



## Cyclic Voltammetry in Chemistry Classes

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### Abstract

*Voltammetric methods have become an indispensable part of chemical research. Cyclic voltammetry (CV), in particular, is considered the most important method in the field of voltammetry [1]. Researchers use CV to determine redox properties, the number of electrons transferred or the reversibility of the reaction. CV also reveals information on the thermodynamics and kinetics of reactions as well as on underlying reaction mechanisms. Despite their great importance and diverse applications, voltammetric methods are rarely taught in school and teacher training courses. Likewise, previous literature and experiments mainly address graduate students and PhD candidates [2].*

*In this contribution, we present simple models and experiments to demonstrate that CV can easily be connected to the donor-acceptor principle and is well suited for repetition, application, consolidation and extension of relevant concepts of chemistry. Furthermore, the method offers the special opportunity not only to recognize the initial and final state of a redox process, but also to follow the course of electron transfer.*

*Our models and experiments help to make CV accessible to undergraduates and students at high school or school labs, providing a more detailed understanding of redox processes and the ability to observe them experimentally. In detail, we present teaching and learning materials students can use to investigate the reversibility of electrochemical reactions, using iron complexes and ascorbic acid. Additional experiments cover the determination of concentrations, redox potentials and the identification of chemical species. These topics are typically part of high school curricula and can be deepened in a more illustrative way by CV measurements. Finally, we present a first evaluation using CV materials in a teacher education lab course.*

**Keywords:** *cyclic voltammetry, donor-acceptor principle, model experiments*

### 1. Introduction

As early as the 1980s, not long after its development in the 1960s, cyclic voltammetry was described as the "spectroscopy of the electrochemist" due to its great importance to chemistry [3]. Cyclic voltammetry (CV) is now firmly established in research and is considered the most important method in the field of voltammetry [1]. The method makes it possible to record characteristic curves (cyclic voltammograms (CVG)) for redox processes. The course of the reaction, the associated redox potentials and the reversibility of the reactions can be retrieved from these curves. This information is of great interest to several fields of research: e.g., in analytical chemistry for the identification of substances, in electrochemistry for the development of sensors or for testing electrode properties in electrochemical cells.

Despite its great scientific significance, CV plays practically no role in school lessons. This is mainly due to a lack of educational introductory literature and simple experiments, both for schools and for student teachers.

In order to close this gap, first educational literature has been published in recent years [1] [2] [4]; however, this literature is mainly addressed at university scholars. The suggestions and experiments presented here go one step further and should also enable students at secondary schools or student laboratories to use CV. In order to ensure an accessible introduction to the method, we advocate an experimental approach to the method.

### 2. An Educational Approach to Cyclic Voltammetry

#### 2.1 Electrochemical Fundamentals and Educational Reduction



The term "cyclic voltammetry" already describes important features of the measurement method: a voltage is applied to an electrochemical cell; unlike in electrolysis, this voltage is changed cyclically (Fig. 2., left diagram). If a chemical reaction takes place in the electrochemical cell at a certain applied voltage, a resulting current is measured. The current/voltage values are recorded as curves.

In contrast to other electrochemical methods such as electrolysis, which use only a working electrode and a counter electrode, CV also requires a reference electrode [2].

A silver/silver chloride electrode with a stable potential is often used for this purpose. Only with this additional electrode, the potential difference to the working electrode can be determined; however, it is not involved in any reaction [5]. The use of a reference electrode can be compared to the standard hydrogen electrode and is therefore easy to understand.

Applying a potential to the working electrode during a measurement immediately results in a reduction or oxidation of the electrochemically active substance in the test solution. As a consequence, an electrochemical double layer forms on the surface of the working electrode. The solution should not be stirred to avoid disruption of the processes within the double layer. This means that diffusion is the only process to occur in the bulk solution.

The position of the redox equilibrium at the electrode can be calculated using the Nernst equation [2]: If at the beginning of the measurement the applied potential  $E$  is significantly smaller than the redox potential  $E^{\text{ref}}$  of the redox couple in the solution (red/ox), there is a significantly greater concentration of the reduced species  $c(\text{red})$  than that of the oxidized species  $c(\text{ox})$  at the electrode. This means that there is hardly any mass transfer and practically no current. Only when the applied potential approaches the value of the redox potential  $E^{\text{ref}}$ , the equilibrium of the redox reaction shifts to the side of the oxidized species. The transfer of electrons to the working electrode is indicated by an increasing current (cf. Fig.1.).

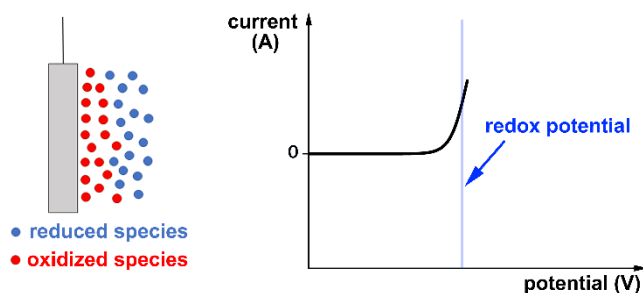


Fig.1. Model of the processes at the electrode when the applied potential is increased (left) and resulting current (right).

Since the solution is not stirred, the layer of oxidized species increasingly covers the electrode and the reaction is slowed down as less reduced species can diffuse to the electrode. This causes the current to drop again, resulting in the characteristic peak of a CVG (Fig.2., right diagram).

When the direction of the voltage advance is reversed, i.e. the potential is continuously reduced again, a reverse reaction takes place: the oxidized species that was formed before switching the potential is now reduced. As a result, a current flows again, now in the opposite direction and a second peak is measured in the opposite direction to the previous one [2]. A deeper consideration of the transfer processes is not necessary for a first interpretation of the curves measured.

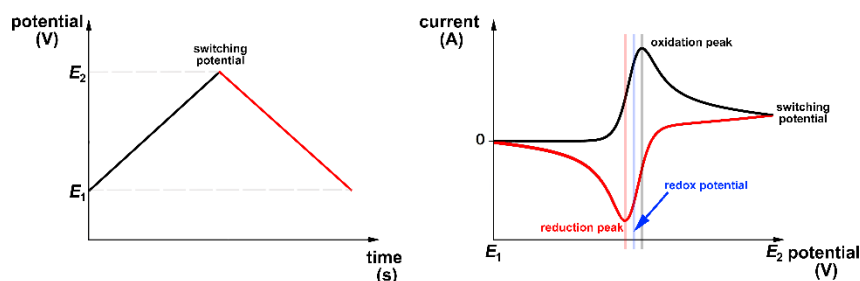


Fig.2. Course of the applied potential (left) and resulting cyclic voltammogram (right).

As this overview shows, CV has many similarities with methods familiar from school (e.g. electrolysis setups, recording current-voltage curves). It is also relatively easy to interpret the CV curves with knowledge from science lessons (Nernst equation, electrochemical double layer, diffusion).



The use of a reference electrode and a potentiostat is the main new element compared to familiar methods. However, it is not necessary to understand the exact mode of operation of a potentiostat. To understand why using a potentiostat is essential, it is sufficient to describe it as a device that sets the voltage change and registers the corresponding current values.

The exact mathematical relationships (e.g. for diffusion processes) are also not necessary for understanding and interpreting the measurement curves. Basic "the more ..., the more ..." relationships can easily be obtained from simple experiments (cf. chapter 3) and are sufficient to explain the observations.

## 2.2 Use of CV at Secondary Schools

Despite providing highly informative measurement results, CV has so far played virtually no role in science lessons. This can be explained by various factors: In order to ensure a uniform, precise rise and fall in voltage and the recording of the associated current, a considerable amount of equipment used to be required. In addition, the measuring arrangement with three electrodes was complicated and the set-up and handling was too time-consuming for teaching purposes. In addition, the costs of these devices and materials used to be too high for most schools.

Recent potentiostats, however, can be easily connected to a computer via Bluetooth. They are now only about the size of a lunch box and are significantly cheaper than they were a few years ago (cf. Fig.3., left). In addition, new computer programs for recording and evaluating the measurement data are beginner-friendly and easy to use.

Also, more advanced electrodes have been developed: Microelectrodes (screen-printed electrodes), in which all three electrodes are "printed" on a thin ceramic plate, are being used more and more frequently in research nowadays (cf. Fig.3. right). Due to the low material consumption during production, they are inexpensive to purchase (a few euros per electrode; graphite electrodes are particularly inexpensive). In many cases, they can be reused for several experiments.

The arrangement of the electrodes on the plate is compact and clear, making it easier for students to understand compared to the relatively complicated set-up of an apparatus with three macroelectrodes. The set-up and dismantling time for experiments is also drastically reduced by using screen-printed electrodes [4].

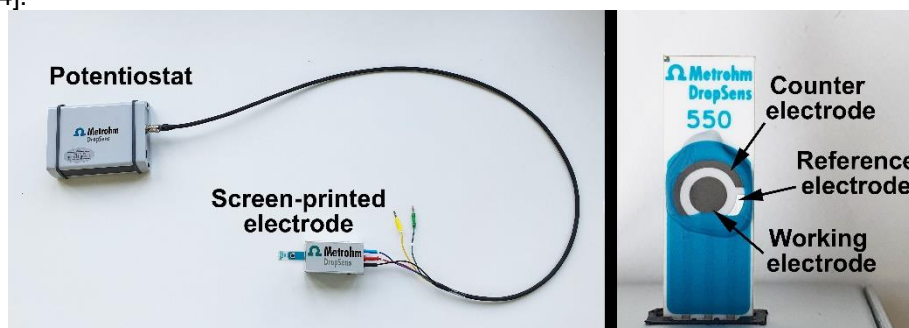


Fig.3. Measurement set-up (left) and structure of a screen-printed electrode with a drop of test solution (right).

To simplify experimental set-ups, experimental tool kits have become commercially available. In addition to the potentiostat, they contain all the necessary equipment such as cables, screen-printed electrodes, reaction vessels and analysis software. However, the price of these kits remains relatively high at several thousand euros.

As opposed to the acquisition costs, however, the costs of the experiments are quite low: Microelectrodes usually only require a single drop of electrolyte (cf. Fig.3. right) and can be used in very small vessels. This offers considerable savings in chemicals.

Another positive factor is the low time effort of the measurements: Depending on the selected voltage range, a measurement often only takes a few seconds to minutes. Accordingly, no time is wasted on technical handling but students can focus on the interpretation of the results.

Overall, CV measurements are easy to perform and provide precise results with little effort: The electrode arrangement is accessible, the voltage change and current registration are performed precisely by the potentiostat and the measurement software takes care of the recording.

The purchase of multiple experiment kits or potentiostats is not realistic for a school due to the financial factors described above. However, schools might consider to purchase a single unit that can be used by small learning groups such as school-based clubs or advanced courses.





It is also conceivable that CV devices could be purchased by extracurricular learning locations or universities; through experimental programs, they can be made available to a large number of pupils.

### 2.3 Connection with Curricular Key Concepts

In order to justify the use of CV for pupils or in teacher training, there has to be a link between standard topics in chemistry lessons and the skills promoted by working with the measurement method. It is therefore of great importance that the measurement method, the new experiments and the knowledge gained by using CV enable repetition, application, consolidation or expansion of familiar school topics and preliminary knowledge. These factors can be memorized with the mnemonic RACE [6].

Most obviously, CV can improve pupils' understanding of the donor-acceptor principle. This fundamental principle of chemistry is an integral part of school curricula. However, different explanatory models for redox reactions that pupils encounter throughout the years (oxygen transfer, electron transfer, change in oxidation numbers), can lead to misconceptions and confusion of models. Studies have also shown that many pupils have problems to describe and interpret the process of electron transfer. On learning about redox reactions, pupils tend to be uncertain as to where electrons come from and where they are transferred to [7].

At this point, CV can be very helpful to clearly understand processes at the particle level:

If a reaction takes place at a certain potential, electrons migrate from the electrode to the substance in the solution (electron acceptance, reduction of the substance) or from the substance to the electrode (electron release, oxidation of the substance). However, these electron transfers are not only recognizable by comparing educts and products, but are also directly visible as a current increase in the CVG. Differentiation between electron acceptance and release is facilitated by spatial separation between the processes in the diagram: Oxidations are always visible as a maximum, reductions as a minimum of the measurement curve.

The biggest asset of the method is therefore that the electron flow in a redox reaction can be observed directly in a resulting diagram and not just as the initial and final state of a reaction.

In addition to this important topic of electron transfer, there are many other school topics to which CV can be linked based on the RACE model (cf. Tab.1.).

| repetition  | application   | consolidation   | extension   |
|---|---|---|---|
| Description of redox reactions as electron transfer reactions, electrochemical series, potential and voltage, electrolysis, Faraday's 1st law, Nernst equation, ... | Identification of unknown substances based on their redox behavior, determination of electrode potentials, determination of concentrations, ... | Diffusion processes, comparison of electrolysis and CV, comparison of electrode potentials and standard electrode potentials, ... | Three-electrode systems, electron transfer at phase boundaries, scientific measurement methods, ... |

Tab.1. Integration of CV into topics taught in chemistry classes.

It is also possible to integrate CV into physical or mathematical topics, e.g. repetition of the concepts of current and voltage, electric circuits, Ohm's law and logarithmic curves using the Nernst equation.

## 3. Experiments on Cyclic Voltammetry

The experiments presented here are designed as basic introductory experiments to the measurement method and have already been tested in university courses and with high school students. A direct experimental introduction appears to be the best way to understand the method, as pupils can directly gain theoretical knowledge on CV from the experiments and measured curves.

All measurements were performed with the "µStat 400" potentiostat and the "DropView 8400" software from Metrohm using "Screen-printed Carbon Electrodes" type 110 from Metrohm.

### 3.1 Experiment 1: Measurement of a reversibly oxidable substance

To prepare an electrolyte solution for all three experiments, dissolve about 0.5 g of potassium chloride in 60 mL of demineralized water. For the first experiment, dissolve 0.1 g of potassium ferricyanide (GHS07, GHS09) in 20 mL of this electrolyte solution. A measurement is then carried out on a screen-



printed carbon electrode starting at +1.2 volts, descending to -0.5 volts and returning to +1.2 volts, at a scan rate of 50 mV/s. The curve obtained is shown in Fig.4 (blue). The ferricyanide ions are reduced to ferrocyanide ions at the working electrode as soon as the applied potential is low enough. This reaction can be observed as a downward reduction peak. When the potential is switched and the voltage is increased back to +1.2 volts, the ferrocyanide ions are oxidized back to ferricyanide ions. The oxidation and reduction peaks of the CVG are approximately the same size and their potentials are close together, indicating a reversible redox reaction.

### 3.2 Experiment 2: Effect of concentration on Cyclic Voltammograms

The remaining potassium ferricyanide solution from the first experiment has a concentration of 15 mmol/L. Dilute 10 mL of this solution with the prepared electrolyte solution in a 1:1 ratio. Dilute 10 mL of the resulting solution in a 1:1 ratio, again. Repeat the measurement of the newly prepared solutions with the settings from experiment 1, resulting in two additional CVGs. These curves are shown in green and red in Fig.4.

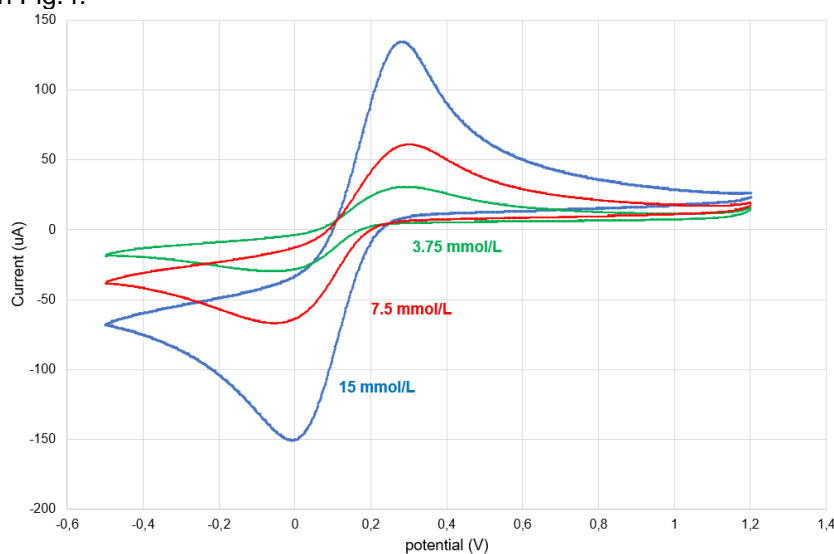


Fig.4. Cyclic voltammogram of potassium ferricyanide at different concentrations (15 mmol/L: blue curve; 7,5 mmol/L: red curve; 3,75 mmol/L: green curve).

The CVGs obtained show that although the heights of the peaks change depending on the concentration, their position remains practically constant. This is easy to understand for students, as they have learnt that the reduction or oxidation is dependent on the redox potential of the substance. To determine this potential, the mean of the potentials of the oxidation and reduction peak needs to be calculated [2]. The measurement in Fig.4. results in an electrode potential of approximately  $E^{ref} = (0 \text{ volts} + 0.3 \text{ volts})/2 = 0.15 \text{ volts}$  compared to the silver/silver chloride reference electrode. To convert this electrode potential to a standard potential, the potential value of the reference electrode (approx. 0.22 volts) must be added to the determined value. The resulting value of 0.37 volts agrees with the literature value of the standard potential (0.36 volts) [5].

The CVG in Fig.4. also shows that the height of the peaks is proportional to the concentration of the solutions. This allows to determine unknown concentrations by comparative measurements and calibration lines from CV measurements. These findings are used, for example, in analytics or in the construction of sensors.

### 3.3 Experiment 3: Ascorbic Acid as a Nonreversible Redox Reagent

For experiment 3, dissolve 0.1 g of ascorbic acid in 20 mL of the electrolyte solution. Subsequently, two consecutive measurements are carried out in the range from -0.3 to +1.2 volts at a scan rate of 50 mV/s.

A clear oxidation peak at around +0.65 volts can be observed in both scans. However, the peak of the second scan is lower than that of the first (cf. Fig.5.). The occurrence of the oxidation peaks can be attributed to the oxidation of ascorbic acid in the solution: The ascorbic acid molecule is present in the solution deprotonated and is reversibly oxidized to a radical by the applied potential. During this oxidation, a proton and an electron are released. The resulting radical is then irreversibly oxidized to



dehydroascorbic acid, releasing a second electron (cf. Fig.6.). As this second oxidation step is irreversible, the dehydroascorbic acid cannot be reduced back to ascorbic acid [8]. Therefore, no reduction peak can be observed.

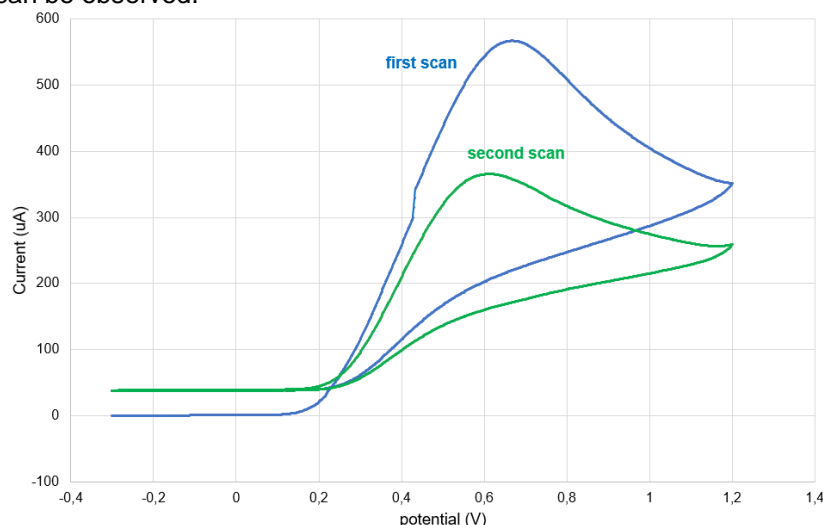


Fig.5. Two consecutive measurements of an ascorbic acid solution (blue curve: first measurement; green curve: second measurement, immediately after the first measurement).

This also explains the lower peak height during the second scan: After the first scan, a layer of dehydroascorbic acid is present on the electrode surface. The layer cannot be oxidized again and diffuses away from the electrode only slowly. For this reason, the scan carried out immediately after the first only shows a low concentration of ascorbic acid on the electrode surface (low peak height). If the electrode is left to rest for a few minutes and another measurement is carried out, a higher peak can be observed again.

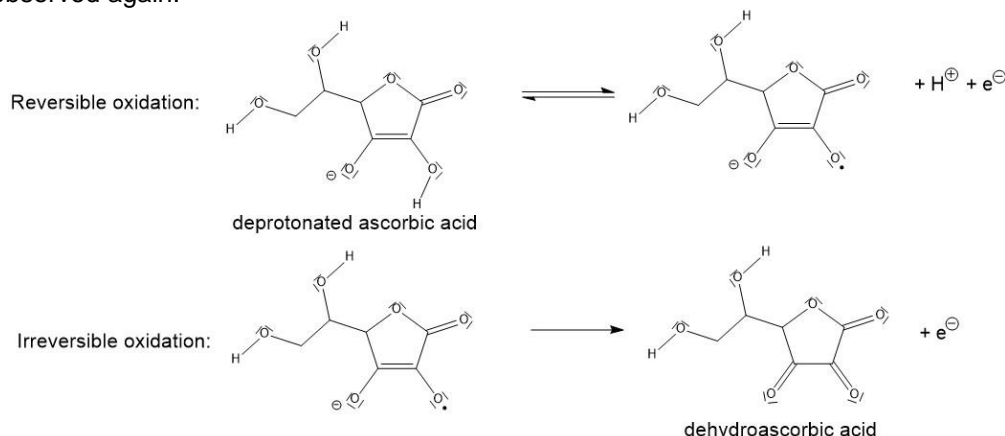


Fig.6. Oxidation mechanism of ascorbic acid.

#### 4. Results of first tests of the experiments in a teacher education lab course

In 2023, the designed experiments were tested and evaluated in a teacher education lab course at the University of Göttingen. First, the students read a short information text on the basics of the measurement method (comparable to chapter 2.1). This text did not cover concrete instructions for the set-up of the measuring apparatus or a technical introduction to the measuring program. Rather, this information was shared while experimenting.

The order of the experiments from chapter 3 proved to be favourable due to its steady increase in difficulty to interpret the curves.

The students described the simultaneous introduction and discussion of theoretical and practical aspects of the measurement method as quite uncomplicated and easy to understand. In addition, the instruction with parallel execution of the experiments only took about 2 hours and no long preparatory work was necessary.



The students particularly appreciated the fact that CV allowed them to directly perceive and "experience" the course of redox processes. Many of them had experienced electrochemistry as a very theoretical field lacking clarity about the exact processes. The use of a modern measuring method and the detective-like interpretation of the peaks was described as motivating and as an interesting insight into current research. The short measurement time and simple digital data analysis were also conceived positively.

The students could well imagine to use CV in combination with teaching units on energy storage or complex chemistry. Even to include CVGs into their classes without taking own measurements seemed conceivable to the participants, as the curves illustrate oxidation and reduction processes very clearly.

These experiments show that prospective teachers are very interested in modern measurement methods which demonstrate basic processes in chemistry clearer than before. Without a comprehensive practical introduction on the method and sufficient practice, however, the students admitted that they would not have felt confident enough to use it in school. These statements strongly emphasize the importance of didactically designed experiments and simple, understandable introductions to the measurement method.

With this in mind, the next step is to find further experiments which use cyclic voltammetry for repetition, application, consolidation and extension of central topics in secondary education.

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