

A Brief History of Electrochemical Impedance Spectroscopy

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Over the past two decades, electrochemical impedance spectroscopy (EIS) has emerged as the most powerful of electrochemical techniques for defining reaction mechanisms, for investigating corrosion processes, and for exploring distributed impedance systems. Although the basis of EIS can be traced to the work on operational calculus by Heaviside and to that of Warburg on diffusion processes, more than a century ago, it was the result of work by Epelboin and his group in Paris in the 1960s that propelled EIS into the forefront as a corrosion mechanism analytical tool. Prior to that time, EIS had been dominated by reactive bridge techniques for measuring interfacial impedance, but these techniques, in general (with one exception), were limited to frequencies above about 100 Hz. The exception is the Berberian-Cole bridge, which, in principle, has no lower frequency limit, but which, in practice, proved to be so laborious to use that it was never adopted on a widespread basis. However, the reactive bridge techniques were used extensively to measure the double layer capacitance at solid and liquid metal electrodes, with the classical work of D. C. Grahame in the 1950s being seminal in nature. The principal reason why EIS did not find extensive use in defining corrosion and electro dissolution reaction mechanisms during this period is that the lowest accessible frequency was too high to detect relaxations involving reaction intermediates, except for the fastest of mechanisms.

It took the combined skills of Epelboin's group and SOLARTRON Instruments, Ltd, to change the EIS world dramatically, with the development of the "frequency response analyzer (FRA)", of which the SOLARTRON 1172 was the pioneer. As with the introduction of the first electronic potentiostat two decades earlier, the FRA revolutionized the field by allowing the impedance to be measured at frequencies down to 0.1 mHz. Together with the pioneering theoretical work of the Epelboin group in France, of Smith et. al. in the USA ("AC polarography"), of Frumkin and coworkers in Russia, and of Armstrong, et al in the United Kingdom, to mention but a few of the groups that have been active in the field over the past forty years, EIS has developed to the point that, over the past decade, it has probably contributed more to our understanding of the *details* of corrosion reaction mechanisms than all other techniques in the preceding history of corrosion reaction mechanism analysis. This theoretical work principally involved the development of techniques for deriving the impedance functions for complex reaction mechanisms, involving coupling between charge transfer, chemical, and mass transfer processes. However, over the past fifteen years, other theoretical innovations have been made, including the development of practical algorithms for performing Kramers-

Kronig transforms for assessing the viability of impedance data by testing for compliance with the constraints of linear systems theory (LST), the definition of alternate perturbation/response transfer functions (e.g., the electrohydrodynamical impedance and the photo-electrochemical impedance function), and the development of harmonic analysis. However, outstanding issues remain to be resolved, including some at the very fundamental level. One such problem is to define the extent to which transfer function analysis (TFA) need conform to the constraints of LST.

The present paper provides a brief review of the history of EIS, with emphasis on those developments that have propelled the technique into the forefront of electrochemical reaction mechanisms.

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