Chapter

Conductive Powder Synthesis Technology for Improving Electrical Conductivity by One-Pot Ultrasonic Spray Pyrolysis Process

Hye Young Koo and Dahee Park

Abstract

In this chapter, we will study the spray pyrolysis process, which is a bottom-up process, and examine the composite electrode powder synthesis process and properties of the core-shell structure. Generally, it is difficult to produce fine particles from metal powders using the top-down method. Thus, the liquid phase method, which is a bottom-up process, is mainly used. However, the liquid phase method has a problem in that impurities exist in the particles. In addition, it is difficult to control the precipitation when synthesizing powder using a solution containing several types of metal salts. The spray pyrolysis process introduced here made it possible to produce composite particles in a one-pot manner without any additional processes for synthesizing the core-shell structure. In the case of core-shell structure of Ag-glass composite powder, the specific resistance of the composite electrode was significantly lowered, compared to the electrode formed by mixing glass frits individually, which improved the dispersibility of the glass. In the case of Cu composite particles with a coating layer, both Ag and glass coating layers formed a passivation layer to improve atmospheric stability, and the introduction of a coating material also improved electrical properties.

Keywords: spray pyrolysis, electrode materials, conductive powder, core-shell structure, composite

1. Introduction

Metals with high intrinsic conductivity, such as gold, silver, and copper, are mainly used as electrodes. Conductive powders using noble metals are easily synthesized into metals even in an oxidizing atmosphere, whereas transition metals are synthesized into metal in a reducing atmosphere [1].

Generally, the powder synthesis technology is divided into top-down and bottom-up methods. The solid phase method can be classified as a top-down method, while the liquid phase method and gas phase method are regarded as bottom-up methods. In the solid phase method, mechanical energy is applied to the raw materials of the

desired composition in order to induce bonding and pulverization repeatedly between the powders, which reduce the particle size and synthesize powder while continuously contacting a new surface. Then, synthesis is completed at room temperature or a desired composition is obtained through post-treatment. The mechanical alloying method is a representative solid phase method. Compared to the bottom-up method, this method has the advantages of relatively easy process operation, low cost, and fewer by-products. However, it is limited in reducing the particle size, and homogeneity of the particles is not secured locally when synthesizing multi-component particles [2–6]. In particular, in pulverization of metals, it is difficult to atomize through crushing due to the ductility of the metal. Furthermore, since spheroidization through crushing is impossible, synthesizing conductive spherical powders through the solid phase method is not possible.

The liquid phase method ionizes a metal salt in a solvent to recover the synthesized particles using a reducing or precipitating agent. Since the raw materials can be mixed evenly at the molecular level, it is possible to control the composition uniformly, and the particle size and distribution can be controlled uniformly as well. Synthesis can be realized at a relatively low temperature, and thus, the method has the advantage of low process cost. However, this method generates substantial amount of chemical solvent byproducts, because particles are precipitated by chemical reaction. Moreover, it is difficult to improve the purity due to residual chemical substances in the particles. In addition, it has the disadvantage of low crystallinity, since it is synthesized at low a temperature [7–10].

The gas phase method is a process in which the raw material is divided into atomic or molecular units by vaporizing a metal salt or solution of metal salt, and then, particles are synthesized through nucleation, growth, and agglomeration during condensation. Examples of such a method include Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD). In the gas phase method, the vaporized molecules are nucleated again to grow into particles, and thus, fine particles can be synthesized. It is an advantageous process for producing high-purity particles with low residues of C, N, S, etc., because the synthesis occurs at a high temperature. However, there are some difficulties in synthesizing alloy powders, because non-uniformity may occur due to the difference in vapor pressure during the vaporizing stage. Additionally, the production cost is also high [11–16].

The spherical shape is preferred for conductive powders, because the density of the electrode must be high after formation. As the dispersion is suboptimal when significantly small particles are applied to the manufacturing paste, mixtures of particles with sub-micron sizes are mainly used. Therefore, synthesis has been performed mainly through the liquid phase process. However, in the case of the liquid phase process, since metal particles are synthesized through a reducing agent, residual carbon is present in the particles, which lowers the purity, thereby lowering the conductivity.

In order to overcome the disadvantages of the liquid phase method, a method for synthesizing metals at high temperature using a gas phase method is introduced, but in the case of PVD and CVD, the process for atomization of 0.2 μm or less. This is due to the nature of the process in which vaporized molecules are condensed and powdered. This characteristic is very advantageous, but there is a limit to synthesizing particles with a size of sub-micron to 1 μm.

The ultrasonic spray pyrolysis process is a process that simultaneously utilizes the advantages of the bottom-up, liquid phase, and gas phase methods. The desired raw material is placed in a solvent to prepare a solution, and fine droplets are generated using an ultrasonic generator, followed by heating in a high-temperature furnace.

It is a process of synthesizing particles in within seconds by passing through drying and thermal decomposition. This is similar to a process of synthesizing particles by generating fine-sized droplets in the form of aerosols, similar to vaporizing a solution using a homogeneous solution at the molecular level. Additionally, it is a process that can utilize both the effects of the gas phase and liquid phase methods, as it starts from the liquid phase to synthesize the powder using the sprayed droplets. Since the spray pyrolysis process performs synthesis using the initial raw material as a solution, it is also advantageous to produce multi-component particles that contain trace elements. Furthermore, this process facilitates synthesizing composite powders using various additives during solution preparation. In particular, the mist comprising a solution with a uniform composition passes through the heating furnace to form particles such that the composition of the entire solution is kept the same, and spherical particles are mainly synthesized in a droplet-like form.

The main requirements for conductive powders are spherical shape, low resistivity, high electrical conductivity, high purity, high crystallinity, low temperature sintering, oxidation resistance, etc. The spray pyrolysis process produces spherical shaped powders, since it maintains the shape of the droplets. Moreover, the pyrolysis process enables synthesizing high-purity and highly crystalline particles with a size of 1 μm or less.

When manufacturing an electrode using a conductive powder, a paste is prepared by mixing the conductive powder and glass frit as an inorganic binder with an organic binder, and printing is used to produce an electrode layer. It is essential to control the surface oxidation of the conductive powder in order to improve the density of the electrode, and the presence or absence of glass frit and particle characteristics are very important [17]. The mixing ratio of the conductive powder of the electrode and the glass frit is generally at least 8–20 times different. In particular, amorphous glass frit generally synthesizes powders through crushing, and realizing uniform dispersion becomes difficult due to the irregular size. Further, in the case of transition metal conductive powders, in addition to the problem of mixing glass frit, an oxide layer is formed on the surface powder after synthesis, since it is easily oxidized even at room temperature. This inhibits the densification of the electrode by decreasing sinterability when forming electrodes and leads to poor conductivity due to oxidation.

In this chapter, a method for synthesizing a composite electrode powder with a core-shell structure using a single-step phase-segregation mechanism using the ultrasonic spray pyrolysis process is described, and the corresponding characteristics are studied. The proposed method overcomes the limitations of the conductive paste process. Moreover, this chapter summarizes some representative studies on the subject.

2. Experimental procedure

In the ultrasonic spray pyrolysis process, a precursor solution with a dissolved salt of a desired composition is generated into fine droplets using an ultrasonic generator, and the generated droplets are dried using a carrier gas in an oxidizing, inert, or reducing atmosphere through a high-temperature heating furnace. It undergoes a pyrolysis process and synthesizes particles of the desired composition through process controls, such as the type of salt used in this process, concentration of the solution, presence or absence of additives, type and speed of the carrier gas, temperature, length, and tube width of the heating furnace. Ag composite powder has the characteristic of being synthesized as a metal powder even if it passes through a high temperature of 900°C or higher using air, and transition-metal-based materials

such as Cu can be synthesized at a temperature of 900°C or higher under a reducing atmosphere. All particles of the core-shell structure used in this chapter were synthesized in one-step through the same process of synthesizing electrode powder of a single composition by including all desired compositions in the solution. The particles maintained spherical shape, because the synthesis was performed without a separate post-processing for composite powder synthesis. The particle morphology was observed through scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and crystal structure analysis was performed with X-ray diffraction (XRD). In addition, by analyzing energy-dispersive spectroscopy (EDS) mapping through scanning transmission electron (STEM), the composition of the surface and the inside was observed. The powder thus synthesized was prepared into paste, screen-printed, and then heat-treated at a uniform temperature to form an electrode layer. The specific resistivities of these heat-treated electrodes were measured and compared through the four-point probe method.

3. Conductive Ag-glass composite powder

Ag has very high conductivity, and thus, it has been used as an electrode for solar cells and various electric circuits [18–20].

The electrode layer formed is mixed with glass frit and an inorganic binder in addition to the conductive powder and organic binder to form a paste through heat treatment after printing. The glass frit plays an important role when sintering power by acting as a pool of liquid sintering agent, as well as in densification by helping to form an electrode layer without pores between the powders. Since a small amount (The mixing ratio of the conductive powder of the electrode and the glass frit is generally at least 8–20 times different) is added compared to the conductive powder, it is very difficult to evenly disperse it throughout. In addition, when a large amount is added to evenly disperse the entire electrode layer, the content of the conductive powder must be relatively low due to the density of the paste, which causes a problem of lowering the conductivity. In order to overcome this problem, the electrode powder synthesis technology in which glass and Ag powder are composited into a core-shell

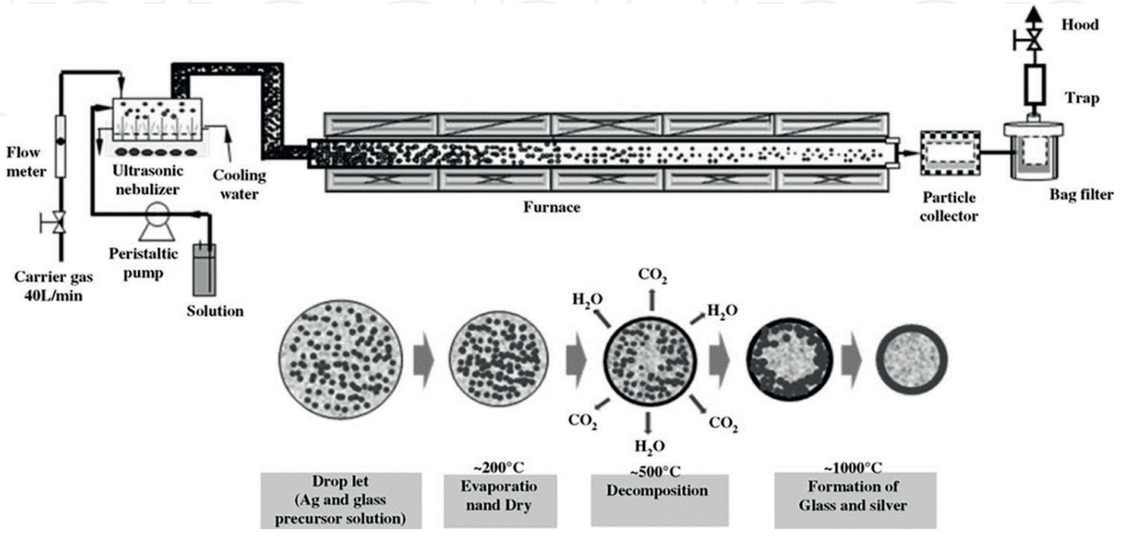
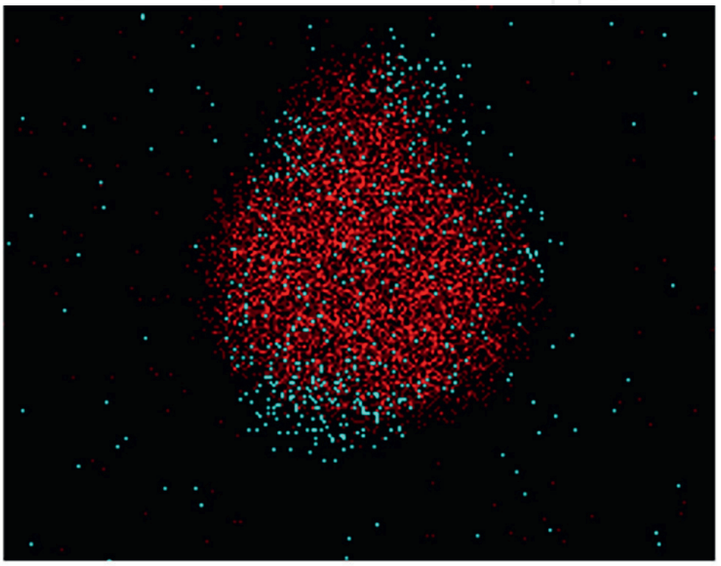
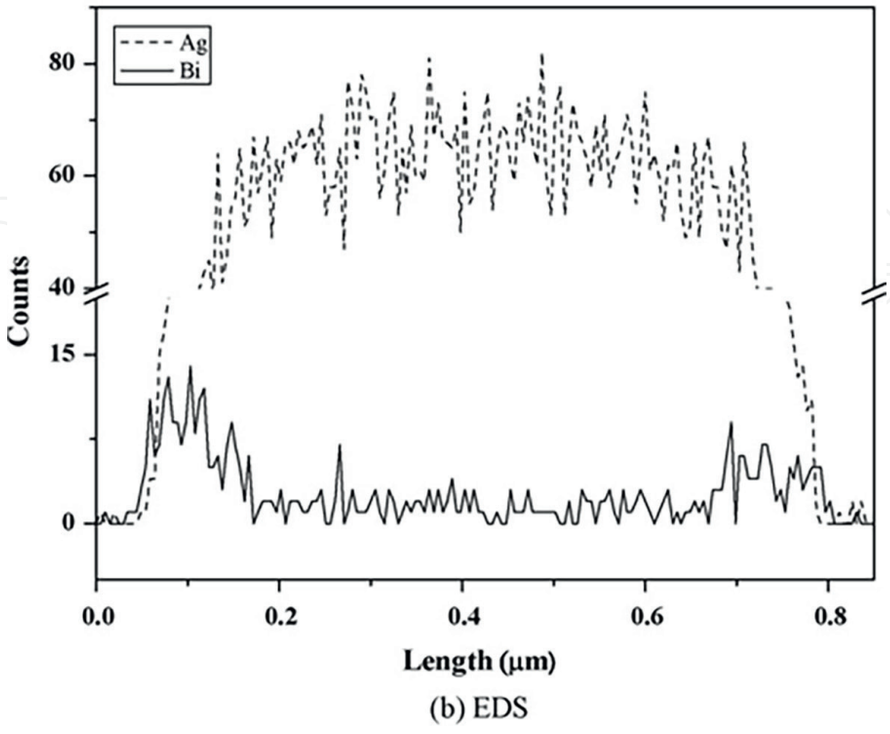


Figure 1.
Formation mechanism of silver-glass composite powder [21].

structure using the spray pyrolysis process has been reported in several papers [21–24]. Composite powders of this structure are manufactured by mixing silver nitrate and a salt comprising glass in a precursor solution under the same process of synthesizing powder (pure Ag) through ultrasonic spray pyrolysis process, as shown in **Figure 1**. It is analyzed that during the pyrolysis and melting process, the glass is pushed into the shell due to the density difference between glass and Ag (glass: 2.4–2.8 g/cm^3, Ag: 10.5 g/cm^3), forming a core-shell structure. Structural analysis of these particles showed that glass is present on the surface by comparing the composition of the shell and core in the DES analysis using STEM, as shown in **Figure 2**. For



(a) element mapping



(b) EDS

Figure 2.
Element mapping and EDS results of the composite powder [21].

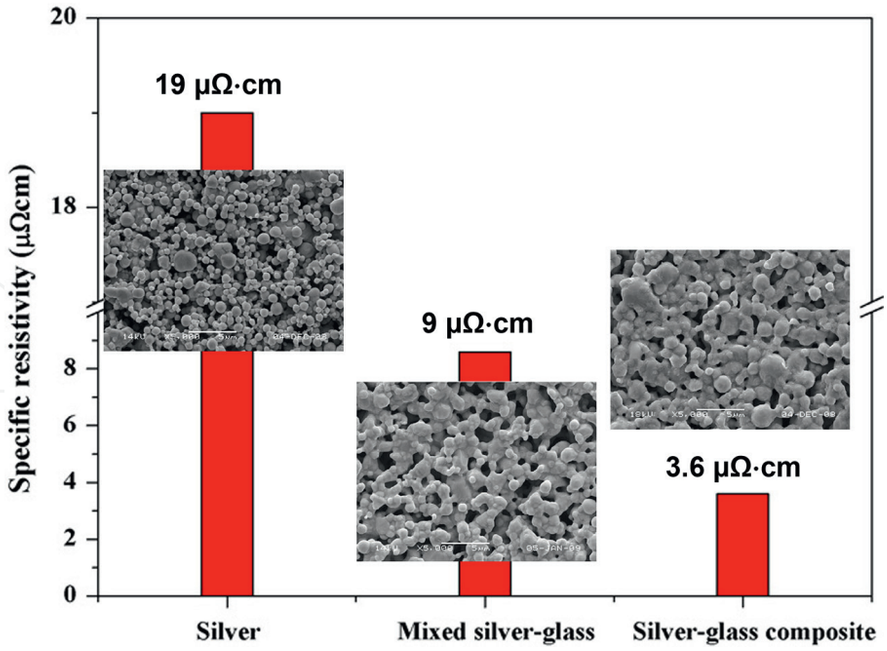


Figure 3.
SEM photographs of surfaces and specific resistivity of silver conducting films sintered at a temperature of 450°C [21].

the electrode layer thus formed, the effect of the composite powder on the densification of the electrode was analyzed through SEM and resistivity analysis as shown in **Figure 3**. As can be confirmed from the SEM analysis, in the electrode layer using only Ag powder, there are several pores without complete connection between the Ag particles, whereas in the case of the electrode layer using the composite powder, the pores on the surface of the electrode layer are significantly reduced, and the contact force between the electrode powders is improved. The specific resistances of the electrodes formed using Ag powder, Ag powder and spherical glass powder mixture, and Ag-glass composite powder were 19 μΩ•cm, 9 μΩ•cm, and 3.6 μΩ•cm, respectively. The specific resistivity was lowered to approximately 50% compared to using only Ag, and approximately 40% compared to the composite powder through ideal

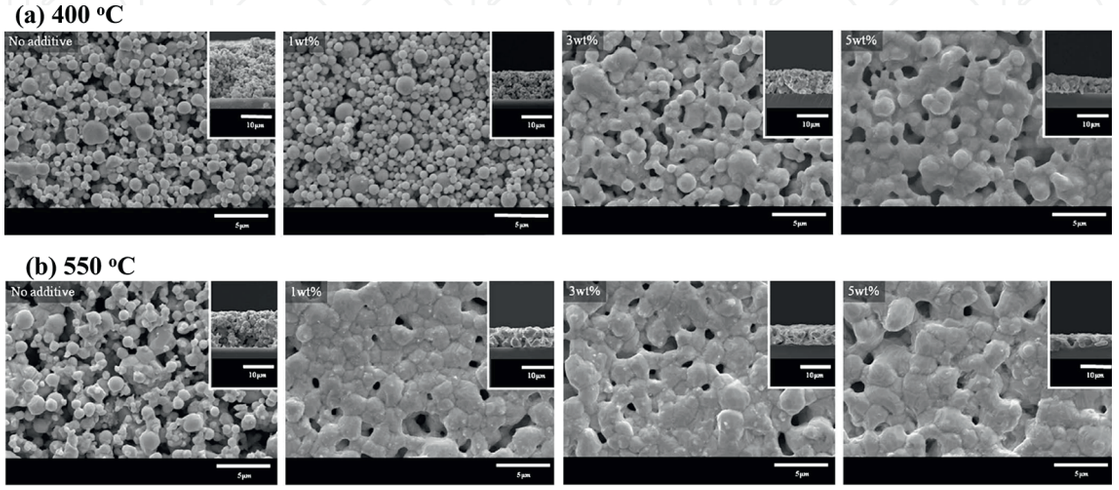


Figure 4.
SEM photographs of surfaces of silver conducting films with various contents of glass sintered at a temperature of 400 and 550°C [24].

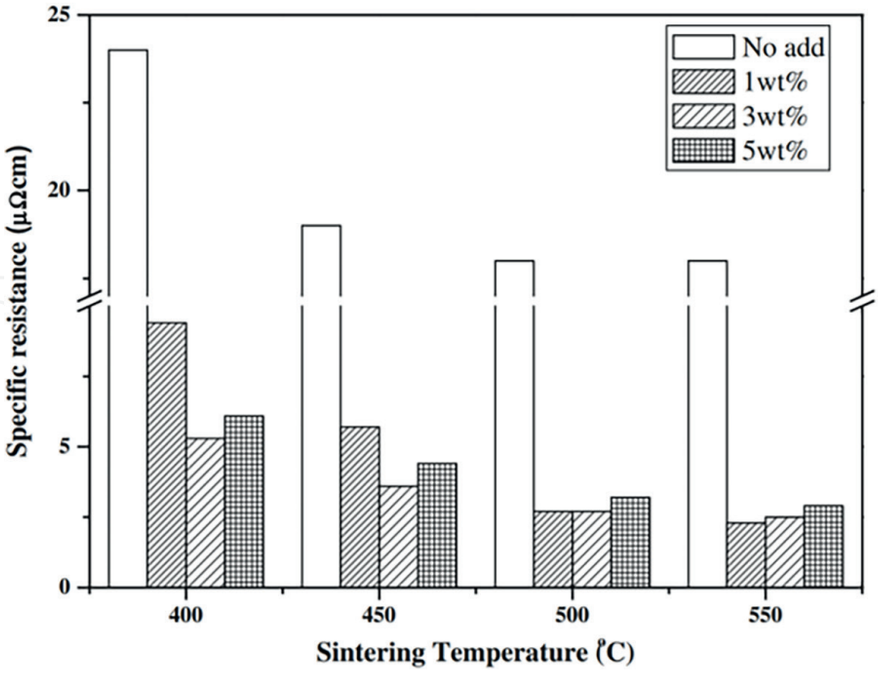


Figure 5.
Specific resistance of silver conducting thick films as a function of sintering temperature and content of glass additive.

dispersing glass frit. This shows that the composite power has the effect of improving conductivity by enhancing the density of the electrode.

Although glass frit can be advantageous in facilitating sintering, it is an amorphous oxide, and should be applied in a minimum amount. Therefore, studies have been reported on the content of glass compared to Ag. Since composite powders can ideally disperse glass and Ag, a previous study observed the density of the electrode according to the glass wt.% through SEM. Further, the effect of glass content on the heat treatment temperature for the electrode was also investigated [24]. As shown in **Figure 4**, an increase in the glass content had a positive effect on the electrode density improvement, and the lowest glass content varied depending on the post-heat treatment temperature. In the results of this study, 5.3 and 2.3 μΩ•cm showed the lowest resistivity values at post-treatment temperatures of 400 and 550°C, respectively, as shown in **Figure 5**. Moreover, the glass content was 3 wt.% and 1 wt.%.

4. Air stable coated copper powder

Ag powder has high utility, but the price of precious metal raw materials is high. Thus, the demand for metals to replace Ag is continuously increasing [25, 26]. Copper, which is relatively inexpensive and has low resistivity, can be used as an alternative, but low atmospheric stability is a major problem. In addition, as the size decreases, the specific surface area increases, and thus, the oxidation problem becomes more pronounced.

In order to solve this problem, efforts have been made to improve atmospheric stability by coating surfactants, conductive polymers, silver, titanium, silica, etc. [27–35]. However, such attempts have led to lowering the conductivity. Further, the method of coating the copper surface with metal requires an additional coating

process after synthesizing the copper powder, which increases the production cost in industrial applications. In addition, these methods present a difficulty in realizing uniform coating.

In this study, a technique for synthesizing coated copper composite particles using the spray pyrolysis process was studied in order to solve problems such as low atmospheric stability, complicated process, and uniform coating. The Cu composite particles developed in this study were prepared into a mixed solution by simultaneously adding copper nitrate trihydrate and silver nitrate salt for producing Ag-coated Cu powder when preparing the precursor solution to be input to the droplet generating device. And hydrogen mixed gas was used as carrier gas for reduction and synthesizing silver-coated copper powder [36]. The melting points of Ag and Cu are 962 and 1084°C, respectively. The results of this study showed that when the synthesis was conducted at 900°C, Cu remained in the core, and Ag was uniformly pushed to the surface. This is because Ag with a lower melting point has relatively better mobility. **Figure 6** shows the result of evaluating the air stability of these uncoated particles, after being left in the atmosphere for 1 month. The uncoated bare Cu powder developed substantial surface irregularities due to oxidation, and its HRTEM elemental profile showed that the oxygen peak on the surface was relatively higher than that on the inside. Further, as shown in **Figure 7**, the surface analysis of the coated particles after 1 month showed smooth characteristics similar to the initial stage, and the HRTEM analysis showed lattice spacing (Ag on the surface and Cu on the core). The elemental profile also confirmed atmospheric stability, showing relatively high Ag on the surface and no major change in oxygen peak. **Figure 8a** shows the sheet resistances of the electrode according to the Ag content of the Ag-coated Cu electrode layer. All samples were sintered at 700°C for 10 min under N_2 atmosphere. In **Figure 8a**, the sheet resistance value showed the lowest value of 2 mΩ square^{-1} when Ag was 15 wt.%, which showed the characteristic that the porosity of the electrode was low, as shown in **Figure 8c**. When Ag was as high as 50 wt.%, large pores were exhibited due to the high mobility of Ag, and the sheet resistance value increased.

Glass-coated Cu particles have been proposed as another structure for synthesizing particles with improved atmospheric stability and electrode properties [37]. In the reported study, one-pot synthesis was performed using the spray pyrolysis process in the same manner as the previously shown process. To prepare glass-coated copper particles, The precursor solution was obtained by combining copper nitrate trihydrate

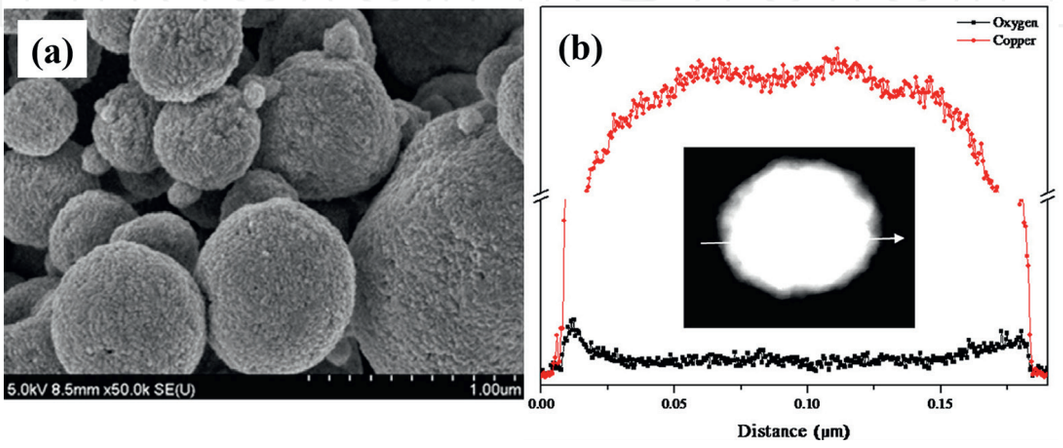


Figure 6.
(a) SEM image, (b) element profile of bare copper particles after 1-month exposure to air [36].

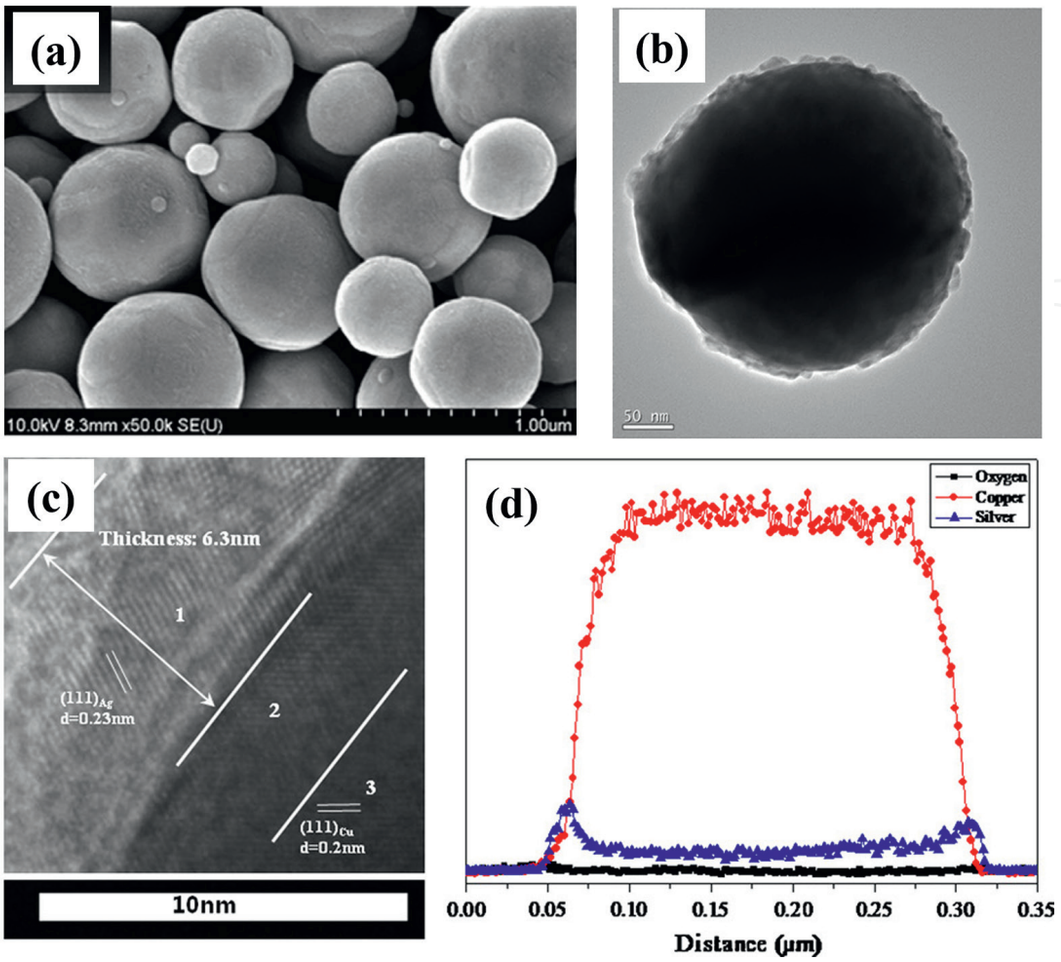


Figure 7.
(a) SEM, (b) TEM, (c) HRTEM images of 20 wt.% silver coated copper, and (d) element profile across the particle diameter direction. The sample was exposed to air for 1 month [36].

($Cu(NO_3)_2 \cdot 3H_2O$), barium carbonate ($BaCO_3$), tetraethyl orthosilicate ($SiC_8H_{20}O_4$), and boric acid (H_3BO_3). The content of the glass precursors in the Cu@BBS particles was varied such that the final weight portion of the glass comprised 0.5–10 wt% of the Cu.

In the Cu electrode, the glass material also serves as an inorganic binder, helping the electrode sinter to increase the density of the electrode, and as an auxiliary agent to improve the electrode conductivity. It simultaneously acts as an inorganic binder and passivation to derive two positive effects in the case of Cu, enabling the synthesis of Cu particles without an additional process, which provides several advantages for mass production.

Figure 9 shows the synthesis process of Cu@BBS particles synthesized in the core-shell structure by the one-pot spray pyrolysis process. It was analyzed that CuO_x is changed to Cu during dry pyrolysis in a reducing atmosphere, and the materials constituting BBS that are not easily reduced are formed into BBS glass. Then, Cu is pushed to the center, and BBS glass is pushed to the surface due to the difference in melting point.

As shown in **Figure 10**, the surface of the synthesized particles was uniformly coated, and the coating layer was amorphous. In addition, the resistance values were compared by forming an electrode using the powder before and after coating, and the Cu and Cu@BBS particles exposure to air for 1 month, followed by heat treatment. As a result, the resistance values of bare Cu and Cu@BBS particles were lowered to 5.1 and

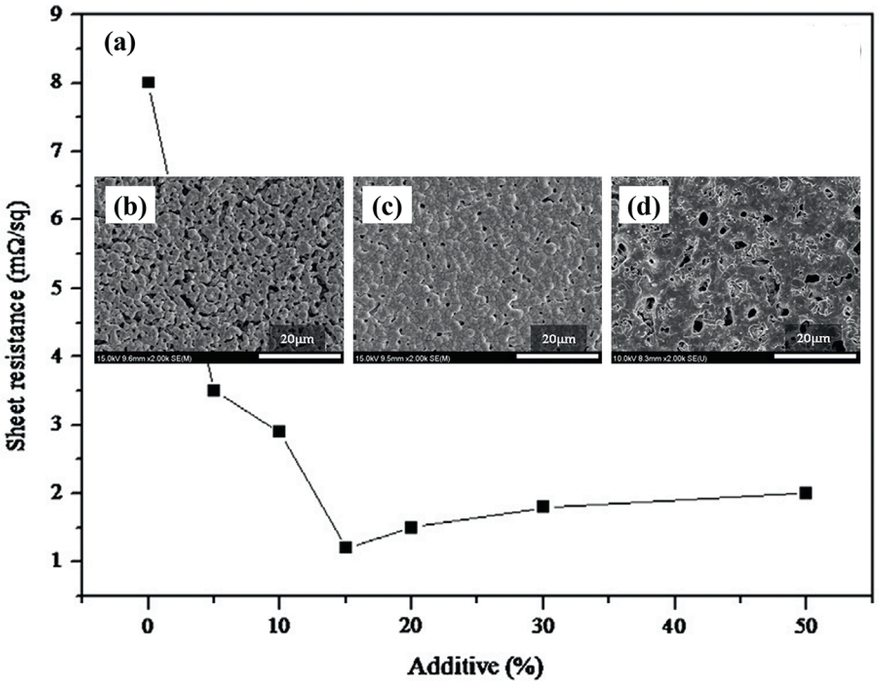


Figure 8.
(a) Sheet resistance of conducting films obtained from silver-coated copper particles with various loadings of silver, sintered at 700°C for 10 min in N_2 atmosphere. SEM photographs of surface section of the prepared conductive films obtained from (b) bare copper, (c) 15 wt.%, and (d) 50 wt.% silver-coated particles [36].

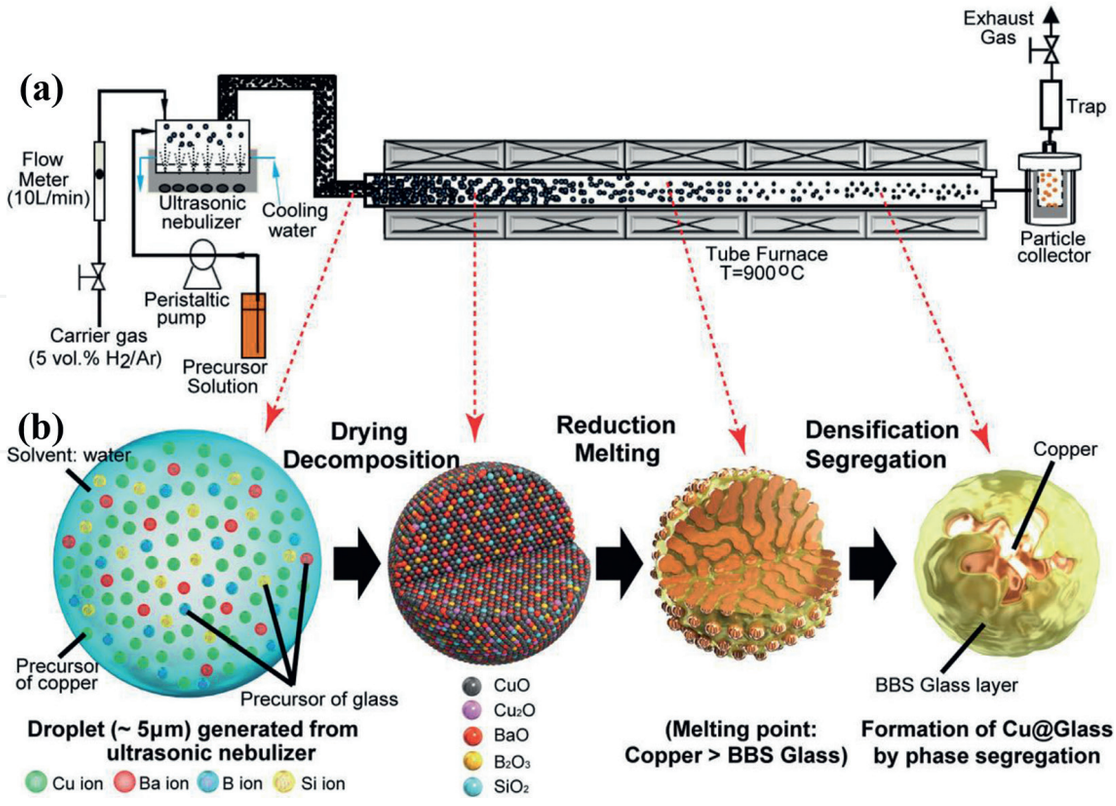


Figure 9.
(a) Experimental setup for ultrasonic spray pyrolysis used in the current investigation. (b) Formation of BBS glass-coated copper particles by phase segregation [37].

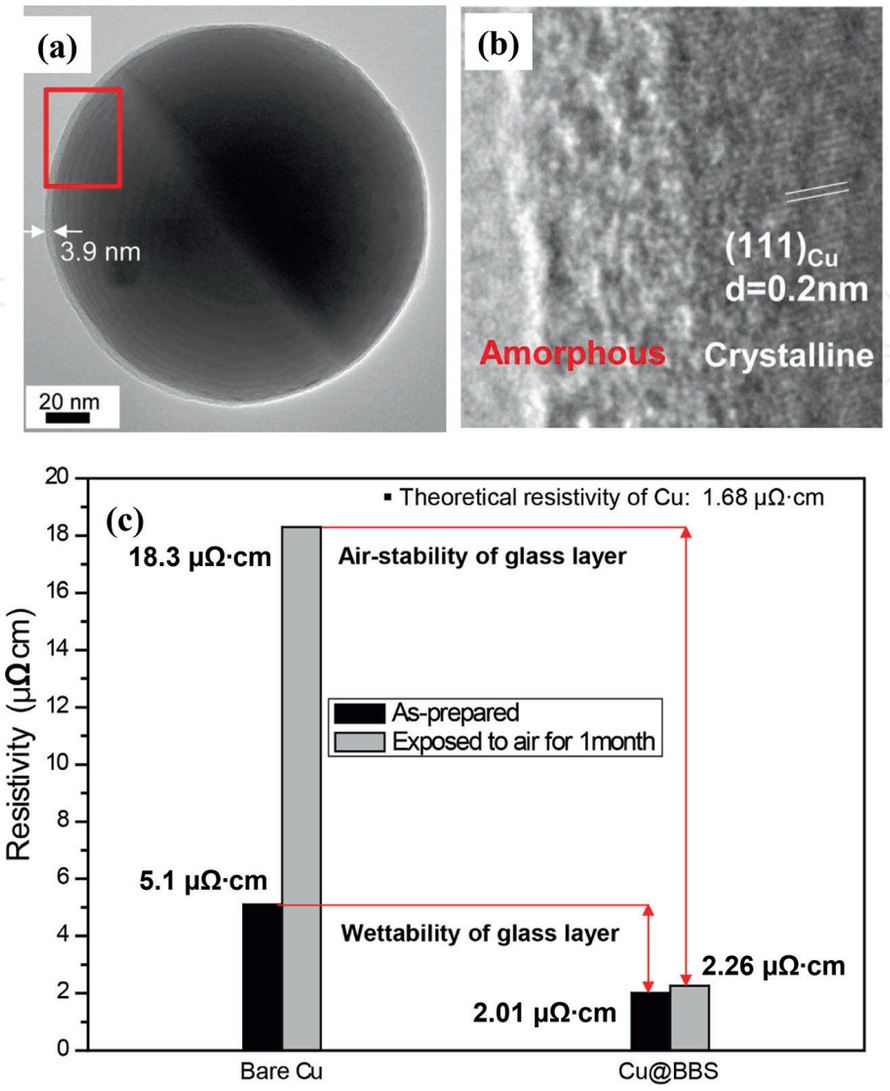


Figure 10.
(a) Transmission electron microscopy (TEM) images of Cu@BBS particles (b) high-resolution TEM image magnified from the red box in (a) showing the amorphous coating layer and (c) resistivities of Cu conductive films based on bare Cu particles and Cu@BBS particles (measured after sintering at 800°C for 10 min under N_2 atmosphere) [37].

2.01 μΩ•cm, respectively, and those for the electrodes formed after 1 month of exposure were 18.3 and 2.26 μΩ•cm, respectively. As a result, the resistivity of bare Cu particles and Cu@BBS particles was lowered to 5.1 and 2.01 μΩ•cm, respectively, and after 1 month of exposure, these values were 18.3 and 2.26 μΩ•cm, respectively. Thus, the resistivity of the electrode comprising bare Cu increased by approximately three times or more than that of the existing electrode, while the Cu@BBS particle showed similar resistivity and presented improved atmospheric stability and electrode characteristics.

5. Conclusions

The ultrasonic spray pyrolysis process simultaneously utilizes the advantages of the bottom-up, liquid-phase, and gas phase methods. It involves the steps of placing the desired raw material in a solvent to prepare a solution, generating fine droplets using

an ultrasonic generator, and passing through a high-temperature heating furnace to synthesize particles within seconds via thermal decomposition. Since the process uses a solution by adding a desired metal salt, it is possible to uniformly distribute the material of the desired composition in a single particle. Furthermore, it is an advantageous process for synthesizing particles of complex structures that are difficult to synthesize top-down in one-pot through only process control of fine metal composite particles.

In this chapter, the process of synthesizing Ag and Cu particles, which are mainly used as electrodes, with glass, one of the electrode components, and the process of synthesizing silver-coated copper powder are summarized. All the composite electrode powders showed the advantage of synthesis in the same process as the electrode powder manufacturing process without a coating layer, and all of the samples showed superior electrical properties and atmospheric stability compared to bare powders.

From the results presented in this chapter, it can be inferred that the ultrasonic spray pyrolysis process can be used to synthesize not only single metals, but also various types of composite metal powders utilizing differences in density and melting point.

Acknowledgements

This research was supported by the National Research Council of Science & Technology(NST) grant by the Korea government (MSIT) (No. CAP22081-000) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea under grant (No. 20011040).

Conflict of interest

The authors declare no conflict of interest.

Author details

Hye Young Koo* and Dahee Park
Department of Metal Powder, Powder Materials Division, Korea Institute of Materials Science (KIMS), Changwon, Republic of Korea

*Address all correspondence to: hykoo@kims.re.kr

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