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Determination of Fast Electrode Kinetics Facilitated by Use of an Internal Reference

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S *Supporting Information*

ABSTRACT: The concept of using an internal reversible reference process as a calibration in the determination of fast electrode kinetics has been developed and applied with the technique of Fourier transformed large amplitude ac voltammetry to minimize the influence of errors arising from uncertainties in parameters such as electrode area (A), concentration (C), diffusion coefficient (D), and uncompensated resistance (R_u). Since kinetic parameters (electron transfer rate constant, k^0, and electron transfer coefficient, α) are irrelevant in the voltammetric characterization of a reversible reaction, parameters such as A, C, D, and R_u can be calibrated using the reversible process prior to quantification of the electrode kinetics associated with the fast quasi-reversible process. If required, new values of parameters derived from the calibration exercise can be used for the final determination of k^0 and α associated with the process of interest through theory-experimental comparison exercises. Reference to the reversible process is of greatest significance in diminishing the potentially large impact of systematic errors on the measurement of electrode kinetics near the reversible limit. Application of this method is demonstrated with respect to the oxidation of tetrathiafulvalene (TTF), where the $TTF^{0/\bullet+}$ process is used as a reversible internal reference for the measurement of the quasi-reversible kinetics of the $TTF^{\bullet+/2+}$ process. The more generalized concept is demonstrated by use of the $Fc^{0/+}$ (Fc = ferrocene) reversible process as an internal reference for measurement of the kinetics of the $Cc^{+/0}$ (Cc^+ = cobaltocenium) process. Via the internal reversible reference approach, a k^0 value of 0.55 cm s^{-1} was obtained for the $TTF^{\bullet+/2+}$ process at a glassy carbon electrode and 2.7 cm s^{-1} for the $Cc^{+/0}$ one at a carbon fiber microelectrode in acetonitrile (0.1 M Bu$_4$NPF$_6$).
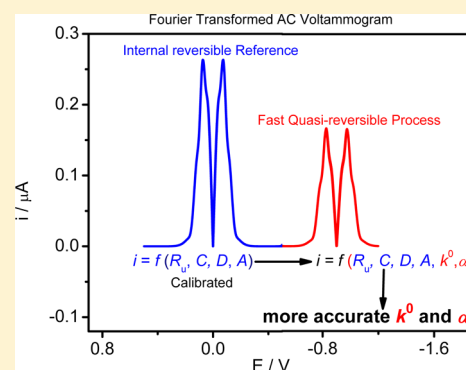
The quest to push the upper limit available for the reliable measurement of the kinetics of heterogeneous electron transfer reactions has been a constant driving force for electrochemists. To date, dc techniques that have been commonly employed for electrode kinetic measurements include polarography at a dropping mercury electrode[1] and cyclic voltammetry at a solid electrode.[2−4] In the case of dc cyclic voltammetry, the theory developed by Nicholson[2] has allowed electrode kinetic information to be acquired from the difference in the reduction (E_P^{red}) and oxidation (E_P^{ox}) peak potentials as a function of scan rate. In principle, use of this method with high scan rates allows the kinetics of rapid electron transfer reactions to be determined. However, significant limitations arise in the high scan rate regime due to the large influence of double layer charging and uncompensated resistance (iR_u effect).[3] In order to minimize the double layer and iR_u effects, microelectrodes and nano-electrodes have been used under either near steady-state dc voltammetric[5−8] or scanning electrochemical microscopic conditions.[8−14] These techniques also allow access to higher scan rate/mass transport rate regimes but they have stricter experimental requirements since the construction and characterization of small interfaces and electrodes are challenging.

In all voltammetric techniques, quantitative measurement of the heterogeneous electron transfer rate constant (k^0) of an electrode reaction close to the reversible limit is always prone to significant inaccuracies due to the relatively large impact of small but important uncertainties in some of the parameters such as R_u that need to be predetermined as part of the electrode kinetic evaluation exercise.[2,15,16] However, it has been established that access to higher order harmonics available with Fourier transformed large amplitude ac voltammetry (FTACV)[17] provides significant advantages over dc methods for the determination of fast electrode kinetics.[15] High kinetic sensitivity was available even under low frequency FTACV conditions in studies of the 7,7,8,8-tetracynoquinodimethane (TCNQ) reduction processes at macrodisk electrodes in acetonitrile (0.1 M Bu$_4$NPF$_6$), where a k^0 value of ~0.30 cm s^{-1} was estimated.[18] FTACV studies on the oxidation of tetrathiafulvalene (TTF) have also been undertaken in the same medium but at higher frequencies, and k^0 values of ≥1.0 and ~0.35 cm s^{-1} were reported for the $TTF^{0/\bullet+}$ and $TTF^{\bullet+/2+}$ processes, respectively.[19] In the FTACV method, the magnitudes of the higher order ac harmonic currents provide a sensitive measure of the electrode kinetics under conditions

where the background current is rejected.[15,18,20,21] Furthermore, k^0 and iR_u influence the characteristics of each harmonic in a distinctly different manner,[15] so that the contributions from these terms can be resolved. Thus, k^0 values up to at least 1.0 cm s^{-1} can be measured at moderate frequencies by the FTACV technique in organic solvents with macrodisk electrodes.[18,19,22]

Despite the undoubted ability of the FTACV method to measure fast rates of electron transfer, as with other voltammetric methods, systematic errors associated with parameters like concentration (C), diffusion coefficient (D), electrode area (A), and uncompensated resistance (R_u) mean that k^0 values reported near the reversible limit can contain significant uncertainty. On this basis, the k^0 values of ~0.30 cm s^{-1} reported for the TCNQ$^{0/\bullet-/2-}$ processes in acetonitrile (0.1 M Bu$_4$NPF$_6$) at low frequency could be considered to be an upper limit.[18]

To improve the reliability of k^0 determinations near the reversible limit, the internal reference concept is introduced in this paper. The method is based on the use of a reversible process as an internal reference for the measurement of the k^0 value for a quasi-reversible process. The kinetics of the fast TTF$^{\bullet+/2+}$ process can be measured accurately with reference to the reversible TTF$^{0/\bullet+}$ process. Additionally, the k^0 value for the quasi-reversible Cc$^{+/0}$ (Cc$^+$ = cobaltocenium) process is also reported using the reversible Fc$^{0/+}$ (Fc = ferrocene) process as an internal reference.

■ EXPERIMENTAL SECTION

Chemicals. Cobaltocenium hexafluorophosphate (CcPF$_6$, 98%, Aldrich), TTF (99%, Aldrich), Fc (≥98%, Aldrich) were used as received from the manufacturer. The supporting electrolyte *n*-tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$, 98%, Wako) was recrystallized twice from ethanol. Bu$_4$NPF$_6$ and distilled acetonitrile (MeCN, 99.9%, Aldrich) were dried and stored under nitrogen in a glovebox.

Instrumentation and Procedures. A CHI 400B electrochemical workstation was used for dc voltammetric studies. A BAS 100B electrochemical analyzer was used to determine R_u by analysis of the R_uC_{dl} time constant obtained from potential step chronoamperometry at a potential where no faradaic process was present.[3] FTACV experiments were undertaken with home-built instrumentation described elsewhere.[17]

All voltammetric experiments were undertaken in a glovebox under a nitrogen atmosphere at room temperature ($T = 22 \pm 1$ °C). A conventional electrochemical cell with a three electrode cell configuration was used. A macrodisk glassy carbon (GC) ($d = 1.0$ mm) or a microdisk carbon fiber ($d = 33$ μm) was used as the working electrode. A Pt wire placed in a glass capillary was used as a quasi-reference electrode and a Pt wire provided the auxiliary electrode. Working electrodes were polished initially with a 0.3 μm alumina slurry and then with a 0.05 μm alumina slurry on a polishing cloth (BAS), sonicated in water for a few seconds, rinsed with water and then acetone, and finally dried under nitrogen before use in electrode kinetic studies.

Simulations and Data Analysis. In the case of voltammetry at a macroelectrode, one-dimensional diffusion applies. For this case, simulated data were obtained with MECSim (Monash Electrochemistry Simulator) software (http://www.garethkennedy.net/MECSim.html). At microelectrodes, where two-dimensional diffusion operates, DigiElch software was used for the simulations.

Simulations of the electrode kinetics were based on use of Butler−Volmer theory[3] and use of the electron transfer reaction given in eq 1:

$$A \xrightleftharpoons{E^0, k^0, \alpha} A^+ + e^- \tag{1}$$

where E^0 is the reversible potential and α is the electron transfer coefficient. The ac voltammetric data obtained experimentally or by simulation were subjected to data analysis in which time-domain current data were converted to the frequency domain using a Fourier transformation algorithm to give the power spectrum.[17] Power spectrum data in the region containing the ac harmonics and aperiodic dc component were then subjected to band filtering followed by inverse Fourier transformation to provide the resolved aperiodic dc or ac components (harmonics) as a function of time or potential. Key parameters in the experiment/theory comparison exercise are C, R_u, E^0, D, k^0, α, T, A, ν (dc scan rate), f (ac frequency), ΔE (ac amplitude), and C_{dl} (double layer capacitance). R_u was determined experimentally from the R_uC_{dl} time constant at a potential where no faradaic current was present; E^0 was estimated from current minima of the second harmonic; C_{dl} was quantified from the background current in the fundamental harmonic at potentials where ac faradaic current is absent and k^0 and α were commonly extracted from a simulation experiment comparisons of higher order (5th and 6th) harmonic components. In order to define the potential dependence of C_{dl}, a nonlinear capacitor model was used where necessary, using the procedure described elsewhere.[23] Values of the D were estimated as described in the Results and Discussion section. Other parameters such as ν, f, ΔE, and T were assumed to be accurately known. Reversible processes were simulated using the same theory as for the quasi-reversible process but a very large k^0 value of 1×10^4 cm s^{-1} and $\alpha = 0.50$.

■ RESULTS AND DISCUSSION

Theoretical Estimation of the Upper Limit for k^0 Determinations. Simulations were initially undertaken to determine the upper limit available for k^0 determination by FTACV when using parameters of $f = 228.0$ Hz, $\Delta E = 80.0$ mV, $\alpha = 0.500$, $\nu = 0.100$ V s^{-1}, $R_u = 510$ Ω, $C = 1.00$ mM, $D = 2.00 \times 10^{-5}$ cm^2 s^{-1}, $C_{dl} = 20.0$ μF cm^{-2}, and $A = 0.00785$ cm^2. These parameters were chosen on the basis that they lie in the range typically encountered in electrode kinetic measurements in organic solvent (electrolyte) media.

In FTACV, k^0 is estimated to a large degree from the magnitude of peak current of the higher harmonic ac components, although of course the potential dependence of the current also is important. The high sensitivity to current magnitude is apparent from examination of the second and sixth harmonic components simulated as a function of k^0 in Figure 1. Analysis of the second harmonic data reveal that in principle, k^0 values ≤0.70 cm s^{-1} could be determined under the conditions relevant to this simulation since the current magnitude with a k^0 value of 0.70 cm s^{-1} is clearly distinguishable from the reversible one (differs by 10%). On the same basis, higher k^0 values ≤2.0 cm s^{-1} could be determined from the sixth harmonic data due to the higher kinetic sensitivity associated with these effectively shorter time scale data.

The peak current magnitude, which as noted above is one of the key factors used in k^0 determinations by FTACV, also is influenced by R_u, C, D, and A. Each of these parameters has an
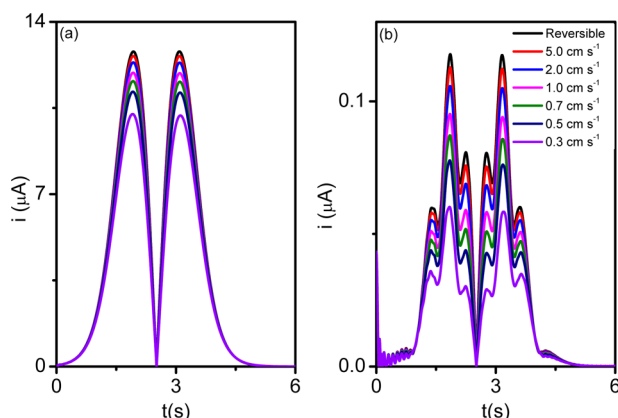
Figure 1. Simulated FTAC voltammograms (a) 2nd and (b) 6th harmonics obtained for the $A^{0/+}$ electrode process as a function of k^0 using parameters f = 228 Hz, ΔE = 80.0 mV, R_u = 510 Ω, D_A = 2.10 × 10^{-5} cm^2 s^{-1}, D_{A+} = 2.0 × 10^{-5} cm^2 s^{-1}, C_{dl} = 20.0 μF cm^{-2}, A = 0.00785 cm^2, C = 1.00 mM, ν = 0.100 V s^{-1}, T = 295 K, and α = 0.500.

uncertainty associated with their value, which affects the reliability of the determination of k^0. Furthermore, during the course of a series of experiments, additional uncertainties may arise for example from variation in R_u due to a change of the separation between working and reference electrodes, an increase in C due to solvent evaporation, or a decrease in A due to surface blocking. D is normally determined from the current values derived from either the dc steady-state or transient voltammetry which means that any uncertainties associated with values of C and A will lead to uncertainties in measured D values. Figure S1 shows the effect of R_u, C, D, and A on the currents associated with the largest peak associated with each ac harmonic component (1st−6th) for a reversible one-electron electron transfer reaction case when the uncertainty associated with each parameter is ±10%. Under the particular conditions chosen for this exercise, the influence of an error in R_u on the peak currents is the largest, although the impact of error in each of the parameters is moderate. In addition, iR_u also results in a unique peak splitting effect to the ac harmonics (not shown).[15] Because of the presence of R_u and C_{dl}, the influences of A and C, which are indistinguishable in their absence, are no longer identical since A and C_{dl} (but not C) influence the double layer charging current and hence alter the iR_u effect. Consequently, the effects from each parameter on the peak current (and other voltammetric characteristics) associated with each ac harmonic component are unique and remain distinguishable by FTACV. This allows k^0 to be obtained with high accuracy provided the electron transfer process differ significantly from that associated with a reversible process.[15] However, in the data analysis region close to the reversible limit, the moderate impact in peak current can translate into a large systematic error in the estimated k^0 as demonstrated in Figure 1. Even worse, the combined effects from the relatively small uncertainties associated with these parameters may result in a scenario where FTACV for a reversible process may be undistinguishable from that for a quasi-reversible process within experimental certainty when the process being determined is close to reversible (Figure S2). Consequently, an apparently measured k^0 value of ≥0.5 cm s^{-1} under conditions of Figure 1 may more realistically and conservatively be regarded as being reversible rather than quasi-

reversible and only a lower limit of k^0 rather than an absolute value should be reported.

Application of an Internal Reference to Assist in the Measurement of k^0. The above analysis suggests that the upper limit of k^0 measurement from the sixth harmonic under the conditions of Figure 1 could be extended from about 0.50 to 2.0 cm s^{-1}, if the impact of the systematic errors R_u, C, A, and D could be minimized from say 10% to 1%. To achieve this goal, it is now suggested that a compound such as Fc that gives rise to a reversible $Fc^{0/+}$ reference process can be introduced into the solvent (electrolyte).

Although, ideally the reference process and the quasi-reversible process of interest are completely independent with respect to kinetics and thermodynamics, the impact of systematic errors associated with A, D, C, and R_u for both processes are expected to be identical. By scanning the potential over a sufficiently wide range, both voltammetric responses can be obtained from a single measurement using exactly the same working, reference, and auxiliary electrode configuration. This condition implies that (a) identical values of A and R_u apply to both processes; (b) systematic error associated with C, if due to say solvent evaporation, will be the same; and (c) if both D values are determined in the same solution using the same electrochemical technique (for example, the limiting currents of a steady-state voltammograms) then errors present in D should be similar. The D value for Fc has been reported commonly to have a value of 2.4 × 10^{-5} cm^2 s^{-1} in acetonitrile (0.1 M n-tetraethylammonium perchlorate) at 25 °C and is not strongly electrolyte dependent.[24] In addition to its usual role as an internal reference for the potential scale,[25−27] the $Fc^{0/+}$ process is now proposed to have a role as a reference in kinetic determinations. In a special case, if a species undergoes two or more well-resolved one-electron processes with one of them being reversible, introducing a reversible reference process is no longer needed since it is already available.

The principles underpinning the internal reversible reference process concept are generally applicable to all forms of voltammetry. However, the method can be very conveniently applied under FTACV conditions at macrodisk electrodes with a single calibration, because all of the aperiodic dc and ac harmonic components, which provide information on different time scales and have different sensitivity to each parameter (Figure S1), are all obtained from the one experiment. By contrast, dc cyclic voltammetry at a macrodisk electrode requires a new experiment for each scan rate and micro-electrode voltammetry under steady state conditions requires a series of experiments with electrodes of different radii, which introduces additional uncertainty and more extensive need for calibration.

Protocol for Using an Internal Reference in Electrode Kinetic Measurements. The following protocol can be adopted when using the internal reference method for the determination of fast electrode kinetics:

Step 1: If not independently known, determine the C, D, A, and R_u values for the species involved in both the internal reference process and the fast quasi-reversible process of interest. Many strategies are available to achieve predetermined values of these parameters: (a) C can be determined based on the known mass of the pure solid form of the electroactive species and known volume of the solution; (b) D may be known from literature report or obtained from peak currents derived from dc transient voltammetry (under reversible conditions and when effect of R_u is negligible) and use of the

Randles–Sevcik relationship[3] or preferably from the plateau current derived from steady-state voltammetry[3] or convolution voltammetry[28−33] since this parameter is devoid of any influence from R_u, k^0, and α; (c) A can be either taken as the geometrical area or more precisely calculated from the peak current of a reversible process, such as $[Ru(NH_3)_6]^{3+/2+}$ or $Fc^{+/0}$, associated with a species (i.e., $[Ru(NH_3)_6]^{3+}$ or Fc) with known diffusion coefficient,[3] and (d) R_u can be estimated from the R_uC_{dl} time constant obtained from a potential step chronoamperometric/chronocoulometric measurement or from impedance spectroscopy.[3] These predetermined or independently known A, C, D, and R_u values are considered to be their original values in this paper.

Step 2: Confirm the accuracy of the relevant original A, C, D, and R_u values by theory-experiment comparisons for the reversible internal process and if necessary introduce new values for these parameters via this calibration process. Excellent agreements between experimental and simulated data need to be achieved for all harmonics when "correct" values of all parameters are employed.

Step 3: If required, the calibrated values for A and R_u obtained for the reversible reference process would replace the predetermined values otherwise used for the fast quasi-reversible process. The calibrated values for D and C used to generate theoretical data for the fast quasi-reversible process can be obtained from the ratio of their original values and calibrated ones established for the reversible internal process.

Step 4: Use the values assigned in Step 3 for the determination of electrode kinetics of the fast quasi-reversible process through a theory-experiment comparison exercise.

It should be noted that under stationary conditions the mass transport limited current associated with a disc electrode is governed by D/a^2 (a = radial of the disc electrode) and nC (n = number of electron transferred). Therefore, in principle, a time dependent mass transport limited current, which is governed by linear diffusion in a short time scale but radial diffusion in a long time scale can be used for the calibration of D, A, and C,[28,33,34] but not R_u, the most crucial parameter for kinetic determination.

Examples of the Use of the Internal Reference Method. To demonstrate the practical utility of the internal reference concept, two example processes were chosen: Case 1, use of $Fc^{0/+}$ as the internal reference process and $Cc^{+/0}$ as a fast quasi-reversible process, where the internal reference is derived from an independent electroactive species; and Case 2, oxidation of TTF, with the initial $TTF^{0/\bullet+}$ process used as the reversible internal reference process to determine the kinetics of the quasi-reversible $TTF^{\bullet+/2+}$ process. Case 2 represents an example where both processes are derived from same electroactive species.

Case 1: Kinetics of the $Cc^{+/0}$ process using the reversible $Fc^{0/+}$ Process As an Internal Reference. The $Fc^{0/+}$ reaction is a well-known reversible process with a k^0 value of 11.6 cm s⁻¹ reported at a Pt nanoelectrode in acetonitrile (0.1 M Bu_4NPF_6),[8] probably being the most reliable value available. This outer sphere process is also very fast at other electrode surfaces and can be assumed to be reversible under all FTACV conditions employed in this study. On this basis, the electrode kinetics of the quasi-reversible $Cc^{+/0}$ process in acetonitrile (0.1 M Bu_4NPF_6) can be determined using the $Fc^{0/+}$ process as a reversible reference. Initial D_{Fc} and D_{Cc+} values were estimated from analysis of peak height versus scan rate data obtained by dc linear sweep voltammetry from a solution containing 1.35

mM Fc and 1.32 mM Cc^+ (concentrations established by dissolving weighed quantities of relevant solute in known solution volume) simultaneously present in acetonitrile (0.1 M Bu_4NPF_6). Oxidation of Fc to Fc^+ and reduction of Cc^+ to Cc^0 give rise to chemically reversible one-electron transfer processes at a GC electrode (A = 0.00785 cm² assumed on the basis of geometric area) (see Figure 2). Since both processes are

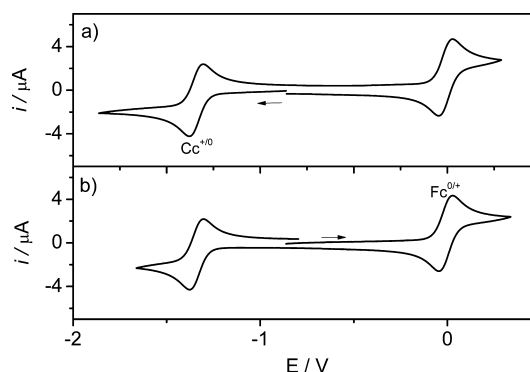**Figure 2.** Direct current voltammograms obtained at a GC macrodisk electrode (d = 1.0 mm) starting with (a) reduction of 1.32 mM Cc^+ and (b) oxidation of 1.35 mM Fc in acetonitrile (0.1 M Bu_4NPF_6), ν = 0.100 V s⁻¹.

reversible on the dc voltammetric time scale, a plot of the magnitudes of the relevant peak currents ($|i_p|$) versus the square root of scan rate was used to determine both diffusion coefficients using the Randles–Sevcik relationship,[3]

$$|i_p| = 0.4463nFA\left(\frac{nFD\nu}{RT}\right)^{1/2}C \qquad (2)$$

On this basis and ignoring any influence of iR_u, D_{Cc^+} is calculated to be 2.2×10^{-5} cm² s⁻¹ (Figure 2a) and close to literature values,[35] and $D_{Fc} = 2.4 \times 10^{-5}$ cm² s⁻¹ (Figure 2b), which also is consistent with literature values.[3,24] $E^0_{Cc^{+/0}}$ for the $Cc^{+/0}$ couple is calculated as −1.326 V vs $Fc^{0/+}$ from analysis of the midpoint potential (average of oxidation and reduction peak potentials) of dc cyclic voltammograms (Figure 2), again consistent with the literature data.[36] Because of the consistency between the measured D_{Fc} with the reported value in the literature, the known geometric area of 0.00785 cm² was therefore considered accurate for A. An independent estimate of R_u = 450 Ω was obtained from analysis of the R_uC_{dl} time constant measured in a potential region in the absence of faradaic processes.

Initial experiments to evaluate k^0 for the $Cc^{+/0}$ process were undertaken by FTAC voltammetry at a GC electrode using a sine wave frequency of 228 Hz and amplitude 80 mV along with a dc scan rate of 0.149 V s⁻¹ over the potential region where both the $Fc^{0/+}$ oxidation and $Cc^{+/0}$ reduction processes are simultaneously present. Under these conditions, excellent signal-to-noise ratios are obtained for the dc aperiodic component and for at least the first seven ac harmonic components for both the $Fc^{0/+}$ and $Cc^{+/0}$ processes.

In order to determine $k^0_{Cc^{+/0}}$, the reference $Fc^{0/+}$ process was modeled on the basis of reversible theory to fit the aperiodic dc and ac harmonic components. Polynomial fitting of C_{dl} based on the formula[23] $C_{dl} = c_0 + c_1E + c_2E^2 + c_3E^3 + c_4E^4$ (where E is the potential versus the reference electrode) was achieved with c_0 = 25.5, c_1 = −5.87, c_2 = 5.64, c_3 = 7.110, and c_4 = −2.40 μF cm⁻² using the non-Faradaic region of the first harmonic.

Excellent experiment-theory agreement has been obtained for the aperiodic dc component and 1st−6th harmonics were obtained for the reference $Fc^{0/+}$ process with this from of estimation of the potential dependence of C_{dl}, along with $D_{Fc} = 2.4 \times 10^{-5}$ cm^2 s^{-1}, $C_{Fc} = 1.35$ mM, $A = 0.00785$ cm^2, and $R_u = 490$ Ω. This result provides reassurance that the concentration and diffusion coefficient for Fc (and Cc^+) and electrode area are correct, with the only change resulting from calibration being made in the value of R_u (450 to 490 Ω). Consequently, $D_{Cc^+} = 2.2 \times 10^{-5}$ cm^2 s^{-1}, $C_{Cc^+} = 1.32$ mM, $A = 0.00785$ cm^2 along with the newly calibrated $R_u = 490$ Ω were then used as known parameters to model the $Cc^{+/0}$ quasi-reversible process with $k^0_{Cc^{+/0}}$ and α values treated as unknown variables. Comparison of the experiment and theory derived on this calibration basis is given in Figure 3, where the dc aperiodic component is plotted
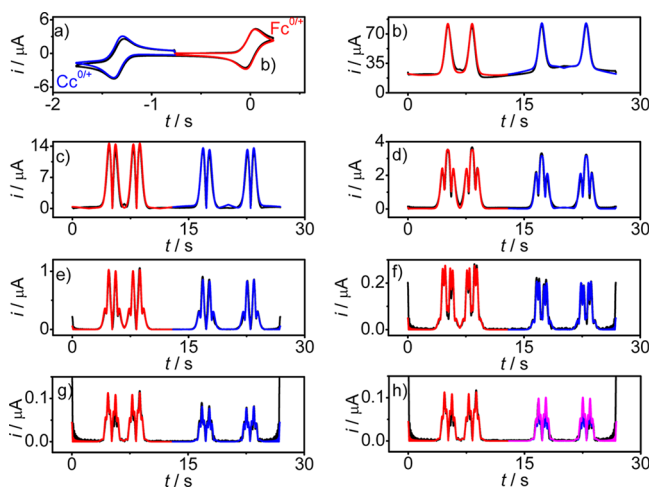
Therefore, to minimize the influence of iR_u, higher frequency FTACV data were obtained for oxidation of Fc and reduction of Cc^+ at a carbon fiber microelectrode (nominal $d = 33$ μm) rather than at the macrodisk GC electrode. Simulations were undertaken with DigiElch to accommodate radial diffusion. A frequency of 1228 Hz was used instead of 228 Hz to achieve enhanced kinetic sensitivity. Simulations based on radial diffusion were undertaken on the $Fc^{0/+}$ process and then calibrated experimental parameters used in simulations of the $Cc^{+/0}$ process also based on radial diffusion with $R_u = 24\,000$ Ω (calibrated value), $A = 8.54 \times 10^{-6}$ cm^2, $D_{Cc^+} = 2.2 \times 10^{-5}$ cm^2 s^{-1} (determined as above), $C_{Cc^+} = 2.20$ mM (calibrated value) and $C_{dl} = 12.88$ μF cm^{-2}. Via this procedure and assuming $\alpha = 0.50$, a value of $k^0_{Cc^{+/0}} = 2.7$ cm s^{-1} was deduced from the theory and experiment comparisons shown in Figure 4 with data on

Figure 3. Comparison of experimental (black —) FTAC voltammograms obtained from 1.32 mM Fc and 1.35 mM Cc^+ in acetonitrile (0.1 M Bu$_4$NPF$_6$) at a GC electrode with simulated voltammograms for $Fc^{0/+}$ (red —) and $Cc^{+/0}$ (blue —) processes (a) aperiodic dc component (b−g) 1st −6th harmonics with simulation and experimental parameters that include $\nu = 0.149$ V s^{-1}, $A = 0.00785$ cm^2, $f = 228$ Hz, $\Delta E = 80$ mV, $D_{Fc} = 2.4 \times 10^{-5}$ cm^2 s^{-1}, $D_{Cc^+} = 2.2 \times 10^{-5}$ cm^2 s^{-1}, calibrated $R_u = 490$ Ω, $k^0_{Cc^{+/0}} = 2.0$ cm s^{-1}, $\alpha = 0.50$ (assumed value), C_{dl} ($c_0 = 25.5$, $c_1 = -5.87$, $c_2 = 5.64$ and $c_3 = 7.11$, $c_4 = -2.40$) μF cm^{-2}, $T = 295$ K and the $Fc^{0/+}$ process assumed to be reversible. (h) Comparison of the 6th harmonic for the $Co^{+/0}$ process with a simulated fully reversible (pink —) process.
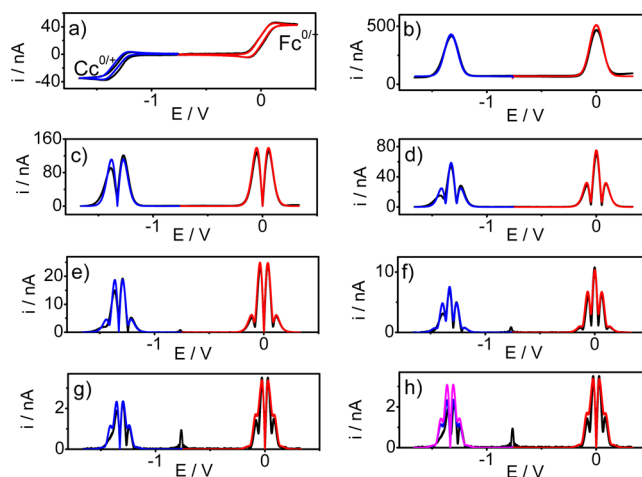
Figure 4. Comparison of experimental (black —) FTAC voltammograms obtained from calibrated 2.40 mM Fc and calibrated 2.20 mM Cc^+ in acetonitrile (0.1 M Bu$_4$NPF$_6$) at a carbon fiber electrode with simulated voltammograms for $Fc^{0/+}$ (red —) and $Cc^{+/0}$ (blue —) processes (a) aperiodic dc component (b−g) 1st −6th harmonics with simulation and experimental parameters that include $\nu = 0.298$ V s^{-1}, $A = 8.54 \times 10^{-6}$ cm^2, $f = 1228$ Hz, $\Delta E = 80$ mV, $D_{Fc} = 2.4 \times 10^{-5}$ cm^2 s^{-1}, $D_{Cc^+} = 2.2 \times 10^{-5}$ cm^2 s^{-1}, calibrated $R_u = 24\,000$ Ω, $k^0_{Cc^{+/0}} = 2.70$ cm s^{-1}, $\alpha = 0.5$, $C_{dl} = 12.88$ μF cm^{-2}, $T = 295$ K and the $Fc^{0/+}$ process assumed to be reversible. (h) Comparison of the 6th harmonic for the $Co^{+/0}$ process with simulated fully reversible (pink —) process.

in the potential domain and ac harmonics in the time domain. Excellent agreement between theory and experiment is obtained with $k^0_{Cc^{+/0}} = 2.0$ cm s^{-1} and $\alpha = 0.50$ (assumed value). However, use of a k^0 value of 2.0 cm s^{-1} produces simulated data that are indistinguishable from that predicted for reversible behavior in the first five harmonics, with a small departure from reversibility only becoming evident in the kinetically more sensitive sixth harmonic. On the basis of assuming complete reliability of a determination based on the sixth harmonic, $k^0_{Cc^{+/0}}$ is estimated to be 2.0 cm s^{-1}, with $k^0_{Cc^{+/0}} \geq 2.0$ cm s^{-1} probably being the preferred form of presentation of the result, although it is clear that $k^0_{Fc^{0/+}} > k^0_{Cc^{+/0}}$.

In order to measure $k^0_{Cc^{+/0}}$ more reliably, in principle a higher frequency ac perturbation could be used to shorten the time scale of the measurement. However, the enhanced iR_u at the macrodisk glassy carbon electrode has a higher impact under higher frequency conditions, which decreases the quality of the higher order ac harmonics, so little, if anything, is gained.

this occasion provided in the current−potential rather than current−time format. The full set of simulation and experimental parameters used in this exercise are provided in the caption to Figure 4. On the basis of our previous study[37] and the results presented in Figure S3, the symmetry of even harmonic components is highly sensitive to α. However, the "asymmetry" present in the negative potential direction scan of the $Cc^{+/0}$ process and not produced by theory based on $\alpha = 0.50$, is not evident if the initial scan direction was positive rather than negative. Although the reason for this particular asymmetry is unknown, the results suggest that $\alpha = 0.5 \pm 0.1$ for the $Cc^{+/0}$ process. Furthermore, under these higher frequency conditions at a microelectrode it is now obvious that current magnitude per unit concentration for the $Cc^{+/0}$ process is significantly less than for that of the $Fc^{0/+}$ process in the higher harmonics when the difference in their diffusion coefficients is taken into account. Lower Cc^+ concentration data could not be analyzed because the contribution of background

is relatively large and its significant potential dependence cannot be modeled using DigiElch software.

$k^0_{Cc^{+/0}}$ values have been reported in a range of solvent/electrolyte media and with different electrodes and techniques. $k^0_{Cc^{+/0}}$ values of 0.052 cm s^{-1} at a 1.6 mm diameter Pt electrode,[35] 0.3 cm s^{-1} at a 25 μm radius Hg hemisphere electrode,[38] and 3.0 cm s^{-1} at a dropping Hg electrode[39] were obtained in acetonitrile (Bu$_4$NPF$_6$ or Bu$_4$NClO$_4$) media with $k^0_{Cc^{+/0}}$ values of 1.55, 0.37, and 1.75 cm s^{-1} at the 25 μm radius Hg/Au hemispherical electrode, 12.5 μm radius Pt electrode, and 5 μm radius Au electrode, respectively, also being reported in dimethylformamide (0.1 M Bu$_4$NClO$_4$).[40] Direct comparison of our estimated value with those reported is not possible since none of the literature values were obtained under identical conditions to those employed in this study. However, our value is one of the highest values reported. Recent work by Mirkin with nanoelectrodes[8] and FTAC voltammetric studies[41] on the kinetics of the Fc$^{0/+}$ and [Ru(NH$_3$)$_6$]$^{3+/2+}$ processes also have generated considerably higher k^0 values than literature ones by minimizing or accounting for iR_u drop.

The inherently slower k^0 value observed at GC and carbon fiber electrodes for the Cc$^{+/0}$ process relative to the Fc$^{0/+}$ one can be explained in terms of Marcus theory where the reorganization energy is predicted to play a vital role in the electrode kinetics.[35,42,43] Plausibly, a higher reorganization energy for the Cc$^{+/0}$ process compared to that for the Fc$^{0/+}$ system[40] leads to the slower kinetics for the former process. However, the Frumkin double layer effect also may be important as the processes occur at very different potentials.[3] Insufficient data are available to introduce double layer corrections to the k^0 values obtained in this study.

Case 2: Determination of the Electrode Kinetics of TTF$^{•+/2+}$ Process Using the Reversible TTF$^{0/•+}$ Process As the Internal Reference. The k^0 values for the TTF$^{0/•+}$ ($k^0_{TTF^{0/•+}}$) and TTF$^{•+/2+}$ ($k^0_{TTF^{•+/2+}}$) processes in acetonitrile (0.1 M Bu$_4$NPF$_6$) have been reported to be $k^0_{TTF^{0/•+}} \geq 1.0$ cm s^{-1} and $k^0_{TTF^{•+/2+}} = 0.30 \pm 0.05$ cm s^{-1}, respectively.[19] If all the experimental parameters are assumed to be correctly known in a conventional simulation-experiment comparison of the TTF$^{•+/2+}$ process derived from oxidation of 1.0 mM TTF (f = 233 Hz, ΔE = 80 mV, ν = 0.089 V s^{-1}, R_u = 590 Ω, C = 1.0 mM, D_{TTF} = 2.1 × 10^{-5} cm^2 s^{-1}, $D_{TTF^{•+}}$ = 1.9 × 10^{-5} cm^2 s^{-1}, $D_{TTF^{2+}}$ = 1.6 × 10^{-5} cm^2 s^{-1} (all D values were obtained previously from the steady-state voltammograms of the corresponding species at a microelectrode[19]), A = 0.00785 cm^2, T = 295 K, $k^0_{TTF^{0/•+}}$ = −0.074 V and $k^0_{TTF^{•+/2+}}$ = 0.311 V vs Fc$^{0/+}$, C_{dl} (c_0 = 10.0 c_1 = 0.02 and c_2 = 4.5) μF cm^{-2} and α = 0.50 (assumed value), then a value of $k^0_{TTF^{•+/2+}}$ = 0.35 cm s^{-1} is found for the TTF$^{•+/2+}$ process which is in good agreement with the previously reported value of 0.30 ± 0.05 cm s^{-1}.[19]

However, with the reversible internal reference method, C, R_u, D, and A parameters associated with the internal reference are calibrated to give C = 1.0 mM, R_u = 590 Ω, D_{TTF} = 1.9 × 10^{-5} cm^2 s^{-1}, $D_{TTF^{•+}}$ = 1.7 × 10^{-5} cm^2 s^{-1}, $D_{TTF^{2+}}$ = 1.45 × 10^{-5} cm^2 s^{-1}, and A = 0.00800 cm^2 through a theory-experiment comparison exercise shown in Figure 5. These calibrated D values were obtained by knowing the ratio of the initial and the calibrated D_{TTF} for the reversible TTF$^{0/•+}$ process. This means that D_{TTF}, $D_{TTF^{•+}}$, $D_{TTF^{2+}}$, and A have now changed from 2.1 × 10^{-5} cm^2 s^{-1}, 1.9 × 10^{-5} cm^2 s^{-1}, 1.6 × 10^{-5} cm^2 s^{-1}, and 0.00785 cm^2, respectively, to 1.9 × 10^{-5} cm^2 s^{-1}, 1.7 × 10^{-5} cm^2 s^{-1}, 1.45 × 10^{-5} cm^2 s^{-1}, and 0.00800 cm^2, respectively. The use of these calibrated A, C, D, and R_u
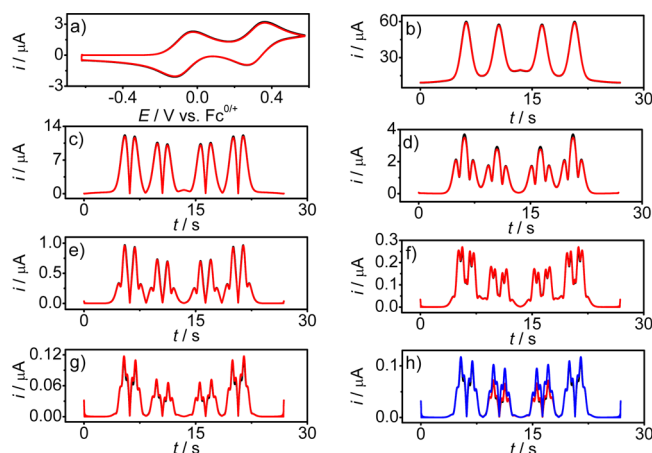

Figure 5. Comparison of simulated (red —) and experimental (black —) FTAC voltammograms obtained for the TTF$^{0/•+/2+}$ oxidation processes with 1.0 mM TTF in acetonitrile (0.1 M Bu$_4$NPF$_6$) at a GC electrode using the TTF$^{0/•+}$ process as a reversible internal reference (a) dc component (b−g) 1st−6th harmonics. Simulation parameters include f = 233 Hz, ΔE = 80 mV, ν = 0.089 V s^{-1}, R_u = 590 Ω, calibrated D_{TTF} = 1.9 × 10^{-5} cm^2 s^{-1}, calibrated $D_{TTF^{•+}}$ = 1.7 × 10^{-5} cm^2 s^{-1}, calibrated $D_{TTF^{2+}}$ = 1.45 × 10^{-5} cm^2 s^{-1}, calibrated A = 0.00800 cm^2, T = 295 K, $k^0_{TTF^{0/•+}}$ = −0.074 V, $k^0_{TTF^{•+/2+}}$ = 0.311 V vs Fc$^{0/+}$, $k^0_{TTF^{•+/2+}}$ = 0.55 cm s^{-1}, $\alpha_{TTF^{•+/2+}}$ = 0.50 and C_{dl} (c_0 = 10.0, c_1 = 0.02, and c_2 = 4.5) μF cm^{-2}, (h) comparison of the 6th harmonic for the TTF$^{+/2+}$ process with simulated fully reversible (pink —) process.

values in the determination of the electrode kinetics of the TTF$^{•+/2+}$ process in a second theory-experimental comparison exercise gives $k^0_{TTF^{•+/2+}}$ = 0.55 cm s^{-1} which is slightly higher than the value of 0.35 cm s^{-1} obtained without the internal reference. It should be noted that agreement of theory and experiment is now almost perfect within the resolution of the Figure 5 plots for both processes. Since the TTF$^{•+/2+}$ process exhibits lower electrochemical reversibility with respect to the measurement time scale in comparison with the Cc$^{+/0}$ process (Figure 4 and Figure S3), the symmetry of the even harmonics associated with this process is even more sensitive to α, as revealed from the results shown in Figure S4. On this basis, an α value of 0.50 ± 0.05 can be assigned to the TTF$^{•+/2+}$ process.

Comparable values for $k^0_{TTF^{•+/2+}}$ and α were also obtained with a lower TTF concentration of 0.12 mM using the internal reversible reference method (Figure S5). Without using the TTF$^{0/•+}$ process as the internal reversible reference process, experimental data for the TTF$^{•+/2+}$ process also agree well with the simulated ones (Figure S6) for a reversible process with C = 0.12 mM, R_u = 910 Ω, $D_{TTF^{•+}}$ = 2.0 × 10^{-5} cm^2 s^{-1}, $D_{TTF^{2+}}$ = 1.7 × 10^{-5} cm^2 s^{-1}, and A = 0.00785 cm^2, instead of those given in the caption to Figure S5, again confirming that application of the internal reversible reference method is crucial in improving prospects for obtaining a correct $k^0_{TTF^{•+/2+}}$ value.

■ CONCLUSION

In FTACV electrode kinetics studies, peak current magnitudes of the ac harmonics are of paramount importance in the estimation of k^0 values. In this study, a heuristic method of data analysis was used to determine k^0. Ideally, it is desirable to provide a full statistical analysis of uncertainties in all parameters,[44] but this is an extremely complex task, as the number of variables contributing to the overall uncertainty is substantial. Calibration based on simplicity available in the theory for a reversible process is therefore proposed as a

method that minimizes the risk of introducing significant levels of systematic error. In this context, use of a reversible electrode process as an internal reference is shown to improve the reliability of k^0 values reported by FTACV for quasi-reversible processes particularly when the kinetics are very fast and approach the reversible limit. The internal reference method reduces systematic errors that result from uncertainties in C, D, A, and R_u. The same strategy also should be useful in the quantitative determination of electrode kinetics by other voltammetric methods.

Finally, it should be noted that while the $Fc^{0/+}$ process is an ideal internal reversible reference for electrode kinetic measurements in organic solvents, addition of the reference compound should not change the physical properties of the solvent (electrolyte) system. In ionic liquids, the D values for both Fc and Cc^+ determined from measurements on solutions containing only one species may be affected when both species are simultaneously present.[45]

ASSOCIATED CONTENT

Ⓢ Supporting Information

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Additional experimental details and data (PDF)

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