Tribute to Bernard Tribollet

The authors of this foreword started their collaboration with Bernard Tribollet many years ago. The dates of the earliest co-authored papers are 1988 for Nadine Pêbêre and Marco Musiani, 1992 for Oscar Mattos, 1996 for Mark Orazem, and 2005 for Vincent Vivier, the youngest person in our group. The fact that there were joint publications ever since testifies to how interesting and rewarding working with Bernard has been for us all.

Bernard's research activities have had a wide scope, covering a variety of materials and processes. His work is characterized by the development and use of innovative techniques of investigation and by rigorous quantitative analysis of experimental data through physico-mathematical models.

Bernard's activity started at the crossroad between electrochemistry and fluid dynamics. In the beginning of the eighties, in the laboratory of Israel Epelboin, in collaboration with Claude Deslouis, Bernard advanced the electrohydrodynamical (EHD) impedance technique (i.e. the frequency response of an electrochemical system to a perturbation of the angular speed of a rotating disk electrode) to study heterogeneous reactions on a uniformly accessible surface [5,9,14,15,24,Cl]. In 1981, Bernard served as a visiting scientist in the laboratory of John Newman at the University of California, Berkeley. John and Bernard made seminal contributions to the theoretical understanding of the convective diffusion impedance response of a rotating disk electrode, including that associated with EHD [16,17]. Bernard's subsequent contributions reflect the foundation he received in the laboratories of Epelboin and Newman.

The EHD technique is particularly suited for cases where mass transport is involved [44,48] and has been used primarily for studying corrosion and anodic dissolution processes [81]. Bernard derived theoretical predictions concerning frequently encountered situations, including diffusion through insoluble corrosion products or 3-D inhibitor layers [32] and diffusion toward interfaces that are partially blocked by adsorption or film-forming inhibitors [6,33]. Bernard's work showed that EHD is especially useful for identifying systems influenced by both diffusion through a surface film and convective diffusion in the electrolyte [32]. Such situations cannot be readily identified by traditional stationary measurements.

In the late eighties, Bernard became interested in conducting polymers and the assessment of their transport properties by EIS. In collaboration with the CNR group in Padova, Bernard explored the use of free-standing conducting polymer membranes [68,76,83,86]. The use of free-standing polymer membranes was novel, as previous work was conducted on films adhered to electrode surfaces. The resulting electrolyte/polymer/electrolyte configuration, with two symmetric interfaces, allowed a simpler data analysis and, with a major contribution by Michail Vorotyntsev, opened the way to the development of a comprehensive kinetic model applicable to different electrolytes containing or not electroactive species and to both symmetric and asymmetric geometries [100].

In the early nineties, Bernard was invited to be a visiting researcher at the Federal University of Rio de Janeiro (FURJ). He not only implemented the technique of EHD impedance in Brazil, but carried in his luggage the instruments needed to deploy this technique. The first work developed in this period was related with iron dissolution in sulphuric acid for which a liquid layer of high viscosity was found to be formed at the interface. This result was totally new because, instead of a commonly accepted precipitated film, a viscosity gradient profile was shown to be involved [54,70].

Later, in the nineties, through a collaborative project between France (INP Toulouse) and Brazil (FURJ), he promoted the use of EHD impedance for exploration of electrodissolution mechanisms under conditions where current is controlled by mass transfer. A more detailed interpretation was made possible by combining...
steady-state (Levich plots), ordinary impedance, and EHD impedance. For copper dissolution in hydrochloric acid and in phosphoric acid, his work revealed the presence of concentration gradients within a solid salt layer on the electrode and in the electrolyte [65,66,79,124]. For nickel dissolution in sulphuric acid media, he showed that a very large Schmidt number is associated with mass transport [85]. He strongly encouraged students to prepare a dual PhD dissertation, jointly supervised by French and Brazilian scientists and recognized in both countries. To date, six students have received such dual diplomas.

At the end of the nineties, Bernard became convinced that local electrochemical measurements were essential to obtain a comprehensive description of the interfacial processes. He developed an elegant way to measure the interfacial pH during an electrochemical reaction [91], and later on, he investigated the physical meaning of a local redox potential measurement [105]. This was the starting point of his involvement in the development of local electrochemical impedance spectroscopy [175,194], in which he pointed out the different local measurements that can be performed [165–167] and the necessity of performing simultaneously local and global measurements [170,218]. These new developments were mainly used in corrosion science, but they also offer new perspectives for a broader field of applications.

In an effort to go deeper into the insight of the physical meaning of the CPE parameters extracted from the EIS technique, he proposed local impedance experiments on disk electrode systems for which the global impedance revealed CPE behavior. The resulting article [154] became one of his most cited papers. In this paper, Bernard proposed that the CPE could be regarded as resulting from a distribution of time constants along the electrode surface or through a film. In parallel to his work on the CPE, Bernard developed a model for the impedance response associated with corrosion of pure magnesium. This model, which involves two electrochemical steps coupled by an adsorbed intermediate species, provided an excellent agreement with both the experimental results of his collaborators and that found in the literature [164]. While there has been some disagreement expressed in the literature over the existence of an adsorbed intermediate species, his model is the only one available that can explain all experimental observations.

In a series of papers dedicated to theoretical and experimental exploration of the impedance response of a disk electrode, Bernard connected features in the local impedance to the observed time-constant or frequency dispersion in the global impedance [165–167]. The mystery of the local impedance, which experimentally presents inductive loops in the high frequency range, was elucidated, thanks to these contributions [208]. The understanding of the origin of the complex character of the Ohmic impedance revealed by these simulations was strengthened by experimental data obtained for galvanic couplings between two metals [175,198,202,224,227].

The frequency dispersion associated with the geometry-induced current and potential distribution for a disk electrode was shown to be representative of a surface distribution [209]. A power-law distribution of resistivity through a film was shown to give rise to a CPE, and the resulting relationship between film properties and CPE parameters was independently verified [210,228]. The importance of this contribution can be seen in the present use of EIS to assess oxide layer thickness as part of a quality assurance program by a major manufacturer.¹

In collaboration with M. Orazem, Bernard shared his vision of impedance spectroscopy in a textbook, published by Wiley in 2008 as part of the ECS monograph series [B1]. This book was the result of eight years of intensive effort during which new ideas were developed and appeared in print as well as in the book. Mark and Bernard are currently working on the second edition of this book with publication expected in 2016.

In recent years, some of us have enjoyed collaborating with Bernard in the frame of the activities of the International Society of Electrochemistry, in which Bernard serves as Treasurer since 2011. He was elected to this position after chairing the 2010 Annual Meeting of the ISE. This meeting, held in Nice, was the largest ISE meeting to date.

Bernard enjoys sharing his knowledge with everybody. He established the links between all of us and also with numerous colleagues in France and in foreign countries. He is always ready to discuss science and things of the life over a caipirinha, casquinha de siri, or a glass of zinfandel.

Finally, working with Bernard has significantly increased our expertise in other fields, besides impedance, notably French and international cuisine and wines, fields where Bernard was and is a daring and successful experimentalist, not just a theoretician.

For all this, many thanks, Bernard, from your friends.

Publications of Bernard Tribollet


Books


Chapters in books

