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Authors

Barry, Michael L.
Tobias, Charles W.

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University of California
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Michael L. Barry and Charles W. Tobias

May 1965

STUDIES OF THE ANODIC OXIDATION OF WHITE PHOSPHORUS

by

Michael L. Barry and Charles W. Tobias
Inorganic Materials Research Division,
Lawrence Radiation Laboratory, and
Department of Chemical Engineering
University of California, Berkeley

Abstract

Coulometric studies were made of the electrochemical oxidation of liquid and solid white phosphorus impregnated in porous conducting matrices in alkaline, neutral, and acidic electrolytes. Comparison with the rates of formation from the spontaneous disproportionation-decomposition reactions of phosphorus at zero current density showed that phosphorus in a silver-amalgam matrix in neutral and acidic media was quantitatively oxidized to phosphorus and phosphoric acids with overall coulombic efficiencies approaching 100% at current densities up to 10 ma/cm^2 . The open-circuit potentials measured for the phosphorus electrodes were considerably lower than the potentials predicted for the oxidation of phosphorus to the phosphorus oxyacids, indicating that the potential-determining reaction was either partial oxidation of phosphorus to an intermediate compound or oxidation of the phosphine produced by the disproportionation reactions of phosphorus.

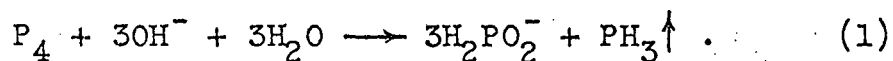
INTRODUCTION

This work involved an exploratory experimental investigation of the electrochemical oxidation of white phosphorus⁽¹⁾. The systematic chemistry and thermodynamic properties of phosphorus and phosphorus compounds have been studied fairly extensively^(1,2,3,4), but very little work has been done to characterize the electrochemical behavior of phosphorus. In addition to providing thermodynamic data by direct electrochemical measurements, the electrochemical oxidation of phosphorus is of interest for practical reasons. Oxidation of elemental phosphorus to phosphoric acid is currently a major chemical operation in the chemical industry; recovery of part of the free energy of the oxidation reaction as electrical energy from an electrochemical cell would be very attractive. Also, use of phosphorus as an anodic reactant in a battery or fuel cell may be of interest. In addition, if phosphorus can be made to undergo electrochemical oxidation, it may well be possible to synthesize electrochemically other phosphorus compounds, such as phosphorus-oxy-halogen compounds, which may not now be readily obtained.

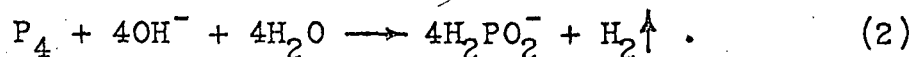
The expected products of the electrochemical oxidation of phosphorus in aqueous electrolytes are the phosphorus oxyacids or their anions. These compounds consist of phosphorus, hydrogen, and oxygen, generally in configurations of four atoms surrounding the central phosphorus atom. The more common of these oxyacids are based on a

single phosphorus atom, but oxyacids based on two, three, and more phosphorus atoms are well known. The oxyacids based on one phosphorus atom are hypophosphorus acid, H_3PO_2 ; orthophosphorous acid, H_3PO_3 ; and orthophosphoric acid, H_3PO_4 ; the apparent oxidation numbers of phosphorus in these acids are 1, 3, and 5, respectively.

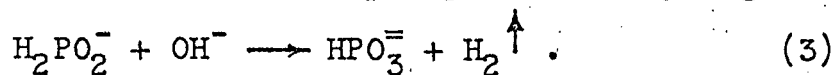
The oxidation potentials estimated for simple oxidation states of phosphorus are quite high; for example, the standard potential for oxidation of phosphorus to hypophosphite in alkaline media calculated from thermochemical data⁽³⁾ is 2.05 v. These high oxidation potentials indicate that phosphorus should undergo a series of disproportionation-decomposition reactions in aqueous media. Thus, white phosphorus in contact with alkaline media disproportionates to the +1 and -3 states, hypophosphite and phosphine:



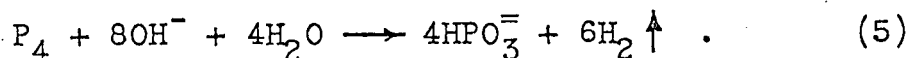
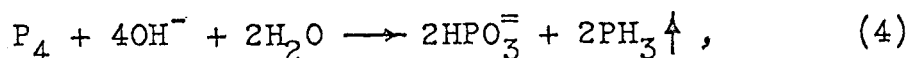
Also, white phosphorus decomposes alkaline solutions to form hydrogen and hypophosphite:



The hypophosphite formed from these reactions also decomposes alkaline solutions to form phosphite and hydrogen:



Other disproportionation-decomposition reactions of phosphorus in alkaline media produce phosphite, phosphine, and hydrogen:



The equivalent reactions in acidic media, as well as the further oxidation of phosphite to phosphate, are theoretically possible, but, as will be shown later, they do not occur to any noticeable extent.

The occurrence of spontaneous disproportionation-decomposition reactions of phosphorus in aqueous media implies that the phosphorus electrode should corrode; that is, there should be an effective internal cell current (and resulting displacement from the equilibrium potential) when the external cell current is zero. A method of analyzing corroding electrode systems has been developed for relatively simple cases⁽⁵⁾, but it is not applicable to systems as complex as the phosphorus electrode. Also, the products of the spontaneous reactions occurring at the phosphorus electrode are themselves electrochemically active and may contribute to the electrode potential. Furthermore, phosphorus is not an electrical conductor and is not soluble in water, so formulation of a suitable electrode is difficult. For all these reasons, open circuit potentials measured for phosphorus electrodes may have little thermodynamic significance, and it has been necessary to develop new techniques to determine the electrochemical characteristics of white phosphorus.

The general procedure used to determine the extent of participation of phosphorus in the electrode reaction was:

1. Development of suitable phosphorus electrodes.
2. Measurement of the open circuit half-cell potentials of the phosphorus electrode over broad ranges of electrolyte pH.
3. Determination of the gross overall electrochemical reactions of the phosphorus electrode by comparing the rates of formation of phosphoric, phosphorous, and hypophosphorous acids, hydrogen, and phosphine at known current densities to the rates of formation of these compounds at zero current density.

In addition, half-cell potentials were measured for the various products of the disproportionation-decomposition reactions of phosphorus.

EXPERIMENTAL APPARATUS AND TECHNIQUES

Since white phosphorus has a very high electrical resistivity and is virtually insoluble in water, normal electrode configurations were not satisfactory. The phosphorus electrodes eventually developed consisted of solid or liquid white phosphorus impregnated in a porous, electrically conducting matrix. In order to provide adequate three-phase contact between phosphorus, conductor and electrolyte, it was necessary to ensure that phosphorus preferentially wetted the conductor surface;

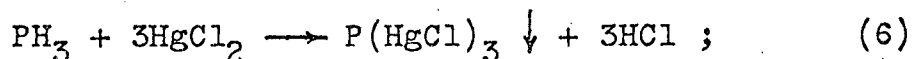
that is, the contact angle at the phosphorus-electrode, electrolyte interface had to be less than 90° . With the exception of mercury, phosphorus does not preferentially wet most pure metal surfaces under normal conditions, and mercury-phosphorus electrodes did not provide large enough regions of three-phase contact. Other conductors tried in these studies were silver, platinum, copper, nickel, tin, lead, iron, amalgams of all these metals, and graphite. Of these systems, only silver-amalgam powder and graphite powder were found to be suitable matrix materials⁽¹⁾.

A simplified diagram of the experimental apparatus is presented in Figure 1. The phosphorus electrode was contained in the main compartment of the electrochemical cell, and the reference electrode (Hg/HgO for alkaline electrolytes and calomel for neutral and acidic electrolytes) and counter electrode were in side compartments. Provision was made to collect and measure the gas produced in both the main compartment and the counter-electrode compartment, and samples of the electrolyte solution could be withdrawn from the main compartment. The electrolyte solution was agitated by a vibrating dasher*, which passed out of the cell through a gas-tight diaphragm. Separate studies of the effectiveness of mixing in this cell indicated that mass-transfer in the electrolyte was not

* Vibro-Mischer manufactured by AG. für Chemie-Apparatebau, Zürich, Switzerland.

the limiting factor in any of the reactions studied. The potential between the phosphorus electrode and the reference electrode was measured by a vacuum-tube voltmeter with an input impedance of 10^{14} ohms* ; the output from the VTVM was reduced by a voltage divider and then put into a recording potentiometer. The polarizing circuit consisted of a D.C. power supply and a current recording device in series between the phosphorus electrode and the counter electrode.

The rates of the reactions occurring at the phosphorus electrode were determined by measuring the rates of formation of the products: H_3PO_2 , H_3PO_3 , H_3PO_4 , H_2 , and PH_3 . These compounds were determined by the following analyses: phosphine was measured by scrubbing the product gas with saturated mercuric chloride solution and titrating the hydrochloric acid which was formed according to the reaction:



hydrogen was determined as the difference between the total dry gas produced and the amount of phosphine produced; hypophosphorous acid was determined by oxidation with sulfatoceric acid at 60°C ; phosphorous acid was determined by oxidation with iodine in neutral solution; and orthophosphoric acid was determined colorimetrically as the phosphomolybdate complex.

There is no a priori reason to expect that the only

* Kiethly Model 200B Vacuum Tube Volt Meter.

products of the electrochemical oxidation of white phosphorus are the mono-phosphorus oxyacids; indeed, oxidation of the tetratomic P_4 molecule to the final product should result in many di- and tri-phosphorus fragments, some of which are known to be relatively stable. However, the separation and analyses of these higher oxyacids are extremely complex, and in these experiments, these compounds were oxidized, hydrolyzed, and determined as orthophosphoric acid.

EXPERIMENTAL RESULTS

The half-cell potentials measured for the phosphorus electrodes and phosphine electrodes are presented in Table I. The phosphorus-electrode potentials varied nearly linearly with the pH of the electrolyte (as shown in Figure 2) but did not vary with hypophosphite or phosphite concentration. The potentials of phosphorus in both silver-amalgam matrices and graphite matrices were the same in alkaline solutions, but differed noticeably in neutral and acidic solutions. Alkaline and acidic solutions of phosphine resulted in potentials very slightly higher than the potentials predicted for the oxidation of phosphine to phosphorus and also only slightly higher than the potentials of the phosphorus electrode in the same electrolytes. The potentials of hypophosphite and phosphite in alkaline solutions are shown in Table II; in effect, these potentials were established only in highly

concentrated alkaline electrolytes (5 N NaOH) where the rate of the decomposition reaction (Eqn.3) to form phosphite and hydrogen was appreciable. However, the electrode potential for these hypophosphite-phosphite solutions, once established, remained constant even though the concentrations of hypophosphite and phosphite each changed by over an order of magnitude during the course of the experiment.

Polarization experiments showed that the potentials of the graphite-matrix phosphorus electrodes were much more sensitive to small changes of the applied current density than were the silver-amalgam-matrix electrodes. This result is shown in Figure 3. In effect, the graphite electrodes could not be used in coulometric studies since current densities large enough to produce measurable quantities of the phosphorus oxyacids polarized the electrode to the point where other electrode reactions (such as evolution of oxygen) took place.

Typical results of the coulometric studies of the phosphorus electrodes are shown in Table III, where the rates of formation of the products of the electrode reactions at a given current density are compared to the rates of formation at zero current density. In alkaline media the effect of the applied current on the electrode reactions appeared very complex; in general, the rate of formation of phosphine decreased, the rates of formation of phosphite increased, and, at relatively high

current densities, the rate of formation of phosphate became significant. It should be emphasized that phosphate was not a product of the disproportionation-decomposition reactions, so the formation of phosphate was a direct indication of the effect of the applied current on the phosphorus electrode. Unfortunately, the coulometry in alkaline media was not quantitative, that is, the net increase in the rates of oxidation did not correspond to the applied current density. In addition, although the electrode potentials were 0.2 to 0.3 v from the oxidation potential of mercury, some attack of the amalgam matrix occurred resulting in the formation of small amounts of mercury compounds (equivalent to less than 5% of the total current passed).

In neutral and acidic media, the rates of the disproportionation-decomposition reactions were negligible, and the evidence of the anodic oxidation of the phosphorus electrode was much clearer. As shown in Table IV, the overall coulombic efficiencies in these cases approached 100%. These coulombic efficiencies were calculated on a basis of a 5-electron transfer for oxidation of phosphorus to phosphoric acid, a 3-electron transfer for oxidation to phosphorous acid, and a 1-electron transfer for oxidation to hypophosphorous acid. No mercury or silver ions or precipitates were found in solution in any of these experiments.

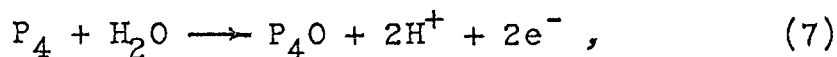
INTERPRETATION

Three hypotheses may be advanced to explain the low potentials measured for the phosphorus electrode: (1) the

corrosion current caused the displacement of the electrode potential from the theoretical equilibrium value; (2) the potential-determining reaction was the partial oxidation of P_4 to some intermediate compound rather than to the mono-phosphorus oxyacids; (3) the electrode potential was established by a product of the spontaneous disproportionation-decomposition reactions.

The first hypothesis can be refuted by examination of the polarization curves of the phosphorus electrode. In Figure 4 the electrode potential is shown as a function of the total current density, that is, the sum of the external applied current density and the internal corrosion current density. The dotted line in this figure represents arbitrarily the polarization caused by the corrosion current alone. At the point where small external currents were applied, the electrode potential appears to be almost discontinuous; this behavior indicates that the potential-determining reaction was not the same as the corrosion reactions.

The second hypothesis does not appear to be unreasonable. If, for example, the potential-determining reaction was of the type:



the free energy of the reaction can be estimated from bond energies as approximately 10 Kcal (assuming entropy differences are relatively small). Then the potential for the two electron transition would be of the order of

0.2 v, relative to the hydrogen electrode in the same solution. Actually, the uncertainties in the bond energies and entropies are large, so this potential would be in the range -0.5 v to +0.5 v. If the succeeding oxidation and reorganization steps leading to the mono-phosphorus oxyacids were fast, then the electrode potentials would not depend upon the concentrations of these oxyacids. Therefore, in these respects, the behavior of an electrode based on a reaction of the type shown in Eqn.(7) would qualitatively resemble the observed behavior of the phosphorus/^{electrode.}

The third hypothesis to explain the low electrode potentials measured for phosphorus also appears reasonable, at least in alkaline media. The potentials established by phosphine were quite close to the measured phosphorus-electrode potentials if the latter were corrected for the partial pressure of phosphine in the gas produced by the disproportionation-decomposition reactions. However, this hypothesis appears inapplicable for neutral and acidic solutions, where the amounts of phosphine produced were negligible.

The quantitative anodic oxidation of phosphorus to phosphorous and phosphoric acid in neutral and acidic media appears very promising. Unfortunately, the experimental data presently available are not sufficient to predict detailed mechanisms for the electrode reactions. The differences in sensitivity to polarization between the silver-amalgam-matrix and the graphite-matrix phosphorus

electrodes and the production of traces of mercuric oxide at high current densities in alkaline media indicate that the silver-amalgam matrix may have been involved in the electrode reaction. Attempts to determine the degree of this involvement have been unsuccessful to date.

CONCLUSIONS

When an electrode consisting of phosphorus impregnated in a conducting matrix is immersed in aqueous solutions of various electrolytes, the potentials established at the electrode are considerably lower than the corresponding potentials calculated for the oxidation of phosphorus to the various phosphorus oxyacids. These low potentials may be caused by partial oxidation of phosphorus to some intermediate compound or, in alkaline solution, by oxidation of the phosphine produced by the disproportionation-decomposition reactions of phosphorus.

Coulometric studies of the anodic oxidation of phosphorus in a silver-amalgam matrix in neutral and acidic media show that phosphorus is quantitatively oxidized to phosphorous and phosphoric acids with a coulombic efficiency approaching 100% at current densities of up to 10 ma/cm^2 . Results of coulometric studies of the phosphorus silver-amalgam-matrix electrode in alkaline media are obscured by the simultaneous disproportionation-decomposition reactions of phosphorus. It appears that

the first step is the oxidation of phosphine, and then, as the current density is increased, other electrode reactions also occur, leading eventually to the formation of phosphate. There are some indications that the silver-amalgam matrix takes part in these reactions in some manner. Further studies should be made to explore the effects of using other metals as electrode matrices, to determine precisely the effects of current density and pH on product distribution, and to determine the amounts and types of di- and tri-phosphorus oxyacids formed at the electrode.

The results of anodic oxidation of phosphorus in a silver-amalgam matrix in neutral and acidic media appear quite promising; it is possible that processes based on this method of oxidizing phosphorus may have direct practical applications.

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REFERENCES

1. M. L. Barry and C. W. Tobias, The Electrochemical Oxidation of White Phosphorus, UCRL-11573, Lawrence Radiation Laboratory, University of California, Berkeley, California (1964).
2. For an extensive and detailed presentation of phosphorus chemistry, see Phosphorus and Its Compounds Vol. 1, by John R. Van Wazer (Interscience, New York, 1958); for a more concise summary, see Systematic Inorganic Chemistry, by D. M. Yost and H. Russell, Jr. (Prentice-Hall, Inc., New York, 1944).
3. T. D. Farr, Phosphorus, Properties of the Element and Some of Its Compounds, Tennessee Valley Authority, Chem. Eng. Rept. No. 8, U.S. Government Printing Office (1950).
4. W. M. Latimer, Oxidation Potentials, Prentice-Hall, Inc., New York (1952).
5. M. Stearn and A. L. Geary, J. Electrochem. Soc., 104, 56, (1957).
M. Stearn, J. Electrochem. Soc., 104, 559, 645 (1957).

Table I. Measured Potentials of Phosphorus and Phosphine Electrodes

Electrode Configuration	Temp. °C	Electrolyte	Concentration moles/liter	Half-Cell Potential (Rel. to std. H ₂), v
Phosphorus Ag-Hg Matrix	60	NaOH	10.0	1.08
"	"	"	1.00	0.90
"	40	"	10.0	1.07
"	"	"	1.02	0.89
"	"	"	0.100	0.83
"	"	"	0.010	0.5
"	"	Na ₂ SO ₄	0.5 (pH=5.5)	0.3
"	"	Na ₂ SO ₄	0.5	0.18
"	"	H ₂ SO ₄	0.0050	
"	"	H ₂ SO ₄	0.050	0.13
"	"	H ₂ SO ₄	0.49	0.08
"	"	H ₂ SO ₄	4.95	0.00
Phosphorus Graphite Matrix	"	NaOH	1.02	0.89
"	"	H ₂ SO ₄	0.49	0.04
Phosphine Ag-Hg Matrix	60	NaOH PH ₃	9.99 (saturated)	1.12
"	40	NaOH PH ₃	1.00 0.0024	0.94
"	"	H ₂ SO ₄ PH ₃	0.49 0.0016	0.11

Table II. Hypophosphite and Phosphite Electrode Potentials
(Silver-amalgam electrode, 60°C)

<u>Electrolyte Composition, molar</u>					<u>Half-Cell Potential, volts</u> <u>(Rel. to standard H₂ electrode)</u>
<u>NaOH</u>	<u>H₂PO₂⁻</u>		<u>HPO₃⁻</u>		
	<u>Initial</u>	<u>Final</u>	<u>Initial</u>	<u>Final</u>	
10.0	0.050	0.004	0	0.05	0.78
10.0	0	0	0.036	0.036	0*
5.84	0.043	0.014	0	0.03	0.70
1.00	0.041	0.041	0	0	0*
1.00	0.096	0.096	0.11	0.11	0*

* The silver-amalgam electrode potential remained equal to the Hg/HgO equilibrium potential.

Table III. Phosphorus Electrode Coulometry (Standard Silver-Amalgam-Matrix Phosphorus Electrodes, 40°C)

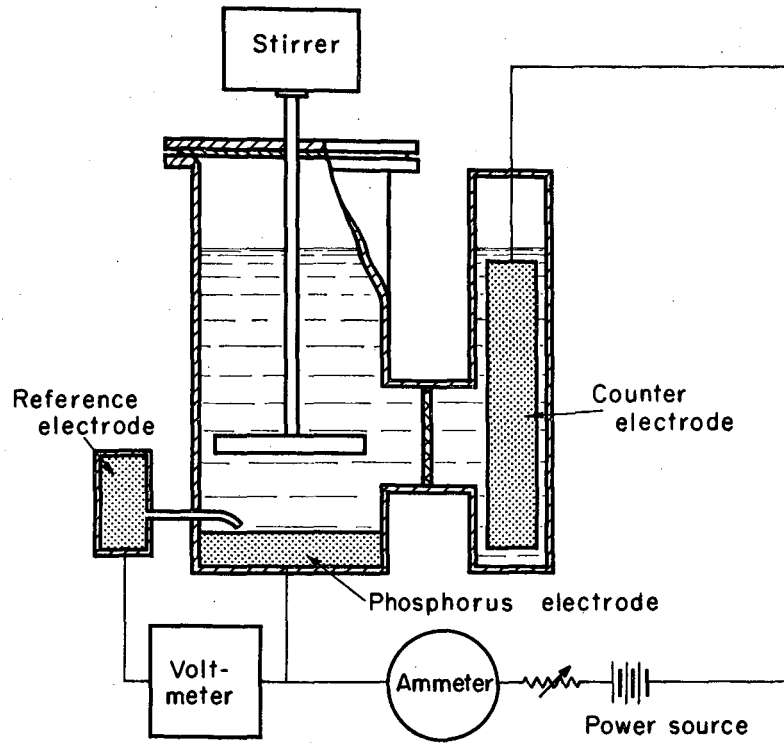
Electrolyte	Conc. Molar	Applied Current Density x 10 ⁴ meq/cm ² min	Rates of Formation, meq/cm ² min x 10 ⁴									
			With Applied Current			With Zero Current Density						
			H ₃ PO ₂	H ₃ PO ₃	H ₃ PO ₄	H ₂	PH ₃	H ₃ PO ₂	H ₃ PO ₃	H ₃ PO ₄	H ₂	PH ₃
NaOH	10.3	28.4	2.4	2.4	10.8	5.6	1.2	2.8	3	0	4	2.3
"	1.02	19.3	25	21	0	18	8.5	20	16	0	18	12.
"	1.02	62.7	20	22	50	11	6.6	20	16	0	18	12.
NaOH	0.010	12.5	0.2	2.1	12	0	0	0	0	0	0	0
Na ₂ SO ₄	0.5											
H ₂ SO ₄	0.055	31.8	0.9	11.1	19	0	0	0	0	0	0	0
"	0.57	11.8	0.3	3.8	7.8	0	0	0	0	0	0	0
"	0.50	60.6	1.6	23	33	0	0	0	0	0	0	0

Table IV. Coulombic Efficiency of the Anodic Oxidation of Silver-Amalgam-Matrix Phosphorus Electrodes

Electrolyte	Concentration Molar	Applied Current Density ma/cm ²	Rates of Formation ma/cm ²			Coulombic Efficiency %		
			H ₃ PO ₄	H ₃ PO ₃	H ₃ PO ₂	H ₃ PO ₄	H ₃ PO ₃	H ₃ PO ₂
NaOH	0.010	2.0	1.9	0.3	0.03	95	15	1.5
Na ₂ SO ₄	0.5							
H ₂ SO ₄	0.055	5.1	3.1	1.8	0.15	61	35	3
"	0.57	1.9	1.2	0.6	0.05	64	32	3
"	0.50	9.7	5.3	3.7	0.3	55	38	3

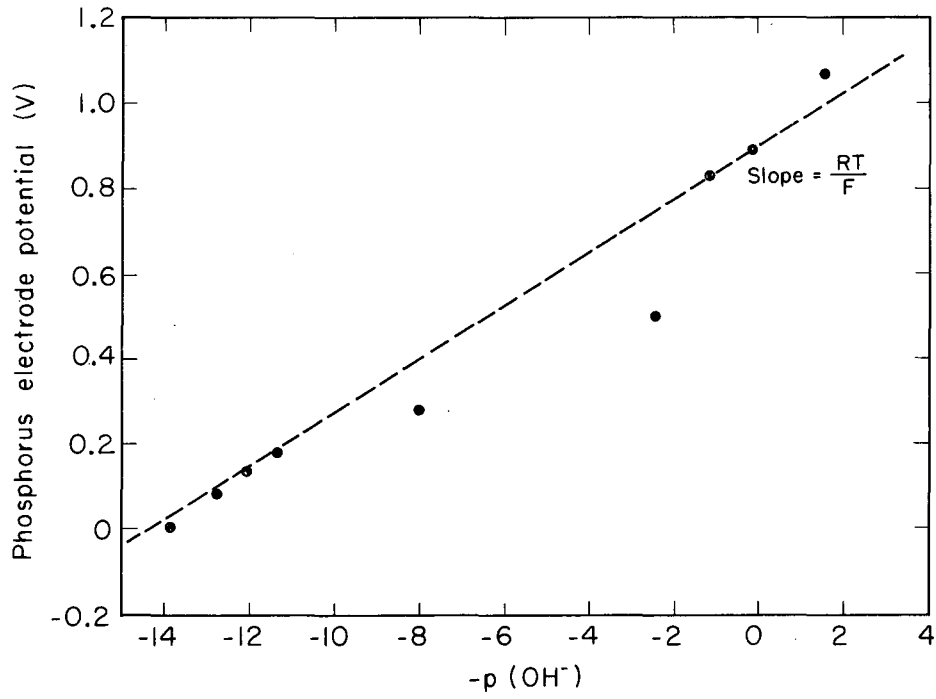
FIGURE CAPTIONS

- Figure 1. Experimental apparatus for phosphorus electrode studies.
- Figure 2. The effect of hydroxyl-ion activity on the phosphorus-electrode potential (white phosphorus in silver-amalgam matrix, 40°C).
- Figure 3. Polarization of phosphorus electrodes (1.0N NaOH, 40°C).
- Figure 4. Polarization of corroding phosphorus electrode. (Current density equals sum of external applied current density and corrosion current density, silver-amalgam matrix, 40°C, 1.0N NaOH.)



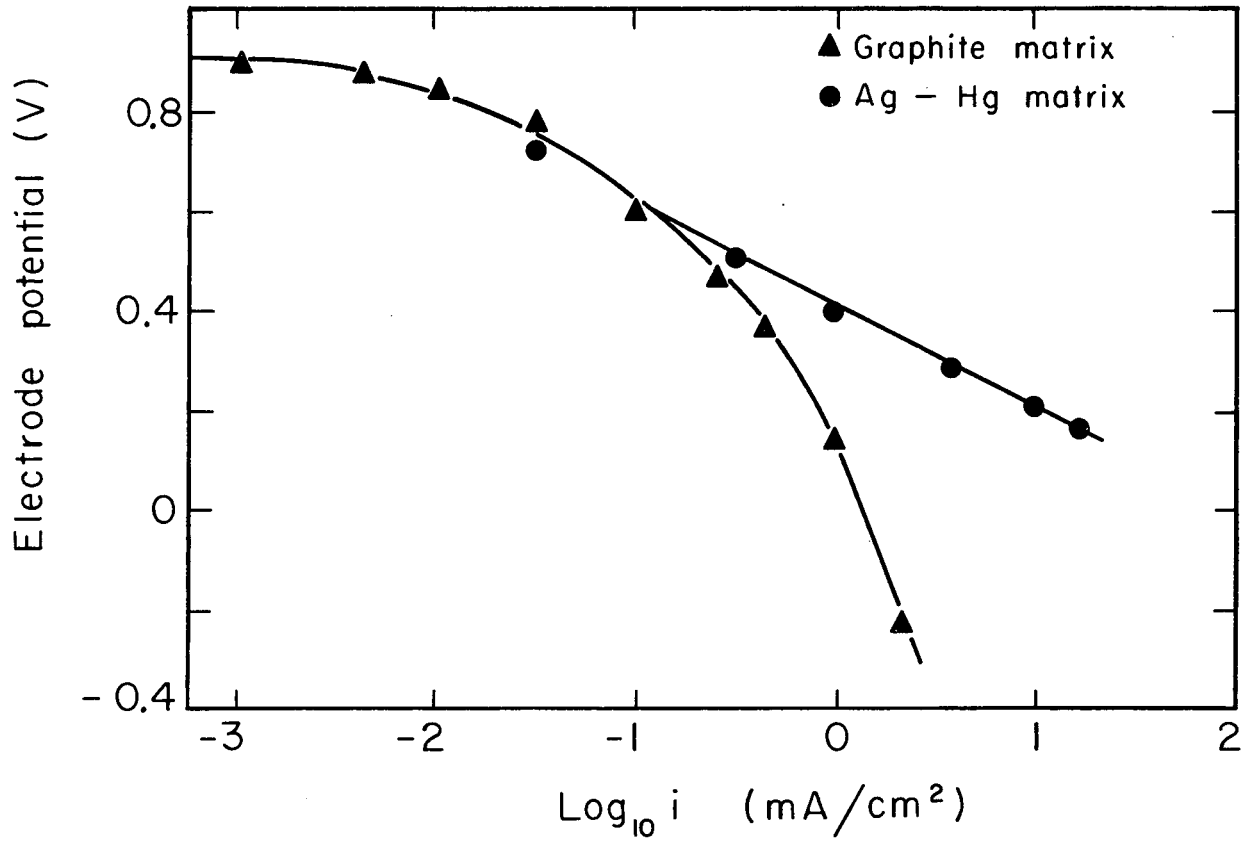
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Fig. 1



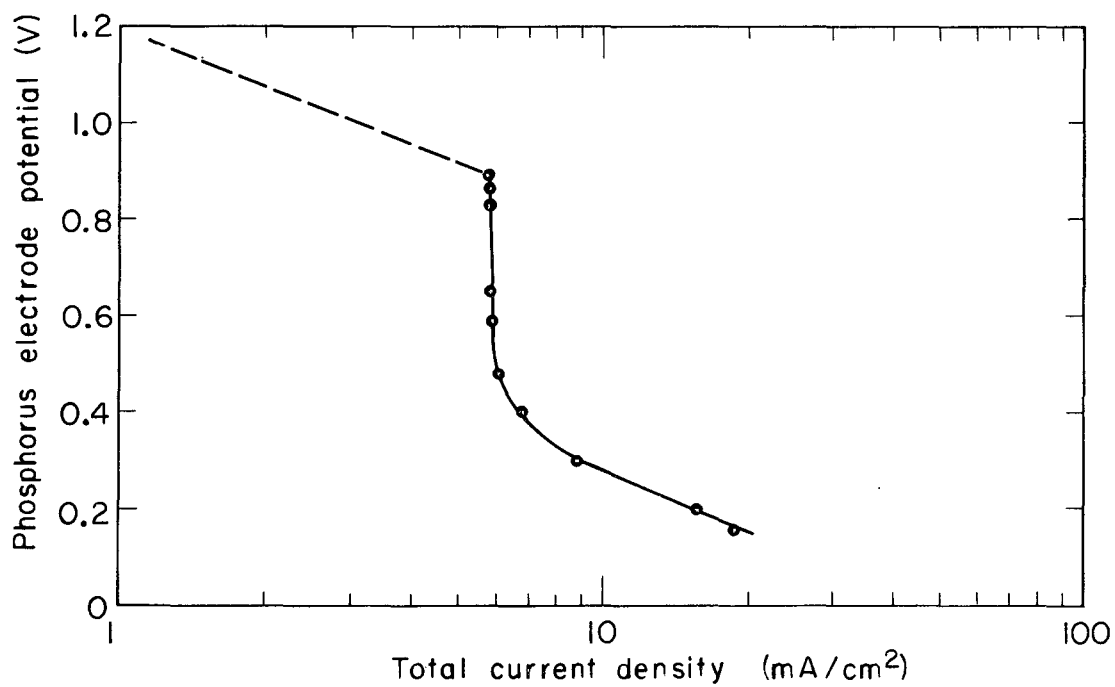
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Fig. 2



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Fig. 3



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Fig. 4

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