ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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PRE-REQUISITES : B.Sc. or B.E.

INTENDED AUDIENCE : PG students, working on electrochemical research

INDUSTRIES APPLICABLE TO : Battery and electric vehicle (EV) companies, those where corrosion is a key problem, or those working in electroplating, will find this useful

COURSE OUTLINE :

This course will introduce electrochemical impedance spectroscopy technique and illustrate its use to characterize electrochemical processes. Details regarding correct method of data acquisition and analysis, along with pitfalls to watch out for, will be discussed

ABOUT INSTRUCTOR :

Prof. S. Ramanathan is a Professor in Dept. Chem. Engg. IIT Madras. His research interests include general electrochemistry (corrosion, electrodeposition etc.) and mechanistic analysis of electrochemical reactions using of electrochemical impedance spectroscopy (EIS). In addition, we have developed new experimental tools and simulation methods to extend the EIS to nonlinear regime.

COURSE PLAN :

Week 1: Introduction to electrochemistry, electrode-electrolyte interface, reference electrode, three electrode cell, supporting electrolyte, rate constant, EIS basics, electrical elements, differential impedance, time domain results, graphical representation of impedance data in Bode and Complex plane plots, other techniques

Week 2: Experimental details: Instrumentation, single and multi-sine inputs, FFT details, frequency range and resolution, cross correlation, multi sine: odd harmonics and non-harmonic choices, crest factor, spectral leakage, windowing

Week 3: Data validation: Kramers Kronig Transforms (KKT), Linearity, causality, stability, impedance vs. admittance, applications and limitations, Alternatives – measurement model analysis and linear KKT

Week 4: Data analysis: Electrical Equivalent Circuits, choice of circuits, confidence intervals, AIC, initial values, distinguishability, zeros and poles representation, charge transfer resistance and polarization resistance, Maxwell, Ladder and Voigt circuits

Week 5: Reaction mechanism analysis, linearization of governing equations, derivation of impedance expression for a simple electron transfer reaction; two step reactions with one adsorbed intermediate

Week 6: Reaction mechanism analysis (continued), development of impedance expression for multiple reactions, an example reaction exhibiting negative resistance, an example three step reaction with 2 adsorbed intermediates

Week 7: Reaction mechanism analysis (continued), development of impedance expression for a catalytic reaction exhibiting negative resistance, reactions with Frumkin isotherm practical challenges in extraction of kinetic information, list of various patterns of complex plane plots reported in literature

Week 8: Diffusion effects, Warburg Impedance, finite and semi-infinite cases, effect of change in dc potential and boundary layer thickness.

Week 9: Constant phase elements (CPE), porous electrodes

Week 10: Passivation and film formation, point defect model (PDM) and extensions. Description of a few selected applications of EIS: Corrosion, biosensors, fuel cells, mechanistic analysis

Week 11: Nonlinear EIS (NLEIS), introduction, mathematical background (Taylor series, Fourier series, modified Bessel functions), NLEIS for a simple electron transfer reaction, reaction with adsorbed intermediates, Nonlinear charge transfer and polarization resistances

Week 12: Effect of instabilities in traditional EIS- calculation using NLEIS methodology, solution resistance effects, Detection of nonlinearities using KKT, NLEIS with Frumkin and Temkin isotherm, evaluation of related technique: electrochemical frequency modulation (EFM)