Supporting Information

Dynamic Impedance Spectroscopy of Nickel Hexacyanoferrate Thin Films

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Supporting Information

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S1 Quasi-Triangular Waveform

The mathematical description for the quasi-triangular wave (QTW) has been defined in previous publication of our research group [1]. The quasi-triangular wave used in this work is shown in Fig.S1a. The amplitude of the QTW was 400 mV peak to peak. The frequency of the QWT was 0.125 Hz corresponding to a scan rate of 200 mVs$^{-1}$. The NiHCF thin films were held at 100 mV vs Ag/AgCl before the QTW and the multi-sine were applied to the NiHCF because NiHCF is more stable in its reduced form than its oxidized form as shown in Fig.S1b.

Figure S1: (a) Quasi-triangular waveform used in this work represented in the time domain (b) Cyclic voltammogram of NiHCF thin films held at 100mV and 900 mV for 5 minutes after every 5th cycle.
S2  Schematics of Transmission Line Model

The transmission line model (TLM) in its generic form for describing the faradaic processes occurring in porous electrode consists of several parallel and serially connected elements which describes the various regions in the porous electrode [2, 3, 4]. $\rho_s$ describes the resistance of the electrolyte within the pores of the NiHCF, $\rho_E$ describes the resistance in the NiHCF while $\zeta$ describes the impedance in the active interface i.e. the interface between the pores/electrolyte. It is assumed that the $\rho_s$, $\rho_E$ and $\zeta$ are independent on the position along the x axis (Fig. S2) which represents the pore depth, thus the impedance of the pore is independent of the position along the pore depth.

Figure S2: Schematic of the transmission line model used in describing the faradaic processes occurring in NiHCF thin film.
S3 Model

The two-step intercalation process can be described as:

\[ A_i^+ \rightleftharpoons A_i^+ \]  
(1)

\[ A_i^+ + ANi[Fe^{III}CN_6] + e^- \rightleftharpoons A_2Ni[Fe^{II}CN_6] \]  
(2)

where equation 1 corresponds to the first step which is the partial desolvation of the cations in solution \( (A_i^+) \) and the formation of an ad-ion \( (A_i^+) \) in the inner Helmholtz plane (IHP) while equation 2 represents the insertion step where the partially desolvated cation \( (A_i^+) \) is inserted into the host structure followed by change in the oxidation state of Fe from +3 to +2 to achieve charge neutrality (second step). The potential distribution at the interface is given by:

\[ \phi_1 = \phi_i \]  
(3)

\[ \phi_2 = \phi_T - \phi_i \]  
(4)

where \( \phi_i \) is the potential drop in the IHP, \( \phi_T \) is the total potential drop in the interface and \( \phi_2 \) is the potential drop due to the insertion step.

The rate of formation of the adsorbed species is the difference between the rate of the desolvation step \( (r_1) \) and insertion step \( (r_2) \) and can be defined as:

\[ N_{ad} \frac{\partial \beta}{\partial t} = r_1 - r_2 \]  
(5)

where \( N_{ad} \) is the number of adsorption sites available. The influence of the adsorbed cation on the potential drop in the IHP \( (\phi_1) \) is expressed as:

\[ \phi_1 = \frac{F\beta N_{ad}}{C_1 + C_2} + \frac{C_2}{C_1 + C_2} \phi_T \]  
(6)

The total current \( (I_T) \) flowing through the system can then be described as:

\[ I_T = -F(1 - \gamma)r_1 - Fr_2 + C_{dl}\phi_T \]  
(7)

\[ \gamma = \frac{C_1}{C_1 + C_2} \]  
(8)

Subsequently, the impedance \( (Z) \) is given by:

\[ \frac{1}{Z} = \frac{\Delta I_T}{\Delta \phi_T} = -F(1 - \gamma) \frac{\Delta r_1}{\Delta \phi_T} - F\gamma \frac{\Delta r_2}{\Delta \phi_T} + j\omega C_{dl} \]  
(9)

where \( \Delta \) denotes the oscillating quantity or variable. The rate of the reactions is a function of the oscillating potential and oscillating concentrations which can be represented with a first order Taylor series as shown below:
\[
\frac{\Delta r_1}{\Delta \phi_T} = \frac{\partial r_1}{\partial \Delta \phi_1} [1 - \gamma] + \left[ \frac{\partial r_1}{\partial \beta} - \frac{\partial r_1}{\partial \Delta \phi_1} \frac{N_{ad}}{C_1 + C_2} \right] \frac{\Delta \beta}{\Delta \phi_T} + \frac{\partial r_1}{\partial C_{A_1}} \frac{\Delta C_{A_1}}{\Delta \phi_T} \tag{10}
\]

\[
\frac{\Delta r_2}{\Delta \phi_T} = \frac{\partial r_2}{\partial \Delta \phi_2} - \gamma + \left[ \frac{\partial r_2}{\partial \beta} + \frac{\partial r_2}{\partial \Delta \phi_2} \frac{N_{ad}}{C_1 + C_2} \right] \frac{\Delta \beta}{\Delta \phi_T} + \frac{\partial r_2}{\partial \theta} \frac{\Delta \theta}{\Delta \phi_T} \tag{11}
\]

The resistance due to adsorption \((R_{ad})\) can be described as:

\[
R_{ad} = \left[ -F \frac{\partial r_1}{\partial \phi_1} \right]^{-1} \tag{12}
\]

Substituting equation 12 into equation 10 leads to the expression below:

\[
\frac{\Delta r_1}{\Delta \phi_T} = \frac{[1 - \gamma] + \left[ \frac{\partial r_1}{\partial \beta} - \frac{\partial r_1}{\partial \Delta \phi_1} \frac{N_{ad}}{C_1 + C_2} \right] \frac{\Delta \beta}{\Delta \phi_T} + \frac{\partial r_1}{\partial C_{A_1}} \frac{\Delta C_{A_1}}{\Delta \phi_T}}{FR_{ad}} \tag{13}
\]

Similarly, the charge transfer resistance \((R_{ct})\) can be described as:

\[
R_{ct} = \left[ -F \frac{\partial r_2}{\partial \phi_2} \right]^{-1} \tag{14}
\]

Substituting it into equation 11 results to

\[
\frac{\Delta r_2}{\Delta \phi_T} = -\frac{\gamma}{FR_{ct}} + \frac{\partial r_2}{\partial \theta} \frac{\Delta \theta}{\Delta \phi_T} + \left[ \frac{\partial r_2}{\partial \beta} + \frac{1}{R_{ct}} \frac{N_{ad}}{C_1 + C_2} \right] \frac{\Delta \beta}{\Delta \phi_T} \tag{15}
\]

The rate of the reaction is related to the concentration gradient of the reacting species and can be expressed with the equations below:

\[
\frac{\partial \Delta C_{A_1}}{\partial t} = D_{A_1} \frac{\partial^2 \Delta C_{A_1}}{\partial x^2} \tag{16}
\]

\[
-D_{A_1} \frac{\partial \Delta C_{A_1}}{\partial t} = -\Delta r_1 \tag{17}
\]

\[
\frac{\partial \Delta \theta}{\partial t} = D_{\theta} \frac{\partial^2 \Delta \theta}{\partial x^2} \tag{18}
\]

\[
-D_{\theta} \frac{\partial \Delta \theta}{\partial t} = -\Delta r_2 \tag{19}
\]

where \(D_{A_1}\) is the diffusion coefficient of the cation in solution, \(D_{\theta}\) is the diffusion coefficient of the cation in the solid. Solving the Fick’s diffusion for \(\Delta C_{A_1}\) and \(\Delta \theta\) using semi-infinite diffusion and finite length diffusion with a reflective boundary respectively leads to [5]:

\[
\frac{\Delta r_1}{\Delta \phi_T} = \frac{\Delta C_{A_1}}{\Delta \phi_T} \sqrt{\frac{\omega}{D_{A_1}}} \tag{20}
\]
where $\tau$ is the diffusion time constant. Substituting equations 20 and 21 into equations 13 and 15 results to

\[
\sqrt{j\omega D_A} \Delta C_{A_e} \Delta \phi_T = \left[ 1 - \gamma \right] \frac{\partial r_1}{\partial \phi_1} \frac{D_A}{R_{ad}} \frac{1}{\Delta \phi_T} \tanh \left( \sqrt{j\omega \tau} \right)
\]

and

\[
\sqrt{j\omega D_\theta} \tanh \left( \sqrt{j\omega \tau} \right) \frac{\Delta \theta}{\Delta \phi_T} = -\gamma \frac{\partial r_2}{\partial \theta} \frac{\Delta \theta}{\Delta \phi_T} + \left[ \frac{1}{R_{ct}} \frac{N_{ad}}{C_1 + C_2} + \frac{\partial r_2}{\partial \beta} \right] \frac{\Delta \beta}{\Delta \phi_T}
\]

The Warburg impedance of the adsorbed cation ($Z_{Wad}$) and the capacitance of the adsorbed layer ($C_{ad}$) can be described as:

\[
Z_{Wad} = -F \frac{\partial r_1}{\partial \phi_1} \frac{1}{\Delta \phi_T} \frac{1}{\Delta \theta \Delta \phi_T} \tanh \left( \sqrt{j\omega \tau} \right)
\]

\[
1 \frac{C_{ad}}{C_{int}} = \left[ F \frac{\partial r_1}{\partial \phi_1} \right]^{-1} \frac{\partial r_1}{\partial \beta} \frac{1}{N_{ad}}
\]

Subsequently, equation 22 can be rewritten as:

\[
\sqrt{j\omega D_A} \Delta C_{A_e} \Delta \phi_T = \left[ 1 - \gamma \right] \frac{\frac{\partial r_1}{\partial \phi_1}}{\Delta \phi_T} \frac{D_A}{R_{ad}} \frac{1}{\Delta \phi_T} \tanh \left( \sqrt{j\omega \tau} \right)
\]

\[
\frac{\Delta \beta}{\Delta \phi_T} = \frac{-\frac{1}{N_{ad}} \frac{1}{\Delta \phi_T} \frac{1 - \gamma}{\Delta \theta \Delta \phi_T}}{\frac{1}{\Delta \phi_T} \frac{1}{\Delta \phi_T} \tanh \left( \sqrt{j\omega \tau} \right) \left[ R_{ad} + Z_{Wad} \right] \frac{\Delta \theta}{\Delta \phi_T}}
\]

Similarly, the Warburg impedance of the cation in the solid host structure ($Z_{Wct}$) and the capacitance of the double layer due to the insertion reaction ($C_{int}$) can be described as:

\[
Z_{Wct} = \left[ F \frac{\partial r_2}{\partial \phi_2} \right]^{-1} \frac{\partial r_2}{\partial \theta} \frac{1}{\Delta \theta \Delta \phi_T} \tanh \left( \sqrt{j\omega \tau} \right)
\]

\[
\frac{1}{C_{int}} = \left[ -F \frac{\partial r_2}{\partial \phi_2} \right]^{-1} \frac{\partial r_2}{\partial \beta} \frac{1}{N_{ad}}
\]
The impedance can thus be defined as:

\[
\frac{\gamma}{j\omega D_A} \frac{\Delta C_{Ae}}{\Delta \phi_T} = \frac{\gamma}{j\omega} \left[ R_ad + Z_{Wa_d} + \frac{1}{j\omega C_{ad}} + \frac{1}{C_1 + C_2} \right] - \frac{1-\gamma}{j\omega} \left( \frac{1}{C_{\text{int}}} + \frac{1}{C_1 + C_2} \right) \left( \frac{R_{ct} + Z_{Wct} + R_ad + Z_{Wa_d}}{C_1 + C_2} \right) \frac{1}{j\omega}
\]

\( (30) \)

At equilibrium, \( C_{ad} \) is equivalent to \( C_{int} \) and equation 32 can be rewritten as:

\[
\frac{1}{Z} \approx \frac{\gamma^2(R_{ad} + Z_{Wa_d}) + (1-\gamma)^2(R_{ct} + Z_{Wct}) + \left( \frac{\gamma}{C_{ad}} + \frac{(1-\gamma)}{C_{\text{int}}} \right) \frac{1}{j\omega} + \left( \frac{1}{C_1 + C_2} \right) \frac{1}{j\omega}}{(R_{ct} + Z_{Wct})(R_{ad} + Z_{Wa_d}) + \left( \frac{R_{ct} + Z_{Wct}}{C_{ad}} + \frac{R_{ad} + Z_{Wa_d}}{C_{\text{int}}} \right) \frac{1}{j\omega} + \left( \frac{R_{ct} + Z_{Wct} + R_{ad} + Z_{Wa_d}}{C_1 + C_2} \right) \frac{1}{j\omega}}
\]

\( (31) \)

The equivalent circuit obtained from equation 33 is shown in Fig. S3 with \( R_u, R_{ad}, Z_{Wa_d} \) corresponding to the uncompensated cell resistance, resistance due to adsorption and the Warburg impedance in the electrolyte described with semi-infinite diffusion. \( R_{ct}, Z_{Wct}, C_{ad}, C_1 \) and \( C_2 \) represents the charge transfer resistance, the Warburg impedance in the solid described using finite diffusion with reflective boundary, adsorption capacitance, the capacitance of the outer and inner Helmholtz plane respectively.
Figure S3: Equivalent circuit obtained from modelling the reversible insertion of cations in aqueous medium as two-step process.
S4 Fitting algorithm

The measured impedance were fitted using the modified non-linear least squares minimization reported previously by our research group [6, 7]:

\[
\chi^2_T = \sum_{k=1}^{N} \chi^2_k + \sum_{n=1}^{N_p} W_n^2 \left| \frac{\partial^2 P_n}{\partial t^2} \right|_{tk} \tag{34}
\]

where \( N \) is the number of impedance spectra to be fitted and \( W_n \) is the weighting factor, which allows for the variation of parameters to be controlled [6, 7]. The last term which is the second derivative of the parameters with respect to time allows for the minimization of the smoothing parameter resulting in the variation of the parameters to change smoothly. The classic \( \chi^2 \) can be described as [6, 7]:

\[
\chi^2_k = \frac{1}{N_{f,k}} \sum_{m=1}^{N_{f,k}} \left( \frac{(Z'_{k,m} - Z'_k(\omega_m, p_n))^2 + (Z''_{k,m} - Z''_k(\omega_m, p_n))^2}{(Z'_{k,m})^2 + (Z''_{k,m})^2} \right) \tag{35}
\]

with \( Z' \) and \( Z'' \) are the real and imaginary part of the impedance respectively while \( N_f \) is the number of frequencies.
S5  Statistical Analysis of the Results

To avoid over parametrization i.e. representation of a physiochemical process by more than one parameter which could arise by the representation of physiochemical processes that occurs too fast to be captured within the frequency range used in this work or processes which maybe negligible a $t$-test was done for every parameter in the equivalent circuit. The $t$-value is given by [7]:

$$ t = \frac{\hat{x}}{\sigma_x} $$  \hspace{1cm} (36)

where $\hat{x}$ is the estimated parameters from the fit of the measured impedance and the model and $\sigma_x$ is the absolute standard error of the parameters obtained from the formal covariance matrix of $\chi^2$ minimization [7]. The $t$ values for each parameter is then compared to the cumulative $t$-distribution for n-1 degrees of freedom with a confidence level of 95 \% [7].

The result obtained from fitting the measured impedance with the equivalent circuit shown in Fig. S3 had a $\chi^2$ in the range of $1.7 \cdot 10^{-5}$ to $6.5 \cdot 10^{-5}$ for both cations. However the $t$ values for both cations of the parameters (Fig. S4a) indicates that $\gamma$, $R_{ad}$, $R_{ct}$, $\sigma_{ad}$, $\sigma_{ct}$ $\tau$ and $C_{ad}$ are below the confidence level for both cations with $C_{ad}$ having the lowest $t$-values as seen in Fig. S4a and Fig. S4b. This indicates that $C_{ad}$ tends to a very small value and can be considered negligible suggesting that the capacitance of adsorption is much higher than the inner Helmholtz plane capacitance, thus $C_{ad}$ can be treated as a short circuit.

The equivalent circuit obtained under this assumption is shown in Fig. S5a and the result obtained using this equivalent circuit indicates that the goodness of the fit was not compromised as the $\chi^2$ was observed to be fairly constant. $R_{ct}$ was however observed to have the lowest $t$ value from the fit obtained using this equivalent circuit (Fig. S5a) as seen in Fig. S4c and Fig. S4d.
Figure S4: t-test for the parameters obtained from fitting the measured impedance using (a) and (b) equivalent circuit obtained from the model (Fig. S3), (c) and (d) equivalent circuit shown in Fig. S5a with \( C_{\text{ad}} \) treated as a short circuit (e) and (f) equivalent circuit shown in Fig. S5b, (g) and (h) equivalent circuit shown in Fig. S5b with mass transport in the solid described using semi-infinite diffusion.
$R_{ct}$ was then removed under the assumption that the charge transfer process occurs so fast resulting $R_{ct}$ becoming negligibly small. The major contribution to the $R_{ct}$ in the two-stage model proposed in this work is the further desolvation of the partially desolvated cations and transfer of this desolvated cation across the electrode/electrolyte interface. The hydrated radii of of Na$^+$ and K$^+$ is 1.83 Å and 1.25 Å respectively while the channels connecting the intercalation sites has been reported to be 1.6 Å [8, 9]. A partial desolvation of the cations can thus result in partially desolvated cation that can be be inserted/extracted through the channels connecting A sites in the NiHCF and could result in $R_{ct}$ becoming negligibly small enough not to be observed in the measured impedance. The result obtained from fitting the measured impedance with the equivalent circuit obtained using the assumption (Fig.S5b) resulted in a good fit with $\chi^2$ values in the same order of magnitude ($10^{-5}$) and the t-values for the parameters in the equivalent circuit were above the confidence level except $\tau$ as shown in Fig. S4e and Fig. S4f.

![Figure S5: Equivalent circuit obtained from the model under the assumption that (a) $C_{ad}$ treated as a short circuit (b) Charge transfer process becomes negligible.](image)

The mass transport in the solid in the model has been described using the finite length diffusion with reflective boundary which is given as [5, 10]:

$$Z_{Wct} = \sigma_{ct} \sqrt{\tau} \cdot \left[ \frac{1}{\sqrt{j\omega}} \coth(\sqrt{j\omega}) \right]$$

(37)

with $\tilde{\omega} = \omega \tau$. If $\tilde{\omega} \gg 1$, equation 37 is reduced to the equation below and can be described as semi-infinite diffusion [10].

$$Z_{Wct} = \frac{\sigma_{ct}}{\sqrt{j\omega}}$$

(38)

For $\tilde{\omega} \ll 1$, equation 37 results to [10]:

$$Z_{Wct} = \frac{\sigma_{ct} \sqrt{\tau}}{3} + j \frac{\sigma_{ct}}{\omega \sqrt{\tau}}$$

(39)

The result obtained from the fit indicates that $\tilde{\omega} \gg 1$, subsequently the mass transport in the solid was described using equation. 38 which resulted in a good fit with $\chi^2$ in the range of $1.3 \cdot 10^{-5}$ to $6.0 \cdot 10^{-5}$ for both cations, and all parameters obtained from the circuit was above the confidence level as
seen in Fig. S4g for Na\textsuperscript{+}. The parameters obtained in K\textsuperscript{+} were observed to be below the confidence level in the potential regions of ca. 0.61 V to 0.67 V where the shouldered peak in the voltammogram in K\textsuperscript{+} occurs. This suggests that the obtained parameters in this region maybe insignificant or the model does not describe the intercalation at this region. The origin of this shouldered peak is still not clear and outside the scope of this paper. It has however been attributed to the intercalation of K\textsuperscript{+} in the two stable forms of NIHCF and could also be attributed to interactions between redox sites and intercalated sites [11, 12]. The equivalent circuit (Fig.S5b) with the mass transport in the solid described using semi-infinite diffusion was subsequently used for fitting the measured impedance of both cations.
Figure S6: Nyquist plot of impedance spectra obtained at different potential within the frequency range of 10 Hz to 125 kHz in 0.5 M Na$_2$SO$_4$ solution during (a) and (b) cathodic scan (c) and (d) anodic scan.
Figure S7: Nyquist plot of impedance spectra obtained at different potential within the frequency range of 10 Hz to 125 kHz in 0.5 M K$_2$SO$_4$ solution during (a) and (b) cathodic scan (c) and (d) anodic scan.
S7 Resistances

The rates of the desolvation step \( r_1 \) and insertion step \( r_2 \) can be expressed as:

\[
\begin{align*}
 r_1 &= k_f^1 \frac{C_A}{C_0} [1 - \beta] - k_b^1 \beta \\
 r_2 &= k_f^2 [1 - \theta] \beta - k_b^2 [1 - \beta] \theta \\
 k_f^1 &= k_{0,f}^1 \exp\left(-\frac{\alpha_1 F \phi_1}{RT}\right) \\
 k_b^1 &= k_{0,b}^1 \exp\left(\frac{(1 - \alpha_1) F \phi_1}{RT}\right) \\
 k_f^2 &= k_{0,f}^2 \exp\left(-\frac{\alpha_2 F \phi_2}{RT}\right) \\
 k_b^2 &= k_{0,b}^2 \exp\left(\frac{(1 - \alpha_2) F \phi_2}{RT}\right)
\end{align*}
\]  

\[
\begin{align*}
 r_1 &= \frac{C_A}{C_0} [1 - \beta] k_{0,f}^1 \exp\left(-\frac{\alpha_1 F \phi_1}{RT}\right) - \beta k_{0,b}^1 \exp\left(\frac{(1 - \alpha_1) F \phi_1}{RT}\right) \\
 r_2 &= [1 - \theta] \beta k_{0,f}^2 \exp\left(-\frac{\alpha_2 F \phi_2}{RT}\right) - [1 - \beta] \theta k_{0,b}^2 \exp\left(\frac{(1 - \alpha_2) F \phi_2}{RT}\right)
\end{align*}
\]

where \( k_f \) and \( k_b \) represents the rate constants for the forward and backward reactions with superscript 1 and 2 specifying the desolvation and insertion step respectively. \( C_A \) is the concentration of the cations in the electrolyte, \( C_0 \) the reference concentration which in our case is 1 M, \( \beta \) is the molar fraction of the adsorbed species, \( \alpha \) the transfer coefficient with subscript 1 and 2 specifying the desolvation and insertion step respectively. \( R \) is gas constant, \( T \) absolute temperature and \( \theta \) represents the molar fraction of the inserted cation in the host structure. The current flowing due to the desolvation and insertion step can be described as:

\[
\begin{align*}
 I_1 &= -n F k_1^0 \left[ \frac{C_A}{C_0} [1 - \beta] \exp\left(-\frac{\alpha_1 F \phi_1}{RT}\right) - \beta \exp\left(\frac{(1 - \alpha_1) F \phi_1}{RT}\right) \right] \\
 I_2 &= -n F k_2^0 \left[ [1 - \theta] \beta \exp\left(-\frac{\alpha_2 F \phi_2}{RT}\right) - [1 - \beta] \theta \exp\left(\frac{(1 - \alpha_2) F \phi_2}{RT}\right) \right]
\end{align*}
\]
At equilibrium, \( r_1 = 0 \), \( r_2 = 0 \) and the net current of the individual step is zero. As a result,

\[
\exp \left( \frac{F \phi_1}{RT} \right) = \frac{C_{A^+}}{C_0} \frac{1 - \beta}{1 - \beta} \quad (50)
\]

\[
\exp \left( \frac{F \phi_2}{RT} \right) = \frac{1 - \theta}{\theta} \quad (51)
\]

\[
\exp \left( \frac{F \phi_T}{RT} \right) = \frac{C_{A^+}}{C_0} \frac{1 - \theta}{1 - \theta} \quad (52)
\]

The individual exchange current \((I_{0,1} \text{ and } I_{0,2})\) can be described as:

\[
I_{0,1} = nFk_1^0 \left[ \frac{C_{A^+}}{C_0} \right]^{1-\alpha_1} [1 - \beta]^{1-\alpha_1} \beta^{\alpha_1} \quad (53)
\]

\[
I_{0,2} = nFk_2^0 [1 - \theta]^{1-\alpha_2} \beta^{1-\alpha_2} [1 - \beta]^{\alpha_2} \theta^{\alpha_2} \quad (54)
\]

\[
I_1 = I_{0,1} \left[ \exp \left( \frac{-\alpha_1 F \phi_1}{RT} \right) - \exp \left( \frac{(1 - \alpha_1) F \phi_1}{RT} \right) \right] \quad (55)
\]

\[
I_2 = I_{0,2} \left[ \exp \left( \frac{-\alpha_2 F \phi_2}{RT} \right) - \exp \left( \frac{(1 - \alpha_2) F \phi_2}{RT} \right) \right] \quad (56)
\]

During the voltage sweep in which the dynamic impedance is acquired, one part of equation 55 and 56 becomes negligible. In the cathodic scan for example, \( \exp(-\alpha_1(F/RT)\phi_1) \gg \exp(1 - \alpha_1(F/RT)\phi_1) \) and \( \exp(-\alpha_2(F/RT)\phi_2) \gg \exp(1 - \alpha_2(F/RT)\phi_2) \), thus equation 55 and 54 leads to

\[
I_1 = I_{0,1} \left[ \exp \left( \frac{-\alpha_1 F \phi_1}{RT} \right) \right] \quad (57)
\]

\[
I_2 = I_{0,2} \left[ \exp \left( \frac{-\alpha_2 F \phi_2}{RT} \right) \right] \quad (58)
\]

At small overpotential, \( e^x \approx 1 + x \) and equation 57 and 58 results to

\[
I_1 = -I_{0,1} \frac{F}{RT} \phi_1 \quad (59)
\]

\[
I_2 = -I_{0,2} \frac{F}{RT} \phi_2 \quad (60)
\]

The \( R_{ad} \) and \( R_{ct} \) can be defined as \([13]\):

\[
R_{ad} = \left[ -\frac{\partial I_1}{\partial \phi_1} \right]^{-1} \quad (61)
\]
Equation 65 predicts the dependence of $R_{ad}$ on $\beta$, however $\beta$ was not experimentally quantified in this work. The relationship between $\beta$ and $\phi_T$ is obtained by substituting equation 6 into equation 50 which results to:

$$\exp\left(\frac{F(1-\gamma)\phi_T}{RT} + \frac{F^2N_{ad}}{RTC_1 + C_2}\beta\right) = \frac{CA_1}{C_0} \frac{1-\beta}{\beta}$$

(67)

Solving equation 67 numerically using $\phi_T$ obtained from $\theta$ indicates that $\beta$ assumes a fractional coverage similar to that of $\theta$ as shown in Fig. S8.

Figure S8: Plot of the total potential drop in the interface ($\phi_T$) versus $\beta$ and $\theta$.

$R_{ad}$ estimated using equation 65 and the fractional coverage of $\beta$ is observed to decrease continuously when $\beta \leq 0.5$ to a minimum which occurs when $\beta = 0.5$.
which occurs around the peak potential in the voltammogram and increases when $\beta \geq 0.5$. This is similar to the dependence observed for $R_{ad}$ obtained from fitting the measured impedances indicating a good agreement with the model and experimental results.

Figure S9: Plot of estimated $R_{ad}$ vs the total potential drop in the interface ($\phi_T$) with $k_1^0 = 5 \cdot 10^{-6}$ cm/s and $\alpha_2=0.5$. 
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