Chapter 16
Instrumental Limitations

Typical EIS measurements are usually carried out in a frequency range from 20 to 50 kHz to 0.1 Hz. However, in dielectric [669] or fast kinetic studies [670], high frequencies up to several megahertz are necessary. Such measurements cannot be carried out with a potentiostat, which is too slow and introduces additional phase shift. On the other hand, very slow frequencies in the millihertz or microhertz range are necessary in studies of intercalation (batteries [671, 672], hydride formation [673]). In addition, the measured impedance varies from several megaohms (or gigaohms) for paints and coatings, corrosion in concrete, or solid materials to milliohms or lower [674] for fuel cells or batteries. This puts high demands on the measurement equipment and can lead to errors and artifacts. This measuring equipment and cell problems will be described below.

16.1 Measurements of High Impedances

Measurements of high impedance, i.e., high-resistance and low-capacitance samples, are very demanding. Each potentiostat is characterized by a certain input impedance that limits its applications. One ISO norm, ISO 16773 (parts 1–4) [675], describes in detail equipment calibration and measurement procedures as well as application notes from Gamry [676] and Solarton [677–681].

As a first step, the potentiostat should be tested in an open circuit in a two-electrode setup. For this experiment the reference and auxiliary electrodes should be connected together with no connection between them and the working electrode (open circuit). Then the impedance measurements should be carried out in a frequency range of 10^5–0.01 Hz. Although in typical electrochemical experiments the amplitude used is 3.5 mV rms (i.e., 5 mV amplitude, 10 mV peak to peak), in these measurements the amplitude might be larger, 20–30 mV rms. A higher amplitude is necessary when the sample impedance is very high and the current flow very low. The open-circuit impedance behaves as a parallel connection of the input resistance and capacitance (RC) (Fig. 2.33). The sample impedance $|Z|$ must

A. Lasia, *Electrochemical Impedance Spectroscopy and its Applications*,
DOI 10.1007/978-1-4614-8933-7_16,

be much smaller than the potentiostat open-circuit impedance; otherwise, erroneous results will be obtained. If the potentiostat's input impedance is too small, one can use another piece of specialized equipment, such as the Solartron 1296 Dielectric Interface, which works with a frequency analyzer and is able to measure impedances up to 100 TΩ [677–681].

Accurate impedance measurements at high frequencies are affected by the input and cable capacitance. Approaches to dealing with this problem are discussed in Solarton Application Notes [679, 680].

Next, the equipment should be checked using a dummy cell, a simple (RC), $R_1(R_2C)$, or $(C_1(R_1(R_2C_2)))$ circuit, but with R_2 within a range of the measured sample resistances, on the order of gigaohms and a capacitance on the order of nanofarads [675]. This will give the accuracy of the measurements. One can also consult the accuracy contour map from the manual of a given potentiostat [676].

Finally, the sample should be measured. It should be kept in mind that an increase in the real surface area of a working electrode decreases its impedance. The counter electrode should be made of a noncorroding material, for example, a noble metal or other low-impedance electrode. Its surface area should be large, comparable to that of a sample, and placed in parallel to the working electrode. It might be necessary to place the measured cell in a Faraday cage.

Certain artifacts are also observed in studies in low-conductivity media [682]. In studies in pure 80 % and 100 % acetic acid a very important influence of the distance between the tip of a Luggin capillary and a working electrode made of stainless steel was observed (Fig. 16.1). These solutions were characterized by very large resistivities, 8–10 kΩ cm for 80 % and 8–12 MΩ for 100 % acetic acid. At short distances, high-frequency capacitive-inductive behavior is apparent. Similar behavior was also observed when a Pt pseudo-reference electrode was used. Such behavior was explained by the capacitive-resistive coupling between working and reference, working-auxiliary, and reference-auxiliary electrodes [682].

Similar artifacts were observed at high frequencies in highly conducting solutions [683] when the Luggin capillary was located too close to the electrode surface. In general, it should be experimentally checked whether the distance between the tip of a Luggin capillary and a reference electrode affects observed impedance spectra. The only effect of changing this distance should be a parallel displacement of the complex plane plot along the real axis, that is, the change in the uncompensated solution resistance. The conditions for the reference electrode will be discussed below.

16.2 Measurements at High Frequencies

The slow response of potentiostats limits studies at high frequencies. Although many manufacturers claim that their potentiostat can work at very high frequencies up to 1 MHz, in practice the upper limit is 50 to 100 kHz and in some cases as low as 20 kHz. This can be easily checked experimentally.

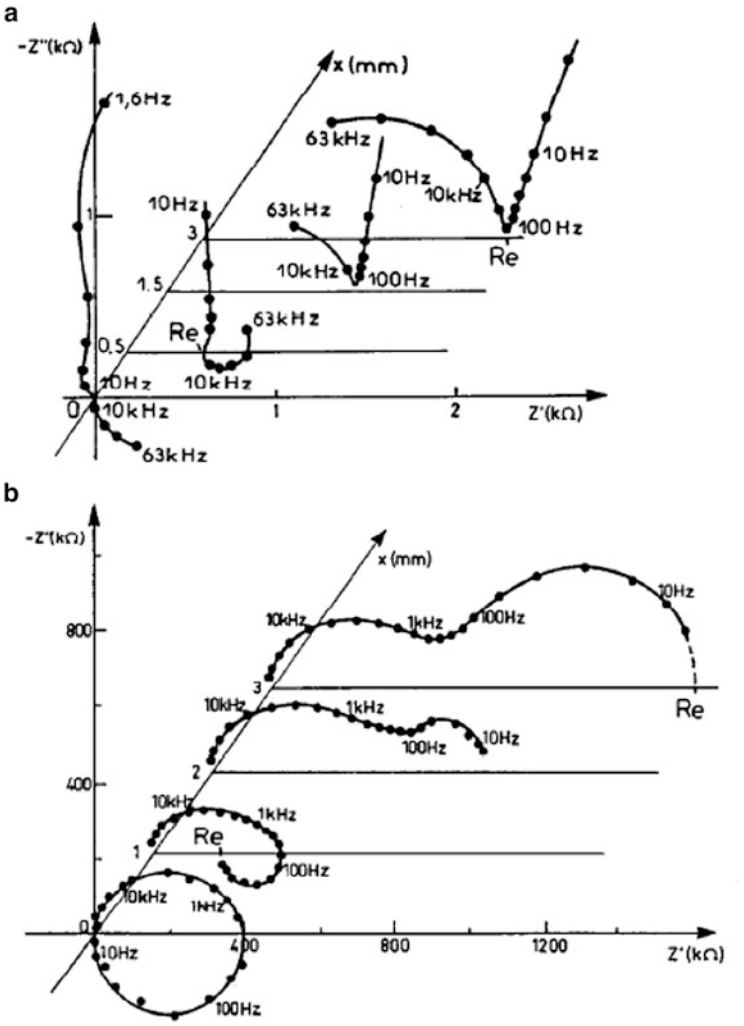

Fig. 16.1 Influence of distance between tip of Luggin capillary and working electrode in 80 % and 100 % acetic acid at stainless steel electrode (From Ref. [682], copyright (1990), with permission of Elsevier)

Schöne and Wiesbeck [684] proposed using two working electrodes (disk-ring) with electronic compensation of the solution resistance and frequency analyzer without a potentiostat. The potentiostat was used only for slow dc polarization of the working electrodes.

The use of two identical working electrodes was proposed by Sibert et al. [685]. The electrodes should be placed close to each other to minimize the solution resistance and be polarized by a small ac amplitude between them by a FRA. The current is measured as a potential drop on a small calibrated resistance

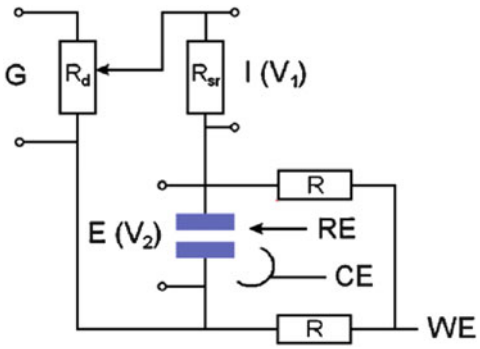

Fig. 16.2 Setup for high-frequency measurements using identical twin electrodes; ac generator G produces higher amplitude, which is divided by potentiometer R_d; current is measured as potential drop (V_1) at R_{sr}; potential is measured at electrodes (V_2), V_1 and V_2 are fed to FRA; both working electrodes are dc polarized through large resistance from potentiostat (From Ref. [686], copyright (2012), with permission from Elsevier)

and fed back to the frequency response analyzer. The dc polarization of these two electrodes at the same potential is assured by a potentiostat through large resistances. The electrical connections are shown in Fig. 16.2. This method was recently used to measure the fast reaction of HUPD at Pt [686]. The system worked well up to 1 MHz.

Fafilek [687] proposed another setup in which a potential is applied without a potentiostat to two electrodes, one working and another a very large-surface-area Pt electrode. In such an arrangement, the impedance of the large-surface-area Pt electrode might be neglected. This method was also used later to measure HUPD kinetics at a Pt electrode [686]. The connections are displayed in Fig. 16.3. This system allowed for measurements up to 1 MHz.

The systems shown previously make it possible to work at high frequencies without potentiostats, which have a limited response time, and to study fast electrochemical processes.

Some studies without a potentiostat or with a specially constructed fast potentiostat were carried out but with small currents at ultramicroelectrodes [688–690].

16.3 Measurements of Low Impedances

In the case of low sample impedances, large currents flow in the system. Large currents generate inductive effects in leads and measuring resistors at higher frequencies [691]. However, even larger inductive effects are generated by cells [692]. An example of such an effect is presented in Fig. 16.4. It appears at high frequencies and is similar to the effect of an inductance in series (compare with Fig. 2.41).

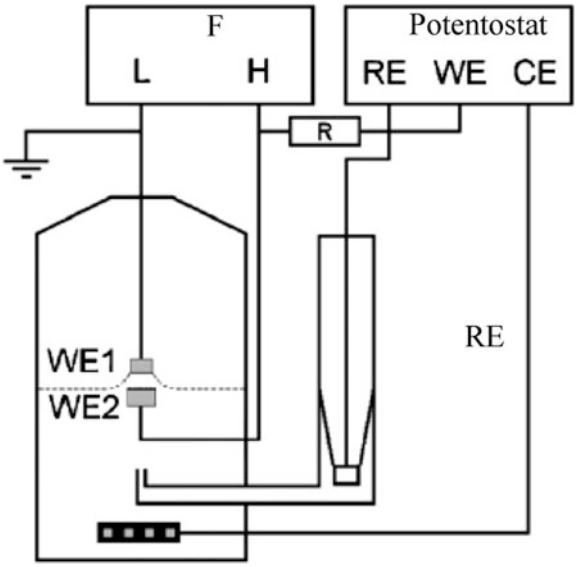

Fig. 16.3 Setup for high-frequency impedance measurements; WE1 working electrode, WE2 high-surface-area Pt electrode. Potential is applied and current measured by FRA; one electrode is polarized by potentiostat (From Ref. [686], copyright (2012), with permission from Elsevier)

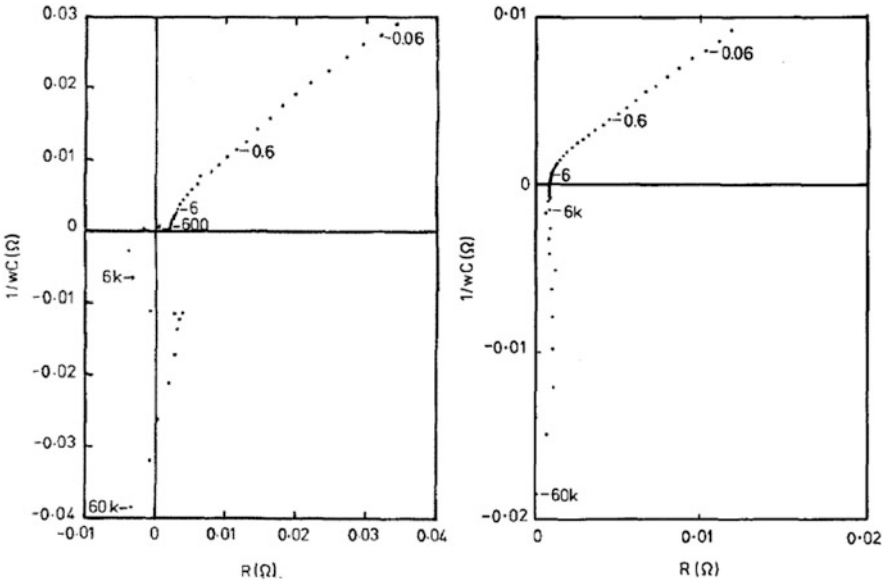

Fig. 16.4 Complex plane plots of impedance of lead acid battery using sense resistor of 10 Ω (*left*) and calibrated shortening bar (*right*) (From Ref. [691] with kind permission from Springer Science +Business Media)

This impedance was acquired using an internal resistance of commercial measuring equipment of 10 Ω. As the cell impedance was less than 0.1 Ω, a lower sense resistor was desirable. The authors used and calibrated a shortening bar as a 0.1245 Ω sensing resistor, determined its characteristics, and subtracted its impedance to obtain the pure impedance of the battery. The result is shown in Fig. 16.4 (right). In these measurements long commercial cables with crocodile clips were replaced by short cables bolted to the cell terminals. It is also recommended to use coaxial cables or twisted cable pairs in which currents flow in opposite directions, decreasing the inductive effect [693, 694].

Impedance measurements in such cases should be carried out in galvanostatic mode. In fact, applying a 5 mV amplitude to a sample having low resistance, e.g., 1 mΩ, causes a current of 5 A and for lower impedances even more. Because it is technically difficult to apply amplitudes lower than 1 mV, the ac current is applied and the ac voltage measured [693, 694]. Potentiostats are usually slower in the galvanostatic than in the potentiostatic mode. However, they are faster in a two- than a three-electrode mode.

Ordinary potentiostats are limited to a highest current of approximately 1 A. To study higher currents, either booster potentiostats [695] or so-called load banks should be used [696, 697]. In load banks, the ac current may be modulated externally and the potential drop on a load resistor (proportional to current) and potential difference at the studied object are applied to the frequency response analyzer to measure the impedance. Analysis of the impedance of fuel cells with the separation of impedances of the anode, cathode, and load were presented by Diard et al. [698, 699]. A similar correction procedure was also described in Ref. [700].

In general, in studies of very low impedances, the ac current might be measured as a potential drop on a very small resistor and the ac voltage as a potential difference at the studied object; both ac voltages should be fed to the frequency response analyzer to measure the impedance. The impedance of the resistor and that of the cables/connections should be subtracted from the total measured impedance.

16.4 Reference Electrode

The quality of the reference electrode is primordial in all EIS studies. Its impedance must be low, below 1 kΩ; therefore, some reference electrodes used in pH determination cannot be used (although they may work in dc experiments). Reference electrodes are usually equipped with a Luggin capillary probe to decrease the uncompensated solution resistance. The tip of the Luggin capillary is usually partially blocked with ceramic frits, Vycor glass frits, or asbestos threads to decrease the flow of the filling solution and possible contamination. Ideally, the inner reference electrode solution and the cell solution should be the same. This may be obtained using calomel or Ag|AgCl electrodes when working with chlorides, Hg|Hg_2SO_4|SO_2^{2-} when working with sulfuric acid or sulfates, or HgO|OH^- when

working in alkaline solutions. The double junction reference electrodes is often used to avoid contamination, but the total impedance must be checked, especially in nonaqueous solutions.

It is simple to measure the impedance of the reference electrode. The reference electrode must be immersed in the electrolyte in a beaker, a large-surface-area inert electrode also immersed in this solution, and the impedance measured at the open-circuit potential [701].

The response time of the measuring circuit is also limited by the resistance of the electrolyte inside the Luggin capillary [702–704]. Strange impedances at high frequencies were also observed in highly conducting solutions [683] when the Luggin capillary was located too close to the electrode surface. To eliminate these problems, a Pt wire connected to the reference electrode through a small capacitor (100 pF to 10 nF) and immersed in the solution can be used [701, 702]. In such a configuration, the high-frequency signal flows through the capacitor and the dc signal through the reference electrode. It was also found that insertion of the Pt wire into the Luggin capillary (with no connections) also improved the response time of the reference electrode [704].

16.5 Conclusions

Modern impedance apparatus are capable of handling low or high impedances in a wide frequency range. However, care must be taken when working in more extreme conditions of high frequencies and very low or very high impedances. The measurement possibilities of the system must be well checked, usually using appropriate dummy cells.

One of the most often found artifacts is related to the reference electrode, its impedance, and the distance of the Luggin capillary from the electrode. Its impedance must be low, and if the distance from the working electrode is changed, only the solution resistance should change without affecting the shape of the impedances.