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QUARTERLY REPORT
OCTOBER 1969

JET PROPULSION LABORATORY
CONTRACT # 952 - 543

STUDY OF THE ZINC-SILVER OXIDE
BATTERY SYSTEM



UNIVERSITY OF PENNSYLVANIA

THE SCHOOL OF CHEMICAL ENGINEERING

PHILADELPHIA, PENNSYLVANIA 19104

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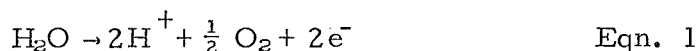
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1. Electrode Studies

1.1 Silver Oxide Electrode

1.1.1 Single Crystal Preparation

An electrolytic method was used to anodically grow starting material for the subsequent preparation of silver oxide surfaces. A graphite rod (6 in. long, $\frac{1}{4}$ in. diameter) anode was enclosed in a glass sheath (9mm o.d.) with a 5mm diameter hole on one side. Electrolysis of 2M silver nitrate solution at 25°C with a d.c. power supply (IP-12 Heath Battery Eliminator) was accomplished with a stainless steel cathode (2 cm x 10 cm) in a 250 ml beaker. Black, shiny crystals (more than 1 cm long and up to 5 mm diameter) were produced at currents of 65-75mA (approximate current density, 250-300 mA/cm²). Other sizes of holes on the anode glass sheath (1 and 3 mm diam.) were tried. However, the 5mm diam. hole turned out to be most favorable for the production of large crystals. According to Brown, [M. J. Brown, Trans. Am. Electrochem. Soc. (1916) V30, p. 327] when silver nitrate solution is electrolyzed between insoluble electrodes, silver is deposited at the cathode and silver peroxyxynitrate ($\text{Ag}_7\text{O}_8\text{NO}_3$) is deposited at the anode, there being presumably a simultaneous formation of nitric acid at the anode as in the reaction:



1.1.2 Anode Reactions

The effect of current density was studied by gradually increasing the current in the system described above (Sec. 1.1.1) together with simultaneous measurement the potential drop between the graphite anode and the reference electrode of pure silver wire. The anode potential varied from 800 mV for a current of 1 mA to 930 mV for 100 mA.

Potential data are insufficient to distinguish discontinuities or slope changes. However, at currents less than 5 mA, only gas (believed to be oxygen) evolved. For currents ranging from 5 to about 80 mA, crystals grew and gas evolved at the same time. At currents greater than 80mA, gas evolved rapidly and the carbon anode disintegrated rapidly.

Some support for Eqn. 1 as a partial anode reaction was obtained by measurement of the change of pH of the solution during the crystal growth. The pH decreased as the crystals grew, varying from 5.5 to 1.0, i. e., the solution became more acidic.

1.1.3 Thermogravimetric Analysis of anode product

To find out the composition of the black shiny crystal, a crude thermogravimetric analysis was obtained from measurements of weight losses during gradual heating up to about 1000°C. Sample crystals were put in a porcelain crucible (2.6 cm in height and 3 cm in diameter at the top opening) with a porcelain cap and were heated gradually in an electric furnace.

Initial weight loss determinations indicated a rapid onset of crystal crumbling above 100°C with attendant ejection loss of material from the crucible. Accordingly, the above-mentioned crucible was seated inside another larger crucible with a cap. Two major weight losses occurred; first at 110°C (typically 200 mg for a 2.5 gm initial crystal weight) followed by a larger loss (typically 280 mg) for heating above 400°C. The residue from heating above 960°C was drops of once molten silver. The composition of the crystal was then calculated on the assumptions that (i) the crystals consist of silver and oxygen, (ii) as the temperature is raised, the crystal ultimately loses all oxygen leaving metallic silver. Based on the initial weight, the composition of the crystal was estimated to be $\text{AgO}_{1.78}$. On the basis of the weight of the residue following the 110°C loss, the ratio of silver to oxygen was calculated to be 1 to 1.04 (approximately 1 to 1, i. e., AgO). For

comparison, commercially prepared Ag_2O powder was analyzed in the same way. The silver to oxygen ratio was measured as 1.94 i. e. within 3% of the expected ratio of 2.0, thus indicating that the relatively crude thermogravimetry with discrete cooling and weighing steps was reasonably accurate. A continuously recording system is being constructed using a linear variable differential transformer as the weight transducing element. Thermogravimetry of silver-zinc battery cathodes may prove to be a useful method for determining conversion efficiency.

1.1.4 Structure Determination of Anode Product.

X-ray diffraction studies of powder (prepared by crushing the brittle shiny black anode product) were performed by Dr. Mel Robin of Bell Telephone Laboratories. The pattern matched that of silver peroxynitrate, $\text{Ag}_7\text{O}_8 \text{NO}_3$ a cage clathrate type of salt. The silver peroxynitrate composition corresponds to an apparent silver-oxygen compound of composition $\text{AgO}_{1.7}$, in fair agreement with the results of thermogravimetry (Sec. 1.1.3).

It is suspected that the metallic conductivity $\text{Ag}_7\text{O}_8 \text{NO}_3$ is due to an electronic transition between two simultaneously existing oxidation states i. e. mono and divalent silver ions in the same crystal unit cell. The possibility for the existence of similar types of compounds as oxidation products in anodic oxidation processes may be of considerable importance to battery technology.

1.1.5 Chemical Stability of Silver Peroxynitrate

The crystal dissolved entirely in acid solutions such as nitric (up to 14N), sulfuric (up to 36N) and hydrochloric (to 0.1N). Dirkse has pointed out that AgO dissolves in nitric acid to give a dark brown solution which is fairly stable in the cold. The same behavior was experimentally confirmed with the crystal.

[T. P. Dirkse, J. Electrochem. Soc. V106 (1959)]

According to Brown, silver peroxynitrate can undergo reaction in water according to the sequence [cf Sec. 1.1.1].



Eqn. 2

This reaction is the basis of the present approach to produce large usable surfaces of AgO from the black anode product silver peroxyxynitrate. In acids, however, the AgO may exist as a transient species, giving rise to AgO behavior as mentioned above for nitric acid.

For acids, the higher the concentration, more rapid the dissolution. In sulfuric acid, the reaction products included a greenish-black colloidal dispersion which simultaneously dissolved. The nature of this substance is unknown. In HCl, a white layer formed on the crystal surface which changed color slowly to purple and dissolved after standing for a few days. It is suspected that this product is AgCl, lending credence to the existence of monovalent silver ion as part of the reaction scheme shown in Eqn. 2.

Finally, the crystal was very stable in alkaline solutions showing no significant change in either appearance or weight.

1.1.6 Leaching of Silver Peroxyxynitrate

Leaching of the crystal in boiling distilled water was performed to obtain a complete silver (II) oxide crystal for application to studies of the equilibrium electrode potential. Some idea of the kinetic behavior of Eqn. 2 is needed for determination of the mechanical aspects of the AgO product. The rate of dissolution of Ag^+ ion out of the crystal was detected quantitatively by the Volhard method (titration with CNS^- using ferric ammonium sulfate solution as indicator in nitric acid medium). As a result of leaching in hot water the black, shiny crystals tarnished to a dull appearing surface. A silver peroxyxynitrate crystal initially weighing 0.1323gm lost 15.6×10^{-5} mol of silver ion as a result of one-hour leaching in hot water. Returned to fresh water, the crystal lost an additional 4.0×10^{-5} mol Ag^+ in the second hour and 1.2×10^{-5} mol Ag^+ during the third hour of leaching. The decreasing rate of silver loss indicates an approach to either completion

or a steady state for the reaction shown in Eqn. 2. Further survey diagnostic tests were based on the thermogravimetric results reported in Sec. 1.1.3. The original crystal crumbles at 110°C , while silver (II) oxide crystal decomposes at about 400°C . Hence, if the original crystal was completely leached with no content of $\text{Ag}_7\text{O}_8\text{NO}_3$, it should not crumble upon heating at 110°C . In a series of black crystals of nearly the same size, leaching for 0.5 hour resulted in rapid decomposition at 110°C . This observation supports the notion of complete reaction according to Eqn. 2. The speed of total crystal leaching, even for solid state diffusion at 110°C , is surprisingly large. The preparation of AgO electrodes thus seems feasible. The microscopic structure of the leached crystal is presently being studied for surface roughness estimation. Experiments are also in progress to quantitatively assess the degree of conversion from resistivity measurements (see Sec. 1.1.7).

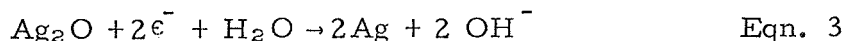
1.1.7 Electrical Resistivity of Silver Peroxynitrate

The regular cross section of the centimeter long needle crystals of silver peroxynitrate permitted good estimation of the resistivity from simple resistance measurements. The crystals were placed in shallow channels milled into the surface of a lucite block. Mercury pools located at the ends of channel provided electrical contact. A simple constant current circuit was used together with measurement of the potential drop across the crystal. The results of several repeat measurements for several different crystals, gave resistivities (based on the slope of the current-potential curve for current approaching zero) ranging from 0.02 to 4.5 ohm cm at 25°C . A non-linear current-voltage behavior observed as current increased may be due to heating of the crystal and deserves further study. First results of leaching studies (Sec. 1.1.6) are for a crystal with an initial resistivity of 0.042 ohm cm. Leaching in hot water (100°C) for one hour resulted in a resistivity of 32.9 ohm cm. Further leaching for one hour produced an increase to 91.7 ohm cm (25°C). Simultaneously, a decrease in the rate of silver removal was noted. Work is needed in

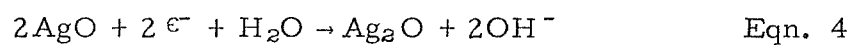
correlating the rate per unit area of Eqn. 2, the resistivity and density variation and the tendency to rapidly decompose at 110°C as noted in the discussion of thermogravimetry (Sec. 1.1.3). The leached crystal retains the shape of the starting substance although in one instance, a needle shape separated into two needles joined at a common base, suggesting leaching attack along a preferential direction, possibly a twin plane.

1.1.8 Equilibrium Electrode Potential

Many interesting side lights of the silver peroxynitrate crystals have been uncovered. However, the main goal is to obtain silver oxide surfaces of clear area definition for study of electrode reactions pertaining to the silver battery electrode. The open circuit potential change versus time with respect to the standard mercury-mercuric oxide reference electrode in 2M KOH was followed for several crystals. As a reference for time-behavior, a commercially prepared Ag₂O powder electrode yielded fairly constant potential of 246 mV compared to the standard mercury/mercuric-oxide reference electrode (well consistent with literature data) over a period of ten days. Peroxynitrate electrodes showed potentials of 630 mV upon initial immersion in 2N KOH. The potential of one crystal drifted steadily downward over 3 days to 150mV, below the potential for equilibrium between Ag₂O and Ag (Eqn. 3).



which is 246 mV, as mentioned above for an actual AgO electrode. After 3 days, the potential rose and decreased from about 400mV after 9 days of immersion. Drifting potential was also noted for a second crystal of silver peroxynitrate which however had received some brief cathodic treatment (total of 8 mA-min). The potential did not go below 490 mV in this case. A third crystal was given intensive cathodic treatment in steps ranging from 0.1 to 100 mA for 10 second intervals. The potential of this crystal was still decreasing slowly after 6 days in the region of 490 to 500 mV. The theoretical e.m.f. for the reaction



is (Hg/HgO reference) 478 mV for 2N KOH. The open-circuit potential measurements need to be correlated with surface composition of leached crystals. Overpotential data for alternating cathodic-anodic (discharge-charge)cycles will be the next area of study with the silver oxide electrodes.

2. Transport Parameters

2.1 Battery Separator Permeability

2.1.1 Permeation Apparatus

The rotating disk permeability apparatus [M. Litt, W. G. Smith, Science 160 (1968) p. 201] has been assembled. A new base was constructed for the rotating membrane unit so that the drive and gear box assembly are mounted separately to reduce vibration. The unit is driven by a variable speed 0-3600 RPM Servotek motor, operating through a 25 to 1 Boston gear reducer. A specially fabricated timing belt drives the rotating disk itself.

Since the unit had originally been designed to operate in dilute salt solutions, changes were necessary to handle the highly concentrated caustic solutions to be used in this study. All "O"rings and other non-plexiglas parts in contact with the solution were replaced by alkali impervious materials. The unit is now complete and ready to run using a passive chemical concentration gradient as the driving force. Calibration studies using potassium chloride solutions are proceeding at the present. A design for incorporating electrodes in the permeation chambers to allow an electrochemical gradient across the system is now being prepared.

2.1.2 Zinc Analysis

The precision of permeability measurement is directly related to the precision of analysis for zinc (as zincate in hydroxide solution). Some preliminary investigations were made to establish the sensitivity and the accuracy of atomic absorption spectrophotometry as an analytical method for Zn determination. Test solutions of zincate in KOH (reported as ppm Zn) were analyzed in a Beekman 440 AA unit. The results were found to agree with the actual concentration of Zn to within 2% over the range 910 to 3270 ppm Zn (5 samples). Null readings were obtained for blank background samples of distilled water and 0.2 N KOH.

The calibration curve ("peak height-absorption" vs concentration) was found to be nearly linear in the range $0 - 2.5 \times 10^3$ ppm but the slope of the curve beyond this concentration decreases, becoming nearly parallel to the concentration axis. With the single beam 440AA, the calibration curve was not stable over a long period of time. Each new observation required redetermination of the calibration curve.

2.2 Electrolyte Diffusivity

2.2.1 Capillary Method

The capillary method [Anderson, J. S., and K. Saddington, J. Chem. Soc., S 381(1949)] of measuring diffusivity, D , in liquid systems has been widely used for the last 20 years. The various difficulties encountered in translating the mathematical boundary conditions into actual practice have been well-documented in the literature. [Richards, S. R., L. Nanis, and J. O'M. Bockris, Rev. Sci. Inst., 36, 5 (1964)]

Difficulties arise when an attempt is made to enforce the boundary condition of constant concentration at the open end of the capillary. This is done by removing the material diffusing out of the open end of the tube by convective transport. Removal by convective transport has led in the past to the so-called " $\Delta \ell$ " effect and consequent errors in the calculated value of D .

The present approach has been to build a diffusivity measurement apparatus, which would not introduce " $\Delta \ell$ " errors. The study by Richards (loc. cit.) revealed that the $\Delta \ell$ - error was primarily a function of the Reynolds number based on internal radius as the characteristic dimension of the tube and velocity of flow over the open end of the capillary. It is apparent that the ' $\Delta \ell$ ' effect errors can be reduced by decreasing the velocity of flow and also the characteristic dimension of the tube.

2.2.2 Reduction in Capillary Dimension

The usual practice is to use a capillary about 3 cm long with a circular bore of 1mm diam. The volume of the test solution contained in

the tube is thus approximately ≈ 0.023 cc. Since this is already a very small volume, any reduction in its magnitude by decreasing the diameter of the bore would cause serious difficulties in measuring the concentration change resulting from diffusion. It would appear that it might be possible to compensate for decrease in diameter by an increase in the length of the capillary. However, in order to achieve the same relative concentration change in the lengthened capillary the duration of the experiment has to be increased as the square of the square of the length. It was therefore decided to design capillaries which would have a length similar to that of a conventional capillary, a characteristic dimension smaller than the characteristic dimension (i. d.) of a conventional capillary, and an outer dimension greater than the bore diameter of a conventional capillary.

A working design was evolved for capillaries with rectangular bores (0.5mm x 1mm) made of the acrylic plastic plexiglass which was found to withstand the corrosive effects of concentrated KOH very well. The 0.5mm side is kept perpendicular to the direction of flow. The rectangular design of the bore will be of advantage for photographic studies of dye streaming to check for the existence of $\Delta \ell$ effect.

2.2.3 Measurement of Capillary Dimensions

The capillary bore volume was measured by filling the capillary with mercury and weighing the Hg required. The other dimensions of the bore were measured under a microscope with a 6x magnification. It is planned to measure the uniformity of the bore at the end of the experiment by measuring the cross sectional area of the bore at various lengths. A rough check is being made by filling the capillary to different lengths.

2.2.4 Reduction in the Velocity of Flow

The Einstein-Smoluchowski equation can be used to calculate the minimum velocity of convective transport to avoid the accumulation of material diffusing out of the capillary at the open end. A typical estimate shows this to be about 10^{-4} cm/sec. This estimate is at least four orders

magnitude lower than the range recommended in the literature. It was therefore decided to design the apparatus in such a way that velocities in the order of 10^{-3} cm/sec could be achieved. For multiple simultaneous capillary studies, a cascade of weired dams was built of plexiglas with the overflow of one pool entering the next lower pool. Control of the flow of liquid from one pool to the next is achieved by using the wick effect of nylon threads. Study of the movement of lycopodium powder in the pool has shown that velocities in the range of 10^{-3} cm/sec can be attained. It was found that because of the non-wettability of the plastic weirs, the head required to start the flow was considerable. However, the use of nylon thread insures a very slow constant flow. A cover has been designed to permit a nitrogen atmosphere to flow above the pools to minimize CO_2 absorption and carbonate formation.

2.2.5 Capillary Wetting

Non-wettability of the plastic produced a serious problem as the solution level was raised to the open end of the capillary. Surface tension effects permitted the pool level to rise above the upper most surface of capillary. Very great flow velocity was observed that at the instant of the break up of this surface effect the resulting scooping up of the test solution from the mouth of the capillary would have defeated the very purpose of the slow flow (Sec. 2.2.4). The problem was overcome by coating the top section of the capillary with a very thin layer of platinum paint. Bonding was improved by baking the painted surface at 120°C . The Pt coating was thin enough not to interfere with visual observations. The wetting properties of such a metallic paint were found to be excellent.