Chapter 15
Nonlinear Impedances (Higher Harmonics)

When linear electrical elements are used in circuits, the measured impedances are independent of the amplitude of the ac perturbation. However, in electrochemistry, the electrical equivalent parameters related to the kinetics, diffusion, and other aspects are nonlinear because the current is a nonlinear function of the applied potential. In such cases, as was already discussed in Sects. 4.2.1 and 13.2, a small perturbation amplitude must be used to avoid the formation of harmonics. Now let us look in more detail at the formation of nonlinearities and the applications of such methods.

Second and higher harmonic responses were studied at the very beginning of the development of impedance spectroscopy [15, 17, 29, 635, 636]. Let us look first at the simplest case of the Tafel equation.

15.1 Simple Electron Transfer Reaction Without Mass Transfer Effects

In the case of a simple one-electron transfer reaction in Tafel conditions (i.e., irreversible electrochemical process without mass transfer effects), the faradaic current is described as

$$i = i_{\text{ex}} \exp(\alpha f \eta), \tag{15.1}$$

where i_{ex} is the exchange current density, and η is the overpotential. Let us apply a sinusoidal potential perturbation $\Delta\eta$ on a dc potential η_{dc}:

$$\eta = \eta_{\text{dc}} + \Delta\eta = \eta_{\text{dc}} + E_0 \cos(\omega t), \tag{15.2}$$

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where E_0 is the applied ac amplitude. The total current is

$$i = i_{\mathrm{ex}} e^{\alpha f \eta_{\mathrm{dc}}} e^{\alpha f E_0 \cos(\omega t)} = i_{\mathrm{dc}} e^{\alpha f E_0 \cos(\omega t)}. \tag{15.3}$$

An oscillating current can be expressed as a Maclaurin series, see also Eq. (4.15) [15, 637, 638]:

$$i - i_{\mathrm{dc}} = \Delta i = i_{\mathrm{dc}} \begin{bmatrix} 1 + b\cos(\omega t) + \frac{1}{2!} b^2 \cos^2(\omega t) + \frac{1}{3!} b^3 \cos^3(\omega t) \\ + \frac{1}{4!} b^4 \cos^4(\omega t) + \ldots - 1 \end{bmatrix}, \tag{15.4}$$

where $b = \alpha f E_0$. Using simple trigonometric identities [637, 639] this expression may be rearranged into harmonics:

$$\begin{aligned} \frac{\Delta i}{i_{\mathrm{dc}}} &= i_0 + i_1 \cos(\omega t) + i_2 \cos(2\omega t) + i_3 \cos(3\omega t) + i_4 \cos(4\omega t) \\ &\quad + i_5 \cos(5\omega t) + \ldots, \end{aligned} \tag{15.5}$$

where i_0 is the frequency-independent term and i_{k} are terms in front of cos($k\omega t$):

$$\begin{aligned} i_0 &= \frac{1}{4} b^2 + \frac{1}{64} b^4 + \frac{1}{2304} b^6 + \ldots, \\ i_1 &= b + \frac{1}{8} b^3 + \frac{1}{192} b^5 + \frac{1}{9216} b^7 + \ldots = \sum_{k=1}^{\infty} \frac{b^{\mathrm{k}}}{2^{2k} k!(k+1)!}, \\ i_2 &= \frac{1}{4} b^2 + \frac{1}{48} b^4 + \frac{1}{1536} b^6 + \ldots, \\ i_3 &= \frac{1}{24} b^3 + \frac{1}{384} b^5 + \frac{1}{15360} b^7 + \ldots, \\ i_4 &= \frac{1}{192} b^4 + \frac{1}{3840} b^6 + \ldots, \\ i_5 &= \frac{1}{1920} b^5 + \frac{1}{46080} b^7 + \ldots. \end{aligned} \tag{15.6}$$

In these expressions, the influence of up to the seventh term is shown. Note that the frequency-independent term, i_0, is not equal to zero; it is called a faradaic rectification current. It approaches zero for small amplitudes E_0. Moreover, a current of odd frequencies contains only odd powers of b^{k} and that of even frequencies contains even powers. In addition, the importance of higher-order terms decreases, and when the amplitude E_0 is small, only the linear term is left out, $i_1 = b$, all the other terms become negligible, and a classical linearized

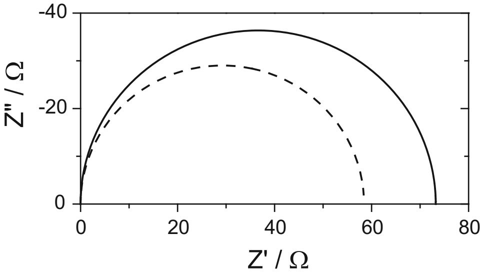

Fig. 15.1 Complex plane plots of fundamental harmonic impedances for simple redox reaction in Tafel zone; ac amplitudes: 5 mV rms – *continuous line*, 50 mV rms – *dashed line*; other parameters: $\alpha = 0.5$, $i_{\mathrm{ex}} = 10^{-4}$ A, $\eta = 0.1$ V

impedance is obtained. It is evident that at larger amplitudes, all terms are influenced by higher-order terms.

The charge transfer resistance at the fundamental frequency, ω, may be obtained as [637]

$$R_{\mathrm{ct}} = \lim_{E_0 \to 0} \left(\frac{E_0}{i_1 i_{\mathrm{dc}}} \right) = \frac{1}{\alpha f i_{\mathrm{dc}}}, \tag{15.7}$$

but the charge transfer resistance, including nonlinearities, $\mathbb{R}_{\mathrm{ct}}$, is

$$\mathbb{R}_{\mathrm{ct}} = \frac{E_0}{i_1 i_{\mathrm{dc}}}, \tag{15.8}$$

that is, it is smaller than the R_{ct} value. This effect is presented in Fig. (15.1) for the fundamental harmonic impedance for two amplitudes of 5 and 50 mV rms. It is obvious that a larger amplitude causes lower charge transfer resistances because the higher harmonics influence the fundamental harmonic results.

Another approach to describing current nonlinearities is to use a Fourier series [640, 641]:

$$\frac{\Delta i}{i_{\mathrm{dc}}} = I_0(b) - 1 + 2\sum_{k=1}^{\infty} I_{\mathrm{k}}(b) \cos(k\omega t), \tag{15.9}$$

where $I_{\mathrm{k}}(b)$ are modified Bessel functions of b of order k. This implies that the currents in Eq. (15.6) converge to $i_0 = I_0(b) - 1$ and $i_{\mathrm{k}} = I_{\mathrm{k}}(b)$. In fact, they are series representations of the $I_{\mathrm{n}}(b)$ Bessel functions. It should be mentioned that the Bessel functions $I_{\mathrm{k}}(x)$ are available in Excel as BESSELI(x,k), and of course they might be computed easily in other programs such as Mathematica or Maple. The plot of the first few Bessel functions $I_{\mathrm{k}}(b)$ is presented in Fig. 15.2 for different values of the ac impedance amplitude and $\alpha = 0.5$. These functions increase with increases of the parameter b. Only I_0 starts at one and all the other functions start at zero. Nevertheless, in Eq. (15.9) the frequency-independent term is $I_0(b) - 1$, which also starts at zero for $b \to 0$.

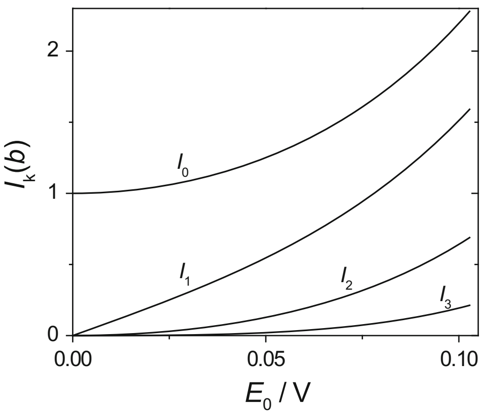

Fig. 15.2 Plot of Bessel $I_k(b)$ for different values of ac amplitude and $\alpha = 0.5$

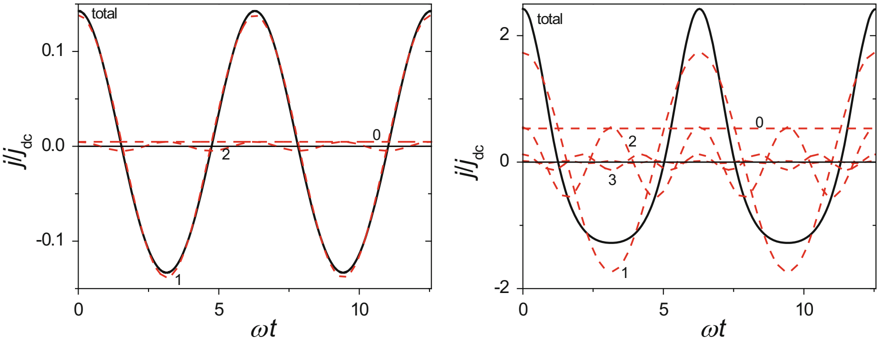

Fig. 15.3 Plots of total (*thick line*) and harmonics (*dotted lines*, harmonic number indicated) for faradaic impedance in one-electron Tafel conditions with $\alpha = 0.5$. Amplitudes: *left* – 5 mV rms, *right* – 50 mV rms

Let us look at the influence of nonlinearities on observed spectra for typical amplitudes of 5 and 50 mV rms, that is, amplitudes of $5\sqrt{2}$ and $50\sqrt{2}$ [641]. They are shown in Fig. 15.3. At small amplitudes, the nonlinear effects are negligible. However, for larger amplitudes the current observed in Tafel conditions is no longer sinusoidal and contains contributions from higher harmonics.

Harrington [641] noticed that measurements of the first harmonics at different amplitudes allow for the determination of the transfer coefficient. The ratio of the fundamental harmonic current using the amplitude E_0 and $2E_0$ equals

$$\frac{i(\omega, 2E_0)}{i(\omega, E_0)} = \frac{I_1(2b)}{I_1(b)} \tag{15.10}$$

and allows for the determination of the parameter b and, as a consequence, the transfer coefficient. Both amplitudes should be in the nonlinear zone, e.g., 30 and 60 mV.

One can proceed in a similar way when the current is described by the Butler-Volmer equation [637, 641, 642]

$$i = i_\mathrm{a}\exp(b_\mathrm{a}\eta) - i_\mathrm{c}\exp(-b_\mathrm{c}\eta), \tag{15.11}$$

where b_a and b_c contain anodic and cathodic transfer coefficients. This leads to

$$\begin{aligned}\Delta i = i - i_\mathrm{dc} &= i_\mathrm{a}\left(e^{b_\mathrm{a}\cos(\omega t)} - 1\right) - i_\mathrm{c}\left(e^{-b_\mathrm{c}\cos(\omega t)} - 1\right)\\ &= i_\mathrm{a}[I_0(b_\mathrm{a}) - 1 + 2I_1(b_\mathrm{a})\cos(\omega t) + 2I_2(b_\mathrm{a})\cos(2\omega t) + 2I_3(b_\mathrm{a})\cos(3\omega t) + \ldots]\\ &\quad - i_\mathrm{c}[I_0(-b_\mathrm{c}) - 1 + 2I_1(-b_\mathrm{c})\cos(\omega t) + 2I_2(-b_\mathrm{c})\cos(2\omega t)\\ &\quad +2I_3(-b_\mathrm{c})\cos(3\omega t) + \ldots].\end{aligned} \tag{15.12}$$

Taking into account that $I_\mathrm{k}(-b) = I_\mathrm{k}(b)$ for k even and $I_\mathrm{k}(-b) = -I_\mathrm{k}(b)$ for k odd Eq. (15.12) becomes

$$\begin{aligned}\Delta i &= i_\mathrm{a}[I_0(b_\mathrm{a}) - 1] - i_\mathrm{c}[I_0(b_\mathrm{c}) - 1]\\ &\quad +2\sum_{k=1}^{\infty}\left[i_\mathrm{a}I_\mathrm{k}(b_a) - (-1)^k i_\mathrm{c}I_\mathrm{k}(b_\mathrm{c})\right]\cos(k\omega t).\end{aligned} \tag{15.13}$$

It simply contains the difference between two series. For small amplitudes the first frequency-independent term and harmonics for $k \geq 2$ become zero and a classical linear response ($k = 1$) is observed. Nonlinear effects are observed for larger ac amplitudes, generating larger values of b_a and b_c.

In the case of large applied amplitudes, the nonlinear effects depend on the solution resistance. In fact, ac voltage is attenuated by solution resistance, leading to the application of a lower amplitude. This effect was discussed in detail by Diard et al. [642–644].

It should be stressed that in the case of nonlinear effects, response at the fundamental frequency is perturbed.

15.2 Other Reaction Mechanism

Harmonic analysis was also applied to other reaction mechanisms. One of the simplest reactions is a reversible redox process with Red and Ox forms in the solution. When bulk concentrations and the diffusion coefficient of both forms are identical, the dc current may be described as [637, 642, 645]

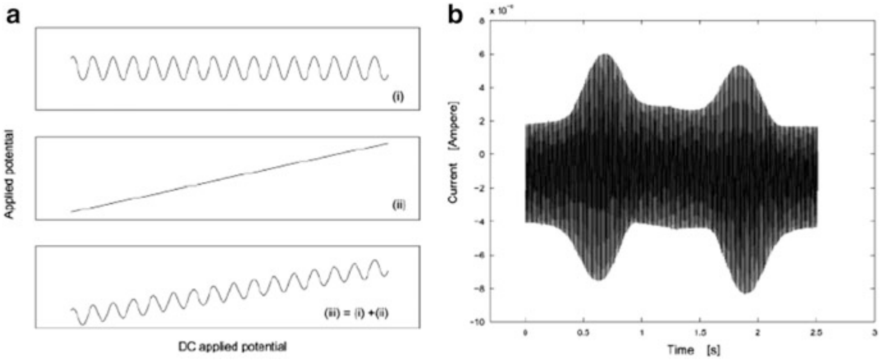

Fig. 15.4 (**a**) Signal applied in large-amplitude ac voltammetry: (i) ac signal, (ii) dc sweep, (iii) sum of two signals; (**b**) total current produced by application of signal (iii) in cyclic voltammetric conditions (Reprinted with permission from Ref. [649]. Copyright 2004 American Chemical Society)

$$i = \frac{nFDC^*}{\delta}\tanh\left[\frac{nf\left(E - E^0\right)}{2}\right]. \tag{15.14}$$

This equation can be written as an infinite series as was done previously. It converges for low ac amplitudes. A detailed analytical method of obtaining harmonic elements was described in Ref. [645]. Harmonic analysis was also applied to quasi-reversible reactions on a rotating disk electrode [642].

Other mechanisms studied include electrosorption with Langmuir isotherm [641] and a Volmer-Heyrovsky type of mechanism [641, 642]. The reader should consult these references for more details.

Bond and coworkers [646–657] have proposed use of the ac voltammetry with large ac signal superimposed on the linear sweep. The applied potential and measured current are presented in Fig. 15.4.

Then, to analyze the obtained current, a Fourier transform is applied and the responses at the fundamental, ω, and harmonic, 2ω, 3ω, 4ω,. . ., frequencies are obtained. Next, the current responses at the fundamental and harmonic frequencies are extracted by an inverse Fourier transform. Harmonics up to the eighth order were obtained. Analysis of the kinetic parameters is carried out by comparison of the experimental and simulated data. Theoretical ac voltammograms were simulated using classical numerical simulations of the diffusion-kinetic process using an implicit finite-difference method [658, 659] with a subsequent Fourier analysis of the simulated data. An example of the comparison of the experimental and simulated data is shown in Fig. 15.5. In this case, oxidation of ferrocenmethanol appeared reversible, and a good agreement was found with the simulated data for the reversible process.

Fourier transform analysis of higher harmonic data is well suited to differentiate between the effects of the solution resistance and kinetics [649, 651]. It is well

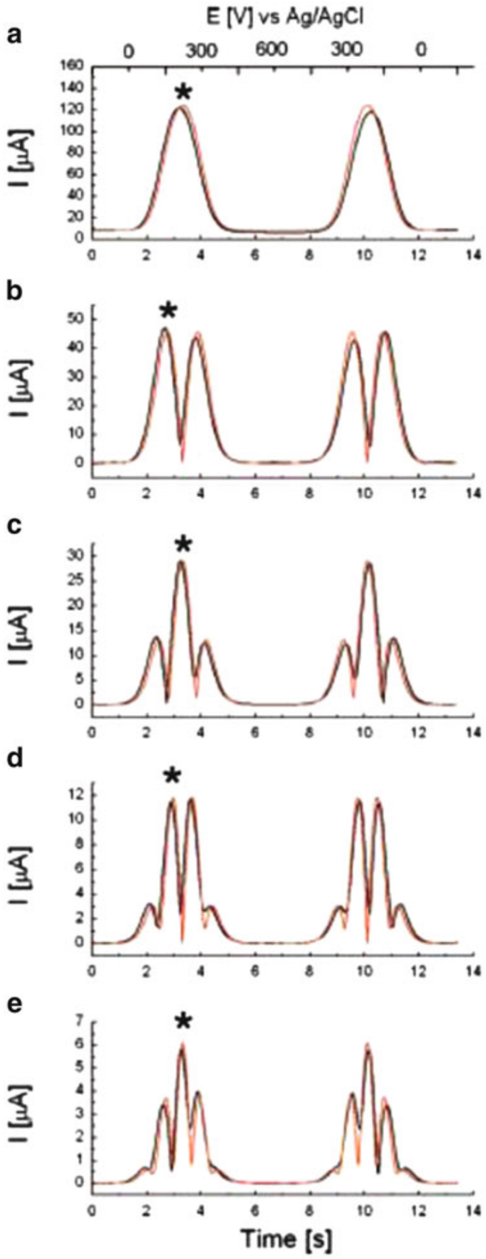

Fig. 15.5 Large-amplitude fundamental to fifth (**a**–**e**) harmonic Fourier transformed ac cyclic voltammograms (*black*) obtained for reversible oxidation of 1 mM ferrocenmethanol, compared with simulations of reversible process (*red*). Conditions employed: $f = 21.46$ Hz, ac amplitude $E_0 = 100$ mV, sweep rate $v = 111.76$ mV s^{-1} (Reprinted with permission from Ref. [652] (Fig. 15.2) Copyright 2008 American Chemical Society)

known that in cyclic voltammetry these two effects lead to an increase in the potential difference between anodic and cathodic peaks. A Fourier transform of higher harmonics can easily discriminate between these effects. An example is shown in Fig. 15.6, where the effects of the solution resistance and electron transfer

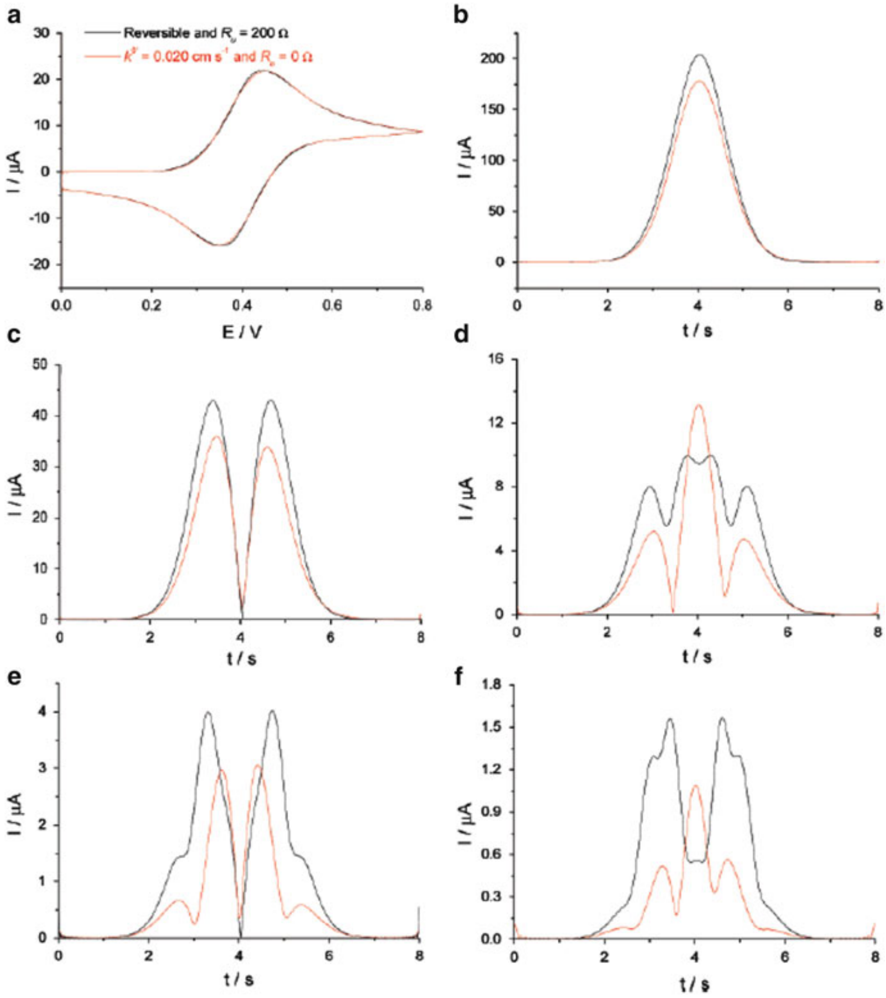

Fig. 15.6 Comparison of simulated FT large-amplitude ac voltammograms for a reversible process with solution resistance R_u of 200 Ω and a quasi-reversible process with $k^0 = 0.020 \text{ cm s}^{-1}$ and R_u of 0 Ω. (**a**) dc component, (**b**) fundamental, (**c**) second, (**d**) third, (**e**) fourth, and (**f**) fifth harmonics (Reprinted with permission from Ref. [651] (Fig. 15.2). Copyright 2007 American Chemical Society)

kinetics are completely different at higher harmonics. In general, linear elements such as solution resistance and double-layer capacitance should disappear at higher harmonics because they do not produce nonlinear effects. Bond and coworkers [649] stated that (a) the dc cyclic component provides an estimate of $E^{0\prime}$ (because the R_u and k^0 effects are minimized); (b) the fundamental harmonic provides an estimate of C_{dl} (because it has a high capacitance-to-faradaic current ratio); and (c) the second harmonic provides an estimate of R_u, k^0, and α (because the C_{dl} effect is minimized). They also studied the influence of noise on obtained results [650]. Fourier transform analysis of higher harmonic data was applied to study the kinetics of surface-bound molecules [647] and adsorbed films [653], chemical reactions coupled with electron transfer [652, 654], fast electron transfer processes [649, 655], and the low concentration of electroactive species [660, 652]. Its wider use is limited by a lack of commercial software to simulate and analyze data. The authors also discussed the use of square wave excitation to obtain similar information [661–665].

Another approach using nonlinear frequency response analysis with the help of the Volterra series expansion and generalized Fourier transform was also proposed and applied to the study of methanol or ferrocyanide oxidation [666–668].

15.3 Conclusions

The use of larger amplitudes generates harmonics and influences responses at the fundamental frequency. Analysis of higher harmonics may be carried out analytically in simpler cases or numerically in more complex cases of ac voltammetry. Careful analysis of higher harmonics allows for the discrimination of solution resistance and double-layer capacitance effects and of the kinetic parameters of electron transfer reactions and homogeneous chemical kinetics coupled with electrochemical reactions.