Preparation of silver powder used for solar cell paste by reduction process

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Abstract

The preparation of fine silver particles is getting great attention due to their applications in electrical fields such as the fabrication of conductive pastes used in solar cell metallization. This study deals with the preparation of silver powders by a chemical reduction method using silver nitrate as a starting material, and either sodium or ammonium hydroxides as reactants, and formaldehyde as a reducing agent. The effects of ratio change between the silver nitrate and the base concentrations, on the characteristics of the silver micro particles, were examined. The physicochemical properties of the powders were evaluated using XRD, SEM, and granulometry. It was shown that the particle size and shape of the powder depend on the molar ratio of silver nitrate to base and, on the base nature.

1. Introduction

Silver powder was extensively used in electronic industry. It confers conductive properties to inks and pastes of thick films of solar cells metallic grids. To obtain the screen printable pastes, a homogeneous
melted mixture of metallic oxides, called glass frit, and additional chemicals, is mixed to the active material. Then, many specific organic substances and solvents are added to get the viscous form of the pastes [1]. Thick film conductive pastes are mainly composed of a specific morphological feature of spherical and/or flakes formed silver powders. Such powders can be constituted of non-agglomerated micron/submicron crystalline particles with a narrow size distribution [2]. They must have suitable properties such as an adequate surface area, particle size and particle size distribution. In the two last decades, many synthesis methods were reported for the preparation of silver particles with tailor-made size, shape, and size controllability [3-5]. Depending on the end use of the powder, these methods include the chemical reduction of silver ions, with or without surfactant (stabilizing) agents, atomization, milling method, and electrochemical processes. Nevertheless, in order to achieve better characteristics of silver particles, which affect directly the mechanical and physical properties of the deposited film, and consequently the solar cell performances, the chemical reduction process was considered as the most appropriate method [2, 6]. It leads to a fine silver powder, controlled in shape and size [2]. In this last method, the silver powder is reduced from an aqueous silver nitrate solution. The reducing agents can be formaldehyde, hydrazine, ascorbic acid, or sugars. And the surfactant agents can be poly(N-vinylpyrrolidone) [7], polyvinyl alcohol [8] or a mixture of these two polymers [9]. These polymers are also used as protective agents, and give high mono dispersive spherical silver particles [3,10,11]. This synthesis method is well suitable for the preparation of nano-sized silver particles of various shapes [12].

In this paper, silver particles were synthesized by the reduction method. This method was chosen because it does not require specific experimental equipments. Furthermore, it offers both homogeneous powder morphology and efficient scale-up for mass production [13, 14]. Silver particles were obtained by heating a mixture constituted of a silver salt solution, a base and a reducing agent, to a temperature of 45 °C. The influence of the ratio (silver salt/base) on the silver particle size was examined.

2. Materials and Methods

2.1. Material

Silver nitrate (AgNO₃) and formaldehyde (CH₂O) were purchased from Sigma-Aldrich. Ammonium hydroxide (NH₄OH) was purchased from Merck. Sodium hydroxide (NaOH) was purchased from Fluka. Deionized water was used for the preparation of mixture solution.

2.2. Samples preparation

Silver (Ag) powders were obtained by the reduction of a 0.865 M, 0.433M, 0.289M solutions of silver nitrate (AgNO₃) as a starting material by formaldehyde (CH₂O), in two different basic solutions. For the first series of experiments, AgNO₃ solution was added drop wise to three different aqueous solutions of ammonium hydroxide (NH₄OH), such that the molar ratios of the reactant agents R (NH₄OH/AgNO₃) were equal to 2.5, 3 and 3.5, corresponding to the samples hereafter termed P1, P2 and P3.

For the second series of experiments, AgNO₃ solution was added drop wise to an aqueous solution of sodium hydroxide (NaOH) to get Ag oxide, which is dissolved with ammonium hydroxide and reduced by formaldehyde in order to obtain an Ag powder. The molar ratios of the reactant agents R (NaOH/AgNO₃) were equal to 2.5, 3 and 3.5, corresponding to the samples hereafter termed P4, P5 and P6. The solutions were heated to 45°C with stirring to maintain the formed Ag particles dispersed until the reaction was completed. The reaction time was estimated at less than 1hour. The solid product was removed from the solid/liquid mixture by centrifugation at 4100rpm during 10 min. The Ag product was washed several times with deionized water and dried in an oven at 65°C overnight to get Ag particles.
The chemical reduction process was conducted according to the following chemical reactions steps:

- In NH₄OH medium:

\[
\begin{align*}
\text{AgNO}_3 + \text{NH}_4\text{OH} & \rightarrow \text{AgOH} + \text{NH}_4\text{NO}_3 \quad (1) \\
2 \text{AgOH} & \rightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O} \quad (2) \\
\text{Ag}_2\text{O} + 4 \text{NH}_4\text{OH} & \rightarrow 2[\text{Ag(NH}_3)_2]\text{OH} + 3 \text{H}_2\text{O} \quad (3) \\
2[\text{Ag(NH}_3)_2]\text{OH} + \text{CH}_2\text{O} & \rightarrow 2 \text{Ag} + \text{HC=OONH}_4 + 3 \text{NH}_3 + \text{H}_2\text{O} \quad (4)
\end{align*}
\]

- In NaOH medium:

\[
\begin{align*}
\text{AgNO}_3 + \text{NaOH} & \rightarrow \text{AgOH} + \text{NaNO}_3 \quad (5) \\
2 \text{AgOH} & \rightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O} \quad (6) \\
\text{Ag}_2\text{O} + 4 \text{NH}_4\text{OH} & \rightarrow 2[\text{Ag(NH}_3)_2]\text{OH} + 3 \text{H}_2\text{O} \quad (7) \\
2[\text{Ag(NH}_3)_2]\text{OH} + \text{CH}_2\text{O} & \rightarrow 2 \text{Ag} + \text{HC=OONH}_4 + 3 \text{NH}_3 + \text{H}_2\text{O} \quad (8)
\end{align*}
\]

2.3. Characterization

The powders X-ray diffraction (XRD) diagrams were determined with a monochromatic Cu Kα (λ=1.5418Å) Philips X’Pert Pro Diffractometer, using Philips X’Pert Plus 2001 software [15]. The analysis parameters were a scan step size of 0.02 °2θ, a time per step of 0.5 s, and 2θ varying from 10 to 90, with I=40 mA and V=40 kV. The particle size was estimated using a Malvern Mastersizer 2000 laser distribution analyzer. Grain image analysis and pore distribution of the powders were performed with two Scanning Electron Microscopes (SEM) JEOL JSM-6360LV and Philips XL30, equipped with an EDX, ESEM-FEG probe. Either secondary electrons or back scattered electrons modes were used, with a variation of energy between 10 and 15 keV.

3. Results and discussion

3.1. Diffraction analysis

Fig.1 displays the XRD diagrams of the Ag powders obtained with NH₄OH promoter agent, for the samples P1, P2 and P3. As illustrated, it can be seen that all the samples present similar diagrams with a good crystallinity. For all the diagrams, the products are well crystallized Ag face-centered cubic phases (fcc), with the group space of Fm-3m, identified to the JCPDS standard data of 00-004-0783 [15]. It can be noted that the presence of the Ag typical super-lattice peaks at 2θ values of about 38° (111), 44° (200), 64° (220) and 77° (311). Typical XRD patterns indicate that the silver powders P4, P5, P6 synthesized using the sodium hydroxide as basic medium were found to possess a face centered cubic
structure (fcc) as shown in Fig. 2. Four distinct diffraction peaks were observed at °2θ values of 38, 44, 64 and 77, corresponding respectively to the (111), (200), (220) and (311) crystalline planes of cubic Ag (JCPDS cards (00-04-0783) [15]. These results are similar to those reported by Zhu et al. [16].

Fig. 1. XRD patterns of Ag powders obtained for different [NH4OH]/[AgNO3] molar ratios

Fig. 2. XRD patterns of Ag powders obtained for different [NaOH]/[AgNO3] molar ratios
3.2. Particle size analysis

The size distributions of the synthesized powders are given in Table 1 for NH₄OH and NaOH mediums respectively. The powder average grain size D[50] varies from 31 to 67 μm when NH₄OH is used and from 4 to 16 μm when NaOH is used. It is clear that the samples prepared with NH₄OH present unrefined powders. The Ag granulometry found in the experiments with the ratios (NaOH/AgNO₃) for the samples P4, P5 and P6, is a suitable result for the Ag powders [17]. The results show that the particle size depends on the nature of the used base and also on the ratio (base/AgNO₃). Higher is the ratio (Base/AgNO₃), smaller is the grain size. The same result is obtained by Hosukura [18]. As the silver nitrate concentration decreases, the particle size decreases. It was shown that the use of NaOH as a base medium promotes the production of Ag powders with smaller size, good spherical shape and homogeneity in grain size, than those obtained with NH₄OH base. It can be concluded that NaOH gives better results than NH₄OH. This base is more appropriate for this kind of synthesis.

<table>
<thead>
<tr>
<th>Powders</th>
<th>D[50] (μm)</th>
</tr>
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<tbody>
<tr>
<td>[NH₄OH]/[AgNO₃]</td>
<td></td>
</tr>
<tr>
<td>2.5 (P1)</td>
<td>67</td>
</tr>
<tr>
<td>3.0 (P2)</td>
<td>41</td>
</tr>
<tr>
<td>3.5 (P3)</td>
<td>31</td>
</tr>
<tr>
<td>[NaOH]/[AgNO₃]</td>
<td></td>
</tr>
<tr>
<td>2.5 (P4)</td>
<td>16</td>
</tr>
<tr>
<td>3.0 (P5)</td>
<td>8</td>
</tr>
<tr>
<td>3.5 (P6)</td>
<td>4</td>
</tr>
</tbody>
</table>

3.3. SEM analysis

The SEM micrographs of the synthesized Ag powders for both NH₄OH and NaOH syntheses are shown in Fig.3, Fig.4 and Fig.5 respectively. From all the SEM micrographs, the average grain size of most Ag particles is between 0.5 and 5 μm, which are much smaller than the mean diameter values obtained in the laser granulometry test. These results are in agreement with those obtained by Liu et al. [19] by using silver nitrate as metal source, ascorbic acid as reducing agent and arabic gum as dispersant under traditional chemical reduction method. It was noted that the Ag powder morphology, for the synthesis with NaOH, is more homogeneous than that for Ag powder obtained by the synthesis with NH₄OH. This is probably due to the supplementary synthesis step of formation of silver oxide, which is a very fine powder. The Ag powder, obtained for a ratio (NH₄OH/AgNO₃) of 3.5 (P3) showed in (Fig.4), is composed by unshaped particles, heterogeneousness in the granular particles. Let us suppose the presence of impurities. The EDX analysis of P3 showed the appearance of the oxygen in its composition which indicate that the reaction is incomplete. In the experiment with a ratio of 2.5, (P1) presented in Fig.3, is constituted by spherical Ag micro particles. The Ag powder exhibits more homogeneous spherical particles with many agglomerates. For a ratio of 3, the SEM image (Fig.3) shows a powder with better properties, compared to those obtained for P1 and P3. In the synthesis experiments with NaOH, the Ag
powders have a spheroidal shape and are not agglomerated compared to the powders obtained in the synthesis with NH$_4$OH.

The shape of Ag particles in the synthesis with a ratio (NaOH/AgNO$_3$) of 3.5 (P6) as shown in Fig.5 is more spherical than that for the samples P4 and P5. It can be noted that the mean diameter of Ag grains resulting from the synthesis with NH$_4$OH is greater than that obtained from the synthesis with NaOH. This proves that the particle size and the shape depend on (NaOH/AgNO$_3$) and (NH$_4$OH/AgNO$_3$) ratios.

Fig. 3. SEM micrographs of Ag powder samples. (a) P1 with [NH$_4$OH]/[AgNO$_3$] = 2.5; (b) P2 with [NH$_4$OH]/[AgNO$_3$] = 3

Fig. 4. SEM micrographs of Ag powder samples. (a) P3 with [NH$_4$OH]/[AgNO$_3$] = 3; (b) P4 with [NaOH]/[AgNO$_3$] = 2.5
4. Conclusion

From the diffraction analysis, it was shown that the Ag products have face-centered cubic phases (fcc). The results of the granulometry study have shown that the powder average grain size varies from 5 to 16 μm when NaOH was used and from 30 to 66 μm when NH₄OH was used. The use of NaOH as a base medium promotes the production of Ag powders with smaller size, and good spherical shape and homogeneity in grain size, than those obtained with NH₄OH base. The particle size depends on the nature of the used base and also on the (base/AgNO₃) ratio. The higher this ratio, the smaller is the grain size. SEM observations have shown that the Ag powder morphology, for the synthesis with NaOH, is more homogeneous than that obtained by the synthesis with NH₄OH.

The experimental results of the so-prepared silver powders demonstrated that the ratios (NaOH/AgNO₃) and (NH₄OH/AgNO₃) play a significant role in controlling the particle shape and size. It can be concluded that NaOH gives better results than NH₄OH. This base is more appropriate for the chemical reduction synthesis.

Acknowledgements

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References


