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STUDY OF THE ZINC-SILVER OXIDE BATTERY SYSTEM

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SUMMARY

1. Electrode Studies

The product of leaching of silver peroxynitrate ($Ag_7O_8\ NO_3$) in distilled water at room temperature has been shown by X-ray diffraction to be AgO.

2. Transport Parameters

Use of the rotating disk method for permeation studies of zincate through polyethylene separator material is justified because of solution side mass transfer resistance in the viscous electrolyte. Permeability of 7.7×10^{-5} cm sec^{-1} at 25°C in 0.4 M ZnO - 40% KOH has been found. Diffusivity of zincate ion, measured by the capillary method, is independent of concentration (0.02 to 0.4M) and is 3.03×10^{-6} $cm^2 sec^{-1}$ at 20°C, and 3.24×10^{-6} $cm^2 sec^{-1}$ at 25°C.

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1. Electrode Studies

1.1 Silver Oxide Electrode

1.1.1 Equilibrium Electrode Potential

In order to obtain large area silver oxide surfaces for electrode studies, electrolytically grown silver peroxynitrate crystals have been converted to AgO through leaching in water. As a general index of the chemical nature of the surface of the treated crystal the open circuit potential (with respect to Hg - HgO reference electrode in 1M KOH) has been followed as a function of time. After leaching for 3 hours in boiling distilled water, a crystal with area $3 \times 10^{-2} cm^2$ exhibited a potential of +580 mV (Hg - HgO). After cathodic treatment at 1mA for a total of 20 minutes, the potential was 496 mV, and drifted slowly down to 484 mV over a 45 day period at 25° C. The expected equilibrium potential is 478 mV for the reaction

$$2AgO + 2\epsilon + H_2O = Ag_2O + 2OH^- \qquad \text{Eqn. 1}$$

From the potential measurements, it is concluded that AgO is prepared as a result of leaching and that Ag_2O is produced by the subsequent reduction step.

1.1.2 X-Ray Diffraction Studies

The potential measurements discussed in Sec 1.1.1 can, of course, indicate only the nature of the surface. The degree of conversion and nature of product was studied by X-ray diffraction (Debye - Scherrer) techniques. X-ray studies were made of the product of slow heating of initial crystals to a temperature slightly greater than the 110° C transition determined from thermogravimetric studies (Sec. 1.1.3, Oct. 1969 Quarterly Report) and of the material produced by leaching initial crystals in distilled water. For comparison, the initial crystals (silver peroxynitrate) and final thermal decomposition product (silver) were also studied. The results are summarized in Table 1 in which the 16 principal lattice spacings have

been listed. All studies were made on powders in standard Debye - Scherrer cameras (114.6mm) with Ni filtered CuK α radiation (8 hr. exposure, 45 KV, 15 mA). The data in the column headed "Leached" matches the standard pattern for AgO (ASTM file 14-646) and also agrees with the data of Scatturin, Bellon and Salkind [J. Electrochem. Soc. 108 (1961) p. 819] . The medium strength line at 2.86 Å is not part of the AgO pattern and corresponds closely to the strongest line (2.84 Å) of the $Ag_7O_8\ NO_3$ starting material. It seems probable that the reaction

$$Ag_7O_8\ NO_3 = AgNO_3 + 6AgO + O_2 \qquad \text{Eqn. 2}$$

is not complete even after one week in distilled water at 25° C. The presence of other strong lines of the $Ag_7O_8\ NO_3$ structure is masked by nearby lines of the AgO lattice i.e. the strong $Ag_7O_8\ NO_3$ lines 2.47 and 1.74 Å appear possibly as the weak 2.46 and 1.741 Å lines of the leached product although an unambiguous assignment is not possible because of the similar medium intensity lines of the AgO structure at 2.421 and 1.743 Å. A further strong $Ag_7O_8\ NO_3$ line at 1.49 Å from residual starting crystals may be reinforcing the weak AgO line at 1.477 Å to produce the line at 1.477 Å in the leached product with anomalous medium intensity. A weak line at 2.03 Å is found in crystals heated to 115° C. The standard lines for AgO listed in Table 1 bracket this region of lattice spacings with no line appearing between 2.287 and 1.743 Å. Thus, the occurrence of the stray 2.08Å line is not accounted for in the AgO structure and is also not in the $Ag_7O_8\ NO_3$ structure. The heated product also has a weak line at 2.36 Åwhich is not in the AgO structure. The 2.36 and 2.08 Ålines are, however, close to the two principal lines of silver (2.359, 2.044 Å). The occurrence of metallic silver is unexpected, according to Eqn. 2, and may be an impurity produced by decomposition of AgO caused by local heating during grinding for powder preparation.

TABLE 1

Principal X-Ray Diffraction Data
(lattice spacing, Angstrom Units)
(S = strong, M = medium, W = weak)

$Ag_7O_8NO_3$ #	Leached*	Heated**	AgO***
5.66 W	2.95 W	4.49 W	2.95 W
4.90 W	2.86 M	4.08 W	2.797 VS
3.48 W	2.79 S	3.63 W	2.776 S
2.84 VS	2.77 VS	3.00 W	2.626 M
2.47 S	2.74 W	2.74 VS	2.421 M
1.74 S	2.62 M	2.71 S	2.287 M
1.65 M	2.51 W	2.62 M	1.743 M
1.49 S	2.46 W	2.52 W	1.703 M
1.13 S	2.41 S	2.41 S	1.676 M
1.10 S	2.28 M	2.36 W	1.622 M
1.01 S	2.03 W	2.28 W	1.477 W
0.952 S	1.741 W	2.08 W	1.460 M
0.874 M	1.699 M	1.74 W	1.435 W
0.837 S	1.533 W	1.69 W	1.409 W
0.825 S	1.477 M	1.67 W	1.397 M
0.783 M	1.395 M	1.62 W	1.386 W

* Leaching treatment: 1 week, 25° C, distilled water.

**Heat treatment: slow heating to 115° C.

***AgO: 16 principal lines from ASTM File 14-646.

#$Ag_7O_8NO_3$: 16 principal lines from ASTM File 6-0434.

The lines listed for the heated product indicate the presence of a lattice in addition to AgO, particularly at large lattice spacings. From Eqn. 2, it is suspected that $AgNO_3$ is present in the heated product. The leaching treatment would dissolve any silver nitrate which formed. Details of the reaction mechanisms associated with Eqn. 2 are of general interest but are being deferred in favor of electrode studies of battery reactions using the AgO surfaces produced by leaching of $Ag_7O_8\ NO_3$.

2. Transport Parameters (Dr. Mitchell Litt, Dr. G. Madan)

2.1 Battery Separator Permeability

2.1.1 Permeation Apparatus

The rotating permeation disk apparatus described in the previous report [Oct. 1969] has been used to make a number of preliminary studies of the battery separator permeability using JPL provided samples of polyethylene grafted with acrylic acid and cross-linked with divinyl benzene in the K^+ salt form. The initial studies used a solution of 0.4 molar zinc oxide in 40% KOH solution. The results are reported in Sec. 2.1.2.

As reported previously, the "O" rings had been replaced by special alkali impervious materials for these studies. However, after making the preliminary runs, it was discovered that solution had leaked into the main aluminum gear drive, causing excessive corrosion. A new gear has been fabricated and is being treated with an alkali impervious plastic coating (Kynar) before reassembly.

2.1.2 Permeation Results

Runs were made using the grafted polyethylene membrane under the following conditions: wet thickness of membrane, 0.003in; temperature, 25° C; area of membrane, 5 square centimeters. The driving force for permeation was provided by a differential concentration of zincate ion with 0.4M ZnO in 40% KOH on the input side and 40% KOH in the exit compartment.

The overall permeability through the apparatus, including resistances due to the membrane and the boundary layers on both sides of the membrane gave a result of 3.8×10^{-5} centimeters/sec. Because of the high viscosity of the solution, it was expected that the boundary layer resistance would be a significant factor. The boundary layer mass transfer coefficient was estimated using the method of Litt and Smith [Science 160 (1968) p. 201] using the relationship

$$Sh = 0.62\ Re^{1/2}\ Sc^{1/3} \qquad \text{Eqn. 3}$$

Calculation of the membrane permeability from the Sherwood number (Sh) requires that the viscosity be known for computation of the rotational Reynolds number (Re) and also the Schmidt number (Sc). For this system it was estimated that the viscosity of the solution was 90 centipoise and the density 1.4 grams per cc. Diffusivity, which was estimated from the diffusion experiment results (to be discussed in Sec. 2.2.3) was 3.2×10^{-6} $cm^2 sec^{-1}$. For these conditions, the Reynolds number is calculated to be 10.5 and the Schmidt number 2×10^5 giving a mass transfer coefficient of 1.53×10^{-4} centimeter per second. Since the two boundary layer resistances are in series with the membrane resistance, the permeabilities all add reciprocally so that the estimated permeability for the membrane itself is calculated to be 7.7×10^{-5} centimeters per second.

For the measured film thickness and diffusivity, a permeability of 42.5×10^{-5} centimeters per second would be expected if the complete surface area of the membrane were available for diffusion. The results therefore indicate that $\frac{7.7}{42.5}$ or only 18% of the membrane area is effective for diffusion, i.e. the membrane retards the diffusion of zincate ion by a factor of 5 over what it would be in water solution alone. It is interesting to note that under the condition used, the combined boundary layer resistances were about equal to the membrane resistance so that the use of the rotating disk apparatus is essential in these viscous solutions to correct for liquid boundary layer effects.

These runs will be repeated with the permeation cell fitted with the new coated driving gear, and will be extended to different concentrations and temperatures to determine if diffusion through the membrane is purely passive, or if there is some interaction between the zincate ion and the membrane material.

2.2 Electrolyte Diffusivity

2.2.1 Capillary Method

The equipment for diffusion measurement using the capillary method described in the previous report was completed. Before running the actual diffusion experiments, dye studies were made to determine loss of material from the capillary as a result of initiating the diffusion process. Six capillaries were filled with methylene blue solution and an extra drop of indicator put on the rectangular mouth of the plexiglass capillaries. The capillaries were inserted into their slots in the diffusion apparatus and the water flow started. Five seconds later the capillaries were removed and the intensity of color in each of the capillaries compared with the intensity of solution in a control capillary. Three different dilutions of the methylene blue were used. No significant difference in the color intensity of the experimental solutions and the control solutions was measurable. The test was repeated using potassium permanganate with similar results. We can conclude that the procedure used does not cause significant error at the start of the diffusion process, i. e. no hydrodynamic removal of material from the mouth of the capillary occurs during start-up.

2.2.2 Diffusion of KCl

To check on the reliability of the method, initial studies were made using potassium chloride in aqueous solution for which literature values are known. The system was kept at temperature for three hours to insure total thermal equilibration before starting the diffusion. The diffusion process was allowed

to proceed for a four to six hour interval and the change in concentration of the potassium chloride solution determined. The solutions were analyzed using atomic absorption spectroscopy. The results for the 0.1 Normal potassium chloride solution gave a diffusivity of 1.79×10^{-5} $cm^2 sec^{-1}$. This result compares very favorably with the well-known [Handbook of Chemistry and Physics] value at 25° C for 0.1N KCl of $1.844 \times 10^{-5} cm^2 sec^{-1}$.

Diffusivity for a 0.1 molar zinc chloride solution was also determined giving a value of $1.02 \times 10^{-5} cm^2 sec^{-1}$. No literature value is known for comparison.

2.2.3 Diffusivity of Zinc Oxide - 40% KOH solution

Diffusivities of the zinc oxide - 40% KOH system were measured at 25° and 20°C using concentrations of zinc oxide ranging from 0.02 to 0.4 molar. The scatter in this data was greater than that experienced with the potassium and zinc chloride solutions, presumably because of difficulties with the analysis of the highly alkaline solution. No significant variation with concentration could be determined from the data. The average values obtained, based on about twenty-five measurements each, are: for 25°C, zincate diffusivity equal to 3.24×10^{-6} $cm^2 sec^{-1}$; for 20°C, $3.03 \times 10^{-6} cm^2 sec^{-1}$.

Further work at other temperatures is necessary to determine if these results are significantly different. Better control of the analysis is also needed to reduce the scatter. Also, future runs will be lengthened to give a larger concentration change which will reduce the influence of the analytical error.