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Method of Evaluation of Electron Transfer Kinetics of a Surface-Confined Redox System by Means of Fourier Transformed Square Wave Voltammetry

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A new form of Fourier transformed square wave voltammetry (FT-SWV) is proposed to simplify and accelerate the electron transfer kinetics evaluation procedures for surface-confined redox systems. Even harmonic frequencies, which are derived from the nonlinear Faradaic response, will arise in the power spectrum after Fourier transformation of the current response of FT-SWV. The profile of the even harmonic power spectra is bell-shaped and shows a maximum at a certain frequency. The electrode kinetics-dependent maximum and the corresponding frequency are equivalent to the so-called “quasi-reversible maximum” and “critical frequency” (f_{\max}) in traditional SWV, respectively. The critical frequency can be regarded as a frequency that is synchronized to the electron transfer rate constant (k^0). As a result, it can serve as a probe of k^0 by means of a very simple equation, $k^0 = k_{\max} f_{\max}$. Compared with traditional cyclic voltammetry, square wave voltammetry, alternating current voltammetry, and several other voltammetric techniques, this method exhibits great advantages for its simplicity, rapidity, and sensitivity.

A surface-confined redox system refers to a type of redox reaction where both the reactant and the product are strongly attached to the electrode surface. Over the past decades, studies on surface-confined redox reactions have gained increased interest in comparison to their well-studied solution phase counterparts. An outstanding example is the investigation of proteins by means of protein film voltammetry.^{1,2} It has been recognized that the immobilization of proteins to an electrode surface can provide a biological model, the reaction mechanisms of which may contribute to a better understanding of biological electron transfer.

The standard electron transfer rate constant (k^0) is an important parameter of an electron transfer process. Numerous voltammetric techniques, each of which was characterized by its own unique advantages and disadvantages, were developed to evaluate this parameter historically. The most commonly used technique is cyclic voltammetry (CV).³ Several alternative electrochemical approaches to CV, such as electrochemical impedance

spectroscopy (EIS),⁴ alternating current voltammetry (ACV),⁵ and square wave voltammetry (SWV),⁶ have been used to study the electrode kinetics of surface-confined redox systems.

Among these methods, SWV is an exceptionally versatile voltammetric technique, which combines the best aspects of several pulsed voltammetric methods. SWV has been adopted to evaluate the electrode kinetics of surface-confined redox systems with a so-called “quasi-reversible maximum” (QRM).^{7,8} Briefly, a series of SWV experiments were carried out at a wide range of excitation frequencies, then the normalized peak current of each SWV experiment was plotted as a function of the logarithmic frequency. The plot shows a maximum value at a so-called “critical frequency” (f_{\max}). The standard electron transfer rate constant can then be calculated from a simple equation, $k^0 = k_{\max} f_{\max}$. This method is much simpler than CV and EIS as it is free of fitting.

All of the traditional approaches listed above use a single-time scale excitation. The time scale is then “scanned” to obtain the time scale-dependent patterns of behavior and, subsequently, the kinetic parameters. However, can we excite an electrochemical system with a multifrequency signal and dissect the response with Fourier transform? Recently, Fourier transformed large-amplitude sinusoidal voltammetry (SV),⁹ ACV,^{10,11} and SWV,¹² initiated by Kuhr, Oldham, and Bond, have been proven to be powerful tools for both quantitative analysis and mechanism studies. On the basis of extensive investigations carried out previously, Bond put forth a similar perspective in an inquisitive manner: “Can FT transform revolutionize voltammetric techniques as it did for NMR?”¹³ Driven by this motivation, and inspired by the previous works of

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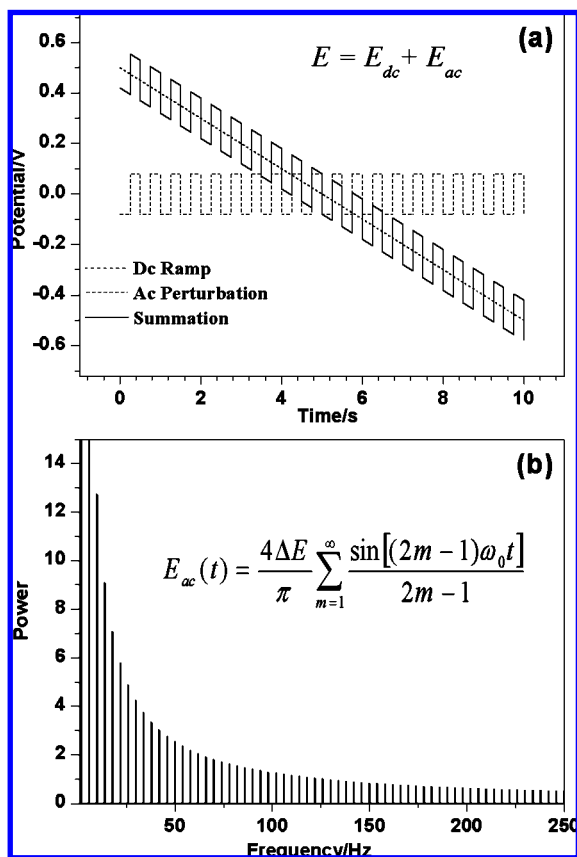


Figure 1. Schematic description of (a) the time domain waveform and (b) the frequency domain power spectrum of a typical multifrequency excitation applied in FT-SWV.

Smith,¹⁴ Park,¹⁵ and Bond, we are excited to report that Fourier transform can also simplify and accelerate traditional voltammetric techniques in the same manner as it did for NMR. The method presented here is Fourier transformed square wave voltammetry (FT-SWV), initially developed by Bond and colleagues.

THEORY

Modeling. Detailed descriptions of the modeling of a surface-confined redox system are available elsewhere.¹² The multifrequency excitation signal we applied is composed of a dc ramp and a large-amplitude square wave of a given frequency (f_0), as shown in Figure 1a. From the point of view of the Fourier series, the ac portion of the excitation signal can be considered as the combination of an infinite number of sine waves of angular frequencies that are the odd multiples of f_0 , as presented in Figure 1b. The assumption that the electrochemical system is linear, which was followed by Smith and Park, is no longer applicable if a large-amplitude excitation is applied. For a nonlinear electrochemical system, the response of such a large-amplitude excitation, as used in FT-SWV, will give rise to a series of measurable harmonic components, the even multiples of f_0 . Unfortunately, because of the inherent complexity of the origins of these harmonic frequencies, we are not able to deduce their exact expressions. We can, however, qualitatively obtain the special properties owned by these even harmonic components. They are derived only from

the faradaic current response and are almost devoid of background charging current. More significantly, they are very sensitive to quasi-reversible processes and insensitive to reversible and irreversible processes.¹²

Since an ideal square wave contains components of all the frequencies that are the odd multiples of f_0 , there must be a certain frequency component that will shift the electron transfer process into the quasi-reversible region and, consequently, induce a maximum harmonic current response. There is a strong implication that the profile of the even harmonic components of the power spectra will show a maximum, which can be regarded as the equivalent of the so-called QRM in traditional SWV as mentioned above. In fact, this form of QRM does exist in FT-SWV. Several figures in previously published papers clearly show this phenomenon.¹² Bond and co-workers have noted that the profile of the even harmonic power spectra was very sensitive to electrode kinetics. They even further used the profile to evaluate the electron transfer rate constant,^{12b} however they obtained the parameter via an experiments vs simulations procedure.

The origin of the QRM in traditional SWV was explained as the consequence of the synchronization between the excitation and the electron transfer rate constant.⁸ When the frequency of the excitation signal is synchronized to the electron transfer rate constant, a multiple and exhaustive reuse of the surface-confined material occurs, and thus a maximum response was induced. We can conclude that the QRM in FT-SWV can also be explained by the same interpretation. The QRMs in both the traditional SWV and FT-SWV reflect a particular frequency at which the excitation is synchronized to the electron transfer rate.

A typical time domain current response of FT-SWV obtained from simulation is depicted in Figure 2a. Generally, we should first transform the current response into a frequency domain power spectrum, as shown in Figure 2b, where the even harmonic components are highlighted. Subsequently, we can obtain the power of each harmonic frequency from the power spectrum, and then plot the ratio of the obtained power to f_0 as a function of the logarithmic frequency, as shown in Figure 2c. We can see that the profile of the even harmonic power spectra is bell-shaped and has a maximum value at a particular frequency, as expected. The maximum, and the corresponding frequency, are equivalent to the so-called QRM and f_{\max} in traditional SWV, respectively. Furthermore, the standard rate constant can be calculated from the critical frequency with the same equation, $k^0 = k_{\max} f_{\max}$, as in traditional SWV.⁷ We further extended our simulation with different values of k^0 ranging in orders of magnitude. The even harmonic power spectra are shown in Figure 2d. The linear relation still exists, and the linear range can theoretically span several orders of magnitude.

The Value of k_{\max} . Once the QRM and the critical frequency have been obtained through a FT-SWV experiment, the value of k^0 can be calculated directly from a linear relation, $k^0 = k_{\max} f_{\max}$. Nevertheless, we must first know the value of the coefficient k_{\max} . The values of k_{\max} , as tabulated in Table 1, are obtained by the simulation of a surface-confined system with known k^0 , following the literature procedure.⁷ The theoretically calculated k_{\max} is independent of the system under study, the frequency of the square wave (f_0), and the scan rate of the linear ramp (v). However, we must note that an apparent requirement of the critical

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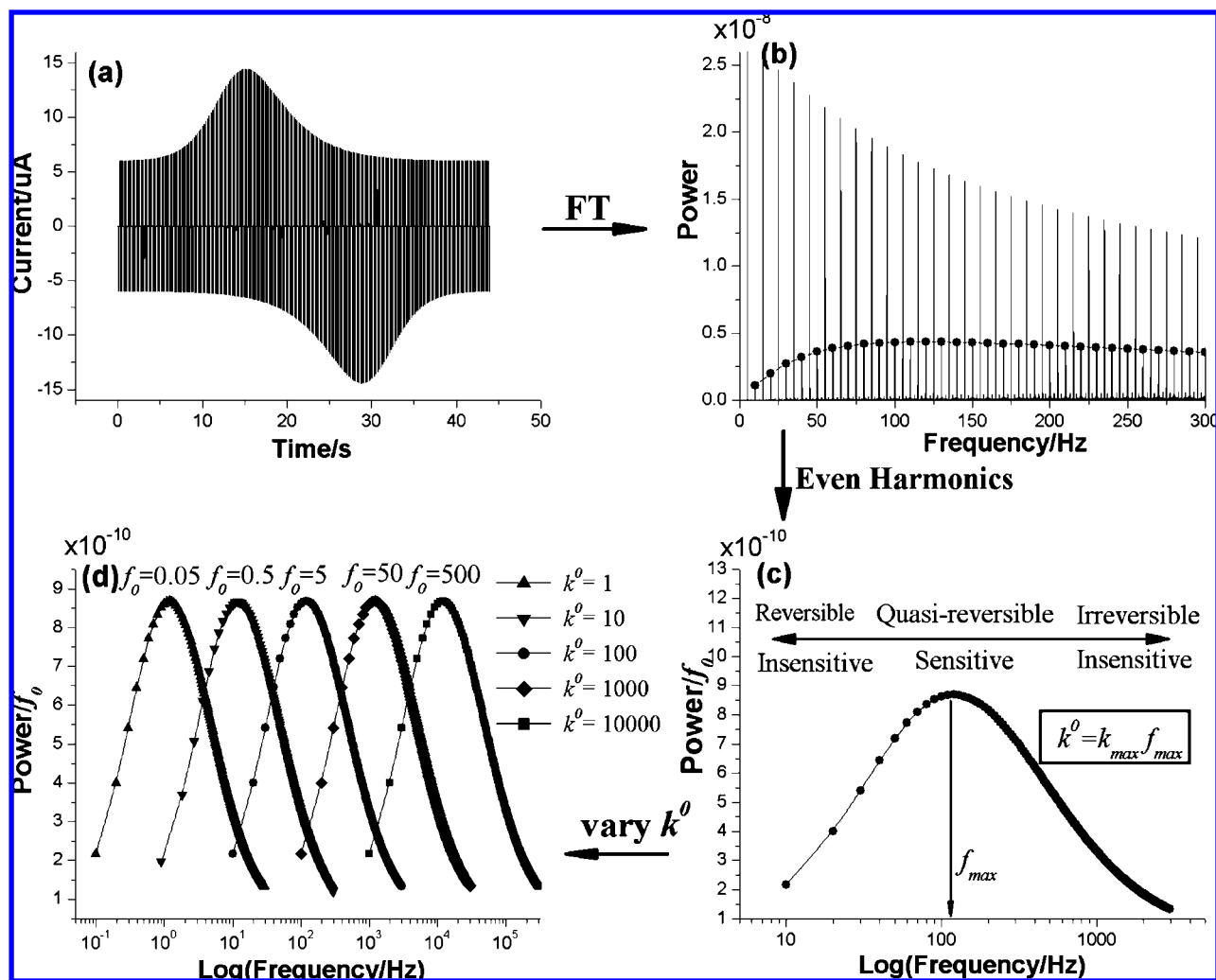


Figure 2. Data processing procedure applied in FT-SWV illustrated with simulated data. The (a) time domain total current is Fourier transformed into (b) the frequency domain power spectrum. Even harmonic components are highlighted and plotted with the frequency axis logarithmically scaled; (c) then a bell-shaped power spectrum is obtained. Even harmonic power spectra associated with different values of k^0 ranging in orders of magnitude are shown in part d; the value of k^0 and f_0 are labeled in the figure.

Table 1. Dependence of k_{max} on the Electron Transfer Coefficient (α) and the Product of the Amplitude of the Superimposed Square Wave and the Number of Electrons Transferred ($n\Delta E$), Obtained via Simulation^a

	$n\Delta E/\text{mV}$				
	40	60	80	100	120
$\alpha = 0.3$	1.72	1.32	0.94	0.72	0.52
$\alpha = 0.4$	1.78	1.39	1.02	0.70	0.48
$\alpha = 0.5$	2.00	1.51	1.11	0.82	0.57
$\alpha = 0.6$	1.85	1.47	1.08	0.80	0.64
$\alpha = 0.7$	1.79	1.39	1.00	0.78	0.60

^a Simulations undertaken with $k^0 = 100 \text{ s}^{-1}$, $v = 10 \text{ mV}$, and $f_0 = 1 \text{ Hz}$.

frequency extraction procedure used in this paper is to make sure that the critical frequency of an electrode process falls within the bandwidth of the applied square wave perturbation, namely, $f_0 < f_{\text{max}}/2$. Theoretically, we can choose any value of f_0 satisfying this requirement, and the extracted critical frequencies are identical. In practice, the use of an excitation with adequate low frequency, such as $f_0 < f_{\text{max}}/20$, is recommended in order to obtain a better result.

The value of k_{max} is unaffected by many factors, but k_{max} varied somewhat with the variation of the electron transfer coefficient (α), the product of the number of electrons transferred, and the amplitude of the square wave ($n\Delta E$). The dependences of these factors are listed in Table 1, from which we can see that the value of k_{max} is mostly affected by ΔE . Generally, a lower amplitude value for the superimposed square wave gives rise to small harmonic responses, while a higher amplitude value always leads to an obvious leakage of the attached material. An intermediate amplitude of the square wave is recommended for best results, and therefore, in our experiments, the amplitude of the applied square wave was 80 mV.

EXPERIMENTAL SECTION

Reagents. Horse heart cytochrome c was purchased from Sigma without further purification and stored at -20°C . The reactants 8-mercaptooctanoic acid (MOTA) and 11-mercaptopundecanoic acid (MUDA) were purchased from Aldrich Chemical. All other chemicals were of analytical grade and used as received. All of the aqueous solutions used in the voltammetric studies were prepared with doubly distilled water.

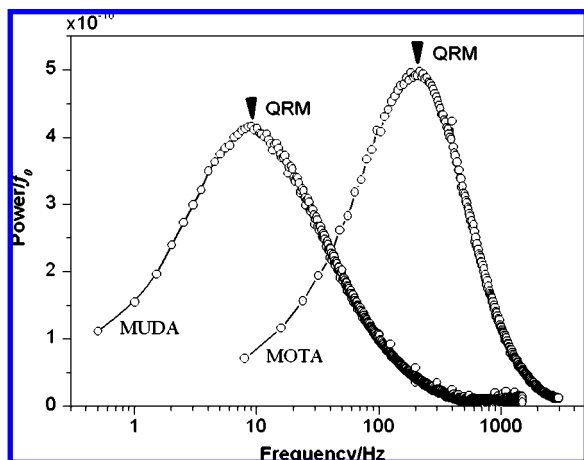


Figure 3. Even harmonic power spectra obtained from FT-SWV for cytochrome c bonded to a gold electrode with MOTA and MUDA. QRMs obtained are labeled in the figure.

Apparatus and Procedures. Detailed description of the home-built versatile arbitrary function voltammetric instrument and the signal processing algorithms used in our studies are available elsewhere.^{16,17} All experiments were arranged so that exactly 2^k (typically, $k = \sim 16\text{--}18$) points of current data were collected at a constant sampling rate of 48 kHz. A moving average of 8 or 16 data points was used for data collection. In order to compare rate constant values obtained using other voltammetric techniques, fast scan cyclic voltammetry (FSCV) and traditional SWV were also performed, using a CHI660B Electrochemical Workstation (Shanghai, China).

A conventional three-electrode configuration cell was employed for all electrochemical measurements, with an Ag/AgCl (saturated KCl, 0.199 V vs SHE) electrode as the reference electrode and a platinum wire as the auxiliary electrode. The gold working electrodes used were made from a gold wire (99.995%) of a radius of 1 mm. Prior to its use in the voltammetric experiments, the gold electrode was treated according to literature.^{12b} Cytochrome c was adsorbed onto the gold electrode as described elsewhere.¹⁸

In FT-SWV, the ΔE was 80 mV, and the dc potential ramp was initiated at 0.285 V and ended at -0.265 V. The f_0 and v parameters were dependent on the system under study: 0.25 Hz, 6.25 mV/s for MUDA and 4 Hz, 12.5 mV/s for MOTA. All experiments were performed at an ambient laboratory temperature, 24–26 °C. All potentials quoted are with respect to the Ag/AgCl electrode.

RESULTS AND DISCUSSION

Figure 3 shows the even harmonic power spectra obtained from FT-SWV for cytochrome c bonded to the gold electrode with MOTA and MUDA. We can see that the profiles of the even harmonic power spectra are bell-shaped and show QRMs as predicted by theory and simulation. The QRM can act as a probe for the rate constant just as in traditional SWV. The principles are identical, but it is much simpler to obtain the rate constant from a single multi-time scale excitation experiment than from multi single-time scale ones.

Previous research has shown that the electron transfer between cytochrome c and the gold electrode is a one electron transfer process and that the electron transfer coefficient is approximately 0.5. The value of the coefficient, k_{max} , is approximately 1.1 for our experimental conditions, according to Table 1. The extracted critical frequencies are 9.5 and 216 Hz for systems of MUDA and MOTA, respectively, indicating that the rate constants are 10 s^{-1} for MUDA and 238 s^{-1} for MOTA.

Generally, the values derived from FT-SWV, FSCV, and traditional SWV agree with each other with acceptable differences, which present a sound verification that the rate constants derived from FT-SWV are reliable. However, the obtained rate constants are smaller than those previously reported.¹⁸ Primitively, we attributed this inconsistency to the effect of the uncompensated resistance. From Bond's finding that the effect of the uncompensated resistance and slow electrode kinetics have the same influence on the amplitudes of the harmonics in large-amplitude Fourier transformed ACV,¹¹ it can be inferred that the uncompensated resistance will shift the critical frequency to a smaller value. However, the extracted critical frequencies remained unchanged even after the application of positive feedback in the experiments. This may be explained by the fact that the uncompensated resistance was negligible. Finally, we attributed this inconsistency to the experimental conditions. For example, almost all of the gold electrodes used in previous papers were Au (111), while the gold electrodes we used were simply fabricated with a gold wire. We also found that the rate constants, evaluated either with FT-SWV or other techniques, were sensitive to many experimental factors.

CONCLUSIONS

SWV performed in the frequency domain with Fourier transform shows great advantages with respect to the kinetics evaluation for surface-confined redox systems. Only a single FT-SWV scan need be conducted, from which the collected current response can be transformed into a frequency domain power spectrum. The even harmonic power spectra with the frequency axis logarithmically scaled is bell-shaped and shows a "quasi-reversible maximum" at the "critical frequency", f_{max} . The standard electron transfer rate constant, k^0 , can be calculated from the critical frequency, f_{max} , with a simple equation, $k^0 = k_{\text{max}} f_{\text{max}}$. Compared with most of the currently widely applied voltammetric techniques, FT-SWV provides a much simpler and faster alternative.

In fact, the "quasi-reversible maximum" can be regarded as the main difference between the quasi-reversible redox reactions of a dissolved and adsorbed redox couple.⁸ It exists not only in surface-confined redox systems but also in other surface processes, such as stripping voltammetry,¹⁹ surface electron transfer coupled with a chemical reaction,²⁰ charge transfer within a thin film,²¹ and ion transfer across a liquid/liquid interface.²² There are strong implications that the kinetic evaluation approach proposed in this paper is workable not only in surface-confined redox systems but also in all other kinds of diffusion limited processes. On the basis of investigations previously carried out

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by other workers, and the findings presented here, we are confident in applying FT-SWV to a wider range of electrochemical problems.

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