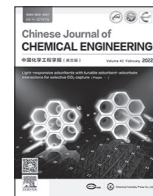




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Full Length Article

Mechanistic insights into homogeneous electrocatalytic reaction for energy storage using finite element simulation

Peng Song*, Yan Li, Shuang Yin

Beijing Key Laboratory for Green Catalysis and Separation, Department of Environmental and Chemical Engineering, Beijing University of Technology, Beijing 100124, China

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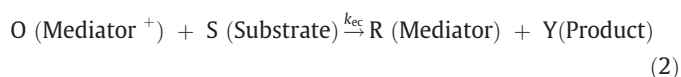
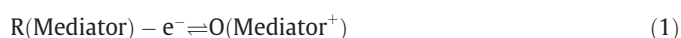
ABSTRACT

The application of homogeneous electrocatalytic reactions in energy storage and conversion has driven surging interests of researchers in exploring the reaction mechanisms of molecular catalysts. In this paper, homogeneous electrocatalytic reaction between hydroxymethylferrocene (HMF) and L-cysteine is intensively investigated by cyclic voltammetry and square wave voltammetry for which, the second-order rate constant (k_{ec}) of the chemical reaction between HMF^+ and L-cysteine is determined via a 1D homogeneous electrocatalytic reaction model based on finite element simulation. The corresponding k_{ec} ($1.1 \text{ (mol}\cdot\text{m}^{-3})^{-1}\cdot\text{s}^{-1}$) is further verified by linear sweep voltammograms under the same model. Square wave voltammetry parameters including potential frequency (f), increment (E_{step}) and amplitude (E_{sw}) have been comprehensively investigated in terms of the voltammetric waveform transition of homogeneous electrocatalytic reaction. Specifically, the effect of potential frequency and increment is in accordance with the potential scan rate in cyclic voltammetry and the increase of pulsed potential amplitude results in a conspicuous split oxidative peaks phenomenon. Moreover, the proposed methodology of k_{ec} prediction is examined by hydroxyethylferrocene (HEF) and L-cysteine. The present work facilitates the understanding of homogeneous electrocatalytic reaction for energy storage purpose, especially in terms of electrochemical kinetics extraction and flow battery design.

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1. Introduction

Research in homogeneous electrocatalytic reaction has grown significantly in the past few decades, especially in the field of energy conversion, energy storage and carbon dioxide reduction [1–3]. In detail, high efficient electrocatalysis facilitates the rapid conversion of electrical energy into chemical energy e.g. hydrogen production [4–6]. Also, such reaction mechanism boosts the energy and power performance of supercapacitors [7], Li-air batteries [8,9] and fuel cells [10–12]. Specifically, a 3-fold improvement has been achieved compared with the electrolyte alone in a redox-mediated redox flow battery [13,14]. Nevertheless, the reaction mechanism associated with the reaction rate determining step as well as the rate constant of the chemical reaction still remains largely underexplored. Thus, the kinetics extraction of homogeneous electrocatalytic reaction is essential for a comprehensive understanding of the redox mediation process [15,16]. In homogeneous electrocatalytic reaction, the mediator undertakes the role of catalyst and the substrate is continuously oxidized as illustrated below:



where k_{ec} ($(\text{mol}\cdot\text{m}^{-3})^{-1}\cdot\text{s}^{-1}$) is the second-order rate constant of Eq. (2). In this reaction mechanism, the redox mediator shuttles the electrons between the substrate and the electrode, leading to a continuous production of the product (Y) in Eq. (2) as demonstrated in Fig. 1a. The introduction of the corresponding redox mediation boosts the performance of the redox flow battery, which makes the obtained battery a powerful candidate in smart grid system as illustrated in Fig. 1a and b. Consequently, the evaluation of the second-order rate constant is vital in the understanding of the aforementioned reaction mechanism.

A number of electrochemical techniques have been employed in the evaluation of homogeneous electrocatalytic reaction. Among these techniques, cyclic voltammetry (CV) [17–19] and square wave voltammetry (SWV) [20–22] have been widely employed in fields of electrochemical kinetics extraction. Particularly, SWV covers the advantages of multiple pulse voltammetry and has the ability to eliminate the influence of non-Faraday current during the

* Corresponding author.

E-mail address: songp@bjut.edu.cn (P. Song).

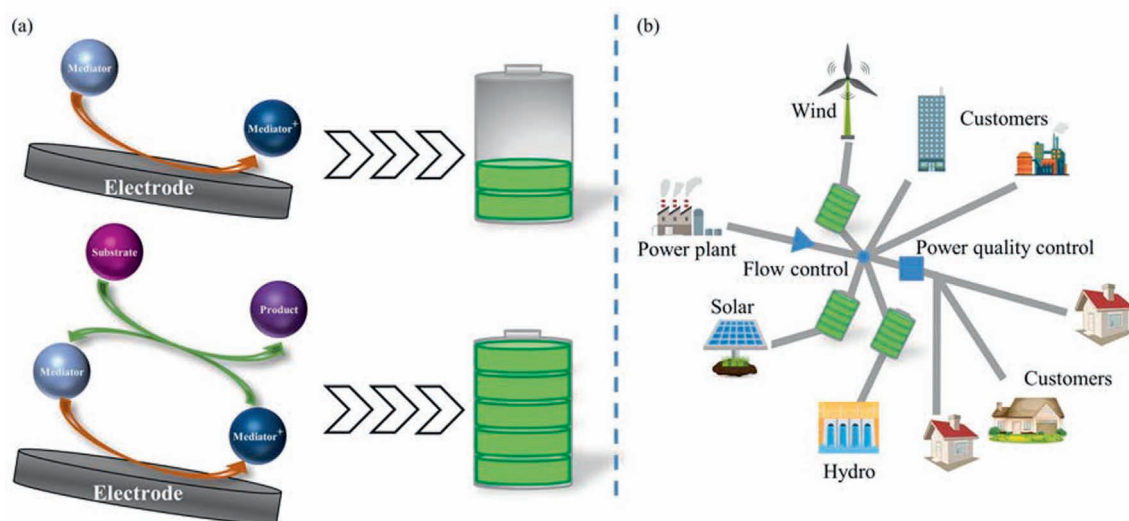


Fig. 1. (a) The schematic of redox reaction vs. homogeneous electrocatalytic reaction; (b) The application of the energy storage device based on homogeneous electrocatalytic reaction in smart grid system.

measurement [23]. Consequently, this technique is extensively employed in intermediate detection of oxidative and reductive reactions simultaneously, which is mostly owing to the continuous forward and reverse pulse potential scanning feature [24]. Based on the advantages mentioned above, researchers have applied SWV in the exploration of electrode reaction mechanisms coupled with chemical reactions such as EC [25–29], CE [27,30,31], ECE [20,29], EC' (homogeneous electrocatalytic reaction) [32–34], CEC' [21] mechanisms. Although extensive research has been implemented in terms of theoretical simulation on EC' mechanism via SWV, most cases treat the k of Eq. (2) as the pseudo-first-order rate constant due to the large excess of substrate compared with the mediator concentration [33–35]. Although this condition facilitates the kinetics extraction under CV and SWV, the substrate is not always in large excess in energy conversion or storage applications. Also, previous research suggests that some of the indicator is not applicable in total catalysis regime of the homogeneous electrocatalytic reaction [36,37], especially when a split wave phenomenon is demonstrated in CV or SWV. Moreover, when second-order rate constant is employed in the study of homogeneous electrocatalytic reaction, few have explored the reaction mechanism by SWV in both experimental and theoretical methods [32,38,39].

In this paper, a homogeneous electrocatalytic reaction under a second-order chemical reaction step is electrochemically investigated by CV and SWV from both theoretical and experimental aspects. The second-order rate constant is calculated by the assistance of the 1D homogeneous electrocatalytic reaction model based on finite element simulation. Moreover, the obtained k_{ec} is verified by experimental and simulated linear sweep voltammograms under various scan rates. In particular, SWV experimental parameters including potential frequency (f), increment (E_{step}) and amplitude (E_{sw}) have been intensively investigated in terms of the effect on homogeneous electrocatalytic reaction. The reported methodology for the determination of k_{ec} is further confirmed by another mediator and the corresponding value is in good agreement with previous research. The proposed numerical methods facilitate the insight into the mechanistic information of homogeneous electrocatalytic reaction as well as the special characteristics of electrochemical applications for energy storage purpose.

2. Experimental and Methodology

2.1. Materials and preparation

In this paper, cyclic voltammetry and square wave voltammetry was used to study the homogeneous electrocatalytic reaction of hydroxymethylferrocene (HMF) and L-cysteine. Hydroxymethylferrocene (HMF, >95.0%), 1-hydroxyethylferrocene (HEF, >95.0%) and L-cysteine (>98.0%), were all produced by Tokyo Chemical Industry. 0.05 mol·L⁻¹ sodium tetraborate (Na₂B₄O₇) and 0.5 mol·L⁻¹ potassium chloride (KCl), which were purchased from Tianjin Guangfu Technology Development Co, were used as pH buffer (pH = 9.0) and supporting electrolyte, respectively. Deionized water (resistivity ≥ 18.25 M Ω ·cm) was supplied from a HUIYIPU UHQ grade water system (Beijing, China). The introduction of electrolyte could effectively avoid the influence of electro-migration of electroactive species and improve the conductivity of electrolyte solution. Before each set of tests, ultrasonic treatment was employed to dissolve ferrocene derivatives in the borate buffer solution.

2.2. Electrochemical characterization

Electrochemical workstation (CHI760e Shanghai Chenhua Instrument Co., China) was employed for all electrochemical tests on a standard three-electrode system. Working electrode is a glassy carbon working electrode ($d = 3$ mm) purchased from Tianjin Aidahengsheng Technology CO, LTD. The platinum mesh electrode and Ag/AgCl reference electrode, which were also obtained from Tianjin Aidahengsheng Technology CO, LTD., served as counter and reference electrode, respectively. Before each test, the working electrode was polished with alumina powder of the median particle size from 1 to 0.05 μ m on a polishing cloth.

2.3. Numerical simulation

Numerical simulation was implemented via COMSOL multiphysics software (version 5.4, COMSOL, Inc., MA, USA). A 1D homogeneous electrocatalytic reaction model based on both cyclic voltammetry and square wave voltammetry was developed for

the theoretical investigation of homogeneous electrocatalytic reaction. All parameters used in the numerical simulation are summarized in Table S1 (Supplementary Material). The heterogeneous electron transfer rate constant is extracted from the experimental data via CHI Version 17.01 software and charge transfer coefficient (α) is fixed at 0.5. The geometry of the established model is in a one-dimensional coordinate system. Both mediator and substrate only diffuse within the diffusion layer length ($6\sqrt{Dt}$). As illustrated in Fig. S1 (Supplementary Material), the largest mesh size is confined within the length of $(6\sqrt{Dt})/8000$ and the corresponding mesh increase ratio is 1.1, which guarantees the convergence of all mathematical calculations. Within the established diffusion layer, both electrochemical reaction and chemical reaction happens simultaneously. In homogeneous electrocatalytic reaction, Eq. (1) is governed by the potential applied on the working electrode. The corresponding current collected from Eq. (1) is defined via Butler-Volmer equation:

$$i = nFA \left(k_a c_R \exp\left(\frac{(1-\alpha)\eta F}{RT}\right) - k_c c_O \exp\left(\frac{-\alpha\eta F}{RT}\right) \right) \quad (3)$$

where n is the electron transfer number, F is Faradic constant, A is the active electrode area, k_a and k_c are anodic and cathodic reaction rate constant, respectively, c_i is the species (I: R and O) concentration in Eq. (1), α is transfer coefficient, η is the electrode polarisation, R is the universal gas constant and T is the temperature. When cyclic voltammetry and linear sweep voltammetry are employed in the simulation, the electrode polarisation is defined as below:

$$\eta = E_{app} - E_{eq} \quad (4)$$

$$E_{app} = E_{start} + \nu t, \quad 0 < t < t_{scan} \quad (5)$$

$$E_{app} = E_{vertex} - \nu(t - t_{scan}), \quad t_{scan} < t < 2t_{scan} \quad (6)$$

$$t_{scan} = (E_{vertex} - E_{start})/\nu \quad (7)$$

where E_{app} is the potential applied, E_{eq} is the equilibrium potential of the electrochemical reaction, E_{start} is the initial potential of the applied potential scan, ν is the scan rate, t_{scan} is the time when the reversed potential is applied, E_{vertex} is the reversed potential. Considering the square wave potential waveform in the simulation, the applied potential consists of a superimposed staircase on a linearly swept potential as shown in Fig. 2:

$$E_{app} = E_{start} + E_{staircase} - f_{wave} \times E_{SW} \quad (8)$$

$$E_{staircase} = \frac{E_{step} \left(t - \text{mod} \left(t, \frac{1}{f} \right) \right)}{\frac{1}{f}} \quad (9)$$

$$f_{wave} = flmsign(\sin(2\pi ft), 0.0001) \quad (10)$$

where $E_{staircase}$ is the modulo operator in COMSOL representing the square wave potential increment (E_{step}) and frequency (f) applied, E_{SW} is the square wave amplitude, f_{wave} is the approximating squares (Heaviside function) stemming from a smoothed step function of sinusoidal frequency. As demonstrated in Fig. 2, the applied square wave potential decreases firstly and then increases with the scale of E_{step} until the end of the potential scanned. The sampled current is collected by the average of current over the last half of each potential wave, rather than only collecting the current obtained by the end of each potential wave change due to the setting-up of the electrochemical workstation used [40].

In terms of Eq. (2), the chemical step is defined as a second-order reaction since the substrate is not in large excess compared with that of the mediator. Thus both mediator and substrate concentrations are considered in the reaction rate:

$$-r_S = -r_O = r_R = r_Y = k_{ec} c_O c_S \quad (11)$$

where $(-)_i$ is the species (I: R, O, S and Y) reaction rate of the chemical reaction, c_i is the species (I: R, O, S and Y) concentration and k_{ec} is the second-order rate constant of Eq. (2). The kinetic-diffusional differential equations within the studied geometry are listed below:

$$\frac{\partial c_R}{\partial t} = D_R \frac{\partial^2 c_R}{\partial x^2} + k_{ec} c_O c_S \quad (12)$$

$$\frac{\partial c_O}{\partial t} = D_O \frac{\partial^2 c_O}{\partial x^2} - k_{ec} c_O c_S \quad (13)$$

$$\frac{\partial c_S}{\partial t} = D_S \frac{\partial^2 c_S}{\partial x^2} - k_{ec} c_O c_S \quad (14)$$

$$\frac{\partial c_Y}{\partial t} = D_Y \frac{\partial^2 c_Y}{\partial x^2} + k_{ec} c_O c_S \quad (15)$$

D_i is the species (I: R, O, S and Y) diffusion coefficient. The boundary conditions of the numerical simulation are shown below:

$$t = 0, \quad 0 < x < 6\sqrt{Dt_{scan}}, \quad c_R = c_R^*, \quad c_O = c_O^* = 0, \quad c_S = c_S^*, \quad c_Y = c_Y^* = 0 \quad (16)$$

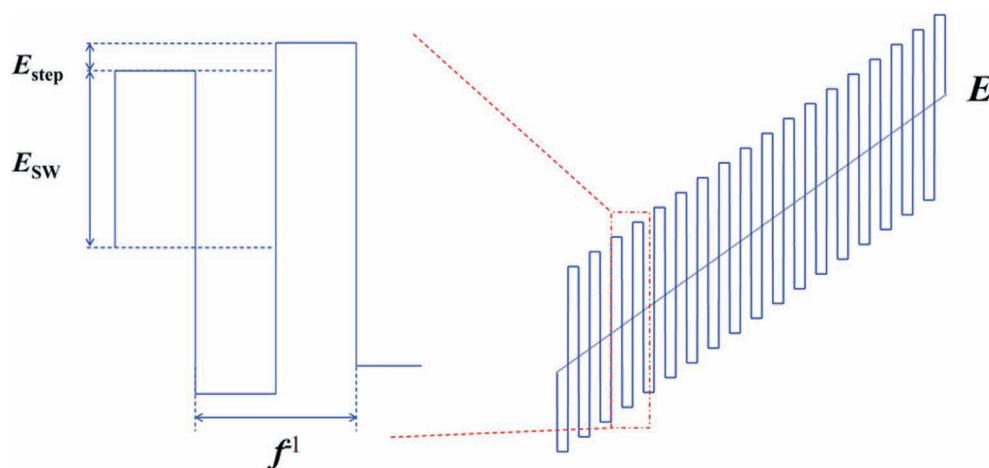


Fig. 2. Simulated square wave potential generated by Eqs. (8)–(10).

$$t > 0, x \rightarrow \infty, c_R = c_R^*, c_O = 0, c_S = c_S^*, c_Y = 0 \quad (17)$$

where c_i^* is the species (I: R, O, S and Y) bulk concentration. A summary of the nomenclature is given in Table 1.

3. Results and Discussion

3.1. Reaction mechanism determination of HMF under cyclic voltammetry

The cyclic voltammograms of homogeneous electrocatalytic reaction via HMF and L-cysteine has been reported for the study of k_{ec} previously [37]. Herein, the corresponding experimental voltammetric waveforms are repeated for the determination of the specific rate constant of the chemical reaction between HMF⁺ and L-cysteine. Simulated linear sweep voltammograms of HMF and L-cysteine at the scan rate of 10 and 100 mV·s⁻¹ are illustrated in Fig. 3a and b. Apparently, a pair of redox peak is observed at +0.24 V (oxidative peak) and +0.18 V (reductive peak) when k_{ec} is zero, indicating a quasi-reversible redox reaction by HMF [37,41,42]. Along with the increase of k_{ec} , an enhanced oxidative peak current is observed and then the single oxidative peak splits to two peaks due to the extremely fast k_{ec} , clearly evincing the voltammetric waveforms enters the total catalysis zone [36]. Similar tendency is observed under a higher scan rate as shown in Fig. 3b except the late appearance of split oxidative peaks under the same k_{ec} . In addition, an increase of oxidative current at the end of the potential scan (+0.6 V) appears at both scan rates. This can be ascribed to the effect of direct oxidation of substrate (L-cysteine). Given the above results, the relationship between the (pre) peak potential and k_{ec} under the scan rate of 10 and

100 mV·s⁻¹ is illustrated in Fig. 3c. As expected, the (pre) peak potential demonstrates a slightly anodic shift and then moves cathodically along with the increase of k_{ec} . Moreover, peak potential shifts of 38 mV ($E_{peak} = -0.038k_{ec} + 0.22$, $N = 8$, $R^2 = 0.996$) and 36 mV ($E_{peak} = -0.036k_{ec} + 0.26$, $N = 7$, $R^2 = 0.998$) are observed for a tenfold increase of k_{ec} when the scan rate of 5 and 100 mV·s⁻¹ is applied, respectively. This potential shift is in consistent with our previous work on k_{ec} between ferroceneacetic acid and L-cysteine [37]. Also, this phenomenon is verified by the cathodic potential shifting (30 mV) of homogeneous redox catalysis of electrochemical reactions reported by Savéant and his colleagues [43]. The relatively larger potential shifting gap can be rationalized by the introduction of substrate direct oxidation and the effect of substrate diffusion coefficient [44]. According to the linearity between the (pre) peak position and k_{ec} , the second-order rate constant between HMF⁺ and L-cysteine is calculated as 1.0 and 6.8 (mol·m⁻³)⁻¹·s⁻¹ at the scan rate of 100 and 5 mV·s⁻¹, respectively (Fig. 3c). Accordingly, the comparison of experimental and simulated linear sweep voltammograms of HMF and L-cysteine is shown in Fig. 3d. Notably, the 1D homogeneous electrocatalytic reaction model is capable in the characterization of HMF electrochemical oxidation (black lines). The current differences after the oxidative peak (>+0.30 V) is mainly caused by the electrochemical oxidation of substituent groups on ferrocene. When a higher scan rate is applied, the corresponding substituent group oxidation is negligible due to the sluggish reaction rate as indicated in Fig. S2. With the addition of L-cysteine, an insignificant split waveform with a sharp tip was observed (red lines). The steep increase in oxidative current is possibly stemmed from mixed valent intermediate in the oxidation of HMF [45], which leads to fast reaction kinetics of both electrochemical and chemical reaction via the hydrogen bonds between HMF molecules. Also, the differences between experimental and simulated voltammetric waveforms in Fig. 3d and Fig. S2 verify the existence of mixed valent intermediates in the studied homogeneous electrocatalytic reaction. Nevertheless, the proposed 1D homogeneous electrocatalytic reaction model is qualified in the description of homogeneous electrocatalytic reaction voltammetric waveforms, clearly indicating that the proposed model is capable in kinetics extraction of homogeneous electrocatalytic reaction for energy storage purpose.

3.2. Homogeneous electrocatalytic reaction with HMF-the effect of potential frequency, increment and amplitude in SWV

The homogeneous electrocatalytic reaction between HMF and L-cysteine was examined by square wave voltammetry in this section. Different from the linearly swept potential in linear sweep or cyclic voltammetry, the square wave feature determined by square wave frequency (f), potential increment (E_{step}) and wave amplitude (E_{SW}) influences the current response of square wave voltammograms. In this section, the effect of wave frequency is firstly investigated. Fig. 4 demonstrates the experimental and simulated square wave voltammograms of 2 mmol·L⁻¹ HMF in the absence of L-cysteine at the frequencies from 1 to 10 Hz. All simulation parameters are extracted from cyclic voltammograms as listed in Table S1 and the obtained forward, backward and net current are collected via the average current of the last half of each potential wave. Apparently the simulated voltammograms (dashed lines) is in good agreement with the experimental ones as shown in Fig. 4, clearly verifying a quasi-reversible redox reaction by HMF as indicated in cyclic voltammograms. Moreover, as one of the most notable benefits of this particular technique, almost no non-faradic current is observed at all frequencies in square wave voltammograms, which indicates the applied technique is able to decouple the non-faradic currents from the faradic ones. This is rationalized by the square wave potential scans, which reduces

Table 1
Nomenclature

Symbol	Definition and units
A	Active electrode area, m ²
c_{HMF}	Concentration of HMF, mol·m ⁻³
c_i	Concentration of species I (R, O, S and Y), mol·m ⁻³
c_i^*	Bulk concentration of species I (R, O, S and Y), mol·m ⁻³
$c_{Lcysteine}$	Concentration of L-cysteine, mol·m ⁻³
$c_{mediator}$	Concentration of mediator, mol·m ⁻³
$c_{substrate}$	Concentration of substrate, mol·m ⁻³
D_i	Diffusion coefficient of species I (R, O, S and Y), m ² ·s ⁻¹
d	Electrode diameter, mm
E_{app}	Applied voltage, V
E_{eq}	Equilibrium potential, V
E_{peak}	Peak potential, V
$E_{staircase}$	Modulo operator, V
E_{start}	Initial potential, V
E_{step}	Square wave potential increment, V
E_{SW}	Square wave amplitude, V
E_{vertex}	Reversed potential, V
F	Faradic constant, C·mol ⁻¹
f	Square wave frequency, Hz
f_{wave}	Approximating squares of Heaviside function, –
i	Current, A
i_{peak}	Peak current, A
k_a	Anodic reaction rate constant, m·s ⁻¹
k_c	Cathodic reaction rate constant, m·s ⁻¹
k_{ec}	Second-order rate constant of the chemical reaction, (mol·m ⁻³) ⁻¹ ·s ⁻¹
n	Electron transfer number, –
R	Universal gas constant, J·mol ⁻¹ ·K ⁻¹
T	Temperature, K
t	Time, s
t_{scan}	Linear sweep time, s
v	Scan rate, V·s ⁻¹
$(-r)_i$	Reaction rate of species I (R, O, S and Y), mol·m ⁻³ ·s ⁻¹
α	Transfer coefficient, –
η	Electrode polarisation, V

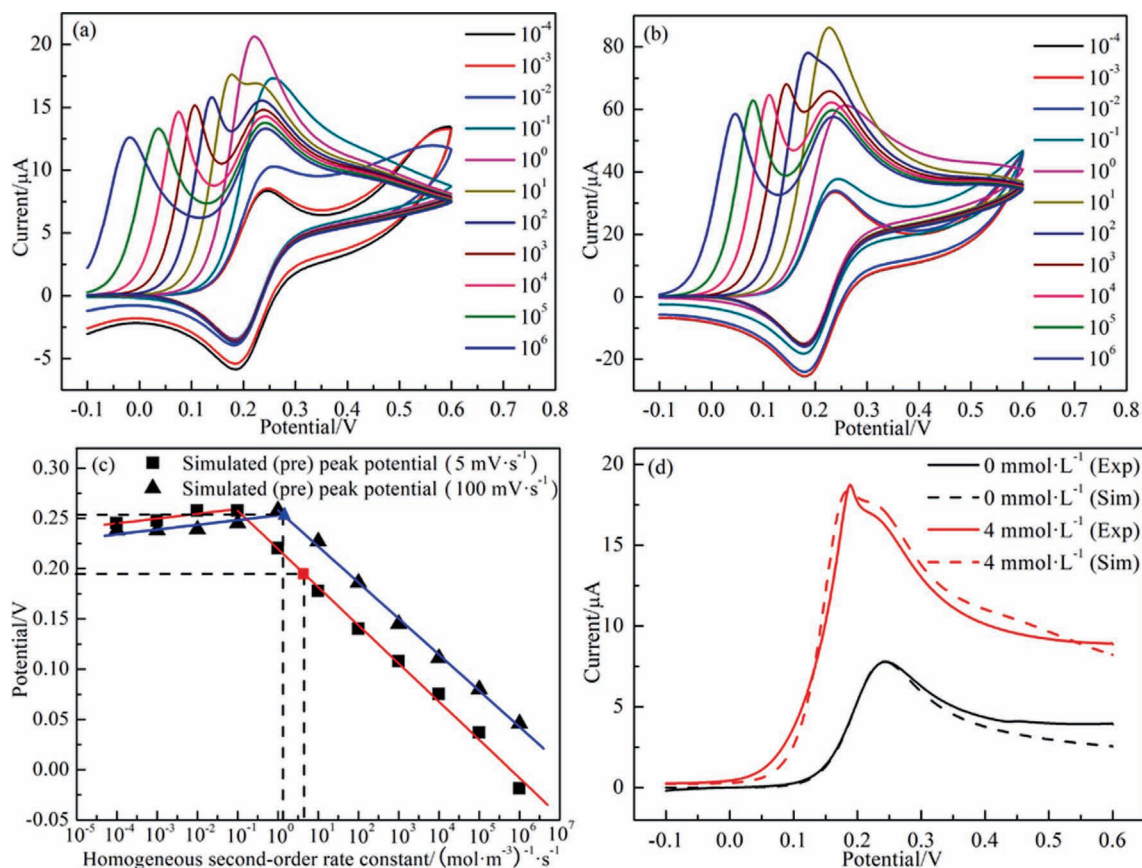


Fig. 3. Simulated voltammograms of 2 mmol·L⁻¹ HMF and 4 mmol·L⁻¹ L-cysteine with various second-order rate constants of the homogeneous chemical reaction step at a scan rate of (a) 5 and (b) 100 mV·s⁻¹; (c) The relationship between simulated (pre) peak potential and homogeneous second-order rate constant at a scan rate of 5 and 100 mV·s⁻¹; (d) Experimental and simulated voltammograms of HMF and L-cysteine at a scan rate of 5 mV·s⁻¹.

the effect of non-faradic current by discontinuous linear potential scan. Hence, this feature would possibly promote the resolution of overlapping redox features in voltammetric waveforms, which guarantees high sensitivity of both potential and current. Notably, the simulated current above +0.30 V is away from the experimental curves only in Fig. 4a, which is stemmed from the side reaction generated by mixed valent intermediates of HMF. This phenomenon appears only when the scan rate is slow in cyclic voltammetry. In square wave voltammetry, the potential scan rate can be expressed as below:

$$\nu = f \times E_{\text{step}} \quad (18)$$

where ν is the potential scan rate of square wave voltammetry. Therefore, f determines the scan rate of potential in the corresponding voltammograms when E_{step} is fixed (0.004 V). As demonstrated in Fig. 4a, the effect of mixed valent intermediates of HMF is observed at the equivalent scan rate of 4 mV·s⁻¹, which is in consistent with the result in cyclic voltammograms in Fig. 3d. When the corresponding scan rates increase from 8 to 40 mV·s⁻¹, no indications can be observed due to the sluggish reaction rate by the mixed valent intermediates of HMF, which is again verified by the linear sweep voltammograms in Fig. S2.

Next, the square wave voltammograms of 2 mmol·L⁻¹ HMF with the presence of 0 to 8 mmol·L⁻¹ L-cysteine was carried out experimentally. As shown in Fig. 5a–f, homogeneous electrocatalytic reaction was investigated by continuously changing the square wave voltammetric scanning frequency. Note that with the continuous addition of L-cysteine in HMF at a frequency of 1 Hz, the initial net current peak increases gradually and the corresponding peak potential moves cathodically from 0.184 to 0.176 V.

Moreover, although the square wave net current has no obvious regularity, the evidence of two overlapping oxidative current peaks is observed along with the addition of L-cysteine as shown in Fig. 5a. The explanation of those two overlapping peaks is as below: the electrochemical oxidative peaks at $\sim +0.184$ V indicates the intrinsic electrochemical oxidation as shown in Eq. (1) while the observed peak shifting is introduced by the electrocatalytic reaction (Eq. (2)). The quick regenerated HMF via the electrocatalytic reaction undertakes the redox reaction of HMF again near the electrode surface. Thus the overlapping oxidative peaks are observed. Indeed, this phenomenon verifies the existence of the homogeneous electrocatalytic reaction with a fast chemical reaction rate, but the corresponding rate constant is still not as large as the example of FAA and L-cysteine ($175 \text{ (mol} \cdot \text{m}^{-3})^{-1} \cdot \text{s}^{-1}$) [37]. Consequently, no high resolution split wave feature is displayed in Fig. 5a. Nevertheless, the benefits of high sensitivity of current in square wave voltammetry is still effective. A linear fit relationship between the obtained current and L-cysteine concentration is demonstrated ($i_{E=0.06\text{V}} = 4.56 \times 10^{-7} C_{\text{L-cysteine}} + 8.19 \times 10^{-7}$, $N = 9$, $R^2 = 0.976$), which indicates the net current is feasible for possible analytical purpose as shown in Fig. S3a. Meanwhile, as shown in Fig. 5b, further efforts have been made for investigating the forward current component of SWV. When no L-cysteine is added, a single peak related to the intrinsic electrochemical oxidation of HMF is demonstrated (black line). Along with the addition of L-cysteine, an obvious protuberance before the intrinsic electrochemical peak is developed initially and then the protuberance and the original electrochemical peak turn into a sharp tip as demonstrated in Fig. 5b, which is similar to the waveforms under cyclic voltammetry at a slow scan rate [37]. The corresponding peak

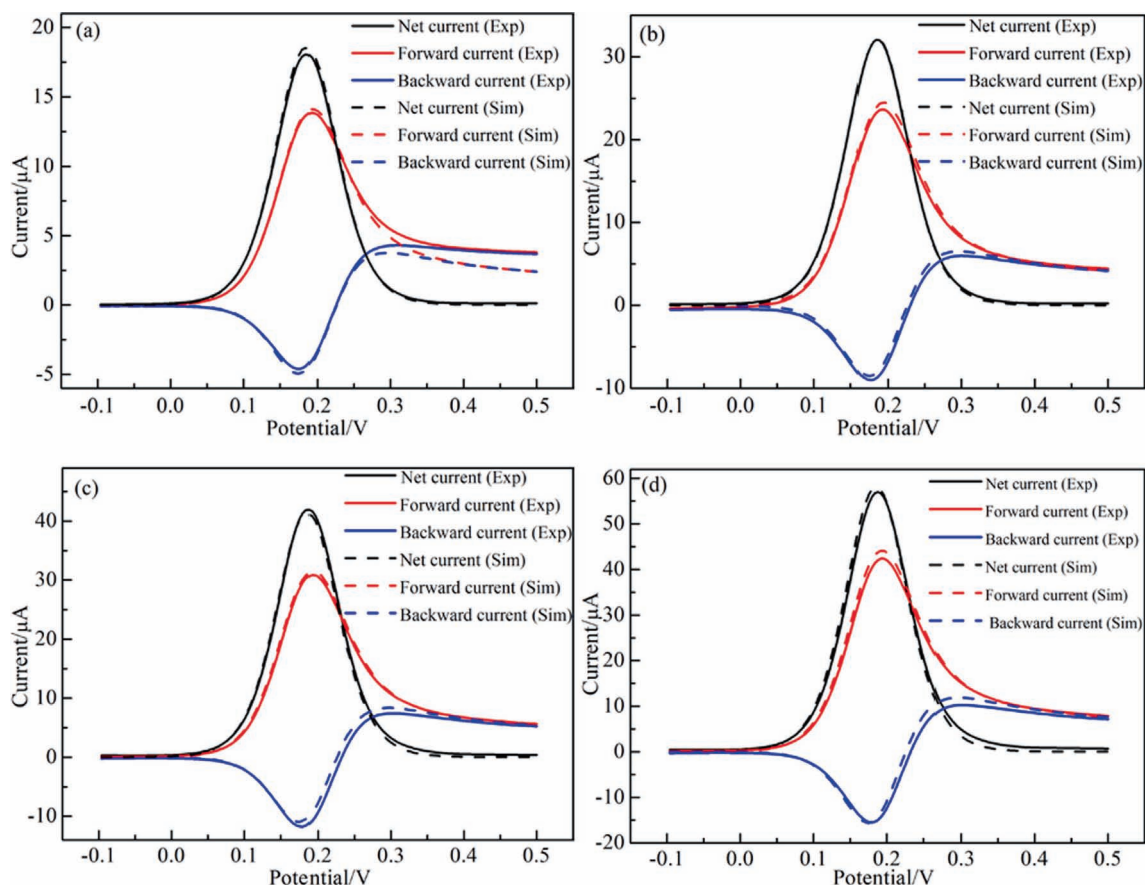


Fig. 4. Comparison of experimental and simulated net, forward and backward current components of square wave voltammograms for 2 mmol·L⁻¹ HMF in a pH = 9 buffer at a frequency of (a) 1; (b) 3; (c) 5 and (d) 10 Hz (Potential increment = 0.004 V; Amplitude = 0.025 V).

position moves cathodically from +0.184 ($C_{\text{L-cysteine}} = 0.0 \text{ mmol}\cdot\text{L}^{-1}$) to +0.172 V ($C_{\text{L-cysteine}} = 4.0 \text{ mmol}\cdot\text{L}^{-1}$) and then stays at +0.176 V ($C_{\text{L-cysteine}} = 8.0 \text{ mmol}\cdot\text{L}^{-1}$), also verifying the development of the waveform transition. As the rate constant between HMF^+ and L-cysteine is two orders of magnitude smaller than that of FAA and L-cysteine, no obvious split wave phenomenon appears. In addition, the linear fit between the forward current and the concentration of L-cysteine is given in Fig. S3b ($i_{\text{peak}} = 3.17 \times 10^{-6} C_{\text{L-cysteine}} + 1.31 \times 10^{-5}$, $N = 9$, $R^2 = 0.997$), clearly indicating the occurrence of homogeneous electrocatalytic reaction between HMF and L-cysteine.

Comparatively, square wave voltammograms at a frequency of 3 and 5 Hz are further discussed as shown in Fig. 5c–f. Different from the waveform under the frequency of 1 Hz, only a single peak is observed under all L-cysteine concentrations from 0 to 8 mmol·L⁻¹. Although the equivalent scan rate is less than $20 \text{ mV}\cdot\text{s}^{-1}$ ($f = 5 \text{ Hz}$, $E_{\text{step}} = 0.004 \text{ V}$), only a slight difference is observed before the intrinsic HMF oxidation peak at different L-cysteine concentrations when net current is considered. Notably, the net current peak value is almost constant along with the addition of L-cysteine. This can be attributed to the competition between reaction kinetics and the diffusion of the reactant and product. As a special type of catalytic reaction, the homogeneous electrocatalytic mechanism employs the electroactive species as the catalysts (mediator). The status transition between reductive and oxidative form of mediator is determined by both electrochemical and chemical reaction. However, both reactions only influence the fraction of a specific status of the mediator, rather than producing more of reactant or product within the diffusion layer while mass transport is the main reason for the supplement

of fresh mediator. In terms of the protuberance structure, the obtained forward current peak is increased with the promotion of frequency while the pre plateau disappears with the increase of frequency, as shown in Fig. 5b, d and f. This can be explicated by the effect of kinetic parameters including potential scan rate (f and E_{step} in SWV) and k_{ec} of Eq. (2), which determine the specific waveform before the electrochemical peak. This also confirms that although SWV has the advantage of decoupling non-faradic current and high sensitivity of electrochemical current, the electrocatalytic feature of reductive and oxidative species recycle hinders the superiority of such features for SWV.

Next, k_{ec} is determined via the square wave voltammograms as demonstrated in Fig. 6. In theory, when k_{ec} increases in the homogeneous electrocatalytic reaction, the peak current increases initially and then splits into two distinguished oxidative peaks. The pre-peak moves cathodically along with the extremely large value of k_{ec} in linear sweep voltammetry [44]. Similarly, the peak current shifting manner in SWV is in consistent with that in LSV as shown in Fig. 6a ($C_{\text{HMF}} = 2 \text{ mmol}\cdot\text{L}^{-1}$, $C_{\text{L-cysteine}} = 4.0 \text{ mmol}\cdot\text{L}^{-1}$). Moreover, as illustrated in Fig. 6b, the relationship between peak current potential is almost constant and then moves cathodically along with the increase of k_{ec} ($E_{\text{peak}} = -0.058k_{\text{ec}} + 0.17$, $N = 7$, $R^2 = 0.997$). This indicates that the pre peak shifting of approximate -58 mV is observed for every ten-fold increase of k_{ec} , apparently verifying the discovery of catalytic parameter and peak-potentials by Gulaboski and his colleagues [32]. Furthermore, the specific k_{ec} between HMF^+ and L-cysteine is determined by SWV and the corresponding value is $1.1 (\text{mol}\cdot\text{m}^{-3})^{-1}\cdot\text{s}^{-1}$ as shown in Fig. 6b. Considering that the voltammetric waveforms of HMF and L-cysteine just falls into the position where the split peaks

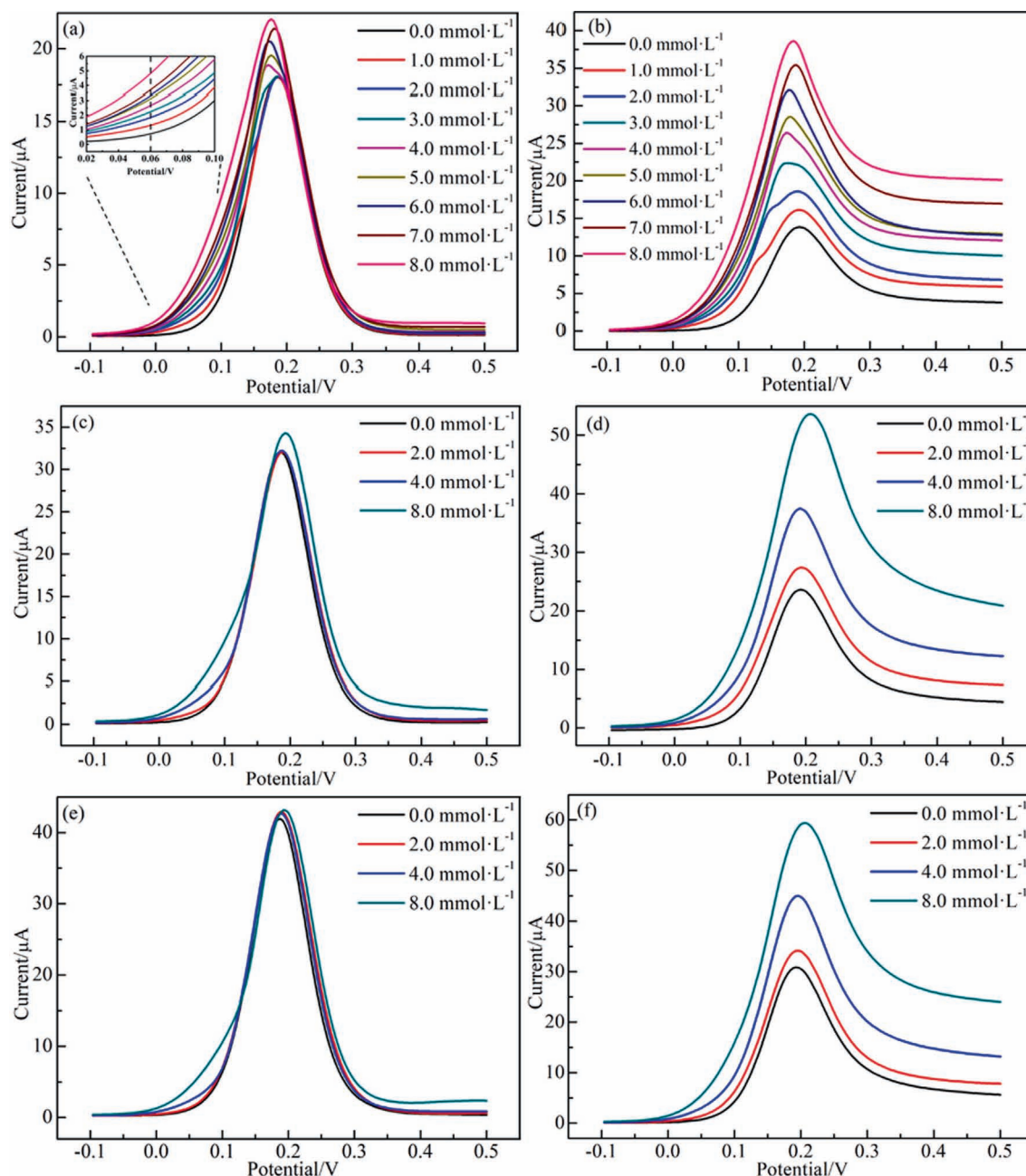


Fig. 5. Experimental net and forward current components of square wave voltammograms for 2 mmol·L⁻¹ HMF and 0–8 mmol·L⁻¹ L-cysteine in a pH = 9 buffer at a frequency of (a–b) 1; (c–d) 3; (e–f) 5 Hz (Potential increment = 0.004 V; Amplitude = 0.025 V).

profile is forming, this value is close to the calculated k_{ec} in LSV. Given the above results, the theoretical results are verified by the 1D homogeneous electrocatalytic reaction model in COMSOL. Both experimental and simulated voltammograms of the forward currents are listed in Fig. 6c and d. Obviously, the simulated waveforms in dashed lines are in good agreement with the experimental results. Specifically, the model simulates the transition of protuberance waveforms to only one oxidative peaks, which is observed under the frequency of 1 Hz. Although the protuberance waveforms toward the SWV profiles become inconspicuous under the frequency of 10 Hz, the simulated waveforms still correspond with the experimental data in Fig. 6d. In summary, the 1D homogeneous electrocatalytic reaction model under SWV is feasible in the description of SWV waveforms of HMF and L-cysteine.

Next, the influence of potential increment is discussed for homogeneous electrocatalytic reaction experimentally. Fig. 7 shows the SWV curves of HMF and different concentrations of L-cysteine under various potential increments. Apart from an oxidative peak at approximately +0.190 V, an obvious protuberance of net current is observed with the increase of L-cysteine concentration in Fig. 7a and c. Besides, a distinguished shoulder profile is obtained when E_{step} is 0.001 V as depicted in Fig. 7b. This phenomenon can be attributed to the role of potential increment in equivalent scan rate as depicted in Eq. (18). In general, a smaller E_{step} leads to a higher resolution of pre peak or shoulder profile since the reaction time of the homogeneous chemical reaction step is relatively abundant, thus an obvious split oxidative peak in forward current component will be demonstrated by the regenerated

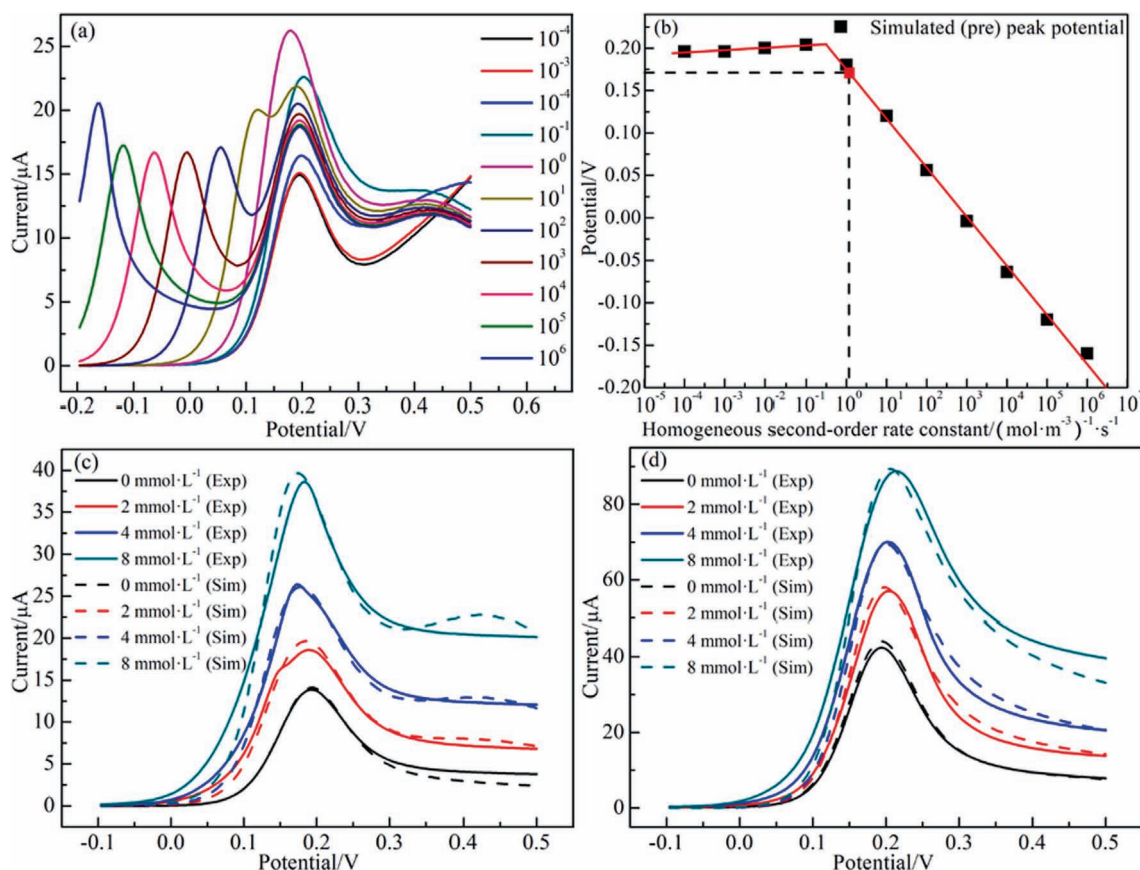


Fig. 6. (a) Simulated forward current components of square wave voltammograms for 2 mmol·L^{−1} HMF and 4 mmol·L^{−1} L-cysteine with various k_{ec} of the homogeneous chemical reaction step at a frequency of 1 Hz; (b) The relationship between simulated (pre) peak potential and homogeneous second-order rate constant; Experimental and simulated forward current components of voltammograms for HMF and L-cysteine at a frequency of (c) 1 and (d) 10 Hz (Potential increment = 0.004 V; Amplitude = 0.025 V).

reactant. Specifically, the transition of split peaks into one single peak is evident along with the increase of E_{step} as a wider voltammetric waveform is demonstrated in Fig. 7d (pink line), which just fall into the position where two obvious peaks (pink line in Fig. 7b) is turning into only one sharp tip (pink line in Fig. 5b). Different from the forward current component which is comparable with linear sweep voltammograms, the waveform transition for net current component accounts for the contribution of backward current, which changes the corresponding voltammetric profile. Although it is evident that the electrocatalytic reaction happens as shown in Fig. 7a, c and Fig. 5a, the relative potential position of the catalytic current should be considered when the net current is employed for the evaluation of homogeneous electrocatalytic reaction for which, the catalytic feature moves anodically with the increase of E_{step} and two overlapping peaks are observed in Fig. 5a. Despite of the waveform transition, the linearity between L-cysteine concentration and net currents at 0.06 V/forward current peaks has been examined. As depicted in Fig. S4 and S5, good linearity is demonstrated ($R^2 > 0.990$) under all potential increment employed, clearly suggesting the existence of homogeneous electrocatalytic reaction between HMF and L-cysteine. Besides, experimental forward current components of SWV for 2 mmol·L^{−1} HMF at the E_{step} ranging from 0.001 to 0.008 V are displayed in Fig. 7e. Apparently the peak current increases with the promotion of E_{step} mainly due to the change of equivalent scan rate. Moreover, with the addition of L-cysteine, the transition of waveforms from a shoulder profile to a single peak is realized in Fig. 7f. This similar trend of waveforms compared with that under different frequencies can be again ascribed to the competition between reaction kinetics and mass

transfer. It is thus revealed that both f and E_{step} effect the SWV waveforms in the same manner as both of them determine the equivalent potential scan speed.

The homogeneous electrocatalytic reaction between HMF and L-cysteine is further investigated under SWV with different E_{SW} . Fig. 8a and c demonstrate the net current component of 2 mmol·L^{−1} HMF and 0–8 mmol·L^{−1} L-cysteine at the E_{SW} of 0.01 and 0.1 V, respectively. Therein, the general voltammetric waveforms become obviously wider with the increase of E_{SW} . Also, the absolute net current increases significantly from approximately 7 μA to more than 40 μA. This can be attributed to the large amplitude carried out in SWV. When the amplitude is 0.01 V, the corresponding voltammetric waveforms are close to that under linearly swept potential techniques, resulting in voltammograms similar to that of LSV, especially when forward current component is considered in Fig. 8b. When E_{SW} is increased to 0.1 V (Fig. 8c and d), both the net current and forward current waveforms are getting wider, which is stemmed from the continuous scanning of large potential amplitude over the equilibrium potential. The application of large amplitude enables the quick redox reaction between mediator and mediator⁺, which obtains wider voltammetric waveforms in Fig. 8c and d. Additionally, the contribution of net current component is almost constant except the accumulation of current from the homogeneous chemical reaction as shown in Fig. 8c. Similar trend has been observed when potential increment varies in last section. Interestingly, the increase of E_{SW} leads to a high resolution of split current peaks in both net and forward current component, whose trend is opposite to those of f and E_{step} . This tendency is mostly owing to the benefit of large peak separation by the corre-

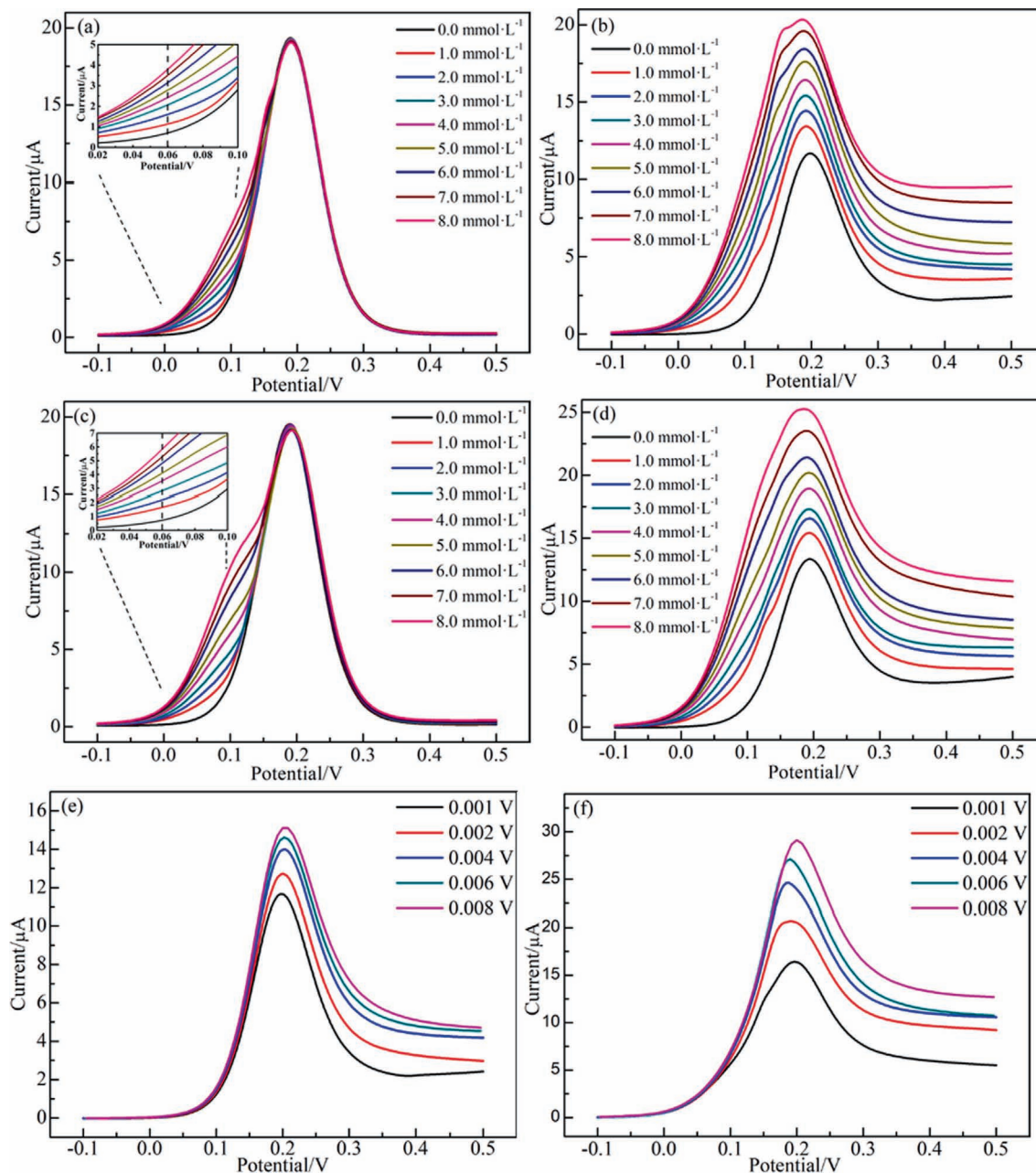


Fig. 7. Experimental net and forward current components of square wave voltammograms for 2 mmol·L⁻¹ HMF and 0–8 mmol·L⁻¹ L-cysteine at a potential increment of (a–b) 0.001 and (c–d) 0.002 V; Experimental forward current components of square wave voltammograms for 2 mmol·L⁻¹ HMF and (e) 0 and (f) 4 mmol·L⁻¹ L-cysteine at a potential increment of 0.001–0.008 V (Frequency = 1 Hz; Amplitude = 0.025 V).

sponding amplitude applied. The relatively large amplitude facilitates the homogeneous electrocatalytic reaction, resulting in the accumulation of oxidative current at a relatively lower potential applied. Also, similar tendency of obtained net current has been achieved *via* changing E_{SW} at a first-order rate constant in homogeneous electrocatalytic reaction by Molina and her colleagues [35]. Although no split wave has been observed due to the excessive substrate used, the net current increases along with the gain of first-order rate constant.

Additionally, the established 1D homogeneous electrocatalytic reaction model is verified under different E_{SW} scoping from 0.01 to 0.1 V in Fig. 8e and f. In general, the simulated voltammograms agree well with the experimental results under the potential amplitude of 0.01 and 0.1 V, clearly suggesting that the reaction between HMF and L-cysteine follows the homogeneous electrocat-

alytic reaction mechanism. But, unlike the agreement of simulated and experimental voltammograms at E_{SW} of 0.1 V, the simulated curves at E_{SW} of 0.01 V demonstrate fairly differences at the excess factor ($c_{\text{substrate}}/c_{\text{mediator}}$) of 1. No protuberance has been shown at the k_{ec} of 1.1 (mol·m⁻³)⁻¹·s⁻¹, obviously indicating a smaller reaction constant is employed and no split peaks is given in forward current component. As illustrated earlier, such circumstance is mainly ascribed to the real k_{ec} value between HMF⁺ and L-cysteine, which just locates in the transition area of voltammetric profiles from on sharp tip oxidative peak to the split peaks phenomenon. Since an obvious protuberance has been observed experimentally, the specific k_{ec} is calculated depending on the voltammogram as shown in Fig. S6a and b. The obtained value is 3.9 (mol·m⁻³)⁻¹·s⁻¹, which is close to the k_{ec} value calculated from CV. Additionally, the corresponding forward current component is

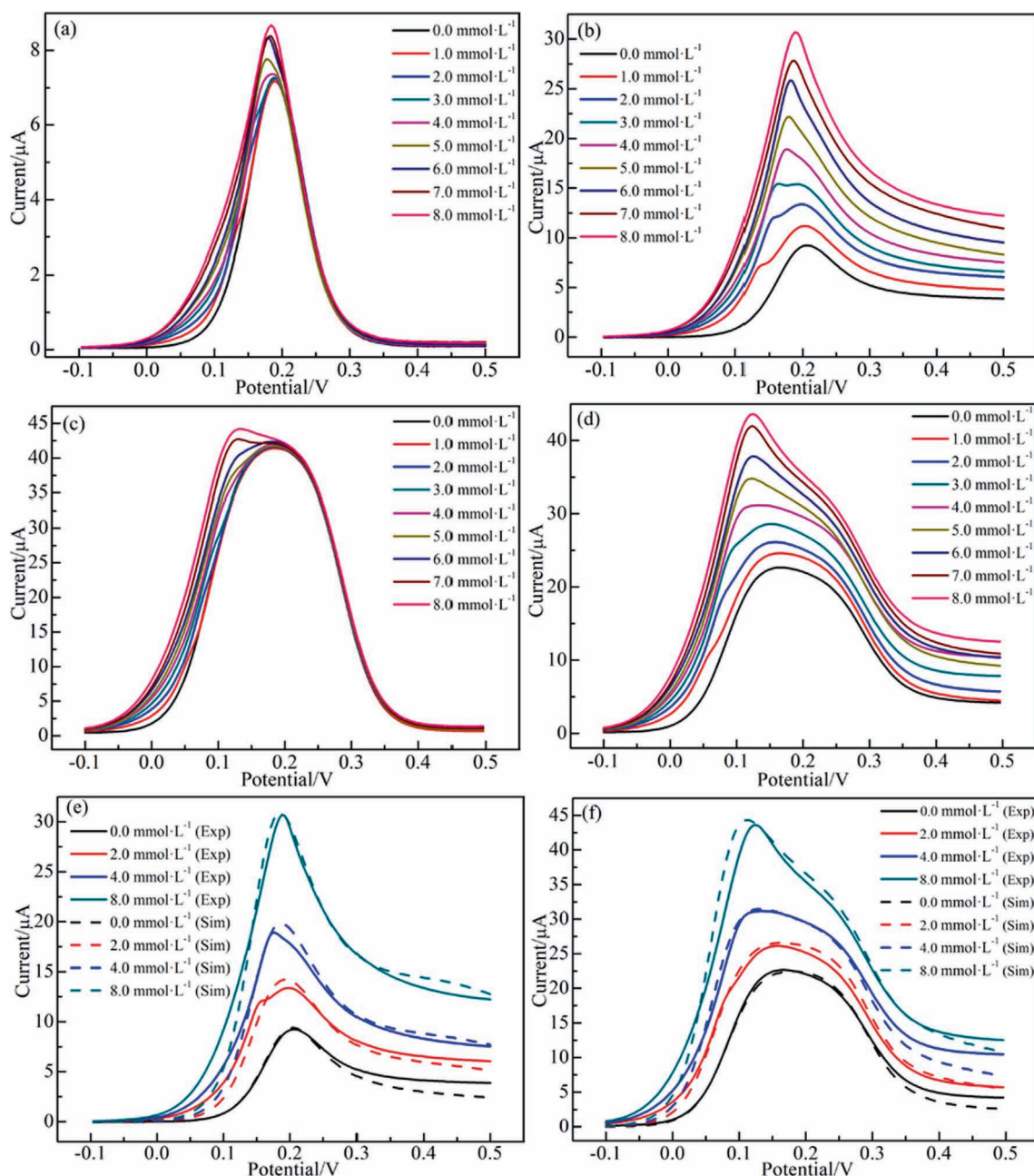


Fig. 8. Experimental net and forward current components of square wave voltammograms for 2 mmol·L⁻¹ HMF and 0–8 mmol·L⁻¹ L-cysteine at a potential amplitude of (a–b) 0.01 and (c–d) 0.10 V; Experimental and simulated forward current components of square wave voltammograms for 2 mmol·L⁻¹ HMF and 0–8 mmol·L⁻¹ L-cysteine at a potential amplitude of (e) 0.01 and (f) 0.10 V (Frequency = 1 Hz; Increment = 0.004 V).

demonstrated with an inconspicuous protuberance as shown in Fig. S6c, obviously evincing a similar waveform feature of the experimental result. Given the above results, it is readily concluded that the k_{ec} of HMF⁺ and L-cysteine lies in a sensitive range, which easily changes the voltammetric profiles of linear sweep and square wave voltammograms.

3.3. Verification of 1D homogeneous electrocatalytic reaction model by HEF

Comparatively, the determination of k_{ec} via square wave voltammograms is further verified by HEF and L-cysteine. As illustrated in Fig. 9a, similar experimental net current component waveform is observed compared with the situation of HMF and

L-cysteine. The evidence of two overlapping oxidative current peaks is demonstrated with the increase of L-cysteine concentration, which further confirms the homogeneous electrocatalytic reaction between ferrocene derivatives and L-cysteine. Moreover, the current at +0.06 V is linearly fitted along with the increase of L-cysteine concentration ($i_{E=0.06V} = 3.11 \times 10^{-7} C_{L-cysteine} + 7.16 \times 10^{-7}$, $N = 9$, $R^2 = 0.981$) in Fig. 9a. Similarly, the forward current peaks is proportional to L-cysteine concentration ($i_{E=0.06V} = 3.27 \times 10^{-6} C_{L-cysteine} + 1.14 \times 10^{-5}$, $N = 9$, $R^2 = 0.997$) in Fig. S7, agreeing well with those obtained from the reaction between HMF and L-cysteine. In terms of k_{ec} between HEF⁺ and L-cysteine, the same methodology introduced for the determination of k_{ec} between HMF⁺ and L-cysteine is employed. Simulation parameters are extracted from the experimental data of the redox reaction of

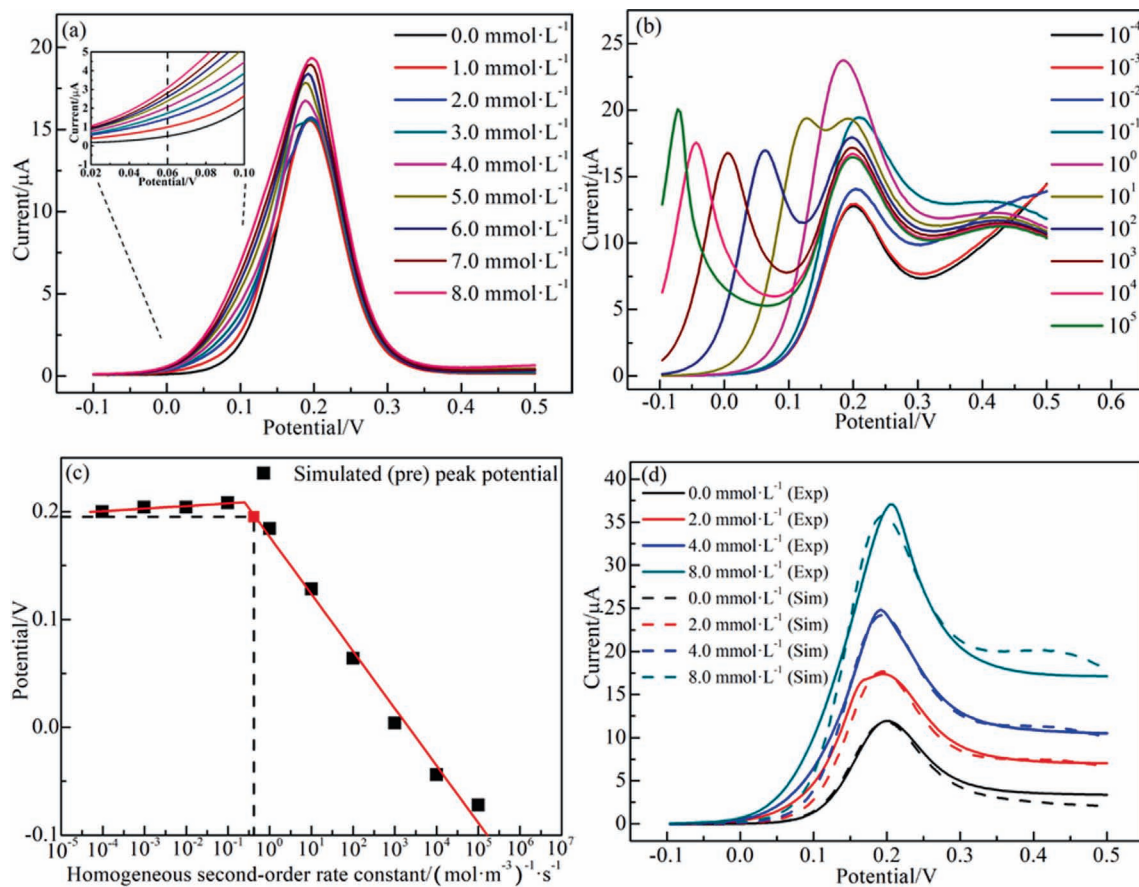


Fig. 9. (a) Experimental net current components of square wave voltammograms for 2 mmol·L⁻¹ HEF and 0–8 mmol·L⁻¹ L-cysteine at a frequency of 1 Hz; (b) Simulated forward current components of square wave voltammograms for 2 mmol·L⁻¹ HEF and 4 mmol·L⁻¹ L-cysteine with various second-order rate constants of the homogeneous chemical reaction step at a frequency of 1 Hz; (c) The relationship between simulated (pre) peak potential and homogeneous second-order rate constant; (d) Experimental and simulated forward current components of voltammograms for HEF and L-cysteine at a frequency of 1 Hz (Potential increment = 0.004 V; Amplitude = 0.025 V).

HEF and the corresponding theoretical simulation of HEF redox reaction is in good agreement with experimental cyclic voltammogram, as shown in Fig. S8. Moreover, similar phenomena occur concerning the voltammetric profiles of changing k_{ec} as displayed in Fig. 9b and the linearity of (pre) peak potential and k_{ec} is shown in Fig. 9c ($E_{peak} = -0.053k_{ec} + 0.18$, $N = 6$, $R^2 = 0.987$). The corresponding k_{ec} of HEF⁺ and L-cysteine is calculated as 0.5 (mol·m⁻³)⁻¹·s⁻¹, which is slightly smaller than that of HMF⁺ and L-cysteine. This result is in consistent with the density functional theory (DFT) calculation by previous research [37]. Furthermore, the calculated k_{ec} is verified in 1D homogeneous electrocatalytic reaction model as demonstrated in Fig. 9d. Apparently the simulated forward current component is in good agreement with the experimental data of HEF and L-cysteine, clearly verifying the excellent compatibility of the established finite element model.

4. Conclusions

As the basics of redox-mediated redox flow battery, homogeneous electrocatalytic reaction is investigated under cyclic voltammetry and square wave voltammetry experimentally and theoretically. A 1D homogeneous electrocatalytic reaction model is established based on finite element methodology and the corresponding model is verified by redox reaction and homogeneous electrocatalytic reaction. The second-order rate constant between HMF⁺ and L-cysteine is calculated as 1.1 (mol·m⁻³)⁻¹·s⁻¹ under square wave voltammetry and this result is verified by linear sweep voltammetry. Notably, the (pre) peak potential shifting

manners with the second-order rate constant in the proposed model under linear sweep voltammetry and square wave voltammetry are both revealed by previous theoretical cases, clearly verifying the feasibility of the established model. Moreover, the effect of experimental parameters including potential frequency (f), increment (E_{step}) and amplitude (E_{SW}) have been comprehensively investigated in terms of voltammetric waveforms. At last, HEF is employed as the mediator to verify the feasibility of the proposed model and good agreement is demonstrated in the prediction of k_{ec} between HEF and L-cysteine. In summary, the proposed model could be utilized as a robust tool for the selection of homogeneous electrocatalytic reaction which possesses a large reaction rate and eventually strengthens the energy and power density of energy storage devices.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2021.12.001>.

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