

This paper is in a collection of

**“Historic Publications in Electrochemistry”**

which is part of

**Electrochemical Science and Technology Information  
Resource (ESTIR)**

(<http://electrochem.cwru.edu/estir/>)

# Journal of the Electrochemical Society

APRIL 1963

VOL. 110 • NO. 4

## CONTENTS

### Editorial

The Woodward Retirement Plan .....	83C
------------------------------------	-----

### Technical Papers

A Study of the Rest Potentials in the Gold-Oxygen-Acid Systems. <i>J. P. Hoare</i> .....	245
Flaws in Anodic Ta <sub>2</sub> O <sub>5</sub> Films. <i>D. A. Vermilyea</i> .....	250
Studies on the Structure of Anodic Oxide Films on Aluminum, II. <i>R. W. Franklin and D. J. Stirland</i> .....	262
Control of Al Corrosion in Caustic Solutions. <i>L. Bockstie, D. Trevelyan, and S. Zaromb</i> .....	267
Properties of Evaporated Thin Films of SiO <sub>2</sub> . <i>D. B. York</i> .....	271
Electrical Resistivity of Stabilized Zirconia at Elevated Temperatures. <i>J. M. Dixon, L. D. LaGrange, U. Merten, C. F. Miller, and J. T. Porter, II</i> .....	276
Thorium Phosphate Phosphors. <i>P. W. Ranby and D. Y. Hobbs</i> .....	280
A Dember Effect Study of Shifts in the Stoichiometry of ZnS. <i>F. F. Morehead</i> .....	285
X-ray Study and Thermoelectric Properties of the W <sub>x</sub> Ta <sub>1-x</sub> Se <sub>2</sub> System. <i>L. H. Brizner</i> .....	289
Improvement in the Electrolytic Preparation of Iodoform. <i>R. Ramaswamy, M. S. Venkatachalapathy, and H. V. K. Udupa</i> .....	294
The Formation of Silicon Carbide in the Electric Arc. <i>W. E. Kuhn</i> .....	298
Electrode Kinetics for Chlorides of Tungsten, Antimony, and Phosphorus. <i>S. W. Mayer and W. E. Brown, Jr.</i> .....	306
Transference Numbers and Ion Association in Pure Fused Alkaline Earth Chlorides. <i>E. D. Wolf and F. R. Duke</i> .....	311
Electrochemistry and Reactions in Molten Li <sub>2</sub> SO <sub>4</sub> -Na <sub>2</sub> SO <sub>4</sub> -K <sub>2</sub> SO <sub>4</sub> . <i>K. E. Johnson and H. A. Laitinen</i> .....	314
Surface Studies on Passive Iron. <i>N. E. Wisdom, Jr. and N. Hackerman</i> .....	318
The Role of Displacement Reactions in the Determination of Activities in Alloys with the Aid of Galvanic Cells. <i>C. Wagner and A. Werner</i> .....	326
Transition from Hydrogen Ionization to Oxygen Evolution on a Platinum Electrode. <i>S. Schuldiner and R. M. Roe</i> .....	332

### Technical Notes

Phenomena at a Solid-Melt Interface. <i>J. R. O'Connor</i> .....	338
The Thermoluminescence of CaF <sub>2</sub> :Mn. <i>W. F. Schmid and R. W. Mooney</i> .....	340
Surface Masking in Gallium Arsenide During Diffusion. <i>T. H. Yeh</i> .....	341
High-Purity CdTe by Sealed-Ingot Zone Refining. <i>M. R. Lorenz and R. E. Halsted</i> .....	343
Stresses in Anodic Films. <i>D. V. Vermilyea</i> .....	345
The Mechanism of the Nickel-Fluorine Reaction. <i>R. L. Jarry, J. Fischer, and W. H. Gunther</i> .....	346

### Brief Communications

Measurement of "Pressure-EMF" in Pure Fused Salts. <i>P. Duby and H. Kellogg</i> .....	349
Preparation of Spherical Single Crystal Electrodes For Use in Electrocrystallization Studies. <i>D. K. Roe and H. Gerischer</i> ..	350

### Current Affairs ..... 89C-100C

Published monthly by The Electrochemical Society, Inc., from Manchester, N.H.; Executive Offices, Editorial Office and Circulation Dept., and Advertising Office at 30 East 42 St., New York 17, N. Y., combining the JOURNAL and TRANSACTIONS OF THE ELECTROCHEMICAL SOCIETY. Statements and opinions given in articles and papers in the JOURNAL OF THE ELECTROCHEMICAL SOCIETY are those of the contributors, and The Electrochemical Society assumes no responsibility for them. Subscription to members as part of membership service; subscription to nonmembers \$24.00 plus \$1.50 for postage outside U.S. and Canada. Single copies \$1.70 to members, \$2.25 to nonmembers. © 1963 by The Electrochemical Society, Inc. Entered as second-class matter at the Post Office at Manchester, N. H., under the act of August 24, 1912.

## EDITORIAL STAFF

**C. L. Faust**, Chairman, Publication Committee  
**Daniel V. King**, Editor  
**Norman Hackerman**, Technical Editor  
**Math G. Sterns**, Managing Editor  
**W. Salzberg**, Book Review Editor  
**Daniel J. Immediato**, Assistant Editor

## ADVISORIAL EDITORS

**C. Vosburgh**, Battery  
**Paul C. Milner**, Battery  
**A. Marsh**, Corrosion  
**C. Makrides**, Corrosion  
**Harry C. Gatos**, Corrosion—Semiconductors  
**Paul J. Frisco**, Electric Insulation  
**Samour Senderoff**, Electrodeposition  
**C. Froelich**, Electronics  
**Wain Banks**, Electronics  
**Charles S. Peet, Jr.**, Electronics—Semiconductors  
**R. Frankl**, Electronics—Semiconductors  
**Wolck Swann, Jr.**, Electro-Organic  
**Wesley Wawzonek**, Electro-Organic  
**John M. Blocher, Jr.**, Electrothermics and Metallurgy  
**W. Westbrook**, Electrothermics and Metallurgy  
**Harley Morley**, Industrial Electrolytic  
**W. Tebals**, Theoretical Electrochemistry  
**deBethune**, Theoretical Electrochemistry  
**A. Hurd**, Theoretical Electrochemistry

## ADVERTISING OFFICE

30 East 42 St., New York 17, N. Y.

## OFFICERS

**LaQue**, President  
 International Nickel Co., Inc.  
 New York, N. Y.  
**Hamer**, Vice-President  
 National Bureau of Standards,  
 Washington, D. C.  
**J. Gilbertson**, Vice-President  
 Aerospace Placement Corp.,  
 1518 Walnut St.,  
 Philadelphia 2, Pa.  
**Yeager**, Vice-President  
 Western Reserve University,  
 Cleveland, Ohio  
**G. Enck**, Treasurer  
 Northampton,  
 Chatham, Mass.  
**Campbell**, Secretary  
 National Steel Corp., Weirton, W. Va.  
**K. Shannon**, Executive Secretary  
 National Headquarters, The ECS,  
 30 East 42 St., New York 17, N. Y.

Manuscripts submitted to the Journal should be in triplicate, to the Editorial Office at 30 East 42 St., New York 17, N. Y. They should conform to the revised Instructions to Authors printed on pp. 35C-36C of the February issue. Manuscripts so submitted become the property of the Electrochemical Society and may not be published elsewhere, in whole or in part, unless permission is requested of and granted by the Society.

The Electrochemical Society does not maintain a supply of reprints of papers appearing in the Journal. A photoprint copy of any paper, however, may be obtained by ordering direct with the Engineering Library, 345 E. 47 St., New York, N. Y.

Microfilm and microfiche copies of volumes should be addressed to University Microfilms, Inc., 313 N. First St., Ann Arbor, Mich. For J. Johnson, Inc., 111 Fifth Ave., New York, N. Y., have reprint rights to out-of-print volumes of the Journal, and also have the right for sale back volumes and single issues with the exception of the current back-year. Anyone interested in securing back issues should correspond direct with them.

Table I. Comparison of transport numbers obtained by different methods

	$T_{Pb}$ in $PbBr_2$	$T_{Ag}$ in $AgNO_3$
Pressure-emf	$0.372 \pm 0.006$ (494°C)	$0.757 \pm 0.025$ (230°C)
Weighing technique (5, 6)	$0.355 \pm 0.015$ (504°C)	$0.781 \pm 0.006$ (219°C)
Bubble technique (4)	$0.347 \pm 0.013$ (500°C)	$0.76 \pm 0.05$ (225°C)

gradient, and we call it the pressure-diffusion potential.

The pressure-diffusion potential arises from the difference between the self-diffusion coefficients of anions and cations which, under the effect of the pressure gradient, migrate with different velocities relative to the bulk of the liquid. If the mechanism proves to be correct, the agreement among the different methods of measuring transport numbers should offer important implications for the validity of the Nernst-Einstein equation in pure fused salts.

Although the measurement of pressure-emf is analogous to the measurement of streaming potential in aqueous solution we believe the two phenomena are fundamentally different. Streaming potential and related electrokinetic phenomena are surface phenomena. We believe our pressure-emf to be a bulk phenomenon, independent of surface effects. We mean to prove this by experiments with porous plugs of different substances but the same molten salt. It is the apparent absence of surface double-layers in fused salt media which makes pos-

sible the measurement of pressure-emf, which would otherwise be obscured by the larger streaming potential.

#### Acknowledgment

This work is supported by the National Science Foundation under grant NSF G 20879. Mr. L. J. Howell provided valuable assistance with the measurements on lead bromide.

Manuscript received Dec. 7, 1962.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1963 JOURNAL.

#### REFERENCES

1. F. R. Duke and R. W. Laity, *J. Am. Chem. Soc.*, **76**, 4046 (1954); *J. Phys. Chem.*, **59**, 549 (1955).
2. P. Duby, Eng. Sc. D. Thesis, Columbia University (1962).
3. D. A. MacInnes, "The Principles of Electrochemistry," pp. 174-180, Dover Publications, New York (1961).
4. R. W. Laity and F. R. Duke, *This Journal*, **105**, 97 (1958).
5. H. H. Kellogg and P. Duby, *J. Phys. Chem.*, **66**, 191 (1962).
6. Results on  $PbBr_2$ , to be published.

## Preparation of Spherical Single Crystal Electrodes For Use in Electrocrystallization Studies

D. K. Roe<sup>1</sup> and H. Gerischer

*Max-Planck-Institut für Metallforschung, Stuttgart, Germany*

Single crystal electrodes have obvious importance in studies of electrochemical processes which are influenced by crystal orientation (1-6). Both flat and spherical crystal surfaces have been used; the latter exhibits all crystal orientation and may be advantageous in certain cases. Elaborate procedures used in preparing single crystal electrodes usually involve mechanical or chemical pretreatment which causes indefinite surface changes and can put the results into question quite seriously. It seemed, therefore, an interesting problem to develop an experimental method which allows convenient preparation of single crystal electrodes so that systematic investigations with a great number of freshly prepared crystals can be done in reasonable time.

The method described here has been used to prepare single crystal spheres, with a diameter of 2-3 mm, of silver, copper, or gold. The method makes use of the technique first applied by Kaishev and Mutafshiev (7), who prepared single crystal spheres by melting the end of a wire containing

single crystal segments. Upon cooling, the sphere was a single crystal if nucleated by a single crystal segment. The concept of this technique has been combined with the procedure described by Conway, Bockris, and Mehl (8) for preparing polycrystalline spherical electrodes. These authors melted the end of a polycrystalline wire in a hydrogen stream by heating the surrounding quartz tube with a gas burner and thereby obtained clean, smooth electrodes free of contamination from mechanical or chemical pretreatment.

The procedure was as follows: Single crystal wires were prepared by the Bridgman method of slow cooling. The wire, 1-2 mm in diameter, was held in a graphite mold in an evacuated quartz tube. The mold was made from spectroscopic graphite electrodes previously baked out at 1000°C in vacuum. Split molds are preferred to bored rods since the latter can produce strains in the wire; the crystals are often held fast in the mold by surface irregularities. There are no major problems associated with the preparation of single crystal wires of silver, copper, or gold. X-ray diffraction patterns

<sup>1</sup> Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Mass.

taken by back reflection show sharp, symmetrically oriented spots.

For convenience in subsequent manipulation, the single crystal wire was attached to the end of a silver or platinum wire; the two ends can simply be melted together in a small flame so that the junction is about the diameter of the wire. A Teflon plug, enlarged in Fig. 1b, was made to fit tightly around the wire and served to hold it to the end of a glass tube. Control of the vertical position of the end of the crystal was possible through the use of a parallel ground K.P.G. tube (Schott and Gen., Mainz), sealed to the inner part of the ground glass joint at the top of the apparatus shown in Fig. 1a. Quartz, Pyrex, or Jena glass is suitable for construction of the apparatus, depending on the diameter.

The end of the wire was located in the center of a tungsten spiral heater made from about 30 cm of 0.4 mm diameter wire and silver-soldered to thick tungsten leads which are sealed through the inner part of a Pyrex joint, as shown. Approximately 80w was necessary to melt the end of the crystal, but the required power will be greatly dependent on the geometry. Hydrogen or an inert gas was used to purge the apparatus. When pure hydrogen was not used, it was found necessary to mix a per cent or two of hydrogen with argon or nitrogen flowing through the tube. Otherwise, as the tungsten heater operated at an extremely high temperature, there was some oxidation of tungsten by traces of oxygen, which caused evaporation of tungsten oxide.

Temperatures, relative to the melting of the silver crystals, were determined by trial and thereafter reproduced by measuring the heater current. The end of the crystal was allowed to melt until a sphere of metal formed, two or three times the diameter of the wire. Freezing times of 10-30 sec were sufficient

for the formation of single crystal spheres. The rate of freezing for a given heater current can be estimated by gently tapping the support stand and observing the vibrations in the liquid portion of the sphere. Approximately the same freezing rate will occur in subsequent operations with crystals of the same size. After some experience it was found possible to remelt a sphere without further melting of the crystal wire.

Although the crystal wires were cleaned in nitric acid prior to forming the spheres, dull deposits were sometimes found on the surface after the first melting. These impurities can be removed by further cleaning in acid, followed by remelting of the sphere. The deposits are apparently due to condensation on the crystal of any volatile oxides which might be formed. Deposits were minimized by a thorough gas purge with the heater on, before the crystal wire is placed in the apparatus. Also a long pretreatment of heating of the spiral helps a great deal.

Cleaning of silver spheres in nitric acid revealed the crystallization state in addition to removing surface deposits. From the symmetry of the etched surface it was possible to see if the sphere was a single crystal. A more selective etch (9) is hot (70°C), concentrated sulfuric acid, which clearly reveals the (100) and (111) planes. Acid cleaning or etching followed by remelting of the sphere can be repeated until a satisfactory crystal is formed. After some experience one usually obtains a crystal sphere ready for immediate use.

After cooling, the wire was pulled up until the crystal sphere contacted the Teflon plug. The glass tube was also drawn upwards until the crystal was close to the end of the K.P.G. tube. Removal of the top portion of the apparatus and transfer to an electrochemical cell was thus possible without exposing the crystal to the atmosphere, provided an adequate flow of inert gas was maintained.

The surface of the crystal sphere was specular like a drop of mercury and, in the case of silver at least, the crystal planes (111) and (100) were often observable as small facets. With microscopic techniques it may be possible to use these individual crystal planes as electrodes. The appearance of these planes gives immediate information about the orientation of the spherical crystal.

The degree of perfection of the surfaces of crystals grown in this manner is, of course, not known. It seems reasonable to assume that gross surface irregularities are less likely on these spheres than on cut and polished metal crystals. Comparative measurements, which are dependent on surface structure, will help to estimate how closely the ideal crystal surface is approached. Preliminary potential and current-potential measurements have indicated that the (111) and (100) planes on silver crystal spheres are relatively free of growth sites. Microscopic examination of the spheres reveals a number of steps surrounding the (111) and (100) facets. The height of each step is estimated to be less than  $0.5\mu$ . The facets themselves appear microscopically flat.

Such spherical electrodes are in use in our laboratory for the study of electrocrystallization pro-

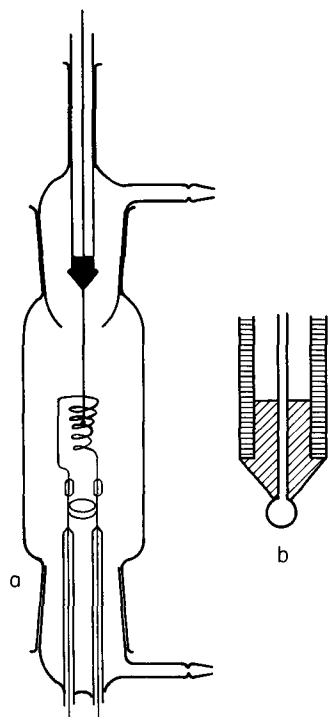


Fig. 1a. Cross section of furnace tube; Fig. 1b. detail of crystal sphere in Teflon holder.

cesses. Some preliminary experiments have also been conducted with small capillaries attached to different parts of the surface for studying the polarization behavior of selected areas on the sphere. The method allows a rapid and quite reproducible preparation of an uncontaminated single crystal surface, which may be useful also in other studies.

#### Acknowledgment

One of the authors (D.K.R.) expresses thanks to the National Science Foundation for a postdoctoral fellowship during the period of this work.

Manuscript received Nov. 26, 1962.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1963 JOURNAL.

#### REFERENCES

1. T. Erdey-Gruz *et al.*, *Z. physik. Chem.*, **A172**, 157 (1935); **A178**, 255, 266 (1937).
2. R. Kaishev, E. Budevski, and S. Malinovski, *Compt. rend. acad. bulgare sci.*, **2**, 29 (1949).
3. W. Kossel, in "Zur Struktur und Materie der Festkörper," p. 56, Springer Verlag, Berlin-Göttingen-Heidelberg (1952).
4. A. T. Gwathmey and H. Leidheiser, *Trans. Electrochem. Soc.*, **91**, 95 (1947); *This Journal*, **98**, 225 (1951).
5. R. Piontelli, G. Poli, and G. Serravalle in "Transactions of the Symposium on Electrode Processes," E. Yeager, Editor, p. 67, John Wiley & Sons, New York (1961).
6. N. A. Economou and D. Trivich, *Electrochim. Acta*, **3**, 292 (1961).
7. R. Kaishev and B. Mutafshiev, *Z. physik. Chem.*, **204**, 334 (1955).
8. B. E. Conway, J. O'M. Bockris, and W. Mehl, *J. Sci. Instr.*, **33**, 400 (1956).
9. M. Yamamoto and J. Watanabe, *J. Japan Inst. Metals*, **17**, 425 (1953).

## Manuscripts and Abstracts for Fall 1963 Meeting

Papers are now being solicited for the Fall Meeting of the Society, to be held at the New Yorker Hotel, in New York, N. Y., September 29, 30, and October 1, 2, and 3, 1963. Technical sessions probably will be scheduled on: Batteries, Corrosion, Electrodeposition, Electronics (including Semiconductors), Electro-Organic (including Symposia on Biochemical Energy Conversion Processes and Radical Formation in Electro-Organic Reactions), and Electrothermics and Metallurgy.

To be considered for this meeting, **triplicate copies of the usual 75-word abstract, as well as of an extended abstract of 500-1000 words** (see notice on page 88C of this issue), must be received at Society Headquarters, 30 East 42 St., Rm. 1806, New York 17, N. Y., **not later than May 15, 1963. Please indicate on abstract for which Division's symposium the paper is to be scheduled, and underline the name of the author who will present the paper.** No paper will be placed on the program unless one of the authors, or a qualified person designated by the authors, has agreed to present it in person. Clearance for presentation of a paper at the meeting should be obtained before the abstract is submitted. An author who wishes his paper considered for publication in the JOURNAL or ELECTROCHEMICAL TECHNOLOGY should send triplicate copies of the manuscript to the Managing Editor of the appropriate publication, 30 East 42 St., Rm. 1806, New York 17, N. Y.

Presentation of a paper at a technical meeting of the Society does not guarantee publication in the JOURNAL or in ELECTROCHEMICAL TECHNOLOGY. However, all papers so presented become the property of The Electrochemical Society, and may not be published elsewhere, either in whole or in part, unless permission for release is requested of and granted by the Editor. Papers already published elsewhere, or submitted for publication elsewhere, are not acceptable for oral presentation except on invitation by a Divisional program Chairman.