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ELECTROCHEMICAL SIGNATURES OF COMMON PITFALLS IN VOLTAMMETRIC EXPERIMENTS: A PRACTICAL GUIDE

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Voltammetry is one of the most widely used electroanalytical techniques owing to its simplicity, low cost, rapid analysis, and ability to provide mechanistic, kinetic, thermodynamic, and analytical information on various redox systems. During the past decades, it has found various applications in biochemistry, pharmaceutical sciences, environmental monitoring, enzymatic electrochemistry, corrosion research, battery development, nanotechnology, green energy conversion, biosensor design, and in analysis of various biomedical materials, among other applications. Despite the apparent simplicity of voltammetric measurements, reliable interpretation of voltammograms often requires substantial theoretical knowledge and careful consideration of numerous experimental factors that may distort electrochemical responses. Incorrect interpretation of such artifacts may lead to erroneous conclusions regarding reaction mechanisms, electron-transfer kinetics, adsorption processes, catalytic activity, or chemical reactivity. Characteristic voltammetric signatures associated with working and reference electrode problems, working electrode memory effects, ohmic drop, dissolved oxygen interferences, convection, adsorption, crystallization, temperature and pH variations, capacitance effects, instrumental noise, peak overlap, chemical reactions coupled to electron-transfer step, bubble formation, and poor repeatability are systematically illustrated and discussed. For each experimental artifact, the major cause of its origin, characteristic voltammetric appearance, methods for recognition, and practical eliminating strategies are presented. By combining representative voltammograms with mechanistic explanations and practical recommendations, this work aims to improve the quality and interpretation of voltammetric measurements. It represents a valuable educational resource for students and all researchers who use voltammetry.

Keywords: voltammetry; pitfalls; IR drop; electrode pollution; instrumental errors

ЕЛЕКТРОХЕМИСКИ МАНИФЕСТАЦИИ НА НАЈЧЕСТИТЕ ГРЕШКИ ВО ВОЛТАММЕТРИСКИТЕ ЕКСПЕРИМЕНТИ: ПРАКТИЧЕН ВОДИЧ

Волтаммetријата е една од најшироко применуваните електроаналитички техники, главно поради нејзината едноставност, достапност, брзина на анализи и можноста да обезбеди механистички, кинетички, термодинамички и аналитички информации за различни редокс-системи. Во текот на изминатите децении, волтаммetријата наоѓа широка примена во важни интердисиплинарни научни подрачја како биохемијата, фармацевтските науки, мониторингот на животната средина, ензимската електрохемија, истражувањата на корозијата, развојот на батерии, нанотехнологијата, конверзијата на зелена енергија, дизајнот на биосензори и анализата на различни биомедицински материјали. И покрај привидната едноставност на волтаммetриските мерења, веродостојната интерпретација на волтаммограмите често бара значително теоретско знаење и внимателно разгледување на бројни експериментални фактори што можат да го нарушат електрохемискиот одговор. Погрешната интерпретација на ваквите артефакти може да доведе до неточни заклучоци во однос на реакциските механизми, кинетиката на електронскиот трансфер, процесите на адсорпција, каталитичката активност или хемиската реактивност. Во рамките на овој труд систематски се илустрирани и дискутирани најважните волтаммetриски карактеристики поврзани со проблеми на работната и референтната електрода, мемориски ефекти на работната

електрода, пад на омскиот отпор, интерференции што потекнуваат од растворен кислород. Покрај тоа, претставени се и волтамметриските карактеристики на проблеми поврзани со процеси на конвекција, адсорпција, кристализација, промени на температурата и промени на pH, капацитивни ефекти, инструментален шум, преклопување на пикови, хемиски реакции спрегнати со чекорот на електронски трансфер, формирање меурчиња и слаба повторливост на мерењата. За секој експериментален артефакт се прикажани главната причина за неговото појавување, карактеристичниот волтамметриски изглед, начините за негово препознавање, а дадени се и практични стратегии за отстранување на артефактите.

Клучни зборови: волтаммetрија; карактеристични проблеми во волтаммetрија; IR пад на отпор; загадување на електроди; инструментални грешки

1. INTRODUCTION

Over the past five decades, voltammetry has evolved from a specialized electroanalytical technique to one of the most versatile and widely used experimental tools in chemistry, biology, medicine, pharmaceutical and biomedical sciences, environmental analysis, and materials research.[1–4] Continuous advances in instrumentation, electrode materials, theoretical modeling, and data processing have considerably expanded the analytical capabilities of voltammetry while making it an indispensable tool in both fundamental research and routine applications.[1–12] Today, voltammetric techniques are explored for studying charge-transfer reactions, reaction mechanisms, biomolecular interactions, corrosion processes, electrocatalysis, batteries, fuel cells, nanomaterials, biosensors, environmental pollutants, and many other electrochemically active systems.[1–10]

One of the major advantages of voltammetry is its experimental simplicity.[3,12] A typical experiment requires only a potentiostat, a conventional three-electrode cell, and a suitable supporting electrolyte, while measurements are rapid, inexpensive, highly sensitive, and require only small sample volumes.[2–4,7,11,12] Beyond quantitative analysis, voltammetry provides valuable information about electron-transfer kinetics, thermodynamic properties, adsorption phenomena, coupled homogeneous chemical reactions to the electron-transfer step, catalytic processes, and mass transport, among others.[2–9,12] These features make voltammetry one of the most informative mechanistic techniques available in electrochemistry.

Despite the apparent simplicity of performing voltammetric experiments, reliable voltammetric measurements are very often more challenging than they initially appear. Recording a voltammogram represents only the first step of an electrochemical experiment,[1–4,12] whereas correct interpretation requires a thorough understanding of both electrochemical theory and experimental methodology. Numerous experimental artifacts–including working electrode contamination, reference electrode instability, uncompensated solution resistance, instrumental noise, dissolved oxygen, convection, capacitive currents, adsorption, crystallization, pH and temperature variations, bubble formation, poor repeatability, chemical reactions coupled to electron transfer, and many more–can substantially affect voltammetric responses. Importantly, many of these phenomena produce voltammetric patterns that closely resemble genuine electrochemical processes and may often lead to incorrect mechanistic or analytical conclusions if not properly recognized.[2–4]

One can find a number of excellent educational papers and books devoted to voltammetric theory, methodology, and data interpretation.[1–4,7,9,12–18] Such work reflects the growing interest of the electrochemical community in improving both teaching and practical understanding of voltammetric experiments. Nevertheless, pitfalls and unwanted phenomena encountered during voltammetric measurements are an almost inevitable part of virtually every electrochemical experiment, regardless of the operator's experience or the sophistication of the instrumentation. Proper recognition of these artifacts/phenomena is therefore essential for obtaining reliable and scientifically meaningful results.

Until now, there had been no comprehensive work that systematically summarizes in one place some of the most common experimental pitfalls in voltammetry. This paper intends to fill this gap. Rather than focusing on rigorous mathematical derivations, its primary objective is to provide a practical visual guide to the most common pitfalls encountered in voltammetric experiments. Representative voltammograms are accompanied by adequate mechanistic explanations and practical recommendations that should facilitate rapid recognition of experimental artifacts and their

distinction from genuine electrochemical phenomena. This work should serve as a useful educational tutorial for students, young researchers, as well as for other electrochemists. The content should contribute to more reliable interpretation of voltammetric measurements and to improved experimental practice.

2. RESULTS AND DISCUSSION

The pitfalls encountered in voltammetry can be broadly categorized into working electrode–related, reference electrode–related, instrumental, electrolyte-related, experimental condition–related, and mechanistic artifacts. Because numerous factors may influence both the quality of voltammetric responses and the reliability of their interpretation, this work focuses on the most common and characteristic pitfalls encountered in voltammetric experiments. Representative voltammetric signatures of these phenomena are presented together with a brief discussion of the underlying causes responsible for their occurrence. Particular emphasis is placed on the practical recognition of each pitfall and on straightforward experimental strategies that can be applied to minimize or eliminate their influence, thereby improving the reliability and reproducibility of voltammetric measurements.

2.1. *Working electrode–related pitfalls*

The selection of an appropriate working electrode is the first and most important step in every voltammetric experiment. Because the use of mercury electrodes is now largely restricted because of their toxicity,[2,18] modern voltammetry mainly relies on three classes of solid working electrodes: carbon-based electrodes, gold electrodes, and platinum electrodes. Each material possesses distinct electrochemical properties that make it suitable for specific analytical applications, but each is also associated with characteristic experimental limitations that should be recognized before interpreting voltammetric data.

Carbon-based electrodes,[2,3,12,18,19] including glassy carbon electrode (GCE), edge-plane pyrolytic graphite electrode (EPPGE), basal-plane pyrolytic graphite electrode (BPPGE), boron-doped diamond electrode (BDD), carbon paste electrode (CPE), and screen-printed carbon electrode (SPCE), are widely used in voltammetric experiments. The extensive application of carbon-based electrodes stems from their chemical inertness, broad potential window, low background current, and high electrical conductivity.[18,19] These properties make carbon-based electrodes excellent platforms for studying pharmaceuticals, biomolecules, organic compounds, and numerous inorganic species.[1–4] Their principal drawback, however, is the pronounced adsorption of lipophilic systems present in voltammetric cell. Strongly adsorbed species may remain on the electrode surface even after the experiment has been completed. In many experimental cases, carbon-based electrodes produce residual peaks during subsequent blank measurements (even after a proper cleaning), a phenomenon commonly known as the *memory effect* (Figure 1a).[2,3,18,19]

Gold electrodes exhibit quite different electrochemical behavior than the carbon-based electrodes.[3,18] Besides their extensive use in stripping voltammetry for trace metal analysis,[2,3,18] they are particularly suitable for investigating sulfur-containing compounds because of the strong gold–sulfur interaction responsible for the formation of self-assembled monolayers.[3] On the other hand, gold surfaces are readily contaminated by strongly adsorbing species. Moreover, at sufficiently positive potentials (typically above approximately +0.9 V, depending on the electrolyte), oxidation of the gold surface generates intense faradaic signals originating from the formation of gold oxide (Figure 1b). These electrode processes may easily overlap with the response of the analyte and complicate voltammetric interpretation.

Platinum electrodes share the excellent conductivity and electrochemical stability of gold but exhibit an additional characteristic associated with hydrogen adsorption.[3,18] Even at relatively low over-potentials (in acidic media), hydrogen evolution is accompanied by adsorption of hydrogen atoms on the platinum surface, producing well-defined hydrogen adsorption/desorption peaks (Figure 1c). Their position and intensity depend on solution pH and the crystallographic structure of the platinum surface.[2,3,18] These intrinsic platinum signals are especially pronounced in acidic media and should always be distinguished from the electrochemical response of the investigated analyte.[3,18]

Most working electrode–related problems can be recognized from characteristic changes in voltammetric responses.[18] Carbon electrodes affected by the “memory effect” typically produce residual peaks in blank electrolytes (Figure 1a), gradual loss of peak intensity, poor repeatability, or distorted baselines caused by surface fouling.[18] The most effective regeneration method is gentle

mechanical polishing using an aqueous suspension of fine aluminum oxide (Al_2O_3) on a polishing pad while moving the electrode in a smooth "infinity" (∞) pattern.[12] After polishing, the electrode should be thoroughly rinsed with distilled water and sonicated to remove residual alumina particles.

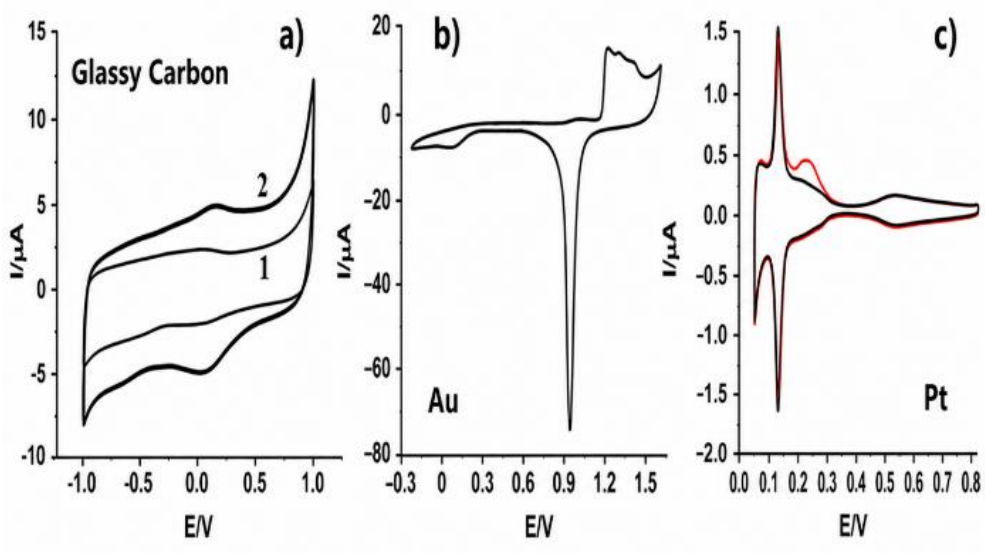


Fig. 1. "Blank" (curve 1) and "memory effect" (curve 2) obtained at a glassy carbon electrode (a), and features of gold (b) and platinum (c) when used as working electrodes in cyclic voltammetry

Gold electrodes are commonly regenerated electrochemically by repetitive potential cycling in 1 mol L^{-1} electrolyte composed of sulfuric acid or hydrochloric acid. Successive formation and reduction of the gold oxide layer efficiently removes adsorbed contaminants.[2,3,18] A similar electrochemical activation procedure is routinely used for platinum electrodes, where repeated oxide formation and reduction restore surface activity. Platinum may also be cleaned chemically using freshly prepared piranha solution (sulfuric acid [H_2SO_4]/hydrogen peroxide [H_2O_2]), aqua regia (hydrochloric acid [HCl]/nitric acid [HNO_3]), or concentrated HNO_3. Because these reagents are highly corrosive and hazardous, such procedures should be performed only under appropriate laboratory safety conditions,[18] followed by extensive rinsing with ultrapure water.

During the last two decades, screen-printed electrodes (Figure 2) have become increasingly popular owing to their low cost, portability, disposable design, and compatibility with point-of-care applications.[19,20] Despite these advantages, they possess several important limitations. Because the working, reference, and counter electrodes are integrated on a single printed substrate, the active surface is particularly susceptible to fouling and gradual degradation of the printed conductive layer (Figure 2). Repeated potential cycling commonly decreases sensitivity of these electrodes, distorts voltammetric peaks, and reduces measurement reproducibility. An additional limitation concerns quantitative analysis of these electrodes. Because each measurement is usually performed by placing a single droplet of solution on the electrode surface, repeated use progressively modifies the working electrode, making reliable calibration curves difficult to obtain using the same device. In addition, because screen-printed electrodes typically operate with very small sample volumes, solvent evaporation can progressively change the sample concentration and composition, thereby affecting the stability and reproducibility of the electrochemical response. Moreover, efficient removal of dissolved oxygen is often difficult or impractical during measurements performed directly on screen-printed electrode platforms, which may introduce background currents or interfere with the electrochemical signals of interest. It is well known that the screen-printed electrodes are generally intended for single use or only a limited number of consecutive measurements for a defined concentration of analyte(s). Under continuous operation, their analytical performance often deteriorates after approximately 1–3 hours, depending on the electrode composition, the investigated system, and the applied potential window. Therefore, whenever quantitative voltammetric measurements are performed using screen-printed electrodes, especially in scenarios when anodic stripping voltammetry protocols are explored, signal stability, reproducibility, and

electrode integrity should always be carefully verified.

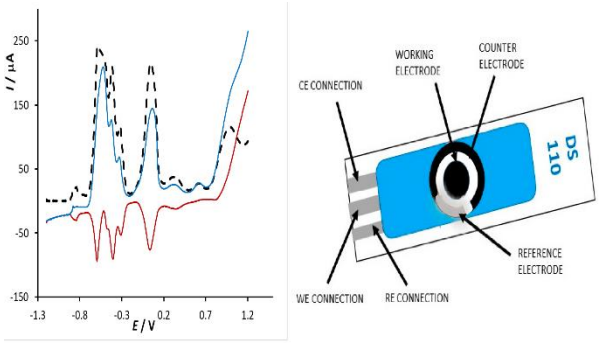


Fig. 2. A scheme of a screen-printed electrode used in voltammetry (right panel) explored for detection of ions of heavy metals dissolved in water (square-wave voltammograms presented in the left panel)

2.2. *Reference electrode–related pitfalls*

The reference electrode is one of the most critical components of every voltammetric system and also one of the most common sources of experimental artifacts.[2,3,9,18] Unlike the working electrode, which generates the electrochemical response, the reference electrode must maintain a constant and reproducible potential throughout the experiment. Even small deviations in its potential can shift peak positions, distort peak shapes, and compromise the interpretation of voltammetric data.

The silver (Ag)/silver chloride (AgCl)/ saturated potassium chloride (KCl) electrode and the saturated calomel electrode (mercury [Hg]/mercury[I] chloride [Hg_2Cl_2]/saturated KCl) are the reference electrodes most frequently used in aqueous voltammetry,[2,3,12,18] whereas double-junction and non-aqueous reference electrodes are employed for specialized applications.[3,12,18] Figure 3 presents an example of voltammograms recorded with a malfunctioning reference electrode. Unstable reference potentials produce distorted voltammetric responses, irregular peak positions, current oscillations, and poor signal reproducibility.[18] In practice, voltammograms containing numerous spikes together with unusually low currents often indicate that the reference electrode is not operating properly. Reference electrode malfunction may arise for several reasons, including aging of the internal saturated KCl solution, clogging or contamination of the porous junction, leakage of the filling solution, trapped air bubbles, crystallization of KCl around the junction, or deterioration of the Ag/AgCl element itself. These processes increase junction resistance, destabilize the reference potential, and introduce both electrical noise and unpredictable potential shifts into the experiment.

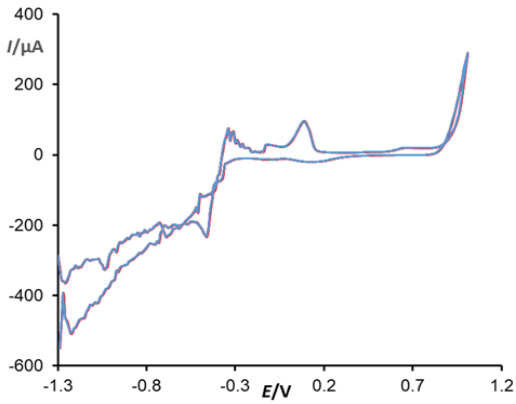


Fig. 3. A cyclic voltammogram recorded with a malfunctioning reference electrode

Most of these problems can be minimized through proper maintenance of the reference electrode. The internal filling solution should be replaced periodically with freshly prepared saturated KCl, while the porous junction should be carefully rinsed with deionized water to remove precipitated salts and adsorbed impurities. High-purity deionized water should also be used for preparing supporting electrolytes and cleaning electrochemical cells, because impurities may gradually contaminate the junction.

Before each experiment, the reference electrode should be inspected for trapped air bubbles and an adequate filling solution level. Proper hydraulic contact through the porous frit is essential for maintaining a stable reference potential. When not in use, Ag/AgCl and Hg/Hg_2Cl_2 reference electrodes should be stored with the junction immersed in saturated KCl solution to prolong their lifetime and preserve junction stability.

It should also be emphasized that several apparent electrochemical phenomena may originate from an unstable reference electrode,[3,18] rather than from the investigated system itself. Unexpected peak-potential shifts, poor scan-to-scan reproducibility, apparently irreversible voltammograms, or seemingly altered electron-transfer kinetics may simply reflect reference electrode instability. Consequently, verification of reference electrode performance should always be one of the first diagnostic steps whenever anomalous voltammetric responses are observed. If unstable potentials, excessive resistance, leakage, or electrical drift persist after cleaning and refilling, then the reference electrode should be replaced. Because reference electrodes have a finite lifetime, their performance should also be verified periodically by calibration against a fresh reference electrode or a well-established internal redox standard, such as ferrocene[2,3,12,18] in

non-aqueous media or a reversible redox couple in aqueous solutions.

2.3. *Ohmic drop in voltammetric cell: recognition and practical solutions*

Ohmic drop (E_{ohmic}), also known as uncompensated resistance (*IR* drop),[2,3,18] is one of the most common instrumental artifacts in voltammetry. It originates from the finite electrical resistance of the solution between the working and reference electrodes. During current flow, part of the applied potential is lost across this resistance instead of driving the electrode reaction.[2,3,18] Consequently, the actual potential at the working electrode differs from the value of the potential applied by the potentiostat according to the relationship $E_{ohmic} = IR$**.** The magnitude of this error increases with both the current passing through the cell and the uncompensated solution resistance.

Although a low supporting electrolyte concentration is the most common cause of *IR* drop, several other factors may contribute to its magnitude. Large currents generated by highly concentrated analytes, large electrode surface areas, and high scan rates all increase the *IR* product.[3,18] Additional sources include a large distance between the working and reference electrodes, poorly conducting organic solvents, resistive surface films caused by electrode fouling, and poor electrical contacts within the electrochemical cell.

The electrochemical consequences of *IR* drop are readily recognized. As illustrated in Figure 4, increasing uncompensated resistance causes progressive separation of oxidation and reduction peaks, shifts peak potentials away from their true thermodynamic values, decreases peak currents, and broadens the overall voltammetric response. Under severe conditions, a fully reversible redox system may incorrectly appear quasi-reversible or even irreversible. Failure to recognize this artifact may therefore lead to erroneous conclusions regarding electron-transfer kinetics, reaction reversibility, heterogeneous rate constants, and reaction mechanisms.

Distinguishing *IR* drop from the capacitive (charging) current (I_c) is a crucial aspect in voltammetry**.** The charging current arises from charging of the electrical double layer and is described by $I_c = vC_d$**,** where v is the scan rate and C_d is the double-layer capacitance. So, large background currents are mainly associated with high scan rates, large electrode surface areas, or highly capacitive electrode materials rather than with uncompensated solution resistance itself.

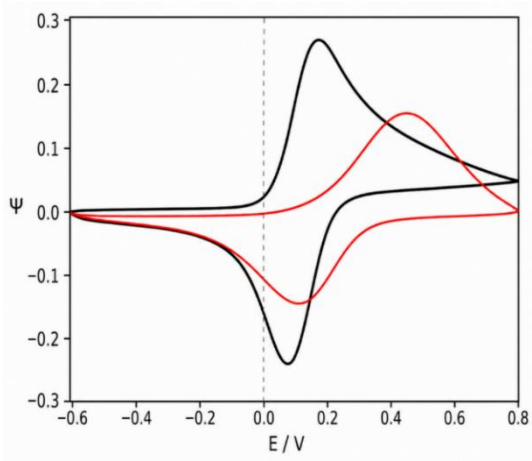


Fig. 4. Normal features of a simulated cyclic voltammogram (black curve), and a cyclic voltammogram featuring significant ohmic drop present in voltammetric cell (red curve)

Fortunately, *IR* drop in voltammetric experiments can usually be minimized through appropriate experimental design. The most effective approach is the use of a sufficiently high concentration of an inert supporting electrolyte (typically > 0.1 mol L^{-1}), which increases solution conductivity and reduces uncompensated resistance. The reference electrode should be positioned as close as possible to the working electrode, preferably by using a *Luggin capillary*,[2,18] to minimize the ionic current path. Proper cleaning of the working electrode and careful inspection of all electrical connections are equally important. When low-conductivity organic solvents are employed, the supporting electrolyte concentration should be increased whenever chemically feasible.[2,3,12,18] Modern potentiostats also provide positive feedback or current-interrupt *IR* compensation, which can substantially reduce uncompensated resistance. However, excessive electronic compensation should be avoided, as it may introduce oscillations and artificial distortions into the voltammogram.[18] Therefore, optimization of the cell geometry and electrolyte composition remains the most reliable strategy for minimizing *IR* drop and obtaining accurate, reproducible voltammetric measurements.

2.4. *Pitfalls due to instrumental noise and bubbles formation*

Instrumental noise is very common factor limiting the quality of voltammetric measurements, especially when small currents are recorded. Unlike faradaic processes, noise originates from the measuring system or from external electromagnetic interferences rather than from the electrode reaction

itself. Typical sources include electronic components of the potentiostat, thermal noise, poor grounding, insufficient electrical shielding, loose cable connections, unstable reference electrodes, temperature fluctuations, mechanical vibrations, and nearby electrical equipment.

Instrumental noise appears as random baseline fluctuations rather than systematic changes in peak position or shape. The voltammograms presented in Figure 5 mainly contain irregular high-frequency oscillations distributed over the entire potential range, resulting in a reduced signal-to-noise ratio. As the amplitude of the noise approaches the magnitude of the analytical signal, reliable determination of peak currents, peak potentials, detection limits, and analytical precision becomes increasingly difficult.

Instrumental noise can usually be minimized by proper experimental practice. The potentiostat should be correctly grounded, all electrical connections should be secure, and shielded cables should be used whenever possible. For current measurements in the nA or pA range, operation inside a Faraday cage is strongly recommended.[2,18] Mobile phones, magnetic stirrers, switching power supplies, fluorescent lamps, and other electromagnetic sources should be kept away from the electrochemical setup. Stable laboratory temperature, minimized mechanical vibrations, and careful optimization of instrumental parameters further improve baseline stability. Signal averaging and moderate digital filtering may also reduce noise, although excessive filtering should be avoided because it may distort genuine voltammetric features.

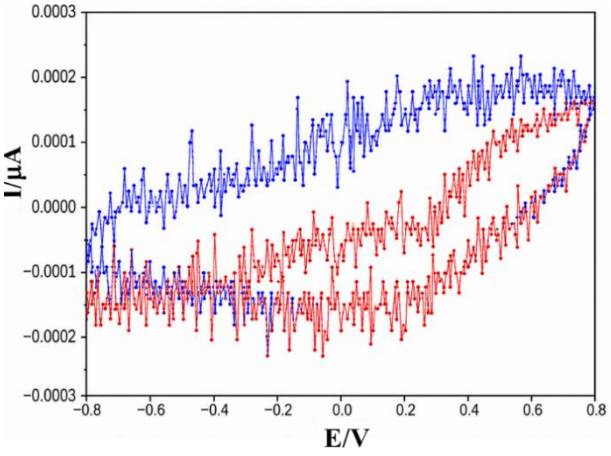


Fig. 5. Consecutive scans showing the effect of instrumental noise on cyclic voltammograms

Bubble formation is another frequently overlooked source of experimental error, often giving voltammetric signatures similar to those of instrumental noise. Bubbles may originate from hydrogen or oxygen evolution at the electrode surface, dissolved gases in the electrolyte, insufficient solution degassing, vigorous stirring, or improper filling of the electrochemical cell. When a bubble adheres to the working electrode, it blocks part of the electroactive surface, reducing the effective electrode area and producing unstable current responses.

The voltammetric signature of bubble formation is usually easy to recognize. Instead of smooth voltammograms, the recorded current exhibits sudden spikes, abrupt jumps, and irregular oscillations superimposed on the faradaic response (Figure 6). Bubbles continuously nucleate, grow, detach, and reform, so the pattern of these disturbances is generally random and poorly reproducible. Persistent bubbles may also reduce peak currents by decreasing the active electrode area and, in extreme cases, completely obscure weak analytical signals.

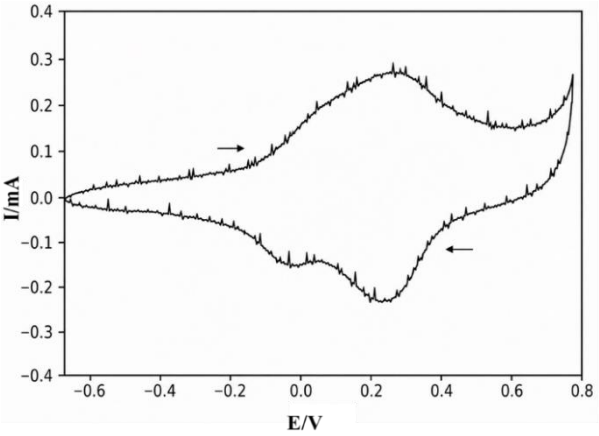


Fig. 6. The shape of a cyclic voltammogram affected by bubbles formed (or persisting) during voltammetric experiment

Bubble-induced artifacts can be eliminated to a large extent by careful experimental practice. Initially, electrolyte solutions should be properly degassed whenever oxygen-sensitive measurements are performed, while excessive gas evolution should be avoided by selecting an appropriate potential window. Before each measurement, the working electrode should be inspected to ensure that no bubbles remain attached. Gentle tapping of the cell, slight movement of the electrode, or brief stirring followed by complete stabilization of the solution is often sufficient to remove adhering bubbles. Appropriate electrode orientation, moderate current densities, and avoidance of excessive gas evolution further reduce bubble attachment. When gas evolution is unavoidable, rotating electrodes or flow-through electrochemical cells can continuously remove bubbles and maintain a stable electroactive surface.

2.5. *Dissolved oxygen interference*

Dissolved oxygen present in an electrochemical cell is very common electrochemical interference in voltammetric experiments, and it should always be considered before interpreting the features of recorded voltammograms. Given that molecular oxygen is electroactive,[3] it is readily reduced within the potential window of many aqueous and non-aqueous systems,[2,3,18] producing a broad cathodic wave (Figure 7) that may overlap with reduction signals of the analyte. The position and intensity of the oxygen reduction peak depend on the electrode material, the supporting electrolyte, solution pH, temperature, the dissolved oxygen concentration, and the voltammetric technique employed. If not removed, oxygen may mask weak analytical signals, and it commonly distorts peak shapes, which often leads to incorrect mechanistic interpretation.

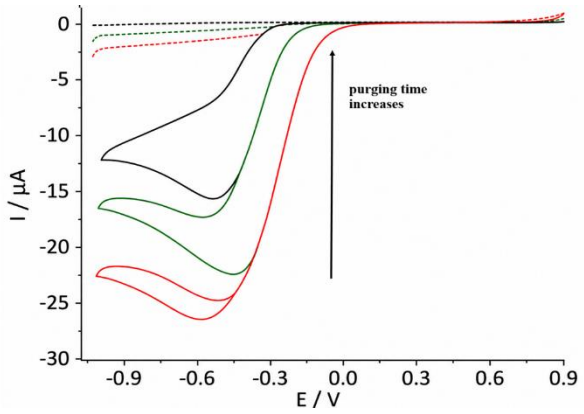


Fig. 7. Voltammetric patterns of dissolved oxygen present in an electrochemical cell. The peak of oxygen reduction decreases (going from the red curve toward the black curve) as the purging time increases in the direction of arrow

Oxygen interference in voltammetric experiments is usually easy to recognize and eliminate. A simple and highly recommended procedure is to record a blank voltammogram of the supporting electrolyte before adding the analyte. The appearance of a broad cathodic wave in the blank indicates the presence of dissolved oxygen. The electrolyte should then be purged with high-purity nitrogen or argon, typically for at least 10 minutes, although larger solution volumes may require longer degassing. During the experiment, a gentle inert-gas blanket above the solution helps prevent redissolution of atmospheric oxygen. Vigorous stirring and unnecessary exposure of the electrolyte to air should also be avoided after degassing. Recording a second blank voltammogram after purging provides a simple verification that oxygen has been successfully removed: The reduction wave should disappear almost completely.

2.6. *pH-related pitfalls*

Solution pH is one of the most influential experimental parameters in voltammetry, as it directly affects both the thermodynamics and kinetics of numerous electrochemical processes. The redox mechanisms of many inorganic and organic compounds involve proton-coupled electron transfer, meaning that electron transfer is accompanied by protonation or deprotonation reactions.[1–4] Consequently, even relatively small changes in pH may shift peak potentials, alter peak currents, modify peak shapes, or even change the overall reaction mechanism. According to the Nernst equation, electrochemical processes involving protons exhibit systematic potential shifts with pH,[2,3,18] so pH control is essential to obtain reproducible and meaningful electrochemical data. Besides affecting redox reactions directly, pH also influences the chemical stability of analytes, the acid-base speciation of electroactive molecules, adsorption processes, the solubility and precipitation of numerous metal ions, and the formation or decomposition of metal complexes.[3] In bioelectrochemistry, pH becomes even more critical because the catalytic activity, structural stability, and electron-transfer properties of redox enzymes strongly depend on the proton concentration.[1,4] Likewise, biological molecules such as proteins, nucleic acids, and many pharmaceutical compounds may undergo conformational or chemical changes outside their optimal pH range, leading to substantial alterations of their voltammetric responses.

The influence of pH is generally easy to recognize from systematic shifts of voltammetric peaks, as those illustrated in Figure 8a. Peak potentials usually move toward more positive or more negative values depending on the reaction stoichiometry, while peak heights and shapes may simultaneously change because of modifications in reaction kinetics. Therefore, recording voltammograms over a series of well-defined buffer solutions often provides valuable mechanistic information regarding proton involvement in the electrode process.

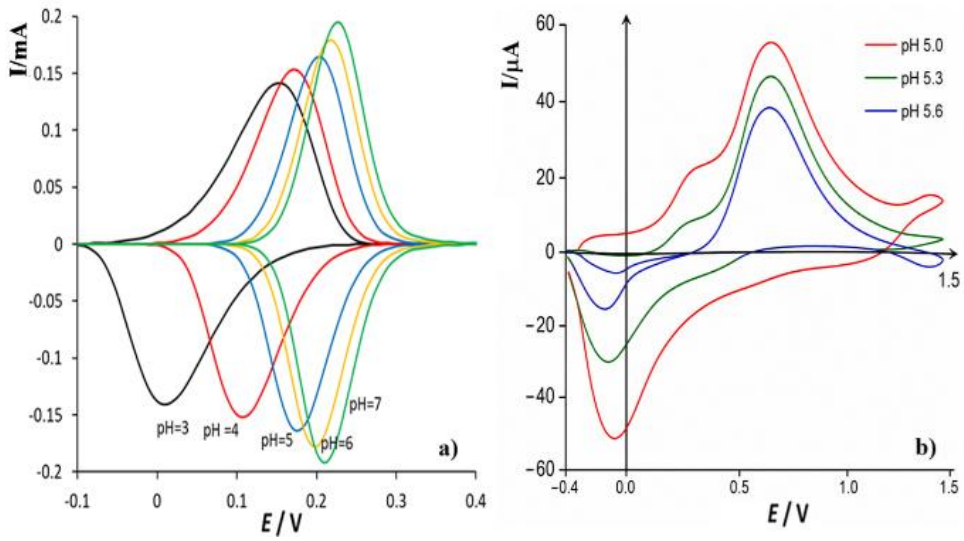


Fig. 8. The effect of pH on the features of cyclic voltammograms. (a) pH-dependent voltammetric behavior of lipophilic surface-active quinone-like systems. (b) The effect of local pH changes in unbuffered solutions on consecutive cyclic voltammograms

In voltammetric experiments, unintended variations in solution pH (Figure 8b) may easily lead to erroneous conclusions concerning reaction mechanisms, electron-transfer kinetics, catalytic activity, or analyte stability. Hence, the pH of supporting electrolytes should always be accurately adjusted using appropriate buffer systems and verified with a calibrated pH meter before each experiment. During prolonged experiments, especially when electrochemical reactions generate or consume protons, pH should be periodically monitored to ensure that local or bulk pH changes do not influence the recorded responses. Careful pH control is a prerequisite for reliable, reproducible, and mechanistically meaningful voltammetric studies.

2.7. *Temperature-related pitfalls*

Temperature is another fundamental experimental parameter that significantly influences every aspect of voltammetric measurements. Increasing temperature generally enhances molecular diffusion, decreases solution viscosity, accelerates heterogeneous electron-transfer kinetics, and increases the rates of homogeneous chemical reactions coupled to electron transfer.[2,3] As a consequence of increased temperature, voltammetric peaks often become broader, peak currents mainly decrease,[2,21] and the rate of coupled chemical reactions might become more pronounced. Conversely, decreasing the temperature slows molecular motion, suppresses many follow-up chemical reactions, and often results in sharper and better-defined voltammetric peaks.[21] This effect is particularly exploited in cryo-voltammetry,[22] where measurements performed at sub-ambient temperatures can stabilize short-lived reaction intermediates and significantly improve the resolution of complex electrochemical processes. Low-temperature voltammetry has therefore become an important tool for mechanistic studies of unstable redox systems and fast coupled chemical reactions. Temperature effects can be recognized by systematic changes in peak position, peak width, peak current, and voltammetric reversibility, as illustrated in Figure 9.

Measurements performed at higher temperatures typically exhibit broader peaks, whereas low-temperature experiments produce narrower peaks with improved resolution.[21,22,23] Temperature also influences adsorption equilibria, catalytic reaction rates, equilibrium constants, solution conductivity, and the stability of passive films formed on electrode surfaces.[1–3] In biological systems, strict temperature control is indispensable because enzymes rapidly lose catalytic activity outside their optimal temperature range owing to partial unfolding or irreversible denaturation.[1,21] Similarly, protective surface films formed on metals or chemically modified electrodes may dissolve, reorganize, or become mechanically unstable at elevated temperatures, thereby altering electrode performance.[3,18] Temperature fluctuations may also change the solubility of gases, salts, and reaction products, potentially introducing additional experimental artifacts. Therefore, voltammetric experiments should always be carried out under carefully controlled thermal conditions, preferably using thermostated electrochemical cells when high reproducibility or reliable mechanistic interpretation is required. Recording all measurements at the same

temperature is essential to ensure that observed changes in voltammetric responses originate from the investigated electrochemical process rather than from uncontrolled thermal variations.

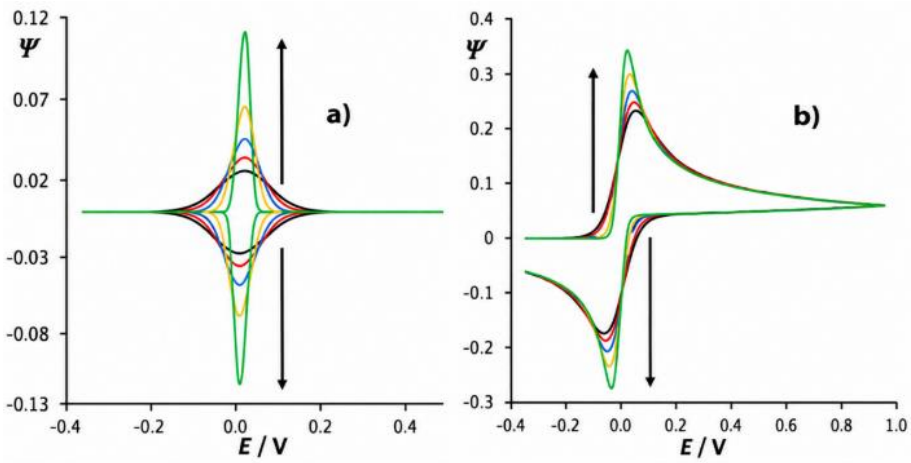


Fig. 9. Temperature-dependent features of theoretical cyclic voltammograms simulated for the simplest one-electron $Ox_{(ads)} - 1e^- \rightleftarrows Red_{(ads)}$ electrode transformation of fully adsorbed (ads) reactants and products (a) and of electrode transformation of fully water soluble reactants and products (b). Temperature decreases from 300 K (black curves) to 100 K (green curves) in the direction of the arrows. To get a better visualization, it is assumed in theoretical model in (b) that diffusion coefficients remain invariable by changing the temperature.

2.8. *Capacitive current effects and baseline drifts*

Capacitive (charging) currents constitute an intrinsic component of every voltammetric experiment and arise from charging and discharging of the electrical double layer formed at the electrode–electrolyte interface.[2,3,9,18] Unlike faradaic currents, which (mainly) originate from electron-transfer reactions of electroactive species, capacitive currents (I_c) result solely from redistribution of electrical charges within the interfacial double layer when the electrode potential is changed. The magnitude of capacitive current is proportional to the scan rate (v) according to the previously mentioned relationship: $I_c = vC_d$. So, capacitive contributions become particularly significant at high scan rates, large electrode surface areas, and rough or highly porous electrodes, while electrodes modified with nanostructured materials possess exceptionally large surface areas.[3,9,18] Additional factors such as high double-layer capacitance of carbon-based materials, poorly defined electrode surfaces, and non-uniform surface films may further increase charging currents. Although capacitance is an unavoidable property of every electrode interface, excessive capacitive currents may severely mask the desired faradaic response and reduce the analytical sensitivity of voltammetric measurements. Capacitive effects can be recognized by the progressive increase in the background current as the scan rate increases, as illustrated in Figure 10.

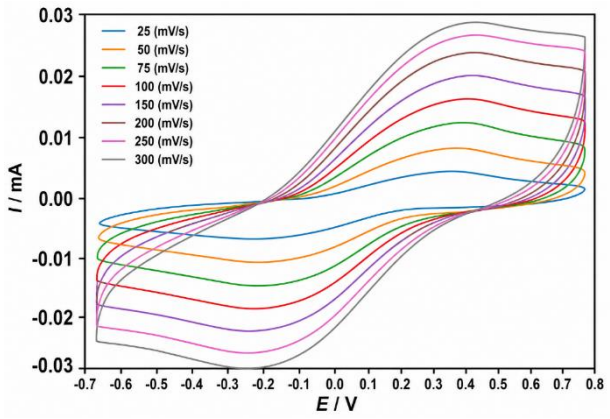


Fig. 10. The effect of scan rate on the capacitance of theoretical current-potential profiles in cyclic voltammetry

Instead of well-defined oxidation and reduction peaks, voltammograms become increasingly dominated by broad, featureless charging currents, often producing a distorted or tilted baseline upon which faradaic peaks are superimposed (see voltammograms recorded at scan rates ≥ 100 mV s^{-1} in Figure 10). As a result, peak heights become more difficult to determine accurately, particularly when analyzing low analyte concentrations or weak electrochemical signals. Excessive charging currents may also lead to an apparent decrease in the signal-to-background ratio, thereby reducing detection limits and analytical precision.

Several practical approaches can minimize the influence of capacitive currents. The simplest strategy is to employ small-to-moderate scan rates whenever measuring fast kinetics is not the primary objective of the experiment. Proper polishing and

cleaning of the working electrode reduce surface roughness and help maintain a reproducible double-layer capacitance. Working electrodes with unnecessarily large geometric surface areas should be avoided when small currents are needed to be detected in given analysis. Modern electrochemical instrumentation also allows electronic background subtraction or digital baseline correction, while pulse techniques such as differential pulse voltammetry[9] and square-wave voltammetry[24] inherently suppress capacitive contributions by sampling the current after the charging component has largely decayed. Therefore, selecting an appropriate voltammetric technique and optimizing the scan rate remain the most effective strategies for minimizing capacitive interference and maximizing the faradaic signal.

Baseline drift is another common experimental artifact that can substantially complicate the interpretation of voltammetric data, particularly in analytical applications performed by fast scan voltammetric techniques.[23] Ideally, the baseline should remain stable throughout the entire potential scan so that faradaic peaks can be accurately identified and quantified. However, numerous experimental factors may cause the baseline to gradually shift with time or potential. Common causes include slow changes in double-layer charging current, gradual adsorption of impurities or reaction products on the electrode surface, incomplete electrode cleaning between measurements, temperature fluctuations, evaporation of the electrolyte, changes in solution composition, instability of the reference electrode, oxygen slowly re-entering previously degassed solutions, instrumental drift of the potentiostat electronics, and gradual changes in electrode surface properties during repeated scans. Chemically modified electrodes may also exhibit baseline drift because of swelling,[1–4] partial dissolution, degradation, or restructuring of the surface film during electrochemical cycling.

Baseline drift is recognized by a gradual displacement or tilting of the background current rather than by random fluctuations or discrete peaks. Successive scanning leads to progressively shifted baselines in voltammetric curves, despite otherwise similar electrochemical conditions. Such behavior complicates peak integration, increases uncertainty in peak current determination, and may produce wrong conclusions regarding changes in analyte concentration, catalytic activity, or electrode kinetics. In severe cases, slow baseline drift may even obscure small faradaic responses completely, particularly in trace analysis or biosensor applications.

Reliable voltammetric measurements require a stable and reproducible baseline, and several practical measures can substantially reduce baseline drift. The working electrode should be carefully cleaned before each experiment to ensure identical surface conditions, while fresh supporting electrolyte should be used whenever contamination is suspected. Electrochemical cells should be performed at a constant temperature (thermostated), while prolonged exposure of the electrolyte to air should be avoided to minimize gradual oxygen dissolution or solvent evaporation. Stable reference electrodes, properly grounded instrumentation, and high-quality electrical connections further improve baseline stability. Recording blank voltammograms before (and at defined times also after the measurements) provides a simple means of verifying baseline reproducibility. All new models of potentiostats also allow for digital baseline correction and background subtraction during data processing. Nevertheless, baseline correction should never replace careful experimental practice, given that the most reliable voltammetric data are always obtained by minimizing the physical causes of baseline drift rather than correcting them mathematically afterward.

2.9. *Pitfalls related to the processes of adsorption and crystallization at working electrodes*

Adsorption and crystallization are two common surface phenomena that may significantly affect voltammetric measurements. If not properly recognized, both can lead to incorrect interpretation of electrochemical data. Although both phenomena occur at the electrode surface, their origins are fundamentally different. Adsorption results from the accumulation of electroactive or non-electroactive molecules, reaction intermediates, or products on the electrode through physical or chemical interactions. This effect is particularly pronounced for proteins, polymers, surfactants, aromatic compounds, thiols, and many pharmaceuticals, especially at carbon-based electrodes with highly active surface sites.[1] Crystallization, by contrast, occurs when insoluble products or metallic species nucleate and grow on the electrode surface during the experiment.[2,3,18] It is commonly observed during metal deposition/stripping,[2,9,18,24] precipitation reactions,[18,24] or whenever the local concentration of electroactive species exceeds their solubility.

Both processes exhibit characteristic voltammetric signatures. Adsorption usually produces relatively sharp and narrow peaks that increase with the accumulation time because progressively larger amounts of analyte adsorb before the voltammetric scan (Figure 11). Unlike diffusion-controlled processes, adsorptive peak currents depend strongly on the accumulation time. Additional evidence for adsorption includes gradual peak suppression during repeated scans due to electrode fouling and a linear dependence of peak current on the scan rate rather than on the square root of the scan rate. Crystallization, on the other hand, generates extremely sharp, spike-like peaks (Figure 12) arising from rapid nucleation, crystal growth, or stripping of crystalline deposits.

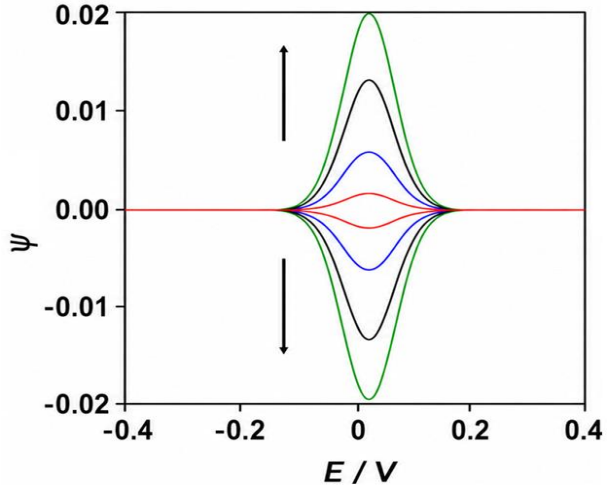


Fig. 11. Theoretical cyclic voltammograms of a simple surface-confined redox reaction as the accumulation time increases. The accumulation time increase in the direction of the arrows

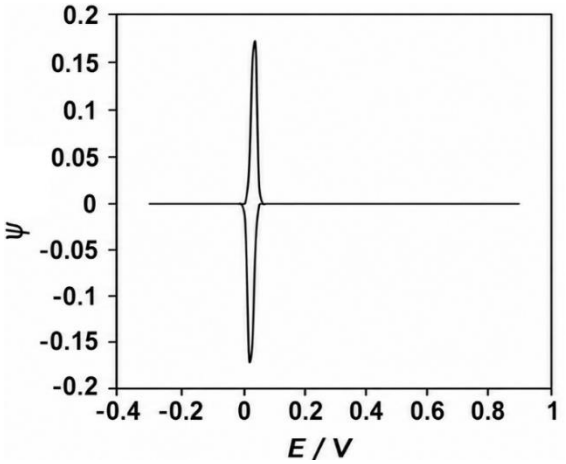


Fig. 12. The typical shape of a cyclic voltammogram when crystallization occurs at the surface of working electrode

Because crystal nucleation is inherently random, peak shape and intensity are often poorly reproducible. Extensive crystal growth may also partially block the electrode surface, resulting in distorted voltammograms and increased peak separation.

Correct identification of adsorption and crystallization is essential because both phenomena strongly influence peak shape, peak current, reproducibility, and mechanistic interpretation, and may otherwise be mistaken for changes in the intrinsic electrochemical behavior of the investigated system. Both phenomena can usually be minimized by proper experimental practice. Adsorption can be controlled thorough regeneration of the working electrode between successive measurements. Carbon electrodes are commonly polished with alumina slurry and rinsed with deionized water, whereas noble-metal electrodes are typically regenerated by repeated potential cycling in acidic electrolytes. Shorter accumulation times, lower analyte concentrations, optimized supporting electrolytes, or the use of less adsorptive electrode materials can further reduce surface fouling. In some applications, antifouling coatings or protective polymer films provide additional protection against nonspecific adsorption.

Unwanted crystallization can be minimized by avoiding excessive analyte concentrations and long deposition times, selecting appropriate potential limits, and optimizing scan rate, temperature, and supporting electrolyte concentration. Gentle stirring during deposition (when applicable), followed by quiescent conditions during voltammetric recording, commonly helps in reducing local super-saturation and crystal nucleation. If crystallization cannot be avoided, then the electrode surface should be completely stripped electrochemically or mechanically cleaned before the next measurement.

2.10. *Pitfalls due to convection during voltammetric experiments*

Convection is often seen as an important source of experimental error in voltammetry because it commonly disturbs the diffusion-controlled transport of electroactive species toward the electrode surface.[2,3] Under normal voltammetric conditions, mass transport (by the fully water-soluble redox systems) occurs predominantly via diffusion, so the measured current reflects only the intrinsic electrochemical behavior of the investigated system. However, mechanical movement of the solution caused by stirring, shaking of the electrochemical cell, movement of the electrodes, thermal gradients, or even gas bubbles rising through the electrolyte may introduce a convective transport. In such scenarios, fresh

analyte is continuously supplied to the electrode surface, producing currents that no longer obey the theoretical relationships developed for diffusion-controlled electrode processes. The effect of convection is usually recognized by poor reproducibility of successive voltammograms and by unusually large or distorted currents, as illustrated in Figure 13.

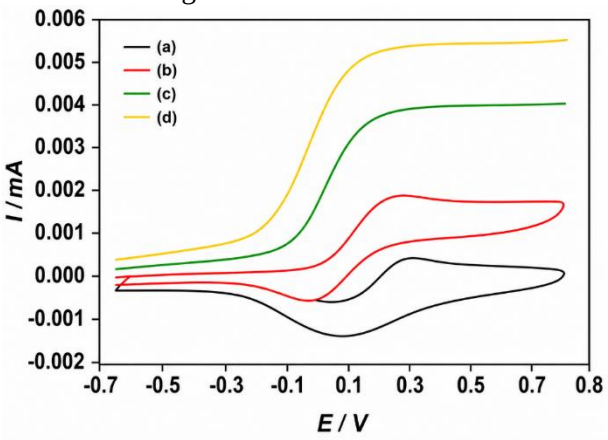


Fig. 13. The effect of an increased convection rate on the features of cyclic voltammograms. The convection rate increases from curve (a) toward curve (d)

Instead of nearly identical voltammograms recorded under identical experimental conditions, repeated scans often exhibit significant variations in peak currents. In more severe cases, convection commonly produces different baselines, irregular current fluctuations, or apparent increases in limiting currents (similar to curves c and d in Figure 13). Because convection enhances mass transport independently of molecular diffusion, diffusion-controlled kinetic analyses may become unreliable, leading to incorrect estimation of diffusion coefficients, heterogeneous electron-transfer rate constants, or analyte concentrations.

Convection can be readily minimized by careful experimental practice. Before recording voltammograms, any stirring used during solution preparation or accumulation should be completely stopped, allowing the electrolyte to become perfectly quiet. A waiting period of several seconds to a few minutes (depending on the cell volume) is generally sufficient for hydrodynamic equilibrium to be re-established. During measurements, the electrochemical cell should remain undisturbed and protected from vibrations, while electrodes should not be moved after the experiment has started. As noted previously, air drafts, rapid temperature fluctuations, and gas bubble formation should also be avoided because they may induce local convection currents. Maintaining a stable laboratory environment and performing measurements only after complete cessation of solution movement ensure that mass transport is governed almost exclusively by diffusion, thereby providing accurate and reproducible voltammetric responses.

2.11. *Peak overlap in voltammetric experiments*

Peak overlap is one of the most common challenges in voltammetric analysis, particularly when complex mixtures or multistep electrode mechanisms are investigated. It occurs when two or more electrochemical processes take place at similar potentials, causing their individual voltammetric responses to merge into a single broad or asymmetric peak. Peak overlap may originate from different electroactive species present in the solution, consecutive or coupled electron-transfer reactions, adsorption phenomena, or chemical reactions that accompany the electrode process. The phenomenon can usually be recognized by unusually broad, asymmetric, or poorly resolved voltammetric peaks (Figure 14a); shoulders appearing on one side of the peak; deviations from the expected peak shape; or changes in the voltammogram upon varying experimental parameters such as the pH, scan rate, accumulation time, or analyte concentration.

Several experimental approaches can substantially improve peak resolution. Decreasing the potential scan rate in cyclic voltammetry or employing smaller potential increments (a low potential step, Figure 14b) in cyclic staircase, differential pulse, or square-wave voltammetry generally improves the separation of closely spaced processes by allowing the system to approach equilibrium more effectively. In addition, optimization of the pulse amplitude, square-wave frequency (for square-wave voltammetry), or potential step in pulse voltammetric techniques[9,24] may also enhance resolution. Electrode surface modification, selection of a more appropriate working electrode material, mathematical baseline correction, digital signal processing, derivative voltammetry, and chemometric deconvolution methods may provide additional improvement when experimental optimization alone is insufficient.

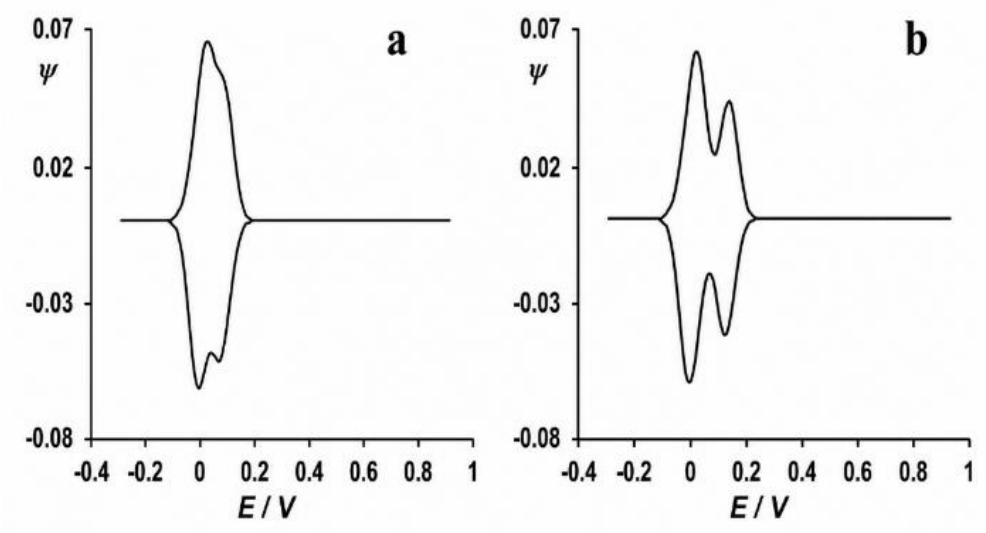


Fig. 14. Overlapping peaks of theoretical cyclic voltammograms for a surface electrode mechanism (a) and resolution of the overlapping peaks by using a smaller potential step (b)

It is important to note that in mechanistic investigations, comparison with theoretical simulations and voltammetric modeling is often indispensable, as overlapping peaks may arise not only from multiple analytes but also from chemically coupled electrode mechanisms that cannot be distinguished solely from experimental voltammograms.[25,26] One must be able to distinguish the overlap of voltammetric peaks originating from different electroactive species (or overlapping peaks that originate from different processes) from peak overlap arising from intrinsically complex electrode mechanisms. In the latter case, a single analyte may undergo successive electron-transfer and chemical transformations through the formation of stable or metastable intermediate species, each possessing its own redox activity. Such multistep mechanisms frequently produce two or more closely spaced peaks that reflect the sequential oxidation or reduction of different reaction intermediates rather than the presence of multiple analytes.[2,24–26] Proper discrimination between these two scenarios often requires systematic variation of experimental parameters, comparison with theoretical simulations, and mechanistic modeling. An incorrect interpretation in such a scenario may lead to erroneous conclusions regarding both the composition of the sample and the underlying electrode reaction mechanism.

2.12. *Coupled chemical reactions and their distinction from experimental artifacts*

Electron-transfer reactions investigated by voltammetric techniques are very often accompanied by homogeneous chemical reactions occurring either before, after, or simultaneously with the electrochemical step.[1–4,24] Consequently, one of the most important objectives in mechanistic electrochemistry is to recognize the nature of the coupled chemical reaction and to distinguish it from a simple electron-transfer process. Depending on the reaction sequence, the electrochemical step may be preceded by chemical equilibrium (the CE mechanism), followed by a chemical transformation (the EC mechanism), or coupled with regenerative (catalytic) reactions (the EC′ mechanism), among many other possibilities. Figure 15 provides representative examples of these mechanisms. Each coupled reaction modifies the voltammetric response in a characteristic manner by changing peak currents, peak potentials, peak symmetry, or the ratio between forward and reverse currents. These characteristic electrochemical signatures have been extensively investigated through theoretical modeling and experimental studies and are comprehensively described elsewhere.[2,4,24,27] Therefore, proper interpretation of voltammetric data frequently requires simultaneous consideration of both electrochemical and homogeneous chemical kinetics rather than the electron-transfer step alone.

In practice, however, interpretation becomes considerably more challenging when coupled chemical reactions are superimposed by experimental artifacts or instrumental pitfalls. Many of the phenomena discussed in the previous sections—including uncompensated resistance (ohmic drop), adsorption, crystallization, oxygen reduction, instability of the reference electrode, baseline drift, excessive capacitance, convection, temperature fluctuations, pH variations, electrode fouling, and instrumental noise—may distort

voltammetric responses in a manner that partially resembles the signatures of genuine coupled chemical reactions. For example, peak broadening caused by uncompensated resistance or temperature changes may be mistakenly interpreted as slow chemical kinetics,[3,18,24] while adsorption or crystallization may produce peak shapes resembling surface-confined intermediates. Similarly, oxygen reduction or unstable baselines may obscure the disappearance or appearance of peaks expected for the EC or CE mechanism, leading to incorrect mechanistic assignments. Such overlapping effects introduce an additional level of complexity that may result in erroneous determination of reaction mechanisms, heterogeneous electron-transfer rate constants, equilibrium constants, catalytic activities, or kinetic parameters of the coupled chemical reaction.

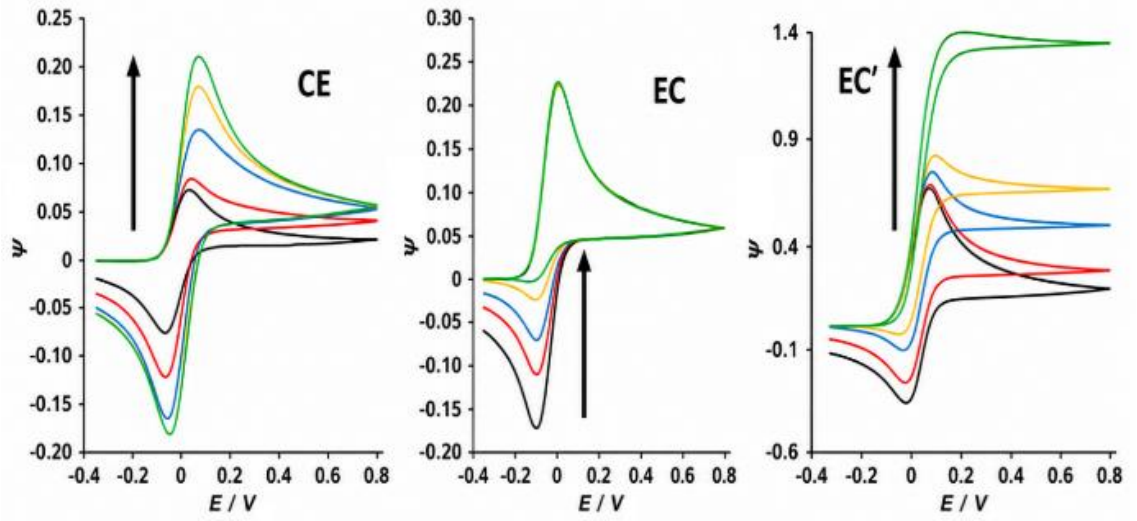


Fig. 15. Examples of cyclic voltammograms of electron-transfer steps coupled with a preceding chemical reaction (the CE mechanisms), a follow-up chemical reaction (the EC mechanism), and a regenerative chemical reaction (the EC′ mechanism), featuring an increased rate of homogeneous chemical steps. The rate of a particular chemical reaction increases in all cases in the direction of the corresponding arrow

For these reasons, reliable mechanistic interpretation requires not only a thorough understanding of theoretical voltammetry but also careful elimination of experimental artifacts before mechanistic conclusions are drawn. Whenever unusual voltammetric behavior is observed, one should first exclude possible experimental pitfalls before attributing the response to a specific coupled reaction mechanism. Verification by blank experiments; systematic variation of the scan rate, temperature, pH, analyte concentration, accumulation time, and supporting electrolyte composition; and numerical simulations based on theoretical models[24–27] often provide the most reliable approach for distinguishing genuine electrochemical mechanisms from experimental artifacts. Ultimately, successful voltammetric analysis relies on the ability to discriminate between electrochemical signatures arising from intrinsic reaction pathways and those produced by undesired experimental conditions, thereby ensuring that mechanistic, kinetic, and thermodynamic conclusions accurately reflect the true behavior of the investigated electrochemical system.

2.13. *Poor repeatability in voltammetric experiments*

Poor repeatability is a strong indicator that one or more phenomena discussed in the previous sections are present during voltammetric measurements. Under identical experimental conditions, successive voltammograms should be nearly superimposable, exhibiting almost the same peak potentials, peak currents, and peak shapes. When significant differences are observed between consecutive scans, there is a strong indication that the reproducibility of the experiment is compromised, making both qualitative interpretation and quantitative analysis unreliable. Poor repeatability may originate from numerous sources, many of which have already been discussed in previous sections as individual pitfalls. In addition, improper positioning of the electrodes, variations in the accumulation time, and inaccuracies in the scan parameters may further contribute to poor experimental reproducibility.

Poor repeatability is readily recognized by comparing several consecutive voltammograms recorded under identical experimental conditions.

In such a scenario, the individual voltammograms no longer overlap perfectly but exhibit noticeable differences in peak current, peak width, peak shape, or occasionally peak potential. The variability may appear as random scatter between successive measurements or as a gradual deterioration of the voltammetric response due to progressive electrode fouling or changes in the electrochemical environment. Such behavior immediately indicates that one or more experimental variables have not been sufficiently controlled. In analytical applications, poor repeatability is reflected by large standard deviations, high relative standard deviations, poor calibration linearity, and reduced precision of quantitative measurements.[2,3,18]

Achieving good repeatability requires rigorous control of all experimental conditions. The working electrode should be carefully cleaned before every measurement using an appropriate cleaning procedure, while the reference electrode should be periodically inspected to ensure a stable potential. Supporting electrolytes should be freshly prepared using high-purity reagents and deionized water, and their pH should be accurately adjusted and maintained throughout the experiment. Dissolved oxygen should be removed by purging the solution with an inert gas before measurements, and the electrochemical cell should remain perfectly quiescent to eliminate convection. Constant temperature should be maintained whenever possible, and instrumental parameters, including the scan rate, potential limits, pulse amplitude, accumulation time, and equilibration time, must remain identical for every measurement. Finally, all electrical connections should be secure, the potentiostat properly grounded, and the electrochemical cell protected from mechanical vibrations and electromagnetic interference. In practice, poor repeatability should not be regarded as an isolated experimental problem but rather as a warning that one or several of the previously discussed pitfalls are present. Careful elimination of these sources of error is therefore essential for obtaining reliable, reproducible, and scientifically meaningful voltammetric data.

2.14. *Additional experimental artifacts less frequently discussed in voltammetry*

Besides the major pitfalls discussed in the previous sections, several additional experimental artifacts (or wrong instrumental selections) may also influence voltammetric measurements, although they receive considerably less attention in textbooks and review articles. While these effects are generally less pronounced than the classical pitfalls, they may also compromise the accuracy, reproducibility, and mechanistic interpretation of voltammetric data if they remain unrecognized. Examples include inappropriate selection of the potential window, impurities present in the supporting electrolyte, counter electrode effects during prolonged experiments, electromagnetic interference (that may manifest itself as instrumental noise), sample (or water) evaporation during long-lasting measurements, and improper selection of the initial potential or scan direction, among others. Although often overlooked, these phenomena should also be considered as potential sources of experimental error, and adequate preventive measures should be implemented whenever necessary to ensure reliable voltammetric measurements.

All aforementioned pitfalls and phenomena in voltammetric experiments are briefly summarized in Table 1 and Figure 16.

Table 1. Major Pitfalls in Voltammetry: Recognition and Practical Solutions

Type of pitfall / phenomenon	Characteristic voltammetric signature (short explanation)	Measures to solve / minimize the problem	Remark
Working electrode – memory effect / fouling	Residual peaks in blank, decreasing peak currents, distorted baseline, poor repeatability.	Polish carbon electrodes (Al_2O_3, ∞ pattern), rinse/sonicate; electrochemically clean Au/Pt; regenerate between runs.	Always record a blank after cleaning.
Screen-printed electrode degradation	Progressive signal loss and poorer reproducibility after repeated use.	Prefer single-use or limited reuse; verify calibration and integrity.	Monitor stability during quantitative work.
Reference electrode instability	Peak shifts, spikes, unstable currents, poor reproducibility.	Replace/refill saturated KCl, clean junction, remove bubbles, recalibrate or replace electrode.	First diagnostic step when unexpected peak shifts occur.
Ohmic (IR) drop	Larger peak separation, broader peaks, lower currents, apparent quasi-irreversibility.	Increase supporting electrolyte, shorten WE–RE distance, use Luggin capillary, *IR* compensation.	Can mimic slow electron transfer.
Instrumental noise	Random high-frequency baseline oscillations.	Ground system, Faraday cage, shield cables, remove Electro-magnetic interferring sources.	Avoid excessive digital filtering.
Bubble formation	Sudden spikes, jumps and irregular oscillations; lower currents.	Degas, remove attached bubbles, avoid gas evolution, adjust electrode orientation.	Often confused with electrical noise.
Dissolved oxygen	Broad cathodic reduction wave overlapping analyte peaks.	Purge with N_2 maintain inert atmosphere, verify with blank.	Always check blank electrolyte.
pH variation	Systematic peak-potential shifts; altered peak currents and shapes.	Use buffers, calibrate pH meter, monitor pH during experiments.	Critical for proton-coupled reactions.
Temperature variation	Changes in peak width, current, reversibility and overall peak shape	Thermostat cell; keep constant temperature.	Temperature affects solubility, diffusion and kinetics of redox active species.
Capacitive current	Large sloping background, poor signal/background ratio at high scan rates.	Lower scan rate, smaller electrode area, pulse techniques (DPV/SWV), baseline correction.	Not a faradaic process.
Baseline drift	Gradually shifting/tilted baseline between scans.	Fresh electrolyte, stable temperature, clean electrodes, blank correction.	Minimize physical causes before mathematical correction.
Adsorption	Sharp peaks increasing with accumulation time; fouling.	Regenerate electrode, reduce accumulation time, antifouling coatings.	Peak current proportional to scan rate.
Crystallization	Very sharp spike-like peaks; poor reproducibility.	Reduce concentration/deposition time, strip deposits, clean electrode.	Common in deposition/stripping.
Convection	Variable peak currents and distorted limiting currents.	Stop stirring, allow solution to rest, avoid vibration.	Mass transport no longer purely diffusion-controlled.
Peak overlap	Broad/asymmetric peaks or shoulders.	Lower scan rate, smaller potential step, optimize pulse parameters.	May arise from different analytes or mechanisms.
Coupled chemical reactions	Characteristic changes in peak ratios, symmetry and reversibility.	Verify by varying scan rate, pH, temperature; compare with theoretical simulations.	Exclude artifacts before mechanistic assignment.
Poor repeatability	Successive scans differ in peak current, shape or potential.	Standardize cleaning, timing, temperature, electrolyte and instrument settings.	Usually indicates one or more underlying pitfalls.
Additional artifacts	Unexpected distortions from poor potential window, evaporation, counter electrode effects.	Optimize experimental design and reagent purity.	Consider when major causes are excluded.

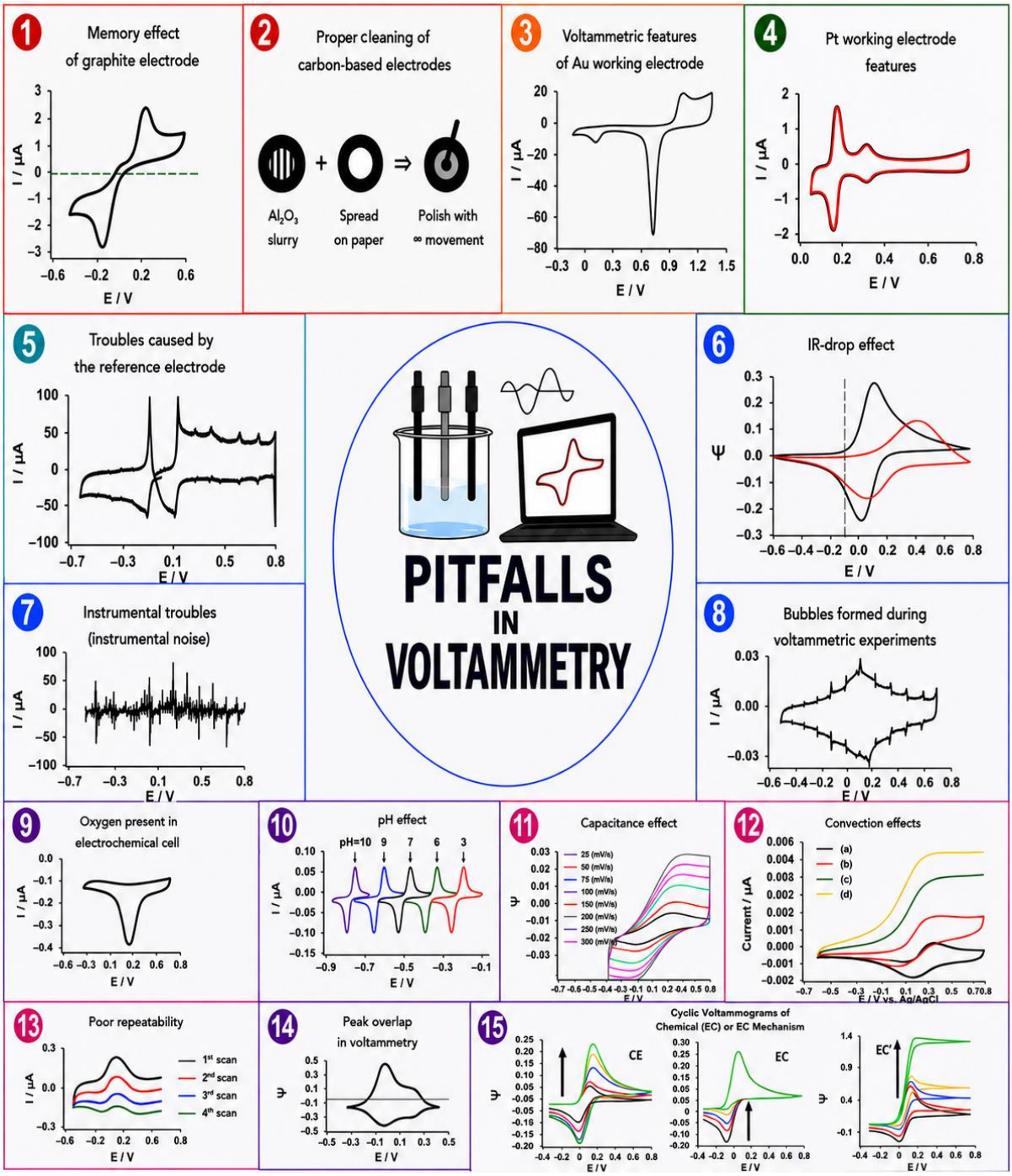


Fig. 16. Schematic summary of the most common pitfalls in voltammetry. Representative voltammograms and illustrations demonstrate the characteristic signatures of each experimental artifact

3. CONCLUSION

Voltammetric techniques are indispensable tools in modern electrochemistry as they provide rapid, inexpensive, and highly informative insight into a wide variety of electrochemical systems. Nevertheless, the apparent simplicity of recording a voltammogram should not create the impression that interpretation of the obtained response is equally straightforward. Numerous experimental artifacts and physicochemical phenomena may substantially modify the shape, position, and intensity of voltammetric signals, while mimicking the genuine electrochemical phenomena. Consequently, successful voltammetric investigations require careful experimental practice as well as a solid understanding of electrode processes and theoretical electrochemistry.

The present work has focused on the visual recognition of some of the most frequently encountered pitfalls in voltammetric experiments. Problems related to the working and reference

electrodes, uncompensated resistance, dissolved oxygen, pH and temperature variations, capacitive currents, baseline drift, adsorption, crystallization, convection, bubble formation, instrumental noise, poor repeatability, and the influence of coupled chemical reactions have been discussed. In addition, important hints have been provided about their characteristic voltammetric signatures, physicochemical origins, and practical approaches proposed for minimizing or eliminating their effects. Recognition of these characteristic signatures represents the first and often the most important step toward obtaining reliable electrochemical data.

An equally important message emerging from this work is that many experimental artifacts may closely resemble authentic electrochemical mechanisms. Therefore, unusual voltammetric responses should never be interpreted immediately as evidence for novel reaction pathways before potential experimental sources of error have been carefully excluded. Proper control of the experimental conditions, systematic variation of experimental parameters, careful maintenance of the electrochemical system, and comparison with theoretical predictions remain essential prerequisites for reliable mechanistic interpretation.

At this stage, it is worth emphasizing one of the less obvious pitfalls in voltammetric experiments: interpretation of the scan rate (or frequency) effects. Although scan rate analysis is among the most powerful tools in voltammetry,[1–4,12,18] it is also one of the most frequently misinterpreted. Varying the scan rate alters the characteristic time scale of the experiment and therefore simultaneously affects every time-dependent process occurring within the electrochemical system.[29] In mechanisms involving coupled chemical reactions, both the electron-transfer step and the kinetics of the chemical transformations respond to changes in the scan rate (or frequency in pulse voltammetric techniques).[29] Therefore, unless the reaction mechanism is first established or independently verified, conclusions drawn solely from scan rate–dependent behavior may be misleading and result in incorrect mechanistic or kinetic interpretations.

The characteristic voltammograms presented throughout this work (summarized in Figure 16 and briefly explained in Table 1) provide a visual guide for recognizing common experimental pitfalls, link each phenomenon to its distinctive electrochemical signature, and suggest appropriate strategies for its elimination. In practical electrochemical measurements, however, individual pitfalls rarely occur in isolation.[28] More commonly, several sources of error act simultaneously, producing complex voltammetric responses that may obscure the true electrochemical behavior of the investigated system. Therefore, reliable interpretation requires a systematic step-by-step diagnostic approach, in which each potential source of error is identified, verified, and eliminated sequentially before attributing the observed voltammetric features to the intrinsic properties of the analyte or electrochemical mechanism. Such a strategy greatly improves the accuracy, reproducibility, and overall reliability of electrochemical measurements.

It is also important to emphasize that this work is intended mainly to serve as a useful educational resource for students entering the field of electrochemistry, young researchers beginning their work with voltammetric techniques, as well as electrochemists seeking a concise practical reference. Indeed, careful recognition and elimination of experimental pitfalls, combined with basic theoretical knowledge, remain essential for obtaining reliable, reproducible, and scientifically meaningful voltammetric results.

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