to be sufficiently large ($L \ge 6\sqrt{Dt_{max}}$) to approximate semi-infinite diffusion (i.e. $C_i(L,t) \approx C_i^*$ for all t). Initial conditions were $C_R(x,0) = C_R^*$ and $C_O(x,0) = 0$. At the electrode surface ($x = 0$), the faradaic flux was defined by Butler–Volmer kinetics:

$$J = k^0 \left[C_R(0,t) exp\left(\frac{\beta F\eta}{RT}\right) - C_O(0,t) exp\left(\frac{-\alpha F\eta}{RT}\right)\right] \qquad \text{(S2)}$$

with boundary conditions

$$J = -D_O \frac{\partial C_O}{\partial x}\bigg|_0 = D_R \frac{\partial C_R}{\partial x}\bigg|_0 \qquad \text{(S3)}$$

and $\eta(t) = E(t) - E^0$, where $E(t)$ follows the experimental triangular waveform at scan rate v. The faradaic current was calculated as $I = nFAJ$.[1] Simulations were performed using the open-source package FreeSim,[2] and the value of k^0 was taken from the experimentally determined value reported in Section 3.7 in the main text.

Figure S1 presents a representative example, showing that the experimentally determined value of k^0 provides a good fit to the observed peak potentials when compared with simulation. The electroactive surface area of each electrode was initially estimated using the limiting forms of the Randles–Ševčík equation. Using the reversible Randles–Ševčík equation (eqn. S4) yielded A values smaller than the theoretically predicted area. In contrast, applying the expression for totally irreversible systems (eqn. S5) gave A values significantly larger than the theoretically predicted area, indicating overestimation.

Reversible Randles–Ševčík equation:[3]

$$I_p = 0.446nFAc^*\sqrt{\frac{nFDv}{RT}} \qquad \text{(S4),}$$

where I_p is the peak current, n is the total number of electron transfer, A is the electroactive surface area, c^* is the bulk concentration, v is the scan rate, F is the Faraday constant (96485 C mol^{-1}), D is the diffusion coefficient, R is the universal gas constant (8.314 J K^{-1} mol^{-1}), and T is the absolute temperature.

Irreversible Randles–Ševčík equation:[3]

$$I_p = 0.496\sqrt{n^{'} + \beta}nFAc^*\sqrt{\frac{FvD}{RT}} \qquad \text{(S5),}$$

where $n^{'}$ is the number of electron transfer before the rate-determining step and β is the anodic transfer coefficient of the rate-determining step. I_p, n, F, A, c^*, v, R, and T have the same meanings as above.

This behaviour is consistent with the $[\mathrm{Fe(CN)_6}]^{4-/3-}$ couple at our electrodes exhibiting quasi-reversible kinetics, lying between the reversible and fully irreversible limits; therefore, neither limiting form is appropriate for accurate determination of A. Nonetheless, although neither the reversible nor totally irreversible Randles–Ševčík expressions yields an accurate absolute A under quasi-reversible conditions, applying a single expression consistently across all electrodes provides a useful comparative (‘apparent’) electroactive area for benchmarking between SPE types.

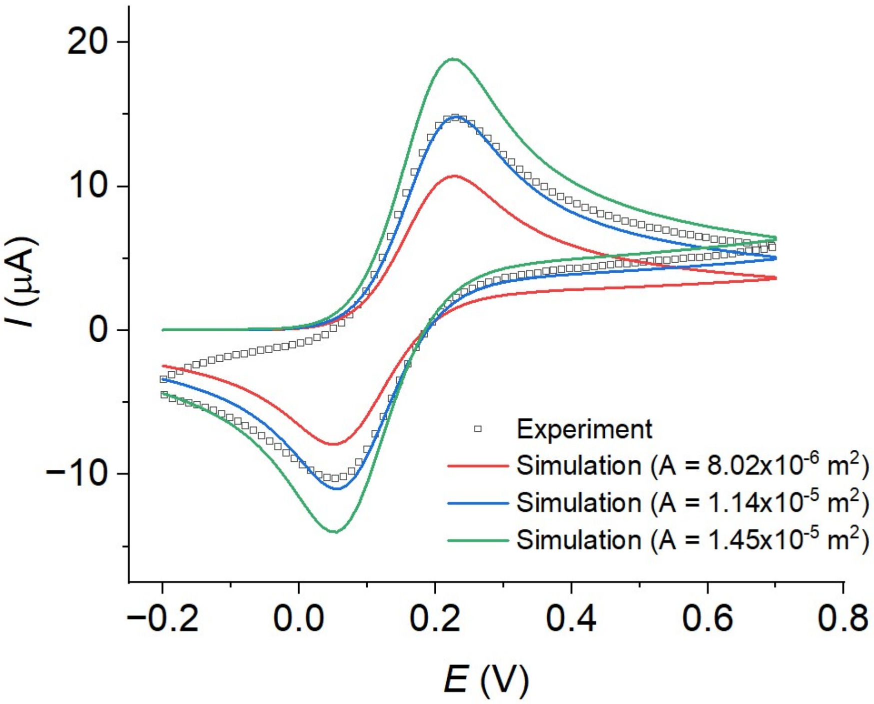

Figure S1: Experimental and simulated CVs of 1.0 mM $[Fe(CN)_6]^{4-}$ in 0.10 M KCl recorded at a scan rate of 50 mV s^{-1} for commercial graphene SPE. Simulation parameters: A = 8.02×10^{-6} m^2 (from the reversible Randles–Ševčík equation, eqn. S4) or 1.45×10^{-5} m^2 (from the totally irreversible Randles–Ševčík, eqn. S5) or 1.14×10^{-5} m^2 (best-fit to the experimental voltammogram), $k^0 = 1.03 \times 10^{-5}$ m s^{-1}, $\beta = 0.5$.

The transfer coefficients (β) obtained experimentally via mass-transport-corrected Tafel analysis (eqn. 15, main text) fall in the range $\beta =$ 0.76 – 0.86 across all SPEs. In contrast, the voltammograms are highly symmetric and are better reproduced by simulation using $\beta = 0.5$ (Figure S2). This discrepancy likely reflects that the experimental β values are apparent parameters extracted under conditions where surface heterogeneity, uncompensated resistance, and non-ideality in the kinetic model can bias Tafel-derived slopes, whereas the simulations assume ideal Butler–Volmer kinetics with a uniform planar interface.

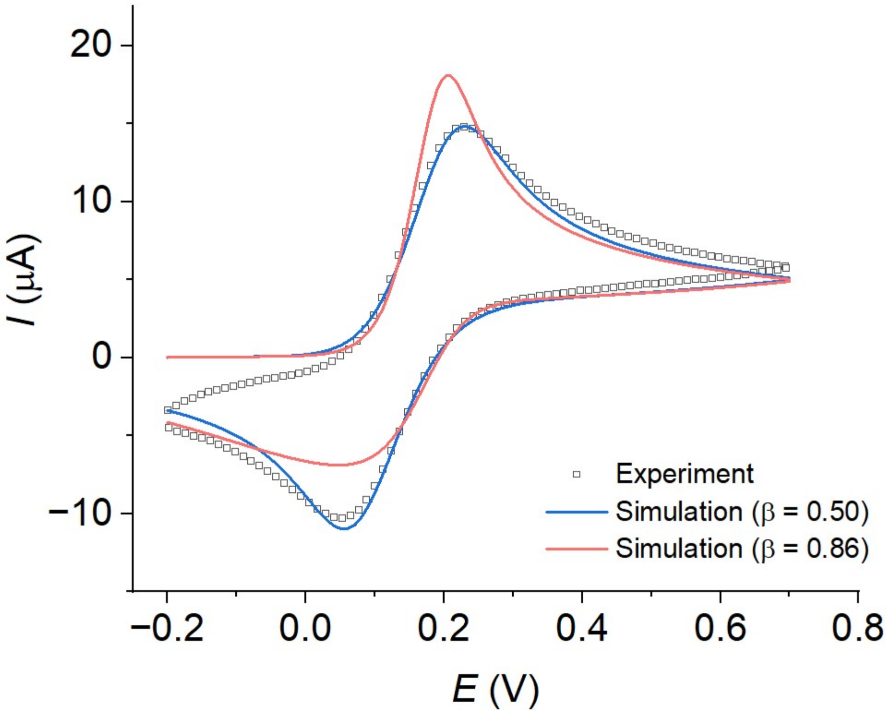

Figure S2: Experimental and simulated CVs of 1.0 mM $[Fe(CN)_6]^{4-}$ in 0.10 M KCl recorded at a scan rate of 50 mV s^{-1} for commercial graphene SPE. Simulation parameters: A = 1.14×10^{-5} m^2, $k^0 =$ 1.03×10^{-5} m s^{-1}, $\beta =$ 0.50 or 0.86.

References

1. Compton, R. G.; Kätelhön, E.; Ward, K. R.; Laborda, E., *Understanding Voltammetry: Simulation of Electrode Processes*. World Scientific: 2014.

2. Chen, H.; Hu, X.; Lu, Y., Advancing Voltammetry Education with FreeSim: An Interactive Toolkit for Teaching Electrochemical Simulation. *Journal of Chemical Education* **2025**.

3. Compton, R. G.; Banks, C. E., *Understanding Voltammetry*. World Scientific: 2018.