

EDITORIAL

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Voltammetric techniques for studying the redox Chemistry of Solids

Commonly, voltammetric studies of redox reactions of interest to organic and inorganic chemists have been undertaken in the solution phase. A solid or mercury liquid electrode placed in solution containing an electrolyte leads to the establishment of the well-recognised double layer at the electrode/solvent/electrolyte interface. Via combinations of diffusion, migration and convection, species dissolved in solution are transported to or from the electrode, and electron transfer takes place in close proximity to the electrode.

The possibility of voltammetrically studying the redox properties of solids on a routine basis emerged when it was realised that composites of the solid and conducting materials could act as electrodes. Thus, formation of composite carbon electrodes in which the redox active solid compound was mixed with conducting carbon material enabled voltammetric studies to be undertaken on the solid. After the discovery of both inorganic and organic conducting polymer materials, electrochemists rapidly showed that it was possible to incorporate redox active centres into the conducting polymers and study their electrochemistry in this new class of “electrode” material. Recently it has been shown that it is possible to mechanically attach redox active solids to electrode surfaces. The electrode of an insoluble material can then be immersed into a (solvent) electrolyte, and voltammetric studies at high scan rates, virtually free of ohmic distortion, can be obtained. Microelectrodes placed into appropriate crystals can give very well-defined voltammograms if the crystals contain say, solvent molecules of crystallisation, and the solid contains cationic and anionic components.

In summary, it has now been recognised that voltammetric studies on virtually any redox active solid are possible because methods of achieving charge neutralisation and electron transfer over relatively large distances are available. It has been recognised in biological electron transfer systems that electrons can be transferred over quite considerable distances at rates that are appropriate for obtaining measurable currents in voltammetric studies. The same situation also appears to

apply with many solids. Naturally, a charge neutralisation process, usually involving the movement of ions, must accompany a redox reaction in the solid state. However, these processes also are sufficiently fast to enable measurable currents to be obtained with many redox active solids.

As in solution phase voltammetry, spectroelectrochemical techniques have greatly increased our understanding of the mechanisms associated with solid state electrochemical reactions. Thus, infrared, Raman, nuclear magnetic resonance, electron spin resonance and other forms of spectroscopy now routinely accompany electrochemical studies associated with solid state reactions. The electrochemical quartz crystal microbalance also has been an invaluable aid in solid state electrochemistry because the uptake or loss of ions to achieve charge neutralisation invariably leads to a mass change.

The ability to undertake voltammetric studies on solids is, of course, extremely important in understanding the mechanism of operation of photovoltaic cells, batteries, electrochromic devices and corrosion, etc., so the ability to expand electrochemical studies into the realm of non-conducting solids, as well as conducting solids, has proved to be of immense value. At present, if a solid material contains a redox active centre, then there is a very high probability that solid state voltammetric studies can be undertaken. Thus, it is no longer mandatory to find a solvent in which to dissolve the compound and to then undertake studies in the dissolved medium. At present the electrochemical solid state nomenclature contains terms such as “thin film studies”, “thick film studies”, “studies on microcrystals”, “studies in conducting polymer media”. In the near future, very close relationships between these various forms of voltammetry probably will emerge rather frequently. For example, is the study of a redox active material embedded in a conducting polymer closely related to the voltammetry of solid materials mechanically attached to an electrode surface? That is, is the conducting polymer really just another kind of

electrode material, and therefore is it possible that voltammetry at arrays of microcrystalline particles occurs in both cases? Similarly, it is likely to emerge that so-called "thin film" voltammetry rarely takes place at thin films. Spectroscopic examination of thin films often reveals that they are actually arrays of microcrystals on a surface.

In conclusion it must be noted that, while limitations on undertaking voltammetric studies on redox active solids have now been eliminated in the majority of

cases, the difficulty of interpreting results will necessarily be much greater than in the case of solution phase studies because of the expanded nature of the interface. Thus, at a minimum, an electrode/redox active solid/solvent (electrolyte) interface exists, which represents a complex system through which to achieve rapid electron and ion transport.

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