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Review

VISIONARY FIGURES IN THE FIELD OF ELECTROCHEMISTRY WHO REVOLUTIONIZED VOLTAMMETRY[1]

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Understanding energetics and electron behavior has been pivotal in elucidating numerous fundamental phenomena, including electricity, corrosion, respiration, energy generation in biological systems, intermolecular interactions within living organisms, organic synthesis, drug development, enzyme functions, and the design of biosensors, among others. As 2024 records the centennial anniversary of the completion of the first polarograph by Nobel laureate Jaroslav Heyrovský (awarded the Nobel Prize in Chemistry in 1959), it presents an opportune moment to pay tribute to several eminent electrochemists who have made significant contributions to the field of voltammetric techniques. Following our recent acknowledgment of the outstanding women who have made substantial contributions to voltammetry in a prior publication, this article aims to briefly highlight the major achievements of several distinguished male figures in the field (Jaroslav Heyrovský, Allen J. Bard, Christian Amatore, Richard Compton, Jean-Michel Savéant, Fraser Armstrong, Fritz Scholz, Joseph Wang, Milivoj Lovrić, Valentin Mirčeski, Alan M. Bond). Given that many of these remarkable personalities have contributed both as authors and referees for the Macedonian Journal of Chemistry and Chemical Engineering, this tribute serves as a fitting acknowledgment of their remarkable accomplishments on the occasion of the journal's 50th anniversary.

Keywords: electrochemistry; giants in voltammetry; polarography; voltammetry; biosensors

ЗНАЧАЈНИ ЛИЧНОСТИ ОД ОБЛАСТА НА ЕЛЕКТРОХЕМИЈАТА КОИ ДОВЕДОА ДО РЕВОЛУЦИЈА НА ВОЛТАМЕТРИЈАТА

Разбирањето на состојбите на енергијата на електроните е еден од најважните сегменти во процесот на разбирање голем број физички и хемиски феномени, вклучувајќи ги електрицитетот, корозијата, респираторниот процес, генерирањето на енергија во биолошките системи, меѓумолекулските интеракции во живите организми, органската синтеза, развојот на лекови, функциите на ензимите, како и дизајнот на различни видови биосензори. Бидејќи во 2024 година се одбележува стогодишнината од дизајнот на првиот модерен поларограф конструиран од Јарослав Хејровски, добитникот на Нобеловата награда за хемија во 1959 година, овој настан е соодветен момент за да се оддаде почит на неколку значајни електрохемичари кои имаат дадено значителен придонес во областа на волтаметриските техники. Додека во нашиот претходен труд беа претставени постигнувањата на неколку извонредни жени-електрохемичари кои дале значителен придонес за волтаметријата, во овој труд се претставени некои од најголемите постигнувања на неколку великани-електрохемичари (Јарослав Хејровски, Алан Џ. Бард, Христијан Аматоре, Ричард Комптон, Жан-Мишел Савеан, Фрејзер Армстронг, Фриц Шолц, Џозеф Ванг, Миливој Ловрић, Валентин Мирчески и Алан М. Бонд). Бидејќи многу од овие електрохемичари придонеле за развојот на Македонското списание за хемија и хемиско инженерство (MJCCE) и како автори и како рецензенти, овој труд нека претставува еден вид признание за нивните постигнувања при одбележувањето на златниот јубилеј на списанието.

[1] Dedicated on the occasion of the Golden Jubilee of the *Macedonian Journal of Chemistry and Chemical Engineering*

Клучни зборови: електрохемија; великани на волтаметријата; поларографија; волтаметрија; биосензори.

1. INTRODUCTION

When discussing electrochemistry in everyday life, batteries and corrosion processes often come to mind. While these are undoubtedly important electrochemical processes, electrochemistry pervades various aspects of our existence. For instance, fundamental processes such as respiration, ion transfer across biological membranes, the establishment of cell-membrane potential, the functionality of numerous 'redox' enzymes and proteins, the generation of energy in the form of adenosine triphosphate (ATP) in mitochondria, among others, inherently possess electrochemical characteristics. From a historical vantage point, among the earliest documented instances of unintentional bioelectrochemical experimentation was those conducted by Galvani, notably his renowned frog legs stretching experiment. Subsequently, giants in the science of that time, such as Faraday, Volta, Davy, Ohm, and others made significant contributions to the establishment of fundamental concepts underpinning electrochemistry as a scientific discipline. In the initial two decades of the 20th century, however, notable progress was witnessed across the spectrum of all physical sciences. Indeed, many advancements in understanding the fundaments of electricity propelled the creation of pivotal technologies that were crucial for the swift industrialization of various nations. The substantial progress in electrochemical science and the ascendance of voltammetry as a preeminent branch of electrochemistry originated from the pioneering contributions of Jaroslav Heyrovský. Just over a century ago, Heyrovský developed what is arguably the most significant electrochemical system designed to investigate the properties of chemical systems capable of exchanging electrons with an electronic conductor under a defined bias controlled from an outside source. The electrochemical technique, for which Heyrovský was awarded the Nobel Prize in Chemistry in 1959, came to be known as 'polarography'. Initially, Heyrovský's experiments focused on utilizing the dropping mercury electrode as a working electrode, achieving a consistent size and renewing the electrode surface with each measurement. Although utilizing mercury in polarography offers notable advantages in respect to its elevated overpotential for hydrogen evolution, capacity to form amalgams with diverse metal ions, and provision of a consistently smooth electrode surface, it also presents several drawbacks that have become increasingly evident over time. These include fluctuations in the size of the working electrode, the inherent toxicity of mercury, and alterations in the surface tension of mercury drops in response to applied potential variations. In contemporary practice, the utilization of mercury as a working electrode material has been largely supplanted by alternative non-toxic materials such as graphite, platinum, and gold. The term 'voltammetry' collectively refers to bias-controlled electrochemical techniques that employ a solid electronic conductor as a working electrode. In our recent publication,[1] we initially reported on women's contributions, delving comprehensively into the significant advancements made by outstanding women electrochemists (Janet Osteryoung, Angela Molina, Šebojka Komorsky-Lovrić, Anna Brainina, Ana Maria Oliveira-Bret, among others) in the field of voltammetry. The current feature article specifically emphasizes the noteworthy contributions made by prominent male electrochemists who have played pivotal roles in revolutionizing voltammetry over the last fifty years.

2. RESULTS AND DISCUSSION

2.1. *He is the father of polarography: Jaroslav Heyrovský (1890–1967)*

Numerous generations of electrochemists recognize that their achievements owe much to the foundational works of **Jaroslav Heyrovský**. Jaroslav Heyrovský, born in Prague (Czech) in 1890, acquired his expertise in electrochemistry primarily at University College London in the period preceding World War I, where he received significant mentorship from Sir William Ramsay. Heyrovský's invention of the polarographic method in 1922 marked a seminal development, and he thereafter dedicated his scientific endeavors to advancing this novel branch of electrochemistry. Working in a more congenial era, devoid of the administrative burdens that contemporary scientists face today, Heyrovský conducted his experiments with joy and simplicity. Armed with only a mirror galvanometer borrowed from the Faculty of Mathematics and Physics at Prague University (Czech Republic), he measured the current's dependence on the applied

potential in a single afternoon. This data, subsequently termed a polarogram, was promptly published in a chemistry journal *Chemické listy* within couple of months.[2] Heyrovský's apparatus measured the current elicited by the application of a predetermined potential across two electrodes submerged in an electrolyte solution. Within a couple of years of the initial demonstration of the first polarographic instrument in 1924, the polarography became a widely adopted electroanalytical method. Despite the challenging circumstances during the Nazi occupation of Czechoslovakia, German fellow J. Boehm provided a sort of protection that enabled Heyrovský to advance his pioneering work during the turbulent times in WW II in Prague. Heyrovský made significant contributions through the refinement of his initial polarographic design, leading to breakthroughs in understanding the hydrogen overpotential issue and elucidating the mechanisms and kinetics of redox transformations of crucial inorganic ions at mercury electrodes, while also investigating the fundamentals of various adsorption phenomena. His research paved the way for the application of polarography in the electroanalysis of diverse chemical systems. Despite his preference for solitary experimentation without the aid of technicians or assistants, Heyrovský's positive demeanor and adept communication of knowledge facilitated the establishment of a new generation of brilliant Czech electrochemists. Notable figures in electrochemistry such as Brdička, Koryta, Zuman, his son Michael Heyrovský, and many others owe much of their success to the foundational works of Jaroslav Heyrovský. A comprehensive biography detailing the life and scientific accomplishments of Jaroslav Heyrovský, along with references of all his published works, can be accessed at Jaroslav Heyrovský, 1890–1967 (royalsocietypublishing.org). Heyrovský's exceptional contributions garnered him 18 Nobel Prize nominations, including 14 for chemistry, one for physics, and three for physiology and medicine. He was awarded the Nobel Prize in Chemistry in 1959. In 1950, Heyrovský was appointed Director of the newly established Polarographic Institute, which was subsequently integrated into the Czechoslovak Academy of Sciences in 1952. Jaroslav Heyrovský passed away in 1967. His enduring legacy in the development of polarography is regarded as a cornerstone for the advancement of modern voltammetric techniques.

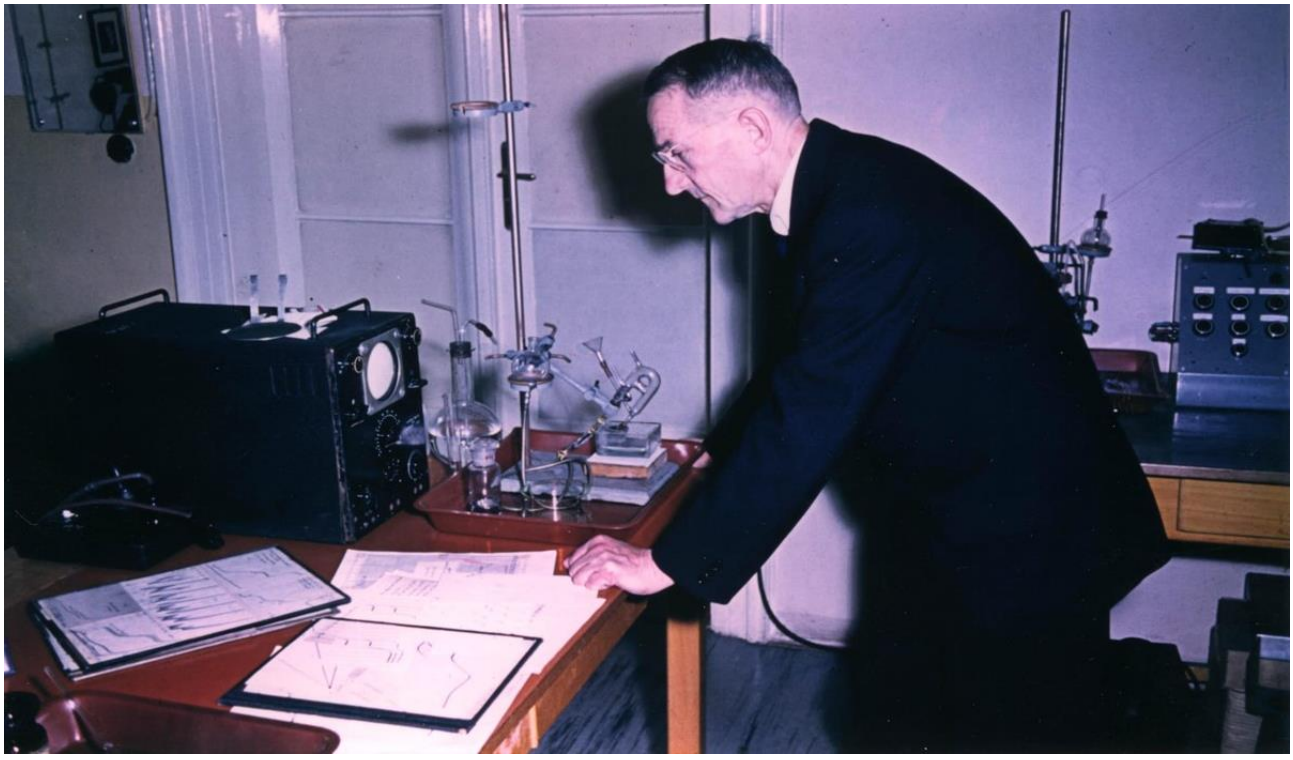

Fig. 1. Jaroslav Heyrovský working with this first polarograph

His contributions served as a pivotal moment in establishing polarography within significant scientific centers in USA, USSR, Italy, France, Canada, Yugoslavia, Japan, and numerous other countries. Despite the evolution of electroanalytical methods leading to the replacement of the dropping mercury electrode with new electrode materials in laboratory settings, mercury remains an invaluable system for investigating the properties and transformations of various substances vital to human health and environmental preservation, including new drugs, chemical carcinogens, pesticides, nanomaterials, and biomolecules. The methodologies and experimental protocols pioneered by Heyrovský[2–10] continue to be employed in diverse fields such as nanotechnology, biochemistry, and other disciplines within the natural and medical sciences.

2.2. *He is the father of modern electrochemistry: Allen Joseph Bard (1933–2024)*

During the preparation of this article, the electrochemical community received somber news on February 11, 2024, with the passing of **Allen Joseph Bard**, a towering figure in contemporary electrochemistry, at the age of 90. Allen Bard epitomized excellence in electrochemistry, dedicating his career to advancing the field, particularly in bringing electrochemistry and voltammetry almost to a molecular level.[11–20] While his primary focus encompassed the application of electrochemical methods to investigate various chemical phenomena, including electro-organic chemistry, photoelectrochemistry, electrogenerated chemiluminescence for DNA analysis, and electroanalytical chemistry, his research group also made significant strides in the development of scanning electrochemical microscopy (SECM).[11] Scanning electrochemical microscopy has emerged as an indispensable tool for studying surface reactivity owing to its ease of use and capacity to deliver quantitative results. The rapid expansion of the SECM field over the past several decades has been propelled by the introduction of novel probes, commercially available instrumentation, and diverse practical applications. The enduring vitality and burgeoning popularity of SECM can be attributed to its versatility and adaptability to evolving scientific and technological landscapes. Recent applications in biomedical and energy-related research underscore the sustained interest and activity in this area.[14–17] Through innovative modifications and theoretical frameworks applied to SECM experiments, Allen Bard and his collaborators extended the utility of voltammetry and electrochemistry to facilitate probing of redox activities at the level of single cells. The capability of SECM to provide high-resolution topographical data across various surfaces has rendered it an indispensable analytical and microscopic tool in contemporary electrochemical laboratories.

Throughout his illustrious career, Allen Bard collaborated with numerous eminent electrochemists and served as an exemplary mentor, overseeing the training of over 100 PhD students from around the globe at the University of Texas at Austin (USA), where he spent his entire academic tenure. With over 1000 scientific papers authored, contributions to over 80 books, over 30 patents, long-term service as chief editor of the iconic Journal of the American Chemical Society, and co-editorship of the excellent edition of "Electrochemical Dictionary" alongside Fritz Scholz and Gyorgy Inzelt, Allen Bard established himself as one of the foremost figures in the field of electrochemistry over the past 50 years. His pioneering research in electrochemistry garnered widespread recognition, including prestigious awards such as the Enrico Fermi Award, the Priestley Medal, and the Wolf Prize in Chemistry. The University of Texas at Austin, where Bard joined the chemistry faculty in 1958, hailed him as the 'father of modern electrochemistry'. In 2013, the US President Barack Obama conferred upon Allen Bard the National Medal of Science for Chemistry, further solidifying his legacy as a preeminent figure in the field. Allen Bard's enduring legacy extends beyond his scientific achievements; his charismatic personality, positive demeanor, and profound understanding of electrochemical phenomena serve as a beacon for future generations of electrochemists. He will forever be revered as an iconic figure whose groundbreaking research and exemplary leadership continue to inspire young scholars in the field of electrochemistry. Allen Bard does not cure diseases. However, his development of the scanning electrochemical microscopy technique has facilitated significant advancements in disease detection and the exploration of transdermal drug delivery methods to combat them. Bard's pioneering work with the scanning electrochemical microscope has provided researchers with enhanced capabilities for high-resolution chemical imaging and the observation of chemical reactions.

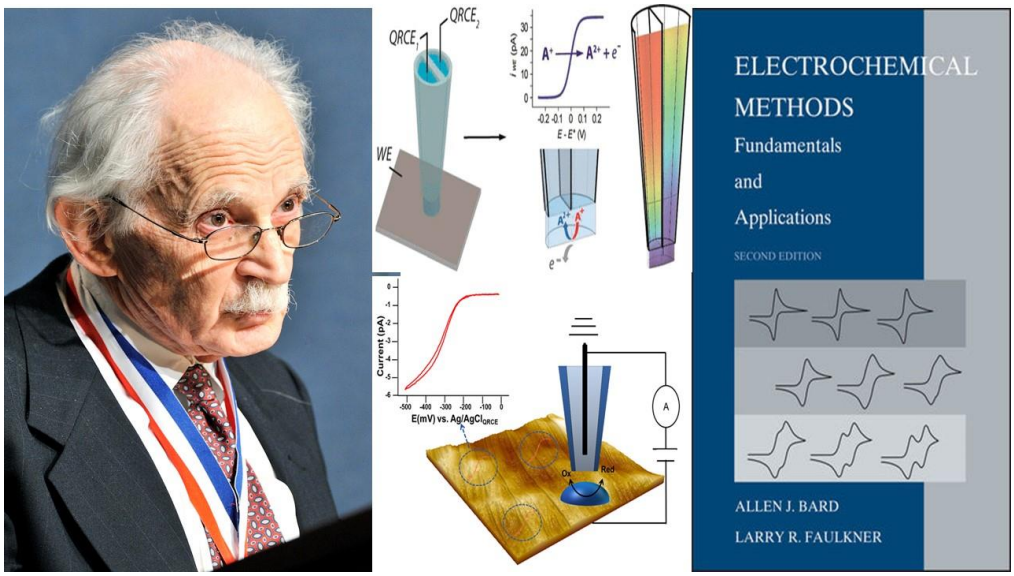

Fig. 2. Allen J. Bard (left), scheme of Scanning Electrochemical Microscopy (middle), and cover of his book "Electrochemical Methods" (right)

2.3. *He is the father of ultrafast voltammetry and ultramicroelectrodes: Christian Amatore (1951–)*

In the field of organic chemistry, a comprehensive understanding of reaction mechanisms often necessitates the elucidation of transient species, such as short-lived free radicals, whose existence may endure for mere nanoseconds. To accomplish this task, voltammetry must be conducted within the framework of nanosecond timescales. **Christian Amatore**, a distinguished researcher of French origin born in 1951 in Algeria, is credited as the pioneer of 'nanosecond voltammetry'. Educated at the Ecole Normale Superieure (ENS), an outstanding French educational and research institution, Amatore held the esteemed position of Director of the Chemistry Department at ENS, previously occupied by Louis Pasteur.

Amatore's seminal contribution lies in the development of algorithms to extract Faradaic current components from nanosecond voltammetric measurements, effectively mitigating the predominant influence of ohmic drop effects and capacitance currents in such experiments. His endeavors in ultrafast voltammetry have facilitated the elucidation of very fast electron transfer kinetics in many crucial chemical and physiological systems. In addition to his profound impact in electrocatalysis, a significant portion of Amatore's research is dedicated to the design of amperometric sensors for detecting essential neurotransmitters and other physiologically relevant systems.

Central to Amatore's innovative approach is the utilization of ultramicroelectrodes, enabling the investigation of various transfer phenomena and the elucidation of electrochemical transformation mechanisms of vital organic molecules at the nanosecond timescale.[21–30] Notably, his collaborative development of the 'artificial synapse' concept with Mark Wightman has yielded significant contributions to the study of cellular behavior at the single-cell or tissue levels, advancing our understanding of biological processes within living cells. Amatore's precise detection and measurement techniques, capable of monitoring minute fluxes as low as 500 molecules per tenth of a millisecond, have enabled the observation of essential messengers emitted by living cells during intercellular interactions within tissues and integrated organisms. His membership in the French Academy of Sciences, along with his knighthood in the French National Order of Merit and the French Legion of Honor, underscore his profound impact and recognition within the scientific community.

With over 550 scientific publications cited more than 30000 times, Amatore's influential body of work extends beyond academic journals to encompass numerous relevant books. His extensive editorial tenure at the Journal of Electroanalytical Chemistry, succeeding the renowned electrochemist Roger Parsons, further underscores his leadership and influence in the field. Amatore's theoretical and practical contributions have solidified his status as a revolutionary figure in voltammetry, elevating the technique to the molecular level and enabling a deeper understanding of critical phenomena in important organic reactions.

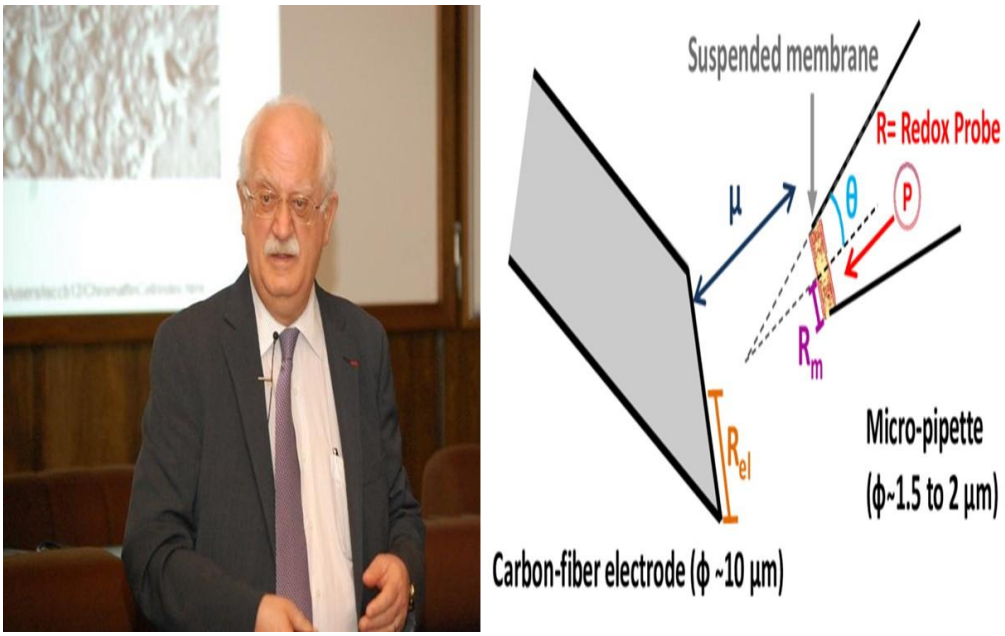

Fig. 3. Christian Amatore (left) and a scheme of ultramicroelectrode set up (right)

2.4. *The most remarkable 'all-rounder' in today's electrochemistry: Richard Guy Compton (1955–)*

Imagine an electrochemist who has authored over 1700 high-quality scientific papers[31–40] and numerous noteworthy books, who explores theories of electrochemical mechanisms in the presence of various chemical reactions and adsorption phenomena, while serving as editor to numerous scientific journals. This individual has developed theories for novel voltammetric techniques, elucidated different types of mass transport, revisited crucial voltammetric theories such as Marcus-Hush and Butler-Volmer, designed voltammetric biosensors for diverse systems, and crafted sensors for dissolved gases in various samples. Additionally, he introduced new types of materials as working electrodes, unraveled mechanisms of electrochemical transformation for critical molecules, detected biomarkers in human bodily fluids, gained deeper insights into electrochemical transformations occurring at electrodes modified with nanoparticles, and conducted research in electrocatalysis and electrosynthesis. Indeed, all this was done by the most remarkable all-rounder in modern electrochemistry, **Richard Guy Compton**. Richard Compton has mentored over 100 PhD candidates and more than 150 master's students, taught regularly, attended numerous electrochemistry-related conferences worldwide, while writing and applying for hundreds of project proposals to secure funding for student research. Remarkably, he has managed to be present at almost all matches of his favorite football club in the English Premier League (Liverpool). Such achievements are made possible by an individual with profound enthusiasm, extensive knowledge in chemistry and physics, substantial capacity for collaboration and idea-sharing, and a dedication to disseminating knowledge.

Richard Compton is a Professor of Chemistry and Aldrichian Praelector at Oxford University (UK) and one of the foremost electrochemists who has bridged the gap between electrochemistry and various scientific disciplines. His positive attitude and ability to elucidate complex phenomena in accessible language have established him as one of the most significant figures in the field of voltammetry and electrochemistry.

Richard Compton, born 69 years ago in the UK, received his PhD in 1980 at Imperial College London, UK, under supervision of Professor Wyndham J. Albery. Richard Compton has been honored with prestigious awards from the Royal Society of Chemistry for his remarkable achievements. He also holds notable positions such as Chinese Academy of Sciences Visiting Professor at the Institute of Physical Sciences in Hefei (2011–16) and Lifelong Honorary Professor at Sichuan University, Chengdu (China). He has received honorary doctorates from the Estonian Agricultural University (Estonia) and National University of Radioelectronics in Kharkiv (Ukraine). Richard is a Fellow of both the Royal Society of Chemistry (since 1999) and the International Society of Electrochemistry (since 2010). Among the numerous awards he has received are the Sir George Stokes

Award from the Royal Society of Chemistry (2011), the Tilden Lecturer Prize from the Royal Society of Chemistry (2005), the Breyer Medal from the Royal Australian Chemical Institute (2006), and the Alessandro Volta Medal from the Electrochemical Society (2004). Compton is the founder and editor of the journal, Electrochemistry Communication, which has become one of the leading electrochemical journals in just over a quarter-century. His book "Understanding Voltammetry" is considered a guideline in voltammetry for electrochemists of all levels.

In a testament to his collaborative spirit, Richard Compton has over 950 coauthors on his papers, showcasing the macrocosm of talented electrochemists he has nurtured. His legacy as one of the most remarkable figures in voltammetry and electrochemistry over the past 50 years is indisputable, as he has democratized access to voltammetry, making it an easy instrumental tool accessible to everyone.

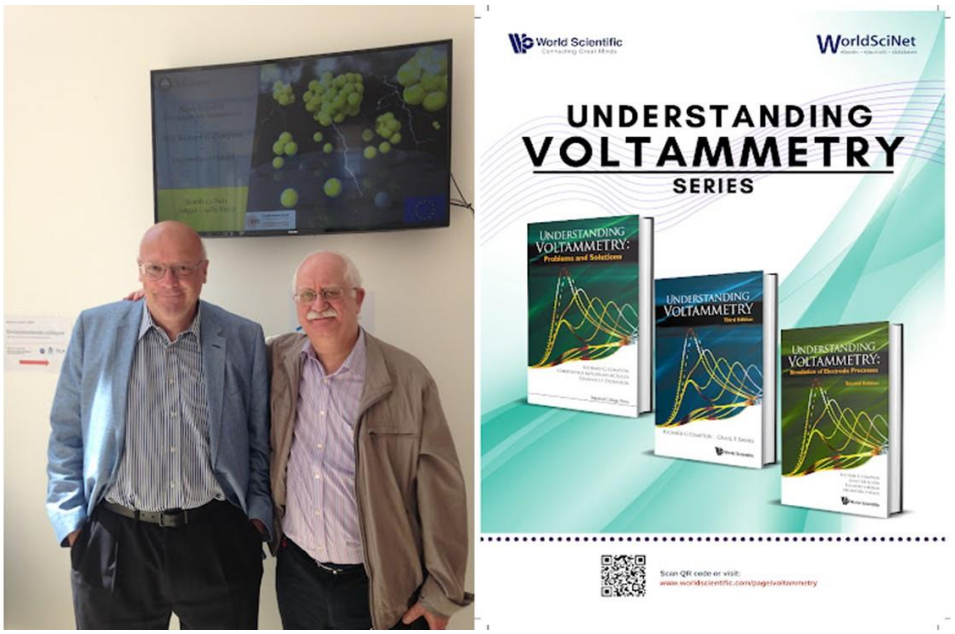

Fig. 4. Richard Compton and Christian Amatore (left).
Right is the cover of iconic book of Richard Compton "Understanding Voltammetry".

2.5. *Nothing works in electrochemistry without understanding cyclic voltammetry: Jean-Michel Savéant (1933–2020)*

Cyclic voltammetry has emerged as a cornerstone technique in electrochemistry, renowned for its efficacy in unraveling electrode mechanisms and physical phenomena occurring at the electrode/electrolyte interface. This method, often dubbed 'electrochemical spectroscopy', offers a straightforward means of comprehending electrochemical processes through the oxidation-reduction patterns depicted in cyclic voltammograms. Its versatility makes it a preferred choice across various electrochemical experiments. The interpretation of cyclic voltammograms, however, presents a significant challenge owing to the multitude of factors influencing their shape. These factors commonly encompass diverse chemical reactions coupled to electron transfer, adsorption phenomena, phase transformations, ion transfers, mass transfer characteristics, crystallization phenomena, among others taking place at the working electrode/electrolyte interface. To elucidate the nature of these processes and assess relevant kinetic and thermodynamic parameters, a molecular approach known as 'molecular electrochemistry' has gained prominence. This branch of electrochemistry focuses on elucidating molecular changes induced by electron transfer to or from an electrode, offering insights into molecular reactivity across chemistry and biochemistry domains.

Jean-Michel Savéant, an outstanding personality in the field of voltammetry, who regrettably passed away on August 16, 2020, dedicated his illustrious career to advancing molecular electrochemistry. With a scholarly record comprising almost 500 publications[41–50] of exceptional quality that attracted more than 40000 citations, Savéant delved into understanding the electrochemistry of pivotal physiological systems at the molecular level. His fascination with the diverse shapes of cyclic

voltammograms led to the development of graphical representations that encapsulate distinct electrochemical mechanisms, facilitating mechanistic recognition by experimentalists, including non-specialists in cyclic voltammetry. Savéant's methodological contributions, particularly the introduction of 'zone diagrams', serve as valuable tools for experimental design in electrochemical catalysis, electro-organic synthesis, biosensor development, kinetic evaluations, drug design, and beyond. Collaborating with eminent electrochemists such as Allen Bard, Christian Amatore, and Fred Anson, Savéant left an indelible mark on the field, characterized by his rigorous scientific approach and formidable intellect.

Born in Brittany in 1933, Savéant obtained his Doctor of Physical Sciences from the esteemed Ecole Normale Supérieure in 1966. He later established the Laboratoire d'Electrochimie Moléculaire at the Université Paris in 1988, where he made significant contributions in the theory and application of cyclic voltammetry. Recognized as a distinguished scientist, he was elected to the French Académie des Sciences in 2000, and as a Foreign Associate of the National Academy of Sciences of the USA in 2001. Over his six-decade career, Savéant received numerous awards, including the Bruno Beyer Award of the Royal Australian Chemical Institute (2005), the ECS Organic and Biological Electrochemistry Division Manuel M. Baizer Award (2002), ECS Olin Palladium Award (1993), and the Faraday Medal of the Royal Chemical Society (1983). His seminal work, "Elements of Molecular and Biomolecular Electrochemistry", remains an indispensable resource in all electrochemical libraries worldwide. The enduring legacy of Michel Savéant lives on through the exemplary scientific and academic pursuits of his former PhD students, who continue to build upon his illustrious contributions.

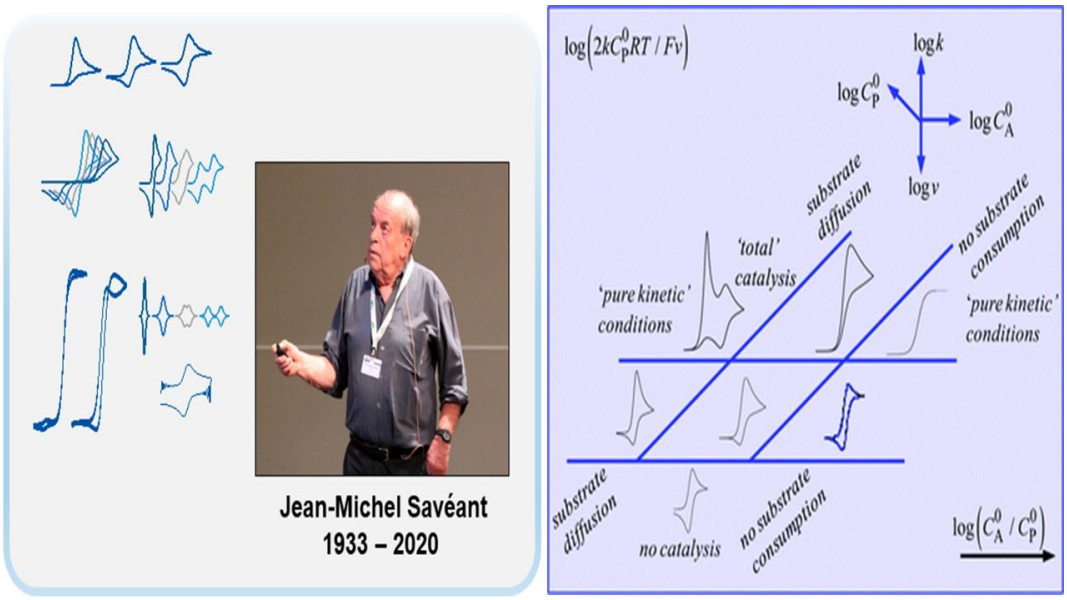

Fig. 5. Jean-Michel Savéant (left) and one of his famous diagrams showing the various kinetic zones of cyclic voltammograms of an electrochemical reaction coupled with a regenerative chemical step (right)

2.6. *He gave artificial life to 'redox enzyme and proteins': Fraser Andrew Armstrong (1951–)*

Redox enzymes and proteins represent pivotal components within physiological systems, and their mechanisms of action, particularly those characterized by high lipophilicity, have long posed challenges for investigation via electrochemical methods. Professor **Fraser Andrew Armstrong** of Oxford University devised a groundbreaking approach to address this issue, enabling the enduring immobilization of lipophilic redox enzymes and proteins for electrochemical study.[51–60] By easily adsorbing these biomolecules onto modified and non-modified carbon-based electrodes, a pathway for electronic communication between the working electrode and the immobilized proteins is established. Within this simplified framework, comprehensive insights into enzyme activity, factors influencing enzyme inhibition, kinetics of enzyme-substrate interactions, and the reactivity of various redox sites within the enzymes can be gleaned from recorded voltammograms. Moreover, the discerned enzyme activity holds

promise for the development of tailored biosensors and biofuel cells. Termed 'protein film voltammetry', Armstrong's approach represents a seminal and highly impactful advancement in voltammetric methodologies, effectively bridging the fields of bioelectrochemistry and biomedicine. In many works performed mainly with metalloenzymes, it has been shown that protein film voltammetry, offers unique insights into the intricate electron-transfer reactions occurring within enzymes and other redox proteins. Armstrong's investigations into the mechanisms of hydrogenases have yielded crucial insights into hydrogen activation, oxygen tolerance, and cofactor assembly. Additionally, his group has explored innovative approaches such as employing enzymes as electrocatalysts in hybrid solar fuel cells and fuel cells and demonstrating their potential for sustainable energy applications. Fraser Armstrong is a Professor of Chemistry at Oxford University and a Fellow of St John's College, Oxford. Following his doctoral studies, Armstrong pursued postdoctoral research at various institutions, including the University of Konstanz (Germany), New Mexico State University (USA), the University of Wisconsin, Madison (USA), and the University of Oxford (UK). From 1983 to 1989, he was awarded a Royal Society University Research Fellowship. Fraser Armstrong returned to Oxford in 1993, where he has been based ever since. In recognition of his contributions to science, Armstrong was elected a Fellow of the Royal Society in 2008. Apart from his research endeavors, he is also a coauthor of a widely used undergraduate textbook on Inorganic Chemistry. He is the author of more than 300 papers that are cited more than 21000 times. Mentoring numerous of PhD students, he formed a great quantum of excellent young researchers that are pursuing his work in protein film voltammetry. Christophe Leger, Julea Butt, Alison Parkin, Lars Jeuken, and Jay Wadhawan stand as exemplary researchers whose substantial contributions have significantly advanced our understanding of the activities exhibited by various classes of crucial redox enzymes and proteins. Their combined efforts have played a pivotal role in the development of theoretical frameworks and experimental methodologies aimed at unraveling the complexities surrounding these biomolecular systems. Of notable mention is the recent milestone achieved by Armstrong's group with the introduction of the 'electrochemical leaf'. This innovative concept represents a pioneering approach that holds promise for harnessing enzyme catalysis in organic synthesis, thereby opening up new avenues for exploration and application in the realm of enzymatic transformations.

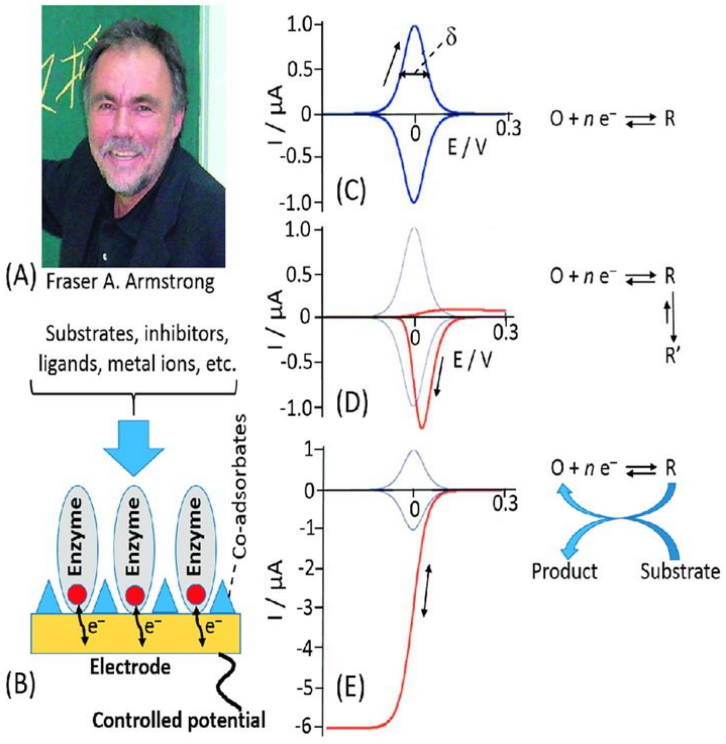

Fig. 6. Fraser Armstrong and a scheme of protein film voltammetry (upper left). On the right side of the figure, voltammetric outputs of a protein film voltammetry experiment is displayed (*Sensors*, **2020**, *20*, 3517, doi:10.3390/s20123517)

2.7. *The father of solid-state electroanalysis and voltammetry at three-phase electrodes: Fritz Scholz (1955–)*

In the field of chemical and electrochemical experimentation, acquiring pertinent thermodynamic parameters is paramount for discerning the equilibrium state of various chemical processes. While electrochemistry serves as a well-established method for elucidating thermodynamic parameters in numerous water-soluble redox systems, it presents considerable challenges when applied to systems exhibiting near-complete insolubility in water. Invented during his research time in former GDR (East Germany) in 1988/1989, and implemented during his research tenure in the laboratory of Alan Bond in Australia in the late 1980's, **Fritz Scholz** pioneered a novel methodology termed "abrasive stripping voltammetry" (later named "voltammetry of immobilized particles").[61] This innovative approach facilitated the voltammetric examination of numerous redox-active water-insoluble crystals by attaching the microparticles of these systems to the surface of a graphite electrode via simple abrasion, subsequently studying them in a water-electrolyte solution (this approach finds enormous application in archaeology mainly via the outstanding works of Antonio Domenech-Carbo and his collaborators). This straightforward approach envisaged coupled electron and ion transfer reactions occurring at the interface of the three distinct phases being in contact. Subsequently, this conceptual framework found application in a novel technique known as the voltammetry of immiscible liquids at so-called 'three-phase electrodes'. Leveraging these methodologies enabled the acquisition of the standard Gibbs energies of transfer for important ions for the first time. Such data hold exceptional significance in electrocatalysis, drug design, drug-drug interactions, and in the evaluation of the efficacy of ionizable drugs during their transmembrane transfer. Collaborating with eminent theoreticians in voltammetry such as Lovrić, Oldam, Mirčeski, Compton, and Molina, Scholz fostered a plethora of theoretical insights elucidating the mechanisms underlying voltammetry at three-phase electrodes. Though renowned as the progenitor of solid-state voltammetry, Scholz was also deeply engaged in diverse projects spanning from the development of various pH electrodes to the design of biofuel cells, demonstrating the manifold applications of analytical electrochemistry in environmental analyses.

As the founder and longstanding editor-in-chief of the distinguished Journal of Solid-State Electrochemistry, alongside his establishment of the educational journal ChemTexts, Scholz remains committed to disseminating captivating works across all branches of chemistry in an approachable manner, even to non-specialists. Moreover, he has authored several great books including "Electrochemistry of Immobilized Particles and Droplets", "Electroanalytical Methods", and "Chemical Equilibria in Analytical Chemistry". Notably, Scholz coauthored and initiated the renowned "Electrochemical Dictionary," a comprehensive compendium encompassing crucial definitions and terms in electrochemistry deliberated by over 300 esteemed electrochemists worldwide. Having actively collaborated with luminaries in electrochemistry such as Allen Bard, Alan Bond, Richard Compton, Milivoj Lovrić, Angela Molina, Valentin Mirčeski, Hubert Girault, Šebojka Komorsky-Lovrić, Zbigniew Stojek, Gyorgy Inzelt, Uwe Schroeder, and Antonio Domenech-Carbo, among others, Scholz has published over 350 publications[61–70] with more than 400 coauthors worldwide, solidifying his stature as a preeminent figure in voltammetry and electrochemistry at large. His affable demeanor, generosity, and willingness to engage in scholarly discourse extend beyond scientific realms, exemplifying his exceptional qualities as a mentor and educator.

He was born in 1955 in Berlin, and received his education and obtained Dr. rer. nat. and the Dr. sc. nat (habilitation) from Humboldt University in Berlin (his supervisor was Professor Gunter Henrion). After completing his education and habilitation at Humboldt University in Berlin (Germany), Fritz Scholz moved for two years to Australia in the late 1980s to collaborate with one of the most eminent electrochemists, Alan Bond. Subsequently, he obtained a professorial position at the Alexander von Humboldt University in Berlin in 1993 before moving to Greifswald University (Germany) in 1997, where he held a professor position at the Institute of Analytical Chemistry and Biochemistry until his retirement in 2021. Throughout his illustrious career, Fritz Scholz has served as a Visiting Professor and Lecturer at esteemed institutions worldwide, delivering over 125 invited talks and participating in over 300 conferences. His election as a Fellow of the International Society of Electrochemistry in 2015 attests to his enduring contributions to the field. Indeed, the significant number of students he guided, a considerable number of whom have gone on to establish distinguished academic trajectories, guarantees the continuation of Fritz Scholz's legacy as a paramount figure in the field of electrochemistry, epitomizing his unmatched enthusiasm and scholarly excellence.

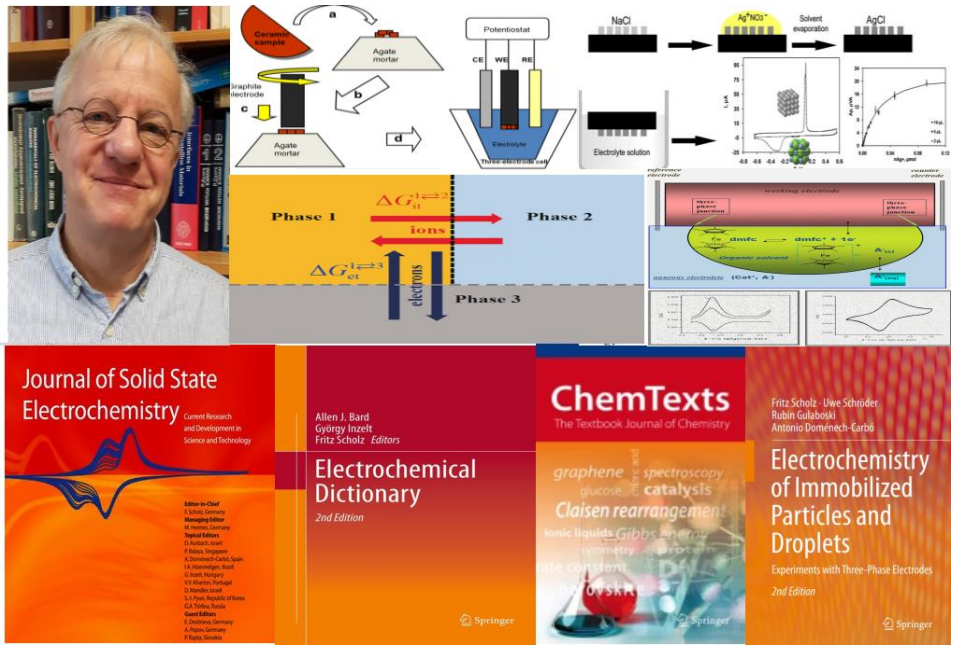

Fig. 7. Fritz Scholz (above left) and schemes of some of his most important developments in three-phase electrodes (above right). In the panel below we see some of the iconic books and journals authored and edited by Fritz Scholz.

2.8. *The champion of electroanalysis and biosensors: Joseph Wang (1948–)*

The primary objective of numerous voltammetric investigations is to establish a fundamental protocol for the development of so-called 'amperometric sensors' - devices tailored to detect specific compounds with high specificity. The advent of nanoparticles, particularly those based on graphene, as surface modifiers for working electrodes has significantly advanced the field of amperometric biosensors.[71–80] Forecasts suggest that within the next few decades, essential bodily functions will be monitored by non-invasive wearable devices situated externally on the body. Among the foremost pioneers in electroanalysis stands **Joseph Wang**, an esteemed professor from the United States, whose lifelong dedication has profoundly influenced the design of wearable sensors and laid down fundamental electrochemical principles for numerous sensing applications. Joseph Wang is the most remarkable electrochemist involved in pioneering the development of sensors worn on the body for monitoring chemical metabolites such as glucose, lactate, and electrolytes, thereby catalyzing the emergence of flexible bioelectronics. These wearable electrochemical devices not only facilitate measurement but also offer avenues for energy application on the body.

Born in 1948, Wang completed his studies at the Technion-Israel Institute of Technology before relocating to the United States in 1978 for postdoctoral research at the University of Wisconsin – Madison (USA). Subsequently, he joined the Department of Chemistry and Biochemistry at New Mexico State University (USA) in 1980, where he rose to become a Regents Professor and the Manasse Chair holder. From 2004 to 2008, Wang served as the Director of the Center for Bioelectronics and Biosensors at Arizona State University (USA), subsequently assuming the position of Chair of the Nanoengineering Department at the University of California, San Diego (USA) from 2014 to 2019. Currently, he holds the title of Distinguished Professor of Nanoengineering and SAIC Endowed Chair at the University of California, San Diego, where he also serves as the Director of the UCSD Center of Wearable Sensors. Wang's research interests span an extensive array of topics including electrochemical biosensors, nanomotors, wearable sensors, biomedical applications of nanomachines, and flexible stretchable materials, among others.

Wang's seminal contributions have earned him numerous international awards, including the Talanta Medal in 2021 and the TÜBA Science Award (Türkiye) in 2022 for his pioneering research in basic and engineering sciences. He has also been recognized with the Bruno Breyer Medal of the Royal Australian Chemical Institute in 2012, alongside multiple honorary doctorates and professorships. With a prolific publication record comprising over 1300 papers and 11 books, as well as holding 30 patents, Wang's impact on the field of

electrochemistry is immense. As the founder of the journal Electroanalysis and a key contributor to the IUPAC project on electrochemical DNA-based biosensors, Wang has played a pivotal role in advancing the field.

Through mentorship of over 50 PhD students and hosting of more than 400 researchers from around the globe, Wang has fostered a cadre of excellent scientists poised to carry forward his legacy. He is revered as a transformative figure in electrochemistry, bridging the gap between experimental sciences and engineering and laying the groundwork for the development of countless electrochemical biosensors. Wang's enduring influence and collaborative spirit serve as a beacon of inspiration for aspiring scientists and engineers, positioning him as an icon and motivator with outstanding personality in the field of electrochemistry.

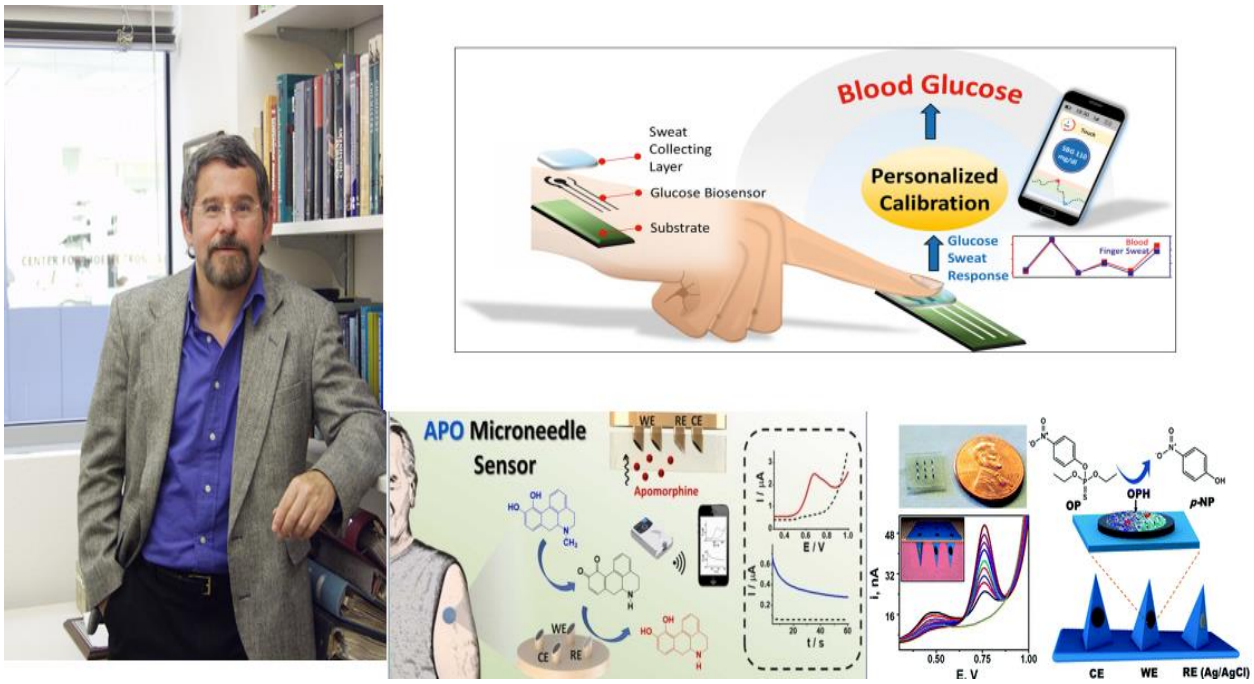

Fig. 8. Joseph Wang (left) and schemes of some of his amperometric sensors (right)

2.9. *They are the most remarkable persons of modern pulse voltammetric techniques: Milivoj Lovrić (1951–) and Valentin Mirčeski (1966–)*

Amidst the plethora of voltammetric operational systems that emerged in the 1950s, cyclic voltammetry stood out as a notable technique valued for both elucidating mechanisms and conducting kinetic measurements. Recognized for its effectiveness in probing various electrode mechanisms and phenomena occurring at the electrode/electrolyte interface, cyclic voltammetry has earned the epithet 'electrochemical spectroscopy'. Simultaneously, several adaptations to the applied potential waveform have been introduced. In this context, the advent of 'pulse voltammetric techniques', encompassing methods such as differential pulse voltammetry, square-wave voltammetry, and cyclic square-wave voltammetry, which have been acknowledged as swift, reliable, and sensitive electroanalytical tools. These techniques maintain the capability to unravel mechanistic intricacies akin to cyclic voltammetry. However, the potential of pulse voltammetric techniques concerning kinetic and thermodynamic evaluations, as well as their analytical applications, surpasses that of cyclic voltammetry. In our recent work,[1] we underscored that pulse voltammetric techniques stand on the shoulders of several pioneering women electrochemists, including Janet Osteryoung, Angela Molina, Šebojka Komorsky-Lovrić, Ana Maria Oliveira Brett, Anna Brainina, and others. Additionally, numerous eminent male electrochemists, such as John J. O'Dea, Robert Osteryoung, Milivoj Lovrić, Valentin Mirčeski, Zbigniew Stojek, Richard Compton, Alan Bond, Eduardo Laborda, Frank Marken, Adrian Miles, Fernando Garay, Lars Jeuken, Fraser Armstrong, Joseph Wang, and many more, have made significant contributions to the advancement of theories and analytical applications of pulse voltammetric techniques. I decided to highlight some of the achievements of **Milivoj**

Lovrić and **Valentin Mirčeski** together in this section of the paper because their scientific trajectories intersect in many aspects, and they both come from very small Balkan countries (Croatia and Macedonia, respectively) that have experienced considerable turbulences over the past 20 – 30 years.

Milivoj Lovrić, born in Croatia in 1951, completed his undergraduate studies at the University of Zagreb (Croatia) in 1974 and attained the title of Doctor of Science in 1983 under the supervision of Professor Marko Branica. He remained affiliated with the Rudjer Bošković Institute in Zagreb throughout his career until his retirement. Over the course of his scientific career, Milivoj Lovrić engaged in active collaboration with prominent figures in electrochemistry, including Alan Bond, Janet Osteryoung, Fritz Scholz, Richard Compton, Zbigniew Stojek, among others. He undertook research visits at various esteemed institutions worldwide, including Humboldt University in Berlin, University Buffalo in New York, University of North Carolina at Chapel Hill (USA), Geelong University (Australia), Greifswald University (Germany), Atomic Institute Julich (Germany), Oxford University (UK), among others.

Lovrić's primary focus lay in advancing theories related to electrochemical mechanisms, particularly in square-wave voltammetry, differential pulse voltammetry, cyclic staircase voltammetry, and other voltammetric techniques.[81–90] His research encompassed a wide array of subjects, ranging from small inorganic ions to complex systems such as enzymes and proteins. Through collaborative efforts, Milivoj Lovrić successfully elucidated numerous electrochemical mechanisms prevalent in the redox chemistry of significant systems, often navigating complexities arising from adsorption phenomena and diverse chemical equilibria.

Notably, Lovrić made substantial theoretical contributions to the understanding of processes inherent in the voltammetry of immobilized particles and droplets, a method pioneered by Fritz Scholz, wherein electron and ion transfers occur nearly simultaneously at the interface of three phases. Furthermore, he played a pivotal role in advancing theories pertaining to ion transfer processes investigated using three-phase electrodes. His coauthorship of the excellent book "Square-Wave Voltammetry–Theory and Application",[81] as well as numerous chapters in other electrochemical texts and entries in the "Electrochemical Dictionary",[64] underscore his significant scholarly contributions.

Throughout his career, Lovrić mentored several PhD students, including Valentin Mirčeski, Dijana Jadresko, and Fernando Garay, who made notable contributions to the field of pulse voltammetric techniques. Recognized as one of the top 2 % most influential scientists of all time by the List of Stanford University since 2018, Lovrić has also served as an editor for numerous esteemed electrochemistry journals. It is very fascinating that Milivoj Lovrić has the ability to articulate complex electrochemical phenomena in simple terms, making them accessible even to non-specialists in voltammetry. During our scientific discussions in Germany, one of my colleagues remarked: "Whenever Milivoj elucidates some complex electrochemical phenomena to me, it's like a veil being lifted from my eyes, and suddenly everything becomes clear." Alongside his collaborators, he developed several straightforward voltammetric methods facilitating the discernment of various electrochemical mechanisms. Moreover, Lovrić devised numerous theoretical voltammetric approaches enabling the exploration of kinetics and thermodynamics of relevant parameters associated with electron transfers, chemical reactions, or adsorption phenomena linked to the electron transfer step. Milivoj Lovrić is highly gifted scientist who can make very nice connections between chemistry, physics, and mathematics in order to explain important phenomena encountered in voltammetric experiments. Milivoj Lovrić has solidified his status as a leading figure in the realm of voltammetric techniques through the publication of over 180 papers, predominantly theoretical, in esteemed electrochemistry journals. Alongside Fritz Scholz and Šebojka Komorsky-Lovrić, their collaborative efforts related to ion transfer with electrochemistry at three-phase electrodes garnered them the award of the best paper in Electrochemistry Communication for the year 2000.[67] Despite his retirement a couple of years ago, Milivoj Lovrić remains actively engaged in publishing and reviewing for numerous journals, sustaining his enduring impact on the field of electrochemistry. He was married to Sebojka Komorsky-Lovrić, also an outstanding researcher in electrochemistry, who regretfully passed away in 2020.

Despite being among the younger cohort of electrochemists, **Valentin Mirčeski**'s significant contributions in both theory and application, notably through the utilization of square-wave voltammetry, have positioned him as one of the foremost individuals in elevating voltammetry to new heights. Born in Macedonia in 1966, he earned his undergraduate and postgraduate education in Mac-

edonia. In 1999, under the supervision of Milivoj Lovrić, he obtained title Doctor of Natural Sciences at the Zagreb University in Croatia. In 2001, he received the highly esteemed fellowship from the Alexander von Humboldt Foundation, undertaking a one-year postdoctoral position at Greifswald University in Germany, with Professor Fritz Scholz as his host. In 2002, he was appointed as a professor at the Faculty of Natural Sciences and Mathematics at Ss. Cyril and Methodius University in Skopje, Macedonia, where he continues to be employed. Throughout his remarkable scientific career, he has fostered fruitful collaborations with numerous prominent electrochemists, including Fritz Scholz, Milivoj Lovrić, Richard Compton, Angela Molina, Šebojka Komorsky-Lovrić, Eduardo Laborda, Maurice L'Her, and many others. Valentin Mirčeski has already contributed over 150 scientific papers to esteemed journals such as the Journal of the American Chemical Society, Electrochimica Acta, Nature Scientific Reports, Analytical Chemistry, Journal of Physical Chemistry, Electrochemistry Communication, Journal of Electroanalytical Chemistry, Journal of Solid State Electrochemistry, ChemTexts, Analytica Chimica Acta, Physical Chemistry Chemical Physics, Bioelectrochemistry, Langmuir, and many more.[91–100] His papers boast coauthors numbering over 200 individuals from around the globe, a testament to his openness to scientific collaboration. Having undertaken numerous research stays at prestigious institutions such as the University of Prague (Czech Republic), University of Greifswald (Germany), University of Saarland (Germany), University of Brest (France), University of Ljubljana (Slovenia), University of Zagreb (Croatia), University of Belgrade and University of Niš (Serbia), the University of Cluj (Romania), and University of Leipzig (Germany), he is currently engaged in multiple projects at the University of Lódź (Poland), where he also works as a professor. Valentin Mirčeski's scientific portfolio is remarkably diverse, encompassing a vast array of theoretical works delving into various electrochemical mechanisms, particularly those complicated by adsorption phenomena and coupled chemical reactions, studied mainly under conditions of square-wave voltammetry. Collaborating with Milivoj Lovrić, they developed straightforward methodological approaches for evaluating the kinetic parameters of electron transfer reactions by exploring phenomena such as 'split net square-wave peaks' and the 'quasi-reversible maximum'. In addition to his significant contributions in theoretical investigations concerning crucial aspects of diverse mechanisms under protein-film square-wave voltammetry conditions, Valentin Mirčeski leveraged his profound expertise in mathematics and chemistry to undertake significant re-evaluations of the iconic Butler-Volmer theory[97] alongside Richard Compton and Milivoj Lovrić as coauthors. Over the past 10 years, Valentin Mirčeski stands out as one of the few electrochemists who have made significant contributions to the theoretical development of innovative voltammetric techniques, specifically electrochemical faradaic spectroscopy[96] and differential square-wave voltammetry.[95] As one of the authors, he made notable contributions to the distinguished book "Square-Wave Voltammetry: Theory and Application"[81] published by Springer in 2007. Additionally, he contributed numerous entries to both editions of the iconic "Electrochemical Dictionary".[64] Valentin Mirčeski's theoretical papers are consistently crafted in a language that is accessible to both electrochemists and non-electrochemists alike. They provide practical insights for experimentalists, offering guidance on designing electrochemical experiments and extracting kinetic and thermodynamic parameters from the measurements. Valentin Mirčeski's experimental prowess is notably diverse. He has significantly advanced the field by designing valuable voltammetric sensors for detecting H_2O_2 in the gaseous phase. Additionally, together with his group, he has made remarkable contributions by developing simple electrochemical sensors capable of detecting important biomolecules directly in human blood serum.[100] Furthermore, he has devised ingenious voltammetric protocols for assessing the redox status of specific types of mouse cells. He has made significant contributions to understanding the kinetics and thermodynamics of processes occurring at three-phase electrodes[81,98,99] by introducing numerous novel theories and innovative experimental protocols in the process. Among his notable achievements is also the discovery of novel functions within couples from the coenzyme Q family.[94] His research, together with the colleagues from Saarland University (Germany), has unveiled entirely new aspects of coenzyme Q systems, particularly regarding their binding and transporting properties of calcium ions.

Due to his remarkable scientific accomplishments, Valentin Mirčeski was elected as one of the youngest members of the Macedonian Academy of Sciences in 2022. He has received numerous national and international awards, with the Young Investigator Award under the age of 40 presented by the French Electrochemical Association being particularly prestigious. Remarkably, his paper titled "Electrode Kinetic Measurements with

Square-Wave Voltammetry at a Constant Scan Rate" (published in Electrochimica Acta, 114 (2013) 667) was recognized as the most innovative study involving a young investigator. Valentin Mirčeski's generosity, willingness to engage in discussions, positive demeanor, and charismatic personality have earned him a reputation as one of the most cherished teachers and supervisors in various scientific and academic institutions. His enduring enthusiasm is a testament to the promising future contributions he will continue to make in the field of voltammetry.

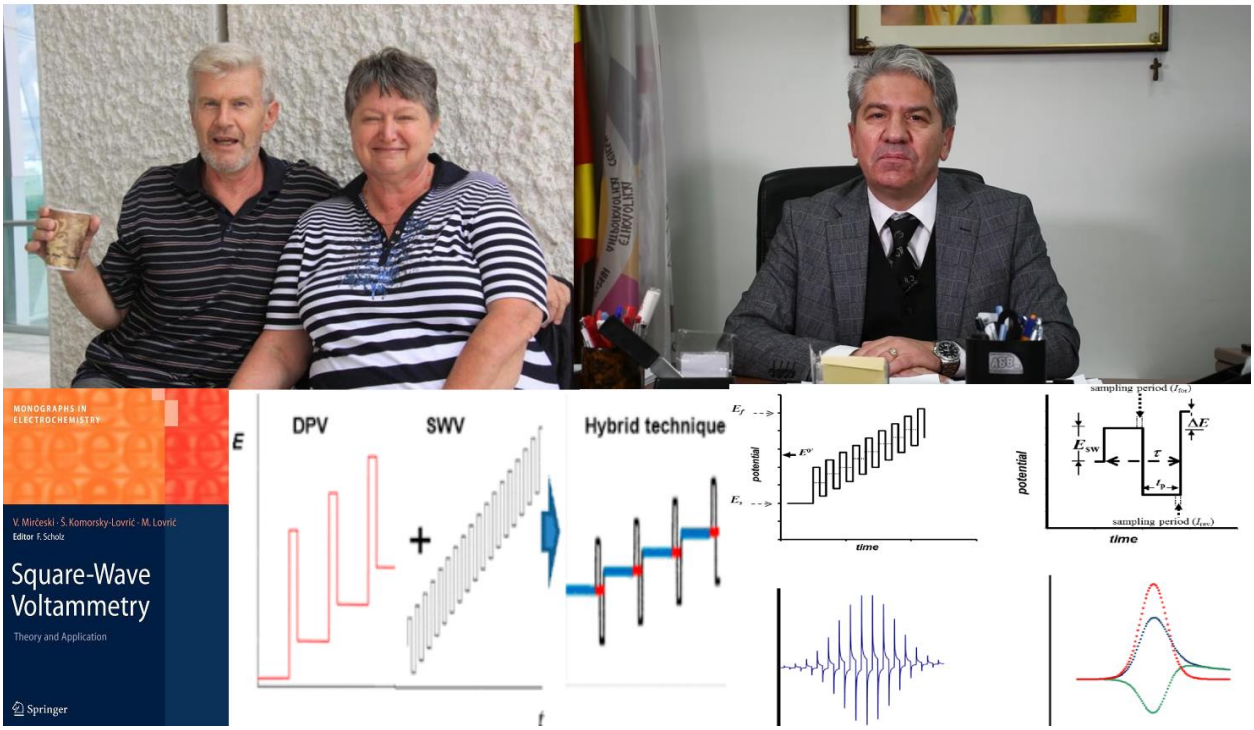

Fig. 9. Milivoj Lovrić (upper left) and his wife Šebojka Komorsky-Lovrić (upper middle) and Valentin Mirčeski (upper right). The lower panel shows some of the schemes of the techniques developed by Mirčeski and Lovrić.

2.10. *He is the father of modern inorganic voltammetry: Alan Maxwell Bond (1946–)*

Closing this overview, I pay tribute to an exceptional electrochemist who have reshaped voltammetry over the past 50 years,[101–110] particularly acknowledging the significant contributions of **Alan Maxwell Bond**, one of the foremost all-rounders in electrochemistry. Born in the small town of Cobden, Australia, in 1946, Alan Bond dedicated his entire scientific career to Australia. Serving as a professor at Melbourne and La Trobe University (Australia), he collaborated with numerous distinguished Australian chemists and initiated scientific partnerships with emerging young electrochemists worldwide. Since the 1980s, Alan Bond's laboratory has resembled a small United Nations, with many scientists mentioned in this overview having collaborated with him or spent some time in his lab.

In 1995, Alan Bond moved to Monash University (Australia), where he was bestowed with an Emeritus position in the School of Chemistry. His achievements in electrochemistry span a wide spectrum, making it challenging to encapsulate all his contributions from the 1970s to the present. With a deep interest in inorganic chemistry, Bond developed numerous theoretical works aimed at elucidating electrochemical mechanisms governing the transformation of various inorganic systems. Bond's significant contributions to steady-state voltammetry at microelectrodes[102–104] have laid foundational principles for utilizing this technique in kinetic evaluations and analytical applications across various systems. He has also made notable strides in exploring electrochemistry at room temperature in ionic liquids,[105] particularly in the field of electrosynthesis. Additionally, Bond's work on modifying carbon nanotube surfaces has facilitated the construction of specific sensors for quantifying various inorganic systems.

Recognizing the potential of multi-frequency Fourier transform alternating currents[108,109] for kinetic evaluations, Bond has played

a pivotal role in establishing novel techniques and voltammetric approaches in electrochemistry. His design of valuable ion-selective electrodes for selective detection of inorganic cations and anions, coupled with his utilization of electron microscopy and x-ray electron analyses, has provided structural insights into many inorganic crystals. Bond's involvement in the establishment of abrasive stripping voltammetry as a simple technique for accessing the redox activity of water-insoluble redox crystals further underscores his pioneering contributions to electrochemistry. He is also the coauthor of several notable electrochemical books, including the widely acclaimed "Modern Polarographic Methods in Analytical Chemistry".[101] In his very recent works, Alan Bond and his team introduced a 'machine learning algorithm',[110] a sophisticated statistical method enabling unsupervised machine learning to organize and categorize voltammetric data independently. This elegant approach provides a clear insight into the mechanisms of specific electrochemical processes, particularly beneficial for individuals not specialized in voltammetry.

Described as a clever and quick thinker, Bond leverages his profound knowledge in physics and chemistry to bridge the gap between theoretical and experimental electrochemistry. With over 1000 published scientific papers in prestigious journals garnering over 32000 citations, Bond has received numerous awards, including the Rennie Medal, Australian Analytical Chemistry Medal, Liversidge Award, Stokes Medal, H.G. Smith Medal, Burrows Award, and The Royal Society of Chemistry and Faraday Medal.

His remarkable scientific journey is detailed elsewhere (A Tribute to Alan Bond on his 70th Birthday: 50 Years of Electrochemistry - Martin - 2018 - ChemElectroChem - Wiley Online Library), and we can only wish Alan Bond continued energy and joy in his future endeavors. Undoubtedly, his achievements have illuminated new pathways in the field of inorganic electrochemistry.

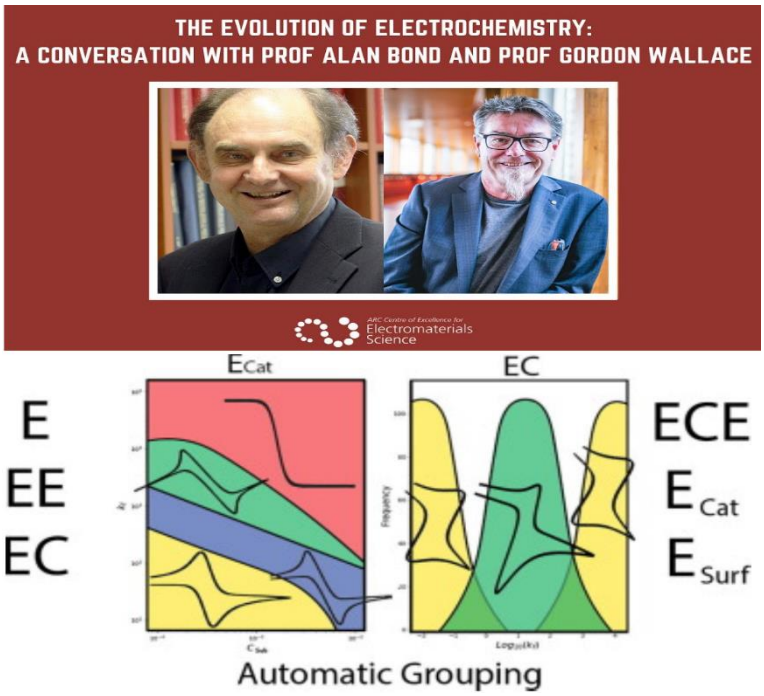

Fig. 10. Alan M. Bond (above left panel) and scheme of machine learning algorithm of different electrochemical mechanisms in cyclic voltammetry (below)

3. CONCLUSIONS

Voltammetry, despite its complexity in theoretical underpinnings, remains pervasive within scientific institutions due to the ease of conducting electrochemical experiments and the valuable insights gleaned from relatively inexpensive and straightforward experimental setups. As I gathered data for this featured article highlighting some of the giants in voltammetry and their notable achievements, I was struck by my limited knowledge of many of the achievements of these remarkable individuals, despite my familiarity with many of them over time. What struck me most about many of these scientists is their enduring enthusiasm for voltammetry, which persists un-

changed from their fervor of three to four decades ago. Even today, a trend in voltammetry is the predominance of 'old school' researchers in publishing new advancements, with only a few emerging young scientists offering innovative perspectives. This raises concerns about the future trajectory of electrochemical sciences. Indeed, the allure of scientific research has diminished over time, potentially creating a void in electrochemistry. While the field has a strong foundation built by the outstanding electrochemists discussed in this brief overview, further progress necessitates more intensive interdisciplinary collaboration to ensure its continued relevance in chemistry, physics, medicine, and engineering. However, the window for such advancements may be closing. In the end, I should apologize that, due to space constraints, I was unable to cover the accomplishments of many other outstanding electrochemists such as Gyorgy Inzelt, Zbigniew Stojek, Hubert Girault, Fred Anson, Keith Oldham, Dieter Kolb, Carlos Pereira, Uwe Schroeder, Ralph Adams, Jurgen Heinze, Frank Marken and numerous others who have elevated electrochemistry to a much higher level over the last 50 years.

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REFERENCES

(1) Gulaboski, R.; Bogeski. I., Review: Women's contribution in the pulse voltammetric theories and applications: Pulse voltammetry stands on the shoulders of outstanding women electrochemists. *J. Electrochem. Soc*. **2022**, *169*, 037519. DOI: 10.1149/1945-7111/ac5cef

(2) Heyrovský, J., Elektrolysa se rtutovou kapkovou kathodou. *Chemické listy*, **1922**, *16*, 256–264.

(3) Heyrovský, J., The processes at the dropping mercury cathode. I. The deposition of metals. *Trans. Faraday Soc*. **1924**, *19*, 692–702.

(4) Heyrovský, J., The processes at the dropping mercury cathode. II. The hydrogen overpotential. *Trans. Faraday Soc*. **1924**, *19*, 785–789.

(5) Heyrovský, J., Researches with the dropping mercury cathode. Part I. General introduction. *Rec. Trav. Chim*. **1925**, *44*, 488–495.

(6) Heyrovský, J., Researches with the dropping mercury cathode. Part II. The polarograph. *Rec. Trav. Chim*. **1925**, *44*, 496–498.

(7) Heyrovský, J., Researches with the dropping mercury cathode. Part III. A theory of overpotential. *Rec. Trav. Chim*. **1925**, *44*, 499–502.

(8) Heyrovský, J., Estimation of oxygen by the polarographic method. *Arhiv. Hem. Farm*. **1931**, *5*, 163–173.

(9) Heyrovský, J., On the limiting currents in electrolysis with dropping mercury cathode. *Arhiv. Hem. Farm*. **1934**, *8*, 11–17.

(10) Heyrovský, J.; Ilkovič, D., The significance of the depolarization potentials derived from intensity-potential curves obtained by electrolysis at the dropping mercury electrode. *Chemické listy*, **1935**, *29*, 234–237.

(11) Liu, H. Y.; Fan, F. R. F.; Lin. C. W.; Bard A. J., Scanning electrochemical and tunneling ultramicroelectrode microscope for high-resolution examination of electrode surfaces in solution. *J. Am. Chem. Soc*. **1986**, *108*, 3838–3839. DOI: 10.1021/Ja00273A054

(12) Shea, T. V.; Bard, A. J., Digital simulation of homogeneous chemical reactions coupled to heterogeneous electron transfer and applications at platinum/mica/platinum ultramicroband electrodes. *Anal. Chem*. **1987**, *59*, 2101–2111. DOI: 10.1021/Ac00144A021

(13) Bard, A. J.; Murray, R. W., Electrochemistry. *Proc. Natl. Acad. Sci. USA*, **2012**, *109*, 11484–6. PMID 22802653. DOI: 10.1073/pnas.1209943109

(14) Fan F. R. F.; Bard, A. J., Scanning tunneling microscopic studies of platinum electrode surfaces. *Anal. Chem*. **1988**, *60*, 751–758. DOI: 10.1021/Ac00159A005

(15) Fan, F. R. F.; Kwak, J.; Bard, A. J., Single molecule electrochemistry, *J. Am. Chem. Soc*. **1996** *118*: 9669–9675. DOI: 10.1021/Ja9610794

(16) Lee, C.; Kwak, J.; Bard, A. J., Application of scanning electrochemical microscopy to biological samples, *Proc. Natl. Acad. Sci. USA*, **1990**, *87*, 1740–1743. DOI: 10.1073/Pnas.87.5.1740

(17) Pierce, D. T.; Unwin, P. R.; Bard, A. J., Scanning electrochemical microscopy. 17. Studies of enzyme-mediator kinetics for membrane- and surface-immobilized glucose oxidase. *Anal. Chem*. **1992**, *64* 1795–1804. DOI: 10.1021/Ac00041A011

(18) *Electrochemical Methods*. Bard, A. J.; Faulkner, L. R., eds.. Wiley, New York, 1980.

(19) Bard, A. J., Between electrode and solution. *Nature*. **1994**, *368*, 597–598.

(20) Fan, F. R. F.; Bard, A. J., Electrochemical detection of single molecules. *Science*. **1995**, *267*, 871–874. DOI: 10.1126/Science.267.5199.871

(21) Amatore, C.; Arbault, S.; Bouret, Y.; Cauli, B.; Guille, M.; Rancillac, A.; Rossier, J., Detection of nitric oxide release during neuronal activity with platinized carbon fiber microelectrodes. *ChemPhysChem.* **2006**, *7*, 181–187. DOI: 10.1002/cphc.200500202

(22) Li, Y. T.; Zhang, S. H.; Wang, L.; Xiao, R. R.; Liu, W.; Zhang, X. W.; Zhou, Z.; Amatore, C.; Huang., W. H., Nanoelectrode for amperometric monitoring of individual vesicular exocytosis inside single synapses. *Angew. Chem. Int. Ed.* **2014**, *53*, 12456–12460. DOI: 10.1002/anie.201404744

(23) Qi, Y. T.; Jiang, H.; Wu, W. T.; Zhang, F. L.; Tian, S. Y.; Fan, W. T.; Liu, Y. L.; Amatore, C.; Huang, W. H., Homeostasis inside single activated Phagolysosomes: Quantitative and selective measurements of submillisecond dynamics of ROS/RNS production with a nanoelectrochemical sensor. *J. Am. Chem. Soc.* **2022**, *144*, 9723–9733. DOI: 10.1021/jacs.2c01857

(24) Wang, Y.; Noel, J.-M.; Velmurugan, J.; Nogala, W.; Mirkin, M. V.; Lu, C.; Guille, M.; Collignon, M.; Lemaitre, F.; Amatore, C., Nanoelectrodes for determination of reactive oxygen and nitrogen species inside biological cells. *Proc. Natl. Acad. Sci. USA.* **2012**, *109*, 11534–11539. DOI: 10.1073/pnas.1201552109

(25) Amatore, C.; Jutand, A., Mechanistic and kinetic studies of palladium catalytic systems. *J. Organomet. Chem.* **1999**, *576*, 254–278. DOI: 10.1016/S0022-328X(98)01063-8

(26) He, Q.; Zeng, L.; Han, L.; Sartin, M. M.; Peng, J.; Li, J. F.; Oleinick, A.; Svir, I.; Amatore, C.; Tian, Z. Q.; Zhan, D., Electrochemical storage of atomic hydrogen on single layer graphene. *J. Am. Chem. Soc.* **2021**, *143*, 18419–18425. DOI: 10.1021/jacs.1c05253

(27) Hillard, E.; Vessières, A.; Thouin, L.; Jaouen, G.; Amatore, C., Ferrocene-mediated proton-coupled electron transfer in a series of Ferrocifen-type breast cancer drug candidates. *Angew. Chem., Int. Ed.* **2006**, *45*, 285–290. DOI: 10.1002/anie.200502925

(28) Amatore, C.; Fosset, B.; Bartelt, J. E.; Deakin, M. R.; Wightman, R. M., Electrochemical kinetics at microelectrodes. Part 5. Migrational effects on steady or quasi-steady state voltammograms. *J. Electroanal. Chem.* **1988**, *256*, 255–268. DOI: 10.1016/0022-0728(88)87002-5

(29) Amatore, C.; Savéant, J.-M.; Tessier, D., Charge transfer at partially blocked surfaces. A model for the case of microscopic active and inactive sites. *J. Electroanal. Chem.* **1983**, *147*, 39–51. DOI: 10.1016/S0022-0728(83)80055-2

(30) Amatore, C.; Savéant, J.-M., Mechanism and kinetic characteristics of the reduction of carbon dioxide in media of low proton availability. *J. Am. Chem. Soc.* **1981**, *103*, 5021–5023. DOI: 10.1021/ja00407a008

(31) *Understanding Voltammetry*, 2nd ed.; Compton, R. G.; Banks, C. E., eds.; World Scientific, UK, 2018.

(32) Yang, M.; Compton, R. G., Voltammetry of adsorbed species: Nonideal interactions leading to phase transitions. *J. Phys. Chem C,* **2020**, *124*, 18031–18044. DOI: 10.1021/acs.jpcc.0c03791

(33) Elliott, J. R.; Le, H.; Yang, M.; Compton, R. G., Using simulations to guide the design of amperometric electrochemical sensors based on mediated electron transfer. *ChemElectroChem*. **2020**, *7*, 2797–2815. DOI: 10.1002/celc.202000674

(34) Miao, R.; Chen, L.; Shao, L.; Zhang, B.; Compton, R., Electron transfer to decorated graphene oxide particles. *Angew. Chem. Int. Ed*. **2019**, *58*, 12549–12552. DOI: 10.1002/anie.201907393

(35) Laborda, E.; Molina, A,; Fernandes Espin, V.; Martinez-Ortiz, F.; Garcia de la Torre, J.; Compton, R., Single fusion events at polarized liquid-liquid interface. *Angew. Chem. Int. Ed*. **2016**, *56*, 782–785. DOI: 10.1002/anie.201610185

(36) Sepunaru, L.; Sokolov, S. V.; Holter, J.; Young, N. P.; Compton, R., Electrochemical red blood cell counting: One at a time. *Angew. Chem. Int. Ed*. **2016**, *55*, 9768–9771. DOI: 10.1002/anie.201605310

(37) Ly, L.; Batchelor-McAuley, C.; Tschulik, K.; Kaetelhoen, E.; Compton, R., A critical evaluation of the interpretation of electrocatalytic nanoimpacts. *J. Phys. Chem C*, **2014**, *118*, 17756–17763. DOI: 10.1021/jp504968j

(38) Nissim, R.; Compton, R., Noneznymatic electrochemical superoxide sensor. *ChemElectroChem*. **2014**, *1*, 763–771. DOI: 10.1002/celc.201300209

(39) Cheng, W.; Zhou, X-F.; Compton, R. G., Electrochemical sizing of organic nanoparticles. *Angew. Chem. Int. Ed*. **2013**, *52*, 12980–12982.

(40) Laborda, E.; Henstridge, M. C.; Batchelor-McAuley, C.; Compton, R. G., Asymmetric Marcus-Hush theory for voltammetry. *Chem. Soc. Rev*. **2013**, *42*, 4894–4905. DOI: 10.1039/c3cs35487c

(41) Savéant, J.-M.; Costentin, C., *Elements of Molecular and Biomolecular Electrochemistry*, 2nd ed.; John Wiley & Sons, Inc., Hoboken, NJ, 2019.

(42) Mastragostino, M.; Nadjo, L.; Savéant, J.-M., Disproportionation and ECE mechanisms. I. Theoretical analysis. Relationships for linear sweep voltammetry. *Electrochim. Acta* **1968**, *13*, 721−749. https://doi.org/10.1016/0013-4686(68)85007-8

(43) Savéant, J.-M., Molecular catalysis of electrochemical reactions. *Chem. Rev*. **2008**, *108*, 2348−2378. https://doi.org/10.1021/cr068079z

(44) Savéant, J.-M.; Vianello, E., Potential-sweep voltammetry. General theory of chemical polarization. *Electrochim. Acta* **1967**, *12*, 629−646.

(45) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat; M'Halla, F.; Savéant, J.-M., Homogeneous redox catalysis of electrochemical reactions. Part V. Cyclic Voltammetry. *J. Electroanal. Chem. Interf. Electrochem*. **1980**, *113*, 19−40. DOI: 0.1016/S0022-0728(80)80508-0

(46) Savéant, J.-M., Catalysis of chemical reactions by electrodes. *Acc. Chem. Res*. **1980**, *13*, 323−329. https://doi.org/10.1021/ar50153a005

(47) Savéant, J.-M., A simple model for the kinetics of dissociative electron transfer in polar solvents. Application to the homogeneous and heterogeneous reduction of alkyl halides. *J. Am. Chem. Soc*. **1987**, *109*, 6788−6795. https://doi.org/10.1021/ja00256a037

(48) Bourdillon, C.; Demaille, C.; Moiroux, J.; Savéant, J.-M., Catalysis and mass transport in spatially ordered enzyme assemblies on electrodes. *J. Am. Chem. Soc*. **1995**, *117*, 11499−11506. DOI: https://doi.org/10.1021/ja00151a013

(49) Savéant, J.-M., Proton relays in molecular catalysis of electrochemical reactions: Origin and limitations of the boosting effect. *Angew. Chem., Int. Ed*. **2019**, *58*, 2125−2128. DOI: 10.1002/anie.201812375

(50) Costentin, C.; Savéant, J.-M., Cyclic voltammetry analysis of electrocatalytic films. J. *Phys. Chem. C,* **2015**, *119*, 12174−12182. DOI: 10.1021/acs.jpcc.5b02376

(51) Morello, G.; Megarity, C.; Armstrong, F. A., The power of electrified nanoconfinement for energising, controlling and observing long enzyme cascades. *Nature Commun*. **2021**, *12*, 340. DOI: 10.1038/s41467-020-20403-w

(52) Evans, R.; Siritanaratakul, B.; Megarity, C.; Pamdey, K.; Esterle, T. F.; Badiani, S.; Armstrong, F., The value of

enzymes in solar fuel research-efficient electrocataysts through evolution. *Chem. Soc. Rev*. **2018**, *48*, 2039–2052. DOI: 10.1039/c8cs00546j

(53) Megarity, C.; Esselborn, J.; Hexterm S. V.; Wittkamp, F.; Apfel, U-P.; Happe, T.; Armstrong, F., Electrochemical investigations of the mechanism of assembly of the active-site H-cluster of [Fe-Fe] hydrogenases. *J. Am. Chem. Soc*. **2016**, *138*, 15227–15233. DOI: 10.1021/jacs.6b09366

(54) Amstrong, F. A.; Evans, R.; Hexterm S. V.; Murphy, B. J.; Roessler, M. M.; Wulff, P., Guiding principles of hydrogenases catalysis instigated and clarified by protein film electrochemistry. *Acc. Chem. Res*. **2016**, *49*, 884–892. DOI: 10.1021/acs.accounts.6b00027

(55) Vincent, K. A.; Blanford, C. F.; Belsey, N. A.; Weiner, J. H.; Armstrong, F. A., Enzyme catalysis on conducting graphite particles. *Nat. Chem. Biol*. **2007**, *3*, 761–762. DOI: 10.1038/nchembio.2007.47

(56) Wijma, H. J.; Jeukem L. J. C.; Verbeet, M. P.; Armstrong, F. A.; Canters, G. W., Protein film voltammetry of copper-containing nitrite reductase reveals reversible inactivation. *J. Am. Chem. Soc.* **2007**, *129*, 8557–8565. DOI: 10.1021/ja071274q

(57) Vincent, K. A.; Cracknell, J. A.; Lenz, O.; Zebger, I.; Friedrich, B.; Armstrong, F., Electrocatalytic hydrogen oxidation by an enzyme at high carbon monoxide or oxygen level. *Proc. Natl. Acad. Sci. USA*, **2005**, *102*, 16951–16954. DOI: 10.1073/pnas.0504499102

(58) Lamle, S. E.; Albracht, S. P. J.; Armstrong, F. A., The mechanism of activation of a [Ni-Fe]-hydrogenase by electrons, hydrogen, and carbon monoxide. *J. Am. Chem. Soc*. **2005**, *127*, 6595–6604. DOI: 10.1021/ja0424934

(59) Jeukem L. J. C.; Jones, A. K.; Chapman, S. K.; Cecchini, G.; Armstrong, F. A., Electron-transfer mechanisms through biological redox chains in multicenter enzymes. *J. Am. Chem. Soc*. **2002**, *124*, 5702–5713. DOI: 10.1021/ja012638w

(60) Armstrong, F. A., Electron transfer and coupled processes in protein film voltammetry. *Biochem. Soc. Trans*. **1999**, *27*, 206–210. DOI: 10.1042/bst0270206

(61) Scholz, F.; Lange, B., Abrasive stripping voltammetry-an electrochemical solid state spectroscopy of wide applicability. *TrAC-Trend Anal. Chem*. **1992**, *11*, 359–367. https://doi.org/10.1016/0165-9936(92)80025-2

(62) Scholz, F., *Electrochemical Methods: Guide to Experiments and Applications*. 2nd ed.; Springer, Berlin, Germany, 2010.

(63) Scholz, F.; Schroder, U.; Gulaboski, R.; Domenech-Carbo, A., *Electrochemistry of Immobilized Particles and Droplets: Experiments with Three-phase Electrodes*. 2nd ed.; Springer, Berlin, Germany, 2015.

(64) *Electrochemical Dictionary*, 2nd ed.; Bard, A. J.; Inzelt, G.; Scholz, F., eds.; Springer, Berlin, Germany, 2014.

(65) Scholz, F.; Mayer, B., Electrochemical solid state analysis: state of the art. *Chem. Soc. Rev*. **1994**, *23*, 341–347.

(66) Grygar, T.; Marken, F.; Schroder, U.; Scholz, F., Electrochemical analysis of solids. A review. *Coll. Czech Chem. Commun*. **2002**, *67*, 163–208.

(67) Scholz, F.; Komorsky-Lovrić, Š.; Lovrić, M., A new access to Gibbs energies of transfer of ions across liquid/liquid interfaces and a new method to study electrochemical processes at well-defined three-phase junction. *Electrochem. Commun*. **2000**, *2*, 112–118. https://doi.org/10.1016/S1388-2481(99)00156-3

(68) Gulaboski, R.; Mirčeski, V.; Scholz, F., An electrochemical method for the determination of the standard Gibbs energy of anion transfer between water and n-octanol. *Electrochem. Commun*. **2002**, *4*, 277–283. https://doi.org/10.1016/S1388-2481(02)00264-3

(69) Rosenbaum, M.; Zhao, F.; Schroder, U.; Scholz, F., Interfacing electrocatalysis and biocatalysis with tungsten carbide: a high performance, nobel-metal free microbial fuel cell. *Angew. Chem. Int. Ed*. **2006**, *45*, 6658–6661. doi.org/10.1002/anie.200602021

(70) Scholz, F., Voltammetric techniques of analysis: the essentials. *ChemTexts* **2015**, *1*, 17. https://doi.org/10.1007/s40828-015-0016-y

(71) Wang, J., *Stripping Analysis: Principles, Instrumentation and Applications*, VCH Publishers, Deerfield Beach, 1985.

(72) Wang, J. In: *Electroanalytical Chemistry* (Bard, A. J.; ed.), Vol 16. Marcel Dekker, New York, **1989**.

(73) Blaedel, W. J.; Wang, J., Mixed immobilized enzyme-porous electrode reactor. *Anal. Chem*. **1980**, *52*, 1426–1429.

(74) Wang, J., Recent advances in stripping analysis. *Fresenius J. Anal. Chem*. **1990**, *337*, 508–511. https://doi.org/10.1007/BF00322854

(75) Wang, J., Amperometric biosensors for clinical and therapeutic drug monitoring: a review. *J. Pharm. Biomed. Anal*. **1999**, *19*, 47–53. https://doi.org/10.1016/S0731-7085(98)00056-9

(76) Wang, J., Carbon-nanotube based electrochemical biosensors: A review. *Electroanalysis*, **2005**, *17*, 7–14. doi.org/10.1002/elan.200403113

(77) Wang, J., Nanomaterials-based electrochemical biosensors. *Analyst*, **2005**, *130*, 421–426. https://doi.org/10.1039/B414248A

(78) Kagan, D.; Balasubramanian, S.; Wang, J., Chemically triggered swarming of gold microparticles. *Angew. Chem. Int. Ed*. **2010**, *50*, 503–506. doi.org/10.1002/anie.201005078

(79) Li, J.; De Avila, B. E.-F.; Gao, W.; Zhang, L.; Wang, J., Micro/nanorobots for biomedicine: delivery, surgery, sensing and detoxification. *Sci. Robotics* **2017**, *2*. DOI: 10.1126/scirobotics.aam6431

(80) Hartel, M. C.; Dongwook, L.; Weiss, P. S.; Wang, J.; Kim, J., Resettable sweat-powered wearable electronic biosensors. *Biosens. Bioelect*. **2022**, *215*, 114565. https://doi.org/10.1016/j.bios.2022.114565

(81) Mirčeski, V.; Komorsky-Lovrić, Š.; Lovrić, M., *Square-wave Voltammetry, Theory and Application*, Scholz, F. ed.; Springer, Berlin, Germany, 2007.

(82) Lovrić, M.; Osteryoung, J., Theory of differential normal pulse voltammetry. *Electrochim. Acta*, **1982**, *27*, 963–968. https://doi.org/10.1016/0013-4686(82)80220-X

(83) Lovrić, M.; O'Dea, J. J.; Osteryoung, J., Faradaic response in derivative and differential normal pulse voltammetry. *Anal. Chem*. **1983**, *55*, 704–708. https://doi.org/10.1021/ac00255a028

(84) Lovrić, M.; Komorsky-Lovrić, Š.; Bond, A., Theory of square-wave stripping voltammetry and chronoamperometry of immobilized reactants. *J. Electroanal. Chem. Interf. Electrochem*. **1991**, *319*, 1–18. https://doi.org/10.1016/0022-0728(91)87064-B

(85) Garay, F.; Lovrić, M., Square-wave voltammetry of quasi-reversible electrode processes with coupled homogeneous chemical reactions. *J. Electroanal. Chem*. **2002**, *518*, 91–102. https://doi.org/10.1016/S0022-0728(01)00695-7

(86) Lovrić, M.; Scholz, F., A model for the propagation of a redox reaction through microcrystals. *J. Solid State Electrochem*. **1997**, *1*, 108–113. https://doi.org/10.1007/s100080050030

(87) Lovrić, M.; Scholz, F., Modeling cyclic voltammograms of simultaneous electron and ion transfer reactions at conic film three-phase electrode. *J. Electroanal. Chem*. **2003**, *540*, 89–96. https://doi.org/10.1016/S0022-0728(02)01279-2

(88) Lovrić, M.; Jadreško, D., Theory of square-wave voltammetry of quasireversible electrode reactions using an inverse scan direction. *Electrochim. Acta* **2010**, *55*, 948–951. https://doi.org/10.1016/j.electacta.2009.09.043

(89) Lovrić, M.; Jadreško, D.; Komorsky-Lovrić, Š., Theory of square-wave voltammetry of electrode reaction followed by the dimerization of the product. *Electrochim. Acta* **2013**, *90*, 226–231. https://doi.org/10.1016/j.electacta.2012.11.101

(90) Lovrić, M.; Pižeta, I.; Komorsky-Lovrić, Š., A square-wave voltammetry in a cathodic stripping mode. *Electroanalysis*, **1992**, *4*, 327-337. https://doi.org/10.1002/elan.1140040311

(91) Mirceski, F.; Gulaboski, R.; Lovrić, M.; Bogeski, I.; Kappl, R.; Hoth, M., Square-wave voltammetry: a review on recent progress. *Electroanalysis*, **2013**, *25*, 2411–2422. https://doi.org/10.1002/elan.201300369

(92) Gulaboski, R.; Mirceski, V., Application of voltammetry in biomedicine-recent achievements in enzymatic voltammetry. *Maced. J. Chem. Chem. Eng*. **2020**, *39*, 153–166. https://doi.org/10.20450/mjcce.2020.2152

(93) Mirčeski, V.; Lovrić, M., Split square-wave voltammograms of surface redox reactions. *Electroanalysis*, **1997**, *9*, 1283–1287. doi.org/10.1002/elan.1140091613

(94) Bogeski, I.; Gulaboski, R.; Kappl, R.; Mirceski, V.; Stefova, M.; Petreska, J.; Hoth, M., Calcium binding and transport by coenzyme Q. *J. Am. Chem. Soc*. **2011**, *133*, 9293–9303. https://doi.org/10.1021/ja110190t

(95) Mirceski, V.; Guziejewski, D.; Stojanov, L.; Gulaboski, R., Differential square-wave voltammetry. *Anal. Chem.* **2019**, *91*, 14904–14910. https://doi.org/10.1021/acs.analchem.9b03035

(96) Jadreško, D.; Guziejewski, D.; Mirčeski, V., Electrochemical faradaic spectroscopy. *ChemElectroChem*. **2018**, *5*, 187–194. doi.org/10.1002/celc.201700784

(97) Mirceski, V.; Lovric, M.; Compton, R. G.; Ullah, N., Revisiting the Butler-Volmer electrode kinetics: Separating the anodic and cathodic current components of a quasi-reversible electrode reactions in staircase voltammetry. *J. Electroanal. Chem*. **2024**, 118111. https://doi.org/10.1016/j.jelechem.2024.118111

(98) Mirčeski, V., Charge transfer kinetics in thin-film voltammetry. Theoretical study under conditions of square-wave voltammetry. *J. Phys. Chem. B*, **2005**, *108*, 13719–13725. https://doi.org/10.1021/jp0487152

(99) Quentel, F.; Mirčeski, V.; L'Her, M., Lutetium bis(tetra-tert-butylphthalocyaninato): A superior redox probe to study the transfer of anions and cations across the water/nitrobenzene interface by means of square-wave voltammetry at the three-phase electrode. *J. Phys. Chem. B*, **2005**, *109*, 1262–1267. https://doi.org/10.1021/jp045914c

(100) Kokoskarova, P.; Stojanov, L.; Najkov, K.; Ristovska, N.; Ruskovska, T.; Skrzypek, S.; Mirceski, V., Square-wave voltammetry of human blood serum *Sci. Rep*. **2023**, *13*, 8485. https://doi.org/10.1038/s41598-023-34350-1

(101) Bond, A. M., *Modern Polarographic Methods in Analytical Chemistry*, CRC Press, 2020.

(102) Bond, A. M., Past, present and future contributions of microelectrodes to analytical studies employing voltammetric detection. A review. *Analyst*, **1994**, *119*, 1R-21R. doi.org/10.1039/AN994190001R

(103) Bond, A. M.; Oldham, K. B.; Zoski, C. G., Steady-state voltammetry. *Anal. Chim. Acta* **1989**, *216*, 177–230. https://doi.org/10.1016/S0003-2670(00)82009-7

(104) Zoski, C. G.; Bond, A. M.; Allinson, E. T.; Oldham, K. B., How long does it take a microelectrode to reach a voltammetric steady state? *Anal. Chem*. **1995**, *67*, 1691–1695.

(105) Zhao, C.; Burrell, G.; Torriero, A. A. J.; Separovic, F.; Dunlop, N. F.; MacFarlane, D. R., Electrochemistry of room temperature protic ionic liquids. *J. Phys. Chem. B* **2008**, *112*, 6923–6936. https://doi.org/10.1021/jp711804j

(106) Bond, A. M.; Duffy, N. W.; Guo, S. X.; Zhang, J.; Elton, D., Changing the look of voltammetry. *Anal. Chem*. **2005**, *77*, 186A–195A. https://doi.org/10.1021/ac00200a008

(107) Ding, L.; Bond, A. M.; Zhai, J.; Zhang, J., Utilization of nanoparticle labels for signal amplification in ultrasensitive electrochemical affinity biosensors: a review. *Anal. Chim. Acta* **2013**, *797*, 1–12. https://doi.org/10.1016/j.aca.2013.07.035

(108) Guo, S.; Zhang, J.; Elton, D. M.; Bond, A. M., Fourier transform large amplitude alternating current cyclic voltammetry of surface-bound azurin. *Anal. Chem*. **2004**, *76*, 166–177. https://doi.org/10.1021/ac034901c

(109) Bond, A. M.; O'Halloran, R. J.; Ruzic, I.; Smith, D. E., Fundamental and second harmonic alternating current cyclic voltammetry theory and experimental results for simple electrode reactions involving solution-soluble redox couples. *Anal. Chem*. **1976**, *48*, 872–883. https://doi.org/10.1021/ac60370a032

(110) Gundry, L.; Kennedy, G.; Bond, A. M.; Zhang, J., Establishing zone regions in cyclic voltammetry using unsupervised machine learning. *J. Electroanal. Chem*. **2023**, 117551. https://doi.org/10.1016/j.jelechem.2023.117551