Supplementary Information

Semi-circular potential sweep voltammetry: Experimental verification and determination of the formal potential of a reversible redox couple

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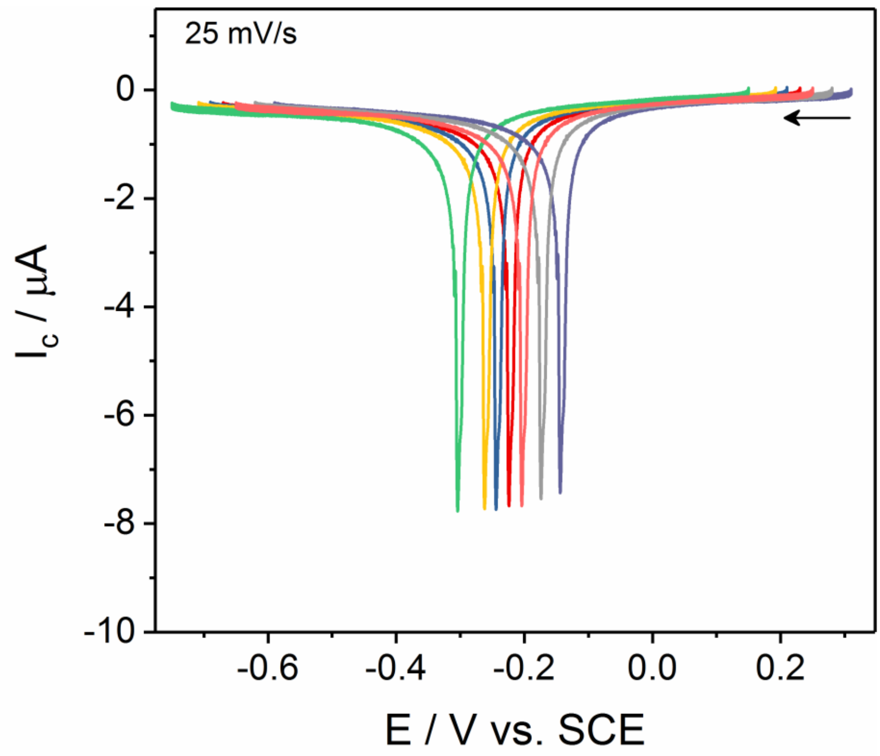

Fig. S1. Voltammograms obtained at a GC electrode at different E_{centre} values using the semi-circular voltammetry in 0.50 M KCl blank solution at an average scan rate of 0.025 V s^{-1} at 298 K. The voltammograms display the capacitive currents without baseline correction.

For the voltammograms using the semi-circular potential wave in a 0.265 mM $[Ru(NH_3)_6]Cl_3$/0.50 M KCl at 0.025 V s^{-1}, the peak heights obtained before any corrections of the voltammograms are compared in Fig. S2. The same trend as after corrections is observed, but the maximum peak current occurs at a potential which is different by about 2 mV from the one after correction. Thus, the correction for the capacitive current is essential.

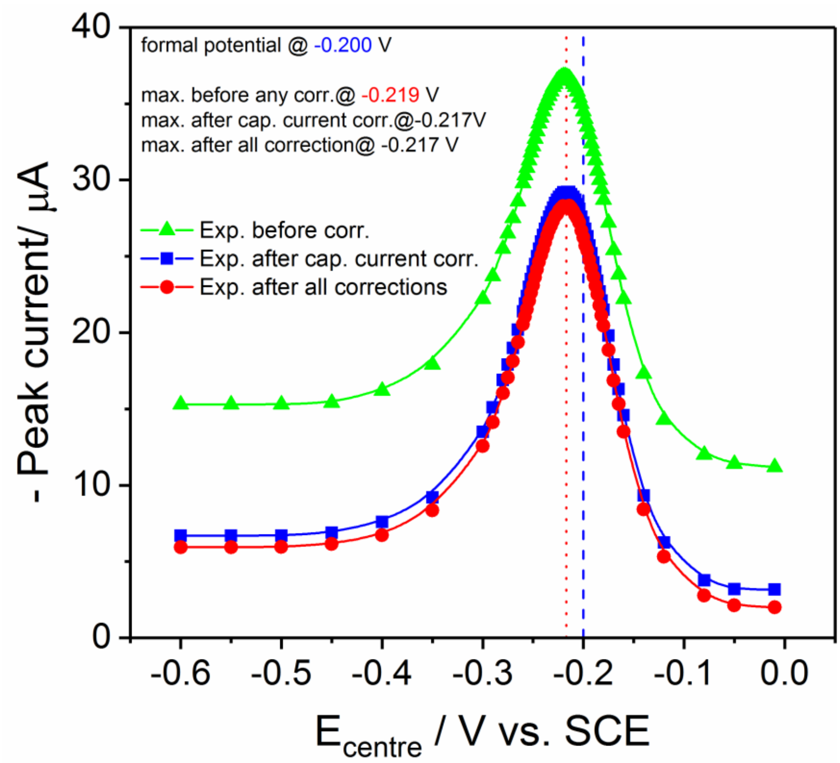

Fig. S2. Plot of the absolute maximum peak currents at different E_{centre} values using the semi-circular potential wave in a 0.265 mM $[Ru(NH_3)_6]Cl_3$/0.50 M KCl at 0.025 V s^{-1}. Data were obtained from the corresponding voltammograms after correction for the capacitive current and the base-line (red spheres), after correction for the capacitive current only (blue squares) and before any corrections (green triangles). The formal potential calculated from the triangular voltammetry is indicated by the dashed blue line, while the potential at the maximum peak current from the semi-circle experiment is indicated by the dotted red line.

A semi-circular voltammetry experiment at a higher scan rate of 0.05 V s^{-1} in the same solution of 0.265 mM $[Ru(NH_3)_6]Cl_3$/0.50 M KCl was conducted, and a plot of peak currents *versus* the corresponding E_{centre} is depicted in Fig. S3. The maximum is observed at −217± 2 mV which is in good agreement with the value obtained from the measurement at 0.025 V s^{-1}, *c.f.* Fig. 6 and S3. The E_{centre}^{max} obtained for this higher scan rate also shows a negative potential shift of 8 ± 1 mV from the formal potential. It is noteworthy that, at this low electrolytic support (1.0 mM $[Ru(NH_3)_6]Cl_3$/0.10 M KCl) at 0.05 V s^{-1} the plot of peak currents *versus* the corresponding E_{centre} reveals the same behaviour with a maximum in peak current, but the potential at which the experimental maximum (−209 ± 2 mV) is observed does not coincide with simulation result (maximum at −187 ± 2 mV), see Fig. S4. The formal potential in this solution, as calculated independently from the triangular wave voltammetry [5] and then implemented in the simulation, is −178 ± 2 mV which is different from the one obtained in highly supported solution. The deviation of 22 ± 2 mV in the position of maximum between simulation and experiment is mainly due to the incomplete electrolytic support [22]. This emphasises the importance of the high ratio of supporting electrolyte to analyte.

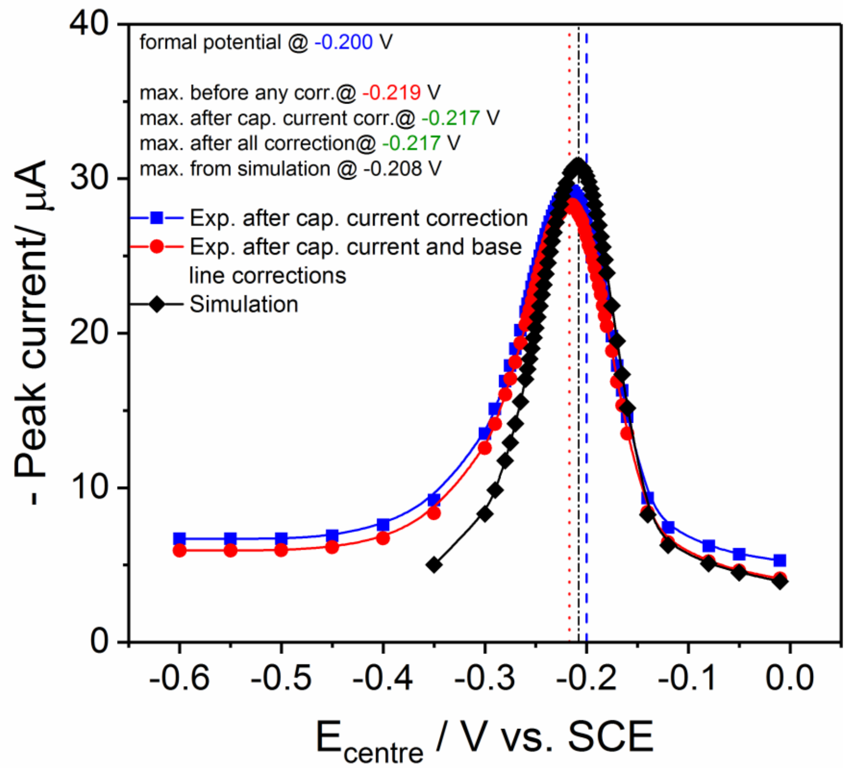

Fig. S3. Plot of the absolute maximum peak currents at different E_{centre} values using the semi-circular potential wave in a 0.265 mM $[Ru(NH_3)_6]Cl_3$/0.50 M KCl at 0.05 V s^{-1}. Data were obtained from the corresponding simulated (black diamonds) and experimental voltammograms after correction for the capacitive current and the base line (red spheres) and after correction for the capacitive current only (blue squares). The formal potential calculated from the triangular voltammetry is indicated by the dashed blue line, while the potential at the maximum peak current from simulation is indicated by the dash-dotted black line and from the semi-circle experiment by the dotted red line.

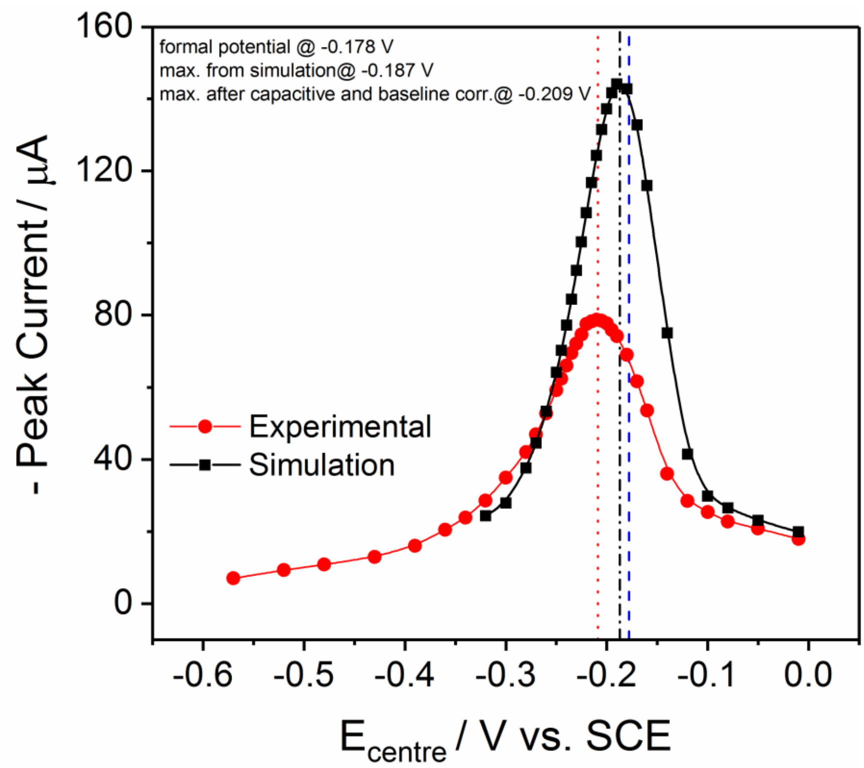

Fig. S4. Plot of the absolute maximum peak currents at different E_{centre} values using the semi-circular potential wave in a 1.0 mM $[Ru(NH_3)_6]Cl_3$/0.10 M KCl at 0.05 V s^{-1}. Data were obtained from the corresponding simulated (black squares) and experimental voltammograms after correction for the capacitive current and the base line (red spheres). The formal potential, calculated from the triangular voltammetry, is indicated by the dashed blue line, while the potential at the maximum peak current from the simulation is indicated by the dash-dotted black line and from the semi-circle experiment by the dotted red line.

Notwithstanding, the maximum obtained from simulation is located at 9 ± 1 mV more negative than the formal potential, which is similar to the results obtained at the high electrolytic support.