Supporting Information

Computational and Experimental Determination of Electrochemical Standard Rate Constant from Cyclic Voltammetry: Insights into α+β≠1

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Table of Contents

I Charge Transfer Coefficients and Diffusion Coefficient Determination of Ferrocyanide Ions Oxidation

The Tafel plots of the obtained cyclic voltammograms for ferrocyanide ion oxidation are represented in Figure S1a. As shown, the slopes enable the determination of the anodic (β) and the cathodic (α) charge transfer coefficients, which are found to be 0.259±0.003 and 0.289±0.005, respectively.

The convoluted current of the cyclic voltammograms was calculated and represented in Figure S1b. Due to the diffusion-limited transfer, the semi-integral (m) approaches a maximum value (m*). The relationship between m* and the diffusion coefficient of the reduced species $D_{Fe(CN)_6^{4-}}$ is given by the following expression [1–4]:

$$m_{max} = nFAD_R^{1/2}C_o^* \quad \text{(S1)}$$

The obtained value of $D_{Fe(CN)_6^{4-}}$ is equal to 6.45 × 10^{-10} m^2 s^{-1}. In aqueous media, the value of the diffusion coefficient $D_{Fe(CN)_6^{4-}}$ typically ranges between 6.10 × 10^{-10} and 8.00 × 10^{-10} m^2 s^{-1} [5].

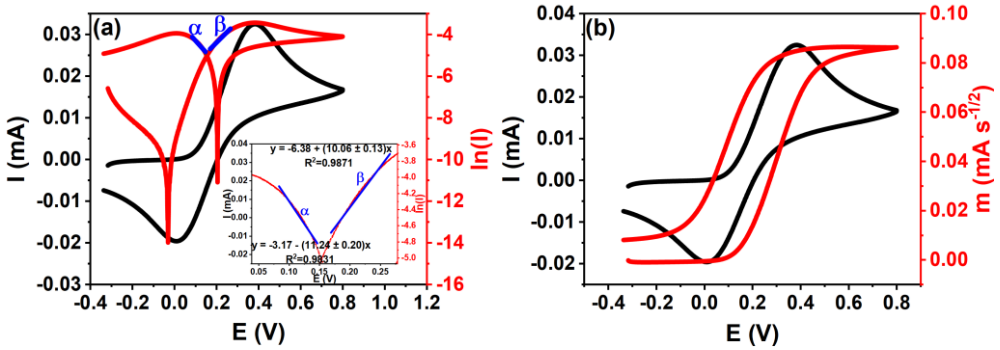

Figure S1. Ferrocyanide oxidation curves: (a) Experimental CV (Black) at 50 mV s^{-1} and its Tafel plots (Red); inset: Tafel plots. (b) Experimental CV (Black) and its semi-integral plot (Red).

II Theoretical Validation of Interpolation Equations

In what follows, Table S1 presents the theoretical calculations for Equations (25) and (34), while Table S2 presents the theoretical validation of Swaddle's equation applied to soluble-soluble systems. The conclusions deduced from these tables are presented in the article.

Table S1. Theoretical validation of Equations 25 and 34. Λ: imposed value; Λ': calculated value

Λ	α	β	α+β	Φa	Φc	ΔΦ	Λ'	
							Eq (25)	**Eq (34)**
10^{-6}	**0.1**	**0.1**	**0.2**	133.628	-134.45	268.078	/	0.70^{E}-6
	0.2	**0.2**	**0.4**	68.578	-68.96	137.538	/	0.66^{E}-6
	0.3	**0.5**	**0.8**	28.398	-46.65	75.048	0.42^{E}-8	0.40^{E}-6
	0.35	**0.65**	**1**	22.058	-40.21	62.268	0.30^{E}-6	0.30^{E}-6
	0.60	**0.60**	**1.2**	23.798	-23.9	47.698	1.91^{E}-5	0.89^{E}-7
	0.75	**0.75**	**1.5**	19.188	-19.27	38.458	1.09^{E}-3	6.84^{E}-6
10^{-5}	**0.1**	**0.1**	**0.2**	110.448	-111.42	221.868	/	1.17^{E}-5
	0.35	**0.65**	**1**	18.498	-33.63	52.128	1.04^{E}-5	1.04^{E}-5
	0.75	**0.75**	**1.5**	16.108	-16.2	32.308	2.71^{E}-3	2.76^{E}-5
10^{-4}	**0.1**	**0.1**	**0.2**	87.198	-88.4	175.598	0.69^{E}-14	1.38^{E}-4
	0.35	**0.65**	**1**	14.938	-27.05	41.988	1.21^{E}-4	1.21^{E}-4
	0.75	**0.75**	**1.5**	13.028	-13.13	26.158	6.96^{E}-3	8.70^{E}-8
10^{-3}	**0.1**	**0.1**	**0.2**	63.788	-65.37	129.158	5.65^{E}-6	1.35^{E}-3
	0.2	**0.2**	**0.4**	33.718	-34.42	68.138	2.45^{E}-5	1.18^{E}-3
	0.3	**0.5**	**0.8**	14.498	-23.62	38.118	0.50^{E}-3	1.06^{E}-3
	0.35	**0.65**	**1**	11.368	-20.47	31.838	1.05^{E}-3	1.05^{E}-3
	0.60	**0.60**	**1.2**	12.218	-12.39	24.608	3.51^{E}-3	1.12^{E}-3
	0.75	**0.75**	**1.5**	9.928	-10.06	19.988	1.94^{E}-2	1.34^{E}-3
10^{-2}	**0.35**	**0.65**	**1**	7.788	-13.89	21.678	0.91^{E}-2	0.91^{E}-2
2×10^{-2}	**0.35**	**0.65**	**1**	6.708	-11.91	18.618	1.82^{E}-2	1.82^{E}-2
6×10^{-2}	**0.35**	**0.65**	**1**	5.008	-8.76	13.768	5.78^{E}-2	5.78^{E}-2
10^{-1}	**0.1**	**0.1**	**0.2**	16.998	-19.12	36.118	0.26^{E}-1	1.30^{E}-1
	0.2	**0.2**	**0.4**	10.108	-11.34	21.448	0.35^{E}-1	1.21^{E}-1
	0.3	**0.5**	**0.8**	5.24	-8.23	13.47	0.78^{E}-1	1.04^{E}-1
	0.35	**0.65**	**1**	4.248	-7.28	11.528	1.03^{E}-1	1.03^{E}-1
	0.60	**0.60**	**1.2**	4.408	-4.77	9.178	1.52^{E}-1	0.88^{E}-1
	0.75	**0.75**	**1.5**	3.678	-4.04	7.718	2.99^{E}-1	0.46^{E}-1
2×10^{-1}	**0.1**	**0.1**	**0.2**	12.458	-11.6	24.058	0.81^{E}-1	2.66^{E}-1
	0.2	**0.2**	**0.4**	7.388	-7.69	15.078	1.04^{E}-1	2.53^{E}-1
	0.3	**0.5**	**0.8**	4.028	-5.83	9.858	1.95^{E}-1	2.38^{E}-1
	0.35	**0.65**	**1**	3.298	-5.26	8.558	2.42^{E}-1	2.42^{E}-1
	0.60	**0.60**	**1.2**	3.278	-3.72	6.998	3.16^{E}-1	2.14^{E}-1
	0.75	**0.75**	**1.5**	2.718	-3.26	5.978	5.35^{E}-1	1.17^{E}-1
10^{0}	**0.1**	**0.1**	**0.2**	7.198	-0.78	7.978	0.74^{E}0	0.80^{E}0
	0.2	**0.2**	**0.4**	4.098	-1.49	5.588	0.97^{E}0	0.89^{E}0
	0.3	**0.5**	**0.8**	2.258	-1.95	4.208	1.32^{E}0	1.20^{E}0
	0.35	**0.65**	**1**	1.808	-2.07	3.878	1.43^{E}0	1.43^{E}0
	0.60	**0.60**	**1.2**	1.538	-2.02	3.558	1.44^{E}0	2.64^{E}0
	0.75	**0.75**	**1.5**	1.118	-2.03	3.148	1.94^{E}0	0.58^{E}0
10^{1}	**0.1**	**0.1**	**0.2**	5.378	0.11	5.268	1.47	0.98
	0.2	**0.2**	**0.4**	2.998	-0.44	3.438	2.31	1.23
	0.3	**0.5**	**0.8**	1.578	-1.02	2.598	3.19	2.25
	0.35	**0.65**	**1**	1.218	-1.21	2.428	3.39	3.39
	0.60	**0.60**	**1.2**	0.948	-1.36	2.308	3.27	8.01
	0.75	**0.75**	**1.5**	0.628	-1.55	2.178	3.76	0.58

The below calculation was made using: n=1, T=298.15 K.

Table S2. Theoretical validation of Swaddle equation. Λ: imposed value; Λ': calculated value

Λ	α	β	α+β	ΔE_p (mV)	Λ'
10^{-6}	**0.35**	**0.65**	**1**	1599.73	14231^{E}-6
10^{-5}	**0.35**	**0.65**	**1**	1339.23	1764^{E}-5
10^{-4}	**0.35**	**0.65**	**1**	1078.72	230^{E}-4
10^{-3}	**0.35**	**0.65**	**1**	817.95	32^{E}-3
10^{-2}	**0.35**	**0.65**	**1**	556.93	5.28^{E}-2
2×10^{-2}	**0.35**	**0.65**	**1**	478.32	6.44^{E}-2
6×10^{-2}	**0.35**	**0.65**	**1**	353.71	9.69^{E}-2
10^{-1}	**0.1**	**0.1**	**0.2**	927.91	0.28^{E}-1
	0.35	**0.65**	**1**	296.17	1.25^{E}-1
2×10^{-1}	**0.1**	**0.1**	**0.2**	618.08	0.46^{E}-1
	0.35	**0.65**	**1**	219.86	1.96^{E}-1
10^{0}	**0.1**	**0.1**	**0.2**	204.96	0.22^{E}-0
	0.35	**0.65**	**1**	99.63	0.97^{E}-0
10^{1}	**0.1**	**0.1**	**0.2**	135.34	0.47
	0.35	**0.65**	**1**	62.38	17.29

III MATLAB Code for Log(Λ) Interpolation Equations Calculation

The purpose of this code is to calculate the Λ. In the implementation, Λ is denoted by the uppercase letter "L". For simplicity, the formulations given in equations (25) and (34) were consolidated into a single equation, which was then used for the numerical evaluation of Λ.

The Matlab code corresponding to Equations (25) and (34), is as follows:

```
dep_value = ;  % replace with your desired ΔEp dimensionless value
alpha_value = ;  % replace with your desired forward transfer coefficient value
beta_value = ;   % replace with your desired backward transfer coefficient value

[logL_result,L_result]= customSolveEquation(dep_value, alpha_value, beta_value);

function [logL,L]= customSolveEquation(dep, alpha, beta)

    % Define the equation
       equation = @(logL) (1 ./ (((7.50978*10^-4) + 0.10944 *exp (1.72596*logL)) + ...
                      ((0.05374+ 0.37723 * exp(0.52667 *logL)) * alpha) + ...
                      ((-0.04452-0.32511 * exp(0.43694 *logL)) * alpha^2))) - dep +...
                      ((1.222-0.189*beta^-1)+(-2.296*beta^-1)*logL - ...
                      ((1.222-0.189*((1-alpha)^-1)+(-2.296*((1-alpha)^-1)*logL)))) ;

    % Set options for lsqnonlin
    options = optimoptions('lsqnonlin','Display', 'off', 'FunctionTolerance', 1e-12,...
              'OptimalityTolerance', 1e-12, 'MaxIterations', 1000);

    % Set lower and upper bounds
    lb = -6;
    ub =6;

    % Generate a random initial guess within the specified range
    initial_guess = (ub - lb) * rand() + lb;

    % Use lsqnonlin for constrained optimization
    logL_solution = lsqnonlin(equation, initial_guess, lb, ub, options);
```

```
    if ~isempty(logL_solution)
        logL = logL_solution;
        L = (10^logL);
    else
        error('No solution found.');
    end
end
```

Nomenclature

A	: Surface area of electrode / m^2
C_{Ox}	: Concentration of the oxidized species / mmol L^{-1}
C_{Red}	: Concentration of the reduced species / mmol L^{-1}
$C_{Ox}(0,t)$	: Concentration of the oxidized species at the electrode surface / mmol L^{-1}
$C_{Red}(0,t)$	: Concentration of the reduced species at the electrode surface / mmol L^{-1}
C_{Ox}^{*}	: Concentration of the oxidized species at t = 0 / mmol L^{-1}
C_{Red}^{*}	: Concentration of the reduced species at t = 0 / mmol L^{-1}
D	: Diffusion coefficient / m^2 s^{-1}
E	: Electrode potential / V
E^0	: Standard potential / V
E_a	: Anodic peak potential / V
E_c	: Cathodic peak potential / V
E_λ	: Switching potential / V
ΔE_p	: Peak-to-peak potential separation / V
F	: Faraday's constant / C mol^{-1}
$J_{Ox}(0,t)$	: Flux of oxidized species / mol m^{-2} s^{-1}
I	: Electrode current / A
I_{pa}	: Anodic peak current / A
I_{pc}	: Cathodic peak current / A
k^0	: Standard heterogeneous rate constant / m s^{-1}
n	: Number of electrons / unitless
R	: Universal gas constant / j mol^{-1} K^{-1}
T	: Absolute temperature / K
t	: Time / s
v	: Scan rate / v s^{-1}
Λ	: Dimensionless rate constant / unitless
α	: Cathodic charge transfer coefficient / unitless
β	: Anodic charge transfer coefficient / unitless
χ	: Dimensionless current / unitless
Ψ	: Dimensionless kinetic parameter / unitless
Φ	: Dimensionless potential / unitless
$\Delta\Phi$	: Dimensionless peak-to-peak potential separation / unitless
η_p	: Dimensionless peak potential / unitless
$\Delta\eta_p$	: Dimensionless anodic peak potentials difference / unitless
σ	: Dimensionless scan rate / unitless

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