Electrolysis of nano-Silver Suspension into Ionic Form via Membrane Electro-Osmosis Process

Kuo Hsiung Tseng, Chih Yu Liao, Der Chi Tien and Tsing Tshih Tsung

***Abstract*—Silver ions (Ag^+) are converted electrophoretically from colloidal solution in two stages. Pre-existing ions are first released to an adjoining cathodic chamber with the application of DC 300 V. The remaining silver nanoparticles are also moved to this chamber after they convert to additional silver ions. The ionic strength here reaches a peak at 0.9 hours. At this point, all silver in the anodic chamber, initially housing the colloidal solution, is depleted. Conductivity study details the system's activity. The arc discharge method for colloidal silver production which is capable of maintaining the nanoparticles in suspension (in DI-water) without adding any conventional chemical surfactants, allowing for accurate interpretation of experiment results.**

***Index Terms*—Conductivity measurement, electrochemical processes, electrophoresis, ions, membranes, silver, ultraviolet spectroscopy.**

I. Introduction

Silver's role as an effective antimicrobial agent has been well established [1]. It can control a wide variety of yeast, fungi, viruses, methicillin- and vancomycin- resistant bacteria [2]. Human health care providers have used silver for diverse purposes for several thousand years [3], however it fell out of use in the last century due to its high cost and the introduction of antibiotics. The development of nano-scale techniques for silver production now promises resurgence in the medical use of silver. Nanoparticles have a large surface area to volume ratio, increasing the ability to interact with other substances at a low cost. Surprisingly, the rise of pathogen resistance to antibiotics makes the exploration of new alternatives essential.

Silver's exact antimicrobial mechanism is unknown. It has been determined yet, however, that the free silver ion is the active agent, with evidence that silver's antibacterial activity is directly proportional to the amount of silver ions released [4]. These ions exhibit an oligodynamic effect by denaturing proteins in prokaryotic cells, typical of microorganisms. Mammalian cells are eukaryotic and so display a strong un-susceptibility to silver's effects, creating the use of silver in treating human disease safe [5].

Though many medical applications for this powerful property have been tried through techniques such as silver plating [6], results have been limited perhaps due to their insufficient surface area and resulting inability to generate sufficient quantities of ionic silver. As it has been confirmed that mode and rate of release are related to the antibacterial effectiveness [7], a method for controlling ion release from nanoparticles holds great promise in uses such as targeting specific wound areas vulnerable to infection.

II. Experimental Methods

A. Preparation of the silver colloid

Several methods of silver (Ag) nanoparticles fabrication exist. Conventional methods add chemical surfactants to maintain a colloidal suspension, leaving these undesired chemicals in the solution after fabrication is complete. The arc discharge method [8], [9], however, is relatively inexpensive. Additionally, any experimental data obtained using these colloids can be confidently measured, as there is no interference from any additional stabilizers.

The Ag colloids used in this experiment were fabricated with the five modules of arc discharge system, shown in Fig. 1. These modules include a 150 Volt DC power supply, two silver electrodes (1 mm diameter), a glass container with deionized water to collect the colloid, a stirring system and a servo control system with a servo feedback loop to maintain a constant gap distance (20-40 μm) in between silver electrodes.

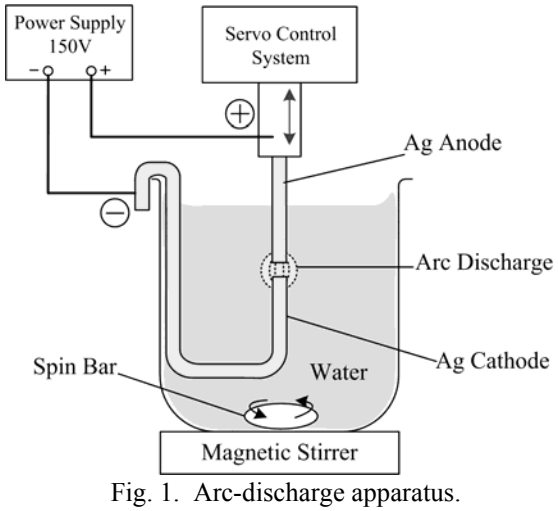

Fig. 1. Arc-discharge apparatus.

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The power supply system provides a stable pulse voltage to etch the Ag electrodes by ionizing the aqueous medium. Ionization in the gap (10-40 µm) is reached after 1-3 µs,. Here, the pulse is maintained at a high open voltage of 80-120 V. Once the medium is ionized, a large discharge current passes through, bringing the applied voltage down to a range of 25-40 V. The on/off discharge pattern is maintained all the way through the entire etching process. Calculation of the energy level is determined, using (Energy) = (Voltage) * (Current) * (Time). By tracking this energy level, the related amount of consumed electrode per energy used can be calculated. This in turn, gives information on amount of nanoparticles formed and solution concentration. Due to the nature of colloidal solutions, silver ions are also fabricated, and are supported by counterions present in the water medium, belonging most likely to the hydroxyl group (OH^-).

B. Electrophoresis setup

The electrophoresis was performed using two glass bottles (600 cm^3) positioned horizontally with a membrane between them, silicone rings to hold the bottles together, and metal electrode wires (99.99%, Gredmann). Inert platinum was chosen for both electrodes because it reacts minimally with water and presents no toxicity to any situation that the end product may be applied to. Colloidal silver solution with a yellow tint (400 cm^3) was placed in the anodic chamber with the anode sticking in through a hole in the bottle, and deionized water (400 cm^3, pH = 6.5, conductivity = 0.7 µS/cm) was placed similarly in the cathodic chamber with the cathode. Cellophane was used as a membrane between the bottles, and its semi-permeability allows for ions to pass through, but not particles or large molecules. Magnetic spin bars were placed in the bottom of both bottles to ensure the solutions' homogeneity, eliminating the concentration variable when monitored by the measuring devices placed within the bottle. Lastly, a 300 Volt DC power supply connected to a current meter was used to provide voltage across the electrodes for three hours. The complete system is shown in Fig. 2. Electrical conductivities (µS/cm) of the two solutions were recorded as the indicators of silver activity.

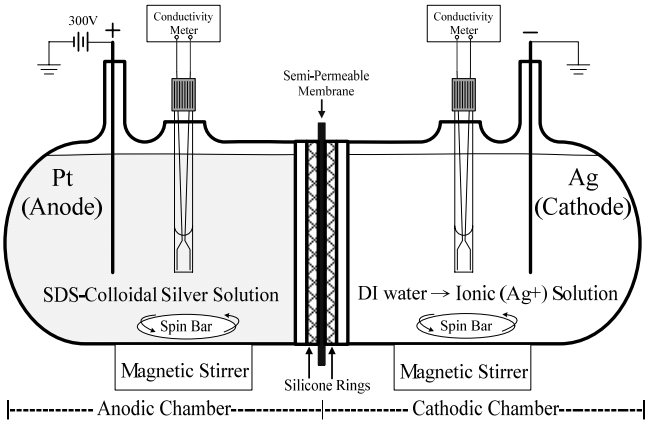
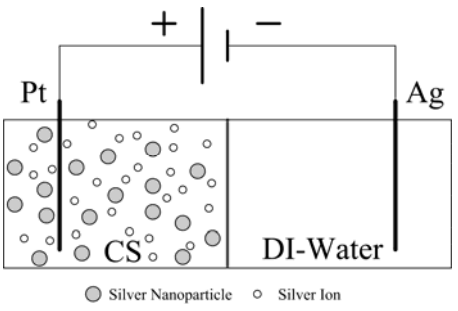


Fig. 2. Electrophoresis system for the production of Ag^+.

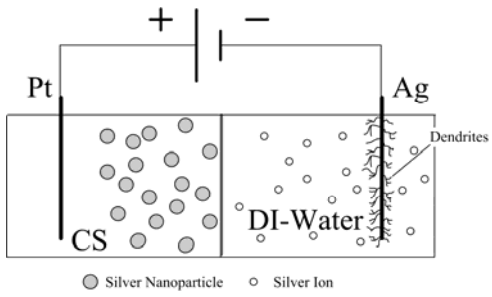
III. Results and Discussion

As soon as voltage is applied to the initial system (Fig. 3a), the first stage (Fig. 3b) of electrophoresis begins. Here, existing Ag^+ are removed from the colloidal solution, as they move rapidly to the negatively charged cathode. Upon contact, the silver ions regain an electron and convert to atomic form, as seen by the increasing formation of dendrites on the rod.

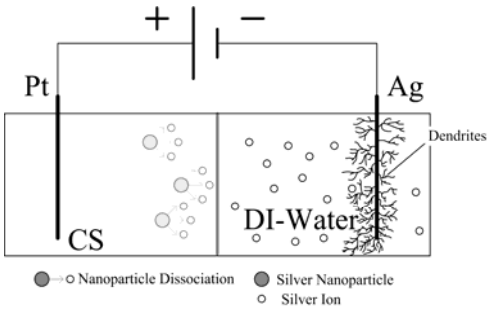
In the second stage (Fig. 3c), all silver nanoparticles dissociate into ionic form, and likewise rush towards the cathode, leaving a water solution free of silver nanoparticles and ions in the anodic chamber. The final cathodic chamber product is an ion-rich solution that can be applied directly into various settings requiring an antimicrobial agent. Though it is possible that some resistance may eventually be formed against silver atoms that restrain its ion release, no pathogenic organisms have succeeded in developing immunity to Ag^+ itself [10]. This entire electrophoresis process could be integrated into a wound dressing so that the ions released in stage one neutralize the Cl^- ions abundant in wound exudates. Then the ions released in stage two would be free to kill the bacteria. Good performance of wound dressings with silver is dependent on a continuous controlled rate of silver ion release, which could be achieved by monitoring the current level and using a feedback loop to adjust voltage accordingly.



(a)



(b)



(c)

Fig. 3. Electrophoresis stages. (a) Initial: before voltage is applied (b) Stage one: 0-30 minutes after voltage is applied. The nanoparticles are too big to pass through the membrane holes, and therefore must stay on the anodic chamber. (c) Stage two: 30-180 minutes after voltage is applied. The yellow color steadily weakens until the anodic chamber is completely transparent.

Conductivity measurements, shown in Fig. 4, confirm the shift in ionic activity from the anodic to the cathodic chamber. The shift begins in stage one, when the anodic chamber conductivity decreases as the ions move to the cathodic chamber. The cathodic chamber conductivity reaches a small plateau around the beginning of stage two (~0.5 hours) as the pre-existing supply of ions is depleted and the nanoparticles begin to dissociate. This then reaches a peak at 0.9 hours (54 minutes), which is not as high as that initially measured on the anodic side. Although more ions reach the cathodic side than were initially present in the colloidal solution, most of them quickly attach onto the cathode, rapidly converting to atomic form. A method that prevents the conversion of ionic to atomic form at the cathode would allow the cathodic chamber peak to increase beyond the initial anodic chamber peak and provide a solution with much higher ionic concentration.

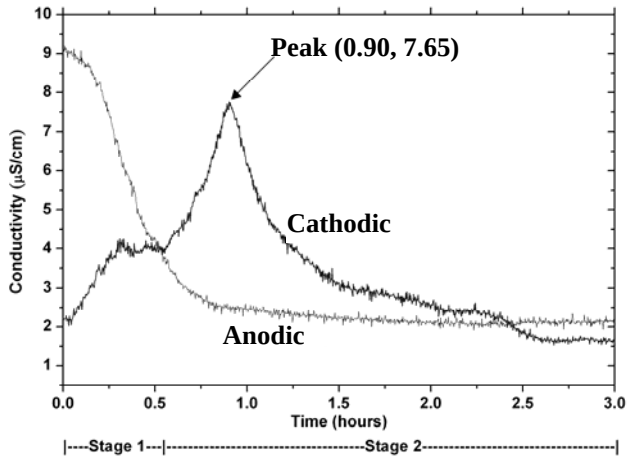


Fig. 4. Anodic and cathodic chamber conductivities indicate changes in ionic activity, which delineate stages 1 (0.0-0.5 hours) and stages 2 (0.5-3.0 hours).

IV. Conclusion

A two stage method is presented for conversion of colloidal silver nanoparticles to a purely ionic solution. The sole governing parameters are amount of applied voltage and type of membrane, making the rate of release quite controllable. The first stage of the process involves the separation of pre-existing silver ions from the colloidal solution, as they move towards the cathode. In the second stage, the nanoparticles are broken down into additional ions, and also moved into the cathodic chamber. Conductivity measurements confirm these results. An ionic silver solution holds potential for introduction into a number of antimicrobial applications, as does a monitored rate of silver ion release. By controlling the transformation from colloids to ions, the method developed here opens the door for further study and application of silver.

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References

[1] C. N. Lok, C. M. Ho, R. Chen, Q. Y. He, W. Y. Yu, H. Sun, P. K. Tam, J. F. Chiu, and C. M. Che, "Proteomic analysis of the mode of antibacterial action of silver nanoparticles," J. Proteome. Res., vol. 5, pp. 916-24, Apr 2006.

[2] C. Dowsett, "The use of silver-based dressings in wound care," Nursing Standard, vol. 19, pp. 56-60, 2004.

[3] L. Goodman and A. Gilman, *The Pharmacological Basis of Therapeutics. Fourth Edition*. Macmillan, New York, N. Y., 1970, pp. 967-969.

[4] A. B. Lansdown, "Silver in health care: antimicrobial effects and safety in use," Curr. Probl. Dermatol., vol. 33, pp. 17-34, 2006.

[5] M. Bicanova and G. Thinschmidt, "Oligodynamic action of silver ions on micro-organisms," Pharmazie, vol. 40, p. 736, Oct 1985.

[6] D. M. Dalgat, R. T. Medzhidov, and R. A. Isadibirov, "Silver electrophoresis in the treatment of lactation mastitis," Khirurgiia (Mosk), pp. 19-22, May 1989.

[7] F. Furno, K. S. Morley, B. Wong, B. L. Sharp, P. L. Arnold, S. M. Howdle, R. Bayston, P. D. Brown, P. D. Winship, and H. J. Reid, "Silver nanoparticles and polymeric medical devices: a new approach to prevention of infection?," J. Antimicrob. Chemother., vol. 54, pp. 1019-24, Dec 2004.

[8] J. K. Lung, J. C. Huang, D. C. Tien, C. Y. Liao, K. H. Tseng, T. T. Tsung, W. S. Kao, T. H. Tsai, C. S. Jwo, H. M. Lin, and L. Stobinski, "Preparation of gold nanoparticles by arc discharge in water," J. Alloy. Compd., vol. 434-435, pp. 655-658, 2007.

[9] D. C. Tien, K. H. Tseng, C. Y. Liao, J. C. Huang, and T. T. Tsung, "Discovery of Ionic Silver in Silver Nanoparticle Suspension Fabricated by Arc Discharge Method," J. Alloy. Compd., to be published.

[10] G. Zhao and S. E. Stevens, Jr., "Multiple parameters for the comprehensive evaluation of the susceptibility of Escherichia coli to the silver ion," Biometals, vol. 11, pp. 27-32, Jan 1998.