Electrochemical Methods

B.E. Conway
Chemistry Department, University of Ottawa,
Ottawa, ON. K1N 6N5, Canada

Studies on electrode processes and electrode interface science can be conducted in several complementary ways: a) by means of recording of current (j) or potential (E) response functions to either discontinuous or continuous modulation of the respective conjugate variables E or j. Such procedures correspond to the electrical methods of potentiostatic or galvanostatic pulsing, linear-sweep voltammetry or continuous AV impedance spectroscopy.

b) By digital recording of potential relaxation over four to five decades of time from μs to terms of s, following interruption of prior DC polarization currents.

Because of the applicability of Faraday's Laws to such processes on a micro or nano scale, a large sensitivity factor, on the order of 10^5, arises in the analysis of respective transfer functions for the above types of processes at electrode surfaces, leading to characteristic high sensitivities of the measurements so that surface coverages, θ, by, e.g., adsorbed intermediates, can be followed down to 1% of a monolayer in time-scales down to 100 μs or less, with response current-densities of μA or even nA.

These procedures are specially valuable as they can distinguish response functions for changes of coverage with potential through the adsorption capacitance from those for changes of charge in the double-layer, the double-layer capacitance. Examples will be discussed.

c) In a different, but equally sensitive way, mass changes can be followed at electrode surfaces at the nanogram level by means of the electrochemical quartz-crystal nano-balance and related to charges for double-layer charging and underpotential deposition, and/or anion adsorption.

d) Coupled with FTIR spectroscopy, electrical modulation procedures allow spectroscopic characterization of monolayer or submonolayer quantities of organic adsorbates, and including even adsorbed H, present at electrode interfaces. The related procedure of optical second-harmonic generation in reflectivity at electrode surfaces sensitively gives complementary information on the behavior of surface species.

e) Related to the electrochemical procedures in (a) above are non-steady state methods associated with recording of current (charge) transients due to displacement of one adsorbed species by another probe molecule such as CO, CH_3CN, $(NH_2)_2CS$ which can give rise to an "*anodic H desorption effect*" or a cathodic anion (HSO_4^- at Pt, with CO) desorption effect. Again high sensitivities are achievable.

f) Finally must be noted various *non-electrochemical* procedures such as surface NMR and surface-enhanced Raman spectroscopies that can be conducted under potential-control. Complementarily there are the surface-structure methods, LEED, RHEED, EXAFS, XANES and in situ STM and Electrochemical STM, the latter four being applicable in the presence of electrolyte solution.

This panoply of sensitive procedures available in electrochemistry makes electrochemical surface science a "cutting edge" in surface chemistry, especially with regard to sensitivity and specificity to surface-substrate structures at single-crystal electrode interfaces.