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PREPARATION, ELECTRICAL AND PHOTOELECTROCHEMICAL PROPERTIES
OF MAGNESIUM DOPED IRON OXIDE SINTERED DISCS

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ABSTRACT

Sintered discs of magnesium substituted iron oxides have been prepared by gel routes or classical solid state reaction techniques and their crystallographic, electrical, and photoelectrochemical properties examined. The discs, sintered between 1200 and 1400°C for 20 hours, contain both α -Fe₂O₃ and a spinel phase. The electrical properties of the discs have been correlated with spinel concentration, the electrical resistivity decreasing with increasing spinel content. The materials were found to be consistently n-type by Seebeck voltage measurements. Photoelectrochemical measurements in aqueous solution showed however that the sintered disc electrodes exhibit photocathodic currents that are characteristic of p-type semiconductors. Evidence is presented which suggests that inhomogeneities in the near surface region of the discs are responsible for the observed photoelectrochemical properties.

Introduction

Over the last decade there has been considerable interest in the use of semiconducting materials as photoelectrochemical diodes for the photosensitized dissociation of water using sunlight as an energy source, and metal oxide semiconductors appear to be promising materials for this application. The photoelectrochemical cell uses two semiconducting photoelectrodes, an n-type semiconductor photoanode where oxidation of OH⁻ to O₂ occurs, and a p-type photocathode for the reduction of H⁺ to H₂. From the standpoint of photoelectrolysis, transition metal oxides have many desirable qualities. They are inexpensive and have bandgaps in the near U.V. or visible which allow utilization of some portion of the solar spectrum. In addition, these materials can exhibit good stability during the oxidation

and reduction processes which occur during photoelectrolysis.

One of the main problems associated with the use of transition metal oxides in photoelectrolysis concerns the availability of materials with appropriate electronic properties. There are numerous n-type semiconducting oxides, but suitable p-type oxide semiconductors, such as the rare earth rhodates (1), are scarce. Thus, the lack of materials with suitable electrical properties has been a severe limitation in the development of an oxide based photoelectrolysis cell.

Recently, it has been suggested that iron oxide, normally an n-type semiconductor at room temperature, might be modified to become a p-type semiconductor which could be used as a photocathode in a p-n photoelectrolysis cell. Gardner et al. (2) have reported that iron oxide doped with a small amount of magnesium oxide showed p-type Seebeck coefficients at high temperatures. Leygraf et al. (3) reported that magnesium substituted iron oxides, sintered at high temperatures and quenched to room temperature exhibited photocathodic currents when used as photoelectrodes in aqueous solution. In addition, it was reported that hydrogen evolution occurs on the surfaces of these photoelectrodes when they are used in a photoelectrolysis cell in short circuit with a silicon doped iron oxide photoanode.

In light of the rarity of p-type semiconducting oxides and the unusual properties of the magnesium-iron-oxygen system, it is worthwhile to examine the solid state and photoelectrochemical properties of these materials more closely. This work presents an investigation of the preparation and characterization of magnesium-substituted iron oxide ceramics.

Sintered discs of magnesium substituted iron oxides were prepared by both gel techniques and conventional slurry milling of the binary oxides. X-ray diffraction experiments show that these materials are multiphase, containing both the Fe_2O_3 corundum phase and a spinel phase. A correlation has been observed between the room temperature electrical resistivity and the amount of spinel present. Although qualitative measurements of the Seebeck voltage showed these materials to be consistently n-type at room temperature, photoelectrochemical experiments using the ceramic discs as photoelectrodes showed cathodic photocurrents under illumination. More important, photochemical techniques have been used to show that the inhomogeneities of these materials in the near surface region may be related to the photoelectrochemical properties of the magnesium substituted iron oxide samples.

Experimental

Magnesium substituted iron oxide samples were prepared using both conventional solid state techniques and gel synthesis. In conventional preparations powders of Fe_2O_3 (MCB reagent) and MgO (Mallinckrodt) were weighed to give the desired compositions of between 0 and 10 mole percent of Magnesium oxide. The powders were mixed by either dry ball milling or by mixing in a methanol slurry.

For the gel preparations the appropriate amounts of the metal chlorides or nitrates were mixed in aqueous solution. The metal hydroxides were then precipitated using an excess of ammonium hydroxide at pH 12. The resultant product was aged for at least thirty minutes then filtered and washed

thoroughly with distilled water. The gels were then dried by heating to about 100°C over 12 hours to remove excess water, resulting in an amorphous xerogel.

500 mg aliquots of the powders obtained by either gel synthesis or conventional techniques were cold pressed into 0.5" diameter discs at 20,000 kg/cm² pressure. The cold pressed discs were then sintered in air using a platinum crucible containing a bed of powder of the same composition as the discs at temperatures between 110 and 1400°C in a vertical tube furnace. After 20 hours the discs were quenched to room temperature in air.

X-ray powder diffraction was carried out on ground sintered discs of magnesium iron oxides using a Siemens model D500 powder diffractometer equipped with monochromated Cu α_1 radiation. X-ray powder patterns were taken using a scan rate of 3° 2 θ /min in the region between 20 and 80° 2 θ . Phase identification was done with the aid of known standards, (spinel and α -Fe₂O₃ commercially available). Qualitative estimations of the relative amounts of each phase present was done using the ratio of the integrated step counted intensities of the (220) spinel reflection and the (012) corundum reflection. The integrated intensities were taken using a step size of 0.1° 2 θ at 2 seconds per step. The relative error in the ratio of integrated intensities is estimated to be approximately 20%. The ratios are not corrected for the relative intensities of either phase relative to corundum (Al₂O₃), and therefore, the absolute error of the ratios is substantial in light of the difference between $I_{\text{Fe}_3\text{O}_4}/I_{\text{cor}}$ versus $I_{\text{Fe}_2\text{O}_3}/I_{\text{cor}}$. Therefore, the ratios are used for qualitative comparative purposes only.

The electrical properties of the samples were determined using the Van der Pauw four probe technique (4). Ohmic contacts to the sample were made using an indium-gallium eutectic alloy, and the ohmicity of the contact was verified by repetitive measurements at current magnitudes between 10 μ A and 100 mA. Carrier type was determined by qualitative measurements of the Seebeck voltage.

Electrodes of magnesium substituted iron oxide discs were prepared using an indium-gallium eutectic alloy to ensure ohmic contact. Each disc was then mounted on a copper plate to which a metallic lead, insulated with a glass tube, was attached. All metallic surfaces were then insulated with a silicon resin, (Dow Corning RTV), so that only the surface of the disc was exposed.

Photoelectrochemical experiments were carried out using a Pine RDE-3 potentiostat in a standard three electrode configuration with a platinum counter electrode and an Hg/HgO reference electrode in an all quartz cell. The electrolyte was 1 M NaOH made from NaOH pellets (Mallinckrodt AR) and distilled deionized water. All potentials reported here are with reference to the reversible hydrogen electrode (RHE).

D.C. photocurrent measurements were performed with a 300 tungsten-halogen lamp. The illumination was passed through an I.R. filter then focused on the sample using a quartz lens. The total illumination intensity was approximately 30 mW/cm², as measured with a calibrated Epply thermopile.

A.C. photocurrent measurements were performed with a 150W high pressure Xenon arc lamp. The illumination from the Xenon lamp was passed through a Heath monochromator equipped with an I.R. filter then chopped at 150 Hz with

a Bulova tuning fork chopper (model 140C) mounted at the monochromator exit slit. The monochromatic chopped light beam was then focused with quartz optics onto the sample. The photocurrents were detected with a PAR model 124A lock-in amplifier with a model 117 preamplifier operating in the differential mode.

Results and Discussion

X-Ray Crystallography and Electrical Properties

X-ray diffraction studies of ground sintered discs of magnesium substituted iron oxides showed the presence of only the hexagonal corundum phase of Fe_2O_3 mixed with a cubic spinel phase. It was found that the transformation from the pure Fe_2O_3 corundum phase to the spinel Fe_3O_4 occurs abruptly at around 1375°C , as reported in the literature (5). The abruptness of this transition is consistent with the known intolerance of $\alpha\text{-Fe}_2\text{O}_3$ for non-stoichiometry. In the case of magnesium containing mixtures, the formation of a spinel phase, most likely $\text{Fe}_{3-x}\text{Mg}_x\text{O}_4$ occurs at lower temperatures. The formation of the spinel phase is directly related to the amount of magnesium oxide present in the mixture, as shown in Figure 1.

FIG. 1

Schematic x-ray diffraction patterns ($\text{CuK}\alpha$) for Mg doped Fe_2O_3 disks, sintered at 1375°C (— full line is corundum, --- broken line is spinel)

Table 1 presents the uncorrected integrated intensity ratio of the spinel (220) reflection to the (012) Fe_2O_3 corundum reflection. This ratio is an indication of the relative concentration of spinel in the ceramic disc. It is evident that the addition of the magnesium to the iron oxide mixture enhances the formation of the spinel phase at lower temperatures.

TABLE 1

Gel Synthetic Route
Temperature = 1350°C for 20 Hours

Initial Composition Mole % Mg	$\frac{I_{\text{spinel}}}{I_{\text{corundum}}}$	Resistivity ($\Omega\text{-cm}$) 300 K
0.0	0	10^6
2.0	0.4	3600
5.0	0.6	100
10.0	1.0	8

Kuczynski (6) investigated the mechanism of the formation of MgFe_2O_4 from the binary oxides and has suggested that the formation of the spinel occurs by diffusion of cations across grain boundaries. At high temperatures oxygen is lost from Fe_2O_3 and exchange of Fe^{2+} and Mg^{2+} can occur by diffusion, resulting in a spinel phase. Further diffusion of Mg^{2+} will eventually result in the formation of the pure spinel. In the present case, it is likely that even in the initial spinel, MgFe_2O_4 , further cation exchange takes place so that the solid solution $\text{Fe}_{3-x}\text{Mg}_x\text{O}_4$ is formed. This would explain the large amounts of spinel formed at temperatures below the corundum-spinel transition temperature of Fe_2O_3 in mixtures containing only a small amount of magnesium oxide, (10% or less).

Table 1 also presents the room temperature electrical properties of the same ceramic discs. In all cases qualitative Seebeck voltage measurements indicated that the materials were n-type semiconductors, as would be expected from the phases present. Figure 2 shows a graph of electrical resistivity versus sintering temperature at constant preparative conditions. A graph of $I_{\text{spinel}}/(I_{\text{corundum}} + I_{\text{spinel}})$ versus temperature for a constant magnesium concentration is also plotted on the same axis. There is an obvious correlation between the amount of spinel present and the electrical resistivity of the samples: an increase in the amount of spinel present lowers the resistivity.

The evolution of the electrical resistivity with composition, coupled with the carrier type, suggests that electrical conduction in these materials may occur through a percolation of carriers provided by the spinel phase inclusions, because $\alpha\text{-Fe}_2\text{O}_3$ is a high resistivity material while as Fe_3O_4 is a semimetal at room temperature (7).

As a further investigation of the electrical properties of these multiphase ceramics, the growth of magnesium doped single crystals by chemical vapor transport was attempted. The charge consisted of 1 mole percent Mg metal with Fe_2O_3 . The concentration of the TeCl_4 transport agent was 2.3 mg/cc and the transport conditions were the same as for Fe_2O_3 (8). The crystals obtained through this synthesis was found by x-ray analysis to be corundum phases which probably contain a small amount of Mg^{2+} . The room temperature resistivity of these crystals was greater than $10^6 \Omega\text{cm}$.

FIG. 2
Resistivity and phase composition versus sintering temperature for Fe_2O_3
disks with 10% MgO

The results of the single crystal experiments show that Mg doping of Fe_2O_3 does not produce a conducting material. Therefore, magnesium substituted iron oxides are not conducting because of a conducting corundum phase, but rather because of spinel phase inclusions.

An interesting result of the electrical properties is the observation of a n-type Seebeck voltage in all the sintered ceramic discs. This is consistent with the presence of spinel in the materials, and shows that the high temperature carrier distribution of Fe_2O_3 is not applicable to the magnesium substituted samples studied here.

Photoelectrochemical Measurements

Figure 3 shows a typical D.C. cyclic voltammogram in 1 M NaOH of an electrode having an initial composition of 10 mole percent Mg in Fe_2O_3 . The sintered disc was heated at 1350°C for 20 hours then quenched into air. The behavior of the electrode in the dark is not characteristic of a true p-type phototelectrochemical diode. The dark currents observed between -0.075 and 1.526 RHE are on the order of 50 $\mu\text{A}/\text{cm}^2$, and the shape of the voltammogram is reminiscent of an n-type semiconductor in solution where hydrogen is evolved at negative bias. The dark currents of these materials evolves with time, reaching values as high as 100 $\mu\text{A}/\text{cm}^2$. It appears that the electrode may not be stable under cyclic voltammetric conditions. Under illumination the electrodes exhibit cathodic photocurrents which have initial values of up to 50 $\mu\text{A}/\text{cm}^2$.

FIG. 3
D.C. cyclic voltammogram for Fe_2O_3 with 10% MgO sintered
20 hours at 1350°C

The A.C. photoresponse as a function of applied potential at several different wavelengths is presented in Figure 4. The A.C. photocurrents were measured between -0.075 and 1.526 V RHE at wavelengths of 300, 400, 500, and 550 nm. The plots display both photoanodic as well as photocathodic currents and have been normalized to a constant photocurrent value at 1.526 V RHE. The plots display p-type photocathodic currents when shorter wavelength irradiation is employed while photoanodic or n-type behavior is observed upon illumination with longer wavelength light. A qualitative comparison of the curves shows that there is considerable inhomogeneity in the A.C. photoresponse of the magnesium substituted iron oxide electrodes.

The A.C. photoresponse allows the photocurrent to be separated from the dark current. Furthermore, the use of monochromatic light allows the examination of a particular region of the space-charge layer because the absorption coefficient of a semiconductor is inversely proportional to the depth of light penetration. In the sintered disc electrodes it appears that a surface region is present which gives photocathodic currents under illumination. From the viewpoint of photoelectrolysis these results are remarkable because, despite the observation of an n-type Seebeck coefficient, the electrode behaves under illumination as if the space-charge layer potential gradients in the near surface region were similar to a true p-type semiconductor. Undoubtedly this behavior is related to the inhomogeneity of the ceramic material itself, as the disc contains multiple phases. If a surface in homogeneity were present, it could in principle be abraded from the surface resulting in different electrochemical behavior.

FIG. 4
A.C. depth profile photocurrent for Fe_2O_3 with 10% MgO sintered
20 hours at 1350°C

Following the hypothesis that the near surface region is different from the bulk of the disk, the electrodes were sandblasted to remove the first 100 microns of the out layer. The A.C. photoresponse of the abraded electrode is shown in Figure 5. It is clear that removal of the near surface region resulted in a complete reversal of the previously observed photocathodic currents. After abrasion, only photoanodic currents are observed. The results of this experiment indicate that, indeed, the near surface region of the discs has a different chemical character than the bulk.

It should be noted, however, that in light of the high temperatures of the preparation of the sintered discs, such inhomogeneities between the surface and the bulk are not surprising. The temperatures of preparation, $1200\text{--}1400^\circ\text{C}$, are high enough to result in reduction of the surface. This is consistent with the observed instability of the electrodes during the cyclic voltammetry experiments.

In an attempt to identify the chemical nature of the near surface region of the discs, the surfaces of the ceramic discs were removed with a jeweler's file. X-ray powder diffraction of the surface powder showed no evidence for phases other than $\alpha\text{-Fe}_2\text{O}_3$ and spinel; however, the x-ray patterns were not of sufficient quality to merit a measurement of the relative ratio of the two phases as was presented previously. At present, photoelectron spectroscopy studies are in progress to determine the oxidation states of iron in the near surface region, and to determine the surface composition more accurately. It is hoped that these studies will elucidate the source of the observed p-type behavior in the near surface layer.

FIG. 5

A.C. photocurrent, before and after surface abrasion for Fe_2O_3 with 10% MgO sintered 20 hours at 1350°C

It should be noted that the instability of the iron oxide electrodes reported here was not observed by Leygraf et al. (9) when these electrodes were used in p-n assemblies, and the reasons for the instabilities of both the dark currents and the photocurrents could be electrochemical corrosion or photocorrosion of the near surface region. We shall also explore the possibility of indium-gallium leaking by surface diffusion to the iron oxide surface, and thereby initiating corrosion. Studies are in progress to identify the causes of the instability of the electrodes.

Conclusions

The preparation and characterization of magnesium substituted iron oxide ceramics has been reexamined. It was found that the sintering of cold pressed discs made from MgO and Fe_2O_3 powders or gels at temperatures between 1200 and 1400°C resulted in an inhomogeneous ceramic material containing both $\alpha\text{-Fe}_2\text{O}_3$ and a spinel phase, most likely of composition $\text{Fe}_{3-x}\text{Mg}_x\text{O}_4$. The formation of the spinel phase is favored by the addition of magnesium oxide to Fe_2O_3 powders.

The electrical properties of the sintered discs having an initial composition of 10 mole percent magnesium in Fe_2O_3 showed a clear correlation between the amount of spinel present and the electrical resistivity of the discs. In all cases n-type Seebeck voltages were observed. These results imply that the spinel phase inclusions give rise to extrinsic conduction through carrier percolation in the Fe_2O_3 matrix.

Despite the observed n-type Seebeck voltages, photoelectrochemical measurements showed that the electrodes prepared from the sintered discs

exhibited photocathodic currents. A.C. photocurrent measurements using monochromatic light indicated that the near surface region of the doped iron oxide discs is responsible for the p-type behavior. This was further verified by abrasion experiments which showed that removal of the near surface layers of the electrode resulted in disappearance of the photocathodic currents.

All of the results presented here suggest that the inhomogeneity of the magnesium substituted iron oxide discs is intimately tied to the photoelectrochemical behavior of these materials. Surface studies are in progress to determine the composition of the surface layer that is apparently responsible for the observed photocathodic currents.

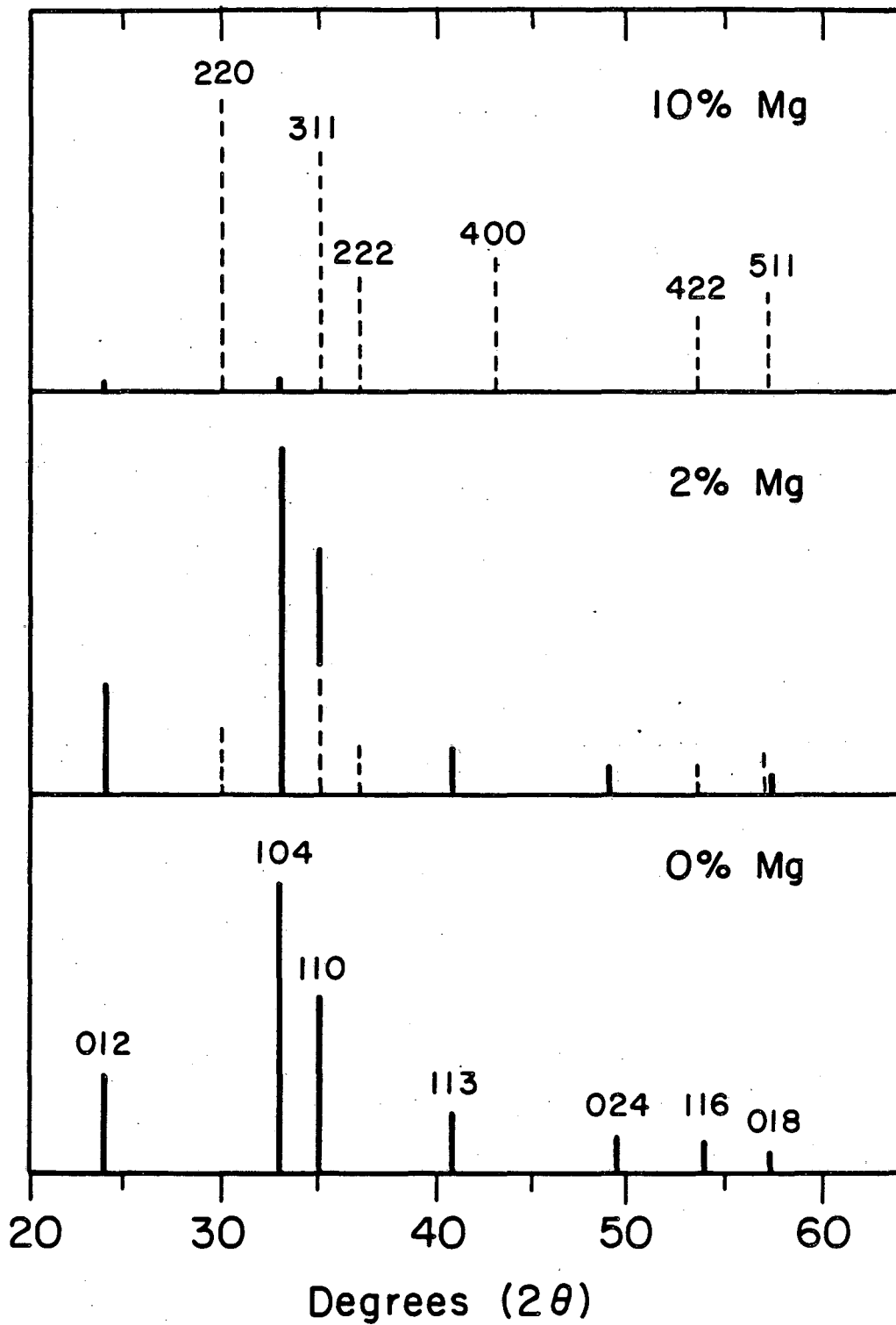
Acknowledgements

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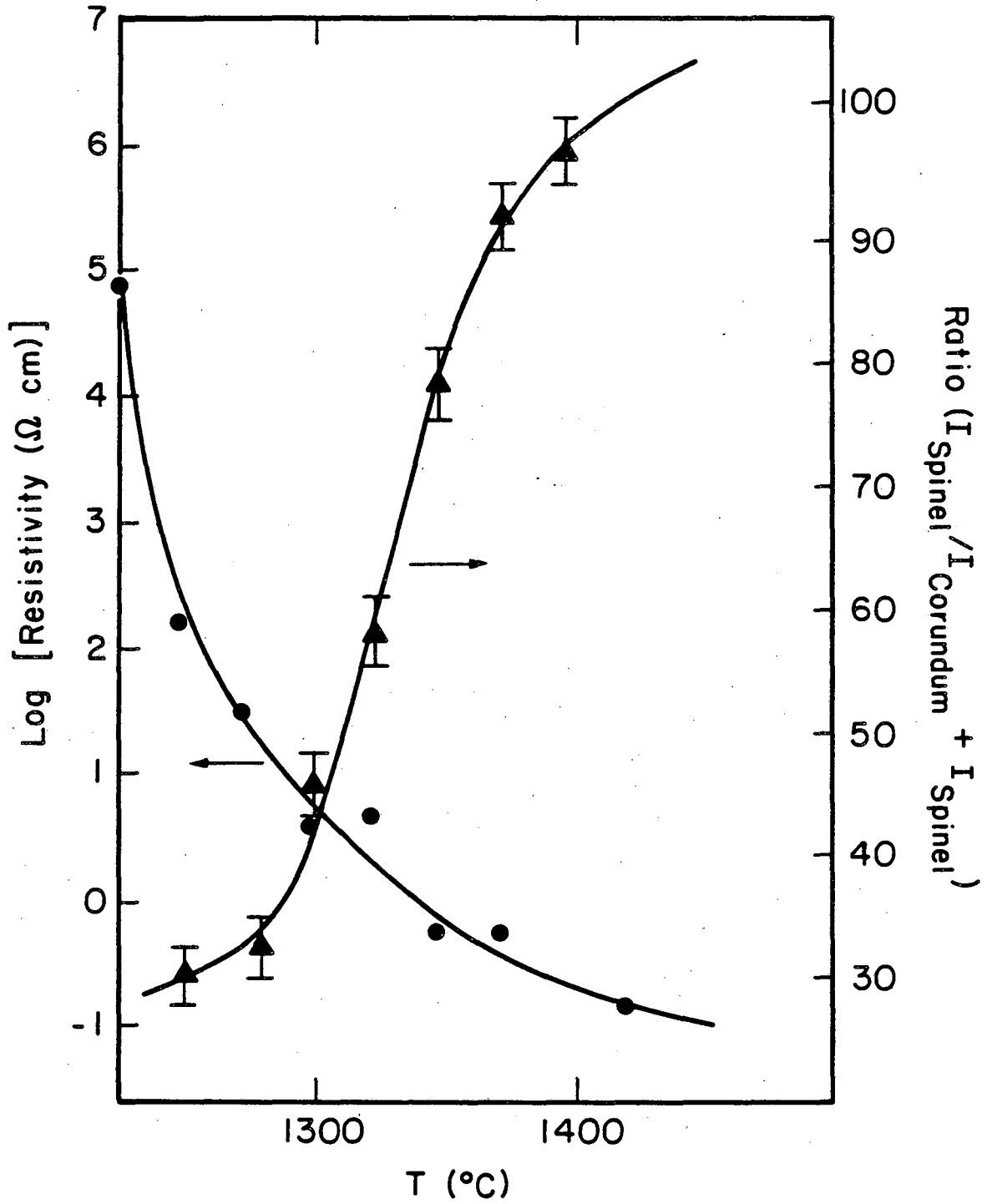
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Fig.1



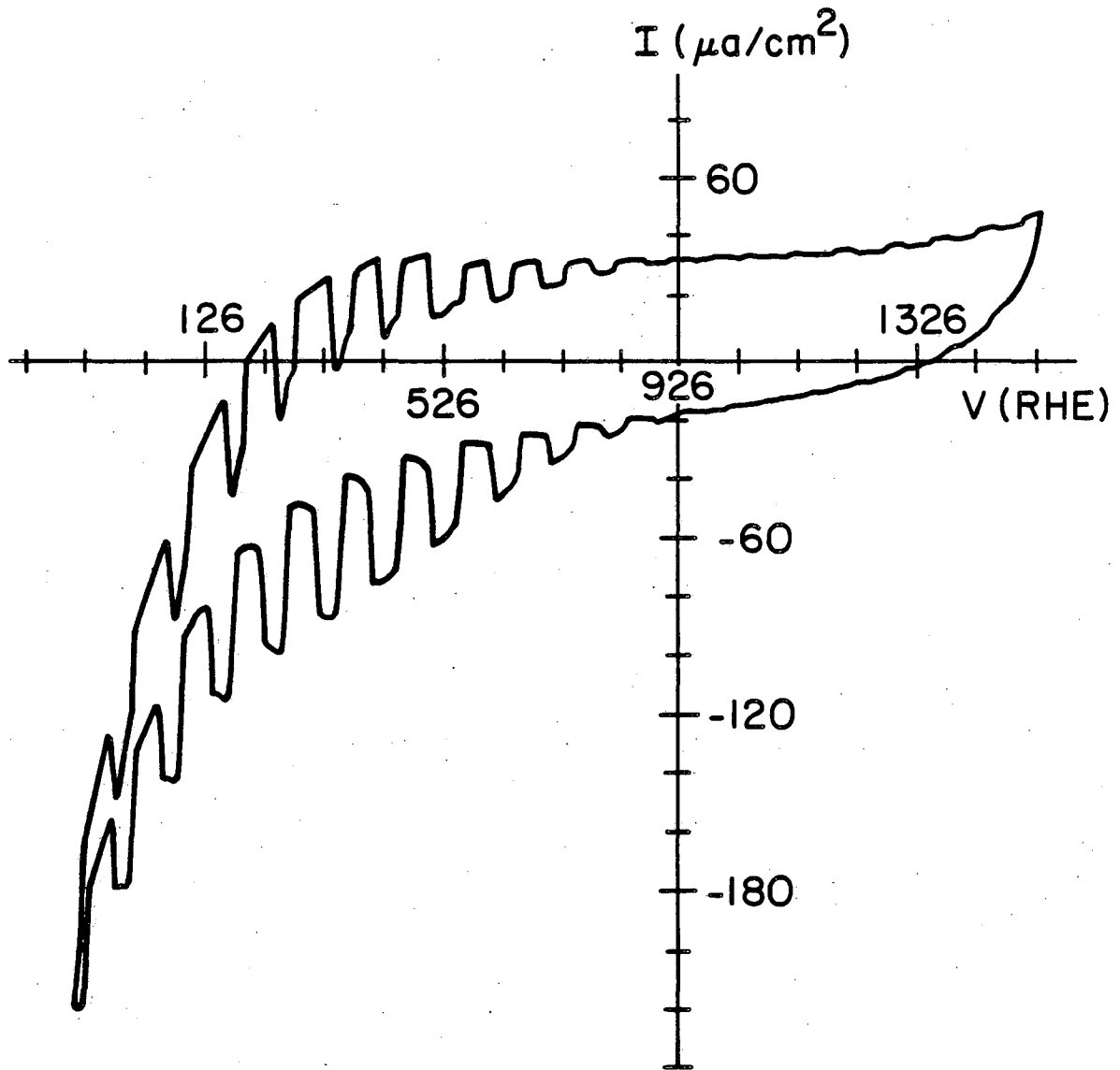
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Fig.2



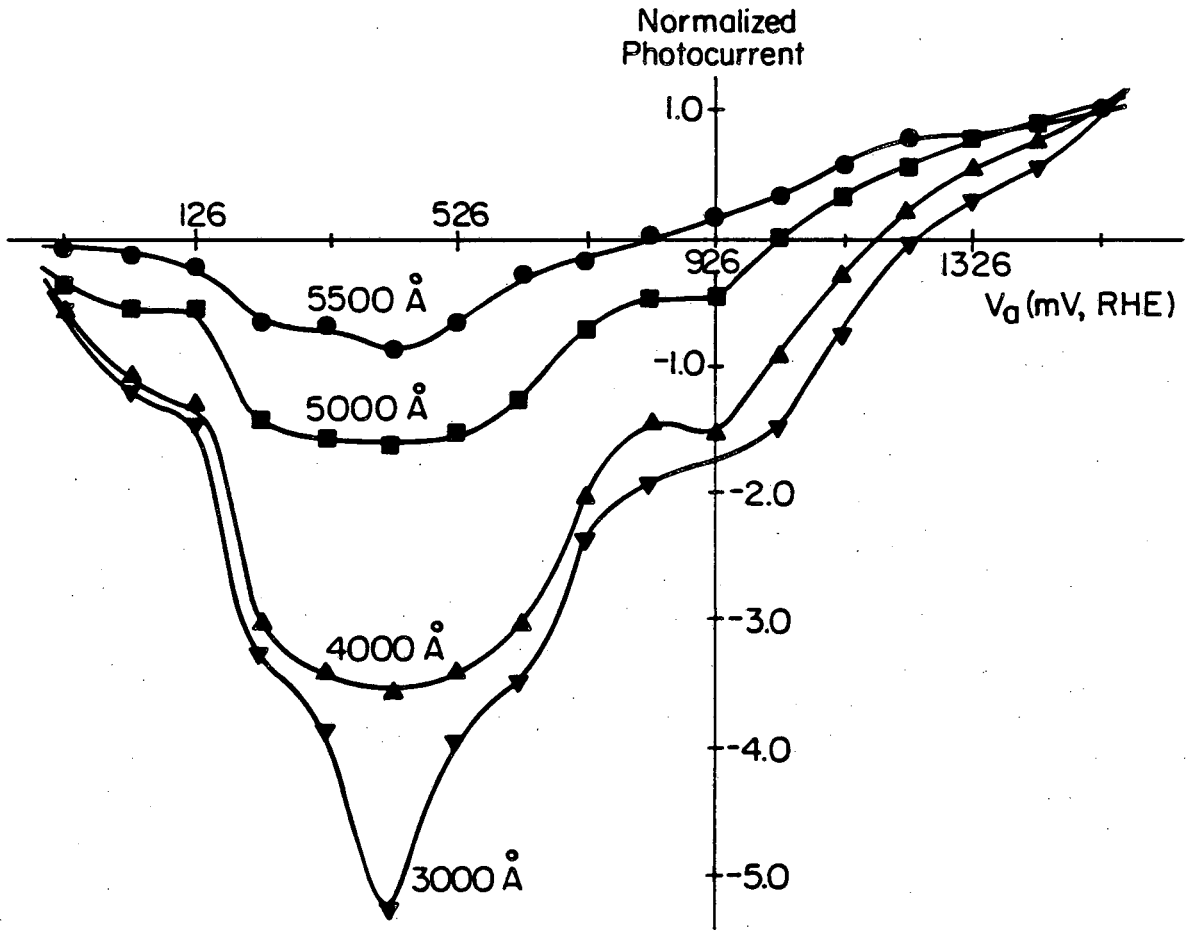
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Fig.3



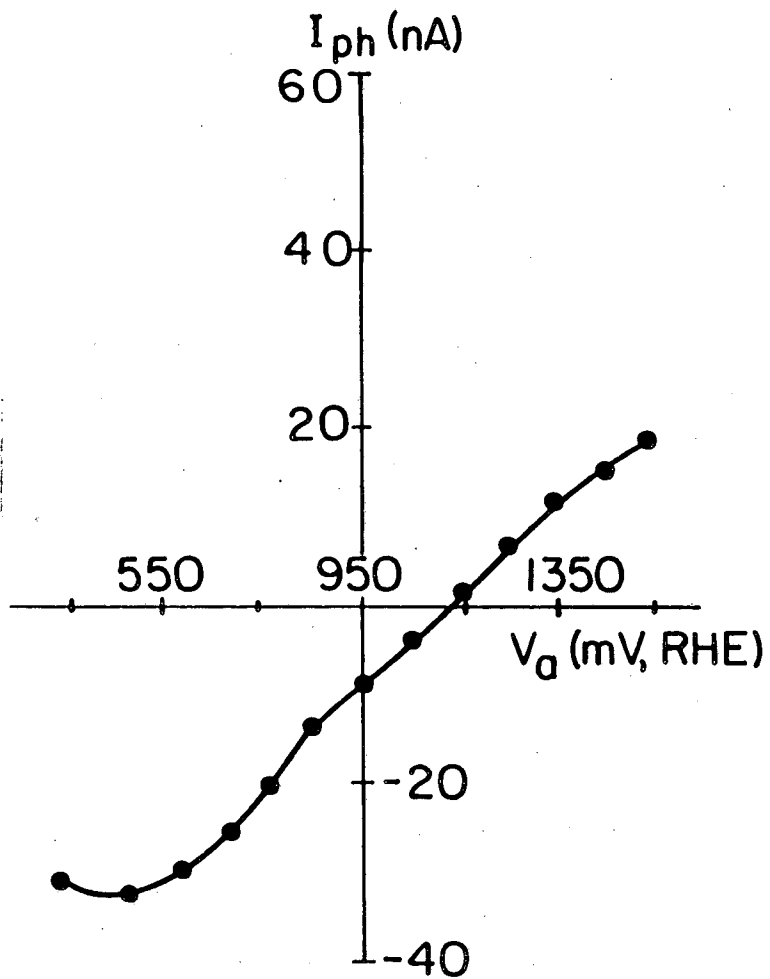
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Fig.4



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Before Surface Abrasion



After Surface Abrasion

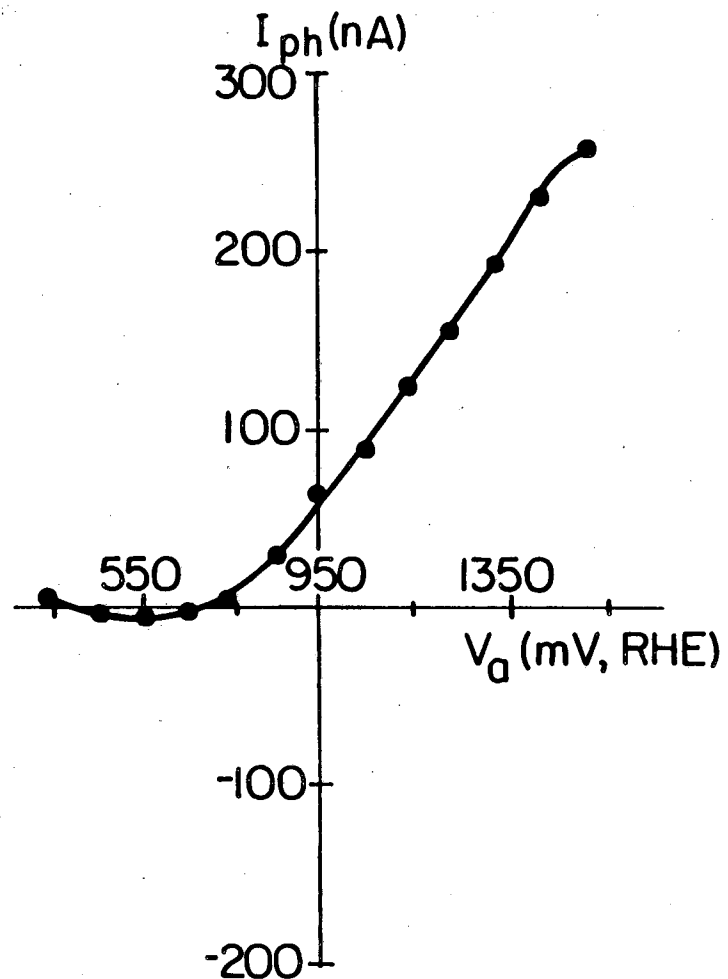


Fig. 5

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