Supplementary Information for

Electrochemistry at Highly Oriented Pyrolytic Graphite (HOPG): Lower Limit for the Kinetics of Outer-sphere Redox Processes and General Implications for Electron Transfer Models

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Contents

1. Voltammetric responses of $IrCl_6^{2-/3-}$ on AM and SPI-3 grade HOPG

The electrochemical reduction of 0.25 mM $IrCl_6^{2-}$, in a supporting electrolyte of 0.1 M KCl, was examined on AM and SPI-3 HOPG surfaces, respectively, with typical CVs shown in Figure S1. Peak-to-peak separation values of 160 ± 1 mV and 112 ± 1 mV at 10 V s^{-1} were seen on AM HOPG in two different cells, respectively, while 86 ± 1 mV and 95 ± 1 mV were observed for SPI-3 HOPG in two different cells. This difference emphasizes the relatively poor reproducibility, due to the impact of ohmic drop effects (see main text) under these conditions, and highlights the need for much higher concentration of supporting electrolyte.
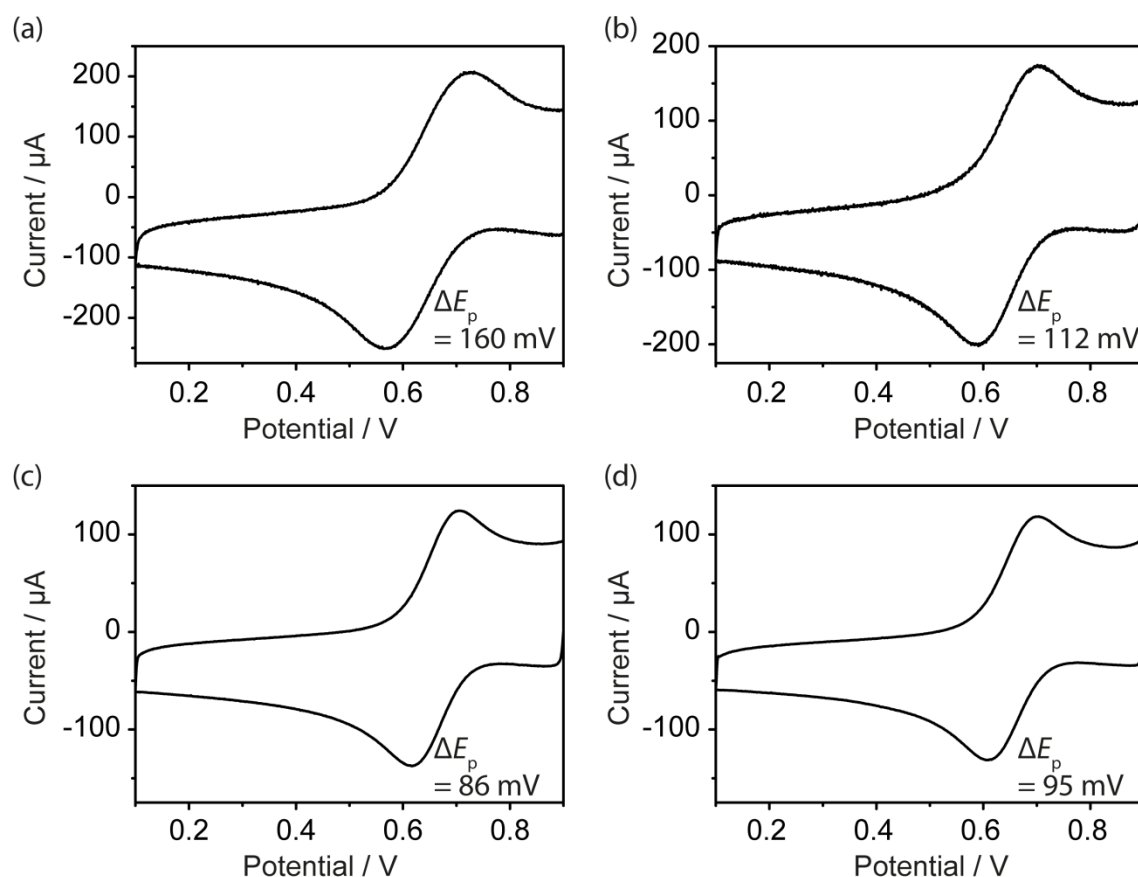

Figure S1. Cyclic voltammograms for the reduction of 0.25 mM $IrCl_6^{2-}$ in 0.1 M KCl on freshly cleaved (a)-(b) AM, and (c)-(d) SPI-3 HOPG, with a scan rate of 10 V s^{-1}, and each grade of HOPG studied in 2 different droplet-cells. The numbers indicated are the peak-to-peak separations.

2. Voltammetric responses of $Ru(NH_3)_6^{3+/2+}$ on AM and SPI-3 grade HOPG

With the optimised experimental condition, where 0.25 mM redox-active mediator and 1 M KCl were used, CV measurements were carried out on freshly cleaved surfaces of AM and SPI-3 HOPG. As seen from Figure S2 and S3, similar peak-to-peak separation values at 10 V s^{-1} were obtained for $Ru(NH_3)_6^{3+/2+}$, indicative of the good reproducibility of CVs under the optimised conditions. It should also be noted that these values are smaller than obtained with a lower concentration (0.1 M KCl) of supporting electrolyte, as a result of significantly reduced ohmic drop .
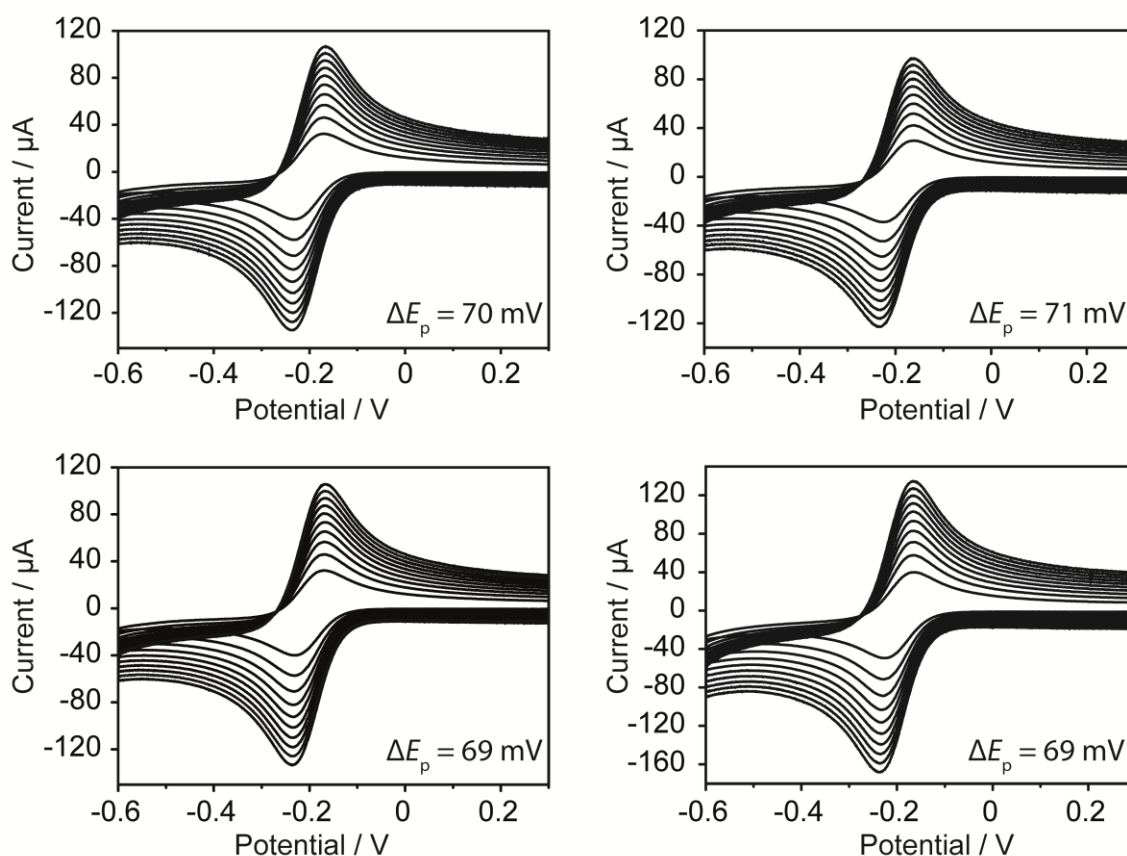

Figure S2. Cyclic voltammograms for the reduction of 0.25 mM $Ru(NH_3)_6^{3+}$ in 1 M KCl on AM grade HOPG in 4 different droplet-cells (each a freshly cleaved piece of HOPG), recorded at a scan rate of 1 (smallest current), 2, 3, 4, 5, 6, 7, 8, 9 and 10 (largest current) V s^{-1}, respectively. The numbers indicated are the peak-to-peak separations at 10 V s^{-1}.
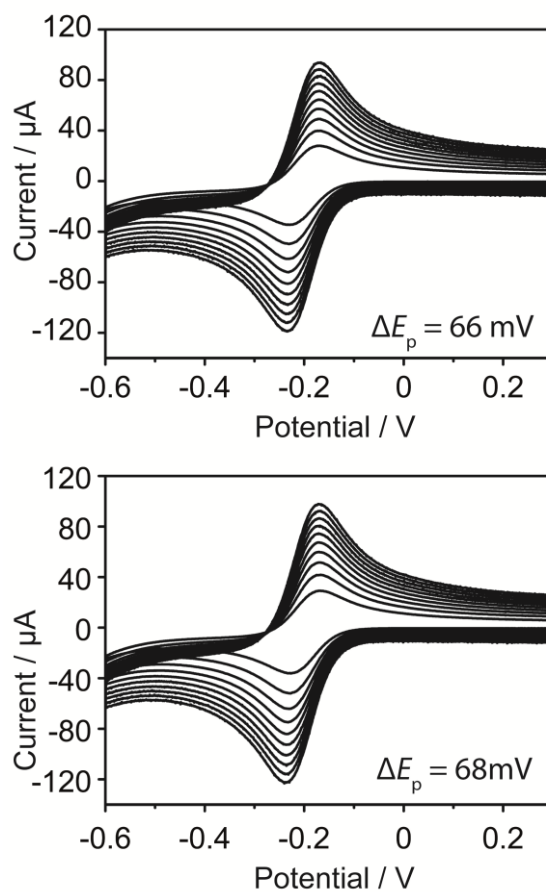
Figure S3. Cyclic voltammograms for the reduction of 0.25 mM $Ru(NH_3)_6^{3+}$ in 1 M KCl on SPI-3 grade HOPG in 2 different droplet-cells (2 freshly cleaved pieces of HOPG), recorded at a scan rate of 1 (smallest current), 2, 3, 4, 5, 6, 7, 8, 9 and 10 (largest current) V s^{-1}, respectively. The numbers indicated are the peak-to-peak separations at 10 V s^{-1}.

3. Voltammetric responses of $Fe(CN)_6^{4-/3-}$ on AM and SPI-3 grade HOPG

CV measurements were also carried out in a solution containing 0.25 mM $Fe(CN)_6^{4-}$ and 1 M KCl, on freshly cleaved AM and SPI-3 grade HOPG. As illustrated in Figure S4 and S5, similar peak-to-peak separation values at 10 V s^{-1} were obtained, indicating the good reproducibility of CVs under the optimised conditions.
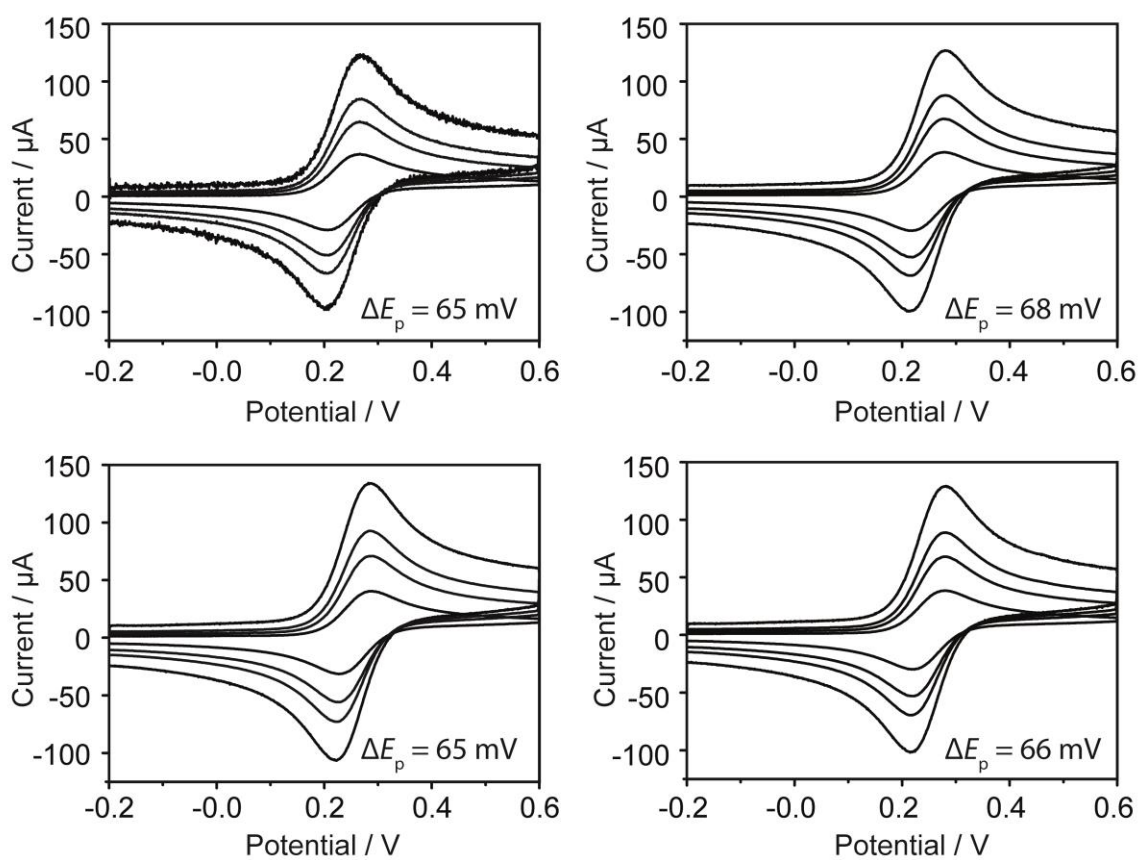

Figure S4. Cyclic voltammograms for the oxidation of 0.25 mM $Fe(CN)_6^{4-}$ in 1 M KCl on freshly cleaved AM grade HOPG in 4 different droplet-cells (4 different pieces of HOPG), recorded at a scan rate of 1 (smallest current), 3, 5 and 10 (largest current) V s^{-1}, respectively. The numbers indicated are the peak-to-peak separations at 10 V s^{-1}.

Figure S5. Cyclic voltammograms for the oxidation of 0.25 mM $Fe(CN)_6^{4-}$ in 1 M KCl on freshly cleaved SPI-3 grade HOPG in 4 different droplet-cells (4 fresh samples), recorded at a scan rate of 1 (smallest current), 3, 5 and 10 (largest current) $V\ s^{-1}$, respectively. The numbers indicated are the peak-to-peak separations at 10 $V\ s^{-1}$.
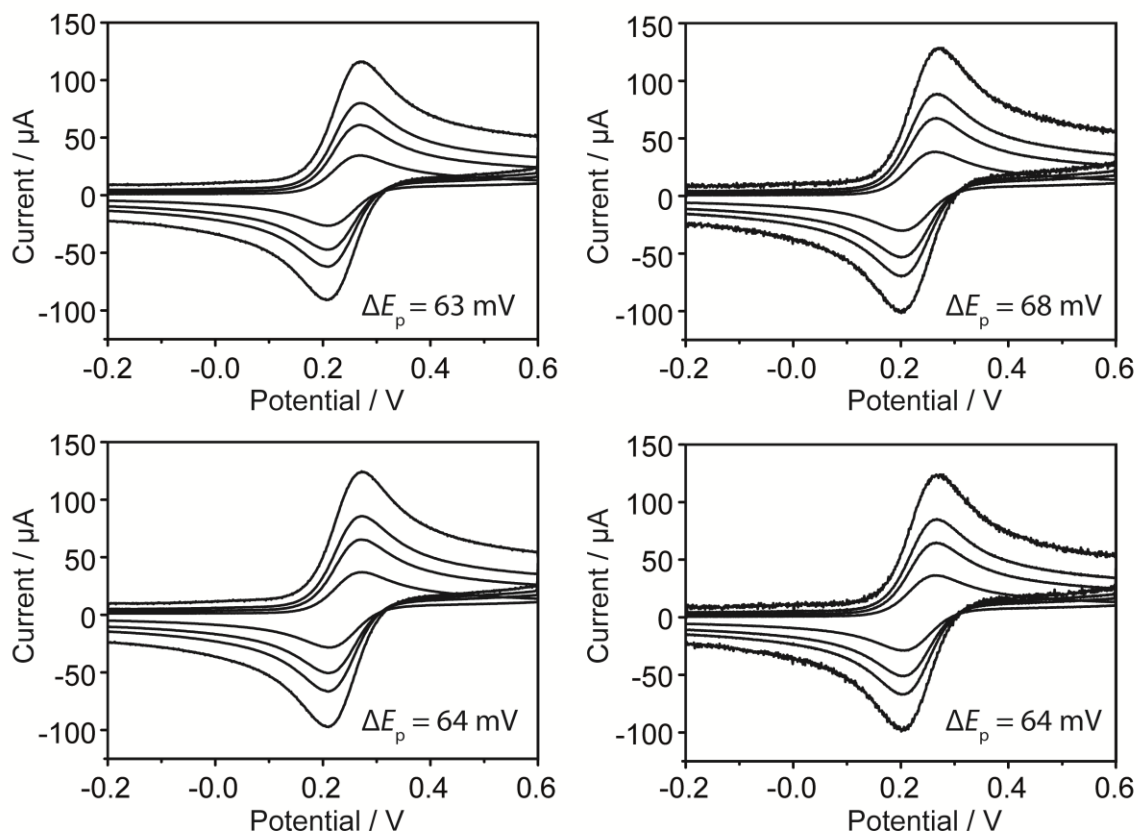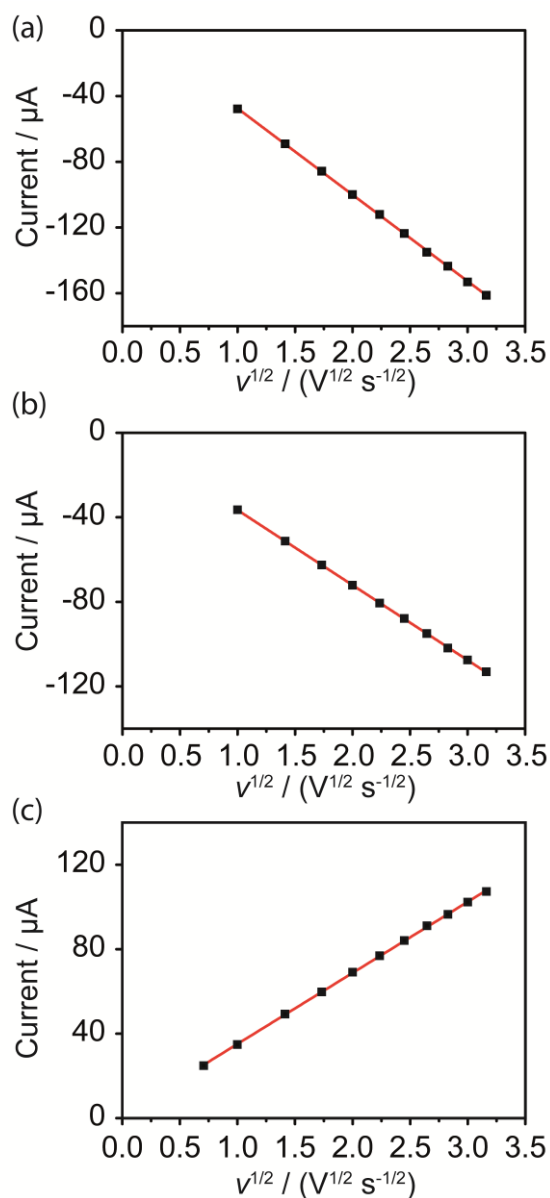
4. Influence of scan rate on the peak current

Figure S6. Plot of the reductive peak current for $IrCl_6^{2-}$ (a) and $Ru(NH_3)_6^{3+}$ (b), and the oxidative peak current for $Fe(CN)_6^{4-}$ (c) against the square root of the scan rate ($v^{1/2}$). Both experimental data (■) and a line of best fit (━) are shown.

It was found that peak current changed linearly with the square root of scan rate, for all the three redox couples, i.e. $IrCl_6^{2-/3-}$, $Ru(NH_3)_6^{3+/2+}$ and $Fe(CN)_6^{4-/3-}$. Together with the ΔE_p analysis herein, this indicted that these redox reactions on HOPG are essentially reversible diffusion-controlled processes.