CHAPTER 2

Cyclic Voltammetric Technique

2.1 INTRODUCTION

It may be surprising to note that cyclic voltammetry is nearly fifty years old. The first cyclic voltammograms of metal ions using the classical dropping mercury electrodes (DME) employed potential sweep rates much faster than the drop time of DME to obtain stationary electrode voltammograms [1]. The theory of linear sweep voltammetry (LSV) and their verifications were reported very much later [2, 3]. With the introduction of carbon paste electrodes [4, 5] and hanging mercury drop electrode (HMDE) [6, 7], more detailed studies of solution phase reactions became possible. The anodic stripping voltammetry (ASV) also obtained a great fillip by the development of HMDE.

In 1960, cyclic voltammetry (CV) was used for the study of H and O monolayers on platinum [8]. This was followed by extensive studies of such monolayers on a number of noble metals. Detailed investigations of electrocatalysis also followed primarily due to the impetus given by fuel cells. Thin layer voltammetry also found extensive use in the characterization of such processes.

As in the case of other analytical techniques, developments in electronics have brought up dramatic changes in cyclic voltammetry as well. Availability of computers enabled numerical simulation works to be carried out with ease, convenience and speed. Theoretical reports containing digital simulation results for a variety of possible reaction schemes were published. Operational amplifiers enabled construction of cheap and reliable potentiostats and other equipments possible. In the late sixties, computers also entered the electrochemical laboratories [9, 10]. Data acquisition, storage and analysis became possible. Simultaneous advancements in theory as well as instrumentation have thus made this technique very reliable for new studies.

At present the emphasis is moving towards application of the technique for individual systems from the development or refinement of the technique itself. Recent developments such as modified electrodes, conducting polymers and photo-electrochemistry also act as catalysts for such developments. However, with each experimental report, a number of refinements is noticed in the experimental approach. Hence new ideas, new insights and new directions are always noticed in the experimental aspects of cyclic voltammetry as well. Fortunately some excellent works describing the experimental

aspects of electroanalytical techniques in general are now available [11-14]. Most of these details are relevant to cyclic voltammetry as well. Some brief reports on cyclic voltammetry are also available [15;16].

The basic experimental approach in cyclic voltammetric method is essentially the same as in the classical polarography with much wider scope for varying the material components involved. In classical polarography one uses dropping mercury electrode alone as the working electrode. In CV a wide variety of liquid and solid electrodes including semiconducting electrodes can be employed (Section 2.2). One can investigate the redox behaviour of the species present in solution or the redox behaviour of these electrode materials, the nucleus (Section 2.2). The redox species may be dissolved in water, alcohol, aprotic solvents and even liquid hydrocarbons, fused melts and solid electrolytes (Section 2.3). The ionic conductivity of these solvents may be enhanced using a variety of supporting electrolytes. The supporting electrolyte also minimises the iR drop, modifies the solvation behaviour of the redox couple and the acid-base properties of the solvent (Section 2.4).

Like polarography, cyclic voltammetry is also a controlled potential technique. The electrode potential is varied in a desired fashion using a stable reference electrode system (Section 2.5). Wide variations in the reference electrode component are also possible. The current flow is again measured between working and counter electrodes as in polarography. All types of new cell designs adapted in modern polarography are adopted in CV. Some new cell designs are also specifically introduced (Section 2.6).

The most striking developments in modern polarography are in the area of electronic instrumentation and computerization. All these developments have found parallel applications in cyclic voltammetry as well (Section 2.7). As wider variations of polarographic methods such as pulse and differential pulse polarographic methods are being developed parallel developments are also noted in linear sweep and cyclic voltammetry (Section 2.8). In short, polarographic and voltammetric methods are based on some types of material components (Fig. 2.1) with a much wider scope for variations in the latter one. Hence most of the details regarding the polarographic methods discussed earlier [1-14] are basically applicable to the CV as well. However, in addition to this, one must also look at the possible

variations in all the material components of the electrochemical as well as measuring systems in cyclic voltammetry.
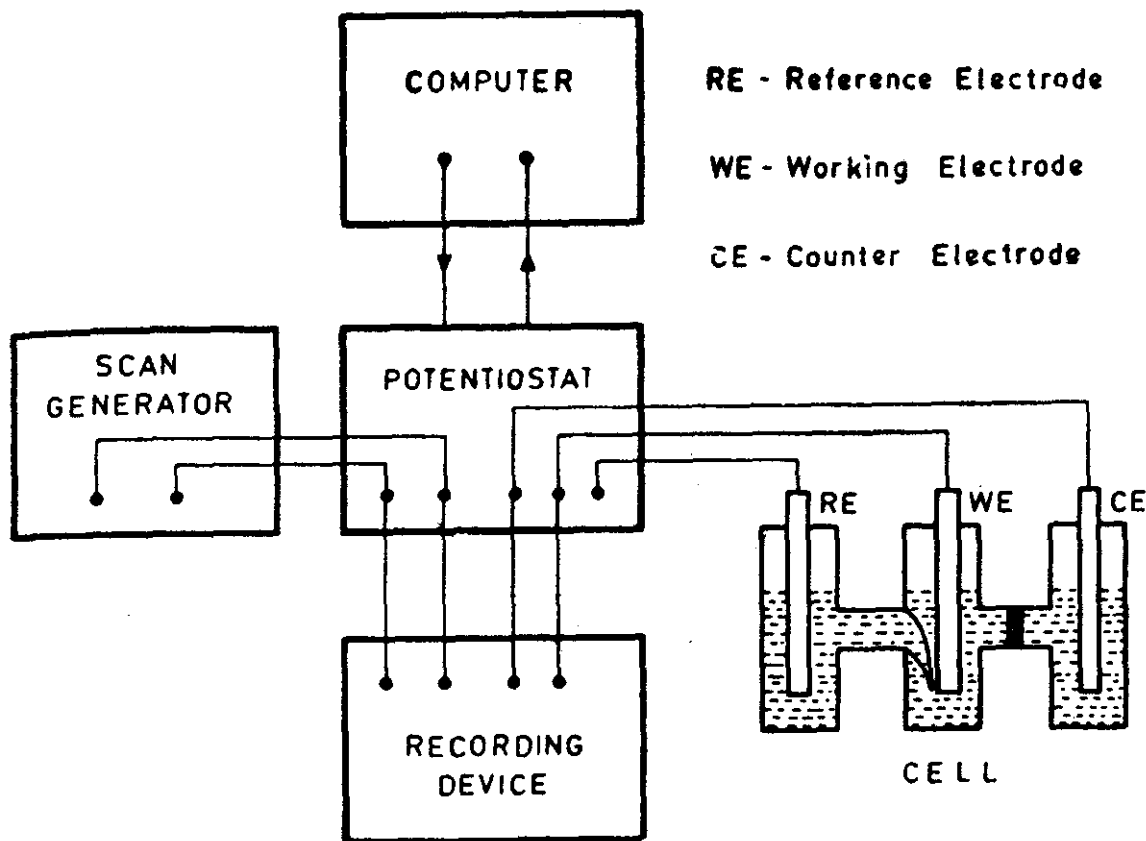

Fig. 2.1   Instrumental set-up for cyclic voltammetric experiments.

Hence, in this chapter, there is a concentration on two important questions in cyclic voltammetric technique. First of all, what specific properties of an electrochemical cell component such as the electrolyte dictate their choice in a particular experiment? Similarly which instrumental method would suit a particular study of an electrochemical system. Once such a choice is made, the second question arises: How is the individual experimental situation practically handled? A comprehensive discussion on the properties and practices of individual electrochemical system components follows.

2.2 THE WORKING ELECTRODES

2.2.1 MATERIALS AND PROPERTIES

For practical convenience, one may classify the working electrodes into four types: (a) inert electrodes, (b) reactive electrodes, (c) photo-

excitable or semiconductor electrodes, and (d) synthesised or chemically modified electrodes. Overlap is very common in this classification. For example, depending on the potential region, one electrode may function either as inert or reactive electrode. This limitation need not, however, restrict one from a convenient discussion of working electrodes employed in electrochemistry.

Inert electrodes, which do not chemically and electrochemically react in the potential region of interest, are the most often sought after electrodes for the study of solution phase reactions. Hg is the most popular electrode of this type [17]. Absence of surface defects (liquid electrode), easier cleaning procedures, and high cathodic overvoltage for hydrogen evolution are factors in its favour.

Since it easily dissolves anodically, Hg is not suitable in anodic regions. For such processes Pt is the electrode of first choice. In aqueous solutions an oxide film is formed in the anodic region and hydrogen evolution limits the cathodic potential region. In non-aqueous solvents, however, Pt provides a very wide potential region. Polycrystalline materials are often employed [11, 13], but some recent works consider single crystal electrodes and their orientational effects (Chapter 7 for example).

In aqueous media, Au offers a wider potential region when compared with Pt. Oxide formation takes place at much more positive potentials (Chapter 7). Polycrystalline as well as single crystal electrodes have been used [11].

A few other metallic inert electrodes such as boron nitrides and some carbides were introduced into electrochemistry [11]. However, either because of poor reproducibility or high electrical resistivity, these electrodes were not very successful.

A number of carbon electrodes has been introduced into voltammetric studies [18, 19]. These electrodes have a very wide anodic as well as cathodic potential region, both in aqueous and non-aqueous solvents. Single crystal graphite materials are quite difficult to obtain and use. A few studies with such materials, however, indicate different behaviour in the basal plane containing the electron rings of graphite crystal and the edge plane which is perpendicular to it [20]. Carbon paste made of graphite powder and a mineral solvent was one of the earliest inert electrodes introduced into electrochemistry [11]. Until recently pyrolytic graphite was widely used in voltammetry [18, 19]. Carbon fibres [21] introduced recently may be considered as the miniature version of this graphite materials formed by pyrolysis and

deposited on a mantle. It may also be formed as a film on other substrates [21 a, b]. However, the vitreous or *glassy carbon electrode* introduced recently into electrochemistry is the most widely used carbon electrode material today [22, 23]. Its high mechanical stability, low porosity, inertness over a wide potential region and good conductivity and reproducibility are some of the reasons for its very wide applications.

Almost any metallic electrode in any environment would become reactive at some sufficiently anodic potential. These electrodes may then directly dissolve into the electrolyte, form some oxide, sulphide or selenide or any other compound solid phase. The thickness, porosity, reactivity and conductivity may vary over a wide range. The processes taking place on such reactive electrodes are of interest to many surface scientists and technologists. The surface processes of many working electrodes such as noble metal electrodes, Fe, Ni, Cd, Ti, Ta and Cu electrodes are considered later (Chapters 6 to 10).

As pointed out above, at sufficiently negative potentials even these reactive electrodes can function as inert electrodes. For example, Ag [24], Cu [25] aud Pb [26] have been used as inert electrodes in cyclic voltammetric studies. Great care must, however, be taken to obtain and retain the inert base metallic surface of these electrodes.

Conducting anodic films formed on the electrodes may also sustain some interesting solution phase reactions. The Hg (1) salt film electrodes were used very early for the study of anodic processes [27]. Many electro-oxidation reactions of organic and inorganic compounds take place on oxidized metallic surfaces (Chapter 12). RuO_2 and IrO_2 electrodes have been employed especially in the synthesis of modified electrodes. Highly doped SnO_2 electrodes have electrical conductivity close to that of metals. In addition, they are optically transparent. These electrodes thus find use in spectro-electrochemistry (Chapter 15). It is very difficult even to state whether these electrodes are in fact inert or reactive. They usually give comparatively higher residual current indicating surface reactions (Chapters 12 to 14).

A notable feature of the third type of electrodes is their photo-excitability. Already the presence of an energy gap between the valence band and the conduction band in a semiconductor has been discussed (Section 1.2.1). Photons may be employed to excite the valence band electrons. The follow up processes after such photo-

excitations are indeed very attractive and are under active research (Chapter 16). A number of such electrodes are employed from narrow band gap (Si, MoS_2) to very wide band gap (TiO_2, ZnO). Both single crystal as well as polycrystalline materials have been employed. Some electrodes may even be prepared electrochemically (28).

Finally one may also employ chemically synthesized materials as the working electrodes. A great variety of such 'chemically modified electrodes' are now available (29; 30]. Cyclic voltammetry is extensively used for their preparation and characterization (Chapters 8 to 10). These types of working electrodes can also catalyse a number of electrochemical reactions (Chapters 13 and 14).

2.2.2 PRACTICES

One might choose any electrode material discussed above for work depending on one's interest, experience and the nature of the problem. But one has no choice with regard to the strict practical procedural standards to be adopted to obtain well-defined, reproducible and meaningful results. The following practical aspects require great emphasis: (a) purity, (b) size and shape, (c) cleaning, (d) fabrication, (e) orientation, (f) material handling, and finally (g) pretreatment [31]. All these aspects are dealt with here, briefly.

a) *Purity requirements*

Purity of the electrode material must be around 99.999 per cent for well-defined results. Mercury may be easily purified to this grade in the laboratory [12-14, 17]. Pt, Au and many other solid electrodes of this level of purity are commercially available. It is also a good practice to report the source of the working electrode along with the purity levels and possible impurities.

Planar electrodes are the simplest ones to treat mathematically, especially when mass transfer effects are also involved. Plane discs of a few mm diameter with proper shielding would represent this situation. Hence this is the shape more often employed in voltammetric studies. Hg can be held only in the form of a drop from a capillary. When using such hanging mercury drop electrode (HMDE), one must always consider the spherical diffusion effects. Small electrodes draw very small currents through the cell. This

eliminates the potential drop due to the resistance of the solution to a great extent ($E = iR_u$ where R_u is the uncompensated solution resistance). Hence very small electrodes have attracted some interest recently. Carbon fibre [21], Pt and Au wires [32, 33] of diameters around 5–10 µm have been introduced recently. The diffusion problems at such micro-electrodes are still unresolved to a great extent (Chapter 3). Electrodes in the form of thin plates or mini-grids may also be employed in, for example, thin layer voltammetry and spectro-electrochemistry.

Commercially obtained pure electrodes may be degreased in acetone or similar solvents to remove the grease impurities carried over during packaging and transit. The solvent must be carefully chosen so that it does not dissolve the electrode itself. Metallic electrodes may also be annealed at appropriate temperatures to relieve the strains on the electrode materials.

b) *Fabrication and storage*

It is always preferable to buy the electrode in the shape in which it is intended to be used. Whenever a shape change is required, recasting or machining may of course be resorted to. However, in such works, one must take care that the electrode material does not get contaminated by the impurities of the crucibles or the machinery. Easily oxidizable materials must be cast and annealed under inert atmospheres.

Only a fixed surface of an electrode must be exposed to the electrolyte. The liquid metal is easily hung through a capillary. The metallic wires and micro-electrodes which can withstand high temperatures may be fused into a soft-glass tube. Pyrex glass may also be used, but its life would be shorter due to uneven thermal expansion. For easily oxidizable metals, the sealing must be carried out under inert conditions [31, 34]. For elecctrode materials that cannot withstand direct flames, heat shrinkable Teflon or Kel F (another plastic material that can withstand normal electrochemical conditions) material may be used for fabrication of the electrodes. Electrodes may also be fixed into a glass tube using epoxy resin. However, in such cases, epoxy material may possibly render the electrode less active if it enters into the working electrode material. If the electrode has some odd geometry and hence may not be

enclosed easily, it may be hung from a Pt hook which, in turn, may be sealed in a glass tube.

In all these fabrication works, care should be taken to see that the electrode is completely sealed by the encapsulating material and the solution does not seep in. All the unwanted portions of the electrode surfaces must also be covered by a non-conducting film. These effects can cause irreproducibility.

When powder materials such as graphite are to be used as electrode materials, it may be formed as a paste with, for example, Nujol and fixed into the cavity of the electrode holder [11]. The electrode may also be formed as a polymer composite. Kel F graphite electrode introduced recently [35] has some good qualities such as machinability.

When detailed studies on single crystal electrodes are undertaken, the electrodes must be mounted in the proper direction. Techniques such as X-ray diffraction may be used for exposing the required plane (111 of silver, for example) alone to the electrolyte.

Even the question of taking ohmic contact from the working electrode may not be a trivial problem, for example, in the case of semiconductors. Silver conducting paste, liquid metal contact, Au plated contact etc. may be employed. Potential drop at this juncture must be carefully avoided.

Fabricated electrodes must be stored in a clean environment. It is also a good practice to avoid touching the electrode surface manually. If the working electrode can undergo easy air oxidation, it may be stored in inert atmosphere. Hg capillaries are normally stored in high purity water to avoid Hg spillage. There is no reason for storing solid electrodes in water for longer times although this practice is reported in the literature. This procedure would, in fact, result in the slow adsorption of minor impurities in the solvent.

c) *Pretreatments*

One may refer to all mechanical, chemical and/or electrochemical treatments given to the working electrode just prior to the voltammetric measurement as electrode pretreatment. Obtaining reproducible results and activating the electrode surface to obtain reproducible results are the two main objectives of a great variety of pretreatment procedures reported in the literature

Reproducible results can be obtained if the electrode is maintained

in the same state of cleanliness. Mechanical polishing is carried out with metallographic papers of increasing fineness. The electrodes may also be polished using alumina or diamond powder of 0.05 μ size. This would remove all surface impurities. However, care must be taken to clean the electrode thoroughly afterwards to ensure that the polishing materials are completely removed. Otherwise, these polishing materials themselves may show some spectific catalytic or inhibitive effects [36].

Chemical cleaning using oxidizing agents starting from permanganate up to *aqua regia* are usually recommended. From experience these methods show that they not only oxidize impurities but also the electrode materials. Some carbon electrodes are quite irreversibly oxidized very strongly. These electrodes produce high background currents and very poor reproducibility. If oxidative or reductive removal of impurities is our primary objective the electrochemists have a much better option, namely, the electrochemical oxidation or reduction. The electrodes can be potentiodynamically swept between some predetermined potential regions (which would vary for each electrode) to obtain the same residual current. The potential range, the sweep rate and the time of potential cycling must be carefully chosen and reported along with the results.

The cleanliness of the electrode and hence the electrode reproducibility may change during the course of an electrochemical experiment. This is termed as time effect. This may happen due to slow adsorption of impurities in the electrolyte solution, slow passivation of electrode surface or the adsorption of products of the electrochemical reaction on the electrode surface. These may normally be removed by potential cycling pretreatment discussed above. At times, other methods may also have to be resorted to. How often one must resort to electrode pretreatment depends on how long one is able to get reproducible current potential curves.

Activation of the electrode surface is primarily achieved by electrochemical oxidation and reduction of the electrode surface or potentiodynamic sweeping discussed above. The electrode activation may be due to resurfacing of the surface atoms of the electrode or increased surface roughness of the electrode (Chapter 7). On carbon electrodes, surface activity may be enhanced by improving the surface hydrophilicity (Chapter 11).

d) *Surface area measurements*

The geometric area of liquid electrodes (normally in the form of drops) and solid electrodes of well-defined geometry may easily be determined. However, determination of a true surface area of most solid electrodes is more involved since even a well-polished electrode may have some microscopic roughness. For some noble metals such as Pt and Au, adsorption coverage of hydrogen or oxygen may be used for surface area determination (Chapter 7). The double layer capacitance value at a fixed potential (Section 1.3) in a selected medium may also be used if the standard value per unit actual surface area is known. The diffusion limited peak current values are often employed for this purpose (Chapter 3). However, it must be remembered that the area determined by this method on most occasions only corresponds to geometric surface area and does not include the roughness factor (Chapter 3).

2.3 THE SOLVENT

2.3.1 MATERIALS AND PROPERTIES

A number of physicochemical properties must be considered while choosing a solvent for electrochemical work: (a) it must be a liquid at room temperature, (b) it must have sufficient solubility for ionic substances to form conducting electrolyte; it must be able to dissolve the electroactive species of interest, (c) it must have a wide enough potential region for the study of the redox process of interest, that is, the solvent itself must not undergo oxidation or reduction in this potential region, and (d) it must possess the required acid-base properties.

A few detailed discussions on the solvents used in electrochemistry are available [12, 37, 38]. Here only the physicochemical properties of a few widely employed solvents are discussed. The dielectric constant is the most important parameter.

The cheapest solvent is water which possesses many physico-chemical properties. It can dissolve ionic components and form highly conducting solutions. Many compounds of electrochemical interest dissolve easily in the solvent. Its acid-base properties are also well understood. However, the solvent itself gets reduced or oxidized to H_2 and O_2 very easily. Hence it only possesses a potential region of 2.0 V for the study of other processes. It reacts so well with radicals

that it is unsuitable for radical ion studies. Water also easily forms oxide films on solid electrodes and hence affects reactivity and reproducibility. Some organic reactants are less soluble in water. This defect is normally overcome by using alcoholic mixed solvents or alcoholic stock solutions of reactants.

Acetonitrile is perhaps a solvent with inert electrochemical properties. It has $+3.0$ V (versus SCE) anodic and -3.0 V cathodic limits. Even these limits are probably set by the supporting electrolyte oxidation and impurity (water) reduction. If impurities are absent, radical ion chemistry may be studied very well. However, this solvent has very poor solubilitry for ionic species. Salts containing organic ions such as tetra-alkyl ammonium salts must be employed. A few electroactive salts such as Ag (1) and Tl (1) salts are also soluble.

Dimethyl formamide (DMF) is one of the aprotic solvents which has very good dissolving power for ionic species. It has a cathodic limit up to -3.0 V anion radicals. Hence, this is the solvent of choice for studies on anion radicals and dianions. In the positive potential regions above $+1.0$ V, the solvent itself decomposes. Cation radicals are less stable in this medium.

Dimethyl sulphoxide has electrochemical properties similar to DMF in the cathodic region. It has somewhat a better anodic potential limit. Since it is not as basic as DMF, cation radicals are somewhat stable in this medium.

Methylene chloride is the solvent of choice for organic oxidation studies. It is stable up to $+3.0$ V as acetonitrile. Cation radicals and dications are quite stable in this medium. Electrolytes are easily soluble when compared with acetonitrile. Even large organic molecules and polymers are soluble in this medium. However, at negative potentials of -1.0 V, the solvent decomposes. The anionic species are less stable in this medium.

A host of other solvents are used in voltammetric studies. Propylene carbonate widely used in battery research can, for example, stabilize both anion and cation radicals. Hexamethylene phosphorylamide may be employed for solvated electron studies. Tetra-hydrofuran is employed to study hardly reducible species. Even totally non-polar solvents such as benzene and other hydrocarbons may be used to study the solution phase [39] as well as surface [40, 41] processes. More details of their properties and uses have already been reviewed [12, 37, 38].

2.3.2 PRACTICES

Most of the solvents with required purity levels for voltammetric studies are commercially available. Some practical details of purification, storage and handling of a few solvents discussed above are considered here.

Water, deionized and repeatedly distilled with alkaline $KMnO_4$, is usually considered as pure. The purity is checked by conductivity measurements. However, this water might still contain some volatile impurities [42]. These may be removed by passing the distilled water vapour through a column containing Pt catalyst at about 800°C over which oxygen also is simultaneously passed. The organic impurities are oxidized completely by this procedure [42].

The main impurity present in non-aqueous solvents is water. This is usually removed by refluxing with anhydrous copper sulphate, alumina, aluminium chloride, P_2O_5 etc and distilling many times and collecting the proper fraction. The distillation is normally conducted at reduced pressure to avoid decomposition of the solvents. Some aprotic solvents may easily absorb moisture. In such cases vacuum lines must be employed during purification, storage and use in voltammetric work [43]. An easier procedure would be to employ a dehydrating agent such as anhydrous alumina as an internal addition [44]. It must, however, be ensured that these materials do not interfere in the voltammetric behaviour in other ways.

Aprotic solvents may contain other impurities. Oxidizable impurities may, for example. be removed by refluxing with $KMnO_4$. Reducible impurities may be removed by refluxing with sodium (Dioxane). Polymeric materials that may be present in acetonitrile are removed by refluxing with CaH_2 and subsequent distillation.

Any metallic electrode surface would contain approximately 10^{15} atoms per cm^2 surface area. This entire surface area may be blocked by just 10^{-8} M impurities in a solution. This should indicate to us the level of purity requirements of the solvent. Sometimes the detection of such low levels of impurities in solvents itself becomes a problem [37, 38].

2.4 SUPPORTING ELECTROLYTES

2.4.1 MATERIALS AND PROPERTIES

Here all ionic salts or ionizable compounds in a solvent are defined as the supporting electrolytes. It is very important to realize that they can influence the electrochemical process in a number of ways: (a) these electrolytes impart conductivity to the solvent and hence enable the continuous current flow in solution; (b) they must remain electroinactive in the potential region of interest if any useful voltammetric study is to be conducted; (c) if the concentration of the supporting electrolytes is very low, they can form a space charge near the surface and the space charge potential can influence the charge transfer kinetics (Section 1.3.1 and Chapter 11); (d) if the ions of the supporting electrolytes are adsorbed on the surface, they can catalyse or inhibit other reactions (Chapters 11 and 12); (e) small cations may form ion pairs with the anion radicals formed in the electrode process and the properties of the ion pairs can be very different from those of the free anion radical; (f) some ions may form complexes with the reactants and/or products (Chapter 6);(g) the supporting electrolytes generally control the acidity of the ionic solution; (h) the liquid electrolyte melts and solid electrolytes act as the medium for the ionic phase; and (i) in a few circumstances such as oxide growth in alkaline media, they may function as the electroactive species.

A number of controversies in the voltammetric behaviour as seen later can be traced back to the use of different supporting electrolytes. Even today a number of voltammetric results at very positive potentials in KCl media is interpreted without possible influence of Cl^- adsorption. Reductions in Li^+ salt solutions are interpreted without consideration of ion-pair effect. One must always consider all possible influences of supporting electrolytes if such pitfalls are to be avoided.

$HClO_4$, H_2SO_4 or HCl are normally employed for studies in acidic aqueous solutions; and $NaOH$ or KOH are employed for alkaline media. In the neutral region, if buffering is important, acetate, citrate and phosphate buffers are usually employed. If the redox process does not involve acid-base reactions, no buffers are needed

and any electrolyte may be used. Alkali metal salts are usually employed.

A number of anions such as Cl^-, OH^-, citrate, tartrate and oxalate added to control acidity may also be involved in complex formation as mentioned above. Some electrolytes such as KCN, KCNS and EDTA may intentionally be added to promote complex formation.

Solubility is the main consideration in selecting supporting electrolytes for aprotic solvents. $LiClO_4$ is quite soluble in a few aprotic solvents. $NaClO_4$ is much less soluble. A number of tetra-alkyl ammonium (TAA) salts shows good solubility in aprotic media. Tetra-ethyl ammonium (TEA) and more recently tetra-n-butyl ammonium (TBA) salts are widely employed for this purpose.

Perchlorate ions are usually oxidized at about + 1.6 V. BF_4^- ions are not oxidizable at least up to + 3.0 V. This is the anion of choice in most recent works. PF_6^- has been introduced recently.

A number of molten electrolyte systems has been characterized. Lewis acid-base characteristics may be varied conveniently by varying the electrolyte composition. A recent work [45] describes the properties and practices of a number of molten salt systems including room temperature melts.

2.4.2   PRACTICES

Most of the inorganic acids, bases or salts are commercially available in the high purity grade.

TAA salts are frequently available in the form of halides. The perchlorates or fluoborates may be easily obtained by double decomposition of these salts with the corresponding sodium salts. The precipitated $TAAClO_4$ or $TAABF_4$ may be recrystallized twice or thrice [12].

Some electrolytes may be hygroscopic. Dehydration may be done in an oven. Dehydrated samples should be stored in desiccators.

Care must be exercised in handling explosive salts such as $NaClO_4$. They must neither be overheated nor ground in mortars with force, and contact with organics should scrupulously be avoided.

2.5 THE REFERENCE ELECTRODES

2.5.1 ELECTRODES AND PROPERTIES

The general requirement of a reference electrode is very simple. Its potential should not vary when the external potential is applied in the working electrode-reference electrode system of the cell. It must also be chemically stable. There is a number of electrode reactions which possess these physicochemical properties [46-48].

The standard reference electrode system is the reversible hydrogen electrode where H^+ ions and H_2 gas are present in an electrolytic half cell with a platinum black electrode. The electrode potential at unit activity of H^+ and H_2 at 25°C is taken as the zero point for the electrochemical scale of potentials. This is the best electrode for the processes where H^+, H_2O or OH^- ion is the reactive species. The pH-dependence of the working and reference electrodes will then be directly related.

The metal/metal ion electrodes may also be employed as reference electrodes. Cu/Cu^{2+} reference electrodes are extensively employed. Ag/Ag^+ (acetonitrile) is used as the reference electrodes in non-aqueous media. Al/Al^{3+} reference electrodes are employed for measurements in non-polar solvents [41] and in molten salt media [49].

The most popular reference electrodes, however, are the so-called electrodes of the second kind where the equilibrium electrode potential depends on an ion that does not directly involve in an electrode reaction. In the most widely used saturated calomel electrode (SCE), for example, the Hg is in contact with Hg_2Cl_2/KCl paste which then is in contact with a saturated KCl solution. The electrode reaction is Hg^+/Hg reaction but because of the low solubility of Hg_2Cl_2, the electrode potential depends on Cl^- concentration. The electrode potentials of such electrodes can very easily be maintained at a constant value. The Hg/Hg_2SO_4, $Ag/AgCl$ and Hg/HgO electrodes also belong to this group.

A film of redox material (say ferrocene/ferrocinium couple) may be produced on an inert electrode material by, say, polymerization. Such a redox film electrode can function as a very good reference electrode [50]. If the stability problems associated with these

electrodes are solved, they may become very popular reference electrodes in future.

The present day instruments generally employ a very high impedance in the working electrode-reference electrode cycle to control the potential. Hence very little current flows through these cycles. This enables the use of even a Pt or Ag wire of some oxidized state [51] to be used as a quasi-reference electrode to maintain a constant potential. However, the electrode potential is not defined by any electrochemical equilibrium. The potential of this quasi-reference electrode must be monitored against another standard electrode or some internal standard redox couple such as ferrocene/ferrocinium ion couple must be used to measure the electrode potential.

2.5.2 PRACTICES

Although a number of reference electrode half cells is available, the choice is very much narrowed down by a number of practical considerations. Some of the practical problems one must consider are:

(a)   The reference system must not contaminate the solvent-supporting electrolyte (SSE) of the working electrode-electrolyte system. Contamination of cations, anions as well as solvent must be avoided.

(b)   The chemical stability of the reference electrode-electrolyte system must not be affected by the SSE of the working electrode and *vice versa*.

(c)   When a liquid junction is created to overcome the contamination effects, it must be ensured that no liquid junction potential is created which would affect the results.

(d)   No undue increase in the uncompensated solution resistance (R_u) must be allowed in constructing a compatible reference system.

(e)   The reference electrode system must, of course, be easy to construct, handle and get well-defined constant electrode potential. There can of course be very few electrodes that meet all these requirements.

Contamination effect in principle can be avoided only when studying processes involving H^+ or OH^- ions (using hydrogen reference electrode) or metal ions (using M/M^{2+} reference electrodes). In all other processes contamination effects will be encountered and overcome. The chemical stability of the electrode must receive primary attention. The Hg/Hg_2Cl_2 electrode cannot be used in CH_3CN medium since Hg_2Cl_2 can disproportionate and drastically change the activity of the reference electrode.

Salt bridges are introduced to minimize ionic contamination. Liquid junction potential is minimized by using salts of ions the mobilities of which are almost equal (for example, KCl), but it must be remembered that even in this type of bridges Cl^- ions can migrate into the working electrode compartments and exhibit adsorption effects.

When studies are carried out in non-aqueous solvents, one must also consider the mixing-up of solvents of the working and reference electrode compartments. Traces of water in non-aqueous media can greatly influence solvent properties [48]. The electrolytes are separated by materials of high mass-transfer resistance to minimize solvent diffusion. Fine frits, fine asbestos fibres sealed in glass, or porous thirsty Vycor are employed for this purpose [12]. A separate compartment containing the test solution may also be interposed between the reference and working electrode cells (Fig. 2.2). This would prevent the mixing up of solvent in the working electrolyte solution.

One may eliminate contamination by increasing bridge length or increasing the number of bridges and intermittent solutions. However, while doing so, simultaneously the electrolyte solution resistance is being increased and this results in additional potential drop. This may become a very severe problem when non-aqueous media are employed or very fast sweep rates are applied. Hence, in the construction of bridges there must always be a compromise between minimizing contamination and resistance. The quasi-reference electrodes [50] mentioned above have the special advantage in this regard. They do not contaminate. They do not practically introduce any resistance component. They have a very fast response and hence are suitable for fast sweep rates [31].

Ultimately, convenience is one of the major deciding factors in the choice of an electrode. This is why hydrogen electrode is not very
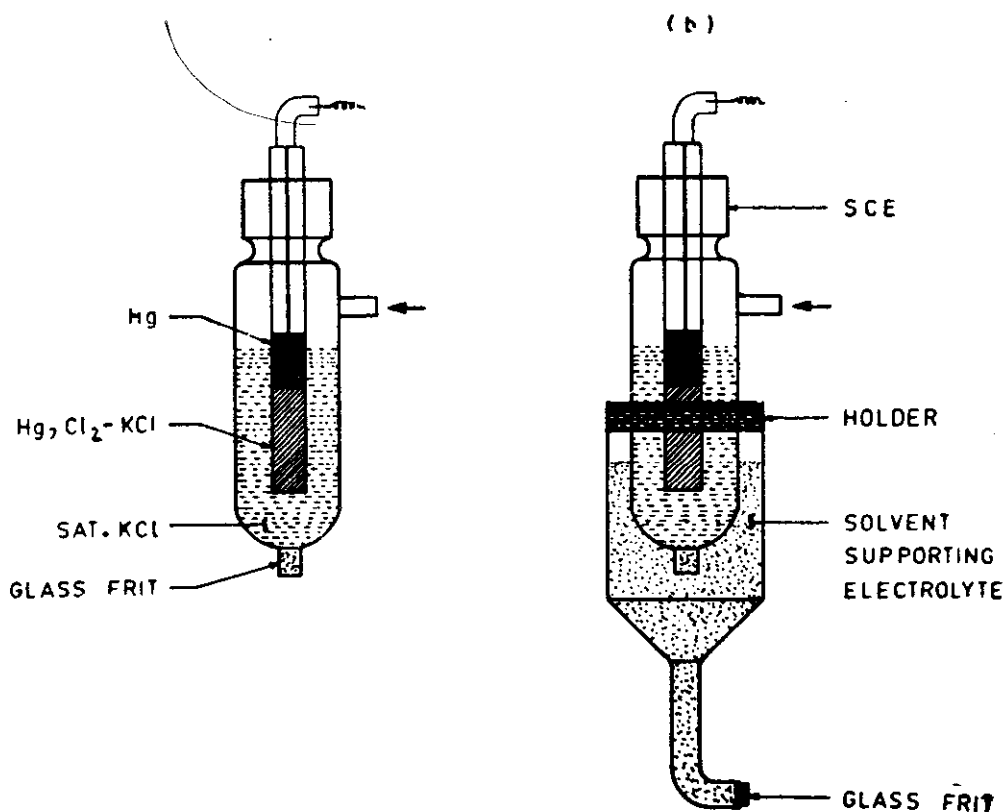
Fig. 2.2   Typical calomel electrode set-up and the solvent supporting electrolyte jacket for eliminating the mixing up of solvents.

often used. The necessity to pass hydrogen at a constant pressure is not at all a   convenient procedure. The high popularity of SCE is also because of the ease with which it can be prepared and handled. If H_2O contamination is noted, the working electrolyte is dehydrated with alumina. However, when using such general purpose electrodes, one must always take note of their limitations.

2.6   CELLS AND OTHER MATERIAL COMPONENTS

In the last four sections the four major components and their variations have been conside. ed. In this section all the other material   components   of   an   electrochemical   cell   are   briefly considered. These aspects are clubbed together not because they are unimportant, but because the choice here is mostly practical and there is not much physical chemistry to discuss about.

2.6.1 CELL TYPES

The simplest electrochemical cell can be a beaker with the three electrodes: (a) the working, (b) the reference, and (c) the counter electrodes, dipping in an electrolyte solution. Oxygen or any other gaseous component in the atmosphere can contaminate this solution. Hence usually a glass cell with a ground joint is used. The ground joint cover has provisions for the three electrodes (Fig. 2.3). There
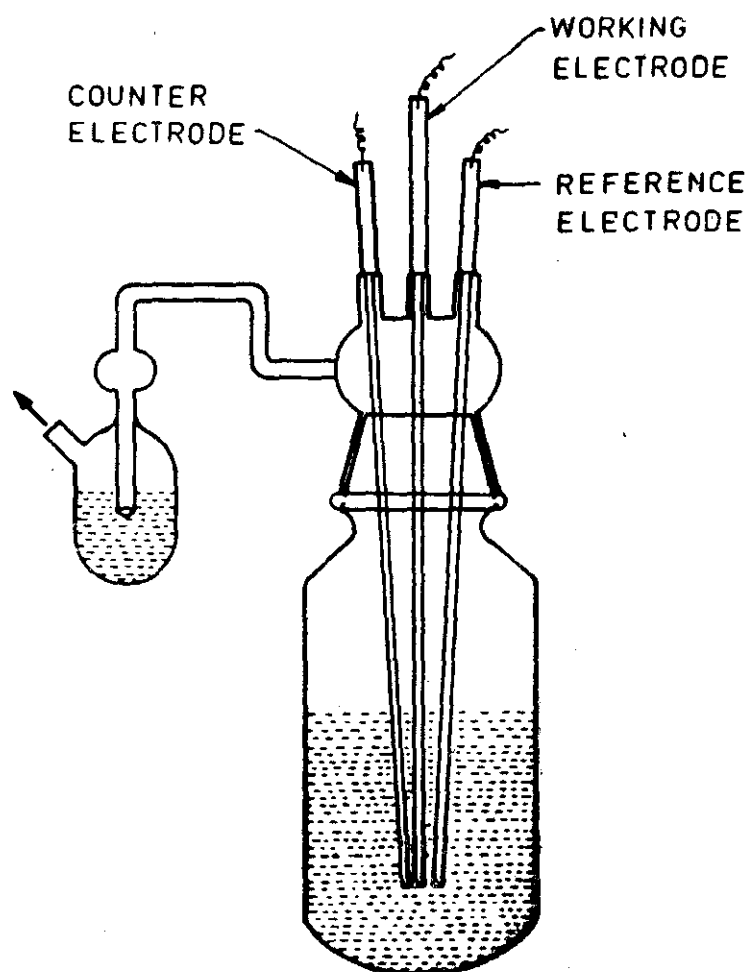

Fig. 2.3   A typical single compartment cell for cyclic voltammetric experiments.

is also additional provision for removal of dissolved oxygen or other gases by passing an inert gas. The electrolyte volume in such a cell is around 25 ml. This is the most convenient cell design for non-aqueous solvents.

In the single component cell described above, the working and counter electrode compartments are not separated. In some situations

the reaction products at counter electrode may interfere with the reactants at the working electrodes. This is specially true if voltammetric experiments are carried out for longer times at slower sweep rates. For such purposes the working and counter electrode compartments may be separated by mass transfer resistant materials such as glass frits (Fig. 2.4). In such cells the reference electrode is

A - Working electrode

B - Counter electrode

C - Luggin capillary

D - Fine porous glass frit

E - Gas inlet

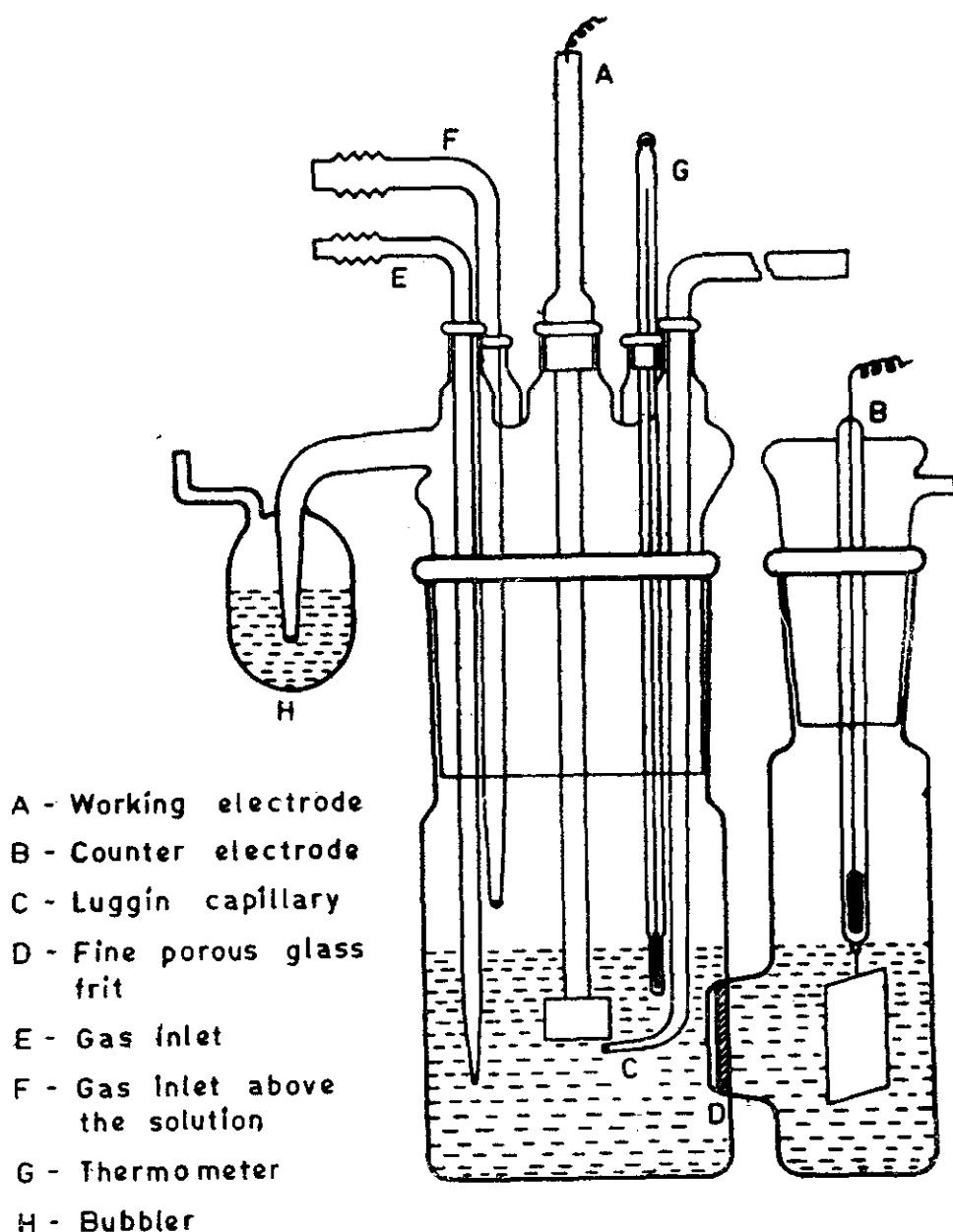F - Gas inlet above the solution

G - Thermometer

H - Bubbler

Fig. 2.4   A typical H type cell for cyclic voltammetric experiments.

connected to the working electrode through a luggin capillary. Sometimes a three compartment cell also may be used. The third
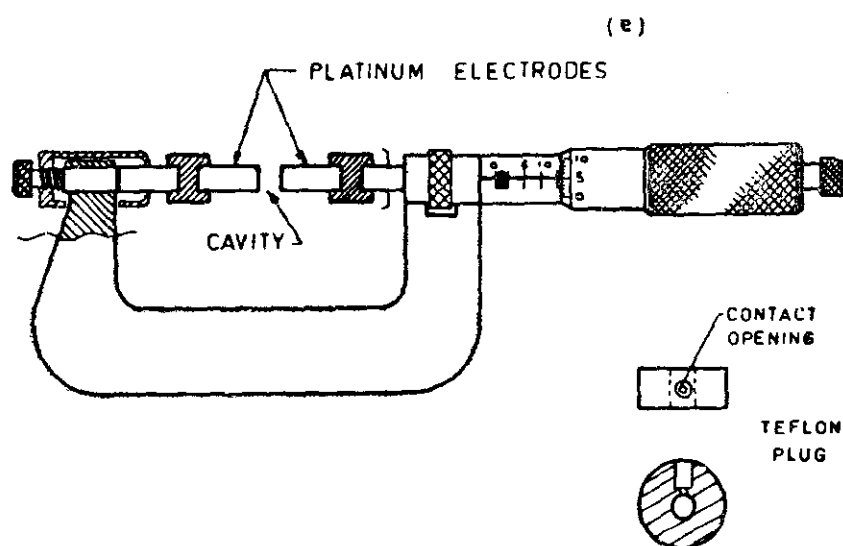
(e)

PLATINUM ELECTRODES

CAVITY

CONTACT
OPENING

TEFLON
PLUG

Fig. 2.5(a)   Micrometer electrode. The teflon plug surrounds the thin layer of solution [From AT Hubbard and FC Anson, Anal Chem 36 (1964) 723].
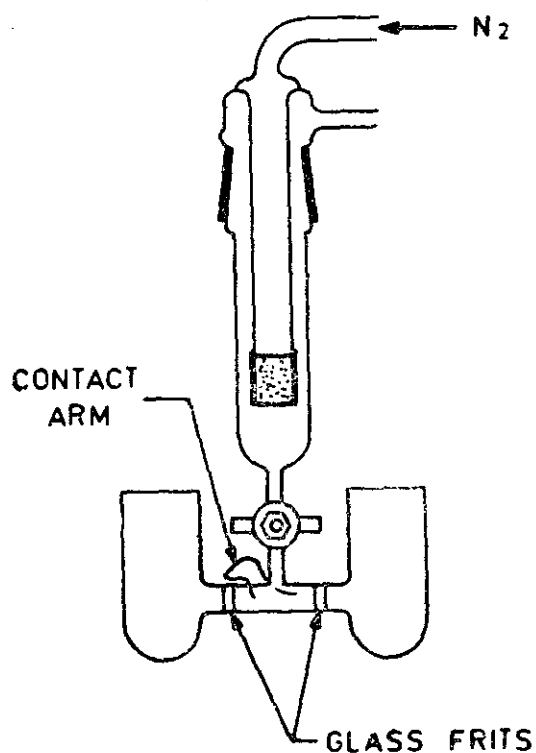
N₂

CONTACT
ARM

GLASS FRITS

Fig. 2.5(b)   H cell for use with the micrometer electrode. One compartment contains the auxiliary electrode and the other compartment contains the reference electrode [From N Winograd and T Kuwana, Electroanal Chem 7 (1974) 1].

compartment will house the reference electrode. These cell designs are more suitable for aqueous medium.

A third type of cell which is becoming popular in recent times is the thin layer cell. These types of cells have a high area to volume ratio and they have many advantages in the mathematical treatment of the problem as well as experimental evaluation of results (Chapter 10). A typical thin layer cell is presented in Fig. 2.5. More variations and details may be found in the literature [52, 53]. Such cell designs with optically transparent electrodes are very popular in spectro-electrochemistry [54; 55].

Electrochemical instrument manufacturers themselves supply most of these general purpose cells. A number of variations in these basic designs may however be seen in individual laboratories depending on the individual nature of studies and also to some extent on the interest and capable sophistication of the research workers.

The cells are usually made of glass materials with ground joints. These are easy to clean (say with nitric acid) and use. They are resistant to most of the solvent media. In some situations where glass is not suitable Teflon or Kel F materials may be used. In fused salts, especially high temperature fused salts, completely different high temperature materials ranging from graphite to silicaware are used. In these cases, in addition to cell fabrication, its insulation, heating and temperature control are also important [45].

2.6.2   COUNTER ELECTRODES

In voltammetric studies, the current flows between the working and counter electrode. Although the main interest is on the working electrode, it must be ensured that the counter electrode does not complicate matters. It must not dissolve in the medium. The reaction product at the counter electrode must reach or react at the working electrode.

Most of these requirements are fortunately met by Pt electrodes and this is the most widely used counter electrode in aqueous, non-aqueous as well as molten salt media. Pt electrodes in the form of coils or thin foils are normally used. Carbon electrodes are also used in molten salts. The electrode area must be sufficiently larger than the working electrode area to ensure that the limiting current is not controlled by the area of the counter electrode.

2.6.3 GASES AND GAS PURIFICATIONS

Dissolved oxygen can give reduction waves on Hg electrodes. Today, the polluted atmosphere might also contain other reducible or oxidizable impurities. Hence it is always advisable to remove dissolved gases from the electrolyte solution.

Usually N_2, H_2 or argon are employed for deaeration purposes. Nitrogen is the most widely used inert gas. Hydrogen gas is convenient since high purity hydrogen can be easily produced in any electrochemical laboratory using Ni cathode in alkaline KOH. However, hydrogen must not be used in oxidation studies where dissolved hydrogen itself can function as an electroactive species. High purity argon is used in some accurate experimental work.

The gases are usually purified before passing into the electrochemical cell. The methods developed for polarographic work have not changed substantially [17, 31]. Pyrogallol solutions are used for removal of oxygen. CO_2 is trapped in alkali solutions. Acid solutions are used to remove alkali. For non-aqueous solvents, the water is removed by passing the gas through molecular sieve (4A type). Oxygen traces can be removed by passing through heated copper coated silica gel at 350°C for N_2 gas and through palladized asbestos at 450°C for hydrogen. Activated charcoal is also used to remove water and trace impurities. Finally the gas is also presaturated with the electrolyte solution before entering into the electrolytic cell. The gases are usually passed through Teflon tubes during the cleaning procedure.

2.7 INSTRUMENTATION

So far the emphasis has been on the electrochemical cells and related material components. For cyclic voltammetric work, a minimum of three electronic instruments are required to accomplish experimental work: a potentiostat for controlling the potential between the working and reference electrodes, a voltage scan generator for changing the potential of the working electrode in the required way and a recording device for the measurement of the resulting current-voltage curves. Recently the revolution brought about by the microprocessor in the electronic industry is also picking up in the electrochemical instrumentation. Microprocessors or

microcomputers can now replace the voltage scan generator and the conventional recording devices completely and also perform some additional jobs.

A new entrant to cyclic voltammetric experiments can pick up either of the following two ways regarding the use of electrochemical instruments. To be sure and steady, one may try to learn the basic principles of how the instruments function electronically. Most of the instruments employ operational amplifiers that can measure and control current/potential input or output. These operational amplifiers and microprocessor chips are now available as single circuit elements. With some basic knowledge on these elements and instrument functions, many of the instruments may be easily fabricated. Some excellent introductions to electronic instrumentatations are available for the interested readers in this line [12-14, 54, 55].

However, for many electrochemists coming from chemical and biological backgrounds the above approach would definitely be more difficult. Fortunately for them a number of manufacturers are now supplying all electrochemical instruments (for example, EG and G Princeton Applied Research, USA; Bioanalytical Systems Inc, USA, Tacussel Electronique, France, EDT, UK, Metrohm Herisau, Switzerland; Wenking, FRG; Bruker, FRG). These instruments are reliable and are competitively priced. Electrochemists may use these instruments for their purposes just as they use a spectrometer or a chromatograph.

In the brief presentation here, no attempt is made to describe the electronics side of the story of electrochemical instrumentation— just a few questions need answering. What is the function of the instrument ? What can it do for one? What are the practical limitations ? How to select a particular instrument ? A beginner can straightaway go in for some experimental work with commercially available instruments. As he gets along and reaches more intricate questions to be answered, he may go in for a detailed understanding of the instruments [12-14, 54, 55]. If needed, he can improve upon the instruments depending upon his requirements.

2.7.1   POTENTIOSTATS

Basically, a potentiostat must be able to bring the working electrode potential (with respect to the reference electrode) to the desired

level in a short enough time. The time taken by the potentiostat for controlling the working electrode potential is called the rise time. For slow sweep rate experiments (say 10 volts/sec) it is enough if the potentiostat has a rise time of 50 μ sec. This is the sweep rate range normally employed. However, in the study of some fast processes, sweep rates of the order of 10,000/volts sec may be employed. In such cases, it is better to have a potentiostat with still shorter rise times in the range 1 μ sec.

Apart from controlling the working electrode potential, the potentiostat also measures the current flowing between the working and counter electrodes. The potentiostat must also have the capacity to provide the required cell voltage for this circuit. Normally a potentiostat with $\pm$ 15 V capacity will serve the purpose. In non-aqueous media the cell voltage can be higher. Hence a $\pm$ 30 V capability is desirable for such purposes.

In the usual cyclic voltammetric studies the current flowing between the working micro-electrodes and the counter electrodes will be in the range of micro-amperes. But whenever larger electrodes and/or very high sweep rates are employed the current flow may be higher. The current capability of 100 mA is sufficient for most purposes. 1 A potentiostats are also available.

Discussion about iR_u drop between the working and reference electrodes and their influence on the accuracy of potential measurement has already taken place. The measured potential E_m is related to the applied potential E_a by equation 2.1

$$E_m = E_a + iR_u \qquad 2.1$$

The previous discussions (Section 2.2 to 2.5) concentrated on the practical ways of minimizing i or R_u and hence minimizing the influence of iR_u on the measured potential. There may, however, be a number of occasions where this cannot be done. Alternatively, a positive feedback circuit in the potentiostat itself can be incorporated. This can apply a variable resistance, if R_f, in the direction opposite to that of R_u. The measured potential then becomes :

$$E_m = E_a + i(R_u - fR_f) \qquad 2.2$$

when R_u equals $f R_f$ oscillations in the voltammetric results would be noticed. This observation is employed to approximately evaluate the R_u value. At about 0.9 $f R_f$ the cyclic voltammogram with minimum effect of R_u may be recorded [56–60]. A more involved

method of completely correcting for R_a using the same positive feedback technique was proposed recently [61]. From the practical point of view, it is better to have potentiostats with positive feedback facilities for more accurate works.

2.7.2   VOLTAGE SCAN GENERATORS

Voltage scan generators serve the very important function of applying a systematically varying potential to the working electrode through the potentiostat at a desired rate. The sweep rates can vary from a few mV/sec to as high as 20,000 volts/sec.

In most of the experimental works, a linearly varying potential sweep (LSV) or a triangularly varying potential sweep (CV) is applied to the working electrode. However, a number of other ways of scanning the electrode potentials is also employed (Fig. 2.6). One
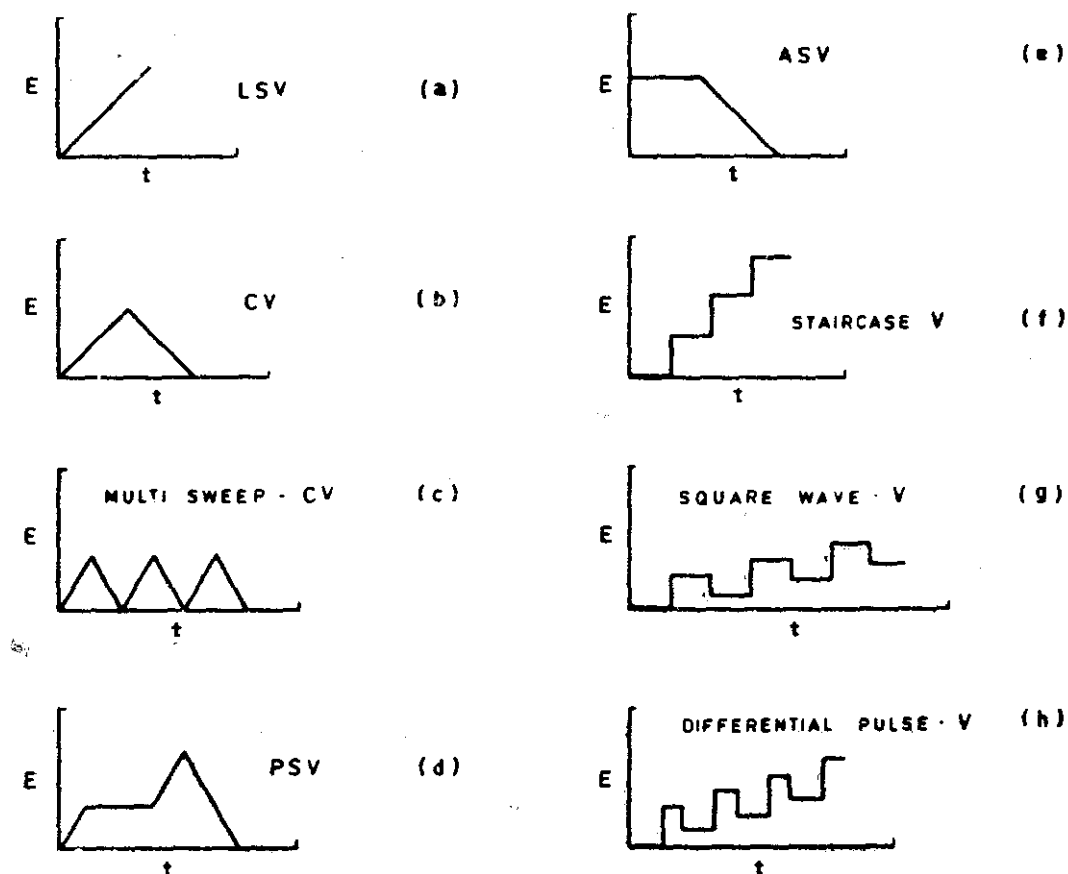

Fig. 2.6.   Typical potential sweep programmes employed in cyclic voltammetry and related experimental techniques.

may employ multiple sweeping [11]. Potentials may be held at any point in between sweeps [62, 63]. Anodic stripping voltammetry can be considered as a limiting form of this method (Chapter 6). One may superimpose a faster sweep rate of short potential width on a slower sweep rate of longer width [64–66]. More recently development of staircase voltammetry [67–69], square voltammetry [70–72] and differential pulse voltammetry [73–75] have demanded very high and accurate capabilities of voltage scan generators.

A number of analog devices are available for the generation of various wave-forms. However the more demanding wave-forms [67–75] require the capability to instruct the wave generator the correct voltage pattern required. This can best be achieved through computers. In recent times digital wave-form generators are more frequently employed for this purpose. The scan rate is then fed to the potentiostat through a D/A converter (see Section 7.3.5).

2.7.3 RECORDING DEVICES

The experimental output in cyclic voltammetric work is the current as a function of potential (or time since potential itself varies with respect to time). Direct ink recordings of the current voltage curves are very convenient for further analysis. X-Y recorders are usually employed for this purpose. However, these recorders have a response time which is not less than one second. Hence one can employ them only when one makes measurements at sufficiently longer durations than this. It is not advisable to use X-Y recorders when sweep rates greater than 500–600 mV/sec are employed.

A great variety of oscilloscopes is available for current-potential measurements at higher sweep rates. They have substantially lower response times, say less than 50 μ sec. The X-Y recordings may then be photographed for further analysis.

In the recent past, computers have also entered this area of instrumental application. The current-potential outputs are digitized using an A/D converter and stored in the memory. Graphic print-outs of the results may be easily obtained whenever required (Sec. 2.7.4).

2.7.4 COMPUTER CONTROLLED INSTRUMENTATION

Computers entered into electroanalytical instrumentation in 1967 [76] or even earlier. Computer applications in stationary electrode

voltammetry [77, 78] and cyclic voltammetry [77–81] were reported quickly thereafter. Computers have also enabled the development and use of a number of new related techniques that require the generation of sophisticated wave-forms [67–75] and even more involved and accurate data analysis methods.

It is impossible in this brief discussion to describe the components of a computer, the languages employed to communicate with it and the method of using it for one's experimental work. A few comprehensive reports on the general aspects of computer applications in electroanalytical chemistry are available [82–84]. Specific references to cyclic voltammetry [85] and anodic stripping voltammetry are also available. At least, three computer controlled general purpose electroanalytical instruments are available in the market (PAR Model 384 B; TAC 2000; BAS 100). These instruments may be employed for cyclic voltammetric analysis as well as for other related methods. The instruction manuals provide enough information about their scope and application. Hence this discussion shall confine itself to a brief discussion of what the computers can do in cyclic voltammetric analysis.

a) Computers can be used to apply any potential programme to the working electrode through the potentiostat. The start potential, range, sweep rate, the nature of the pulse etc. may be instructed to the computer in the digital form. In addition to the potential programme required for various analytical techniques (Section 2.7.2) potential programmes for pretreating the electrode may also be applied (Section 2.2.2). The digital data input is converted to the analog one using the D/A converter before applying the programme to the electrochemical cell.

b) A computer can be used to control a number of mechanical operations that may require precise timing. It can thus be used to knock off a standing mercury drop used as the electrode at the end of each measurement. It can be used to control the rotation rate of an electrode in a controlled way in hydrodynamically modulated AC [86] or square wave [87, 88] voltammetry. It can be used for operating a mechanical stirrer for a prescribed period in between voltammetric measurements. A number of applications of this type may be thought of.

c) Computers can be used very effectively in data acquisition and retrieval (Section 2.7.3). The applied potential values and the

resulting current values may be converted to digital information by an A/D converter. This information can be stored in the computer memory. At any convenient time, this information may be recalled and obtained in digital or graphic form.

d) Computers can improve the signal-to-noise ratio of the experimental cyclic voltammograms. Computers can repeat each experiment under identical conditions a number of times and average out the current value at each potential point of the cyclic voltammetric curve. The random errors that may appear due to any type of noise effects [89, 90] may thus average out. It is generally known that if the voltammetric curves are recorded, say 10 times, and averaged out, the signal will improve 10 times. This method is extremely useful at very high sweep rates and very low electroactive species concentration.

e) Computers can be used for data analysis. The analytical objectives can be very different. It may be to measure the peak current or peak potential very accurately [91, 92]; subtraction of background current may be attempted [79]; and separating individual peak characteristics from overlapping peak may also be attempted [79]. Voltammetric curves may be differentiated to obtain peak potentials with greater precision [93]. The information thus obtained such as peak current, peak potential and peak width at various concentrations may then be correlated with theoretical predictions for establishing the nature of the process and evaluating the rate parameters.

Recently a host of new cyclic voltammetric techniques has emerged that depends very much on the analytical capabilities of the computer. These include semi-integral (94, 95] convolution sweep [96, 97] and normalized potentiat sweep [98, 99] voltammetry (Section 28).

f) Computers are extensively used to simulate and obtain cyclic voltammetric curves using the right phenomenological equations (Chapter 1), defining appropriate boundary conditions(Chapters 3 to 10) and selecting proper values of the rate and thermodynamic parameters. This purely mathematical simulation works are known for a very long period [82, 100]. However, in many recent works, cyclic voltammograms are simulated and matched with the experimentally observed curves. By properly matching the curves, the required rate and thermodynamic parameters may very accurately be determined [101, 102].

g) Computers can also be used for carrying out some closed loop operations. For example, the computer may be programmed to hold the working electrode potential at a point where the current minimum occurs after a first peak. This procedure can be very useful for example in stripping an analysis of multicomponent mixtures [103]. This type of computer application is definitely one of the most difficult ones to achieve at present [84].

The above discussion does not exhaust the possible applications of computers. Each experimental worker may in fact have his own specific requirement. Commercial instruments cannot provide all software programmes for such potential applications. It will be sufficient to start with simpler equipments. As one reaches more and more sophisticated problems, he may have to develop his own software for the specific application.

2.8 CYCLIC VOLTAMMETRIC METHODS

With the experimental set-up described in the above sections. one can develop a number of voltammetric methods. These methods either vary in the way the potential sweep is applied in the system (Section 2.7.2) or in the way the experimental data are analysed further (Section 2.7.4). Only a few variants of these methods are widely employed and hence would attract our attention throughout the book. However, it is better to conclude this chapter with a brief discussion of the methods that are extensively used at present and the methods that have great potentiality in future. The AC voltammetric methods and the methods employing a growing electrode surface (polarography) will not be considered within this framework.

2.8.1   EXPERIMENTAL METHODS

Linear sweep voltammetry (LSV) employs a linearly varying potential sweep from an initial potential to a final potential (Fig. 2.6 a). Theoretical simulations for all types of processes have been developed for this technique. This is also the most widely employed technique for quantitative work.

In cyclic voltammetry (CV) the voltage is linearly varied from an initial to a final potential and immediately swept back at the same sweep rate to the initial (Fig. 2.6 b). This method is very useful to characterize the nature and reactivity of the products formed in

an electrochemical reaction. A number of methods are used to accurately estimate the reverse current characteristics [11, 55, 104, 105]. The theoretical solutions are also available for a number of processes. In addition to quantitative work, a number of qualitative characterizations are also possible when this technique is employed.

Most of the LSV and CV experiments are carried out in the normal cells. Semi-infinite linear diffusion conditions normally prevail under these conditions (Chapter 3). When a very thin layer of solution is held near the working electrode (Section 2.5) the behaviour is very different. The LSV and CV studies in such thin layer cells are usually denoted as thin layer voltammetry (TLV). The theoretical models of such a cell are very similar to the cases where a thin insoluble electroactive film is present on the electrode surface. Hence this technique will be discussed with such thin layer redox processes in this work (Chapter 10).

The potential sweep in CV need not be confined to one sweep. In fact, a great deal of qualitative information on the products formed following the electrode reactions can be obtained by employing mutiple sweeps (Fig. 2.6 c). Recent computer simulation and matching facilities [101; 102] have enabled quantitative calculations to be made using such multisweep cyclic voltammetry (MCV).

In the potential step voltammetry (PSV [62, 63] one holds the potential in LSV or CV sweep programme to generate more of a particular species or to eliminate the influence of previously reduced or oxidized species (Fig. 2.6 d). This technique is primarily resorted to achieve improved sensitivity in the analysis.

The electrode may also be held at a characteristic cathodic potential and deposit the metal ions present in solution. Subsequently one can employ an anodic potential sweep (Fig. 2.6 e). This anodic stripping voltammetry (ASV) is the most widely used analytical technique encountered in this work (Chapter 6). Cathodic stripping voltammetry (CSV) is the analog of ASV where the oxidized species is held by the electrode and the product is then stripped cathodically.

All the above techniques have reached a matured state of development and are very widely used. A few newer techniques that may find potential applications in future are discussed in the following paragraphs.

When a staircase type of potential input (Fig. 2.6 f) is employed and the current is measured just before the next potential increment is employed, the charging current component is eliminated. The theory of this staircase voltammetric technique requires much further development [67-69].

The square wave voltammetry [70-72] and differential pulse voltammetry [73-75] are the offshoots of analogous developments in polarography. The potential inputs (Fig. 2.6 g, h) are very similar to their polarographic analogs. These techniques substantially improve the analytical sensitivities. But the demands of these techniques on both theory and instrumentation are really very much.

All the voltammetric techniques discussed above employ stationary working electrodes. The theoretical derivations on stationary electrodes presume absence of convection effects. When a rotating disc electrode (RDE) is employed the diffusion layer thickens and hence the mass transfer effects are substantially reduced. In the study of some surface processes, rotating disc electrodes are employed to minimize mass transfer effects (Chapters 12 and 13) if the linear sweep voltammograms are found to be independent of rotation speed of the electrode. This is taken as an evidence for the absence of mass transfer effects. However, these techniques are closer of RDE voltammetry than the transient LSV and CV.

In the recent past, however, transient voltammetric studies involving convective diffusion are also being developed. The transient response of LSV on a RDE has, for example, been described [106-107]. Hydrodynamic modulation of square wave voltammetry [87, 88] are also reported. The latter work, in fact, is an extension of hydrodynamic modulation in AC voltammetry [86].

2.8.2 DATA ANALYSIS METHODS

The extraction of the correct information from the cyclic voltammetric curves is definitely a very challenging and rewarding activity. Throughout, the rest of this book is more concerned with this aspect. A great deal of work, of course, depends on the characterization of peak currents and peak potentials at various experimental conditions. These analyses may be performed by manual collection and evaluation of data.

However, it must be admitted that in the above types of data analysis, only a small portion of the total voltammograms obtained is used (say peak current, peak potential or half-peak width). Semi-integral analysis (SA) [94, 95] attempts to eliminate the influence of mass transfer and hence enables the analysis of the whole voltammetric curve which is quite similar to the analysis of steady state voltammetric curves. Convolution sweep voltammetry (CSV) is very similar in approach to this technique [96, 97]. Very recently normalized potential sweep voltammetry (NPSV) [98, 99] has been developed. This method depends on the three dimensional analysis of the current-potential-time information. All these methods require the use of a computer for data analysis and hence still require widespread application. Another recently developed method, the linear curent potential analysis (LCP) [91] does not require a computer for the analysis, but its scope is quite limited to the estimation of Tafel slope values.

Convective diffusion controlled processes can also be analysed using such methods. CSV analysis of RDE data for example has been analysed by this method [108]. In the present chapter, then, a fairly comprehensive view is presented of the experimental aspects of cyclic voltammetric techniques. With the help of the literature cited, one can certainly take up any experimental work. A newcomer may, in fact, have another question. When there are so many possible variations right from the choice of electrode to the method of analysis, how does one exactly choose his own approach for an experiment? A straightforward answer to this question is certainly not possible.

The nature of the problem, the availability of materials, the instruments and the experience generally narrow down the choices to a very great extent. However, the nature of the work is the most important factor. Close analysis of earlier experimental works on the processes of related interest to one's own work would indicate the choice of experimental conditions. Some preliminary experiments may then be carried out to establish the reproducibility. Many pretreatment procedures are selected at this stage. The level of reproducibility required may also depend on the requirements. In general, then, one normally picks up most of the experimental conditions from previous experience. This definitely implies that a little also depends on the individual's ingenuity and choice; and it

is exactly this 'little bit' by a 'number of individuals' that keeps the cyclic voltammetric technique so different, lively, interesting and challenging.

REFERENCES

1   LA Mathson and N Nicholas, Trans Electrochem Soc 73 (1938) 193.

2   A Sevcick, Collect Czech Chem Commun 13 (1948) 349.

3   JEB Randles, Trans Farad Soc 44 (1948) 327.

4   RN Adams, Anal Chem 30 (1958) 1576.

5   C Olson and RN Adams, Anal Chim Acta 22 (1960) 582.

6   W Kemula and Z Kublik, Roczmiki Chem 32 (1958) 941.

7   W Kemula, Advances in Polarography, Vol 1 (IS Langmuir, Ed.), Pergamon, London (1960) 105.

8   FG Will and CA Knorr, Z Electrochem 64 (1960) 258.

9   G Laver, R Abel and FC Anson, Anal Chem 39 (1967) 765.

10   SP Perone, JE Harrar, SB Stevens and RE Anderson, Anal Chem 40 (1968) 899.

11   RN Adams, Electrochemistry at Solid Electrodes (Marcel Dekker, New York) 1969.

12   DT Sawyer and JL Roberts Jr. Experimental Electrochemistry for Chemists, Wiley Interscience, New York (1974).

13   E Gileadi, E Kirowa-Eisner and J Penciner, Interfacial Electrochemistry —An Experimental Approach, Addison Wesley Reading, Massachusetts (1975).

14   Laboratory Techniques in Electrochemistry (PT Kissinger and WR Heineman. Ed.) Marcel Dekker, New York (1984).

14a   LR Faulkner, Physical Methods of Modern Chemical Analysis, Vol. 3. (T Kuwana, Ed.) Academic Press, New York (1983) 137.

15   GA Mabbott, J Chem Educ 60 (1983) 697.

15a   PT Kissinger and WR Heinerman, J Chem Educ 60 (1983) 702.

16   VD Parker, Adv Phys Org Chem 19 (1983) 13.

17   L Meites, Polarographic Techniques, 2nd Ed., Wiley Interscience, New York (1958).

18   RE Panzer and PJ Elving, Electrochim Acta 20 (1975) 635.

19   JP Randin, Encyclopedia Electrochem Elements 5 (1976) 1.

20   VF Gaylor, PJ Elving and AL Conrad, Anal Chem 25 (1953) 1078.

21 MA Dayton, JC Brown, KJ Stutts and RM Wightman, Anal Chem 52 (1980) 946.

21a C Urbaniczky and K Lundstran, J Electroanal Chem 157 (1983) 221.

21b K Lundstran, Anal Chim Acta 146 (1983) 109.

22 HE Zittel and FJ Miller, Anal Chem 37 (1965) 200.

23 WE Van Der Linden and JW Dieker, Anal Chem Acta, 119 (1980) 1.

24 S Thangavelu, Ph.D. Dessertation, MK University, Madurai, India (1984).

25 M Noel and PN Anantharaman, Advances in Electrochemicals, CECRI Karaikudi, India (1984) 47.

26 M Noel, R Kanakam Srinivasan and S Chidambaram, Proc 3rd Internat Symp Electrochem, SAEST India (1984).

27 T Kuwana and RN Adams, J Amer Chem Soc 79 (1957) 3609.

28 LM Peter, Electrochemistry 9.

29 RW Murray, Acc Chem Res 13 (1980) 135.

30 M Noel, PN Anantharaman and HVK Udupa, Trans SAEST 15 (1980) 49.

31 H Angerstein Kozlowska, Comprehen Treatise Electrochem 9 (1984) 15.

32 JO Howell and RM Wightman, Anal Chem 56 (1984) 524.

33 JO Howell and RM Wightman, J Phys Chem 88 (1984) 3915.

34 JO'M Bockris and BE Conway, J Chem Phys 28 (1958) 707.

35 JE Anderson, DE Tallman, DJ Chesney and JL Anderson, Anal Chem 50 (1978) 1051.

36 J Zak and T Kuwana, J Electronal Chem 150 (1983) 645.

37 CK Mann, Electronal Chem 3 (1969) 57.

38 H Lund, Organic Electrochemistry (MM Baizer and H Lund, Ed.) Marcel Dekker, New York (1983) 161.

39 R Lines and VD Parker, Acta Chem Scand B31 (1977) 369.

40 E Peled, A Mitavski, A Reger and E Gileadi, J Electroanal Chem 75 (1977) 677.

41 M Elam, I Lahatt, E Peled and E Gileadi, J Phys Chem 88 (1984) 1609.

42 BE Conway, H Angerstein-Kozlowska, WBA Sharp and E Criddle, Anal Chem 45 (1973) 1331.

43 A Demertier and AJ Bard, J Amer Chem Soc 95 (1973) 3495.

44 O Hammerich and VD Parker, Electrochim Acta 18 (1973) 537.

45 Molten Salt Techniques (DG Lovering and RJ Gale, Ed.) Plenum, New York (1983).

46 DJG Ives and GJ Janz, Reference Electrode, Academic Press, New York (1961).

47 JN Butler, Adv Electrochem and Electrochem Engg 7 (1970) 77.

48 CK Mann and KK Barnes, Electrochemical Reactions in Non-aqueous Systems, Marcel Dekker, New York (1970).

49 RJ Gale and RA Osteryong. J Electrochem Soc 127 (1980) 2167.

50 PJ Peerce and AJ Bard, J Electroanal Chem 108 (1980) 121.

51 LR Faulkner and AJ Bard, Electroanal Chem 10 (1977) 1.

52 AT Habbard and FC Anson, Electroanal Chem 4 (1971) 129.

53 FE Woodard and CN Reilley. Comprehensive Treatise in Electrochem 9 (1984) 353.

54 AT Hubbard and FC Anson, Anal Chem 36 (1964) 723.

54a N Winograd and T Kuwana, Electroanal Chem 7 (1974) 1.

55 T Kuwana and WR Heineman, Acc Chem Res 9 (1976) 241.

56 RS Nicholson, 37 (1965) 667.

57 WT de Vries and E Van Dalen, J Electroanal Chem 10 (1965) 183.

58 S Roffia and M Lavacchielli, J Electronal Chem 22 (1969) 117.

59 CP Andrieux, L Nadjo and JM Saveant, J Electroanal Chem 26 (1970) 147.

60 JC Impeaux and JM Saveant, J Electroanal Chem 28 (1970) 325; 31 (1971) 183.

61 E Ahlberg and VD Parker, J Electroanal Chem 107 (1980) 197; 121 (1981) 57.

62 L Papouchado, J Bacon and RN Adams, J Electroanal Chem 24 (1970) App. 1.

63 A Renlan, O Hammerich and VD Parker, J Amer Chem Soc 95 (1973) 210.

64 BE Conway, H Angerstein Kozlowsta, FC Ho, B Mac Dougall and S Gottesfield, Farad Discuss Chem Soc 56 (1973) 210.

65 CM Ferro, AJ Calandra and AJ Arvia, J Electroanal Chem 59 (1975) 239.

66 JO Zerbino, NR de Tacconi, AJ Calandra and AJ Arvia, J. Appl Electrochem 11 (1981) 703.

67 DR Ferrier and RR Schroeder, J Electroanal Chem 45 (1973) 343

68 JJ Zipper and SP Perone. Anal Chem 45 (1973) 452.

69 S Stefania and R Seeber, Anal Chem 54 (1982) 2524.

70 R Tamamushi and K Matsuda, J Electroanal Chem 80 (1977) 201.

71 Ch. Yarnitsky, RA Osteryoung and J Osteryoung, Anal Chem 52 (1980) 1174.

72 JJ O'Dea and RA Osteryoung, J Physchem 87, 20 (1983) 3911.

73 HE Keller and RA Osteryoung, Anal Chem 43 (1971) 342.

74 SC Rifkin and DH Evans, Anal Chem 48 (1976) 1616.

75 MR Jaun and WF Smyth, Analyst 109 (1984) 1187.

76 G Lauer, R Abel and FC Anson, Anal Chem 39 (1967) 765,

77 SP Perone, JE Harrar, FB Stephens and RE Anderson, Anal Chem 40 (1968) 899.

78 SP Perone, DO Jones and WF Gutknecht, Anal Chem 41 (1969) 1154.

79 SP Perone, JW Frazer and A Kray, Anal Chem 43 (1971) 1485.

80 SC Creason, RJ Loyd and DE Smith, Anal Chem 44 (1972) 1159.

81 PE Whitson, HW Vanden Born and DH Evans, Anal Chem 45 (1973) 1298.

82 Computers in Chemistry and Instrumentation, Vol. 2 Electrochemistry Calculation, Simulation and Instrumentation (JS Mattson, HD Mac Donald Jr. and HB Mark Jr. Ed.) Marcel Dekker, New York (1972).

83 D Jagner, Marine Electrochemistry, Wiley Interscience, New York (1981) 123.

84 TH Ridgway and HB Mark Jr. Comp Treatise in Electrochem 8 (1984) 99.

85 DE Smith, Anal Chem 45 (1973).

86 B Miller, MI Bellavance, S Bruckenstein, Anal Chem 44 (1972) 1983.

87 WJ Blaedel and RC Engstrom, Anal Chem 50 (1978) 476.

88 DS Austin, DC Johnson, TG Mines and ET Berti, Anal Chem 55 (1983) 2222.

89 T Coor, J Chem Educ. 45 (1968) A 533, A 583.

90 GC Barker, J Electroanal Chem 39 (1973) 484.

91 B Aalstad and VD Parker, J Electroanal Chem 112 (1980) 163.

92 R Eliason and VD Parker, J Electroanal Chem 170 (1984) 347.

93 E Ahlberg and VD Parker, J Electroanal Chem 121 (1981) 57, 73.

94 KB Oldham and J Spanier, J Electroanal Chem 26 (1970) 331,

95 KB Oldham, Anal Chem 44 (19/2) 196.

96 L Nadjo, JM Saveant and D Tessier, J Electroanal Chem 52 (1974) 403.

97 JM Saveant and D Tessier, J Electroanal Chem 65 (1975) 57.

98 B Aalstad and VD Parker, J Electroanal Chem 122 (1981) 183.

99 B Aalstad, E Ahlberg and VD Parker, J Electroanal Chem 122 (1981) 195.

100 SW Feldberg, Electroanal Chem 3 (1969) 199.

101 T Matsue, DH Evans and I Agranat, J Electroanal Chem 163 (1984) 137.

102   DH Evans, PJ Jimenez and MJ Kelly, J Electroanal Chem 163 (1984) 145.

103   OV Thomas, RA Depalma SP Perone, Anal Chem 49 (1977) 1376,

104   ML Olmstead and RS Nicholson, Anal Chem 38 (1966) 150.

105   R Nelson, ET Seo, D Leedy and RN Adams, Z Anal Chem 224 (1967) 184.

106   PC Andricacos and HY Cheh, J Electrochem Soc 127 (1980) 2153.

107   PC Andricacos and HY Cheh, J Electroanal Chem 144 (1983) 77.

108   JL Valdes and HY Cheh. J Electroanal Chem 181 (1984) 65.