

Review

# How to Improve the Performance of Electrochemical Sensors via Minimization of Electrode Passivation

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**Abstract:** It follows from critical evaluation of possibilities and limitations of modern voltammetric/amperometric methods that one of the biggest obstacles in their practical applications in real sample analysis is connected with electrode passivation/fouling by electrode reaction products and/or matrix components. This review summarizes possibilities how to minimise these problems in the field of detection of small organic molecules and critically compares their potential and acceptability in practical laboratories. Attention is focused on simple and fast electrode surface renewal, the use of disposable electrodes just for one and/or few measurements, surface modification minimising electrode fouling, measuring in flowing systems, application of rotating disc electrode, the use of novel separation methods preventing access of passivating particles to electrode surface and the novel electrode materials more resistant toward passivation. An attempt is made to predict further development in this field and to stress the need for more systematic and less random research resulting in new measuring protocols less amenable to complications connected with electrode passivation.

**Keywords:** electrode passivation; electrode surface renewal; electrode pretreatment; electrode modification; measurement in flowing systems; electrode protection; novel electrode materials resistant to passivation



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## 1. Introduction

The immense potential of modern electroanalytical methods in monitoring of organic compounds is generally recognized and appreciated [1–7] because of their low investment and running costs, reasonable and in many cases “fit for the purpose” sensitivity and selectivity, easy automatization, easy miniaturization resulting in portability of corresponding instrumentation, user friendliness, and environmental friendliness (“green electroanalytical chemistry”). For the same reason, electrochemical sensors are frequently used nowadays. Recent advances in electrochemical biosensing with special emphasis on universal point-of-care systems can be found in minireview [8]. The heart of any electrochemical sensors is a working electrode on which the electrical signal is generated via an electrochemical process and which serves as a transduction element. In more complex and sophisticated biosensors, it can be covered with a sensing and biorecognition layer. Advances in the development of electrochemical sensors for clinically relevant biomolecules, including small molecules, nucleic acids, and proteins are reviewed in [9]. Excellent review [10] is focused on advancing the speed, sensitivity, and accuracy of biomolecular detection using multi-length-scale engineering from more general view not limited to electrochemical sensing. Modular construction of an autonomous and programmable multi-function biochemical network that can identify, transform, translate, and amplify biological signals into physiochemical signals based on logic design principle [11] is another possible approach. Similarly, a scalable system of reporter enzymes cleaves specific DNA sequences in solution, which results in an electrochemical signal when these newly liberated strands are captured at the surface of a nanostructured microelectrode [12]. These sensors utilized complex chemistry to achieve high-accuracy sensing of large biomolecules, but the electrochemical interface is actually very simple. All above mentioned papers [8–12] are focused mainly on large

molecular analytes and comprehensively describe the construction of various types of electrochemical sensors, which can be beneficial to readers of this review, too. Nevertheless, this review pays attention mainly to smaller organic molecules.

Here, the big problem connected with the use of modern electrochemical techniques in practical analysis remains the passivation of working electrodes by products/intermediates of electrochemical reactions or by components of complex samples, which can adsorb on the electrode surface, thus fouling the electrode and complicating the determination or even making it impossible. Strategies to combat passivation must be tailored to the type of sensors, electrode materials, mechanism of passivation, used electroanalytical method, and type of matrix. It is obvious that surface chemistry plays a decisive role in this process. Generally, the problems with passivation can be addressed (eliminated, diminished, or minimised) by the following approaches:

- a. To renew the surface of the working electrode after each measurement. An ideal example is dropping mercury electrode, the surface of which is renewed spontaneously every few seconds, thus minimising problems with passivation [1–7]. However, problems with mercury toxicity prevent widespread use of this excellent tool. Similar surface renewal is used in the case of dropping gallium-based electrode [13], so far not too frequently used. The same holds for renewable liquid Cd-Ga electrode [14] and In-Ga electrode [15]. Another possibility is to use carbon paste electrodes with easily mechanically renewed surface [16,17], solid amalgams electrodes with mechanically or electrochemically renewed surface [18–20], or mechanical, chemical, or electrochemical cleaning of the working electrode after each measurement [1–7]. However, these approaches (with notable exception of electrochemical cleaning) require human involvement and complicate desirable automatization. This complication can be at least partially eliminated by using retractable-pen-based renewable silver amalgam film electrode [21]. Another interesting possibility currently under investigation in our laboratory is to use analogously the renewable gallium film. Carbon electrodes electrochemical pretreatment can play a very useful role in this field [22] due to its simplicity, efficiency, and low cost and due to resulting undistorted, well-defined, and reproducible signals.
- b. To use disposable electrodes just for one measurement. This approach is frequently used in medical diagnosis, where exchange of working electrodes is imperative for each sample to eliminate any risk of cross-contamination [23]. Increased price of the determination and generation of waste of used disposable electrodes (a not too “green” situation) makes this approach not well suited for large scale monitoring. However, recently proposed electrodes based on aluminium wrapping foils [24], gold on the surface of used CD [25], or carbon rods from used batteries [26] present an inexpensive alternative to commercial disposable electrodes. The same holds for carbon film electrodes where only the film is disposable [27,28], resulting in decreased price and more “green” attitude. A novel approach can be demonstrated by the use of disposable pencil graphite electrodes for detection of SNP (single nucleotide polymorphism) in human mitochondrial DNA [29].
- c. To use surface modifications preventing passivation [5–7]. Many papers on modified electrodes confirm increasing interest in this approach. However, this approach still remains a combination of art and science, with limited robustness and shelf-life of modified electrodes [30–32] complicating to a certain degree routine applications of modified electrodes in large scale monitoring.
- d. To use measurements in flowing systems minimizing passivation [33–35] or to use RDE (rotating disc electrode) [36–46] or hydrodynamic electrodes [37]. In all these cases, products/intermediates of electrochemical reaction are washed away from the electrode surface thus minimizing their deposition on working electrode. Here, HPLC-AD (HPLC with amperometric detection), FIA-AD (flow injection analysis with amperometric detection), and BIA-AD (batch injection analysis with amperometric detection) are frequently used for large scale monitoring [47,48]. This approach

is useful only if electrode products/intermediates are responsible for passivation. Combination of BIA with passivation resistant BDDE (boron doped diamond electrode) [48] can further amplify antifouling effect.

- e. To use novel separation methods preventing access of passivating components of environmental matrices towards the working electrode surface (membrane separation, HFME (hollow fibre membrane microextraction) [49–53]. This approach is useful only if matrix components are responsible for passivation.
- f. To use novel electrode materials more resistant toward passivation. This approach is generally most promising and acceptable for practical laboratories. This is the most attractive and appealing approach and most welcome one from the point of view of large scale and high throughput monitoring. Moreover, it is well compatible with continuous monitoring. Probably the best known “passivation resistant” electrode material is boron doped diamond [54–56] especially if its surface is –H terminated. Another more recently developed “antifouling” material is tetrahedral amorphous carbon with incorporated nitrogen (ta-C:N) [57] and sp<sup>3</sup>-carbon dominated hydrogenated surface [58,59]. However, in all cases, passivation depends on conditions, analysed solutions, potential program, electrode surface, and on many other parameters.
- g. To use various heated electrodes (metallic [60] or carbon based [61]) to remove deposited substances from the electrode surface. This approach can also improve S/N ratio, mass transport, and reaction kinetics resulting in improved figures of merits. However, it is experimentally more demanding and so far not too widely used.
- h. To use various enzymes converting organic analytes prone to electrode fouling into simple inorganic products with negligible danger of electrode fouling [62]. Enzyme based electrodes are very frequently used for their selectivity and sensitivity so that antifouling possibilities are not too frequently accentuated.
- i. To use intentional electrode fouling by adding strongly adsorbable organic compounds (e.g., mercapto-hepta(ethylenelycol) forming SAM (self-assembled monolayer) on electrode surface), thus minimising further electrode fouling by analytes/electrode reaction products. This “fighting fire with fire” approach results in the decreased signal of an analyte after formation of SAM but then the signal remains stable after multiple repetition of voltammetric scans, thus enabling standard addition of calibration curve evaluation. The above mentioned SAM exhibits strong antifouling properties against proteins adsorption, and thus it can be useful for biosensors construction [63].

It can be summarized that in spite of a number of papers dealing with electrode passivation, a non-systematic and more or less random approach still prevails in this field. Therefore, it is desirable to investigate the relationship between structure of the electrode surface, structure of passivating substance, and electrochemical behaviour of passivating substances to clarify the nature and mechanism of these processes and to find ways to diminish, suppress, or completely eliminate passivation and connected negative effects complicating electroanalysis of real samples.

The growing interest in the problems connected with electrode passivation can be demonstrated by the results of literature search, when in Web of Science nearly 5000 papers with keywords “electrode passivation” can be found, even though most of them are connected with electrode passivation in batteries and fuel cells. However, nearly 550 of them are connected with electroanalytical applications, and the rest of them can be most inspiring for electroanalytical chemists, namely, those connected with the mechanism of technical electrodes passivation and ways of their elimination with new electrode modifiers, application of protecting films, and novel electrode materials. Probably the best and most comprehensive treatment of problems connected with electrode passivation and critical evaluation of used approaches for its minimization can be found in the excellent review [64] and abundant references therein.

## 2. Importance of Electrode Passivation—Reasons and Consequences

It is obvious that the main reason for electrode passivation is adsorption/deposition of a passivating compound on working electrode surface. The most pronounced consequences are the decrease of the rate of electrode reaction resulting in the shift of half-wave or peak potential to more negative (in the case of cathodic reaction) or to more positive (in the case of anodic reaction) potentials and in the decrease of peak current, which is especially in the case of pulsed technique influenced by this rate. Decreased active surface of the working electrode naturally results in the decrease of limiting currents observed in CV (cyclic voltammetry), LSV (linear scan voltammetry), DCV (direct current voltammetry), and in amperometric methods. The most usual symptom of electrode passivation is the decrease of an electrochemical signal with repeated scans in voltammetric and with time in amperometric techniques. It is clear that electroanalytical methods can provide sufficient evidence of electrode passivation and valuable information about its mechanism and are most frequently used for these purposes. However, a number of other techniques used for surface characterization in material sciences should be exploited in this field more frequently to monitor changes in the course of electrode passivation and opening new pathways for its minimisation/elimination. Moreover, the obtained knowledge regarding characterization of chemical composition and electronic structure of electrode surfaces may eventually lead to rational design of new (smart) electrode materials and measuring protocols resistant to electrode passivation for monitoring of organic compounds. Last but not least, this approach could close the gap between quickly growing number of electroanalytical methods for organic substances and their practical applications for large scale monitoring still somewhat hindered by problems with electrode passivation. It is worth noting that the same phenomenon (adsorption) that helps to increase the sensitivity of adsorptive stripping techniques in other cases complicates and even prevents the application of electroanalytical methods in large scale monitoring, making it even more important topic for basic research. Moreover, understanding the mechanism of passivation will pave the way for its minimisation/elimination.

## 3. How to Minimise Electrode Passivation

The following different approaches to eliminate unfavourable influence of electrode passivation are pursued most frequently, the first one being the most challenging and most promising, as documented by selected papers from our UNESCO Laboratory of Environmental Electrochemistry [1,16–21,27,28,47,50,51,54–56,65–72].

- A. Search for materials resistant to passivation and investigation of the relationship between surface properties and proclivity to passivation. This general strategy can be successful, whether the passivation is caused by some matrix components or by products/intermediates of electrode reaction. Moreover, the detailed structural investigation of the electrode surface before and after passivation can reveal the mechanism of passivation and contribute to the elimination of its unfavourable effects. Passivation resistant electrodes would be definitely the most useful electroanalytical tool. This research is scientifically the most complicated, and it requires intensive co-operation of experts in surface analysis (both in pre-passivation and “post-mortem” (after passivation) electrode surface analysis), in new electrode materials and in the development of novel electroanalytical instrumentation/measuring protocols. Without this synergy, it would be impossible to reach this very ambitious goal.
- B. Investigation of electrochemical polishing/cleaning/pre-treatment of electrode surface between successive measurements to eliminate unfavourable effects of electrode passivation together with using less common potentials programs and currents response treatments. The possibility of electrochemical activation in situ will be again applicable irrespective of the mechanism of passivation; this is the most simple and user-friendly approach from the point of view of an electroanalytical chemist if the antifouling electrode is not available for the given analyte and matrix. Many inspiring details on the application of electrochemically pretreated electrodes can be found

in an excellent review [22]. The electrochemical assisted antifouling strategy using continuous CV was used, e.g., for voltammetric determination of clenbuterol and ractopamine at phosphorene nanocomposite modified electrode [73]. Antibiofouling strategy for optical sensors by chlorine generation using low-cost, transparent and highly efficient electrodes based on platinum nanoparticles coated oxide [74] can be inspiring for electrochemical removal of organic compound fouling the electrode surface.

- C. The use of disposable electrodes with a low number of repeated measurements limiting the influence of passivation on obtained electrochemical signal. This approach is most frequently used in medical laboratories because of low risk of cross contamination. However, the electrode passivation should not be too pronounced to enable at least a few measurements on one electrode necessary for standard addition method. However, the large piles of disposed electrodes are not too compatible with the idea of “green electroanalytical chemistry”. Electrodes with renewable surface, either bare or modified, are more acceptable from this point of view.
- D. Elimination of electrode passivation by measurements in flowing systems resulting in removal of the products of electrochemical reactions, which can cause passivation by dimerization/polymerization and deposition on electrode surface. This approach can be useful only in the case where electrode passivation is undoubtedly caused by electrode reaction products/intermediates, which can be revealed by detailed surface investigation of the electrode before and after passivation. Moreover, the instrumentation is slightly more complicated than for batch analysis. On the other side, determination is faster. Here, most promising areas are HPLC-AD (HPLC with amperometric detection), FIA-AD (flow injection analysis with amperometric detection) [75], and BIA-AD (batch injection analysis with amperometric detection) [47,48,76,77], the last one being the most interesting because of its so far untapped potential in the field of large-scale monitoring.
- E. Prevention of passivating molecules from matrix to access the electrode surface via preliminary separation of the analyte from those molecules, e.g., using membrane filtration or HF (hollow fibre) microfiltration [49–53]. This approach is used quite frequently in the analysis of biological liquids but not so frequently in environmental and food analysis. Obviously, it can be used more frequently, but it will have some limitations for high throughput large scale monitoring of organic compounds. Here, the development of miniaturised solid electrodes compatible with this approach is an imperative.
- F. Application of electrodes with easily renewable surface. This approach mirrors a fascinating property of dropping mercury electrode, the surface of which is automatically renewed with each new drop. This is a very promising approach both from the point of view of the fundamental research and its practical applications. Renewable amalgam, carbon paste, solid carbon-based, bismuth, gallium, and antimony electrodes will play decisive role in this field. An interesting possibility is to use the renewal of the PGE (pyrolytic graphite electrode) surface by using the adhesive tape, which is more laborious than renewing the mercury drop but still much simpler than many typical polishing procedures required for most solid electrodes [78]. Another undoubtedly very useful fouling resistant electrode with easily renewable surface can be commercially available bismuth drop electrode [76].
- G. Modification of the electrode surface by fouling resistant polymers, films, or nanoparticles (either metallic or carbon-based). This is a most “high-risk–high-gain” research with sometimes unpredictable results. However, it can open new frontiers in the fight against passivation. Therefore, this kind of fundamental research should be pursued more frequently, because it can bring really new knowledge, combining the successful elimination of problems with passivation with increased sensitivity and selectivity connected with the application of nanoparticles. Silver nanoparticles on the black phosphorene surface and its amino-functionalized multi-walled carbon

nanotubes nanocomposite and the application of this nanohybride nanozyme sensor for voltammetric monitoring of uric acid, xanthine, and hypoxanthine [79] is an interesting example of this approach. Similarly, Pt nanoparticles and other metal nanoparticles can be used for these purposes.

- H. The use of different solvents that can help to minimize electrode fouling is well documented by a detailed study of electrooxidation of phenol on platinum electrode in different solvents [80]. This simple and straightforward approach definitely deserves further detailed investigation.
- I. The fascinating development in 3D printed sensors has led to new generation of sensors with good passivation characteristics, wearable sensors being just one of many examples [81]. Undoubtedly, further fast development of fouling resistant electrodes/sensors can be envisaged.

#### 4. Methodology for Electrode Passivation Investigation and Minimisation

The following general strategies should be followed:

- A. **Elucidation of the relationship between the electrode surface structure and its passivation** by organic compounds or products/intermediates of their electrochemical transformations using both electrochemical methods (CV, DPV (differential pulse voltammetry), SWV (square wave voltammetry), SV (stripping voltammetry), DPAdSV (differential pulse adsorptive stripping voltammetry), EIS (electrochemical impedance spectroscopy), and microscopic and spectroscopic methods currently used in solid state chemistry (AFM (atomic force microscopy), TEM (transmission electron microscopy), SEM (scanning electron microscopy), X-ray microdiffraction, EELS (energy loss spectroscopy), SAED (selected area electron diffraction), ESCA (electron spectroscopy for chemical analysis), etc.). To reach this goal, an intellectual and instrumental potential of experts on electroanalytical chemistry, experts on solid state chemistry, and experts on electroanalytical instrumentation and its industrial and environmental applications should work together to create a “critical mass” necessary to address this challenging problem.
- B. **Outlining general principles for preparation/fabrication of sensors and electrodes of novel electrode materials and their pre-treatment** with higher probability of resistance to passivation based on at least partial knowledge of the relationship between electrode surface structure and the proclivity to its passivation. Here an attempt should be made to substitute the prevailing “trial and error approach” in eliminating problems with electrode passivation by a more rigorous “prediction based on knowledge approach”. The following novel electrode materials selected on the basis of long term experience and extensive literature search seems to be most promising:
  1. Boron doped diamond (BDD) and its different modifications and versions [54–56,82–87] are well known for their resistance to passivation, even though their antifouling properties (attributable to their hydrophobic characteristics arising from sp<sup>3</sup>-hybridised carbons on a diamond surface) were recently found less pronounced than previously thought [54–56]. Moreover, the surface termination and boron content can play a significant role together with other structural parameters [54,55]. Both constant potential [54] and constant current [82] pre-treatment influencing the surface termination should be investigated with respect to antifouling properties. BDD and Ti composite prepared by spark plasma sintering at the surface of Ti matrix possess characteristics of a BDD material, including wide potential window, high oxygen evolution potential, and low background current and much longer lifetime than that of a BDD coating electrode produced by conventional CVD (chemical vapour deposition) [83]. Therefore, it can be another promising material with antifouling properties.

2. Tetrahedral amorphous carbon with incorporated nitrogen (ta-C:N) is similar to BDD, and it can be expected that it will have pronounced antifouling properties. Moreover, it can be deposited at room temperature by physical vapour deposition [57]. Again, the thorough investigation of the relationship between surface character and passivation is necessary.
3. Sp<sup>3</sup>-carbon dominated hydrogenated surface [58,59], which can be prepared by pyrolysing acetylene and following hydrogenation by plasma or by one-pot chemical procedure involving a tris(pentafluorophenyl)-borane catalysed n-butylsilane reduction, and which seems to pose pronounced antifouling properties as well. The clarification of the structure–adsorption behaviour relationship is again very desirable.
4. Carbon film electrodes [27,28,65] and pencil graphite electrodes [88] with easily renewable surface substituting less “green” disposable electrodes. It should be interesting to use boron doped diamond particles and tetrahedral amorphous carbon with incorporated nitrogen (ta-C:N) particles for the preparation of similar carbon film electrodes. Interesting comparison of carbon film and carbon and gold screen printed electrodes can be found in [89]. Quite promising from this point of view seem to be different graphite powder-based electrodes [90].
5. Paper-based sensors represent another potential alternative, because they are cost effective, disposable, and customizable [91]. Moreover, they can be simply fabricated by hand drawing the electrode with a suitable ink based on MWCNT (multiwall carbon nanotubes) [92].
6. Carbon composite electrode [93], the surface of which (0.3–0.5 mm layer) is cut off by special commercially available device [94], resulting in fresh unpassivated surface is another interesting possibility. Unfortunately, number of renewals is limited in this approach.
7. Bismuth film [66,67,95,96] and bulk [68] electrodes and antimony film electrodes [69] with mechanically and/or chemically (electrochemically) renewable surface are another promising material with envisaged antifouling properties and easily renewable surface.
8. Silver solid amalgam electrodes [18–20] with electrochemically easily renewable surface have excellent electrochemical properties nearly comparable with liquid mercury. Both electrochemical [18–20] and mechanical [21] surface renewal can suppress problems with their passivation. Other interesting applications of amalgam film electrodes can be found in [97] (renewable film) and in [98] (amalgam electrode fabricated with nanoparticles).
9. Polymer modified carbon electrodes [70,99] can in some cases be also more passivation resistant than bare electrodes.
10. Electrodes modified with MOFs (metal organic frameworks), which can be functionalized as electrochemically functional frameworks with perfect electrochemical properties, are quite promising, even though this research is still in its infancy [100–102]. The functionalization of carbon nanomaterials (e.g., graphene, graphene oxide, carbon nanotubes, and fullerenes) with POSS (carbon nanostructures containing polyhedral oligomeric silsesquioxanes) can be also used for fabrication of electrochemical sensors [103].
11. Silica sol–gel films that modify working electrode to protect it from passivation by adsorption of macromolecules with emphasis on pore size, structure, and orientation are thoroughly discussed in review [104].
12. A refreshable electrochemical aptasensor based on a hydrophobic electrode and a magnetic nanocomposite had been developed to solve the problem of the sensor passivation. The hydrophobic electrode was fabricated by modifying SPCE (screen printed carbon electrode) with PDMS (polymethylsiloxane) to avoid adsorption of molecules on modified electrode due to its hydrophobicity [105].

13. Sputtered metallic film electrodes [71] and silver amalgam particles electrochemically deposited on optically transparent indium-tin oxide substrate [106] are definitely suitable candidates for fouling-resistant sensors. The same holds for novel solid amalgam electrode decorated by silver nanoparticles [107]. Further interesting possibilities are offered by the use of various nanomaterials [108].
  14. Novel perforated Fe electrodes or Al hollow cylindrical electrodes preventing the passivation introduced in [109] can have some antifouling potential as well.
- C. **Search for new antifouling strategies.** Some principles used in antibiofouling strategies for water monitoring instrumentation can be inspiring as well [110,111], namely, those connected with the use of electrode cleaning via mechanical means (wipers, tapes), laser or UV radiation, UV LED devices, ultrasound, antifouling sprays, or other techniques inspired by nature. A transparent organogel layer with self-repairing property for the inhibition of marine biofouling can be an inspiring example [110] and the same holds for the electrochlorination system based on platinum nanoparticles coated oxide [74]. Electrochemistry could be a very efficient tool for biofouling prevention in two ways, either by local biocide production through seawater electrolysis or by immobilizing electrogenerated biocides using antimony doped tin dioxide as an electrode material [111].

It is worth mentioning that sometimes more frequent calibration can at least partially eliminate unfavourable effects of electrode passivation. The choice of antifouling strategy is governed by sensor operating principle, intended application, matrix, and analytical requirements. Obviously the economic reasoning plays important role as well. However, in many cases increased cost is compensated by better performance and longer life-time of the sensor.

## 5. The Structural and Phase Characterization of the Electrode Surface

The structural and phase characterization of the electrode surface is a complex analytical problem. It is necessary essentially to analyse a thin layer, sometimes inconsistent, the thickness of which is in the order of 10 nm to several  $\mu\text{m}$ . Moreover, the electrodes are often curved, miniaturized, or sterically hindered so that it is difficult to approach the surface to be analysed. In some cases, the electrode material can be analysed indirectly in the powder form. However, in most cases, it is necessary to directly examine the real surface in situ. The basic task of electrode surface analysis is the precise structural and morphological analysis of the surface. In addition, however, other issues need to be addressed:

1. to get information about the functional groups on the electrode surface of the carbon material (e.g., via Raman based techniques)
2. to get information about crystallographic characterization and orientation of the electrode surface structures (e.g., via X-ray techniques)
3. to get information about the size and nature of the nanoparticles on the surface of the electrode (e.g., via TEM)
4. to get information about the organic substances adsorbed on the surface of the passivated electrode (e.g., via Raman based techniques)
5. to get information whether we have removed this organic substance from the surface (by combination of above mentioned techniques)

Structural characterization of the solid electrode surface is very important supplementary information to its electrochemical characterization and can reveal the situation on the electrode surface before and after passivation. To solve these problems, X-ray diffraction [112,113] and electron microscopy analytical techniques [114,115] can be used. For analysis of morphology and phase composition of the surface and for investigation of adsorbed organic compounds on the electrode surface, TEM is a suitable technique; carbon containing particles coming from the electrode surface can be analysed by SAED. Obtained diffraction patterns enable to distinguish crystallography of the surface carbon layer. Further characterization can be performed by EELS. This method is suitable for

measuring especially light elements, such as carbon. The EELS spectra give two main pieces of information—the position of peak designates the element, and the shape of the peak determines the bounding of the element. EELS spectra from carbon containing materials are well described in literature and their analysis together with SAED can bring detailed information about the electrode surface. The use of ESCA and XPS [116,117] and AFM techniques is also recommended. For ESCA technique, it is specific that it brings surface information important for the study of electrode passivation. Application of AFM techniques can solve the problem of specimen fixation and the nonplanar surface of the electrodes. Very inspiring from the general point of view is monograph [99].

## 6. Advantages and Disadvantages of Different Antifouling Approaches

All above mentioned approaches have their advantages and disadvantages from the point of view of practically oriented electroanalytical laboratories. An attempt to analyse these approaches using the currently popular SWOT analysis is summarised in Table 1.

**Table 1.** SWOT analysis of different approaches to the minimization of electrode fouling.

<b>I. Novel electrode materials resistant to passivation</b>	
S	User friendly, attractive to practical laboratories, simple, straightforward, low personal requirements
W	Limited sortiment of so far available materials, higher price, need to buy new electrode
O	Great future potential, increasing market for producers
T	Ambivalent attitude of practical laboratories to new materials
<b>II. Disposable electrodes</b>	
S	Commercially available, used and accepted by practical laboratories
W	Slightly higher price per analysis, too intensive passivation can prevent several measurements necessary for standard addition method, not too “green”
O	Combination with flowing systems
T	Usually not only working but also reference and auxiliary electrodes are unnecessarily disposed off
<b>III. Polishing/cleaning/pre-treatment of electrode surface</b>	
S	Generally applicable in any lab, various possibilities of cleaning, easy automation of electrochemical cleaning, relatively simple, medium personal requirements
W	Chemical and mechanical cleaning can be time consuming and require certain skills, its efficiency must be verified
O	Automated electrochemical and mechanical (e.g., retractable pen electrode) cleaning, new possibilities of chemical cleaning (e.g., new solvents)
T	Influence on electrode life-time
<b>IV. Measurements in flowing systems</b>	
S	Easy automation, shorter time of analysis, higher productivity, possibility to couple with preliminary separation (HPLC-AD)
W	Only when passivation is caused by electrode reaction products/intermediates, more complex instrumentation
O	Commercially available RDE, FIA-AD, and BIA-AD [76,77], great number of HPLC-AD systems
T	Passivation by matrix components
<b>V. Preliminary separation of passivating molecules preventing their access to electrode</b>	
S	Effective elimination of passivating compounds from matrix
W	Inefficient when passivation is caused by electrode reaction products/intermediates, sometimes somewhat complex and personally demanding
O	Development of solid electrodes compatible with this approach (e.g., with HF application)
T	Low recovery, decreased approach of analyte to electrode surface

Table 1. Cont.

<b>VI. Application of electrodes with easily renewable surface</b>	
S	Highly efficient, applicable for any kind of fouling, usually relatively simple and user friendly, many different possibilities and combinations
W	Problems with mercury toxicity for DME, insufficient information/experience with dropping electrodes based on other metals/conductors
O	Fascinating possibilities for new dropping electrodes based on different novel materials (e.g., hundreds of different carbonaceous particles) dispersed in different novel solvents (e.g., hundreds of different RTILS (room temperature ionic liquids))
T	Lack of useful applications convincing enough for practical laboratories, possible toxicity of RTILS
<b>VII. Modification of electrode surface by fouling resistant polymers, films, or nanoparticles</b>	
S	Improved antifouling properties sometimes combined with increased sensitivity and selectivity
W	Lack of verified working examples, results are difficult to predict and must be carefully verified, higher personal and training requirements
O	Perspective approach opening new pathways, many different options, fascinating field for new basic research
T	Limited life time of modified electrodes
<b>VIII. The use of different solvents to minimize electrode fouling</b>	
S	Technically simple removal of passivating films
W	Not generally applicable, not too “green”, require trial and error approach
O	New more “green” solvents
T	Unpredictable influence of matrix components
<b>IX. 3D printed sensors with good passivation characteristics</b>	
S	Expanding possibilities of 3D printing with vast number of various combinations of new materials, decreasing price and increasing speed can be expected
W	Too many combinations will require large number of studies verifying their usefulness and practical applicability
O	Tailor made electrodes and cells can be produced in many laboratories
T	Too many possibilities can complicate validation of novel approaches

S = Strengths, W = Weaknesses, O = Opportunities, T = Threats.

## 7. Conclusions

For many determinations of electrochemically active small organic molecules, electrode fouling is one of the biggest complications preventing their broader practical applications. It follows from the above given brief overview of the state of art in the field of available antifouling approaches that in spite of many available possibilities, there are still many limitations in so far proposed solutions of this problem. It is clear that practice will accept only simple, inexpensive, user friendly, and not too time-consuming and labour intensive solutions with obvious antifouling effect. From the above mentioned possibilities, probably the most acceptable options are the use of novel passivation resistant electrode materials (both bare and modified (by various films, polymers, nanoparticles, etc.)), disposable electrodes, electrodes with renewable films and measuring in flowing systems. So far untapped potential can be found in combination of several antifouling principles, e.g., using disposable or renewable electrodes in flowing systems, etc. However, it is necessary to keep in mind that none of them are the best one, because it is always necessary to take into account the nature of electrode and of analyte, matrix, and applied electroanalytical technique. Finally, authors of an increasing number of sophisticated, ingenious, and effective fouling resistant electrodes must devote energy to convince practical laboratories to apply them (and of course practical laboratories must actively search for

these new approaches). The best way how to reach this goal is to apply novel antifouling approaches to as many analytes of interest as possible and thus attract attention to novel electrodes. It is worth mentioning that some of the strategies discussed in this review can be also used in general electrochemical biosensor development and for electrochemical monitoring of large biomolecules, because general electrochemical principles are adhered to in all these cases.

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