HIGH SURFACE AREA SILVER POWDER AS AN OXYGEN CATALYST

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Introduction

The major voltage loss at current densities below 100 ma/cm^2 in modern hydrogen-oxygen fuel cells is due to the high overvoltage for the oxygen reduction reaction. Hence, much research has been expended in efforts to develop catalysts that are more active toward the reduction of oxygen. While the platinum group metals are well known oxygen catalysts, they have the disadvantage of being very expensive.

Boron carbide [1] and carbon black [2] have been suggested as less expensive oxygen reduction catalysts. Other catalysts of interest are certain organic materials such as cobalt phthalocyanine [3] and oxide materials such as the spinels. For the alkaline cell, however, the most promising catalyst to date appears to be silver [4,5,6].

Silver as an oxygen reduction catalyst may not possess a significant advantage over the platinum metals from technical considerations, but the difference in cost is significant. Silver will almost certainly replace the noble metals as the cathode in the alkaline hydrogen-oxygen fuel cell unless a less expensive and/or more active material is discovered.

The amount of the catalyst's surface area exposed to the fuel cell reactant in part limits the reaction rate. If the surface area is increased, some increase in reaction rate results. Therefore, we attempted to make a silver powder with a surface area 5-10 times higher than the surface area of commercially available silver powders. Further increases in surface area have diminishing returns and sometimes even adverse effects.

Silver powder with varying properties has been prepared in several ways. Some well known methods are chemical and electrolytic reduction of silver solutions and the decomposition of silver salts. Many investigators have studied the preparation and decomposition of silver oxalate [7,8,9,10,11]. It was shown by Erofeev et al [7] that the gradual acceleration of the decomposition of silver oxalate is due to the catalytic effect of the product, silver. They observed that for the first 20-30% of the decomposition the fraction decomposed, α, is given by the equation $\log(1-\alpha) = -kt^n$, where t represents time and k and n (≈ 4) are constants. The decomposition reaction is essentially $Ag_2C_2O_4 \xrightarrow{\Delta} 2Ag + 2CO_2$.

Macdonald [8] and Tompkins [9] found that partially decomposed silver oxalate crystals darkened uniformly and there was no preferential decomposition of the surface nor did the decomposition spread from a few isolated nuclei. These investigators were interested in the kinetics of the controlled decomposition and did not study the explosive decomposition reaction or the properties of the product of this reaction. Poltorak and Panasyuk [10] investigated the activity of sintered silver, produced by the decomposition of silver oxalate

in vacuo, for the decomposition of hydrogen peroxide. The catalytic activity reached a maximum for silver powder sintered at 600° C. Sviridov and Branitskii [11] investigated the catalytic activity of partially decomposed silver oxalate for the decomposition of hydrogen peroxide. The activity of this mixture of silver and silver oxalate was found to be a maximum after 35% of the initial silver oxalate was decomposed.

We investigated the rate of reduction of oxygen in alkaline media on silver powder made by the explosive decomposition of silver oxalate. It was found that silver powder with a surface area of 2-6 m^2/g could be made by the rapid explosive decomposition of silver oxalate [12].

Experimental Technique

Preparation and Decomposition of Silver Oxalate

Silver oxalate was made by adding crystalline silver nitrate to a saturated solution of oxalic acid at ambient temperature. The silver oxalate precipitate was filtered and the resultant slurry dried under a bank of heat lamps. It was crushed and sized and only particles between 0.5 and 2.0 mm were decomposed.

The silver oxalate was decomposed by dropping the particles onto a hot surface. The decomposition temperature of silver oxalate is 140° C but to increase the rate of decomposition the particles are dropped on a surface at 250-500° C. At higher temperatures the silver powder formed begins to sinter, thus lowering its surface area. The decomposition is accomplished in a container since otherwise the force of the explosion would scatter the silver. The container must be properly vented to exhaust the large volume of carbon dioxide released during the decomposition reaction. A schematic diagram of the decomposition apparatus is shown in figure 1. The silver decomposition product is screened to less than 0.15 mm in diameter to remove any oxalate particles or hard pieces of silver formed when the product is scraped from the decomposition chamber.

Electrode Preparation

Electrodes were prepared from the silver powder by incorporating poly-tetrafluoroethylene as a binder and pressing the mixture onto a metal screen in a method similar to that reported by Niedrach and Alford [13]. Electrodes 7.5 cm x 7.5 cm were used to determine the catalytic activity of the material in terms of fuel cell performance, while electrodes 10 cm x 23 cm were used in life tests. In life tests two cells in parallel were used to insure reliability and more significance in testing.

Determination of Catalytic Activity

The activity of electrodes for the reduction of oxygen was determined in a hydrogen-oxygen fuel cell using an asbestos matrix to contain the electrolyte. The test conditions are given in Table I. The same conditions were used for life tests.

TABLE I

Test Conditions

Thickness of Asbestos Matrix	- 0.75 mm
Electrolyte	- 30% KOH
Temperature	- 90° C
Gas Pressures	- 18 psig (26 psia)
Anode	- 3.0 mg Pt and 3.0 mg Pd per cm^2 plated on a porous sintered nickel plaque.

A transistorized 60 cps sine wave commutator [14] was used to drive the cell. For short term tests, such as those to determine the initial activity (electrical performance), no elaborate water removal system was required. Water may simply be removed by purging the gas cavities with the respective reactants. The asbestos is soaked with electrolyte until saturated. The gases are then applied to the cell and the cell is subjected to a load of 300 ma/cm^2. The gas cavities were purged until a maximum voltage was reached at the applied load of 300 ma/cm^2. A reverse current scan was adopted since it normally yielded better reproducibility than the forward scan. Total cell voltage, resistance-free voltage and the resistive voltage losses of the cell were then measured as a function of current density. The time required to determine the voltage-current curve is 2-5 minutes.

Voltammetric measurements were made using a potentiostat. It was developed in our laboratories and is capable of handling anodic and cathodic loads of up to 25 amperes. The test cell consisted of a working electrode held in place by an asbestos matrix with electrolyte flowing behind the asbestos. To keep oxygen from bubbling through the electrode a counter pressure was applied to the electrolyte. The oxygen pressure was approximately 3 psig higher than the electrolyte pressure. If a smaller differential pressure was used the working electrode flooded.

TABLE II

Conditions of Voltammetric Experiments

Temperature	- 90° C
Oxygen Pressure	- 18 psig (26 psia)
Electrolyte	- 30% KOH
Electrolyte Pressure	- 15 psig
Scan Rate	- 10 mv/sec
Reference Electrode	- Hg/HgO

Results and Discussion

Physical Properties of the Silver Powder

Particles of silver produced by the rapid thermal decomposition of silver oxalate are irregular in shape with many nodules. The nodules are approximately 0.1 μ in diameter. Analysis by X-ray indicates that the silver is crystalline.

The specific surface area of the silver powder, measured by the B.E.T. method, was in the range of 2-6 m^2/g. Decomposition of the hardest and driest silver oxalate particles yielded the highest surface area silver powder. Material decomposed rapidly also had higher surface areas than material heated slowly. Photo electronmicrographs of the rapidly decomposed material are shown in figure 2. Figure 2B shows in greater detail a portion of the particle shown in figure 2A. Figures 2B and C show different particles under the same magnification.

Catalytic Activity

The activity of the catalyst for the reduction of oxygen was determined in a hydrogen-oxygen fuel cell. Total cell voltage, resistance free voltage and resistive voltage losses of the cell were measured as a function of current density after optimizing the cell at 300 ma/cm^2. Representative total cell and resistance free voltages vs. current are shown in figure 3. All the voltage-current curves shown in figure 3 were obtained by reverse current scans. Half cell potentials are cited with respect to the potential of the standard hydrogen electrode unless stated otherwise.

The curve in figure 3 shows that appreciable reduction, say 10 ma/cm^2, commences at a potential of 1.05 volts with respect to the hydrogen electrode at 26 psia in the same solution. Voltage current curves for low loaded Pt-Pd electrodes (3.0 mg Pt and 3.0 mg Pd per cm^2 plated on a porous, sintered nickel plaque) and heavily loaded Pt-Pd electrodes (13.5 mg Pt powder and 27 mg Pd powder per cm^2, teflonated and pressed on a nickel screen) are shown for comparison (see figure 3). The Pt-Pd electrodes were tested in the same manner as the silver electrodes. On the basis of half cell measurements we believe that total reaction polarization of the cell (see figure 3), exclusive of resistive losses, occurs essentially at the oxygen electrode. The polarization losses indicated in figure 3 are therefore essentially those of the silver electrode.

Effect of Oxygen Pressure

The effect of oxygen pressure on cathode polarization was studied in a half cell. The resistance free curves are therefore a direct measure of the cathode polarization. The polarization increases nearly linearly with decreasing pressure for pressures exceeding one atmosphere of oxygen. The slope of the curve increases by a factor of five from 32 psia to 12 psia. This increase in slope is especially prominent at current densities above 200 ma/cm^2. Pressure vs. resistance free voltage of a typical high surface area silver electrode is plotted in figure 4.

Effect of Temperature

The effect of cell temperature on cathode polarization was also studied. A resistance free voltage vs. temperature curve for a typical electrode is plotted in figure 5. The slope is essentially independent of temperature between 50° and 90° C.

Performance at High Current Densities

Voltammetric measurements on these silver electrodes showed that the limiting current lies above 6000 ma/cm^2. A voltage vs. current

density curve is shown in figure 6. The measurement was carried out at such a sweep rate that build up of water during the voltage current measurement is so small that control problems do not arise. In manual testing the water build up is too rapid to study the limiting current density with any validity.

Corrosion of Silver

Voltammetric data indicate that silver tends to corrode at potentials exceeding 1.05 volts vs. the potential of the hydrogen electrode for the conditions specified in table I. Therefore, the silver electrode will tend to corrode at current densities less than 10 ma/cm^2. Since silver oxide is appreciably soluble in the fuel cell electrolyte at 90° C, the electrode will gradually dissolve. Furthermore, the silver oxide will be reduced on the anode after migration through the asbestos matrix. Both these effects, dissolution and redeposition of silver, are detrimental to fuel cell performance. In practice, the voltage of fuel cells operating at practical current densities is well below that required for the onset of corrosion. The problem of corrosion of the silver electrode is, therefore, eliminated by the relatively high overvoltage for the reduction of oxygen.

Life Tests

Life tests have shown that electrodes made from this high surface area silver are stable for more than 6000 hours. The increase in polarization for the total cell at a constant current density of 100 ma/cm^2 is about 10 μv per hour in a hydrogen-oxygen fuel cell at 90° C. We have no data available to indicate the rate of voltage degradation for the single electrodes. Since the total degradation for the cell is 10 μv/hour the cathode degradation is certainly less. Life test data is plotted in figure 7.

Conclusions

The rapid thermal decomposition of hard, dry particles of silver oxalate produces a silver powder with a surface area of 2-6 m^2/g. This powder is extremely active as an oxygen reduction catalyst in alkaline media. It exhibits lower polarization losses at all current densities than Pt-Pd electrodes when used in a hydrogen-oxygen fuel cell under the conditions cited in the text.

The dependence of the activity of this material on oxygen pressure is nearly linear for pressures above 18 psia. At pressures between 10 and 18 psia the polarization increases rapidly with decreasing oxygen pressure.

The dependence of activity on temperature is essentially linear from 50° C to 90° C in a hydrogen-oxygen fuel cell. At temperatures below 50° C the polarization increases at a much faster rate.

Life tests show that electrodes made from this material are stable for more than 6000 hours. The average voltage degradation was less than 10 μv/hour.

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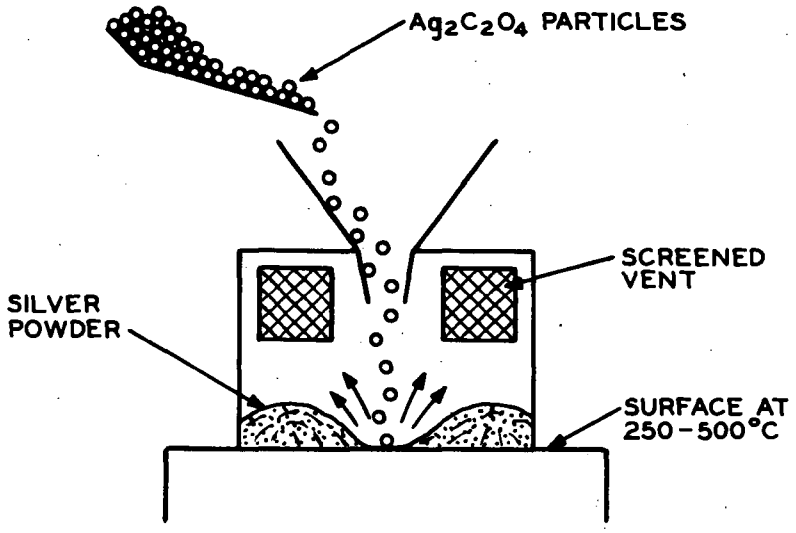

FIG. 1. APPARATUS FOR THERMALLY DECOMPOSING SILVER OXALATE PARTICLES.

REPLICA, 3800 X (A) REPLICA, 19700 X (B) REPLICA, 19700 X (C)

FIG. 2. ELECTRONMICROGRAPHS OF HIGH SURFACE AREA SILVER POWDER

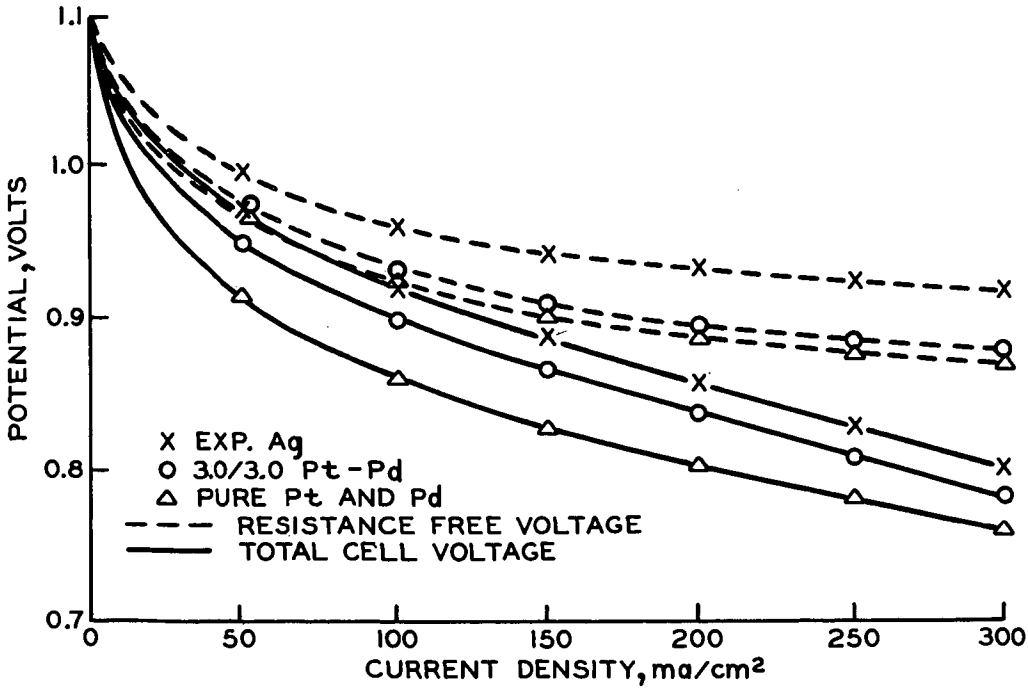

FIG. 3. PERFORMANCE CHARACTERISTICS FOR A FUEL CELL CONTAINING HIGH SURFACE AREA SILVER CATHODES.

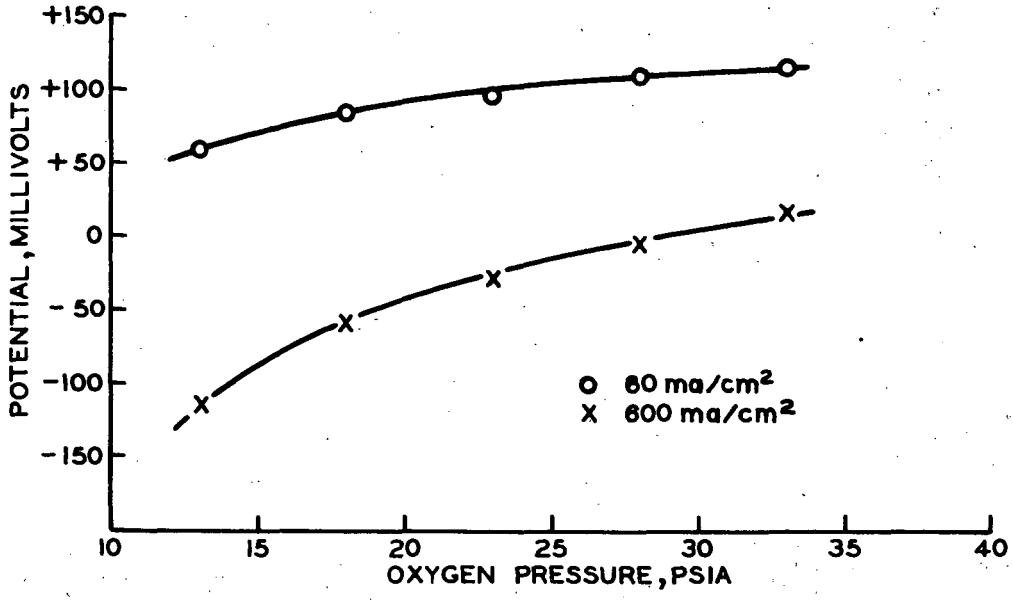

FIG. 4. EFFECT OF P_{O_2} ON THE POLARIZATION OF SILVER CATHODES.

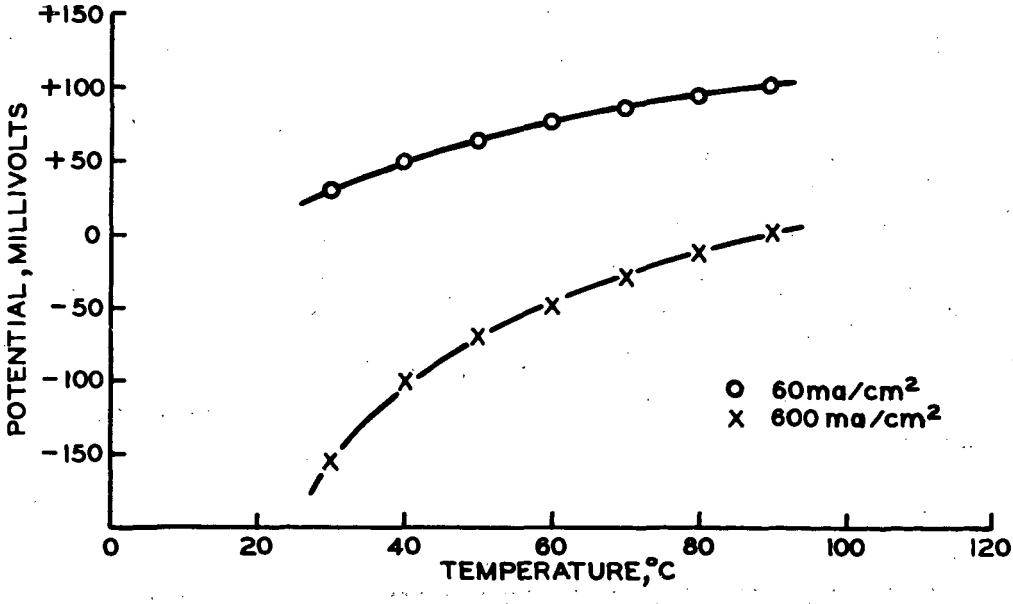

FIG. 5. EFFECT OF TEMPERATURE ON THE POLARIZATION OF SILVER ELECTRODES.

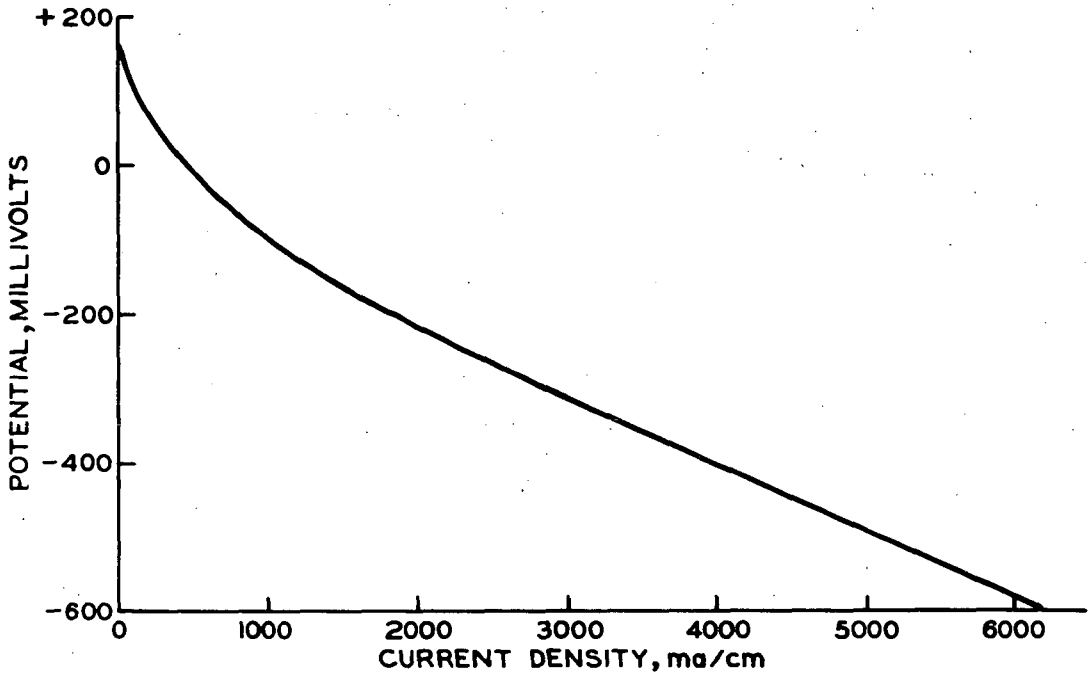

FIG. 6. PERFORMANCE OF HIGH SURFACE AREA SILVER CATHODES AT HIGH CURRENT DENSITY.

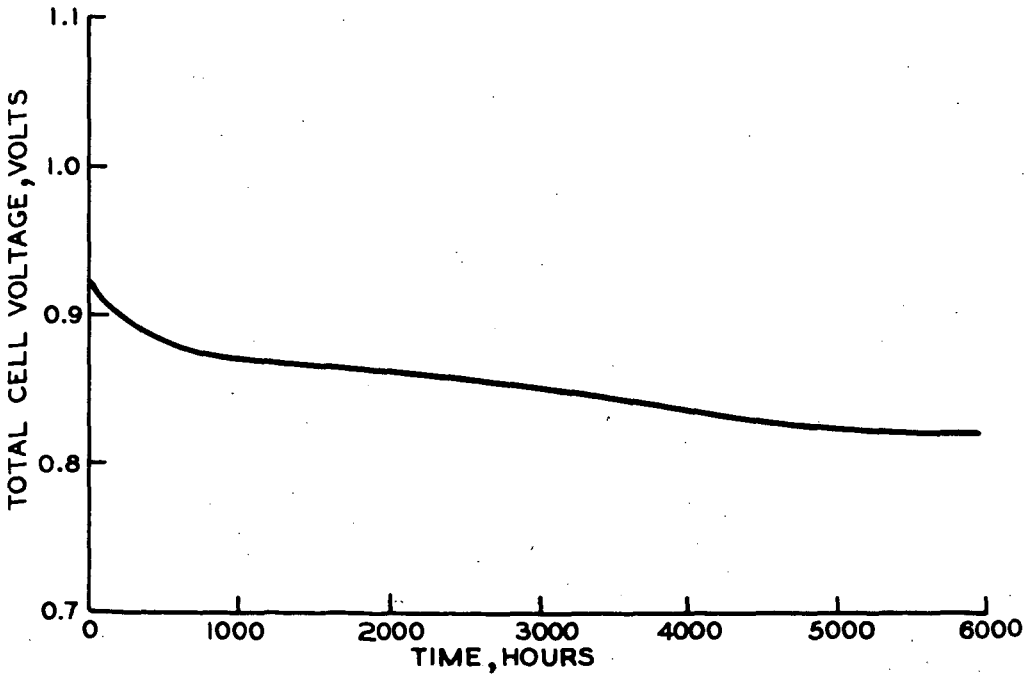

FIG. 7. LIFE TEST PERFORMANCE