



Review—Women's Contribution in the Pulse Voltammetric Theories and Applications: Pulse Voltammetry Stands on the Shoulders of Outstanding Women Electrochemists

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It is exactly a century since polarography was developed, which is seen as a predecessor of all voltammetric techniques. As cyclic voltammetry (CV) is the most prominent member in the family of voltammetric techniques for mechanistic studies, the so-called "pulse voltammetric techniques" emerged as simple and viable alternatives to CV for mechanistic characterizations and analytical application, as well as for kinetic and thermodynamic evaluations. The theories and practical application of pulse voltammetric techniques were largely developed by several women electrochemists. In this short overview, we outline some of the major achievements of five women electrochemists who contributed immensely to the theoretical and practical application of pulse voltammetric technique. Since the theory and application of pulse voltammetric techniques largely relies on the works of Janet Osteryoung, Sebojka Komorsky Lovric, Angela Molina, Anna Brainina, and Oliveira Brett, we give in this review a short historical overview of the major accomplishments of these five exceptional women electrochemists.

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Short Overview of the Historic Development of Pulse Voltammetric Techniques

The first two decades of last century brought radical developments in all physical sciences. Alongside with the evolution of quantum mechanics and relativity theories, the new findings on electricity led to development of new technologies that were important for quick industrialization of many countries. The discovery of the Volta's battery at the very beginning of 19th century, together with the Faraday's, Luigi Galvani's and Hamphry Davy's experiments, are events that are seen as initial cornerstones in application of electrochemistry in the industry and everyday life. However, the real development of electrochemical science and the voltammetry as a branch of electrochemistry, started with the pioneering work of Jaroslav Heyrovsky. Exactly a century ago, Jaroslav Heyrovsky developed probably the most important electrochemical system designed to study the redox features of chemical systems able to exchange electrons with an electronic conductor at which a defined potential is applied.¹ The name of the technique, for which Heyrovsky was awarded with Nobel Prize in Chemistry in 1959, was *polarography*. The term "polarography" was introduced to explain an electrochemical polarization of dropping mercury electrode. In other words, polarization in electrochemistry is linked to changing the amount of surface charge on given conductor (working electrode) by means of an outside-controlled electrical source. In the initial experiments, by exploring the dropping mercury as a working electrode, Heyrovsky achieved a permanent size and a renewable electrode surface in each measurement. Since the first polarographic experiments were conducted mainly to make electrolysis of metal ions from solutions, in the early 30ties years from last century polarography was a very important technique in the metallurgy, but also in the war industry as well. Although this revolutionary technique had many good sides due to specific features of mercury (it has very high overpotential of hydrogen evolution, possibility to form amalgams with many metal ions, always a new fresh smooth surface of working electrode), there were much more negative aspects coming out within the years. Major troubles of this technique were seen in high ratio of capacitance vs Faradaic current, non-constant size of the working electrode, toxicity of mercury, the changes of the surface tension of mercury drop as a function of applied potential etc. The initial promising results of polarography, mainly obtained from the Czech and US electrochemical scientists, led to several improvements of

original technique. These were mainly modifications of the form of applied voltage done by superimposing various forms of potential amplitudes.²⁻⁴ Such modifications resulted in a better sensitivity and replacement of the polarographic wave with a peak having maximum at the half-height of polarographic wave. A few decades later came the introduction of hanging mercury drop electrode (HMDE, which is a stable electrode form) as a replacement of the dropping mercury. Since then, the bias-controlled electrochemical methods that use a firm electronic conductor as a working electrode have a common name "voltammetry."⁵ Afterwards, polarography is considered as a subclass of voltammetry, where the working electrode is a dropping mercury. In the coming years, the stable mercury working electrode was started to be replaced by other non-toxic materials made of graphite, or some noble metals such as platinum and gold. In the initial years, polarization of all these solid (or liquid stable) electrodes could have been achieved via a single linear or a cyclic potential scan. These potential modifications opened up a space to get insight into the nature of mechanisms of electrode transformation of many important chemical systems, ranging from small cations and anions, but also of many industrially important and physiologically active organic molecules. In that generation of voltammetric operative systems, which appeared in 50ties of the last century, the cyclic voltammetry emerged as one of leading electrochemical techniques both for mechanistic and kinetic measurements. Because of its powerful features to recognize the nature of various electrode mechanisms and physical phenomena (adsorption, crystallization, phase transformation) going on at the electrode/electrolyte interface, cyclic voltammetry has been named as "electrochemical spectroscopy." A nice historical overview dedicated on the polarographic techniques and cyclic voltammetry is presented in the paper of Bard and Zoski.⁶ In the coming years, it has been recognized that there is a need to design a voltammetric technique that will keep the advantages of cyclic voltammetry, which will be able to achieve a better sensitivity for analytical purposes. This could have been accomplished via modification of the applied potential bias by superimposing potential pulses with different height and width. By doing this, the so-called "pulse voltammetric techniques"⁷ emerged as an important class of voltammetric techniques that get dominant electrochemical tools in last 50 years for analytical applications on various organic and inorganic substrates, but also for kinetic and thermodynamic measurements, and mechanistic applications as well. The introduction of pulse voltammetric techniques came as a need to achieve higher ratio of desired Faradaic vs undesired capacitance (charging) currents. Since the rate of decay of charging currents is exponential with time, and that of Faradaic currents is inversely

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proportional of square-root of time (for “diffusional” redox analytes), one easily recognizes that the rate of charging currents decay is much faster than that of Faradaic currents. Consequently, sampling the current in a tiny time segment at the end of applied potential pulse is a successful approach that allows significant domination of Faradaic vs the charging measured currents. In the newest techniques, the potential ramp is not linear, but it varies in a series of small steps ranging commonly from 0.1 mV to 20 mV. The most relevant parameters of all pulse voltammetric techniques are:

Pulse width-defined as the time duration of potential pulse; *Pulse amplitude*-that is defined as a height of given potential pulse (measured in mV). It is important to note that the pulse amplitude can be constant or permanently changeable parameter that depends on the technique used. *Sampling period*-is the time-frame at the end of each applied potential pulse where the current is sampled.

There are several different pulse voltammetric techniques available commercially that differ in the form of applied potential, in the number of current sampling points, and in current measuring manner. The Normal pulse voltammetry (NPV); Differential pulse voltammetry (DPV), Square-wave voltammetry (SWV); Cyclic square-wave voltammetry (CSWV), and Double sampled square-wave voltammetry (DSSWV) are the most representative members so far. Relevant books revealing comprehensive overview on all these techniques are Refs. 8–13.

Women-Electrochemists That Contributed to the Development of Theories and Practical Application of Pulse Voltammetric Techniques

Alongside with the introduction of pulse voltammetric techniques, it has been a number of famous male electrochemists that developed scores of relevant theories for different mechanisms on various systems. Samuel Kounaves, Hiroaki Matsuda, Robert Osteryoung, Zbigniew Stojek, Richard Compton, Milivoj Lovric, Alan Bond, Ch. Amatore, Jan Myland, Fred Anson, Frazer A. Armstrong, Fritz Scholz, Keith Oldham, Valentin Mirceski, Stephen Feldberg are just some of the electrochemical giants that worked on developing plenty of relevant pulse voltammetric theories. It is our aim in this short historical overview to outline major achievements of outstanding women electrochemists that made significant contributions towards theoretical and experimental developments of pulse voltammetric electrochemical systems (Fig. 1).

One of the most important woman-researcher in field of electrochemistry, who introduced the “square-wave voltammetry” and made immense development in the theories of pulse voltammetric techniques is **Janet G. Osteryoung**. Janet Osteryoung made significant impact (and she still does) to the development of pulse voltammetry from theoretical and experimental point of view. Janet Osteryoung was born in 1930 in Pennsylvania, while at Swarthmore College she got her undergraduate education in 1961. The graduate education of prof. J. Osteryoung was achieved under the supervision of Prof. Fred Anson at California Institute of Technology, where she got her PhD in 1967. In that time, Janet was a fellow of a National

Science Foundation and the Woodrow Wilson Foundation. In 1967 she started her academic career as an Assistant Professor at Department of Chemistry at Montana State University. Soon afterwards, Janet moved to Colorado State University, where she stayed for 10 years. In 1979 Janet Osteryoung moved to work at the Department of Chemistry at the State University of New York at Buffalo. She was there promoted to Full Professor in 1982. In 1992, Janet made a transfer to the North Carolina State University as a Head of the Chemistry Department. Since 1994 Janet served as a Director of the Chemistry Division at the National Science Foundation in several terms. Janet Osteryoung has received many honors and awards, of which the most important are that of the National Science Foundation Guggenheim and the prestigious US Fulbright Fellowship. In 1987 she was awarded by the prestigious Garvin Medal of the American Chemical Society. She also got the ANACHEM Award from the Association of Analytical Chemists. The ACS Division of Analytical Chemistry awarded prof. Janet Osteryoung for her contribution in Electrochemistry in 1996. In 1998 prof. J. Osteryoung received the Pittsburgh Analytical Chemistry Award from the Society for Analytical Chemists of Pittsburgh. Prof. Janet Osteryoung was a member on several editorial boards of prestigious journals from the field of analytical chemistry and electrochemistry. Janet Osteryoung is a Founding Member of the Society of Electroanalytical Chemistry, where she acted as a president in 1986.

Janet Osteryoung’s main contributions are recognized for her theoretical works developed for pulse voltammetric techniques^{14–19} and in particular for square wave voltammetry.²⁰ Together with R. Osteryoung in 1985 they established the basis of the most advanced pulse voltammetric technique i.e. the “square wave voltammetry.” Working together with R. Osteryoung, Aoki, Lovric, Stojek, J. J. O’Dea and many other outstanding electrochemists, professor Janet Osteryoung contributed to the expansion of major theories for pulse voltammetric techniques at planar and disk microelectrodes.^{21–27} In the 80’s and 90’s of the last century, Janet Osteryoung et al. established plenty of theoretical models relevant to many diffusional^{28–31} and adsorption affected^{32–35} electrode mechanisms under conditions of square-wave voltammetry. Her SWV theories developed for one or two-step electron transfer mechanisms coupled by various chemical equilibria represent a cornerstone for all further electrode mechanisms developed in the coming years. From the kinetic and thermodynamic point of view, theoretical works of Janet Osteryoung are quite important since she presented several simple fitting voltammetric methodologies relevant to extract kinetic and thermodynamic parameters related to the electron transfer step(s) and to the coupled chemical reaction(s) as well. Indeed, her theoretical works served also as a basis to optimize instrumental conditions needed for defined analytical applications with SWV and with other pulse voltammetric techniques.^{19,36} Next to her outstanding achievements in the theory of pulse voltammetric techniques, Janet Osteryoung is recognized expert in analytical applications of SWV. For example, she published score of experimental works where she presented methods for quantification of low



Figure 1. Frol left to right: Janet Osteryoung, Sebojka Komorsky Lovric, Angela Molina, Anna Brainina and Oliveira Brett.

levels of pesticides, heavy metals, carcinogens and pharmaceuticals in a variety of media.^{37–41} Janet Osteryoung authored several books related to theory and application of pulse voltammetric techniques, while publishing more than 250 original papers and gaining over 6000 citations. With all her achievements, she is one of the outstanding women, not only in the field of voltammetry, but also one of the leading female figures in world's electrochemistry.

Another woman-electrochemist that has made immense contribution in the theory and application of pulse voltammetric techniques in last 40 years is Dr. **Šebojka Komorsky Lovric**. Dr.Šebojka was born in Zagreb, Croatia, where she got undergraduate and post-graduate education, and became a doctor of sciences in the field of chemistry in 1984 at the Faculty of pharmacy and biochemistry, University of Zagreb. Her first university position was as an assistant professor of analytical chemistry in the Military school for technical science in Zagreb from 1988. At the Institute "Ruđer Bošković" in Zagreb she worked from 1991 until her retirement in 2016. The scientific career of Dr.Šebojka Komorsky Lovric is quite impressive. She started the post-doctoral specialisations in the laboratory of prof. L. L. Spremulli, (Department of Chemistry, University of North Carolina at Chapel Hill, USA) in period 1985–1986, then in the Institute of Applied Physical Chemistry, Atomic Institute in Jülich, Germany (1986–1987) and in the laboratory of prof. A. Bond, Department of Chemistry, Deakin University, Geelong, Victoria, Australia (1989–1990). In the framework of the scientific cooperation with prof. Fritz Scholz that lasted from 1993 till 2006, Dr. Komorsky Lovric spent two years all together as the visiting scientist at the Humboldt University in Berlin and at the University Ernst Moritz Arndt in Greifswald, Germany. In 2003 she was visiting scientist at the Oxford University, Oxford, England.

Dr. Komorsky-Lovrić was author of more than 160 scientific papers, which are cited more than 4500 times, and participated in scores of scientific meetings with lots of oral presentations. She authored one book,⁸ several chapters in books and many entries in the giant edition of "Electrochemical dictionary."⁴² She was acting as a leader scientist of many national and international scientific projects. For the publication⁴³ she received "Best Cited paper Award 2003" from the Elsevier and the Electrochemistry Communications. For the book "*Square-Wave Voltammetry. Theory and Application*", Springer, Berlin, 2007⁸ she received in 2008 the highest Macedonian state award for science "Goce Delčev" together with prof. Valentin Mirčeski and Dr. Milivoj Lovrić. From 2009 till 2014 she served as the regional representative of the International Society of Electrochemistry.

The scientific achievements of Dr. Šebojka Komorsky-Lovric are a sort of combination of theories of various electrode mechanisms mainly coupled with adsorption phenomena in pulse voltammetric techniques,^{44–65} and developed experimental methodologies with the purpose to establish new electroanalytical methods for kinetic characterizations^{66–69} and electroanalytical applications.^{70–81} After the discovery of phenomenon of "quasireversible maximum" in square wave voltammetry,⁸² this method has been explored by Dr. Komorsky-Lovric for the evaluation of kinetics of surface electrode reactions of many important redox systems.^{83–85} Starting from 1999, Dr. Komorsky-Lovric worked intensively in the field of the transfer of ions across the boundary of two immiscible liquids with the help of so-called "three phase electrode" set up. By using the standard three electrodes cell she contributed (together with prof. Fritz Scholz and Dr. Milivoj Lovric) in the development of a simple voltammetric method to get access to Gibbs free energy of transfer of many important ions.⁴³ This approach was of immense importance to many fields such as interfacial catalysis, ion extraction, drug activity and many more.^{86–88} Dr. Komorsky-Lovric was also involved in analyzing the electrochemical properties of solid microparticles of insoluble inorganic salts and organic substances that are mechanically attached to the surface of inert solid electrode and immersed into aqueous electrolyte.^{89,90} The purpose of this abrasive methodology in solid-state electrochemistry was to study the possibilities

for direct analysis of powders. Dr. Komorsky-Lovric worked on electrochemical identification of active components in pharmaceutical preparations and on the analysis of other biologically important substances, such as cocaine, benzoylecgonine, ciprofloxacin, azithromycin, benzocaine, cinchocaine, lidocaine, procaine, codeine, lutetium bisphthalocyanine, catechins, stevioside, chlorophyllin, myricetin, cannabinoids, capsaicinoids and carotenoids and many more.^{91–96} Sebojka Komorsky-Lovrić was collaborating and co-authoring in her works with more than 200 scientists all around the globe, and they all agree that she was humorous, cheerful and collegial person. Regretfully, Dr. Komorsky-Lovrić passed away in 2020.

One of the leading women-electrochemists that still makes an impressive impact to theory and application of pulse-voltammetric techniques is **Angela Molina**. Professor Angela Molina (born in Spain) got her Doctoral thesis in Spain with title "Study of the ECE mechanism in normal polarography and pulse polarography" under a supervision of Professor Jesús Gálvez. From her PhD thesis prof. Angela Molina published several outstanding publications related to voltammetry of complex two-step electrode mechanism, in which both electron transfer steps are bridged by a chemical reaction (in electrochemical terminology name of this mechanism is "ECE"). This mechanism is quite important since it is seen as an adequate model to understand the electrochemical behavior of many redox enzymes involved in energy-generating systems, whose multielectron redox transformation takes place in two consecutive electron transfer steps that are commonly bridged by a protonation reaction.^{97–99} In the early years of her professional career, major scientific interest of prof. Molina was oriented to the study of electronic transfers in the DME/solution interface.¹⁰⁰ Later on, prof. Molina started to study electron transfer at interface of solid electrodes solid microelectrode/electrolyte solution.^{101–105} In the last 15 years, the group of prof. Molina extended their studies to understand electron/ion transfer phenomena at liquid-liquid interfaces,^{106,107} while they also focused on semiconductor electrodes and Spectroelectrochemistry. Main research interest of prof. Angela Molina is largely focused on the theoretical and experimental analysis of reaction mechanisms in different voltammetric techniques comprising single, double and multi-pulse potential (NPV, DPV, triple pulse techniques, SWV, CV, etc.). These techniques have been applied to study electronic and ion transfer processes taking place at different interfaces (macro and micro) with or without coupled chemical reactions. A special interest in her studies is given to multiple charge transfers and electrocatalytic processes due to their important role in energy transfer and energy generation processes, biological processes, and in electroanalysis in general. In many of theoretical studies considered, the major focus of prof. Angela Molina and her group was to obtain explicit analytical expressions for the electrochemical responses that reveal the fundamental parameters and/or limit behaviors of the experimental results obtained. This possibility was unfeasible to be obtained from a numerical resolution. During the 80's and 90's of last century, prof. Molina's group developed theories corresponding to the use of chronopotentiometric techniques with the current being constant and variable over time. They designed technique called: "Chronopotentiometry with variable programmed current with time." The initial publication on this technique that appeared in 1987¹⁰⁸ was an important advance in experimental application and theoretical development of direct chronopotentiometry and current-inversion chronopotentiometry in DME for many different reaction mechanisms.¹⁰⁹ Prof. Angela Molina made great contribution in the study of slow electronic transfer processes with triple-pulse electrochemical techniques (also designed in her research group), while proposing new very simple methods for the determination of the electron transfer coefficient and standard rate constant of electron transfer.¹¹⁰ It is important to stress that these analytical developments could not have been carried out with the method of Laplace's transform. In 1995 prof. Molina and her group published a scientific work that is considered as a milestone in the development of their research, while

serving as a basis for many subsequent studies.¹¹¹ In that publication¹¹¹ it was found that the fulfilment principle of superposition holds for a Nernstian thermodynamically reversible charge transfer process in any voltammetric technique for the most usual geometries of the diffusion field. This is because the surface concentrations of the participating species are independent of time, while depending only on the applied potential. From the rigorous application of this principle, it was possible to find explicit analytical expressions for the current of given electrochemical mechanism in any electrochemical technique. With this approach, an explicit analytical equation for planar, spherical and cylindrical geometry for a reversible electrode process applicable in DPP, DPV, RPP, RPV, SWV and in CV was obtained. Further on, this approach was applied regardless of the geometry and size of the interface. This fact was verified in 2011 for disks, bands, and microelectrodes.^{112,113} The reasoning used in this work was then expanded and applied rigorously to study catalytic and multielectron charge transfer systems.¹¹⁴ The group of prof. A. Molina contributed largely in the design of new electrochemical techniques such as the “Additive differential pulse voltammetry” (ADPV) introduced in 2001,^{115–119} and the “square wave voltacoulometry” introduced in 2007.¹²⁰ The last technique has been applied to mono-electronic, multi-electronic and catalytic charge transfer processes.¹²¹ Access to the expression of the concentration profiles of the absorbent species allowed the Molina’s research group to obtain expressions corresponding to the curves Absorbance-time and Absorbance-potential in UV both in normal mode and in parallel for different electrode.¹⁰⁵ The voltammetric theoretical background of prof A. Molina’s group was also applied to investigate effects of the electric field generated within the semiconductor on their redox behavior. Alongside to her involvement in the development of novel methods to study various electron transfer systems coupled with chemical equilibria, prof. Angela Molina and members of her group also contributed to the theoretical study of ion transfer in interface between two immiscible electrolyte solutions (ITIES), by using a single polarizable ITIES or two polarized ITIES and applying the Superposition Principle rigorously.^{122–125} The theoretical results obtained from these studies have been applied to the evaluation of mechanism and thermodynamic parameters of transfer of ionized drugs such as antidepressants and anesthetics.¹²⁶ A segment of her recent interest is to consider a system of two polarized ITIES consisting of one or more mediated or electronic transfer-conditioned ion transfers that take place on electrodes modified with organic films.¹²⁷ Impact experiments on polarized liquid-liquid interface due to simple or facilitated ion transfer of an analyte introduced into the droplets of organic phase emulsions in aqueous phase and vice versa are also part of recent achievements of prof Molina’s research group.¹²⁸ The research of prof. Angela Molina is quite important to understand redox behavior of many important redox systems under physiological conditions, especially applicable in enzymatic voltammetry and the protein-film voltammetry. In last 20 years, the group of prof. Angela Molina is probably a world leading electrochemists group that published scores of relevant theoretical works related to pulse voltammetric techniques.

Prof. Molina is a fellow of the International Society of Electrochemistry (since 2017). She is currently an associate editor of *Electrochimica Acta*, and she acted as co-editor in the volume dedicated to “Fundamental and Theoretical Electrochemistry” of “Current Opinion in Electrochemistry” journals. She is also a member of editorial committees of *Electrochemistry Communications*, *Journal of Electroanalytical Chemistry*, *International Journal of Electrochemical Science*, *Chem Electrochem* and *International Journal of Electrochemistry*. She is a full member of the Academy of Sciences of the Region of Murcia of Spanish Institute. In 2020, prof. Molina was awarded from the Spanish group of electrochemistry to her exceptional achievements in her research career. Prof Angela Molina authored more than 260 publications, many of them published in some of the most prestigious chemical and electrochemical journals. She is author of many book chapters, and author of a recent book.⁹ Indeed, her intensive current research and collaboration with many famous electrochemistry groups all over the world is seen as a

cornerstone for further developments in pulse voltammetric theory in the coming years.

Since it has been a special issue published elsewhere in 2012¹²⁹ dedicated to scientific achievements prof. **Khiena Zalmanovna Brainina** (or **Anna Brainina**, as most people know her, born in 1930 in Stalingrad, USSR), in this review we just shortly outline some of her biggest accomplishments. This is because the most of her excellent achievements in analytical pulse voltammetry came in the times of the “cold war,” and she was one of the very few scientists coming from a “closed world” (the former “Soviet Union”) that published research works in “western” journals, while making great contribution towards the practical application of pulse voltammetric techniques. Prof. Brainina’s work was greatly focused on the development of anodic stripping voltammetry (or inverse stripping voltammetry according to her established terminology in late 1960s), an electroanalytical technique that has been proven for detection of nano-molar concentrations of many metal ions.^{130–133} Prof. Brainina’s initial applications considered modification of surface of a glassy carbon electrode with a thin film made of mercury. By applying a defined negative potential on such film-modified electrode that is submerged in a water-electrolyte containing metal ions, it could have been possible to make reduction and dissolution of the corresponding metals in the form of amalgams. With application of a defined initial time, a large preconcentration of many metals could have been achieved. Afterwards, by applying oxidation potentials, amalgamated metals can be stripped off from the Mercury film and subsequently detected. Professor Brainina made significant contribution to the detection of heavy metal pollutants in water, drinks and food^{134–138} and in biological samples.^{139–143} She also modified this method for the quantification of nucleic acids.¹⁴⁴ As many of her achievements are described in special issue dedicated to her achievements published in 2012 elsewhere, in this review we can just confirm that prof. Brainina is one of leading women pioneers of the modern pulse voltammetry applied in electroanalytical and environmental chemistry. She published more than 200 original scientific publications, while she authored several monographs devoted to the stripping voltammetry. In 1995 prof. Brainina was awarded as an Honored Russian Scientist. She is a member of Russian Academy of Science. She got her PhD in Physical Chemistry in 1957 under the supervision of one of the giants in electrochemistry, prof. Armin Stromberg, while the Doctor of Science she became 10 years later in 1967 under supervision of another Russian giant in electrochemistry, prof. Alexander Frumkin. Prof. Brainina’s works attracted very high score of citations. Although she is already 91 years old, Prof. Brainina is still active in electrochemistry, and even in 2020 she still authored in several papers.^{145–147} Her enthusiasm to still work in electrochemistry is certainly a huge inspiration of many young women fellows.

Professor **Ana Maria Oliveira Brett** is another outstanding woman electrochemist that contributed significantly in application of pulse voltammetric techniques in the field of bioelectrochemistry and bioelectroanalysis during her outstanding scientific career. Prof. Oliveira Brett was born in Portugal, while she got her BSc in Chemistry at the University of Coimbra in 1973. In 1980 prof. Oliveira Brett obtained her PhD in Electrochemistry at the Imperial College in the University of London. Major part of scientific research activity of prof. O. Brett is focused on bioelectrochemistry, while she makes immense contribution in studying (theoretically and experimentally) by pulse voltammetric techniques processes of electron transfer reactions of many systems of interest such as anti-cancer drugs, antioxidants, drugs of abuse and many more. Moreover, prof. Oliveira Brett also works successfully on the development of enzymatic biosensors. She also contributes in understanding mechanisms of action between DNA and some anticancerogenic drugs, and interactions between DNA and some heavy metal ions that are known to make oxidative damage to DNA. A part of her current work is also focused on comprising of the mechanisms of actions of some free-radical species to important biological systems (DNA). Prof. Oliveira Brett is author of two

books^{12,148} and many chapters in various books, while she authored more than 250 publications, and got over 12000 citations up to now. Prof. Oliveira Brett was acting as an associate editor of Bioelectrochemistry journal between 2000 and 2016. For eight years between 2007 and 2015, she served as a President of International Bioelectrochemical Society. Currently she is a part of the Editorial Boards of several respected journals from the field of Electrochemistry and the Analytical Chemistry. Prof. Oliveira Brett is fellow of Royal Society of Chemistry, IUPAC, while she acts as a member of most prestigious scientific foundation in Portugal the Fundacao para Ciencia e Tecnologia. She is still engaged as a Professor at the Department of Chemistry in University of Coimbra, while she serves as a director of the Laboratory of electroanalysis and corrosion at Coimbra University in Portugal. She has active collaboration with many famous electrochemistry groups all around the globe. Prof. Oliveira Brett and the members of her group are probably among the leading electrochemists in the world that successfully apply various pulse voltammetric techniques in scores of important bioelectrochemical studies. Their studies are quite relevant to designing bioelectrochemical sensors and to closer understanding of the mechanism of action of many important biological systems. While there will be a special issue coming soon in another journal dedicated to the achievements of professor Oliveira Brett, we present in this work just some of her major scientific contributions. As the antioxidant activity of many redox systems present in biological samples is of utmost importance to understand relevant physiological processes, prof. Oliveira Brett focused intensively on the development of voltammetric sensors to assess the activity of some natural antioxidants such as resveratrol,¹⁴⁹ catechin,¹⁵⁰ para-substituted phenols,¹⁵¹ quercetin¹⁵² and many more described comprehensively in Ref. 153 A large segment of the research interest of prof. Oliveira Brett is focused on designing pulse-voltammetric amperometric sensors for detection of DNA.^{154–157} Many of this DNA bioelectrochemical sensors have been applied to study damaging effects induced on DNA by many drugs such as adriamycin,¹⁵⁸ carboplatin,¹⁵⁹ ions of some heavy metals,¹⁶⁰ hydroxyl free radicals,¹⁶¹ s-triazine derivatives,¹⁶² thalidomide,¹⁶³ gamma radiation¹⁶⁴ and other systems.^{165–168} Prof. Oliveira Brett's scientific research also considers designing of pulse voltammetric sensors for detection of important pharmaceutical compounds and drugs,^{169–174} and drugs of abuse.^{175–178} With all these achievements in bioelectrochemistry, professor Oliveira Brett is surely one of the leading women in electrochemical sciences that largely explored the pulse voltammetric techniques for analytical purposes.

Conclusions

It was a great honor to write about some of the major achievements of five women-electrochemists that contributed greatly to the development of pulse voltammetric techniques from theoretical and applicative point of view. Writing about Janet Osteryoung, Šebojka Komorsky Lovric, Angela Molina, Anna Brainina and Oliveira Brett is like writing a part of the history of voltammetry. Although electrochemistry is a complex science, this short historical overview should serve as a sort of motivating contribution to encourage many young women scientists to follow the steps of Janet, Šebojka, Angela, Anna, and Oliveira.

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