A Brief Study of Cyclic Voltammetry and Electrochemical Analysis

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Abstract: Electrochemistry is defined as the branch of chemistry that examines the phenomena resulting from combined chemical and electrical effects. This paper covers some of the common voltammetry techniques which are currently in use. Cyclic voltammetry is a widely used technique in electrochemistry. The cyclic voltammetry is a powerful tool to study the electrochemical behavior of a system by systematic study of current-voltage measurements of a given electrochemical cell. Brief study of cyclic voltammetry and the analysis of an electrochemical cell from cyclic voltammogram is described.

I. Introduction

Owing to the good stability, high power density and moderate energy compared to the conventional capacitors and batteries, electrochemical capacitors (supercapacitors, also called ultracapacitors) are the attractive power sources. The application of electrochemical capacitors lies in the field where high power density is required with small or short currents such as during start-up of electric vehicles or in power back-up systems (UPS)¹. Energy storage in supercapacitor is due to the pure electrostatic interaction between the charged capacitor plates and the ions from the electrolyte solution and the processes associated with the redox reactions of electrode material. Usually, in the electrical double layer capacitors the materials used as electrodes are activated carbons, metal oxides or conductive polymers. The high effective surface area, the geometry and size of the pores are the factors affecting the capacitance values. Use of such materials improves the efficient utilization of electrode surface increasing the capacitance value. Mass of the electrode, volume of the electrode or surface of the electrode, all is related with the specific capacitance. As a part of pores is available for the electrolyte and few involves in the formation of electric double layer, the capacitance values are low. However the porous electrode materials having pores with suitable pore size matching with electrolyte ions are advantageous in order to reduce the time required to obtain all the energy stored in the capacitor with a better efficiency and an increase in the value of capacitance ².

In short, the capacitance of the capacitor depends mostly on the capacity of electrode material expressed in F/g, while the voltage and the resistance of such device depend mainly on the electrolyte.

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The oxidation or reduction that is taking place at the electrode surface is related with the potential of the electrode. The potential forces electrode ions in solution either to gain or to lose an electron. The more negative potential implies more strongly reducing electrode and on the other hand more positive potential implies more strongly oxidizing electrode. Therefore, the redox reaction taking place on the electrode can be controlled by controlling the electrode potential of an electrochemical cell. So the study of electrochemical reaction that is occurring at the electrode /electrolyte interface is necessary. Hence, the cyclic voltammetry is a powerful tool to study the electrochemical behavior of a system by systematic study of current-voltage measurements of a given electrochemical cell.

The branch of electrochemistry known as voltammetry is developed from the discovery of polarography. Currently there are various forms of voltammetry such as Polarography, Cyclic Voltammetry, Normal Pulse Voltammetry (NPV), Differential Pulse Voltammetry (DPV), Square-Wave Voltammetry (SWV), Anodic Stripping Voltammetry, Cathodic Stripping Voltammetry, Adsorptive Stripping Voltammetry, etc which are used for different analytical purposes. In all these techniques, the potential is applied and current is measured but slight difference is the way and timing for applying potential. These differences can moreover give various chemical, electrochemical, and physical information, such as highly quantitative analyses, rate constants for chemical reactions, electrons involved on redox reactions, and diffusion constants.

Polarigraphy

Polarigraphy has unique place in electrochemistry mainly because of its unique working electrode, the dropping mercury electrode (DME). This electrode consists of a glass capillary through which mercury flows under gravity to form a succession of mercury drops. Each new drop provides a clean surface at which the redox process takes place, giving rise to a current increase with increasing area as the drop grows, and then falling when the drop falls. The potential when the current attains half the value of the plateau current is called the half-wave potential and is specific to the analyte’s matrix. The variation in current is proportional to the concentration of analyte. But Mercury is oxidized at potentials more positive than +0.2 V versus SCE, which makes it impossible to analyze for any analytes in the positive region of potential. Another limitation is the residual current that results from charging of the large capacitance of the electrode surface.

Normal Pulse Voltammetry (NPV)

A cycle of potential pulses of increasing amplitude is used in this technique. The current measurement is made near the end of each pulse, which allows time for the charging current to decay. It is generally carried out in an unstirred solution at either DME (called Normal Pulse Polarography) or solid. The resultant voltammogram exhibits the sampled current on Y axis and the potential to which the pulse is stepped on the X axis.

Differential Pulse Voltammetry (DPV)

Like NPV, here also the potential is scanned with series of pulses but the difference is each potential pulse of small amplitude is fixed and overlaid on a slowly changing base potential. Before the application of pulse and at the end of the pulse, at these two points current is measured. The difference between current measurements at these points for each pulse is determined and plotted against the base potential.

Square-Wave Voltammetry (SWV)

A symmetrical square wave pulse is superimposed on a staircase waveform. Here the forward square pulse coincides with the staircase step. Forward current and reverse currents are measured, the difference between them gives the net current. The concentration of electroactive species is proportional to the peak height. Excellent sensitivity, elimination of background currents and the speed are the advantages of this technique. SWV is used to study the electrode kinetics with regard to prior, following, or catalytic homogeneous chemical reactions.

Anodic Stripping Voltammetry

Stripping voltammetry is a very sensitive technique for trace analysis. ASV is generally used for trace metal determination. This low detection limit is coupled with the ability to determine simultaneously four to six
trace metals using relatively inexpensive instrumentation. Metal ions in the sample solution are concentrated into a mercury electrode during a given time period by application of a sufficient negative potential. These amalgamated metals are then stripped (oxidized) out of the mercury by scanning the applied potential in the positive direction. The resulting peak currents, $i_p$, are proportional to the concentration of each metal in the sample solution.

**Cathodic Stripping Voltammetry**

CSV can be used to determine substances that form insoluble salts with the mercurous ion. A potential scan in the negative direction will reduce the deposited film into solution.

**Adsorptive Stripping Voltammetry**

In this method, instead of accumulation (by electrolysis), adsorption on the electrode surface takes place by reactions occurring at electrodes. The adsorbed species is calculated by using a voltammetric technique such as DPV or SWV in either the negative or positive direction to give a peak-shaped voltammetric response with amplitude proportional to concentration.

**Cyclic Voltammetry**

Cyclic voltammetry (CV) has become a significant and broadly used electroanalytical technique in many areas of chemistry. It is generally used for the study of redox processes, in the analyses of electrochemical reactions between ions and surface atoms of electrodes under the investigation for understanding reaction intermediates for obtaining stability of reaction products, for qualitative information on electrode reaction mechanisms, qualitative properties of the charge transfer reactions between electrolyte ions and electrons from the electrode surface. Thus it is a powerful technique to study the redox reaction which plays a key role for charge storage mechanism in the study of supercapacitor.

Cyclic voltammetry, a three electrode electrochemical cell, is based on varying the applied potential at a working electrode in both forward and reverse directions (at some scan rate) while observing the current. This technique involves a linear and a cyclic variation of electrode potential between the working and reference electrodes within a potential window by measuring the current that flows between working and counter electrodes. Cyclic voltammetry (CV) is a potentiodynamic electrochemical measurement in which working electrode’s potential is ramped in the opposite direction to return to its initial potential. These cycles may be repeated many times. Cyclic voltammogram gives the plot of current versus applied potential.

**II. General Theory**

A chemical reaction takes place in electrochemical cell. These electrochemical reactions occupy charges species. The energy of these species is related with the potential of the phase containing these species. The transfer of ions or electrons across the interface of two adjacent species is the fundamental step in these reactions. An interfacial reaction which involves the charge transfer inevitably is known as electrode reaction. The rate of this type of reaction can be determined and the overall rate is related to the unit area of the interface. The processes such as chemical reaction, adsorption, structural reorganization that are associated with charge transfer are included in interfacial or electrode reactions and all the changes and processes occurring at the electrode during the current flow through the cell are included in electrode processes. Thus electrode reactions and mass transport processes are there in electrode processes. Figure 1 shows the simple schematic of a electrode reaction.
Consider an electrochemical reaction taking place at an electrode with the application of suitable potential to it.

\[ O + ne^- \leftrightarrow R \]  

The reduction or oxidation of a substance at the surface of a working electrode, at the appropriate applied potential, results in the mass transport of new material to the electrode surface and the generation of a current. The three possible mass transport processes are Diffusion, Migration and Convection. The movement of charged ions in the presence of an electric field is known as Migration. The movement of electroactive species by thermal currents, by rotating the electrode or stirring the solution is known as Convection. As the reactant species move in the direction of the electrode surface and product molecules leave the interfacial region, the Diffusion should always be considered.

In general, initially the reactant diffuses from the solution to the electrode interface that is mass transport. Then the potential is applied to the cell which induces the exchange of electrons between the electrode surface and the species in solution.

The rate of the reaction can be determined in a simple way by measuring the current through the circuit as the current is proportional to the surface area of the electrode.

\[ I = \frac{dQ}{dt} \]  

The current density is given by,

\[ j = \frac{I}{A} \]

The current is a measure of how fast a species is being reduced or oxidized at the electrode surface. Actually this current is influenced by many additional factors, mostly the concentration of the redox species, the size, shape and material of the electrode, the solution resistance, the cell volume, and the number of electrons transferred.

Actually in voltammetry, the change in current due to redox reactions with applied potential can be described by various well known laws. The Nerst and Butler–Volmer equation gives that the applied potential controls the concentration of the redox species at the electrode surface and the rate of the reaction respectively.
For a reversible redox reaction as in equation (1), the applied potential forces the concentration of oxidized species \( C_O \) and reduced species \( C_R \) at the electrode surface. The Nerst equation is given by,

\[
E = E^* - \frac{RT}{zF} \ln Q_R \tag{4}
\]

Where,

\( E = \) Cell potential at the interest of temperature,

\( E^* = \) Standard cell potential,

\( T = \) Temperature in Kelvin,

\( R = \) Universal Gas Constant = 8.314 J/K/mol,

\( z = \) number of electrons transferred,

\( F = \) Faraday Constant,

\( Q_R = \) Reaction Quotient = \( \frac{C_R}{C_O} \)

This \( Q_R \) changes with applied potential. When the ratio is larger, \( O \) is reduced as the applied potential is more negative and \( R \) is oxidized for more positive applied potential as the ratio is smaller.

A well-known Butler-Volmer equation is given by equation (5) which gives the relation between current, potential and concentration.

\[
\frac{i}{zFA} = k \left[ C_O \exp(-\alpha \theta) - C_R \exp\left( l-\alpha \right) \right] \tag{5}
\]

Where,

\( A = \) Area of the electrode,

\( K = \) Heterogenous Rate Constant,

\( \alpha = \) Transfer Coefficient,

\[
\theta = \frac{zF \left[ E - E^* \right]}{RT}
\]

Two important parameters can be obtained by this equation i.e. \( i \) and \( k \).

The current flow is also related with the flux of the surface electrode material. Flux is the moles of material diffusing per unit area per unit time. The concentration will increase when there will formation of new \( O \) or \( R \). Now in this case there will be diffusion towards the bulk of the solution. On the other hand, when \( O \) or \( R \) will be destroyed this leads to the decrease in concentration and in this case there will be diffusion of new material from the bulk solution. Fick’s law gives the resultant concentration gradient and mass transport which shows that flux of matter is proportional to the concentration gradient given by equation (6).

\[
\Phi = -AD_O \left( \frac{\partial C_O}{\partial x} \right) \tag{6}
\]

Where,

\( D_O = \) Diffusion coefficient of \( O \),
The similar equation can be written for R. The rate of the reaction and thus the current in the cell can be controlled by flux of O and R.

Various voltammetry methods are followed by their distinctive laws and theoretical relationships which describe the various details of current versus voltage variations that includes the shape, width, height and position etc. of the curve.

III. Cyclic Voltammogram

In CV technique, the electrode potential increases linearly with time in cyclic manner. Scan rate is given by the rate of voltage variation over time during each cycle. The voltage is applied between the working electrode and reference electrode and current is measured between working electrode and counter electrode as shown in figure 2.

Cyclic voltammetry consists of variation of working electrode’s potential using a triangular wave form as shown in figure 3. In the initial forward scan between \( t_0 \) to \( t_1 \), the potential is increased. The current (cathodic) also increases over time because of the analyte species. During this period, the reduction takes place. At some point the reduction potential of the analyte reaches (at \( t_1 \)), the current decreases as the analyte concentration is lowered. During the reverse scan (from \( t_1 \) to \( t_2 \)) the reduced analyte starts to re-oxidize which gives rise to a current (anodic) of reverse polarity to before.
Figure 3. Cyclic voltammetry Potential waveform.

The oxidation and reduction peak will be more similar if the reaction is more reversible. Hence cyclic voltammetry data provides the information about the redox potentials and electrochemical reaction rates. In this way the potential is swept from $E_1$ to $E_2$ at a given scan rate. Single or multiple cycles can be performed. In a given potential range, the potentiostat gives the resulting current according to voltage. A graph of current versus potential is known as cyclic voltammogram as shown in figure 4.

Figure 4. Cyclic Voltammogram.

IV. Analysis from Cyclic Voltammogram

Cyclic voltammetry is a widely used technique in electrochemistry. It gives the basic information about a capacitive electrochemical cell which includes:

1. Capacitance,
2. Voltage window,
3. Cycle life.

Peak potentials ($E_{pc}$, $E_{pa}$) and peak currents ($i_{pc}$ and $i_{pa}$) of cathodic and anodic peaks are the important parameters in a cyclic voltammogram. The peak current $i_p$ is given by,
\[ i_p = (2.69 \times 10^5 \text{ nA})^{3/2} AD^{1/4} V^{1/2} C \] ..........................(7)

where,
\[ i_p = \text{peak current in Amp}, \]
\[ n = \text{number of electrons passed per molecule of analyte oxidized or reduced}, \]
\[ A = \text{electrode area (in cm}^2\text{)}, \]
\[ D = \text{diffusion coefficient of analyte (in cm}^2\text{ / sec)}, \]
\[ V = \text{Scan rate (in V / sec)}, \]
\[ C = \text{concentration of analyte in bulk solution (in moles / cm}^3\text{)}. \]

The midpoint potential of the two peaks in the voltammogram is given by:

\[ E_{\text{mid point}} = \frac{(E_{p, \text{cathodic}}) + (E_{p, \text{anodic}})}{2} \] ..........................(8)

\[ = E_o' + \frac{RT}{nF} \ln \left( \frac{D_R^{1/2}}{D_0^{1/2}} \right) \]

where,
\[ E_o' \text{ is redox potential and } D_0 \text{ and } D_R \text{ are the diffusion coefficients for the oxidized and reduced halves of that couple.} \]

It is practically assumed that \( D_0 \) and \( D_R \) are nearly equal. In such case, the midpoint potential is very nearly equal to the redox potential.

Separation between the two peaks of the voltammogram is given by,

\[ \Delta E_p = \left| E_{p, \text{anodic}} - E_{p, \text{cathodic}} \right| \] ..........................(9)

Hence from a single technique, it is possible to determine the concentration, the diffusion coefficient, the number of electrons per molecule of analyte that are oxidized or reduced and the redox potential of the analyte.

The charge storage capacity can be quantitatively evaluated by the expression,

\[ \text{Specific Capacity} = \frac{\text{Voltammetric Charge}}{(\text{Potential window} \times \text{Mass})} \] ..........................(10)

Voltammetric charge is given by sum of anodic and cathodic voltammetric charges. It is given by integral area of CV curve / scan rate. Hence the specific capacity is given by,

\[ C = \frac{1}{2} \int_{E_1}^{E_2} [i(E) \text{d}E] \sqrt{2(E_2 - E_1) m v} \] ..........................(11)

where,
\[ C = \text{specific capacity}, \]
\[ i(E) = \text{instantaneous current}, \]
\[ (E_2 - E_1) = \text{potential window width}, \]
\[ m = \text{mass deposited}, \]
\[ \int [i(E) \text{d}E] = \text{voltammetric charge obtained by integration of positive and negative sweep in CV}. \]

A voltage sweep applied to an ideal capacitor generates a current due to the equation,
\[ I = \frac{dQ}{dt} = C \cdot \frac{dV}{dt} \] .................................\( 12 \)  
where,  
\[ \frac{dV}{dt} = \text{scan rate}. \]

Scan rates at lower end allow slow processes to occur but take a lot of time. Fast scan rates often show lower capacitance than slower scan rates. The increase in capacitance by decreasing scan rates can be explained by kinetically slow faradaic reactions on the electrode surface and by the transmission line behaviour caused due to electrode porosity. At slow scan rates, faradaic currents have the time to flow which increases the total current and capacitance. So, the average capacitance is given by,

\[ C = \frac{I}{dV/dt} \] .................................\( 13 \)

The interfacial capacitance is given by,

\[ C_i = \frac{C}{A} \] .................................\( 14 \)  
where,  
\[ A = \text{area of the material dipped in the electrolyte}. \]

The specific capacitance is given by,

\[ S_c = \frac{C}{W} \] .................................\( 15 \)  
where,  
\[ W = \text{weight of the material deposited on the substrate}. \]

The cycle life can also be estimated by CV. Poor cycle life and potentially useful cycle life can be differentiated by CV. The first cycle exhibits a quite bigger current compared to other as the initial electrochemical reactions that occur on the surface of the electrodes lead to the higher currents.

V. Experimental Setup

Cyclic voltammetry experiments are carried out on a solution in a cell fitted with electrodes. The electrochemical cell, where the voltammetric experiment is carried out, consists of a working electrode, a reference electrode, and usually a counter (auxiliary) electrode.

The \textit{working electrode} is the electrode where the potential is controlled and the current is measured. This is the electrode at which the electrochemical phenomena (reduction or oxidation) being investigated are taking place. The working electrode serves as a surface on which the electrochemical reaction takes place.

The \textit{reference electrode} is used to measure the working electrode potential. It should have a constant electrochemical potential as long as no current flows through it. Commonly used reference electrodes are the silver-silver chloride electrode (Ag/AgCl) or the Saturated Calomel electrode (SCE).

The \textit{counter or auxiliary electrode} which serves as a source or sink for electrons so that current can be passed from the external circuit through the cell. Simply, it is a conductor that completes the cell circuit. The current that flows into the solution via the working electrode leaves the solution via the counter electrode. The counter electrode should be a non-reactive, high surface area electrode such as platinum or carbon.

These three electrodes are immersed in an electrolyte. The collection of the electrodes, the solution, and the container holding the solution are referred to as an electrochemical cell. Electrolyte provides the sufficient conductivity. The solvent, electrolyte and the material used for working electrode, all these factors determine the potential range that can be accessed during the cyclic voltammetry experiment. Figure 5 gives the electrochemical cell.
Cyclic voltammetry can be performed with most of the commercially available potentiostats. Potentiostats are the generally used tools in electrochemical analysis. Presently several companies manufacture high quality potentiostats capable of performing various voltammetric techniques. Cypress systems, ACM Instruments, EcoChemie Netherlands, EG & G Princeton Applied Research are the top manufacturers. As per the requirement, the potentiostats may vary by size, power, sophistication and price. Though number of companies are manufacturing potentiostat instruments that deliver high precision but they are at equally high cost. These manufacturers usually make available the software for data analysis, electrochemical cells and the electrodes.

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Potentiostat Model</th>
<th>Max. Compliance Voltage (V)</th>
<th>Current Range</th>
<th>Website</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gamry Instruments</td>
<td>G 300 Potentiostat /ZRA</td>
<td>±20</td>
<td>1pA-300mA</td>
<td><a href="http://www.gamry.com">www.gamry.com</a></td>
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<td>Cypress Systems</td>
<td>66-EI400 Bipotentiostat</td>
<td>±10</td>
<td>10pA-10mA</td>
<td><a href="http://www.cypresshome.com">www.cypresshome.com</a></td>
</tr>
</tbody>
</table>
Typically, these instruments along with software cost from $5,000 to $20,000. Due to such a high cost, these instruments are not easily reachable for academic reason or for preliminary research study. Table 4.1 details some of the commonly used potentiostats with features.\textsuperscript{16}

Also there are a number of low cost potentiostats which deliver low accuracy or resolution.

VIII. Applications

Cyclic voltammetry is used in various fields.

- 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, reaction.
- Analytical chemists routinely use voltammetric techniques for the quantitative determination of a variety of dissolved inorganic and organic substances.
- Inorganic, physical, and biological chemists widely use voltammetric techniques for a variety of purposes, including fundamental studies of oxidation and reduction processes in various media, adsorption processes on surfaces, electron transfer and reaction mechanisms, kinetics of electron transfer processes, and transport, speciation, and thermodynamic properties of solvated species.

Potentiostat is prime devices in modern electrochemical research particularly in the investigation of mechanism reaction related to redox chemistry reaction and other chemical phenomena. Now a days, there is increase in interest in developing potentiostat application such as for metal corrosion analysis, environmental monitoring, quality control of food and medicines, biosensor, chemical sensor etc.\textsuperscript{17-21}

IX. Conclusion

Various methods used for voltammetry are described with details of cyclic voltammetry. The different analysis related with the study of the electrochemical reaction that is taking place at electrode-electrolyte interface of an electrochemical cell is detailed. Currently available instruments in market with their specification are also listed.

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