

Spectroelectrochemistry at Optically Transparent Electrodes: An Historical Perspective

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Two quite different techniques, electrochemistry and spectroscopy, can be combined to study the redox chemistry of inorganic, organic, and biological molecules (1-3). Oxidation states are changed electrochemically by addition or removal of electrons at an electrode while spectral measurements of the solution adjacent to the electrode are made simultaneously. Such "spectroelectrochemical" techniques are a convenient means for obtaining spectra and reduction potentials and for observing subsequent chemical reactions of electrogenerated species.

Spectroelectrochemistry was stimulated by the availability of optically transparent electrodes (OTEs), which enabled spectral measurements to be made directly through the electrode. The origin of spectroelectrochemistry at an OTE appears to date from a conversation held at the University of Kansas in the late 1950's between young assistant professor Ralph Adams and his first graduate student Ted Kuwana (4). As recalled by Kuwana, Adams, while observing the production of an intense yellow color in the solution near a platinum anode during the oxidation of o-tolidine commented that "...it would be nice to have a 'see-through' electrode to spectrally identify the colored species being formed...". Later, Kuwana obtained samples of a conducting glass (antimony doped tin oxide-coated glass), and the first spectroelectrochemistry at an OTE was performed on o-tolidine (5). Other early OTEs consisted of very thin films of other conductive materials such as gold and platinum (6,7), which were deposited on a transparent substrate such as glass or quartz. Germanium electrodes were used in the infrared (8). Another category of OTE consisted of micromeshes in which the holes provided transparency to light (9). Gold minigrad with 100 to 1000 wires per inch was used.

Early spectroelectrochemistry consisted of visible light being passed through the OTE either perpendicularly for transmission measurements (5) or at an angle for internal reflection spectroscopy, IRS (8,10). IRS was also done in the infrared (8). These optical methods were coupled with constant current (5), potential step (11) and potential scan (9) electrochemical techniques. Experiments were done under conditions of semi-infinite diffusion (5) and restricted diffusion as in the case of the optically transparent thin layer electrode, or OTTLE (9).

The development of spectroelectrochemistry at OTEs will be traced from these origins to current methodology such as spectroelectrochemical sensors (12).

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