Optically Transparent Thin-Layer Electrodes: Ninhydrin Reduction in an Infrared Transparent Cell

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The construction and application of an infrared transparent thin-layer electrochemical cell are described. The properties of large optical thickness and small diffusional thickness are combined in the cell by use of multiple, spacer-separated gold minigrids. The cell is evaluated using the reduction of ninhydrin in acetonitrile solvent. Ninhydrin is reduced in two one-electron steps in this solvent, and the infrared spectra of its products are used as a basis for suggested equilibrium semidione and dianion product mixtures of dehydrated and hydrated structures.

DEVELOPMENTS in the youthful area of spectral observations at optically transparent electrodes now encompass three basic methodologies:

(a) internal reflection spectrometry (IRS) using electrodes composed of solid germanium (*1, 2*) or of tin oxide (*3–5*), or metal films (*6*) coated on glass

(b) spectral transmission through (semi-infinite) diffusion layers at optically transparent electrodes (OTE) composed of tin oxide coated glass or quartz (*7–9*)

(c) spectral transmission through optically transparent thin-layer electrode (OTTLE) cells employing gold minigrids (*10*) or metal films (*11*) and glass or quartz walls

These techniques have a potential, with continued development, of broad applicability to the study of electrochemical processes and to the solution of analytical problems. Illustration of the usefulness of the bounded diffusion OTTLE and semi-infinite diffusion OTE methods has been made in recent electrode process studies (*8, 9, 12*).

For greatest utility as investigative tools, it is desirable that the spectro-electrochemical methods include access to as many different spectral responses as possible. Extension of the early visible range work to an ultraviolet capability was readily accomplished with quartz substrates for tin oxide (*8*) and metal (*11*) films. Fluorescence response has also been achieved now (*11*). The wealth of spectral information available in the infrared region has, however, not yet been adequately tapped. Although several hints of explorations involving infrared-transparent electrodes have appeared (*1, 4, 11*), two accounts (*1, 2*) of an *in situ* spectro-electrochemical infrared experiment have employed, with IRS, the germanium electrode with its attendant, substantial complexities.

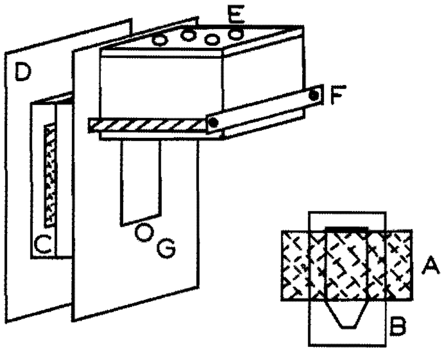

Figure 1. Infrared transparent thin-layer electrode

A. Gold minigrid electrode
B. Teflon spacer
C. NaCl plates
D. Steel frame
E. Holes for reference and auxilary electrodes, nitrogen inlet and outlet
F. Teflon cup and support bar
G. Outlet to draw solution from cell

This report describes application of a thin-layer electrode based on multiple gold minigrids sandwiched between NaCl plates to *in situ* infrared measurements. The cell is evaluated using ninhydrin reduction in acetonitrile solvent. Ancillary data taken from visible and ultraviolet transparent OTTLE cells are included.

EXPERIMENTAL

Ninhydrin (1,2,3-indantrione monohydrate) was obtained from Matheson, Coleman, and Bell. Acetonitrile (Eastman Spectrograde) contained $0.2M$ tetraethylammonium perchlorate as supporting electrolyte. Experiments with *o*-tolidine (Eastman) were conducted in aqueous $1.0M$ $HClO_4$–$0.5M$ acetic acid.

Visible and ultraviolet spectral and coulometric measurements utilized OTTLE cells according to previously described design (*10*) and general experimental procedure (*12*). The cells employed a 1000 lines per inch (lpi) gold minigrid working electrode, quartz plates (Quartz Scientific Co.) for ultraviolet experiments, Teflon tape spacers (Dilectrix Corp., Farmingdale, N. Y.) to fix the thin solution layer thickness, and epoxy cement to seal the cell perimeter.

The infrared-transparent OTTLE cell design is illustrated in Figure 1. The cell contains four gold minigrids alternated

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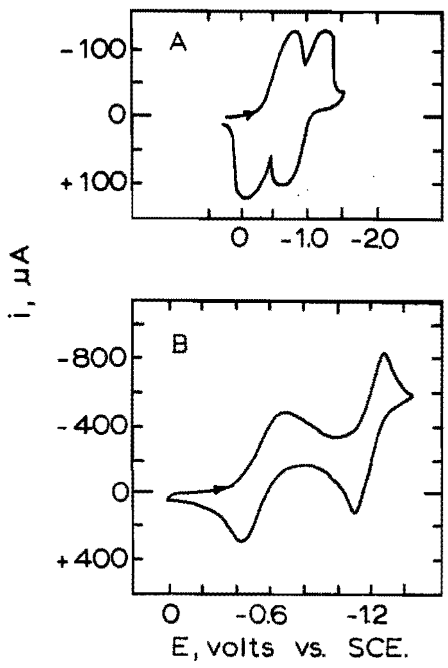

Figure 2. Ninhydrin cyclic voltammetry in 0.1*M* TEAP-CH_3CN

Curve *A*. OTTLE, wall:s:mg:s:wall, l = 113 μ, 1000 lpi mg, 0.01 V/sec, 2.72 m*M* ninhydrin
Curve *B*. Gold wire in bulk solution, 0.1 V/sec, 4.27 m*M* ninhydrin

between five 75-micron Teflon tape spacers, cut as shown, and pressed between two NaCl plates using a modified steel frame similar to Beckman Model F05. The total thin solution layer thickness is approximately 400 microns. Minigrids of relatively coarse mesh (100 lpi, 82% T each, 227 micron wire-to-wire) are used to achieve acceptable overall transparency (30% T) of the multi-electrode cell. A $^1/_{16}$ × $^5/_{16}$ inch hole in the side of the capped Teflon solution reservoir cup is centered over a similar hole in the adjacent NaCl plate for connection to the thin solution layer cavity. The cavity is gravity-fed from the reservoir and can be drained at the bottom.

To obtain quality spectra throughout the infrared range, special attention must be given to compensation of the minigrid transparency and the substantial absorbancies of the solvent and supporting electrolyte. A standard variable spacer cell (Perkin Elmer Model 0751) is placed in the reference beam of the infrared spectrophotometer (Perkin Elmer Model 421). With both sample and reference cells empty, the spectrophotometer reference beam is partially blocked to compensate for the beam attenuation by the sample cell minigrids. Acetonitrile–tetraethylammonium perchlorate solution is then placed in both cells and the variable spacer cell "dialed" to balance out the background absorbance. (Use of a fixed thickness OTTLE cell for the reference beam compensation proved impractical because of the tedium of preparing exactly matched cells.) Previously degassed sample solution is now added to the sample cell, which also contains the Pt auxiliary and (aqueous) SCE reference electrodes, and potential stepping and spectral observations are made as desired. To minimize thermal effects of the infrared beam, the sample cell was darkened until exhaustive cell electrolysis, as indicated by current–time curves, was complete.

Epoxy-cemented infrared cells can be readily prepared in the same manner as the visibly-transparent microscope slide OTTLE, but the present arrangement allows more convenient disassembly of the cell, degassing of sample solution, and salvage of the NaCl windows.

RESULTS AND DISCUSSION

Ninhydrin exhibits convenient spectral and electrochemical properties for use as a model compound in nonaqueous thin-layer spectro-electrochemical studies. Its ultraviolet absorption is intense, its reduction products are under most circumstances visibly colored, and its reducible carbonyl groupings afford strong absorptions for infrared observations. Previous electrochemical reductions of ninhydrin have been conducted in aqueous (*13–16*), aqueous–alcoholic (*17*), and LiCl–methanolic (*18*) media. Two-electron reductions are observed under these conditions. Reduction in acetonitrile containing tetraethylammonium perchlorate electrolyte reveals, however, stepwise one-electron reduction to the semidione and dianion forms. The semidione radical anion can also be prepared by chemical reduction in aqueous–alcoholic (*19*) and DMSO (*20*) media and by electrochemical reduction in DMF (*21*).

Bulk solution and thin-layer cyclic voltammetry of ninhydrin in acetonitrile is illustrated in Figure 2. The two waves are well-formed, although imperfectly reversible, and their one-electron character is established by potential step thin-layer coulometry: n_1 = 1.00, n_2 = 0.90. The ultraviolet and visible spectra of ninhydrin, semidione, and dianion were measured in OTTLE cells and are summarized in Figure 3. The semidione and dianion forms are yellow and blue in acetonitrile, respectively, and the absence of any spectral changes over a period of observation indicates substantial stability. Their stability is likewise indicated by reverse potential step coulometry, $(Q_{cath}/Q_{anod})_1 = 0.97$ and $(Q_{cath}/Q_{anod})_2 = 1.02$, and by the quantitative reversion of each spectrum to that of its predecessor upon anodic potential stepping.

Because of the relatively weak intensities of infrared absorptions as compared to those at shorter wavelengths, special attention to the problem of optical sensitivity is required in the infrared OTTLE experiment. If an absorbance of 0.1 is desired, as a minimum, for a strong infrared absorption band ($\epsilon \approx$ 1,000; *e.g.*, carbonyls of ninhydrin), a sample concentration of 10m*M* suffices in a "thick" OTTLE having l = 100 microns. Observation of less prominent spectral features, say bands having $\epsilon \approx$ 100, would on the other hand require an uncomfortable 100 m*M* sample concentration in this cell. An increase in the OTTLE thickness without concurrent sacrifice of rapid thin-layer electrolysis capability is desirable in the latter case to circumvent, at least in part, the need for such high sample concentrations.

The minigrid electrode provides a unique route to construction of a thick but rapidly responding thin-layer cell. Figure 4 illustrates the manner in which this is done. Alternating Teflon tape spacers and minigrid electrodes permits accumulation of a long optical path while restricting diffusional distance to one spacer thickness (for a wall:minigrid:spacer gap)

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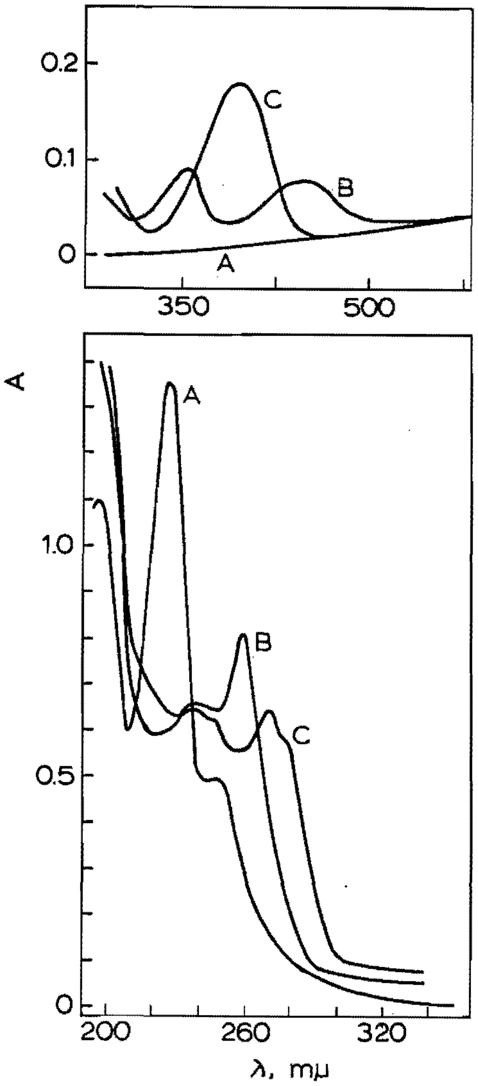

Figure 3. Visible and ultraviolet spectra of ninhydrin and reduction products in 0.2M TEAP-CH$_3$CN. Quartz OTTLE. Upper spectrum: l = 112μ, 4.34mM; lower spectrum: l = 135μ, 2.21mM

Curve A. Open circuit or $E = +0.2$ V (before or after electrolysis at -1.0 or -1.8 V)
Curve B. $E = -1.0$ V
Curve C. $E = -1.8$ V

or to one half a spacer thickness (for a minigrid:spacer:minigrid gap). In the cell shown, a six-fold enhancement of optical sensitivity is accomplished; the diffusional path length to an electrode is 50 microns whereas the cell's optical thickness is 300 microns.

Figure 4 is an idealized picture inasmuch as a small amount of "wrinkling" of the minigrid within the thin layer is difficult to avoid during cell construction unless rather small electrode areas are employed. This effect slows the thin-layer electrolysis by creating longer diffusional paths in parts of the cell. Several potentiostatic experiments using *o*-tolidine oxidation in aqueous medium show, however, that the net effect is apparently minor. The responses of two cells of similar optical thickness but differing, ideally, by a factor of two in diffusional thickness are compared in Curves A and B of Figure 5. A noticeably faster electrolysis occurs for Curve A. A more extreme comparison is given in Curves C and D. The cell of Curve C has a diffusional thickness 5 to 10 times shorter than that for Curve D, and the electrolysis rate is drastically improved by the alternating arrangement. It is apparent that the sensitivity–response advantages of OTTLE cells thus constructed apply to low intensity ultraviolet and visible measurements as well as those in the infrared region. OTTLE cells like that of Curve A were employed to obtain the spectra of Figure 3 and have been used for other low intensity situations as well (*12*).

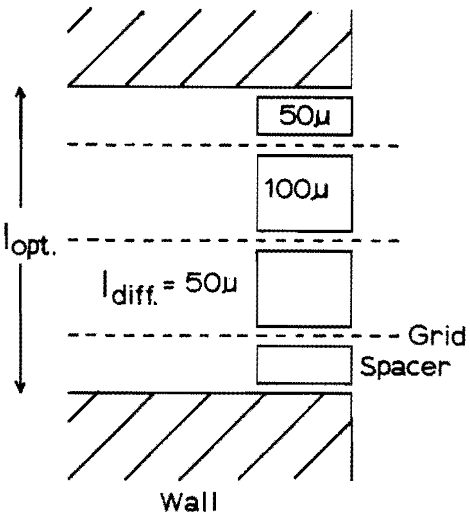

Figure 4. An optically "thick", diffusionally "thin" electrode

The spacer:minigrid configuration of Curve C, Figure 5, is that chosen for use in the infrared-transparent cell of Figure 1. Electrolyses of ninhydrin therein reveal a comparably fast response at 1 mM concentrations. Some increase in electrolysis time occurs at the higher concentrations required for infrared spectral observations, because of the increased resistance drop through the thin solution layer generated at the higher current levels. At 10mM concentrations, adequate for close observation of the intense carbonyl absorptions, complete electrolysis requires 1 to 2 minutes. A 30mM concentration, useful for examination of less prominent spectral details, required about 3 minutes for complete electrolysis.

The infrared spectra of ninhydrin and its one- and two-electron reduction products were measured in the infrared OTTLE and are shown in Figure 6. The spectral range 1800–2700 cm^{-1} exhibits no absorptions and is omitted. Acetonitrile absorbs heavily in the ranges 1000–1100 and 1300–1600 cm^{-1} and measurements in these ranges were accordingly limited. Some attenuation of resolution is evident in these spectra. This arises largely from scattering of infrared radiation by the multiple minigrids. However, substantial spectral differences between ninhydrin, semidione, and dianion are nevertheless apparent.

The strongest ninhydrin bands at 1725 and 1750 cm^{-1} are the carbonyl stretching vibrations. The broad band at 3350 cm^{-1} has been assigned (*22, 23*) to the associated OH stretch of the *gem* dihydroxyl group. Some carbonyl overtone may also contribute to this absorption.

Noticeable changes occur in these bands upon one-electron

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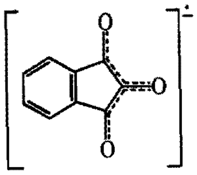
reduction. The 3350 cm^{-1} band disappears and a weak band at 2860 cm^{-1} becomes evident. The two intense carbonyl stretches are replaced by three bands at 1710, 1680, and 1660 cm^{-1}.

Russell and Young (*20*) have chemically reduced ninhydrin in anhydrous DMSO and obtained an ESR spectrum consistent with the dehydrated radical anion I:



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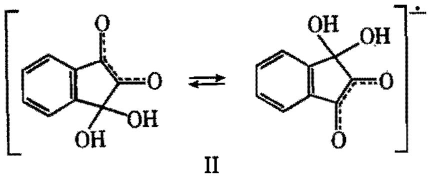
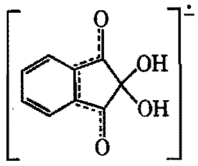


II



III

The spectrum obtained at low pH in aqueous solution was likewise interpretable in terms of structure I, but it was noted that it could also be viewed as a time-averaged spectrum resulting from rapid interconversion of structures II. Structure III was discounted for reasons of expected instability.

Gem diols are usually isolatable only when the diol site is heavily substituted with electron withdrawing groups. Such is the case with the ketone groups flanking the 2-diol site in ninhydrin. One-electron reduction of ninhydrin attenuates the stabilizing influence of these groups, and dehydration of

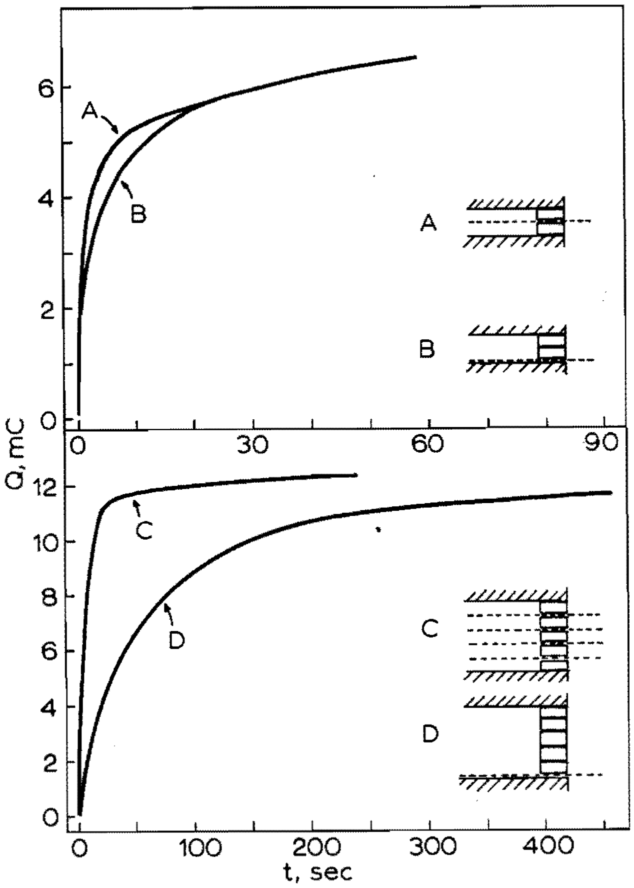


Figure 5. Potentiostatic response of several spacer-minigrid configurations

o-tolidine, aqueous 1*M* $HClO_4$–0.5*M* acetic acid. 50-micron spacers, thicknesses are spectrophotometric, coulometric

Curve *A*. wall:s:mg:s:wall; *l* = 133,133 μ; 1000 lpi; 2.00 m*M* o-tolidine

Curve *B*. wall:s:s:mg:wall; *l* = 146,139 μ; 1000 lpi; 2.00 m*M* o-tolidine

Curve *C*. wall:s:mg:s:mg:s:mg:s:mg:s:wall; *l* = 314,312 μ; 100 lpi. 1.00 m*M* o-tolidine

Curve *D*. wall:s:s:s:s:s:mg:wall; *l* = 298,288 μ; 100 lpi; 1.00 m*M* o-tolidine

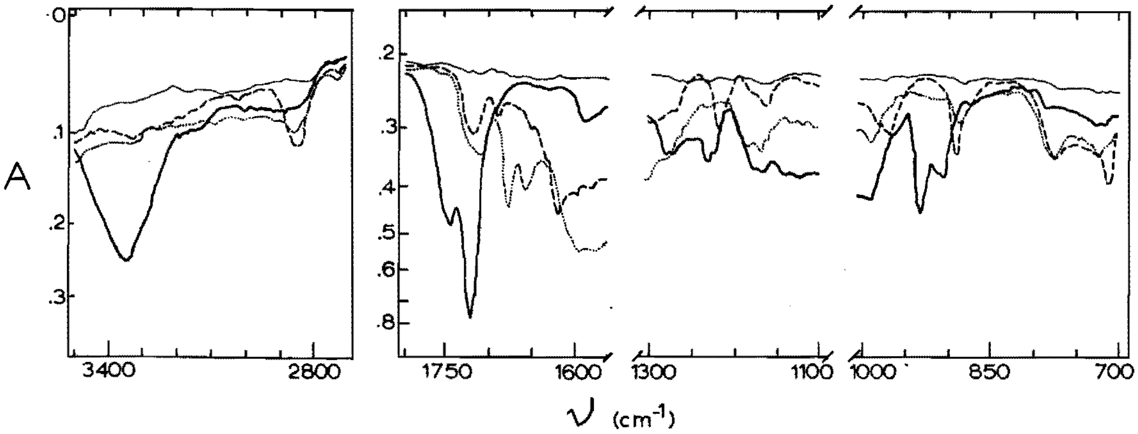


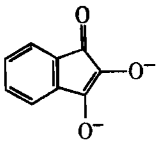
Figure 6. Infrared spectra of ninhydrin and reduction products in 0.2*M* TEAP-CH_3CN. NaCl OTTLE, configuration wall:s:mg:s:mg:s:mg:s:wall, *l* ~ 400 μ, 100 lpi mg, 30.5m*M* ninhydrin, 5-minute electrolysis

—— **TEAP-CH_3CN**
━━ **Open circuit**
•••··· ***E* = −1.1 V**
‑‑‑‑ ***E* = −1.9 V**

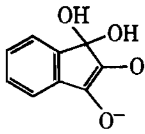
the reduction product in the anhydrous DMSO medium is thus to be expected. Association with water as in structure II is also plausible in aqueous solution.

Disappearance of the 3350 cm^{-1} band assigned to the associated OH stretch provides evidence that the dehydrated structure I results from one-electron reduction of ninhydrin in the acetonitrile medium. The presence of the carbonyl absorptions of lowered bond order is consistent with this structure. The appearance of the 2860 cm^{-1} absorption in the semidione spectrum is disturbing, however. This peak is in the general spectral region for absorption by hydrogen-bonded OH stretches, and suggests the presence of the hydrated structure, II, in which OH hydrogen bonds with an adjacent semidione oxygen, or an intermolecularly hydrogen bonded complex of structure I with residual water (~50m*M*) of the acetonitrile solvent. A possible explanation is that the semidione solution is actually an equilibrium mixture of structure I and either structure II or a structure I–water complex.

Further reduction to the dianion form results in intensification of the 2860 cm^{-1} band and modification of the carbonyl region to absorptions at 1720 and 1692 cm^{-1}. The 3350 cm^{-1} absorption remains absent. As above, these spectral features suggest the presence of an equilibrium mixture of a dehydrated structure, such as IV, and either a hydrated, intramolecularly hydrogen-bonded structure V or a structure IV–water complex. It is surprising that the hydrogen bonded stretch of V is not shifted by the increased charge to somewhat lower energy than the 2860 cm^{-1} absorption of the semidione. Published documentation of the sensitivity of this effect in analogous compounds could not be located.



IV



V

Until further study can more firmly substantiate the existence of the suggested equilibria in the semidione and dianion solutions, attempts to assign bands of lower energy than those considered above do not seem warranted.

Although the objective of this work was to establish the feasibility of an infrared OTTLE, the results obtained for ninhydrin serve to emphasize the utility of infrared data in spectro-electrochemical investigations. The complications revealed in the infrared spectra were not obvious from the electrochemical results alone or in combination with visible and ultraviolet spectra. While the infrared OTTLE described herein is afflicted with a loss of spectral resolution not encountered in its visible and ultraviolet-transparent counterparts, it nonetheless offers the same simplicity of construction and use and can provide valuable supplementary insights into electrochemical studies.

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