Exploring Advances in Electrochemical Impedance Spectroscopy: A Comprehensive Review of Critical Factors and Recent Progress in Studying Corrosion and Metal Protection

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EIS proves to be a versatile and robust technique, adept at unravelling concurrent physical and chemical processes within electrochemical systems. Despite its advantages, extracting meaningful information from EIS faces challenges, as impedance spectra must adhere to causality, linearity, and stationarity. These aspects are sometimes overlooked due to the increasing automation of the process and the ease of data fitting. In electrochemistry, processes often exhibit nonlinearity, such as the exponential relationship between current and potential. Time-induced inherent changes of the electrode, typical in corrosion, introduce non-stationarity during EIS measurements. It's crucial to recognize that stationarity in the measured electrochemical system limits the use of EIS for high-to-low frequency measurements as electrode changing can be expected in the time frame that measurements are done. Additionally, inherent noise in EIS measurements, stemming from hardware and often neglected, complicates the fitting of electrical equivalent circuits. Addressing these complexities, our research group at VUB pioneered the Odd Random Phase multisine excitation signal EIS (ORP-EIS). This technique selectively excites specific odd harmonics, allowing for the quantification of nonlinearities, nonstationarities, and noise. Access to this information enhances the reliability of data and leads to a better understanding of signal-to-noise ratios, facilitating more accurate fitting. While EIS demands linearity, many electrochemical processes inherently exhibit nonlinearity. Our group recently developed a method to detect and quantify nonlinear distortions, estimating the Best Linear Time-Varying Approximation (BLTVA) for nonlinear time-varying systems. A cutting-edge advancement is the operando ORP-EIS, facilitating EIS on rapidly evolving systems over time. This innovation enables EIS measurements on all non-stationary systems, opening novel applications like monitoring fast battery charging, studying the corrosion and protection of magnesium, assessing inhibitor actions, and observing the initial ingress of water and ions in organic coatings. Furthermore, operando ORP-EIS extends its utility to monitor surface modification processes directly. Unlike classical EIS, which is a post-mortem analysis, operando

EIS allows us to observe processes like anodizing or the application of conversion systems in real-time.

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