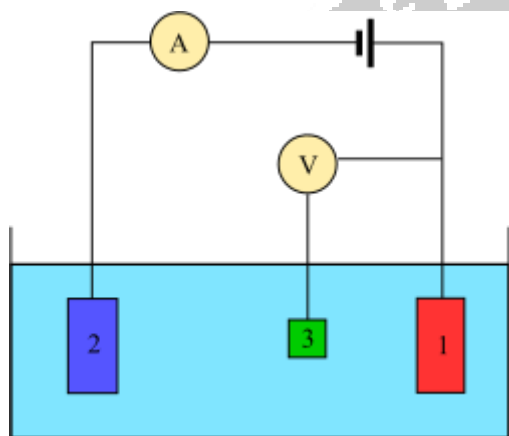


5.3 VOLTAMMETRY

Voltammetry is a category of electroanalytical methods used in analytical chemistry and various industrial processes. In voltammetry, information about an analyte is obtained by measuring the current as the potential is varied.^{[1][2]} The analytical data for a voltammetric experiment comes in the form of a voltammogram which plots the current produced by the analyte versus the potential of the working electrode.¹



Voltammetry experiments investigate the half-cell reactivity of an analyte. Voltammetry is the study of current as a function of applied potential. These curves $I = f(E)$ are called voltammograms. The potential is varied arbitrarily either step by step or continuously, and the actual current value is measured as the dependent variable. The opposite, i.e., amperometry, is also possible but not common. The shape of the curves depends on the speed of potential variation (nature of driving force) and on whether the solution is stirred or quiescent (mass transfer). Most experiments control the potential (volts) of an electrode in contact with the analyte while measuring the resulting current (amperes).^[4]

To conduct such an experiment one requires at least two electrodes. The working electrode, which makes contact with the analyte, must apply the desired potential in a controlled way and facilitate the transfer of charge to and from the analyte. A second electrode acts as the other half of the cell. This second electrode must have a known potential with which to gauge the potential of the working electrode; furthermore it must balance the charge added or removed by the working electrode. While this is a viable setup, it has a number of shortcomings. Most significantly, it is extremely difficult for an electrode to maintain a constant potential while passing current to counter redox events at the working electrode.

To solve this problem, the roles of supplying electrons and providing a reference potential are divided between two separate electrodes. The reference electrode is a half cell with a known reduction potential. Its only role is to act as reference in measuring and controlling the working electrode's potential and at no point does it pass any current. The auxiliary electrode passes all the current needed to balance the current observed at the working electrode. To achieve this current, the auxiliary will often swing to extreme potentials at the edges of the solvent window,

where it oxidizes or reduces the solvent or supporting electrolyte. These electrodes, the working, reference, and auxiliary make up the modern three electrode system.

There are many systems which have more electrodes, but their design principles are generally the same as the three electrode system. For example, the rotating ring-disk electrode has two distinct and separate working electrodes, a disk and a ring, which can be used to scan or hold potentials independently of each other. Both of these electrodes are balanced by a single reference and auxiliary combination for an overall four electrode design. More complicated experiments may add working electrodes as required and at times reference or auxiliary electrodes.

In practice it can be important to have a working electrode with known dimensions and surface characteristics. As a result, it is common to clean and polish working electrodes regularly. The auxiliary electrode can be almost anything as long as it doesn't react with the bulk of the analyte solution and conducts well. It is (or was?) common to use mercury as working electrode e.g. DME and HMDE, and also as auxiliary, and the voltammetry method is then known as polarography. The reference is the most complex of the three electrodes; there are a variety of standards used and it is worth investigating elsewhere. For non-aqueous work, IUPAC recommends the use of the ferrocene/ferrocenium couple as an internal standard.^[5] In most voltammetry experiments, a bulk electrolyte (also known as a supporting electrolyte) is used to minimize solution resistance. It is possible to run an experiment without a bulk electrolyte, but the added resistance greatly reduces the accuracy of the results. With room temperature ionic liquids, the solvent can act as the electrolyte.

- Linear sweep voltammetry
- Staircase voltammetry
- Squarewave voltammetry
- Cyclic voltammetry - A voltammetric method that can be used to determine diffusion coefficients and half cell reduction potentials.
- Anodic stripping voltammetry - A quantitative, analytical method for trace analysis of metal cations. The analyte is deposited (electroplated) onto the working electrode during a deposition step, and then oxidized during the stripping step. The current is measured during the stripping step.
- Cathodic stripping voltammetry - A quantitative, analytical method for trace analysis of anions. A positive potential is applied, oxidizing the mercury electrode and forming insoluble precipitates of the anions. A negative potential then reduces (strips) the deposited film into solution.
- Adsorptive stripping voltammetry - A quantitative, analytical method for trace analysis. The analyte is deposited simply by adsorption on the electrode surface (i.e., no electrolysis), then electrolyzed to give the analytical signal. Chemically modified electrodes are often used.
- Alternating current voltammetry
- Polarography - a subclass of voltammetry where the working electrode is a dropping mercury electrode (DME), useful for its wide cathodic range and renewable surface.
- Rotated electrode voltammetry - A hydrodynamic technique in which the working electrode, usually a rotating disk electrode (RDE) or rotating ring-disk electrode (RRDE), is rotated at a very high rate. This technique is useful for studying the kinetics and electrochemical reaction mechanism for a half reaction.

- Normal pulse voltammetry
- Differential pulse voltammetry
- Chronoamperometry

Cyclic voltammetry (CV)

It is a type of potentiodynamic electrochemical measurement. In a cyclic voltammetry experiment, the working electrode potential is ramped linearly versus time. Unlike in linear sweep voltammetry, after the set potential is reached in a CV experiment, the working electrode's potential is ramped in the opposite direction to return to the initial potential. These cycles of ramps in potential may be repeated as many times as needed. The current at the working electrode is plotted versus the applied voltage (that is, the working electrode's potential) to give the cyclic voltammogram trace. Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution^{[1][2][3][4]} or of a molecule that is adsorbed onto the electrode.

The cell[edit]

A standard CV experiment employs a cell fitted with three electrodes: reference electrode, working electrode, and counter electrode. This combination is sometimes referred to as a three-electrode setup. Electrolyte is usually added to the sample solution to ensure sufficient conductivity. The solvent, electrolyte, and material composition of the working electrode will determine the potential range that can be accessed during the experiment.

The electrodes are immobile and sit in unstirred solutions during cyclic voltammetry. This "still" solution method gives rise to cyclic voltammetry's characteristic diffusion-controlled peaks. This method also allows a portion of the analyte to remain after reduction or oxidation so that it may display further redox activity. Stirring the solution between cyclic voltammetry traces is important in order to supply the electrode surface with fresh analyte for each new experiment. The solubility of an analyte can change drastically with its overall charge; as such it is common for reduced or oxidized analyte species to precipitate out onto the electrode. This layering of analyte can insulate the electrode surface, display its own redox activity in subsequent scans, or otherwise alter the electrode surface in a way that affects the CV measurements. For this reason it is often necessary to clean the electrodes between scans.

Common materials for the working electrode include glassy carbon, platinum, and gold. These electrodes are generally encased in a rod of inert insulator with a disk exposed at one end. A regular working electrode has a radius within an order of magnitude of 1 mm. Having a controlled surface area with a well-defined shape is necessary for being able to interpret cyclic voltammetry results.

To run cyclic voltammetry experiments at very high scan rates a regular working electrode is insufficient. High scan rates create peaks with large currents and increased resistances, which result in distortions. Ultramicroelectrodes can be used to minimize the current and resistance.

The counter electrode, also known as the auxiliary or second electrode, can be any material that conducts current easily, will not react with the bulk solution, and has a surface area much larger than the working electrode. Common choices are platinum and graphite. Reactions occurring at the counter electrode surface are unimportant as long as it continues to conduct current well. To

maintain the observed current the counter electrode will often oxidize or reduce the solvent or bulk electrolyte.

Solvents[edit]

CV can be conducted using a variety of solutions. Solvent choice for cyclic voltammetry takes into account several requirements.^[4] The solvent must dissolve the analyte and high concentrations of the supporting electrolyte. It must also be stable in the potential window of the experiment with respect to the working electrode. It must not react with either the analyte or the supporting electrolyte. It must be pure to prevent interference.

Electrolyte[edit]

The electrolyte ensures good electrical conductivity and minimizes iR drop such that the recorded potentials correspond to actual potentials. For aqueous solutions, many electrolytes are available, but typical ones are alkali metal salts of perchlorate and nitrate. In nonaqueous solvents, the range of electrolytes is more limited, and a popular choice is tetrabutylammoniumhexafluorophosphate.

Applications

Cyclic voltammetry (CV) has become an important and widely used electroanalytical technique in many areas of chemistry. It is often used to study a variety of redox processes, to determine the stability of reaction products, the presence of intermediates in redox reactions,^[10] electron transfer kinetics,^[11] and the reversibility of a reaction.^[12] CV can also be used to determine the electron stoichiometry of a system, the diffusion coefficient of an analyte, and the formal reduction potential of an analyte, which can be used as an identification tool. In addition, because concentration is proportional to current in a reversible, Nernstian system, the concentration of an unknown solution can be determined by generating a calibration curve of current vs. concentration.

Differential pulse voltammetry (DPV) (also differential pulse polarography, DPP) is a voltammetry method used to make electrochemical measurements and a derivative of linear sweep voltammetry or staircase voltammetry, with a series of regular voltage pulses superimposed on the potential linear sweep or stairsteps.^{[1][2][3]} The current is measured immediately before each potential change, and the current difference is plotted as a function of potential. By sampling the current just before the potential is changed, the effect of the charging current can be decreased.

By contrast, in normal pulse voltammetry the current resulting from a series of ever larger potential pulses is compared with the current at a constant 'baseline' voltage. Another type of pulse voltammetry is squarewave voltammetry, which can be considered a special type of differential pulse voltammetry in which equal time is spent at the potential of the ramped baseline and potential of the superimposed pulse.