Supplementary Information for

Kinetic Study of Ferrocenium Cation Decomposition Utilizing an Integrated Electrochemical Methodology Composed of Cyclic Voltammetry and Amperometry

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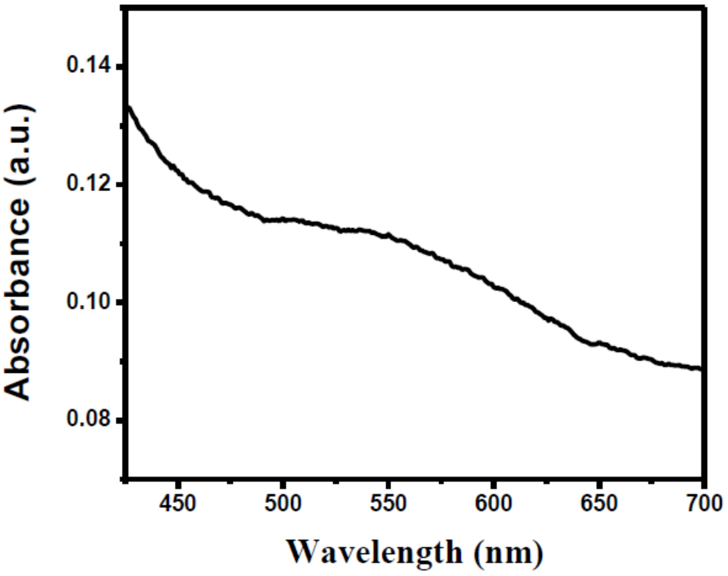

Figure SI 1: UV-Vis spectrum of iron oxide deposited on indium-tin oxide (ITO) electrode in 0.5 M Bu_4NPF_6/ACN.

Integration methodology in cyclic voltammetry to obtain charge (Q) versus potential (E) plot: The CVs obtained in the present study were integrated by using the “Baseline and Peaks” option of origin software. This option has multiple threads that together lead to the stepwise baseline creation, baseline subtraction, peak fitting, and then integral of the X-function of the data points.

In the first step, the anodic component of the CV was plotted in origin (Figure SI 2A). After that Baseline and Peaks option was used in origin software. Baseline of the data point was created using a single rectangle method. In this method, baseline was created by choosing the potential at which the redox process just started, i.e. the potential at which the current sharply started to increase. This method generated a background subtracted CV i.e. Y=0 (i.e. current equal to zero below the potential where redox process started) (Figure SI 2B). Once the base line corrected CV was generated, the integration was achieved by calculating area under the whole CV. Thus it provided a figure of $\int I.dE$ versus E (Figure SI

2C). Subsequently, the charge (Q) was obtained by dividing the total integrated area by the scan rate (ν) of CV and then charge (Q) versus *E* was plotted (Figure SI 2D). These integrated plots are also shown in Figure. 2B.

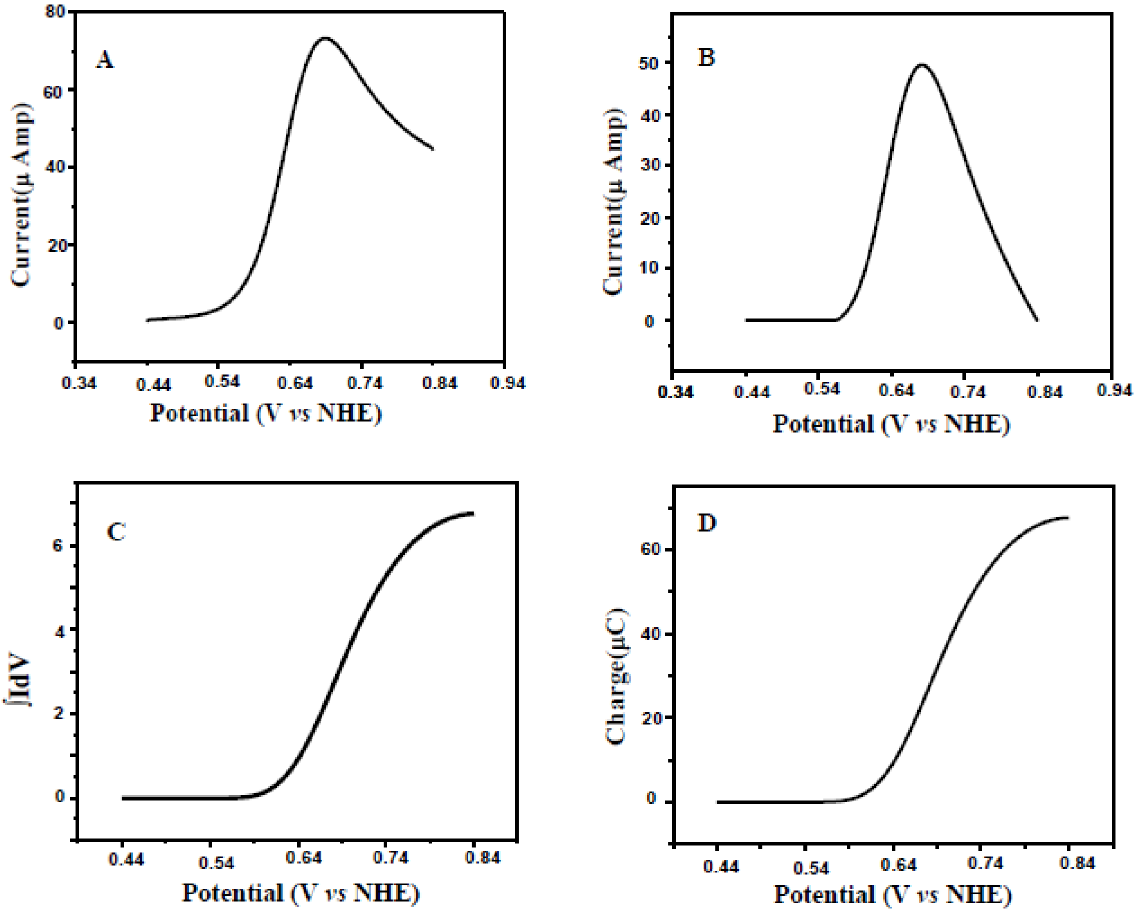

Figure SI 2: (A) Anodic component of 1st cyclic voltammogram collected during CV-(i-t)-CV cycles for 0.5 mM in 0.5 M Bu_4NPF_6/ACN at a scan rate of 100 mV/s (B) Background subtracted voltammogram generated from Figure SI 2A. (C) $\int I.dE$ *versus* potential (E) plot generated from Figure SI 2B. (D) Charge *versus* potential (E) plot where charge was obtained by dividing $\int I.dE$ with scan rate (ν).

Rate Law for Ferrocenium Cation Decomposition:

$$Fc^{+} + O_2 \Leftrightarrow Fc^{+}O_2$$
$$Fc^{+}O_2 + Fc^{+} \rightarrow Fc^{+}O_2Fc^{+}$$
$$Fc^{+}O_2Fc^{+} + O_2 + H_2O \rightarrow \mathrm{Pr}oducts$$

k_1 and k_{-1} are the rate constants for forward and reverse reaction for step 1. k_2 and k_3 are the rate constants for step 2 and step 3 respectively.

$Fc^{+}O_2$ and $Fc^{+}O_2Fc^{+}$ will be symbolized as X and Y respectively.

According to the steady-state approximation methodology

Rate=k_3[Y][O_2][H_2O] (1)

Applying the steady-state approximation to Y

$$\frac{d[Y]}{dt} = 0 = k_2[X][Fc^+] - k_3[Y][O_2][H_2O] \quad (2)$$

Using (2) in (1)

Rate=k_2[X][Fc^+] (3)

Applying the steady-state approximation to X

$$\frac{d[X]}{dt} = k_1[Fc^+][O_2] - k_{-1}[X] - k_2[X][Fc^+] = 0$$

Hence, $[X] = \frac{k_1[Fc^+][O_2]}{k_{-1} + k_2[Fc^+]}$ (4)

Using (4) in (3)

$$Rate = \frac{k_1 k_2 [Fc^+]^2 [O_2]}{k_{-1} + k_2[Fc^+]}$$

Since, $k_2[Fc^+] >> k_{-1}$

So, $Rate = k_1[Fc^+][O_2]$

Since, oxygen was abundant

So, $Rate \propto [Fc^+]$