

The preparation and properties of metallic optically transparent electrodes

Citation for published version (APA):

Janssen, L. J. J., & Kuhn, A. T. (1983). The preparation and properties of metallic optically transparent electrodes. *Surface Technology*, 20(1), 41-49. [https://doi.org/10.1016/0376-4583\(83\)90075-4](https://doi.org/10.1016/0376-4583(83)90075-4)

DOI:

[10.1016/0376-4583\(83\)90075-4](https://doi.org/10.1016/0376-4583(83)90075-4)

Document status and date:

Published: 01/01/1983

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

THE PREPARATION AND PROPERTIES OF METALLIC OPTICALLY TRANSPARENT ELECTRODES

L. J. J. JANSSEN

Department of Chemical Technology, Laboratory of Electrochemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven (The Netherlands)

A. T. KUHN

Department of Biomaterials Science, Institute of Dental Surgery, Eastman Dental Hospital, 256 Gray's Inn Road, London WC1X 8LD (Gt. Britain)

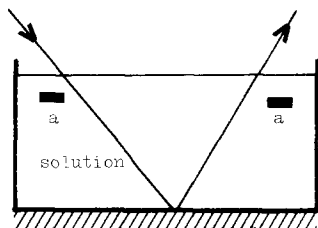
(Received May 25, 1983)

Summary

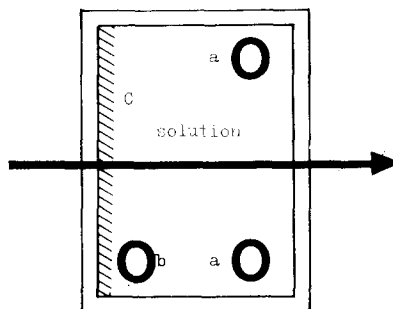
The uses of optically transparent electrodes (OTEs) are briefly discussed together with the different types of OTE. The review is focused on metallic OTEs and a survey of the various types, their means of preparation and their optical and electrical properties is included.

1. Introduction

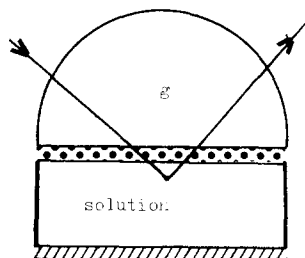
All too often, electrochemists or corrosion scientists find themselves, like the blind, curious to "see" actually what is taking place at the interface which is usually the focus of interest. Although "seeing" might mean actually viewing an electrode or an electrode process with the naked eye or with a microscope, it will more probably involve the more sophisticated methods of spectroscopy to detect the presence of a given species or to monitor its concentration with time. It is now accepted that a very limited number of conceptual approaches exist. They include (a) specular reflectance, (b) transmission and (c) attenuated total reflectance (ATR). The configurations for these are shown in Fig. 1. Specular reflectance will not be considered further beyond the obvious comment that, although it makes no demands on the properties of the electrode itself, the incident and the reflected beams of light must pass through a solution which will certainly attenuate them to a greater or to a lesser extent. Nevertheless, various workers [1] have made remarkable strides in bringing this method (over a wide wavelength band) to the point where it is routinely used. In the other two approaches, however, the method is based on the transmission of incident and reflected light through an optically transparent electrode (OTE). To achieve this, a material or combination of materials is required, and it is the achievement of such a combination that will be considered here.



(a)



(b)



(c)

Fig. 1. Three alternative configurations for spectroelectrochemistry: (a) specular reflectance through solution (C, working electrode; a, counterelectrodes); (b) transmission (plan view) (C, platinum OTE; a, counterelectrodes; b, reference electrode); (c) ATR using a germanium hemicylinder g with a platinum film OTE C (a, counterelectrode).

Two preliminary comments are required. Firstly, even if a single material was found to possess the criteria of high transmission of light and good electrical properties (subjects which will be considered below) it might be of limited interest in that the majority of electrochemical reactions relate to a small number of electrode materials, notably lead, mercury and platinum, and (unless the material in question had remarkable electrocatalytic properties) most interest, rightly or wrongly, is in these materials. The second comment is that, although the transmission configuration (Fig. 1(b)) is historically probably the oldest and most well established, it suffers the disadvantages of both the reflectance method (*i.e.* light passing through the solution) and the OTE systems (in which the electrodes are difficult to prepare and not as robust as massive materials). Only the simplicity of use, in that hopefully such cells can be inserted into commercial UV-visible spectrometers with minimal adaptation, can be set against these disadvantages. Given all the above factors, an entirely healthy "competition" is expected between the users of the various approaches and, in this competition, developments in electronics (*e.g.* phase-sensitive detection) have overwhelmingly favoured the reflectance approach. In addition, novel materials (perhaps as "spin-offs" from aircraft applications, solar energy developments or electrochromic displays) might be expected to make an impact on OTE developments, and optical fibre technology could be equally important. To

some extent, the choice of approach is governed by the information desired in the experiment. ATR is, by its nature, useful only to monitor the layer of solution very close to the electrode surface. True transmission will embrace changes whether at the surface or in bulk solution, as will specular reflectance. However, the use of twin-beam spectroscopy to offset background or solution absorbance is one means by which surface phenomena can be emphasized, *e.g.* as shown by Goelz and Heineman [2] who examined specific adsorption of anions. Modulation of electrode potential, an approach highly developed by Bewick and coworkers, gives even more accurate results.

2. Applications

Although OTEs have been used to view processes such as bubble evolution, their main importance must lie in spectroscopic analysis of reaction products or intermediates in solution or adsorbed species on the electrode surface. In either case, steady state or non-steady-state conditions may be of interest. A review of the literature shows that not all workers have been aware of the correct use of OTEs (*e.g.* their useful potential range) and in the present review their preparation, cells for their use and related methodology are considered.

3. Types of optically transparent electrode

Existing OTEs can be divided into three categories as follows.

(a) Thin conducting films can be supported on glass, quartz or special IR-transparent materials. Such films can be conducting oxides (such as SnO_2) or metals (platinum or gold). They may be "duplex" films where one metal film is deposited onto another metal film or onto an oxide layer.

(b) "Massive" OTEs are made of doped silicon, germanium or other materials.

(c) "Minigrd" electrodes are those where a material such as gold is fabricated as a fine grid, exposing a high surface area to the transmitted light.

We shall focus on the first of these categories in the present review, and the criteria of importance will be (a) the optical properties (transmission as a function of wavelength), (b) the electrical resistance of the film (in ohms per square) and (c) the chemical and electrochemical properties including the potential range over which the OTE can be employed and the electrocatalytic behaviour.

4. General characteristics of thin film optically transparent electrodes

A most valuable review by Haacke [3] entitled "Transparent conducting coatings" is mainly directed towards applications such as solar

energy, liquid crystal displays and other technologies using similar materials. Haacke began with a consideration of the “figure of merit” approach to the classification of OTEs:

$$\phi_{\text{TC}} = \frac{T^{10}}{R_s}$$

where ϕ_{TC} is the figure of merit, T is the optical transmission and R_s is the sheet resistance of the material (coating). As he showed, the figure of merit can also be expressed by the equation

$$\phi_{\text{TC}} = \sigma t \exp(-10\alpha t)$$

where σ ($\Omega^{-1} \text{ cm}^{-1}$) is the electrical conductivity and α (cm^{-1}) is the optical absorption coefficient.

Haacke presented a plot of figure of merit *versus* film thickness for thin films of copper, gold and Cd_2SnO_4 and for a “hypothetical semiconductor”. The performance of the Cd_2SnO_4 is seen to approach that of a hypothetical semiconductor. With such an approach, the individual materials considered as OTEs can be discussed. These materials can be divided into metallic (and quasi-metallic) films on the one hand and semiconductors on the other hand.

5. Metallic film optically transparent electrodes

As Haacke pointed out, the manner in which thin films of metal are formed results in much higher sheet resistance values for such films than might be expected from data on bulk conductivity. A number of tricks exist to minimize the island formation of clusters of metal atoms with intervening gaps; Haacke described a few of these tricks briefly, although he emphasized that the production of such metallic film OTEs is mainly a matter of undisclosed “know-how”. It is generally accepted that, for the very small thicknesses in question, these metal films do not obey the Beer–Lambert law. Haeman [4] has shown that the logarithm of transmission T (%) decreases linearly with the thickness (for thicknesses greater than 0.1 - 0.2 μm) with a proportionality factor which depends on the metal used. Some values of transmission taken from the literature for platinum, gold, nickel and lead films 0.6 μm thick are 0.08% (at 550 nm), 5% (at 550 nm), 0.03% (at 503 nm) and 0.5% (at 503 nm) respectively. Among the materials which have been investigated by electrochemists are gold, platinum and carbon and various alloys. The problem is to deposit a thin and coherent film of a metal with sufficient corrosion resistance to allow its use over a reasonably wide range of potentials. The trade-off between thicker films (improved electrical conductance) and thinner films (improved optical transmission) is now evident. A further danger is that, although the film remains unattacked, it may be lifted away from the substrate by hydrogen gas evolution or by similar phenomena.

The means by which metal film OTEs have been prepared have passed through several phases. Initially, a metal such as platinum was painted onto a substrate using a preparation in which the metal was dissolved in organic oils. After the metal had been painted on, it was fired. Workers such as Pons *et al.* [5] gave directions as to the best means of application of the paint, the number of coats etc. Later [6] the technique of "spinning" was employed to ensure the most even application of the paint. However, most recently, the preferred method of application has been some form of vacuum evaporation. Simultaneous with these ideas has been the recognition that annealing after application improves the electrical characteristics of the film and also that, rather than deposition of the metal directly onto glass or quartz, an improved result is obtained when the metal is deposited onto an oxide [7]. More recently [8], the use of tin oxide has been advocated so that not only do the general benefits of oxides result but also the additional conductivity of the oxide layer can be usefully employed.

Thus Pons *et al.* [5] have described how a platinum OTE may be formed by brushing Liquid Platinum 1 (Engelhard Industries Ltd.) onto glass with a fine brush and by firing the film so formed at 650 - 680 °C, just below the fusion temperature of the glass (borosilicate in their case) onto which it was applied. Either a single coat or successive applications and firings may be employed. Pons *et al.* reported a number of tricks such as the importance of the direction of the brush stroke. The platinum paint may be thinned with a thinner such as dichloromethane before application. Inspection under the microscope shows that these films are not quite uniform and that they contain holes. Annealing is thus beneficial as might be expected and results in an optical density of about 0.4%, with a sheet resistance value of 25 Ω/\square . Even further details are contained in the paper by Van Benken and Kuwana [9] who mentioned that such OTEs are stable to anodization, boiling in HNO_3 or immersion in HCl solution. However, even a brief period of hydrogen evolution will suffice to lift off the film. Mercuric ions (although not mercury metal) are also damaging. Gold films have a lower electrical resistance than platinum films for the same optical density and a plot showing typical optical densities is given in Fig. 2. Pons *et al.* [5] also suggested that palladium films, especially when deposited onto KRS5 may have special use with a wider IR window (5 - 16 μm) than those obtainable on germanium

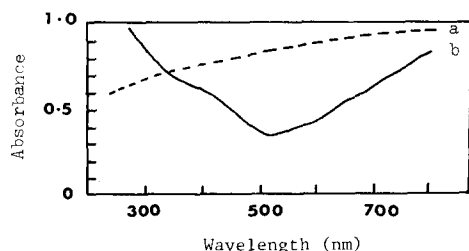


Fig. 2. Absorbance vs. wavelength: curve a, platinum on quartz (electrical resistance, 11 Ω/\square); curve b, gold on Bi_2O_3 on quartz (electrical resistance, 2.5 Ω/\square). (After ref. 10.)

(2 - 10 μm). The same workers suggested that palladium might have IR transparency over a wider range (5 - 16 μm) on HRS5 than it has on germanium (2 - 10 μm).

Van Benken and Kuwana [9] described the deposition of platinum films directly onto borosilicate or other glasses or quartz by evaporation in a vacuum of $(1 - 7) \times 10^{-3}$ Torr. The glass was first cleaned by using a glow discharge. For gold the film was applied over a Bi_2O_3 or PbO_2 coating. All films were annealed after use.

The platinum surfaces were bright, uniform and silvery. They were mechanically stable, except when oxidized after hydrogen evolution for a few seconds or during the deposition of mercury. Normal washing and cleaning, boiling in concentrated HNO_3 or prolonged immersion in HCl solution did not disturb the film, nor did contact with metallic mercury.

On the basis of equal resistance, gold films were more transparent than platinum films. The undercoating used with gold films improved their mechanical and electrical characteristics and, in this, the present authors can be said to have anticipated the Pt-SnO₂ OTE of Laitinen [8].

The characteristics of these films are seen in Figs. 2 and 3. There appear to be few equally detailed accounts of preparation and properties of such electrodes. Nasielski *et al.* [11] mentioned gold electrodes prepared by "subliming gold onto glass". The average thickness was 50 nm and the transmittance at 550 nm was $25\% \pm 5\%$.

Once the platinum and the gold OTEs had been developed, other types of OTE followed. The Hg-Pt OTE is formed by taking a platinum OTE (formed by vapour deposition) and electrochemically depositing metallic mercury onto it from a dilute aqueous solution. A relatively thin layer of mercury (5 - 50 nm) imparts to the platinum a "mercury-like character", *i.e.* the high hydrogen evolution overvoltage which allows cathodic processes to be studied at this electrode is unhindered by hydrogen formation. Heineman and Kuwana [12] described the preparation of platinum OTEs (resistance, about $10 \Omega \text{ cm}^{-2}$), which were washed and dried and then cleaned in a plasma discharge for 5 min. After this the platinum OTEs were inserted into a cell which was filled with a 0.5 mM solution of $\text{Hg}_2(\text{NO}_3)_2$ in an acetate buffer of pH 4. This was deoxygenated for 30 min and the OTE was switched from open circuit to a potential of 0.00 V measured with respect to a saturated calomel electrode. The optical response was

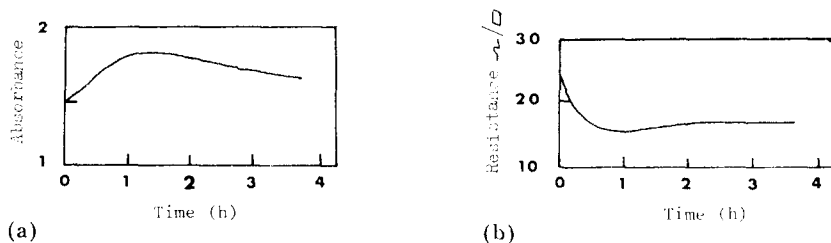


Fig. 3. The effect of annealing on platinum films: (a) optical absorbance vs. time; (b) electrical resistance vs. time. (After ref. 10.)

monitored at 609 nm and the current passing at the same time was integrated to allow an estimation of the charge of the mercury deposition and hence its thickness. A correction for the background current was made in this case. 10 mC of mercury per square centimetre (corresponding to a layer about 15 nm thick) yielded a mercury-like OTE. Heineman and Kuwana [13] also described a cell design which allows admission of a deoxygenated solution directly into the cell, and a further modification is shown [14] in which the electrode area is reduced to 3 mm² and the hold-up volume of electrolyte is reduced to about 1 ml. Heineman and Goelz [15] have described the application of an Hg-Pt OTE in the transmission mode to monitor the specific absorption of anions. A more detailed account of the same work was subsequently reported [2]. Goelz and Heineman [16] have reported a study in which these electrodes were characterized in terms of their electrochemical behaviour on voltammetric stripping and their appearance under the optical microscope. For a useful stable electrode, Goelz and Heineman advocated a mercury layer 5 nm thick. Transmission values of 85% are shown. Optical microscopy taken in conjunction with the voltammetric data shows how excess mercury deposition leads to globules of the metal on the surface. These globules can be removed by anodic oxidation, leaving behind the Pt-Hg intermetallic phase which is the desired structure. Discussing the longevity of these OTEs, Goelz and Heineman suggested that too much mercury leads to amalgamation of the platinum all the way down to the glass substrate, resulting in peeling. If just sufficient mercury is deposited to form the amalgam, but without the formation of droplets, a lifetime of 8 h or more can result. In addition to their use in the transmission approach, the use of Pt-Hg OTEs in internal reflection spectroscopy has also been described [17] using a commercially available cell unit. Data are shown for methylene blue, using a single reflection and time-averaging methods.

The greater opacity of metals to light of longer wavelength led to problems with IR-transparent OTEs. Mattson and Smith [18] described attempts by earlier workers to overcome such problems. Metal films of less than approximately 3 nm thickness are IR transparent. However, they do not have sufficient electrical conductivity. For this reason, Mattson and Smith devised the carbon film OTE using a germanium internal reflection element. The carbon was coated by a commercial organization and, when deposited, had a resistance of 2000 - 5000 Ω/\square for a film about 30 nm thick, corresponding to a value greater than that of bulk graphite by a factor of 10. In their paper [18] a comparison is made between background scans for platinum, carbon and germanium prism OTEs and data for proteinaceous films and other organic species are shown. The carbon films afford transparency over the entire range of use with the substrate (germanium). Large germanium prisms with 13 reflections at the Ge-C interface gave transmissions from 4% to 8%. Germanium microprisms with three reflections gave 15% transmission. Uncoated prisms gave 25% - 30% transmission.

A nickel OTE has been used by Janssen and coworkers [19, 20]. These are also commercially prepared by the deposition of nickel (0.35×10^{-4} mm)

onto an SnO_2 (7×10^{-4} mm) layer on a glass substrate. The transmission was about 12% and typical electrical resistances were 10 - 20 Ω/\square . Electrolytic bubble formation (both hydrogen and oxygen) on these electrodes was viewed through a microscope. KOH solutions of up to 7 M were used at temperatures from ambient to 80 °C. Generally, these electrodes lasted for at least 1 day and because of its chemical stability an Ni-SnO₂ electrode was most useful for oxygen evolution [21].

The Au-Cr OTE has also been used by one of us (L.J.J.J.) to study hydrogen bubble formation in KOH. This electrode was based on an under-layer of chromium 10 nm thick with 40 nm of gold above. The transparency was 9% and the electrical resistance was 2.7 Ω/\square . However, oxygen evolution led to lifting of the gold film from the surfaces.

De Angelis *et al.* [14] described a carbon OTE deposited onto glass or quartz and a mercury-coated version of a similar electrode. As in the previous work of Mattson and Smith [18] the electrodes were prepared by a commercial organization which used electron beam evaporation of carbon. Film resistances of 1000 - 1700 Ω/\square were obtained, and the Hg-C OTE behaved electrochemically in a similar way to mercury itself.

Finally, the use of OTEs in non-aqueous media should be mentioned, the paper by Osa and Kuwana [22] being an excellent overview of this area of the subject. Other information pertaining to non-aqueous solvents and OTEs can be found in ref. 10.

In this short paper the "hardware" aspects of metallic OTEs have been reviewed (semiconducting types including the important SnO₂ types have not been covered here). In addition, the electrical and electrochemical properties of OTEs, which basically resemble those of the parent metals, with the caveat that hydrogen evolution (and presumably also oxygen evolution) marks the danger zones in which they cannot be used, have also been discussed. For a description of cells incorporating these OTEs and the methodology underlying their use, especially for the derivation of transient data, one of the fullest, best and most detailed accounts is given in ref. 10, to which the reader is referred and from which some information has been obtained for this short review.

Acknowledgment

The authors are grateful to Dr. Alan Bewick for his valuable comments on this paper.

References

- 1 A. Bewick, *J. Electroanal. Chem. Interfacial Electrochem.*, 60 (1975) 163; 119 (1981) 175.
A. Bewick, *Electrochim. Acta*, 25 (1980) 931.
J. D. E. McIntyre, *Adv. Electrochem. Electrochem. Eng.*, 9 (1973) 61.
E. Yeager, *Surf. Sci.*, 46 (1974) 1.

- 2 J. F. Goelz and W. R. Heineman, *J. Electroanal. Chem.*, 103 (1979) 155.
- 3 G. Haacke, *Annu. Rev. Mater. Sci.*, 7 (1977) 73.
- 4 D. Haeman, *Balzers Hochvakuum Fachber.*, 4 (1965) 8.
- 5 B. S. Pons, J. S. Mattson, L. O. Winston and H. B. Mark, *Anal. Chem.*, 39 (1967) 685.
- 6 A. Prostack, H. B. Mark and W. N. Hansen, *J. Phys. Chem.*, 72 (1968) 2576.
- 7 L. Holland, *Vacuum Deposition of Thin Films*, Chapman and Hall, London, 1958.
- 8 H. A. Laitinen, *U.S. Patent 4,273,624*, June 1981.
- 9 W. Van Benken and T. Kuwana, *Anal. Chem.*, 42 (1970) 1114.
- 10 T. Kuwana and N. Winograd, *Electroanal. Chem.*, 7 (1974) 1.
- 11 J. Nasielski, A. Kirsch-de Mesmaeken and L. Lempoel, *Electrochim. Acta*, 23 (1978) 605.
- 12 W. R. Heineman and T. Kuwana, *Anal. Chem.*, 43 (1971) 1075.
- 13 W. R. Heineman and T. Kuwana, *Anal. Chem.*, 44 (1972) 1972.
- 14 T. P. De Angelis, R. W. Hurst, A. M. Yacynych, H. B. Mark, W. R. Heineman and J. S. Mattson, *Anal. Chem.*, 49 (1977) 1395.
- 15 W. R. Heineman and J. F. Goelz, *J. Electroanal. Chem.*, 89 (1978) 437.
- 16 J. F. Goelz and W. R. Heineman, *J. Electroanal. Chem.*, 103 (1979) 147.
- 17 J. F. Goelz, A. M. Yacynych and H. B. Mark, *J. Electroanal. Chem.*, 103 (1979) 277.
- 18 J. A. Mattson and C. A. Smith, *Anal. Chem.*, 47 (1975) 1122.
- 19 L. J. J. Janssen and S. J. D. Van Stralen, *Electrochim. Acta*, 26 (1981) 1011.
- 20 R. M. De Jonge, E. Barendrecht, L. J. J. Janssen and S. J. D. Van Stralen, *Proc. 3rd World Hydrogen Energy Conf., Tokyo, June 23 - 26, 1980*, Pergamon, Oxford, 1980.
- 21 C. W. M. P. Sillen, *Thesis*, Eindhoven University of Technology, Eindhoven, 1983.
- 22 T. Osa and T. Kuwana, *J. Electroanal. Chem.*, 22 (1969) 389.