Chapter

Cyclic Voltammetry and Its Applications

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Abstract

Cyclic voltammetry is a versatile method for scientific investigation and innovation due to the fact that most processes involve electron transfer, which makes them be able to be monitored by this technique. Its uses cover characterization, synthesis, mechanisms, and analysis. In all applications, the technique can work well with a large variety of compounds including organic, inorganic, polymer, films, and semiconductors, among others. Furthermore, the method operates satisfactorily whether in a direct or an indirect approach. It can be considered to be an essential part at the very beginning that leads further to the grand project. As an analytical tool, it plays an important role in not only chemistry but also other involving areas. This review sheds the light on the way the technique proves to become one of the important instruments in research, development, and application labs.

Keywords: cyclic voltammetry, electrochemistry, electrochemical applications, characterizations, analysis

1. Introduction

Cyclic voltammetry has long been well known for its versatile applications in a number of areas involving electron transfer process, both directly and indirectly. It should be recognized at first that the techniques are normally not the main or the most important one in the research. Rather, their data are really useful in fulfilling the work as an essential complementary technique. It has been well applied in monitoring electrochemical behavior of a great variety of substances due to the fact that it can provide the insights into the relationship of structure, potential, and characteristic activities. The technique is prominent with its advantages of simplicity, sensitivity, speed, and low costs, among others, which results in a wide range of applications so far. Only important cases of previous studies are presented. Brief information for examples of recent applications is focused here along with corresponding references for further studies in specific area of interest. Furthermore, due to the fact that there have been a large variety of applications, it is not easy to categorize. Therefore, the content has been arranged to suit its further use, vision extension, and initiation of new research. Finally, it has to be emphasized that at this point, readers are supposed to be familiar with basics of this technique as well as involving theories (for example, ref. [29] and [30]). If not, available pertaining literature can be very useful. In discussing the application of cyclic voltammetry, we are going to talk about the three main uses of cyclic voltammetry first for different types of compounds, then continue with involving areas that cyclic voltammetry is considered useful. CV is used starting from here instead of cyclic voltammetry for convenience.

2. Classifications of usage

2.1 Characterization and synthesis

General concepts on using CV for the characterization of polymers as well as inorganic materials can be found elsewhere [1].

2.1.1 Organic compounds and polymers

CV has been proved to be helpful in characterizing xanthone, a bioactive compound, revealing that catechol is the key moiety to make it an effective scavenger for reactive species [2]. CV in methanol of antibiotic named amoxicillin revealed quasi reversible behavior and the change of redox potential upon the interactions with both metal ions and amino acids, which helps guiding in prescribing the medicine that they should not to be used together with the antibiotic [3–5]. Electrochemical behavior of ibuprofen and its degradation could be monitored closely by CV and found to be different for various types of electrode; for example, adsorption was observed on silver composite electrode, providing the insights into selecting the suitable electrode for removing this pollutant [6]. Together with EIS, CV is also found to be very useful in characterizing redox designing biosensors their behaviors depend on diffusion and capacitance, which might well shed the light on designing biosensors [7]. N-dodecylacrylamide (DDA) can form copolymer well with ferrocene derivatives on ITO to be applicable in the catalytic and sensor devices [8]. Its electron transfer characteristic is determined by the formation of monolayer or multilayer on the surface. A polymer-modified electrode namely poly(vinylferrocenium) on Pt was investigated and developed successfully by CV technique to make it applicable in analyzing organic compounds such as adenine [9]. The film of ruthenium complex can be synthesized via electropolymerization and then modified onto Pt electrode as a sensor for hydrazine with the characterization by CV [10]. Due to the fact that pyrrole is electroactive, the behavior of various types of polypyrrole can be conveniently followed by electrochemical methods, especially CV, and they were widely investigated in the 1990s and beyond [11–14]. CV could also be applied well in characterizing polyaniline to get suggestion in film preparations that its kinetic behaviors have the influence from the dopant acid [15]. Our work has also proved that CV can be used in electrografting born-doped diamond (BDD) surface via CV cycling without the use of reducing agent to prepare ex-situ working electrode for Cd determination [16]. With its advantage of speed, fast scan CV has been used to recommend the use of paraffin wax as a sealant instead of epoxy in making electrode for both in vivo and in vitro applications [17]. For natural polymers, CV has paved its way in analyzing specific electroactive compounds such as quinones in natural rubbers, which is very helpful in understanding their properties [18]. It is therefore clear that CV will still be greatly used for organic synthesis and characterizations for a number of years to come.

2.1.2 Metals, metal complexes, and inorganic compounds

Due to the fact that complex formation involves electron transfer, understanding the behavior of metal-ligand interaction can be studied well by CV and proven satisfactorily for simulations for both higher and lower ligand concentrations as well as for obtaining overall formation constants [19]. Our contribution has shown the use of CV to support the results from X-ray crystallography to explain the behavior of copper-thiourea-halide complexes [20]. Redox potential and reversibility obtained by CV have been proved to be useful in studying metalloenzymes with cofactor of molybdenum complexes as a model to describe its physiological role [21]. The characterizations of metal complexes have also been indicated to help investigate the catalytic activities

of complexes for the removal of toxic phenolic substances, especially dyes [22]. At quantum level, redox potentials from CV can be used in calculating LUMO and HOMO as well as the gaps of new organic semiconductors, which are applicable in everyday life [23]. CV has been proved to be advantageous in characterizing quantum dots (QDs), particularly in terms of their stabilities in vivo [24]. CV has been shown to be effective in following molecular imprinting of copper complexes [25]. CV can also be used in tracing activated iridium oxide film (AIROF) microelectrode via the variation of scan rate during the steps of fabrications and animal implantation [26]. In particular, CV from gold rotating disk electrode (Au RDE) has also been proved to be useful in determining surface coverage of silica microparticle monolayer and revealing that the adsorption is stronger with increasing diameter and surface coverage, which sheds the light on the deposition of a variety of particles onto the surface [27]. In terms of fuel cells, CV has been used to characterize the synthesized Pt-Ru catalysts and their catalytic activities [28]. CV has been used in the characterization of metal hydride. Using NaOH instead of KOH reduces hydrogen adsorption/desorption, resulting in better performance of nickel-metal hydride batteries [29].

2.2 Mechanism

Generally, CV has been widely recognized to be able to identify the mechanism of coupled chemical reaction [30–32]. For recent applications, cyclic voltammetry was applied together with voltabsorptometry in understanding the reaction of lumazine [33]. Special technique of fast Fourier transform continuous cyclic voltammetry was developed to be used well in investigating the mechanism of 4-nitrocatechol and its electrochemical synthesis [34]. This technique is also used in investigating proteolysis of milk protein by the research group in the same country [35]. The nontriangular waveform of CV has also been adopted with the advantage of convenient determination of transfer coefficient and electron transfer rate constant [36]. Additionally, staircase was compared with linear scan to assist in investigating adsorbed species [37]. Surprisingly, CV can also be used in studying the mechanism of surface coating [38]. Cyclic voltammetry was used together with potentiometry in understanding interactions between nicotine and metal ions [39]. The mechanism of electropolymerization and catalytic reaction of phenol red can be explained well by CV in order to analyze acetaminophen and dopamine [40]. The technique is also helpful in interpreting Ni electrodeposition for extending methanol oxidation [41]. Additionally, it can be used in understanding the mechanism of synthesizing graphene-coated graphene-coated electrode conveniently and fast in only one step [42]. The technique has been proved to be a helpful tool for mechanistic modeling for biosensors [43].

2.3 Analysis

CV can be used extensively for a wide range of both inorganic and organic compounds. In addition, it can be applied indirectly to analyze other types of characteristics, for example, microorganisms or antioxidant properties. Here the focus is on recent examples for analysis applications.

2.3.1 Organic compounds

For the analysis of organic compounds, cyclic voltammetry can be considered versatile in terms of a great variety of compounds. The technique has been used in the detection of glucose with graphene modified electrode [44]. Due to the overlapping of redox peaks in cyclic voltammetry, mathematical operation such as deconvolution has been applied in analyzing electroactive species including explosives, especially nitro

compounds. With modern technology in data analysis, the techniques can be used in the determination of pesticides [45]. Separation technology, for example, electromembrane is also helpful in eliminating interferences in diclofenac analysis [46]. Carbon black-modified GCE was used in estradiol by voltammetry in cooperation with FIA and amperometry [47]. Another important natural compound that has been widely used is curcumin, and its characteristics from CV can shed the light for its analysis in various corresponding products [48, 49]. CV was also proved to be supersensitive for hydrazine sensing [50]. Boron-doped diamond also exhibits its performance as an electrode with superb sensitivity for metronidazole in the analysis by CV [51], whereas bismuth electrode proved its specific characteristic in monitoring thiol content in fossil fuel [52]. The determination of 2,4,6-trichloroanisole in cork stoppers to reduce the wine defect can be accomplished satisfactorily with CV [53]. Recently, CV has played very important role in the analysis of juice [54] and wine [55] with particular analytes such as phenolic compounds. The analysis by CV helps in investigating perspective ionic liquids (ILs) to be used as solvents and electrolytes with their specific properties of cation and anion dependence [56]. It is also important to state here that CV can be used in analysis with the increase or decrease of the current signals of indicator compounds such as quinones [57] or ferricyanide [58]. Analyses of organic compounds by CV are sure to appear extensively in the near future in the analytical literature.

2.3.2 Inorganic compounds

Cyclic voltammetry can be used well with numerous inorganic compounds. It is normally applied to simple inorganic compounds probably because their electrochemical behavior is less complicated. It is worth mentioning here that metal ions are normally monitored by stripping voltammetry, so it is not going to delve into details here. Certainly, voltammetry is sensitive to metal ions, but its specificity can be enhanced by electrode modifications and stripping potential. Those who are interested in this area are suggested to get more details elsewhere [59–61]. An example of application of cyclic voltammetry to complicated inorganic compounds is the case of nanostructured iron oxides [62]. Additionally, corrosive impurities can be monitored closely in molten chloride by CV, which is very useful for energy storage [63]. With the use of chitosan and silver nanocomposite modified electrode, hydrogen peroxide can be detected [64], and this can be further extended to the determination of other compounds involving hydrogen peroxide such as glucose.

2.3.3 Other aspects of analysis

With electrochemical characteristics of CV, various analytical aspects of applications in analysis can be achieved as well. It was used in the valuation of antioxidant potential, which is very important in making wine [65]. The technique, along with EIS, CV can be used in assessing emulsion stability [66]. Furthermore, CV can be used in determining HOMO and LUMO levels with an acceptable accuracy [67]. Surprisingly, it can be applied in monitoring the formation of biofilms [68]. With its sensitivity for antioxidant, CV can be used in classifying black tea [69]. It is clear that indirect uses of CV can be used in the future in a variety of applications.

3. Areas of applications

3.1 Chemistry

Electron transfer definitely plays an important role in all reactions; therefore, electrochemistry and CV in particular have an essential part in all aspects of

Areas of chemistry	Typical applications
Analytical chemistry	Preparation and synthesis
	Analysis
	Mechanism
Inorganic chemistry	Metal interactions and reactions
	Structure characterizations
	Analysis
Organic chemistry	Synthesis
	Analysis
	Characterization
	Mechanism
Physical chemistry	Thermodynamic studies
	Kinetic studies
	Theoretical equations
	Surface and adsorption
	Analysis
	Mechanism
Biochemistry (and biology)	Metabolic processes
	Continuous monitoring
	In vivo and in vitro analysis
	Kinetic of enzymes
	Biosensors

Table 1.
Summary of the main uses of CV in chemistry.

chemistry as summarized in **Table 1**. Typical examples have already been mentioned in the previous text.

3.2 Other areas

Due to the fact that CV provides essential information for better understanding and the instrument is quite cost-effective now, thanks to modern technology, not to mention the way that it is easy to access, cyclic voltammograph in the form of potentiostat and specific programs is a must in most research and development labs. **Table 2** summarizes the use of CV in other areas besides chemistry.

4. Conclusive remarks

Cyclic voltammetry has long provided essential information in a number of areas and obviously will continue to facilitate research work as an analytical tool. The technique gives researchers an insight into the systems they are working on. For chemistry, the technique has shed the light on the mechanism of electron transfer reactions as well as their quantitative and synthetic relevance. The way that the electron transfer responses to the parameters of the surrounding environment leads scientists to be able to follow the behavior of target substances and therefore supports their characterizations. With smaller and cheaper instruments in addition

Areas	Reference for typical example
Paint	[70]
Medical	[71]
Engineering	[72]
Pharmaceutical sciences	[73–75]
Polymer and polymer films	[76]
Material sciences • microporous materials • semiconductors	[77]
Surface science and interface	[78]
Corrosion	[79]
Energy	[80]
Battery	[81]
Fuel	[82]
Fuel cell and microbial fuel cell	[41]
Processing and production	[83]
Flow detection	[84]
Food • wine product • antioxidant • preservation	[85]
Environment	[86]
Catalysis	[87]
Forensics	[88]

Table 2.
Summary of the main uses of CV in other areas besides chemistry.

to the ease the ease to operate, the technique can be available anywhere to serve all types of needs. The given examples are just only a handful of its usefulness in applications to initiate the understanding and further search. It is hoped that this review can form fundamental database to be implemented for further uses in the areas of individual interest. The opportunity is still there to investigate as well as to develop beneficial innovations. The more newly things are discovered and invented, the greater role the CV data play in feeding the world with much more meaningful scientific prosperity.

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