Fourier transformed alternating current voltammetry in electromaterials research: direct visualisation of important underlying electron transfer processes

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Abstract

Recent advances in materials science have significantly broadened the range of electrodes available for use in dynamic forms of electrochemistry. In the modern era of dc voltammetry when the kinetic-based model of electron transfer with coupled chemical reactions was introduced, initial emphasis in theory-experiment comparison was placed on use of the ideal homogenous liquid mercury electrode with significant attention also given to polycrystalline and faceted metal electrodes. Nowadays, there are a plethora of carbon-based electrodes such as glassy carbon, edge and basal plane graphite, boron doped diamond, graphene and carbon nanotubes that may be extremely heterogeneous. These are supplemented by chemical modifications designed for example to improve the efficiency of electrocatalysis. In this review, it is shown that analysis of the higher harmonics available in large amplitude Fourier transformed alternating current
voltammetry (FTacV) allows key processes to be detected, that are masked under commonly used dc voltammetric conditions. In particular it is shown how underlying fast electron processes that facilitate carbon dioxide reduction at tin electrodes and oxygen evolution at cobalt modified carbon based electrodes can be directly detected and analysed for the first time. FTacV also experimentally reveals that structural defects or ad atoms can give rise to well-defined higher order ac harmonics suggesting that a fast electron transfer process is associated with the active sites during electrocatalytic oxidation or reduction. Importantly, electron transfer processes often can be evaluated by FTacV in the presence and absence of the electrocatalysts, unlike dc voltammetric methods. The ability to analyse third and higher order ac harmonics that are essentially devoid of background charging current and which allow the electron transfer and catalytic steps to be resolved presents new opportunities for fundamental advances in understanding complex electrochemical reaction mechanisms taking place at heterogeneous electrodes. Related advantages in studying electron transfer of surface confined metallo-enzymes or proteins in the presence and absence of their catalytically oxidised or reduced biologically relevant substrate partners are also surveyed. Finally, prospects for providing quantitative accounts of complex reactions at highly heterogeneous electrodes by FTacV are considered.

**Introduction**

Electrocatalysis coupled with renewable energy including solar, wind and hydro represents a sustainable pathway to achieving a viable energy future. Important fuels and chemicals, such as hydrogen, hydrocarbons, oxygenates and ammonia, can in principle be produced from water, carbon dioxide and nitrogen using electricity [1]. Electrocatalysis also can have a significant impact in diverse field such as organic synthesis, sensors and degradation of pollutants [2].
Although existing paradigms summarising the accumulated experience in the design of efficient catalysts implemented with the aid of advances in materials science are useful, challenges still exist in achieving further breakthroughs. In particular, opportunities for the development of more efficient chemical technologies could be enhanced if underpinned by a detailed quantitative understanding of electron transfer and coupled catalytic reaction mechanisms. A major obstacle to understanding the electrochemical behaviour of catalytic reactions is the inability of direct current (dc) voltammetry to resolve the electron transfer and coupled chemical reactions.

The majority electrocatalytic reactions can be divided into three classes [3’’]: (a) heterogeneous (Equations 1-2); (b) homogeneous (Equations 3-4); (c) mediated homogeneous catalytic processes (Equations 5-7). In these equations, R(surf or soln) and O(surf or soln) are the surface-confined or dissolved reduced and oxidised forms of the catalyst, respectively; S(soln) and P(soln) are the dissolved substrate and product, respectively; MR(soln) and MO(soln) are the dissolved reduced and oxidised forms of the mediator, respectively.

(a) Heterogeneous electrocatalytic processes:

\[ R(\text{surf}) \leftrightarrow O(\text{surf}) + e^- \]  

\[ O(\text{surf}) + S(\text{soln}) \rightarrow R(\text{surf}) + P(\text{soln}) \]  

(b) Homogenous electrocatalytic processes:

\[ R(\text{soln}) \leftrightarrow O(\text{soln}) + e^- \]  

\[ O(\text{soln}) + S(\text{soln}) \rightarrow R(\text{soln}) + P(\text{soln}) \]
(c) Mediated homogenous electrocatalytic processes:

\[ M_R(\text{soln}) \rightleftharpoons M_O(\text{soln}) + e^- \] \hspace{1cm} (5)

\[ R(\text{soln}) + M_O(\text{soln}) \rightarrow O(\text{soln}) + M_R(\text{soln}) \] \hspace{1cm} (6)

\[ S(\text{soln}) + O(\text{soln}) \rightarrow P(\text{soln}) + R(\text{soln}) \] \hspace{1cm} (7)

In all cases, the electron transfer (E) reaction is coupled with one or more chemical (C) reactions, which makes a catalytic (EC') process highly challenging with respect to quantitative modelling [4', 5-6]. An EC' process can be summarised as \( A \pm e^- \overset{E^0, k^0, \alpha}{\leftrightarrow} B \overset{k_f or k_b}{\leftrightarrow} C \), where \( E^0 \) is the reversible formal potential for the E step; \( k^0 \) is the heterogeneous electron charge transfer rate constant at \( E^0 \); \( \alpha \) is the charge transfer coefficient for the E step and \( k_f \) and \( k_b \) are forward and backward rate constants for the C step.

The vast majority of existing mechanistic studies of catalytic reactions are based on dc voltammetry. However, in general this method only provides information on the magnitude of the increase in current under catalytic turnover conditions, which usually does not allow the full details of both the electron transfer and coupled chemical reactions to be resolved or the impact of heterogeneity in modern electrodes to be assessed. Conversely, alternating current (ac) voltammetry provides a much more powerful tool to resolve and parameterise the electron transfer processes underpinning the catalytic reaction. Ac voltammetry, when subjected to Fourier transformation (FT), allows a series of resolved harmonic data to be obtained. The third and higher harmonic ac components are highly sensitive to electron transfer kinetics, devoid of non-faradaic background current contributions and can be insensitive to the coupled catalytic reactions.
A schematic representation of the technique of FTac voltammetry (FTacV) is provided in Figure 1. The waveform is generated from superimposition of a large amplitude time dependent, usually sinusoidal wave onto the ramp used in dc voltammetry. The current is initially recorded as a function of time and then converted into a power spectrum or frequency domain version using FT. By selecting the frequency region of interest in the power spectrum, the dc, fundamental and higher harmonic components are obtained by inverse FT (IFT) [7-9]. Hardware for FTacV instrumentation can be constructed by interfacing custom built [7-9] or commercially available components [10, 11] such as a waveform generator to a potentiostat. Recently, the possibility of undertaking FTacV measurements has also been provided to users of commercially available electrochemical workstations by Gamry and CH Instruments. Parameterisation of complicated catalytic processes can be achieved via comparison of experimental and simulated data, where simulations are most easily based on theoretic models available in either commercially available packages (e.g. DigiElch) or in open-source software (e.g. MECSim) [12”].

In the simplest EC’ process, when the reversible electron transfer step is coupled to a pseudo first order catalytic reaction, analytical solutions are available that provide a theoretic explanation as to how the second and higher ac harmonics can separate the electron transfer reaction from the coupled catalytic chemical reaction [13]. The definition of all the dimensionless parameters used in the equations given below and the derivations are available in reference [13]. In principle, the terms without $K_{cat1}$ (blue components in equations 8-10) represent the contribution from the E step and are identical in the presence and absence of the C step while the terms containing $K_{cat1}$ (red components in equations 8-10) represent the contribution of the C step. Examination of equation 8 predicts that the C step effects both the shape and current magnitude of the dc component as illustrated in Figure 1a while equations 9-10 reveal that the shape of ac components is irrelevant.
to the presence of the C step. Furthermore, since the contribution of the C step to the current is governed by the ratio of $K_{\text{cat}1}$ and $n\Omega$ (for the $n$th harmonic), the impact on the ac components becomes less significant in the higher harmonic data, which is extremely helpful in probing the electron transfer aspects associated with electrocatalytic reactions (see Figure 1c-e).

Dc component:

$$I_{\text{dcnorm}} = -\frac{K_{\text{cat}1}}{2} - \sum_{N=0}^{\infty} g(N+1) \left( \frac{E_{\text{dcnorm}}(\tau) - E_{\text{norm}}^0}{2} \right)^2 \frac{\Delta E_{\text{norm}}(2N+1)}{(2N)!}$$

(8)

Ac components:

$$I_{\text{norm,odd}} =$$

$$\sum_{N=0}^{\infty} g(N+1) \left( \frac{E_{\text{dcnorm}}(\tau) - E_{\text{norm}}^0}{2} \right)^2 \frac{\Delta E_{\text{norm}}(2N+1)}{(2N)!} \sum_{i=0}^{N} (-1)^i \left[ K_{\text{cat}1} \sin[(2i+1)\Omega \tau] + (2i+1)\Omega \cos[(2i+1)\Omega \tau] \right]$$

$$\frac{1}{(N-i)!(N+i+1)!}$$

(9)

$$I_{\text{norm,even}} =$$

$$\sum_{N=0}^{\infty} g(N+2) \left( \frac{E_{\text{dcnorm}}(\tau) - E_{\text{norm}}^0}{2} \right)^2 \frac{\Delta E_{\text{norm}}(2N+2)}{(2N)!} \sum_{i=0}^{N} (-1)^i \left[ -K_{\text{cat}1} \sin[2(i+1)\Omega \tau] + 2(i+1)\Omega \cos[2(i+1)\Omega \tau] \right]$$

$$\frac{1}{(N-i)!(N+i+2)!}$$

(10)

In this review, we survey the use of FTacV to detect underlying electron transfer processes associated with structural defects present in polycrystalline gold electrodes that mediate
electrocatalytic reactions [14] and probe the mechanistic details of electrocatalytic reactions associated with a molybdenum enzyme [15*], tin catalysed carbon dioxide reduction [16*] and cobalt catalysed water oxidation [17*]. These studies may utilise advanced materials in the design of the electrodes and details of the impact of heterogeneity associated with new electrodes are also revealed in a manner not possible with conventional dc methods. Historically, theory-experiment comparisons of catalytic reaction schemes were usually undertaken by dc voltammetry at much simpler ideal homogeneous liquid mercury electrodes or at slightly more complex polycrystalline or faceted metal electrodes.

**Figure 1.** A schematic representation of data analysis in Fourier transformed ac voltammetry applied to a catalytic $EC'$ process. Simulated (a) total current, (b) power spectrum, (c) dc, (d) fundamental, (e) second and (f) third ac harmonic components for a reversible heterogeneous
electron transfer process coupled to a pseudo first order catalytic process. Parameters: fundamental frequency $f = 10 \text{ Hz}$, amplitude $\Delta E = 0.050 \text{ V}$, scan rate $v = 0.050 \text{ V s}^{-1}$, $E^{0'} = 0 \text{ V}$, $T = 273 \text{ K}$. In (a) and (b), $k_{\text{cat}1} = 0$. In (c) – (f), $k_{\text{cat}1} = 0$ (curve 1), 100 (curve 2), 500 (curve 3) and 1000 s$^{-1}$ (curve 4). Adapted from reference [13].

**Identification of defect sites in metal electrodes: adatoms and catalysts**

In electrocatalysis it is commonly stated that surface modification lowers the overpotential of a reaction. However, FTacV [14, 18] has allowed other mechanistic scenarios to be identified, including those arising from surface defects. The importance of surface active sites in heterogeneous catalysis was introduced by Taylor in 1925 [19]. Later on, Ertl [20] pointed out that atomic defects are present on all solid surfaces (e.g. polycrystalline gold). The atoms at such defect sites exhibit unusual coordination geometry, and hence kinetics and energetics that differ from those of terrace atoms on the same surface. Somorjai [21] added to this model by demonstrating that their protruding surfaces are unusually electropositive, so that they tend to lose electrons to the bulk phase. The abnormal properties of oxide-supported gold nanoparticles are assumed to be a major contributor to the catalytic properties [22, 23].

Concepts related to atomic defects led Burke to introduce a new interpretation of the electrocatalytic behaviour of many transition metal electrodes which is known as the incipient hydrous oxide adatom mediator model [24, 25]. In this model, the metal electrode contains surface atoms that have low energy and high coordination or high energy and low coordination. The former are dominant and their oxidation occurs in the normal monolayer oxide formation potential region [26]. The latter are of very low coverage but are easily oxidised, usually in the electrochemical
double layer region and are catalytically active. In alkaline media, their oxidation involves a fast reversible or quasi reversible metal adatom hydrous oxide transition not seen in dc voltammetry, but which can be detected in the higher harmonics of FTacV. The surface confined metal hydrous oxide species (M*$_{ads}$) then functions as a mediator in a catalytic reaction scheme. Figure 2a summarises the combination of electron transfer and coupled catalytic reaction that occurs at these highly active sites where the underlying electron transfer reaction (equation 12) can be identified directly by FTacV.

\[
\text{Au}^{+}_{\text{ads}} + n\text{OH}^- \rightleftharpoons \text{Au(OH)}_n + ne^- \tag{11}
\]

Figure 2b illustrates the aperiodic dc (the term “aperiodic” was introduced to distinguish the dc component derived from FTac and conventional dc voltammetry [27]) and fundamental to fifth harmonic ac components derived from FTacV when the potential is scanned over the range of -1.2 to 0.7 V vs. Ag/AgCl at a polycrystalline gold electrode in 0.5 M NaOH. The dc data are essentially featureless until the onset of monolayer Au$_2$O$_3$ formation at 0.06 V vs. Ag/AgCl. However, in each of the fundamental to fifth harmonic responses there is an additional well-defined premonolayer oxidation response centred at about -0.15 V vs. Ag/AgCl (Equation 11) prior to Au$_2$O$_3$ formation that is enhanced by electrochemical activation [14]. Significantly, the fourth and fifth harmonics exhibit features predicted for a close to reversible surface confined process. Electrocatalytic oxidation of hydrazine (Equation 12), glucose and other molecules [14] takes place at a gold electrode in the potential region where the reaction summarised in equation 11 participates in the overall reaction scheme depicted in Figure 2a. Use of FTacV therefore significantly facilitates understanding of electrocatalysis at metal electrodes which may occur via a mediated electron transfer route.
\[ \text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 4\text{e}^- \] (12)

**Figure 2.** Electrocatalysis at gold electrodes. (a) Schematic representation of electrocatalytic reduction of compound (Red) to product (Prod) at electrochemically active defect (adatom) sites. (b) FTacV for aperiodic dc and fundamental to fifth ac harmonics for a polycrystalline gold electrode (black) and activated form of electrode pre-polarised at -1.2 V vs. Ag/AgCl for 5 min (red) and 20 min (blue) in 0.5 M NaOH. Conditions employed for (b): \( f = 21.46 \text{ Hz}, \Delta E = 0.150 \text{ V}, v = 0.052 \text{ V s}^{-1} \). Adapted from reference [14].

**Redox active biomaterials**

Bioelectrochemical experiments typically use electrodes functionalised with very small amounts of protein. Consequently, typical dc protein voltammetric experiments exhibit poor faradaic-to-background current ratios, which hampers analysis of the electron transfer mechanisms. Introduction of FTacV minimises this and other limitations [6, 15**, 28-34, 35**].
In the case of mononuclear molybdenum enzyme *Escherichia coli* YedY (Figure 3), adsorption onto a carbon electrode enables direct electron transfer to both the molybdenum centre and the pyranopterin cofactor. Electron transfer is detected by dc voltammetry as two surface-confined processes separated by approximately 0.42 V (Figure 3b). The process at more positive potentials arises from the proton-coupled Mo$^{IV/V}$ transition, while the two-electron two-proton redox transformations of pyranopterin give rise to the process at more negative potentials. Importantly, adsorbed YedY preserves the enzymatically active state as inferred from the pronounced reductive catalytic currents in dc voltammograms recorded with the solutions containing dimethylsulphoxide (Figure 3c). However, the amount of enzyme adsorbed in these experiments is so low that the faradaic-to-background current ratio is below 1:15 under dc voltammetric conditions (Figure 3b-c), which precludes precise quantitative analysis of the electron transfer.

FTacV of the Mo$^{IV/V}$ transition shows no significant current in ac harmonics, which attests to a very slow rate of electron transfer ($k^0 < 10$ s$^{-1}$). Conversely, the higher order harmonics of ac voltammograms exhibit large faradaic currents associated with redox transformations of pyranopterin and negligible background contribution (Figure 3d). Modelling of these high-quality data [10$^{**}$] allows the redox mechanism to be established and parameterised. FTacV experiment-simulation comparisons attested that the reduction of pyranopterin cofactor in YedY is best described by two consecutive very fast one-electron transfers ($k^0 > 2 \times 10^4$ s$^{-1}$) with very close formal $E^0$ (-0.24 and -0.26 V vs. NHE at pH = 7) [15$^{**}$]. This level of mechanistic understanding is difficult or impossible to achieve from dc experiments only.

Another key conclusion of the study [15$^{**}$] was derived from comparisons of the onset potential for the enzymatic current and formal $E^0$ for pyranopterin reduction derived from FTacV analysis.
Juxtaposition of the aperiodic (Figure 3c) and higher ac harmonic components (Figure 3e) clearly reveals that measurable catalytic currents appear only at potentials more negative than those required for the reduction of the organic cofactor. This identifies redox transformations of pyranopterin rather than that of metal centre as being catalytically relevant in YedY. This is a unique mechanism for mononuclear Mo proteins.

Figure 3. (a) Protein structure and redox transformation of an active site of *Escherichia coli* YedY. (b) dc voltammetry (*v* = 0.100 V s\(^{-1}\)), (c) aperiodic dc, (d) 8\(^{th}\) and (e) 6\(^{th}\) ac harmonic components of FTac voltammograms (*f* = (c, e) 219 and (d) 9, 39 or 219 Hz, Δ*E* = 0.150 V, *v* = 0.016 V s\(^{-1}\)) for YedY adsorbed on a pyrolytic graphite edge plane electrode (0.03 cm\(^2\)) in contact with N\(_2\)-saturated aqueous 50 mM Mes + 2 M NaCl (pH 7). In panel (b), black curve shows raw data, red curves show simulated background, grey
curve shows background-corrected response multiplied by a factor of 20. In panels (c) and (e), black data were obtained in the pure electrolyte solution, while grey curves (solid in (c), dashed in (e)) show voltammetric data recorded in the presence of 200 mM DMSO; Solid grey trace in panel (c) shows data obtained with no YedY present on the electrode. In panel (d), grey and black dashed curves show experimental and simulated data, respectively. Adapted from reference [15**].

**Carbon dioxide reduction**

Electrochemical conversion of CO₂ into high-value industrially important chemicals is attracting major interest [36, 37]. CO₂ can be electrochemically reduced to many products in aqueous electrolyte media via reaction pathways involving two to at least twelve electrons [38], depending on the electrocatalyst used. Electrochemical CO₂ reduction, which may also be accompanied by the hydrogen evolution, is exceptionally complex.

FTacV has been used to separate the fast electron transfer step from the other steps, and provide new mechanistic insights when tin electrodes are used as catalysts. Details of the three types of tin electrode used in the electrocatalytic CO₂ reduction study are given in reference [16**]. Under dc voltammetric conditions, only the Sn⁰/Sn²⁺ and Sn³⁺/Sn⁴⁺ processes and H₂ evolution commencing at -1.5 V vs. Ag/AgCl are observed under N₂, while CO₂ reduction commences at -1.2 V vs. Ag/AgCl when CO₂ is present (Figure 4a). Important additional processes, detected under fifth and higher order ac harmonics, can be attributed to fast electron transfer reaction(s) (Figure 4b). Two closely spaced processes with reversible potentials of around -1.27 and -1.4 V vs. Ag/AgCl are distinguished from these additional features in a series of time (CO₂ concentration)-dependent experiments. As detailed in reference [16**], these processes are attributed to CO₂(aq) and H₂CO₃(aq) reduction chemistry, respectively. Experiment-simulation comparisons focused on the
use of a smaller amplitude sinewave and the lower (third) harmonic component implied that the process at -1.27 V vs. Ag/AgCl is a one- rather than two-electron transfer process associated with °CO₂ (Figure 4c), i.e. °CO₂ + e⁻ ⇌ °CO₂⁻. The fact that this reaction is reversible with the second electron transfer reaction (°HCO₂ + e⁻ → °HCO₂⁻) not contributing to the third harmonic ac response implies that the protonation of °CO₂⁻ to form °HCO₂⁻ is the rate determining step. Definitive conclusion on the process at -1.4 V vs. Ag/AgCl could not be established due to its non-reversible nature.

These FTacV studies again allow direct observation of the underlying electron transfer processes in the presence of chemical steps leading to an enhanced understanding of the active form of the catalyst and the rate determining step(s).

**Figure 4.** Dc and ac voltammograms obtained in CO₂- or N₂-saturated aqueous 0.5 M NaHCO₃ electrolyte, with a Sn(SnOₓ)-modified electrode or a bare glassy carbon (GC) electrode: (a) dc voltammograms, v = 50 mV s⁻¹; (b) fifth harmonic components of FTac voltammograms, displayed with abscissa axis as time (lower) or potential (upper) formats, f = 9.02 Hz, ΔE = 0.080 V, and v = 0.037 V s⁻¹. (c) Comparison of (black) third harmonic components of experimental FTac
voltammograms, obtained with a Sn(SnOx)-modified GC electrode in a CO2-saturated aqueous 0.5 M NaHCO₃ solution \( (f = 9.02 \text{ Hz}; \Delta E = 0.040 \text{ V}; \nu = 0.037 \text{ V s}^{-1}) \), and \textit{(red and green)} simulated data (obtained with the MECSim software package \[10\]) for a surface-confined reversible one-electron transfer and reversible two-electron transfer and quasi-reversible \( (k^0 = 10 \text{ s}^{-1} \text{ and } \alpha = 0.50) \) two-electron transfer surface confined processes. The simulated data have been scaled to match the maximum current found in experimental data to emphasise the shape comparison. The vertical dashed lines visually display the degree of agreement between theory and experiment with respect to peak locations. Adapted from reference \[16\].

**Water oxidation**

Electrooxidation of water (equation 13) provides an attractive source of sustainable and abundant electrons and protons needed for synthesis of energy-rich fuels. Yet again, analysis of the harmonic components of FTac voltammograms for water oxidation catalysed by metal oxides/oxyhydroxides has enabled detection of hitherto unknown redox transformations that are catalytically relevant \[17, 39-40\].

Critical insights into the water oxidation mechanism have been derived from extensive experiment-simulation comparisons of dc and ac voltammetric data obtained as a function of concentration of Co-, Mn- or Ni-based catalysts \[17\]. In the case of the Co catalyst, processes occurring prior to the catalytic response (process I, Figure 5a) are not involved in the catalytic mechanism. In contrast, the well-defined ac process evident at potentials where dc catalytic current is significant (process II, Figure 5b) shifts to more negative potentials and is enhanced as the catalyst loading and the water oxidation rate are increased. Thus, FTacV demonstrates that for the
Co case, process II is a key electron transfer step in the catalytic mechanism that controls the rate of water electrooxidation. Analogous correlations were identified for cobalt-, manganese- and nickel-based catalysts, which suggests that closely related electrocatalytic mechanisms apply in all cases.

Another important outcome of this work was the creation of a parameterised model of the water oxidation reaction that excellently mimics the experimental behaviour over a wide range of conditions (Figures 5a and b). The model uses the “molecular” catalytic mechanism that involves a redox transformation of a surface-confined species coupled to a catalytic reaction with a substrate in solution and accounts for the important role of a Brønsted base (Figure 5c). By using this model, the pseudo-first order rate constants for the reaction of the oxidised state of the catalysts with the substrate was found to be within the range $2\times10^3$ to $4\times10^4$ s$^{-1}$, which is at least an order of magnitude higher than previously reported values [41-43]. The effective reversible potentials for the catalytically relevant redox transformations of Co, Mn and Ni-based oxides (viz. process II in Figure 5b) were also for the first time quantified and determined to be within the range of 1.9-2.1 V vs. reversible hydrogen electrode.

\begin{align}
4\text{OH}^- &\rightleftharpoons \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-, \text{pH} > 7 \quad (13a) \\
2\text{H}_2\text{O} &\rightleftharpoons \text{O}_2 + 4\text{H}^+ + 4\text{e}^-, \text{pH} < 7 \quad (13b)
\end{align}
Figure 5. (a) Aperiodic and (b) 4th harmonic components of FTac voltammograms ($f = 9.02$ Hz, $\Delta E = 0.080$ V, $v = 0.075$ V s$^{-1}$) for water oxidation (0.1M borate buffer, pH 9.2) catalysed by cobalt oxide/hydroxyoxide electrodeposited on F-doped SnO$_2$ flat electrodes at loadings of 11 (orange), 51 (red) and 104 pmol cm$^{-2}$ (brown). Insets show magnified plots of the processes preceding the catalytic water oxidation wave. *Light blue* curves show simulated data based on the mechanism in panel (c). Currents are normalised to the geometric surface area of the electrodes. Adapted from reference [17••].
Conclusion and outlook

FTacV, which allows resolution of the total response into aperiodic dc and ac harmonic components, effectively provides access to a wide time domain and hence electrokinetic regime from a single experiment. This feature, plus an ability to reject background charging current and resolve catalytic and electron transfer reactions provides new mechanistic insights not available in dc voltammetry. This review demonstrates how the attributes of FTacV may assist in unravelling the significantly enhanced level of complexity often associated with studies at highly heterogeneous electrodes being introduced to exploit advances in materials science combined with sophisticated forms of chemical modification to advance the efficiency of electrocatalysis of technologically important processes. Similarly, understanding of the nuances of surface confined voltammetry of biologically important enzymes and proteins is greatly enhanced in both the presence and absence of the relevant catalytically activated substrate. Even though models needed to mimic experimental data obtained at such highly heterogeneous electrodes will almost certainly consist of many parameters than need to be assigned, the high speed of modern computers incorporating web accessible mathematical software and data optimisation fitting routines including for example Bayesian inference methods to provide an account of uncertainties in the modelling, should make this tractable [44••]. Until recently, the FTacV technique required the construction of home-built instrumentation and for this reason was predominately used by specialists in dynamic electrochemistry. However, the method is now being introduced into commercially available electrochemical workstations [45]. Interestingly, even a mobile phone device has been adapted so it can be used as a FTacV second harmonic instrument for analytical applications [46]. In principle, introduction of the FTacV technique into a wide range of electrochemical workstations should be straightforward since the key hardware and software
features are closely related to those present in the commonly used technique of electrochemical impedance spectroscopy [47]. Ideally, in the future, users of electrochemistry, who may not be specialists in instrumentation, mathematics and computing science, should therefore also have access to sophisticated hardware and simulation packages that allow them to provide quantitative accounts of the complex electrocatalytic and other practically important electrochemical reactions.

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Advantages in studying electron transfer of surface confined metallo-enzymes or proteins using
FTAC voltammetry.

   Transfer Reactions Underpinning the Tin Catalyzed Electrochemical Reduction of CO₂
   https://doi.org/10.1021/acscatal.7b01305.

In this work, FTac voltammetry is used to probe the electron transfer aspects of the tin-catalyzed
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followed by a rate-determining CO₂⁻ protonation step is proposed.

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Quantitative FTac voltammetric studies on understanding of mechanistic aspects of water
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The work showcases, for the first time, the unique advantages provided by implementation of Bayesian inference in electrochemical analysis.

