Reduction of Silver Ions With Polyhydroxy Alcohols

by Stojan S. Djokić*

This paper describes the preliminary results on the reduction of silver ions with propylene glycol, ethylene glycol and glycerol. Glycerol and propylene glycol can be used for the reduction of silver ions from $AgNO_3$ and $[Ag(NH_3)_2]OH$ solutions or Ag_2O suspensions. Using the ethylene glycol, the reduction of Ag_2O and $[Ag(NH_3)_2]OH$ to silver was successful. However, reduction of silver ions from $AgNO_3$ to silver metal was not observed with ethylene glycol.

Reduction of silver ions to the metallic state is a well-known art. This process, commonly referred to as the silvering reaction, is used in the production of mirrors, as well as for various electronic, biomedical and decorative devices. The following silver ion reducing agents have been used or reported in the literature: formaldehyde, dextrose, potassium sodium tartrate (Rochelle salt), glyoxal, a boiled mixture of Rochelle salt and crystallized sugar, sugar inverted by nitric acid, aldonic acid and aldonic acid-lactone, potassium borohydride or dimethylamine borane,[1] cobalt ion,[2] sodium sulfide,[3] triethanolamine[4] and polyhydroxy alcohols of type $CH_2OH(CHOH)_nCH_2OH$, where n = 1 - 6 (*i.e.*, mannitol, sorbitol, etc.).[5]

In a U.S. patent, polyhydroxy alcohols as silver ion reducing agents were selected from the group consisting of erythritol, threitol, arabinitol, ribitol, xylitol, allitol and glycero-altrohepitol.[5] Although glycerol, as a polyhydroxy alcohol, belongs to this group, for n = 1 (*i.e.*, $CH_2OHCHOHCH_2OH$), it was not mentioned in the invention[5] as a silver ion reducing agent . Similarly, other alcohols such as ethylene glycol or propylene glycol were not reported in the literature as possible reducing agents. This paper describes preliminary observations and results on the silvering reaction using ethylene glycol, propylene glycol or glycerol as silver ion reducing agents.

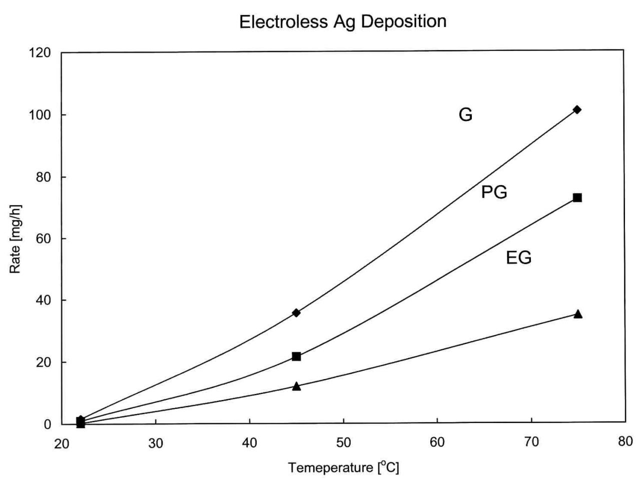

Fig. 1—Rate of silver deposition from $[Ag(NH_3)_2]OH$ solution versus temperature using ethylene glycol (EG), propylene glycol (PG) or glycerol (G) as reducing agents.

Nuts & Bolts: What This Paper Means to You

This paper deals with an interesting form of deposition, rarely covered in these pages, called silvering. Reduction of silver ions to the metallic state is a well-known art and is used in the production of mirrors, as well as for various electronic, biomedical and decorative devices. This paper describes the preliminary results on the reduction of silver ions from solutions of silver nitrate or ammoniated silver salt or suspensions of silver oxide. Propylene glycol, ethylene glycol and glycerol are used as reducing agents. You will see that the process is not an electroless one, nor is it quite simple immersion plating.

Experimental

The sources of silver ions used in this work were $AgNO_3$ and Ag_2O. The reduction was carried out using the following aqueous solutions: $AgNO_3$ (0.1M $AgNO_3$, pH 6.5) and $[Ag(NH_3)_2]OH$ (0.1M $AgNO_3$ mixed with 28% NH_4OH to a clear colorless solution, pH 11.5). To 100 cm^3 (3.38 fl. oz.) of these solutions or an Ag_2O suspension, 10 cm^3 (0.34 fl. oz.) of glycerol, propylene glycol or ethylene glycol was added. Deposition of silver was carried out on flat polyethylene substrates. For this purpose the polyethylene substrates were sensitized and activated in the usual manner using $SnCl_2$ and $PdCl_2$ solutions.[1] The rate of silver deposition was determined by weighing the silver deposited at different temperatures. In some experiments, as explained later, deposition of silver was observed on beaker walls and in the bulk solution.

In order to produce silver powder in 100 cm^3 (3.38 fl. oz.) of an Ag_2O suspension, containing 10 g/L Ag_2O (pH 9.3), 10 cm^3 (0.34 fl. oz.) of glycerol, propylene glycol or ethylene glycol was added. Alternatively, silver powder was produced from $AgNO_3$ and $[Ag(NH_3)_2]^+$ solutions using the same reducing agents. The silver powder was carefully washed with water and ethanol, dried and then analyzed by x-ray diffraction (XRD) and scanning electron microscopy (SEM).

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Results & Discussion

An important observation in this work was that the reduction of silver ions with propylene glycol or glycerol can be carried out from both slightly acidic (or neutral) and alkaline solutions. Reduction of silver ions from an aqueous solution of $AgNO_3$ with propylene glycol can be described by the following reaction:

$$CH_3\text{-CHOH-}CH_2OH + 4AgNO_3 + H_2O \rightarrow CH_3\text{-CHOH-COOH} + 4HNO_3 + 4Ag \quad (1)$$

In the suspension of Ag_2O in water, which was slightly alkaline (pH 9.3), upon addition of propylene glycol at 50°C (122°F), Ag_2O powder was converted to silver. Some deposition of silver on the walls of the beaker also occurred. The reaction of Ag_2O with propylene glycol is described by the following reaction:

$$CH_3\text{-CHOH-}CH_2OH + 2Ag_2O \rightarrow CH_3\text{-CHOH-COOH} + 4Ag + H_2O \quad (2)$$

Silver deposition on the walls of the beaker, for this experiment, was attributed to the reduction of silver ions produced through the dissociation of Ag_2O. It is worth noting that the solubility product of Ag_2O is $K_{sp} = 2 \times 10^{-8}$.[6]

The reduction of silver diammino complex to silver metal in alkaline ammoniacal solution is described by the reaction:

$$CH_3\text{-CHOH-}CH_2OH + + 4[Ag(NH_3)_2]OH + H_2O \rightarrow CH_3\text{-CHOH-COOH} + 8NH_4OH + 4Ag \quad (3)$$

The important conclusion from the above reactions is that propylene glycol and Ag^+ ion react in the ratio of 1:4. Reduction of the Ag^+ ion is a consequence of oxidation of propylene glycol to lactic acid. Similar reactions are applicable for the experiments where glycerol was used as the reducing agent.

When ethylene glycol was used as the reducing agent, production of silver powder was observed in the Ag_2O suspension and the $[Ag(NH_3)_2]OH$ solution, while in the $AgNO_3$ solution the reaction did not occur within the time frame of the present experiment.

Using these systems, silver can be deposited on flat surfaces or as a powder. In the case of flat non-metallic surfaces, sensitization/activation steps common to electroless plating (*i.e.,* $SnCl_2/PdCl_2$ catalyst) can be used. For deposition on metallic substrates it is obvious that, on metals more negative than silver, the first reaction will be a galvanic displacement reaction, followed by electroless deposition in which the reducing agent, *i.e.*, glycerol, propylene glycol or ethylene glycol, are utilized. Electroless deposition of silver on metals more positive than silver proceeds with a consumption of reducing agent (*i.e.*, glycerol, propylene glycol or ethylene glycol).

Figure 1 shows the influence of temperature on the rate of silver deposition from $[Ag(NH_3)_2]OH$ solution for all reducing agents studied. The silver deposition rates at room temperature had comparable values for all three reducing agents. With an increase in temperature, the rate of silver deposition increased as has been observed for other electroless deposition processes. However, it is to be noted that depending on the reducing agent, the rate of silver deposition increased in the order:

glycerol > propylene glycol > ethylene glycol

The reason for this observation should be investigated further.

Figure 2 shows the XRD patterns for the silver powder produced in this work. As shown, there are no significant differences in the XRD patterns for the silver powders produced from the $AgNO_3$ solution, Ag_2O suspension or $[Ag(NH_3)_2]^+$ solution using propylene glycol as a reducing agent. In all XRD patterns the Ag(111), Ag(200), Ag(220), Ag(311) and Ag(222) peaks appeared, with approximately the same intensities. Crystallite sizes were evaluated from the half width of the Ag(111) peak and $2\theta = 38.294°$. Using propylene glycol as a reducing agent, the crystallite sizes were: 26.77 nm for silver powder produced from $AgNO_3$ solution, 29.46 nm for silver powder from the Ag_2O suspension and 17.88 nm for silver powder produced from $[Ag(NH_3)_2]^+$ solution. Similar values of crystallite size were determined for the other reducing agents (glycerol and ethylene glycol). The crystallite size for silver films deposited on the flat substrates from the $[Ag(NH_3)_2]^+$ solution, using glycerol as a reducing agent was 33.3 nm.

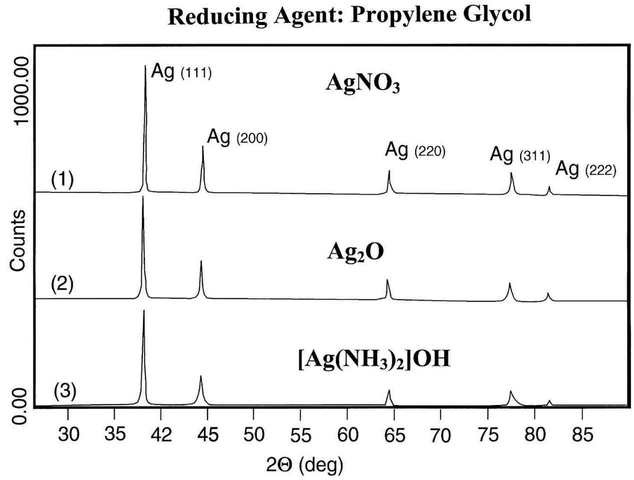

Fig. 2—XRD patterns of silver powder produced by the reduction of (1) $AgNO_3$ solution, (2) Ag_2O suspension and (3) $[Ag(NH_3)_2]OH$ solution with propylene glycol.

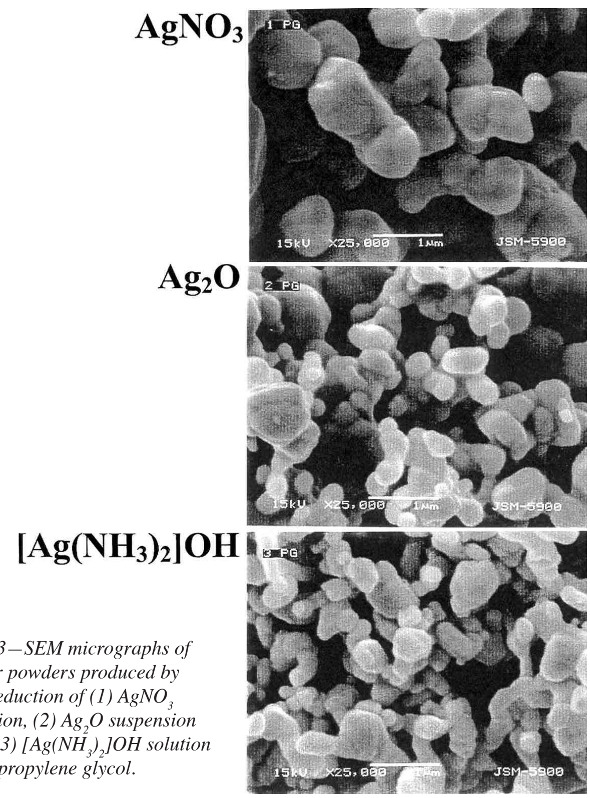

Fig. 3—SEM micrographs of silver powders produced by the reduction of (1) $AgNO_3$ solution, (2) Ag_2O suspension and (3) $[Ag(NH_3)_2]OH$ solution with propylene glycol.

Figure 3 shows the SEM micrographs of silver powders produced from $AgNO_3$ solution, Ag_2O suspension or $[Ag(NH_3)_2]^+$ solution using propylene glycol as a reducing agent. As these micrographs show, irregularly shaped silver particles were obtained. No dendritic growth, typical for silver deposits, was observed.

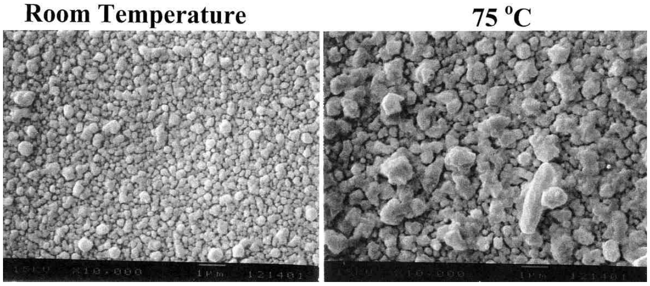

Fig. 4—SEM micrographs of silver films produced from $[Ag(NH_3)_2]OH$ solution and using glycerol as a reducing agent at (1) room temperature and (2) 75°C (167°F).

Thin silver films were deposited on flat plastic substrates (HDPE). The appearance of these films depended strongly on the solution, reducing agent and working temperature. Thin, shiny silver films were produced from the $[Ag(NH_3)_2]^+$ solution using glycerol as a reducing agent. As shown in Fig. 4, an increase in the deposition temperature led to an increase in the roughness of the silver deposits.

Conclusions

Glycerol, propylene glycol and ethylene glycol can be used as silver ion reducing agents. Using these agents, silver can be deposited onto substrates as a continuous film or as a powder. Reduction of silver ions with glycerol or propylene glycol can take place in slightly acidic or neutral and alkaline solutions. However, using ethylene glycol, silver ions can be reduced from a Ag_2O suspension or from a $[Ag(NH_3)_2]OH$ solution, but not from $AgNO_3$ solutions. In order to determine the precise features of these reactions, further systematic studies are required.

References

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Stojan S. Djokić is director of Elchem Consulting Ltd., Edmonton, Alberta, Canada. He holds a BS in Chemical Engineering, an MS in electrochemical energy conversion and PhD in Electrochemistry/Material Science from the University of Belgrade, Yugoslavia. As a Postdoctoral Research Associate at the University of Ottawa, he has worked in the field of molten salt electrochemistry. Dr. Djokić has published more then 50 papers including three chapters in Modem Aspects of Electrochemistry, coauthored the book Fundamental Aspects of Electrometallurgy and holds several U.S. patents. His professional experience covers both industrial and academic environments in electrochemistry, polymeric composite materials, biomaterials, materials science and analytical chemistry. His current interests include electroless and electrodeposition, kinetics, corrosion, electronics materials and biomaterials.