

SYNTHESIS OF BATTERY GRADE REDUCED SILVER POWDER

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Process for production of battery grade reduced silver powder, an active positive material for zinc-silver oxide batteries, having specific characteristics has been optimized and the synthesized reduced silver powder was characterized. Results reveal that the values of bulk density ($1.25 \pm 0.1 \text{ g/cm}^3$) and activity (73.27 %) of synthesized reduced silver powder lies within the recommended range for use as battery material. It has purity $\geq 98\%$ and contains Fe and Cu as traces in the concentration range of $30 \pm 5 \text{ ppm}$ and $15 \pm 7 \text{ ppm}$ respectively. Others determined values of surface and pores parameters are; surface area $2.6 \pm 0.4 \text{ m}^2/\text{g}$; pore volume $3.10 \text{ cm}^3/\text{g}$; pore diameter $0.043 \mu\text{m}$ and porosity 20%. XRD studies reveal that reduced silver powder has a cubic structure.

Keywords: Synthesis, Characterization, Silver powder, Battery grade, Activity

1. Introduction

Silver oxide (AgO), acetic and reduced silver powders having specific characteristics are used as cathode materials in the fabrication of high tech zinc-silver oxide batteries [1]. Particular selection of a material depends upon the nature and the type of zinc-silver oxide batteries. Acetic silver, reduced silver and silver oxide (AgO) powders are being used in the fabrication of the positive electrodes of high current primary (non-rechargeable), secondary (rechargeable) and low current primary (non-rechargeable) zinc-silver oxide batteries respectively. The cost of the imported battery grade positive active materials is very high which increases the price of the zinc-silver oxide battery. In order to reduce the price of the battery, it was decided to synthesize the battery grade positive active materials in our laboratory. We have already developed the processes for the production of battery grade silver oxide [2] and acetic silver powder [3] having specific characteristics. Reduced silver powder is produced by thermal decomposition of silver (I) oxide (Ag₂O), which in turn is produced by reaction between KOH and AgNO₃ solutions. Various process parameters involved in the synthesis of reduced silver play significant role in getting the required product. Small changes in the process parameters may change the end product

specifications and the quality, which in turn affect the electrical performance of zinc-silver oxide battery. This paper describes the details of the process for the synthesis of the reduced silver powder having specific characteristics. Results of the characterization and the electrical activity test of the synthesized reduced silver powder are also described.

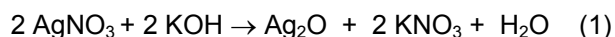
2. Experimental

2.1 Chemicals used

The chemicals used in this study are: silver nitrate (locally available having purity 99.9%); potassium hydroxide (85% ACS Reagent, Aldrich # 22147.3); de-ionized water (locally prepared, conductivity $< 2.0 \mu\text{S/cm}$)

2.2 Synthesis of reduced silver powder

Silver (I) oxide (Ag₂O) was synthesized at varied process parameters such as flow rate of limiting reactant (AgNO₃), stirring motor speed, dropping distance of limiting reactant (AgNO₃) and drying temperature of silver (I) oxide as per following reaction:



The decomposition of synthesized silver (I) oxide powder was carried out in a furnace at

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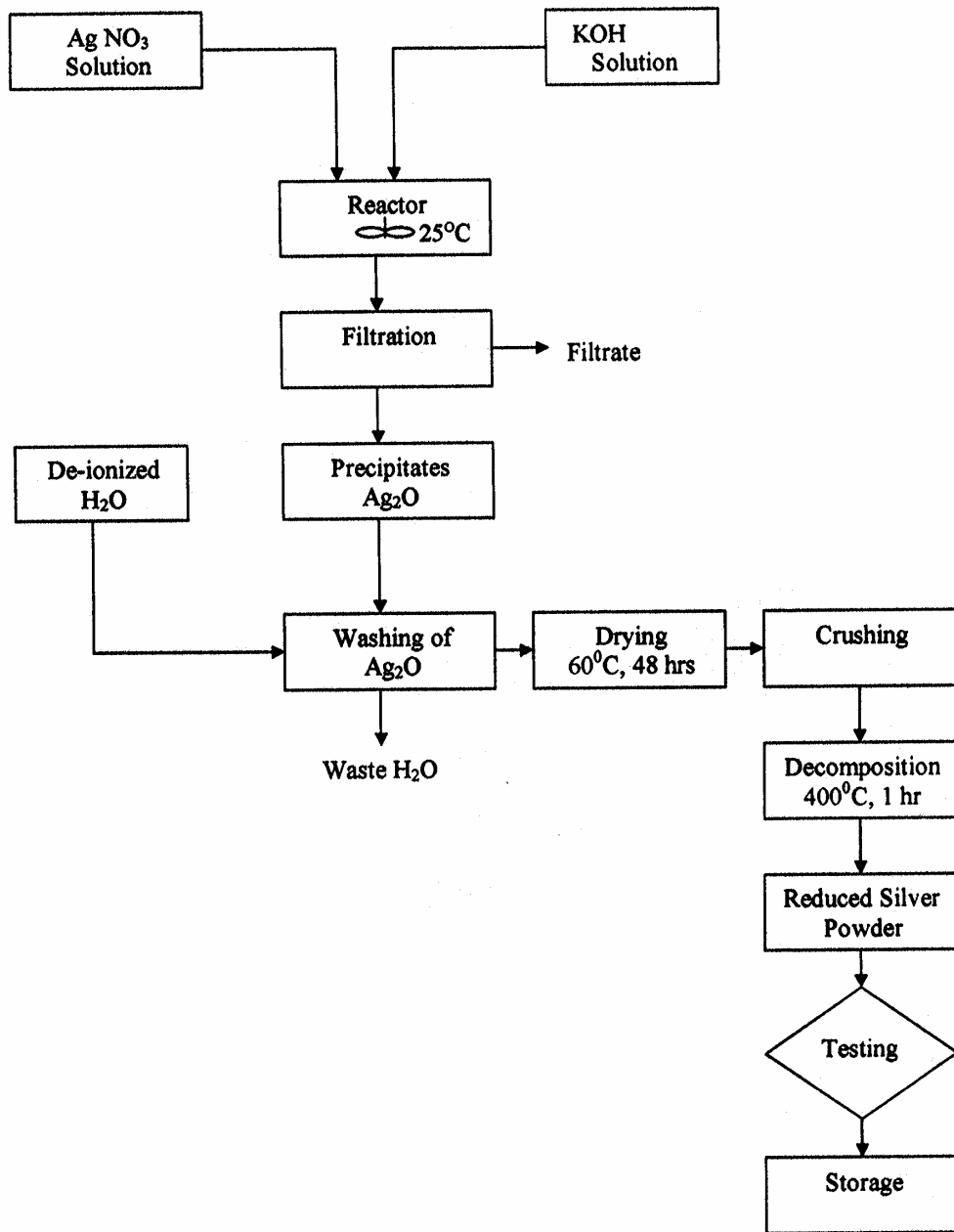
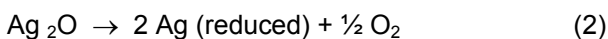


Figure 1. Flow chart for the production of reduced silver powder.

temperature 400 °C for 1 hour, which proceeded via the following reaction:



The optimized flow sheet diagram for the synthesis of reduced silver is given in Figure 1.

2.3 Characterization of synthesized reduced silver powder

The bulk density of reduced silver powder produced was measured according to ASTM standard method No. D-2854-70. Here, an empty cylinder of known volume was weighed, filled with silver powder and weighed again. The bulk density value was calculated in a usual way and is given in Table 1.

Energy dispersive x-rays fluorescence spectrometer (XR-500) from M/S Links System was used to measure the content of silver. The system is equipped with 860 analyzer and 10 mm² x 3 mm deep Si(Li) detector with 155 eV resolution. Rh anode primary x-ray tube was used. Samples were presented to spectrometer in sample cups and x-ray spectrum was collected at voltage 25kV and current 0.04 mA. AgL α was selected as an analytical line, and the measured silver concentration is given in Table 1.

The measurement of Fe and Cu concentration in reduced silver powder as trace metal impurities was carried out by atomic absorption spectrometer after dissolving the reduced silver powder in nitric acid. The description of the equipment and analytical conditions can be seen elsewhere [4]. The measured values of Fe and Cu concentrations in reduced silver powder are given in Table 1. Fe and Cu ions are important because they affect the cell/battery capacity when present in silver powder above recommended level.

The particle size distribution of synthetic reduced silver powder was measured by sieve analysis and detail of the particle size distribution is as follows:

Sieve used (micron)	Weight retained (g)	% of weight retained
400	1.59	5.15
280	7.89	25.58
200	7.77	25.19
140	5.71	18.51
100	3.73	12.09
71	2.23	7.23
-71	<u>1.53</u>	<u>4.96</u>
	30.45	98.71

Total weight of silver powder taken = 30.85 g

Rate of vibration = 90/min.

Time of vibration = 15 min.

1.29 % silver powder has been lost during sieving.

Surface area of synthesized reduced silver powder was determined using Quantasorb Sorption system from Quantachrome Corporation New York by continuous flow method [5]. Nitrogen gas was adsorbed on the sample at liquid nitrogen

Table 1. Measured and recommended values of different parameters of synthesized reduced silver powder

Parameter	Measured value	Recommended value
Silver concentration	98.5 \pm 0.5 %	> 97 %
Fe content	30 \pm 5 ppm	\leq 40 ppm
Cu content	15 \pm 7 ppm	\leq 50 ppm
Bulk density	1.25 \pm 0.1 g/cm ³	1.1-1.50 g/cm ³
Surface area	2.6 \pm 0.4 m ² /g	2 - 4 m ² /g

Table 2. X-ray diffraction data of reduced silver

2 θ	d (Å)	I/I ^o
38.00	2.36	100
44.30	2.04	39
64.44	1.44	29
77.40	1.23	25
81.50	1.18	15

temperature from a stream of nitrogen and helium (carrier gas). It was then desorbed and the liberated nitrogen was measured by a thermal conductivity detector. Single point B.E.T. equation [6] was used to calculate the surface area value, and its determined value is given in Table 1.

Mercury porosimetric study was carried out to measure different pore parameters and pore-size distribution of synthesized reduced silver powder using AUTOPORE 9220 mercury porosimeter from M/s Micrometrics, USA. Mercury was intruded into the pores of synthesized silver powder as a function of pressure. The intrusion/extrusion and pore size distribution curves are shown in Figures 2 and 3 respectively.

X-ray diffraction pattern of reduced silver was obtained with a Philips PW 1069/70 diffractometer goniometer. The detector was argon filled proportional counter linked to a PW 1390 rate meter and channel analyzer. The radiation was CuK α (1.5414Å) generated in a Philips PW1730 generator operated at 40kV and 30mA. XRD data of synthesized reduced silver powder, given in Table 2, was obtained by reflection from the surface of the sample spread on cellophane tape.

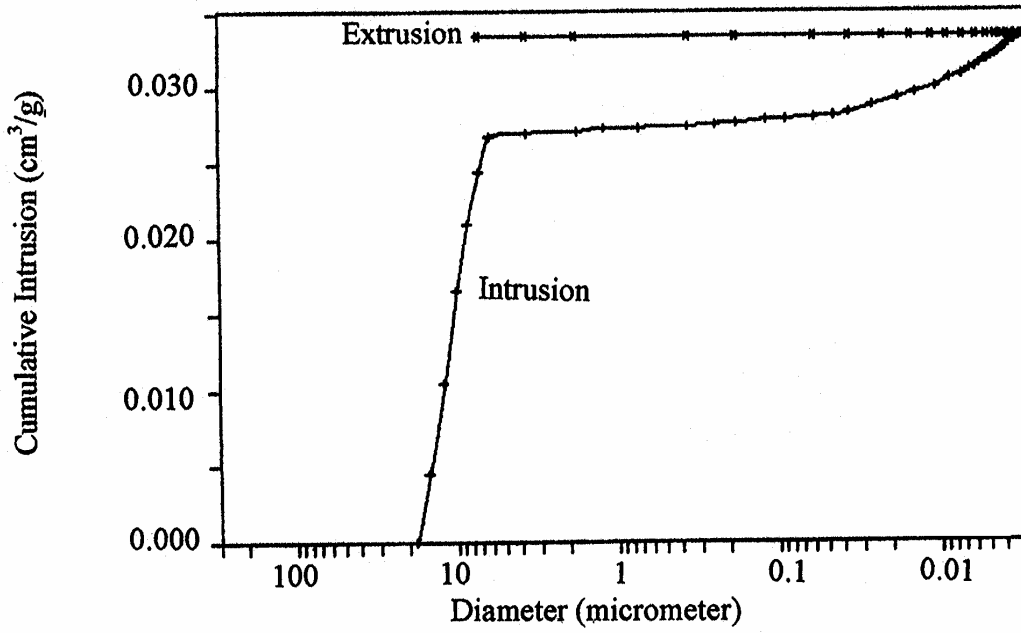


Figure 2. Mercury intrusion/extrusion plots for reduced silver.

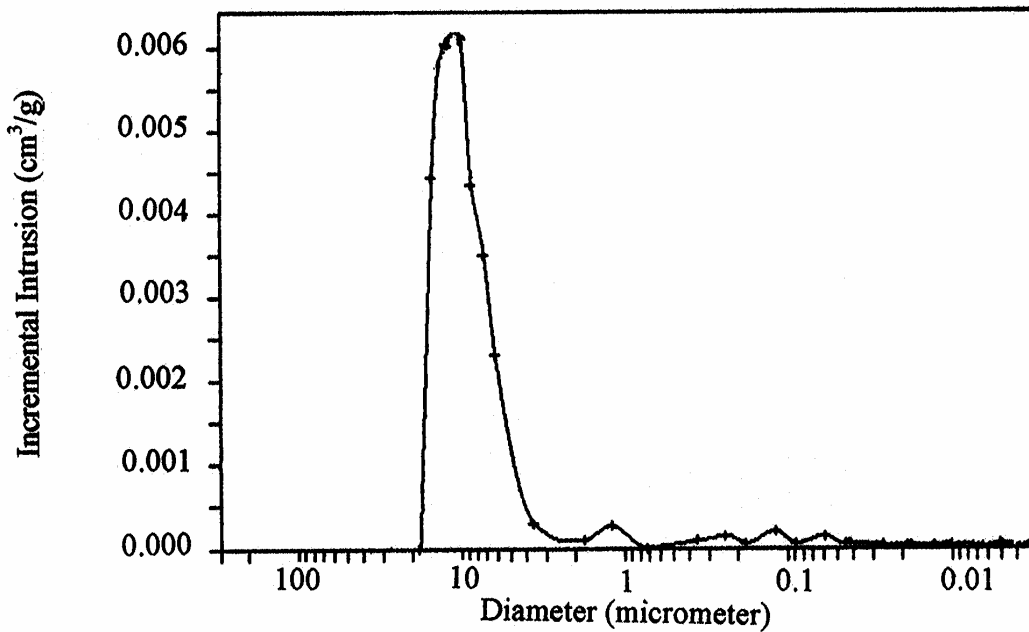


Figure 3. Pore size distribution for reduced silver powder.

2.3 Activity test of synthesized reduced silver powder

Electrodes of known area and thickness were fabricated using synthesized reduced silver

powder, and charging and discharging of the electrodes were carried out at constant current as per details given in Table 3. Set up used in the charging of the electrodes is shown in Figure 4. From the discharged data cells capacity (Ah) and

Table 3. Data of activity test of synthesized reduced silver powder

Cycle		I_d mA/cm ²	Current A	Final voltage V	Discharge time mins
1	Charge	20.2	1.0	2.05	
	Discharge	50.5	2.5	0	64 mins.
2	Charge	50.5	2.5	2.05 ~ 2.10	
	Discharge	50.5	2.5	0	65 mins.
3	Charge	50.5	2.5	2.05 ~ 2.10	
	Discharge	50.5	2.5	0	62.5 mins.
Average discharge time					63.83 mins.
Measured capacity					2.66 Ah
Theoretical capacity					3.63 Ah
Calculated activity					73.27 %
Recommended activity range					70-80 %

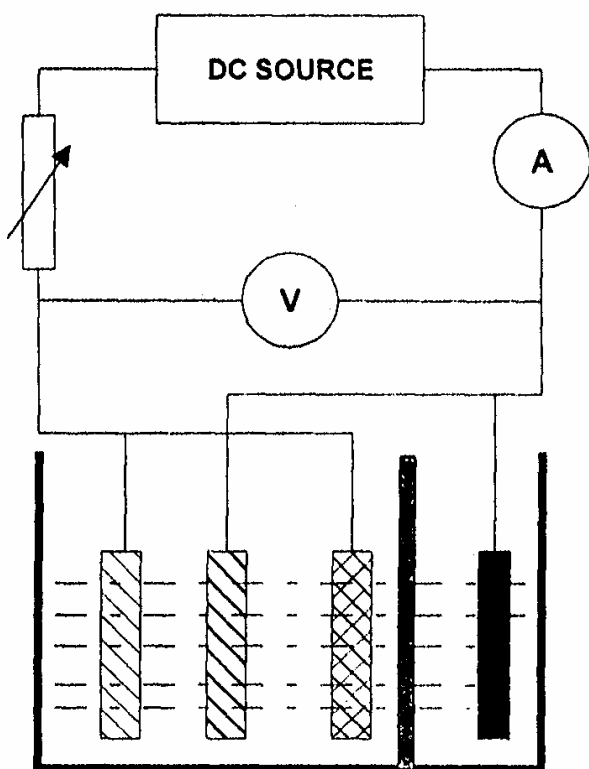


Figure 4. Set up for the charging of the electrode.

% activity were calculated from Electro-chemical equivalents value of silver and their calculated values are also given in Table 3.

3. Results and Discussion

The synthesized reduced silver powder was silvery white in colour and has a yield of 96%.

Silver, Fe and Cu contents, given in Table 1, are within the recommended level of concentration. Synthesized reduced silver powder is macro porous in nature as evident from its surface area value of $2.6 \pm 0.4 \text{ m}^2/\text{g}$.

Plots of mercury intrusion and extrusion as a function of applied pressure for reduced silver powder, Figure 2, shows that there is a steep initial portion in the intrusion plot followed by a relatively flat portion. With further increase in applied pressure, there is a gradual increase in the intrusion volume of mercury. Initial steep slope of intrusion plot may be considered to be a consequence of penetration of mercury into the inter-particulate space [7]. Once the mercury has gained entry into the inter-particulate space, the slope of the curve flattened. Second rise in the slope of the curve indicates that the intrusion occurs within the pores of silver powder. The extrusion plot shows that the mercury extrusion did not follow the same path as that of intrusion, and almost entire volume of mercury has been retained within the pores of silver powder. The retention of intruded mercury within the pores indicates the presence of ink-bottled pores [8]. On reducing the pressure, mercury does not leave due to the presence of the pore potential, which traps mercury once it intrudes into pores [9].

The result of pore size distribution in which volume of mercury is transferred to pores as function of effective radii, r is shown in Figure 3. This plot indicates one large peak maximum at effective radii 12 micrometer and others small peak maxima at 1.3 and 0.15 micrometers. The peak

maximum at radii 12 micrometer is due to the penetration of mercury in the inter-particulate spaces. Height of the other peaks shows that the contributions of pore of radii 1.3 and 0.15 micrometers are less significant to the total pore volume. Pore surface area of reduced silver powder, determined by mercury intrusion, comes out to be $3.10\text{m}^2/\text{g}$. This value is quite similar to the surface area value determined by nitrogen adsorption, which is $2.6 \pm 0.4 \text{ m}^2/\text{g}$. Values of other pore parameters of reduced silver powder, calculated from mercury intrusion, are; total pore volume $0.0335 \text{ cm}^3/\text{g}$; median pore diameter (volume) $10 \mu\text{m}$; median pore diameter (area) $0.005 \mu\text{m}$; average pore diameter $0.043 \mu\text{m}$ and porosity 20%. The pore parameters alongwith the particle size plays significant role in the fabrication of the electrodes, the details of which will be published separately.

X-ray diffraction data presented in Table 2 show that reduced silver powder has a crystalline structure. Main diffraction lines appearing at 2.36, 2.04, 1.44, 1.23 and 1.18 have relative intensities 100, 39, 29, 25, and 15 respectively. These values coincide with the literature cited values [10]. XRD study point towards a cubic crystal structure of the synthesized reduced silver powder.

The electrical performance (activity) of the synthesized reduced silver powder can be assessed from the results given in Table 3, which indicates that the calculated activity (%) value falls within the recommended range of activity (%) for use in the fabrication of zinc-silver oxide batteries.

4. Conclusion

Based on the above reported observations, it is concluded that the quality and the activity of the

battery grade reduced silver powder manufactured in our laboratory is fairly good for use in the manufacturing of zinc-silver oxide batteries.

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