Optimization of Process Parameters for the Production of Battery Grade Acetic Silver Powder

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Summary: Various process parameters involved in the production of battery grade acetic silver powder having specified characteristics have been optimized and the acetic silver powder produced at optimized process parameters was characterized. Results reveal that the activity of synthesized acetic silver powder matched fairly well with the activity of imported material and is also economical cost wise. It has purity ≥ 99% and contains Fe and Cu as traces having concentration of 20 ± 6 ppm and 30 ± 5 ppm respectively. XRD studies show that acetic silver powder has a cubic structure.

Introduction

Silver powders having specific characteristics are used as cathode materials for high tech zinc-silver oxide batteries. Acetic and reduced silver powders are being used for the fabrication of positive electrodes of high current primary (non-rechargeable) and secondary (rechargeable) zinc-silver oxide batteries respectively [1]. Generally, the acetic and reduced silver powders are being prepared by the thermal decomposition of silver acetate and silver oxide (Ag_2O) respectively. The cost of the imported battery grade silver powders 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 acetic silver powders in our laboratory. Various process parameters involves in the synthesis of silver acetate plays 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 affects the electrical performance of zinc-silver oxide battery. This paper describes the details of the optimization of the process parameters for the synthesis of the acetic silver powder having specific characteristics. Results of the characterization and the electrical performance test of the synthesized acetic silver powder are also described in this communication.

Results and Discussion

Acetic silver powder for use as positive active material in zinc-silver oxide batteries should have the bulk density value in the range of 0.4 – 0.68 g/cm^3. The recommended level of silver, Fe and Cu contents are given in Table 1. The bulk density value of the acetic silver powder for use in ordinary primary zinc silver cell should be ≤ 0.6 g/cm^3 where as for high powered primary zinc-silver cell, the bulk density of acetic silver powder should be ≥ 0.60 g/cm^3. Bulk density is main controlling parameter to get the required end product. The general flow chart for the synthesis of acetic silver powder is shown in Figure1 and the chemical reactions involved in the synthesis of acetic silver powder are given in equations 1 and 2. Small changes in the different production steps may change the bulk density of the acetic silver powder produced, which in turn affects the electrical performance of zinc silver oxide batteries. The important process parameters, which affect the bulk density of the acetic silver powder, are as follows:

Table-1: Measured and recommended values of acetic silver powder

Parameter	Measured values	Recommended values
Ag content (%)	99.30	≥ 98
Cu content (ppm)	30 ± 5	50
Fe content (ppm)	20 ± 6	40
Surface area (m^2/g)	0.25 ± 0.05	0.2-0.3

- Flow rate of limiting reactant ($AgNO_3$)
- Stirring motor speed
- Dropping distance of limiting reactant
- Drying temperature of silver acetate

The effects of these parameters on bulk density of acetic silver powder have been studied in detail and conditions were optimized to get the product of required bulk density for use in the

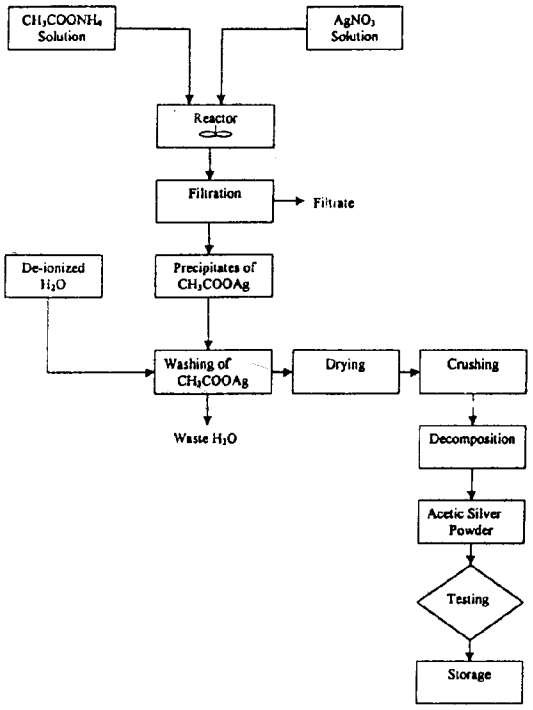

Fig. 1: Flow Chart for the Preparation of Acetic Silver

manufacturing of high powered primary zinc-silver oxide batteries. The details of these studies are given below:

Effect of the flow rate of limiting reactant ($AgNO_3$)

The effect of flow rate of limiting reactant on the bulk density of the acetic silver powder has been studied by producing the acetic silver powder at various flow rates of adding silver nitrate solution at fixed conditions of stirring motor speed (50 rpm), dropping distance of silver nitrate solution (10 cm) and drying temperature of silver acetate (60 °C). Figure 2 shows the variation of the bulk density of the acetic silver powder produced with the flow rates of silver nitrate solution. This figure shows that the bulk density of the acetic silver powder increases with the increase of flow rates and attained constant value around 60ml/min. Therefore, 60 ml/min flow rate of silver nitrate was used in all the subsequent studies.

Effect of the stirring motor speed

The variation of the bulk density of the acetic silver powder with the stirring motor speed is shown

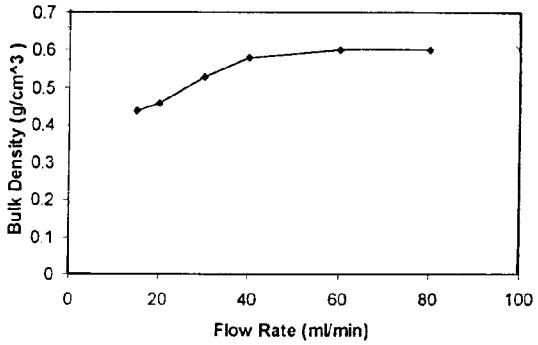

Fig. 2: Variation of Bulk Density of Acetic Silver Powder with Flow Rate of Limiting Reactant

in Figure 3. Dropping distance of silver nitrate solution, flow rate of adding silver nitrate solution and drying temperature of silver acetate were fixed at 10 cm, 60 ml/min and 60 °C respectively. Bulk density values of acetic silver powder increases with the increase in the string motor speed. It was also observed that the required value bulk density of acetic silver powder is achieved around 125 rpm and this value of stirring motor speed was selected and used in the subsequent studies.

Effect of the dropping distance of limiting reactant ($AgNO_3$)

Figure 4 shows the variation of the bulk density of the acetic silver powder with the dropping distance of silver nitrate solution at fixed flow rate of silver nitrate (60 ml/min) and stirring motor speed (125 rpm). Dropping distance of silver nitrate has no effect on the bulk density of acetic silver powder produced.

Effect of drying temperature of silver acetate precipitate

The effect of drying temperature of silver acetate on the bulk density of acetic silver is shown in Figure 5, which indicate that the drying temperature has no effect on the bulk density of the acetic silver powder and 45°C drying temperature was selected to dry the silver acetate precipitate for 48 hours.

Acetic silver powder produced at optimized conditions of flow rate of silver nitrate solution (60 ml/min); stirring motor speed (125 rpm); dropping distance of silver nitrate (10cm); drying temperature of silver acetate precipitates (45°C) was characterized

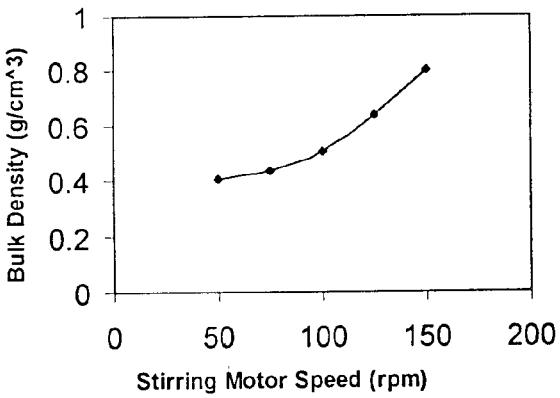

Fig. 3: Variation of Bulk Density of Acetic Silver Powder with the Stirring Motor Speed

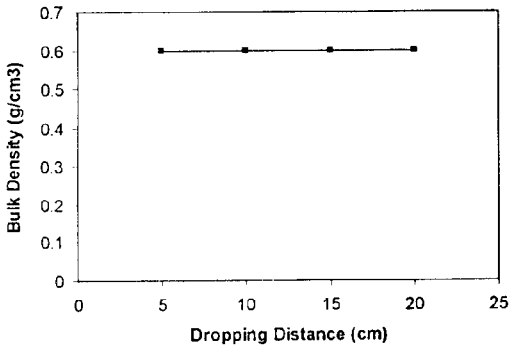

Fig. 4: Variation of Bulk Density of Acetic Silver Powder with Dropping Distance of Limiting Solution

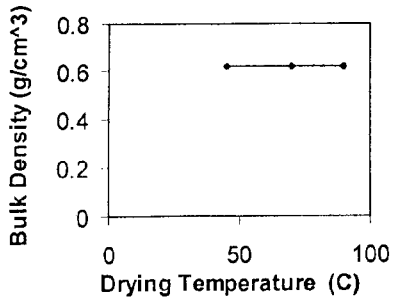

Fig. 5: Variation of Bulk Density of Acetic Silver Powder with the Drying Temperature of Silver Acetate Precipitates

for various parameters and the measured values of different parameters are given in Table 1. This table shows that measured values of different parameters of acetic silver powder matched fairly well with the recommended values for use in the manufacturing of high powered primary zinc-silver oxide batteries.

X-ray diffraction data presented in Table 2 show that acetic 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, 46, 27, 27, and 10 respectively. These values coincide with the literature cited values [2]. XRD studies points towards a cubic crystal structure of the synthesized acetic silver powder.

The electrical performance of the synthesized acetic silver powder can be assessed from the results given in Table 3, which indicates that, the performance of the locally synthesized acetic silver powder match fairly well with the performance of the imported acetic silver powder. The cost of the locally synthesized acetic powder was calculated as US$ 220.00/kg. This cost include the raw materials and the over and above expenditures. The price for the same imported materials varies from US$ 450.00 to US$ 550.00 per kilogram.

Experimental

Chemical used

The chemicals used in this study are: silver nitrate (locally prepared having purity 99.9%); ammonium acetate (Aldrich cat.# 23807-4); de-ionized water (locally prepared, conductivity < 2.0 μS/cm)

Synthesis of acetic silver powder

Synthesis of silver acetate at varied process parameters

Silver acetate was synthesized at varied process parameters such as flow rate of limiting reactant ($AgNO_3$), stirring speed, dropping distance of limiting reactant ($AgNO_3$) and drying temperature of silver acetate as per following reaction using molar ratios:

$$CH_3COONH_4 + AgNO_3 \text{ -------} CH_3COOAg + NH_4NO_3 \quad (1)$$

Decomposition of silver acetate

The synthesized silver acetate powder was spread in a tray and decomposed in a furnace at 300 °C for one hour to obtain acetic silver powder. The decomposition process proceeds via following reaction:

$$CH_3COOAg \text{ ---------} CO_2 + H_2O + Ag \text{ (acetic)} \quad (2)$$

The general flow sheet diagram for the synthesis of acetic silver is given in Figure 1, and the yield of the acetic silver powder produced was ≥ 98 %

Bulk density measurement of acetic silver powder

The bulk density of acetic 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 acetic silver powder and weighed again. The bulk density value was calculated in a usual way. Variations of bulk density of acetic silver powder produced at varied parameters are shown in Figures 2-5.

Characterization of synthesized acetic silver powder

X-ray diffraction studies of acetic silver powder

X-ray diffraction pattern of acetic 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 CuKα (1.5414A) generated in a Philips PW1730 generator operated at 40kV and 30mA. The XRD data of synthesized acetic silver powder, given in Table 2, was obtained by reflection from the surface of the sample spread on cellophane tape.

Table 2: X-Ray diffraction data of Ag

2θ	D(Å)	I/I°
38.00	2.36	100
44.30	2.04	46
64.44	1.44	27
77.40	1.23	27
81.50	1.18	10

Estimation of silver content

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 mm^2 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 a sample cups and x-ray spectrum was collected at voltage 25kV and current 0.04 mA. AgLα was selected as an analytical line, and the concentration of silver was measured as 99.30 ± 0.20 %. The result was confirmed by performing the potentiometric titration and the estimated value of silver as 99.13 ± 0.15 % matched fairly well with the value determined by XRF.

Estimation of Fe and Cu content in acetic silver as impurities

The measurement of Fe and Cu concentration in acetic silver powder as trace metal impurities was carried out by atomic absorption spectrometer after dissolving the acetic silver powder in nitric acid. The description of the equipment and analytical conditions can be seen elsewhere [3]. The measured values of Fe and Cu concentrations in acetic silver powder are 20 ± 6 ppm and 30 ± 5 ppm respectively.

Estimation of particle size of synthesized acetic silver powder

The particle size distribution of synthetic acetic 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	0.87	2.35
280	10.24	27.70
200	8.58	23.20
140	5.60	15.15
100	3.21	8.68
71	2.31	6.26
-71	5.91	15.98

Total weight of acetic silver powder taken = 37 g
Rate of vibration = 90/min
Time of vibration = 15 mins.

Estimation of surface area of synthesized acetic silver powder

Surface area of synthesized acetic silver powder was determined using Quantasorb Sorption system from Quantachrome Corporation New York by continuous flow method [4]. Nitrogen gas was adsorbed on the sample at liquid nitrogen temperature from a stream of nitrogen and helium (carrier gas). It was then desorbed and the librated nitrogen was measured by a thermal conductivity detector. Single point B.E.T. equation [5] used to calculate the surface area value, which comes out to be 0.25 ± 0.5 m^2/g.

Table 3: Discharge data of cells manufactured by using locally developed and imported acetic silver powder.

Parameters	Single cell		Three cells connected in series	
	Locally developed acetic silver	Imported acetic silver	Locally developed acetic silver	Imported acetic silver
Open circuit voltage (V)	1.846	1.854	5.53	5.55
On load voltage (V)	1.394	1.393	4.11	4.04
Discharge current (A)	50.22	50.22	50.22	50.22
Time of discharge (min)	11.88	11.95	12.08	12.41
Calculated capacity (Ah)	9.94	10.00	10.11	10.39

Electrical performance test of synthesized acetic silver powder

Zinc-silver oxide single cells of 10Ah capacity were prepared using locally synthesized and imported acetic silver powders as cathode material. The anode was prepared using zinc oxide powder (commercial, purity 99.99%). After doing the chemical treatment, the cells were discharged using potassium hydroxide as an electrolyte at 50A constant current as per detailed given in Table 3.

Conclusions

On the basis of the above mentioned observation, it is concluded that the activity of the battery grade acetic silver powder manufactured in our laboratory matched fairly well with the activity of the imported one and is also economical. This enables us to save the foreign exchange incurred on the import of the battery grade materials and also reduces the price of the battery.

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