Impact of synergy effect of SDBS and PVP on morphology and performance of electrolytic copper powder

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Abstract
Copper powder is prepared by electrolysis, and additives Sodium dodecyl benzene sulfonate (SDBS) and polyvinyl pyrrolidone (PVP) are added to the electrolyte. Through the synergy effect of the two additives, the shielding effect between metal atoms is enhanced, and as a consequence the microscopic morphology is changed and the powder performance is improved. Scanning electron microscopy (SEM), x-ray diffraction (XRD) and Electrochemical Impedance Spectroscopy (EIS) are used to characterize the copper powder. The results show that when the content of SDBS and PVP is 5 g l$^{-1}$ and 1.5 g l$^{-1}$ respectively, the new type of thin and long dendrite copper powder can be obtained by electrolysis.

1. Introduction
With the upgrading and transformation of national economic enterprises, new materials, as an important component, have a high potential for development. Copper powder, is an indispensable basic material for most new materials. It is thus favored due to its superior conductivity, ductility, moderate price and other advantages, and has a broad development prospect. On the other hand, however, the continuous development of new materials has also put forward more stringent requirements on the copper powder microstructure [1, 2].

There are many preparation methods for copper powder, such as electrolysis, gas reduction, atomization, plasma volume, mechanization, chemical reduction, etc [3–10]. In recent years, several copper powders with different microscopic morphologies have been developed. For example, single crystal copper nanorods are obtained by electron beam irradiation [11], and spherical copper powder by using phosphorus as an auxiliary additive [12]. Using electrolysis and at a certain current density, dendritic copper powder can be deposited on the cathode. Dendritic copper powder has attracted extensive research interest due to its large specific surface area, special microscopic morphology and excellent properties. With electrolysis method, slight changes in the electrolysis condition, may produce copper powders of different performance. Moreover, copper powders obtained in this way have higher purity, extremely high activity, good forming, high pressing strength, wide powder particle size and loose packing density range, thus meeting different requirements. The properties of copper powder are mainly determined by the crystal morphology and grain size while in an electrolysis process, the morphology of deposited copper powder is strongly influenced by electrolysis parameters and metal properties [13–17]. Therefore, copper powders with different morphologies were obtained. The addition of additives, such as polyvinylpyrrolidone(PVP), sodium dodecyl sulfate (SDS), polyethylene glycol (PEG), cellulose and thiourea (Tu), significantly affects the morphology of the particles [18]. The properties of copper powder are closely related to its microscopic appearance. The microscopic morphology of copper powder prepared by electrolysis has been studied and classified systematically [19–21]. At present, there are many reports on different morphologies and particle sizes of copper powder, but few reports on thin and long dendritic copper powder.
In this paper, we discuss a new thin and long dendritic copper powder prepared by electrolysis. To study the impact of synergy effect of adding sodium dodecylbenzene sulfonate (SDBS) and/or polyvinylpyrrolidone (PVP) in the electrolyte on the microstructure of dendritic copper powder, will provide reference to the control of micro morphology of dendritic copper powder as well as process improvement.

2. Experiments

2.1. Preparation of electrolyte
In this experiment, preparation of copper powder is through the constant current method and the chemical reagents used to prepare the electrolyte are all analytically or chemically pure. Take a certain amount of CuSO₄·5H₂O and H₂SO₄ and have them dissolved in deionized water to mix them into electrolyte of a certain concentration. The additives sodium dodecylbenzene sulfonate (SDBS) and polyvinyl pyrrolidone (PVP) are added, and the electrolysis process is carried out in a cylindrical electrolytic cell. The liquid temperature is constant at 25 °C the cathode current density at 1500 A m⁻², the anode made of graphite electrodes, the cathode of stainless steel, and the distance between the two electrodes is 10 cm. The area ratio of Cathode and anode plates is 1:2. Powder scraping is done every 25 min (see table 1 for specific parameters). After the electrolysis is completed, the scraped copper powder is washed in anhydrous ethanol and dried in a drying oven at 53 °C.

2.2. Experimental device
The device for preparing copper powder in this experiment is shown in figure 1. It mainly includes silicon rectifiers, glass electrolyzers and cathode and anode plates. The anode adopts graphite insoluble electrode, and the cathode adopts 316L stainless steel plate. The output voltage of the silicon rectifier is adjusted to control the current density of the cathode in the electrolysis process. At a suitable current density, the Cu²⁺ in the electrolyte obtains electron nucleation crystals on the cathode, reducing and depositing copper powder.

2.3. Characterization
For the convenience of explanation, copper powder deposited in the electrolyte without additives (blank solution) is labeled as A₀; copper powder, when the additive PVP is added, is labeled as A₁; copper powder, when the additive SDBS is added, is labeled as A₂; copper powder, when both additive PVP and SDBS are added is labeled as A₃. The phase composition of copper powder is determined by D8A advance x-ray diffractometer. The microstructure, crystal structure and dispersion of copper powder are characterized by XL30ESEM-TMP scanning electron microscope. Electrochemical polarization curves and Electrochemical Impedance Spectroscopy (EIS) measurements are performed using the DH7000 electrochemical workstation. The working electrode is a smooth stainless steel disc (area 1cm²), the auxiliary electrode is a platinum plate (area 1cm²), and the reference electrode is an Ag/AgCl/Cl⁻ electrode. When the polarization curve is measured by linear voltammetry, the scanning rate is 0.6 mV s⁻¹ and the scanning potential range is −0.20~−2.10V. During the measurement of AC impedance spectrum, the bias potential is set to −0.6V, the amplitude of sinusoidal wave disturbance signal is 10mV, and the frequency is 100 kHz ~ 0.01 Hz.

3. Results and discussion

3.1. X ray diffraction analysis(XRD)
The x-ray diffraction patterns of copper powders obtained by electrolysis under different conditions and copper standard PDF card (JCPDS Card No. 04-0836) are shown in figure 2. It can be seen from figure 2 that the diffraction spectrums of copper powders produced under different conditions are basically the same, indicating that it is mainly composed of pure copper phase (FCC lattice structure) and a small amount of copper oxide phase. The presence of CuO may be caused by the following process. During the drying process of wet copper powder, the not yet dry copper powder provides water vapor and the copper powder already dry is exposed to air at high temperature for a long time so oxidation occurs. Alternatively the oxidation may have occurred during the cooling process in the air after the sample has just been dried at a high temperature.

3.2. Polarization curve
Figure 3 shows the cathodic polarization curves of copper powders deposited under different electrolyte conditions. The cathode polarization of A₀ (Blank) is small. As the cathode potential continues to move negatively, the influence of diffusion and mass transfer on the electrolysis process increases sharply. When the additive PVP is added, the cathodic polarization phenomenon is more prominent, the adsorption of copper ions on the electrode surface is reduced, and the thickness of the cathode diffusion layer is increased, which leads to the continuous decrease of the limit current density, indicating that the addition of PVP played a role of
Table 1. Solution composition of electrolyte and process conditions for copper powder.

| Cu$^{2+}$ concentration | $\text{H}_2\text{SO}_4$ concentration | Cathode current density | SDBS | PVP | Anode materials | Cathode materials |
|-------------------------|-------------------------------------|-------------------------|------|-----|----------------|------------------|
| 0.64 g l$^{-1}$         | 25 g l$^{-1}$                       | 1500 A m$^{-2}$         | 5 g l$^{-1}$ | 1.25 g l$^{-1}$ | graphite         | smooth stainless steel plate |
| 0.64 g l$^{-1}$         | 25 g l$^{-1}$                       | 1500 A m$^{-2}$         | 5 g l$^{-1}$ | /   | graphite         | smooth stainless steel plate |
| 0.64 g l$^{-1}$         | 25 g l$^{-1}$                       | 1500 A m$^{-2}$         | /   | 1.25 g l$^{-1}$ | graphite         | smooth stainless steel plate |
| 0.64 g l$^{-1}$         | 25 g l$^{-1}$                       | 1500 A m$^{-2}$         | /   | /   | graphite         | smooth stainless steel plate |
inhibitor. However, with the continuous increase of the cathode current density, compared with A₀, the change in amplitude of cathode polarization potential is insignificant. This indicates that although the addition of PVP has an inhibiting effect on the electrolysis process, this effect of the single use on the deposition process is obviously limited. Similarly, when SDBS is added alone, the cathodic polarization phenomenon is also enhanced correspondingly, but the amplitude is limited. The physical mechanism is similar to that of PVP, which raises the
reaction resistance of the cathode, thus hindering the charge transfer and acting as an inhibitor, but the inhibition effect is relatively limited. When both SDBS and PVP are added to the basic electrolyte, the polarization electromotive force continued to shift negatively and the cathodic polarization phenomenon continued to enhance, indicating that the synergy effect of the two additives is significant and played a role in jointly enhancing polarization. The reaction resistance increases, the shielding effect of ions is enhanced, and the likelihood of internal clusters is reduced.

3.3. Micromorphological analysis (SEM)

Figures 4(c) and 4(d) are the SEM images of electrolytic copper powders without additives. The microstructure is the bulk structure of highly agglomerated copper grains, with a grain size of 15 μm low degree of dispersion, and large grains without obvious branching. Figure 4(e) is the SEM image with only SDBS added, and the dendritic orientation is obvious, but the crystal grains have thick ends. When only PVP is added to the solution (figure 4(f)), the crystal grains tend to be refine without obvious dendrites. (figures 4(a) and 4(b)) are SEM images.
of copper powders obtained by electrolysis with both SDBS and PVP added. The microscopic morphology of the copper powder becomes thin dendrites composed of thin and approximately spherical copper particles. Without obvious agglomeration, the trunk and branches of the dendrites are slender. At this point, the main ongoing reactions in the solution are as follows:

\[
\text{Anode: } H_2O - 2e^- = 2H^+ + \frac{1}{2}O_2 \tag{1}
\]
\[
\text{cathode: } Cu^{2+} + 2e^- = Cu \tag{2}
\]
\[
2H^+ + 2e^- = H_2 \tag{3}
\]

Cu\(^{2+}\) in the vicinity of cathode receives continuous electrons and at the same time, Cu\(^{2+}\) in solution continuously approaches the cathode depending on the diffusion and the directional transfer of charge.

In the process of electrochemical deposition, since the crystal grows too fast or the required components can only be transported to the precipitation interface by means of long-term diffusion, the concentration field will be seriously uneven. Therefore, dendritic crystals are one of the fractal structures formed by diffusion limited aggregation in the liquid phase [22]. At the tip of the fractal branch, the surface tension wave disturbs the random nucleation, and the crystal nucleus is the basic unit of the aggregate. The main reason for its formation is that when Cu\(^{2+}\) ions in the solution get electrons on the surface of the cathode, copper crystals begin to nucleate and grow into the liquid phase, and the small protrusions randomly extending into the liquid phase will be in a state of supercooling higher than the interface. It is conducive to the growth of crystals, and the local negative temperature gradient is conducive to the dissipation of the latent heat of phase change, so that the small potrusion deep in the liquid phase crystallizes into a branch bud. At this time, the number of crystals obtained is small, the trunk of the branches is short, and the dendritic shape is not obvious as the agglomerates of copper particles. As the reaction progresses, the number of nucleation increases, the crystal trunk gets longer, and the liquid phase has a relative negative temperature gradient perpendicular to the primary branch. Thus secondary branches grow on the trunk and branching structures begin to appear. As the reaction time increases, the dendrite trunk and branches begin to get thicker, and the secondary branch crystal structure appears with the branch as the new trunk. As the reaction further branches and grow, the dendrites adhere to each other [22]. Due to the existence of diffusion limiting aggregation effect in the liquid phase, the part precipitating at the cathode first obstructs the superposition of the same part, so that the grains precipitating later are difficult to nucleate and grow in this part. As a result, the microscopic morphology of the precipitated copper particles presents a loose dendritic structure under the influence of shielding effect.

SDBS is an anionic surfactant that produces dodecylbenzene sulfonate ions and Na\(^+\) in the solution, while PVP is a water-soluble polymer, both of which contribute to the uniformity of ions dispersion in the solution during the electrolysis process and prevent overlap. When SDBS and PVP are added to the solution at the same time, the sulfonic acid group of SDBS will be adsorbed to the lactam group by PVP, which will form free micelles or bound micelles, which will inhibit the growth of polarization of particles [23, 24]. When copper powder is obtained by constant current method, other contents in the electrolyte remain unchanged, and additives SDBS and PVP are added. The additives interact with each other and form a specific association structure with Cu\(^{2+}\). During the cathode deposition, the reduction rate of Cu\(^{2+}\) electrons in the solution decreases, which breaks the equilibrium state of Cu\(^{2+}\) and H\(^+\) precipitation at the cathode. The current efficiency of the cathode decreases, resulting in the decrease of the reduction deposition rate of Cu\(^{2+}\). However, the diffusion mass transfer efficiency was enhanced, the dispersion and mass transfer rate of ions in the solution were increased, and the limiting aggregation and shielding effect of Cu\(^{2+}\) in the liquid phase were enhanced. It reduces the likelihood of agglomeration of the internal atoms, thus controlling the precipitation rate of Cu\(^{2+}\) while ensuring sufficient dispersion. Further, through limited induction a new slender copper powder is formed, so that the microscopic morphology of the dendritic crystal trunk and the slender branches is displayed.

### 3.4. Electrochemical Impedance Spectroscopy (EIS)

As can be seen from figure 5, the curves obtained in the high frequency region and the low frequency region are of semicircle shape. The semicircles in the high frequency region represent the electron e\(^-\) and ion transfer reaction resistance, and the semicircles in the low frequency region represent the diffusion mass transfer resistance [25]. The influence of diffusion resistance relative to reaction resistance is however relatively weak. When PVP and SDBS (A\(_1\), A\(_2\)) are added separately to the solution, the radii of the semicircles in the high frequency zone increase relative to those without additives (A\(_0\)), and the charge transfer reaction resistance increases accordingly. This indicates that the electron placement rate decreases correspondingly, which reduces the adsorption of Cu\(^{2+}\) on the cathode surface. Due to the increase of reaction resistance, the cathode polarization effect is enhanced to a certain extent, which hinders the cathode deposition process. The radii of the semicircles in the low frequency region are correspondingly smaller, and the diffusion and mass transfer resistance in the solution is reduced, which is conducive to the diffusion of ions, and improves the flow and
dispersion of them in the solution. When the additives SDBS and PVP \((A_3)\) are added to the basic electrolyte simultaneously, the radii of semicircles in the high frequency region continue to increase, while those of the low frequency region continue to decrease. As a result, the reaction resistance increases, which ensures, under the condition of highly dispersed ions, that the cathode polarization effect continues to enhance. The diffusion-limiting aggregation effect in the liquid phase is reinforced, so is the shielding effect of atoms, and the likelihood of agglomeration during deposition is significantly reduced. As the fractal dimension of sediment decreases, new slender dendritic copper powder is generated through the synergy effect of additives.

The migration and diffusion of atoms in the solution follow the Arrhenius equation:

\[
D = D_0 \exp \left( -\frac{Q}{RT} \right) 
\]

In the formula, \(R\) is the gas constant and its value is \(8.314 \text{ J} / (\text{mol} \cdot \text{K})\); \(Q\) represents the activation energy per mole of atom, and \(T\) is the thermodynamic temperature. The expressions of the diffusion coefficients of different diffusion mechanisms are the same, but the value of \(D_0\) and \(Q\) are different \([22]\). Due to the interaction between additive (SDBS, PVP) and \(\text{Cu}^{2+}\) in the solution, the activation barrier of ions is reduced to different degrees. As a result, the activation energy required for atomic diffusion is reduced, which leads to an increase in the diffusion coefficient and makes diffusion easier. Therefore, the ions in the solution have a higher transfer rate and degree of dispersion.

4. Conclusions

(1) When copper powder is prepared by constant current electrolysis, a certain amount of PVP and SDBS are added to the electrolyte at the same time, which will form micelle with \(\text{Cu}^{2+}\). Compared with cases without adding additives or adding a certain additive alone, it has higher reduction reaction resistance, lower diffusion resistance, and enhanced cathode polarization and diffusion mass transfer effects. It ensures that the ions have a large cathodic polarization effect under the condition of high mass transfer effect and high dispersion.

(2) Under the conditions of 5 g l\(^{-1}\) of SDBS and 1.25 g l\(^{-1}\) of PVP respectively, constant current electrolysis can produce new fine and long dendrite copper powder.

(3) The addition of additives can reduce the activation energy needed for atomic diffusion and increase the transfer rate and dispersion degree in the reaction process. The order of influence is as follows: \((\text{SDBS} + \text{PVP}) > \text{SDBS} > \text{PVP} > \text{Blank})\).

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