Chapter III.4
Experimental Setup

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III.4.1 Introduction

To run a successful electrochemical experiment it is essential that the experimental setup is electrically correct and appropriate for the experiment planned. There are several points that should be carefully considered before the experiments are started. They include proper choice of the working, reference and auxiliary electrodes, proper selection of the solvent and supporting electrolyte, proper selection of the electroanalytical technique and its parameters, proper wiring of the electrochemical circuit and, finally, proper setting of the parameters of the potentiostat/voltammograph used.

III.4.2 The Working Electrode

The working electrode is the electrode at which the investigated processes occur. The investigator can choose one of the electrodes listed in Chap. III.1. The main criterion is the available potential window, which should meet the requirements of the investigation. Usually, in the range of positive potentials, platinum, gold and carbon (graphite, glassy carbon) electrodes are used. The surfaces of these materials are partially oxidised in aqueous solutions at this potential range. Thin layers of oxides are formed at gold and platinum, and various functional groups, such as –C=O and –OH, are attached to the carbon materials. In the negative range of potential, in aqueous solutions and other protic solvents, mercury electrodes are superior due to high overpotential of the reduction of hydrogen. On the other hand, many organic compounds strongly adsorb on mercury, which may complicate the analysis of voltammograms. In aprotic solvents, Pt, Au and C electrodes can be used in both positive and negative ranges of potential. Electrodes made of other noble metals, such as Ir and Ag, are less frequently used.

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A solid electrode, in comparison to a mercury drop, usually requires very careful pretreatment. The electrode surface should be clean and polished on a very wet pad to mirror gloss. This can be done using abrasive powders (or their suspensions in water), such as diamond and alumina, of various particle sizes. Depending on the actual state of the surface the polishing should start with the appropriate size of the abrasive material, followed by polishing with smaller particles. Usually, at the end of this process, 0.1 and 0.05 μm particles are used. After polishing, the electrode surface should be carefully cleaned (removal of abrasive material) with a dynamic stream of water, and dried with, e.g. methanol if a nonaqueous solvent is used in the experiments. Water-based suspensions of both diamond and alumina are available commercially. Oil-based suspensions are not recommended for polishing, since they lead to hydrophobic properties of the polished surfaces and this limits substantially the applicability of the electrode. An examination of the quality of the electrode surface with a microscope should always be carried out before the polishing procedure and before the experiments. This also helps to ensure that the abrasive material has been quantitatively removed from the surface. Traces of alumina attached to the electrode surface may alter, e.g. pH at the electrode/solution interface. For particular electrochemical purposes cheap disposable electrodes are proposed to ensure a good reproducibility of the measurements. To obtain well-defined voltammograms, it is also important that the electroactive part of the electrodes is perfectly sealed into the electrode body. Otherwise, the background for the voltammograms is usually excessive and steep.

Often, to obtain reproducible curves/waves, the solid electrode needs an electrochemical activation/regeneration. This is usually done by cycling the potential in an appropriate range while keeping the electrode in an appropriate solution. There is no universal range of potential and universal solution that can be employed for such activation. In the work with Au and Pt electrodes, often the voltammetric cycling/activation is done in a diluted sulphuric acid.

Solid electrodes covered by membranes or modified with polymers, gels and various composite materials cannot be treated by polishing. The only way to make them work reproducibly is to apply an appropriate conditioning potential (or a sequence of potentials) before the voltammetric experiments.

It is important that, before carrying out voltammetric experiments with analytes, the available potential window (range) is known and that there are no peaks of unwanted impurities in that range. The available potential window is determined by the currents of reduction/oxidation of the supporting electrolyte/solvent and, in the experiments, one should avoid entering potentials where these processes visibly occur. The products generated at the potential limits may interfere with the system under investigation and may affect the electrode surface.

After use, the working electrode should be thoroughly rinsed and dried to avoid crystallisation of the substrate on the electrode surface.

III.4.3 The Reference Electrode

The selection of a proper reference electrode is equally vital in voltammetry especially when accurate and precise data on the formal potentials of the red-ox

couples under examination are needed. Traditional electrodes based on Hg and Ag (Hg/HgCl, Hg/Hg$_2$SO$_4$, Ag/AgCl, see Chap. III.2) can always be used; however, their concentrated electrolytes should be well separated from the analysed solution. In other words, everything should be done to prevent a leakage of the solution from the reference electrode to the cell, and vice versa. Therefore, first of all, a good electrolyte bridge filled with the analysed solution and well sealed with appropriate, conductive stoppers should be used. Such a bridge may well protect the solution in the cell against a leak of unwanted ions, but not the reference electrode as well. Also, it is usually advised to use the same solvent in the cell and in the reference electrode compartment.

When the experiments are performed with a two-electrode system, the current flows through the reference electrode. Under such conditions the reference electrode potential may not be stable over time. The smaller the working electrode the smaller is the risk of affecting the potential of the reference electrode. In the work with microelectrodes (electrodes with the dimensions of their active parts in the range of micrometers or less) as the working electrodes, the use of the two-electrode system is justified. If the three-electrode system is used, the reference electrode is practically charged with a very small current only; this current is in the range of pA. Such small currents cannot affect substantially the activities of the species that determine the potential of the reference electrode. So, in justified situations, when the voltammetric half-wave potential or peak potential does not have to be known precisely and what really matters is the peak or wave height, the so-called quasi-reference electrodes can be used. Most often a piece of platinum foil immersed into the examined solution is used as the quasi-reference electrode. Quasi-reference electrodes are especially useful when voltammetry at a very low ionic strength solution is performed [1].

III.4.4 The Counter Electrode

The counter (auxiliary) electrode is used in the three-electrode system only. In this system, the current flows between the working and the counter electrode. Either a piece of platinum foil or a platinum or titanium wire is usually employed as the counter electrode. Carbon rods are also used. It is recommended that the area of the counter electrode is substantially larger than that of the working electrode. If this condition is met, the counter electrode should not affect the current measurement due to, e.g. passivation, deactivation and blocking of the surface.

III.4.5 Instrumental Parameters and Wiring

What determines the quality of a potentiostat? Obviously, the ideal potentiostat should be fast, of low noise and of high input impedance. These three requirements rarely go together. Often the user has to choose between "high speed" and "high stability". High stability or low noise in voltammetry is usually achieved in instruments by inserting extra capacitors in the electronic circuit. This solution leads to

distorted voltammetric signals: peaks are smaller and thicker, and waves are more sloped; however, calibration plots constructed for analytical purposes can still be linear. For a more detailed description of the potentiostat construction the reader is referred to the appropriate chapter in ref. [2].

High-input impedance ($>1 \times 10^{12}$ Ω) allows the use of electrolyte bridges of high resistance. It may even be possible to fill the bridge with just deionised water. It is important to realise that any resistance in the cell leads to an ohmic drop in the potential applied to the electrode. Fine instruments offer a possibility of positive-feedback compensation of the ohmic drop. To do this well the value of the solution resistance should be known and inserted either manually or through the appropriate dialog box of the software. The system works in such a way that an extra potential is added to the applied potential to counter the ohmic drop related to the resistance of the solution. If the solution resistance is not known, the method of "set and try" may also be satisfactory. A declaration of a too large resistance usually results in the oscillation of the system and the appearance of faulty peaks. Another possibility of eliminating the ohmic drop is to use the current interrupt method introduced by EG&G in their potentiostats. In this method, while the voltammetric curve is run, the circuit is repeatedly disconnected for several microseconds to analyse the decay of the potential at the working electrode, and an appropriate correction to the potential is applied. Usually, the potentiostats can compensate up to 12 V of ohmic drop, which means that up to 12 V can be imposed between the working and the auxiliary (counter) electrodes. Some EG&G potentiostats can apply up to 100 V. It is worth noting here that a lost connection to the reference electrode during the measurement will result in the application of the maximum potential difference between the counter and working electrodes and possibly in a heavy damage to the electrode surface. Some instruments, those with an impedance-measuring circuit built in, offer an on-line compensation of the ohmic potential drop without any current interrupt.

III.4.6 Nonaqueous Media

Electrochemical investigations are often carried out in aprotic solvents such as dimethylformamide, dimethyl sulfoxide, acetonitrile, propylene carbonate, nitromethane and others. Electrode processes are different in these solvents compared to water. Often well-defined one-electron waves/peaks are obtained. However, to be sure that the results obtained are reliable, one should know the concentration of water in the applied solvent. This concentration cannot be equal to or higher than the analyte concentration to achieve real nonaqueous characteristics. An extra attention should be also paid to the ohmic potential drop, since the resistance of nonaqueous solutions is usually higher compared to aqueous solutions.

III.4.7 Elimination of Electrical Noise

Electrical noise often distorts obtained voltammograms. This may be especially troublesome when the concentration of the examined species is very low. If the frequency of the noise is sufficiently high, the experimental data can be easily

smoothed with most of the commercial electrochemical and graphical software. A simple moving average method as well as the Fourier transform method will give satisfactory results. It is much more difficult to eliminate low frequency (of a few Hz) noise from the voltammograms: usually, the routines applied will affect the faradaic signals too. Even more complicated is the situation when the frequency and the magnitude of the noise change with either potential or time.

Good protection against electrical noise is provided by the application of a Faraday cage during the experiments. A Faraday box can be built quickly by covering a regular carton with aluminium foil. The entire cell with all non-screened electrical connections should be enclosed in the box. Only very small openings should be made for the potentiostat cables. For the best results the Faradaic box (in fact the aluminium foil) should be well grounded.

References

1. Ciszkowska M, Stojek Z (2000) Anal Chem 72: 754A
2. Bard AJ, Faulkner RF (2000) Electrochemical methods, 2nd edn. John Wiley, New York