

参赛学生姓名：李溪若

中学：北京师范大学附属实验中学

省份：北京市

国家/地区：中国

指导老师姓名：李琦

指导老师单位：北京大学化学与分子工程学院

指导老师姓名：孔婀娜

指导老师单位：北京师范大学附属实验中学

论文题目：Electroless-Plated Magnesiophilic 3D Current Collectors for Long-Cycle-Life Magnesium Metal Anodes

Electroless-Plated Magnesiophilic 3D Current Collectors for Long-Cycle-Life Magnesium Metal Anodes

Name of Participant: Xiruo Li

Experimental High School attached to Beijing Normal University

Name of Advisor: Qi Li

College of Chemistry and Molecular Engineering,
Peking University

Name of Advisor: Ejing Kong

Experimental High School attached to Beijing Normal University

Abstract:

Rechargeable magnesium batteries (RMBs) are one of the promising energy-storage systems in the post-lithium era, due to their high volumetric capacity, low cost, and abundant Mg resources. Unfortunately, non-uniform Mg deposition in the metal anodes always shortens cycle life and poses a short circuit. In this work, we developed a simple and scalable electroless plating process on the carbon fiber paper to produce a Cu-coated current collector with a 3D pore structure for Mg metal anodes, in which a 3D interconnected framework is naturally integrated with the copper-coated carbon fibers. The Mg initial nucleation potential was proposed as the key factor for characterizing the Magnesium affinity of the current collector in the process of Mg deposition, and it was successfully applied to guide the fabrication of the composite 3D current collector. In half-cell tests, the optimized Cu@CF-based anode achieved a Coulombic efficiency of 99.17% and demonstrated stable cycling over 350 cycles at a current density as high as 4 mA cm^{-2} . In full-cell tests with Mo_6S_8 cathodes, the optimized Cu@CF-based cell retained about 94% of its initial specific discharge capacity after 300 cycles at 0.8C, achieving a specific discharge capacity of 127 mAh g^{-1} .

Keywords: rechargeable magnesium batteries, Mg metal anode, 3D current collector, carbon fiber paper, electroless plating, electrochemical performance

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1. Introduction

The ever-increasing demand for high-performance energy-storage systems in electric vehicles, portable electronic devices, and renewable-energy integration has driven the development of advanced batteries.^{1,2} Lithium batteries currently dominate the market due to their high energy density and long cycle life.^{3,4} However, safety problems arising from dendrite problems and the relatively limited lithium resources have motivated the search for alternative batteries.⁵⁻⁷ In the post-lithium era, rechargeable magnesium batteries (RMBs) have attracted great attention because of their high volumetric capacity (3833 mAh cm^{-3}), abundant Mg resources, low cost, and improved safety.^{2,7,8}

Although owning these advantages, Mg batteries' commercialization faces significant challenges, largely due to issues associated with Mg metal anodes. Key challenges include uneven Mg deposition, surface passivation, dendritic growth, poor anode and electrolyte compatibility, and volume changes during repeated plating and stripping.^{7,9,10} Among these challenges, nonuniform deposition of Mg can compromise the reversibility and pose potential safety risks.¹¹ Therefore, regulating Mg plating and stripping behavior through rational current-collector design is critical for the development of advanced Mg metal batteries.

Three-dimensional (3D) current collectors are a promising solution for achieving uniform surface regulation. Their structure reduces local current density, provides numerous nucleation sites, and accommodates volume changes during cycling. In addition, the functionalized surface has a strong affinity for magnesium, which facilitates uniform deposition.¹² To date, significant advancements have been made in developing 3D current collectors, showing certain methods in overcoming critical challenges in metal battery anodes. Kwak et al. constructed Ag@Cu by introducing magnesiophilic Ag nanoparticles onto porous Cu foam, enabling stable performance for over 1200 cycles at 0.2 mA cm^{-2} .¹³ Liu et al. developed a nitrogen-doped carbon layer derived from ZIF-8 on carbon cloth, known as ZIF8-900@CC, achieving stable Mg plating/stripping for over 2200 h at 2.0 mA cm^{-2} .¹⁴ Zhou et al. developed a 3D Cu-

coated carbon cloth (Cu@CC) that improved the compatibility between the Mg metal anode and the Celgard separator, resulting in a high average CE of 99.35% over more than 2000 cycles.¹⁵ From these studies, we can summarize that an important aspect in current collector design is enhancing magnesiophilicity. Whether through the use of metal substrates, surface modification, or metal coating, the primary purpose is to improve the affinity of the current collector toward Mg, thereby enabling uniform deposition of magnesium metal on the 3D current collector.

However, the design of anodes and current collectors when considering magnesiophilicity often relies on density functional theory (DFT) calculations, in which the affinity between the current collector and Mg metal is assessed through static adsorption energies.^{16–18} This approach has inherent limitations. DFT calculations based solely on thermodynamic adsorption energies neglect several significant electrochemical factors, including interfacial electric-field effects, the work function associated with electron removal from the current-collector surface, and Mg²⁺ desolvation kinetics. These omissions may lead to significant discrepancies between theoretical predictions and experimentally observed deposition behavior.

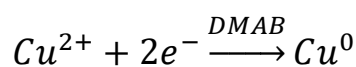
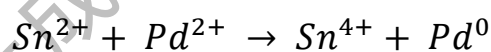
Therefore, this work proposes an evaluation method based on the electrochemical performance of the half-cells for magnesiophilicity. Specifically, Mg initial nucleation potential is measured to evaluate the affinity to Mg, and the cycle life is considered to assess the long-term stability of the current collectors. The Cu@CF 3D current collector designed based on electrochemical performance achieved a CE of 99.17% and demonstrated stable cycling over 350 cycles at a current density of 4 mA cm⁻² in half-cell tests. In full-cell tests with Mo₆S₈ cathodes, the Cu@CF-based cell retained about 94% of its initial specific discharge capacity after 300 cycles at 0.8C, achieving a specific discharge capacity of 127 mAh g⁻¹ (128 mAh g⁻¹ theoretically).

2. Design of 3D current collector

In our work, the current collector was fabricated by coating carbon fibers with copper. Carbon fiber (CF) paper has excellent porosity, providing sufficient space for

magnesium deposition and allowing for higher magnesium loading while also being lightweight and cost-effective.^{19,20} Its relatively poor conductivity and magnesiophilicity were improved by surface metallization through electroless plating. Unlike electroplating, electroless plating can produce highly uniform coatings on 3D substrates without current input, which reduces the production cost and simplifies the process.^{21,22} Copper was chosen as the coating material in this study due to its affinity for magnesium, high electrical conductivity, and affordability. So, the magnesiophilic 3D current collector for magnesium metal anodes was designed and fabricated.

As shown in Figure 1a, the uniform and porous Cu@CF 3D current collector is produced by electroless plating through several steps, including functionalization, sensitization, activation, and Cu deposition. Plasma treatment is first applied to the carbon fiber paper to enhance its wettability and introduce functional groups (such as –OH and C=O–COOH) to increase its reactivity. Then, the KH550 silane coupling agent is used to functionalize the carbon fiber paper surface by introducing active sites (–NH₂, Si–OH), thereby allowing easier attachment of subsequent ions. Next, Sn²⁺ ions are introduced onto the carbon fiber paper surface as reducing agents, enabling the subsequent reduction of Pd²⁺ to Pd⁰. Subsequently, Pd²⁺ ions are introduced into the system, and Pd⁰ clusters are formed. The subsequent copper plating process can then proceed at the active Pd catalytic sites.



Lastly, the modified carbon fiber paper is immersed in the plating solution containing Cu²⁺, TEA (triethanolamine), EDTA-2Na (disodium ethylenediaminetetraacetic acid), and DMAB (dimethylamine-borane). Cu²⁺ is the copper source in the system. TEA and EDTA-2Na are complexing agents that coordinate with Cu²⁺ ions, thereby regulating the Cu reduction and deposition rate and preventing excessively rapid Cu reduction; this is because their N and O atoms possess lone-pair electrons capable of forming coordinate bonds. Because the Cu deposition rate is controlled, more homogeneous nucleation is promoted, resulting in a relatively

uniform coating. DMAB functions as the reducing agent, as the B–H bond can provide a reducing equivalent and release H_2 . The whole process is autocatalytic and redox, without any external current.

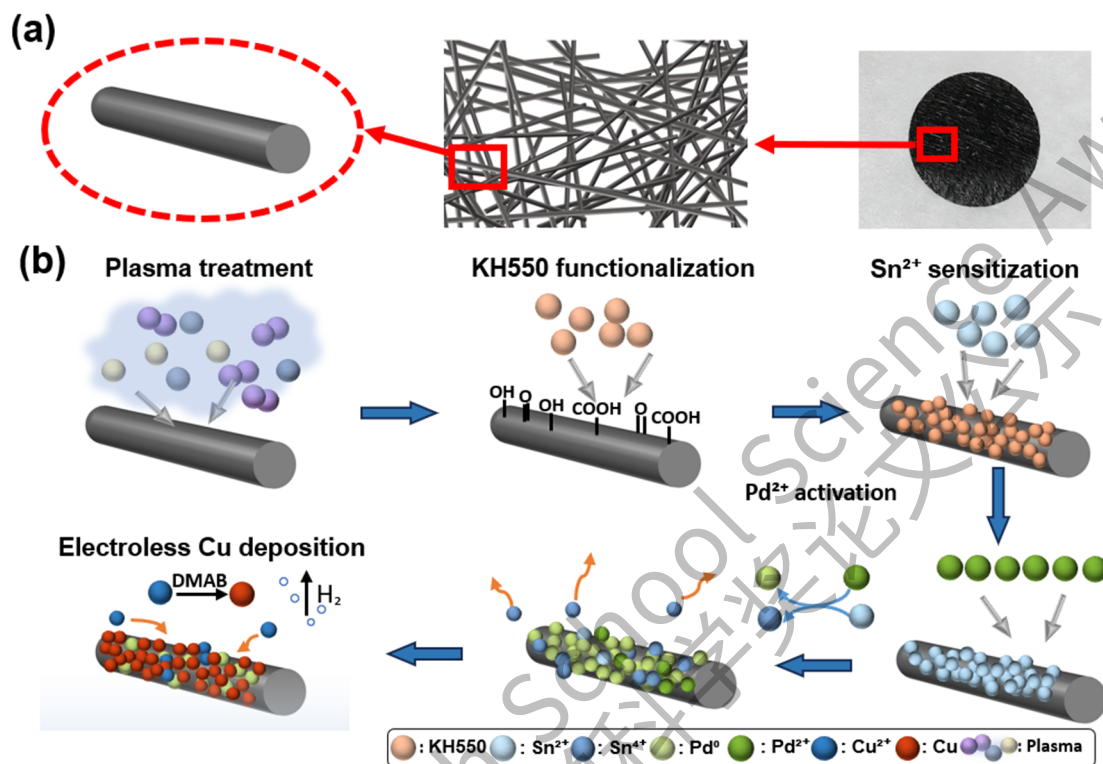


Figure1. (a) The structure of the CF paper; (b) The schematic illustration of the process of electroless plating.

Figure 2a shows the scanning electron microscopy (SEM) image of a single CF in the CF paper, which is the substrate of the current collector. After the electroless plating process, the pattern of the coating is shown in Figure 2b. The Cu@CF has a layer of dense, smooth, and uniform copper particles. In Figure 2c, the X-ray diffraction (XRD) schematic shows that the characteristic peaks at 25.5° and 43.6° are from the carbon fiber paper, and the 43.4° , 50.6° , and 74.1° peaks belong to the crystal planes of Cu (111), Cu (200), and Cu (220), respectively. Figures 2d and 2e show the current collector at low magnification before and after the electroless plating process. After plating, the current collector remains porous and has sufficient space, since the coating is relatively thin and extends along the fiber. Figure 2f shows the magnified view of the Cu grains, which range from approximately 200 nm to 800 nm. Figure 2g-i shows the

energy-dispersive X-ray spectroscopy (EDS) of the coated material. The Cu coverage is relatively high, and its distribution is broad and uniform, confirming that electroless plating yields a dense and uniform Cu coating. The above analyses demonstrate that a porous Cu@CF 3D current collector with a uniform Cu coating was successfully fabricated, preserving the porous structure of pristine CF while incorporating a Mg-friendly copper coating.

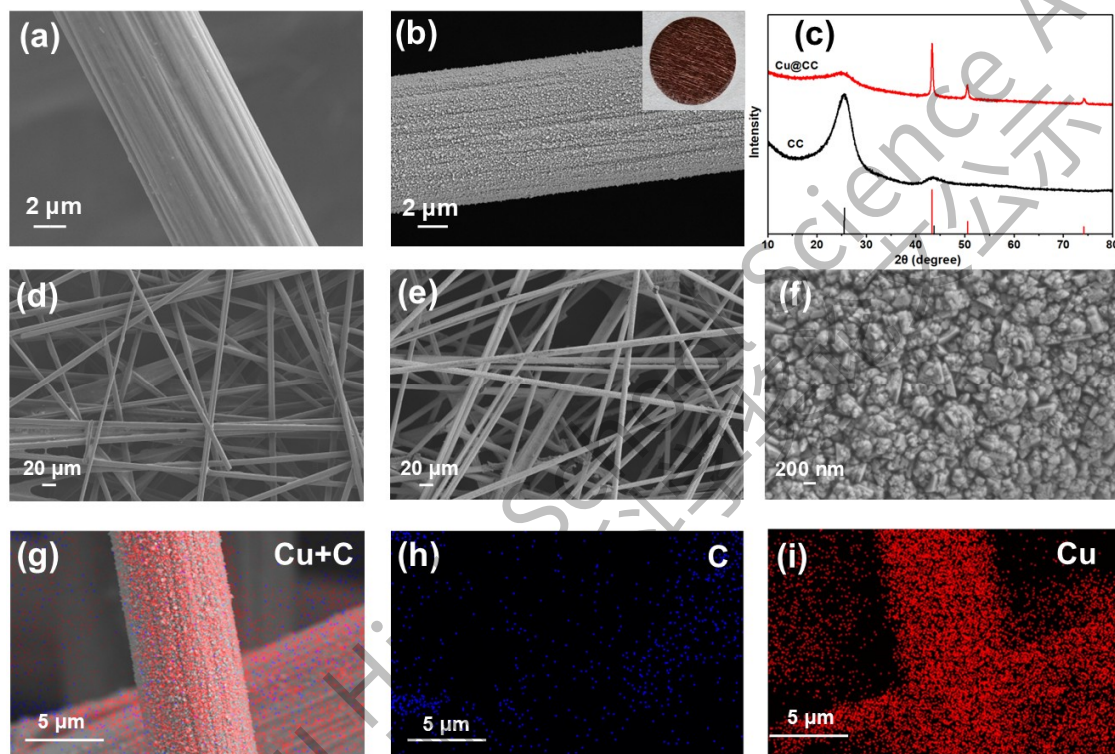


Figure 2. (a) SEM images of the carbon fiber paper at high magnification, (b) SEM of the Cu@CF at high magnification, (c) XRD of Cu@CF. (d) SEM images of the carbon fiber paper at low magnification, (e) SEM of the Cu@CF at high magnification, (f) SEM image of the coated copper particles. (g)-(i) EDS of the Cu@CF, (g) both Cu and C elements, (h) C element, (i) Cu element.

Conventional evaluation methods for 3D current collectors mainly focus on physical characterization, including coating morphology, particle size, compactness, and electrical conductivity,^{15,23,24} which reflect only the static structural features of the coating and cannot directly capture its dynamic behavior during actual electrochemical deposition. Optimizing the current collector based on this is clearly defected. Therefore, in our study, we proposed a method of optimization based on the electrochemical performance of a half-cell, specifically using the initial nucleation potential to reflect

magnesiophilicity and the cycle number to reflect the long-term stability.

3. Result and discussion

3.1 The fabrication of Cu@CF 3D current collectors

For evaluating the performance of the Cu@CF 3D current collectors, we systematically investigated the influence of the key factors in electroless plating, including plating temperature, plating time, CuSO_4 concentration, reducing agent concentration, and additives. The coating morphology was characterized by scanning electron microscopy (SEM). The electrochemical measurements were performed using 200 μL of APC electrolyte and a glass-fiber (GF/D) separator at a current density as high as 4 mA cm^{-2} and an areal capacity of 4 mAh cm^{-2} .

3.1.1 Influence of electroless plating time

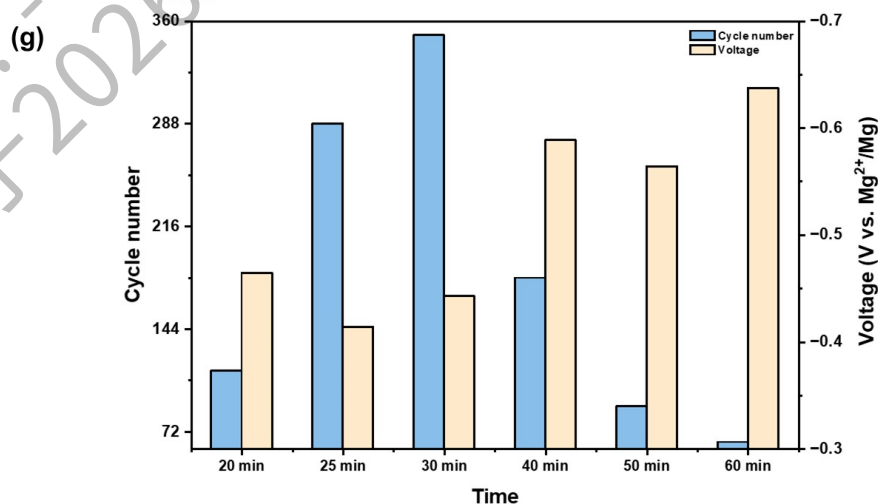
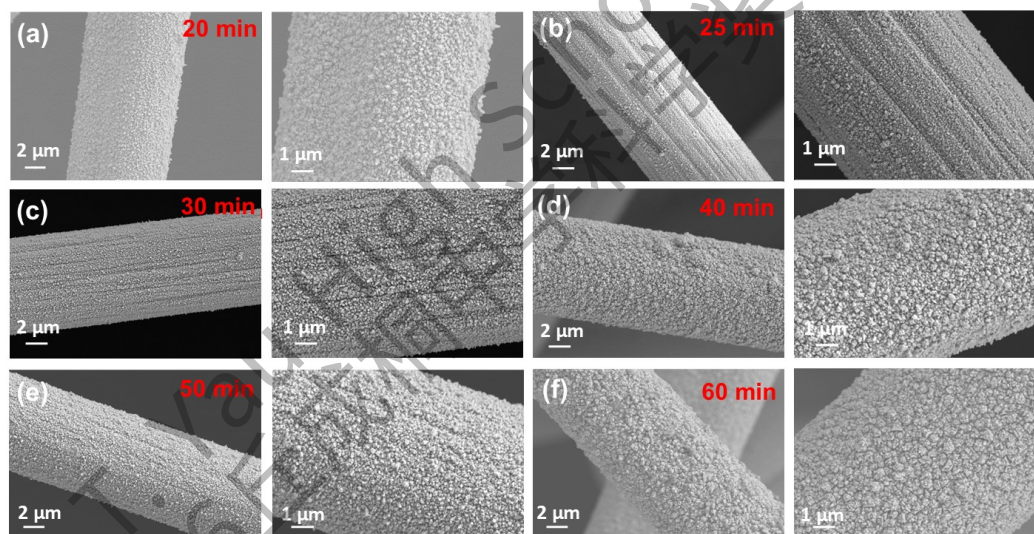


Figure 4. (a)-(f) The SEM images of the time-ranging samples, (g) Half-cell electrochemical data of the samples.

The electroless plating time plays an important role in the nucleation and growth of Cu on the CF. It was systematically varied to investigate the changes in Cu morphology and its corresponding Mg electrochemical behavior.

In Figure 4, the morphology of the Cu coating from 20 min to 60 min is shown in Figure 4a-f, while the half-cell electrochemical data are shown in Figure 4g. Samples with plating times less than 20 min are not considered because their coatings lack adequate coverage.

As the electroless plating time increased, the Cu deposits gradually transitioned from isolated clusters to a more uniform coating. Within an optimal timeframe, the coating became continuous and uniform. Prolonged electroless plating time could result in excessive Cu growth and particle agglomeration. From the morphology (Figure 4a-f), the 30min and 50min samples are considered optimal, as they both exhibit uniform, compact coatings, with the 30min having smaller particles and the 50min having larger ones.

However, according to the electrochemical data (Figure 4g), the optimized electroless plating time is between 25 and 30 min, as they both have less negative nucleation potential and long cycle life. The 25 min sample has the least negative initial nucleation potential, while the 30 min sample has the longest cycle life.

3.1.2 Influence of electroless plating temperature

The electroless temperature significantly affects the reaction kinetics of electroless plating and consequently the Cu coating morphology. It was systematically varied to investigate the resulting changes in Cu coating morphology and the Mg electrochemical behavior.

The morphology of the Cu coating at 20°C to 70°C is shown in Figure 5a-f, while the half-cell electrochemical data are shown in Figure 5g.

With rising electroless temperature, the Cu nuclei tend to grow larger due to accelerated reduction kinetics and enhanced surface diffusion. At low temperatures, the

Cu nuclei may be insufficiently grown. When the electroless temperature reaches a high level (60-70°C), the Cu nuclei agglomerate and a rough surface is formed. Based on the morphology in Figure 5a-f, the 30°C and 50°C samples both have a uniform, compact surface with fine grain sizes. The 60°C and 70°C samples have rough and nonuniform surfaces.

According to the electrochemical performance (Figure 5g), the sample deposited at 50°C was optimal, exhibiting the longest cycling lifespan and the least negative initial nucleation potential. In addition, although the morphology of the 60°C and 70°C samples is highly unfavorable, the electrochemical performance is acceptable.

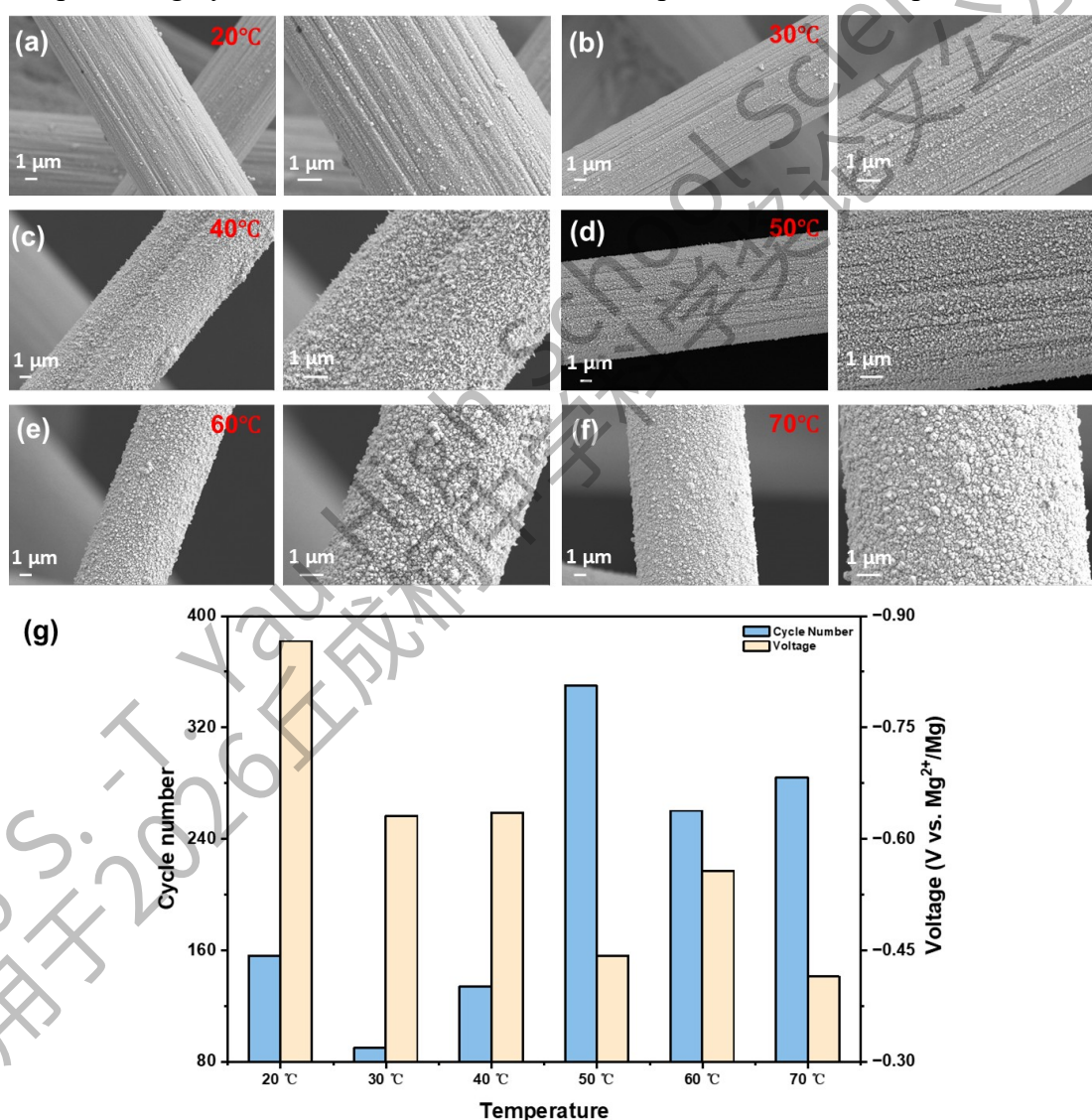


Figure 5. (a)-(f): The SEM images of the electroless temperature-ranging samples, (g): Half-cell electrochemical data of the samples.

3.1.3 Influence of Cu^{2+} concentration

As the source of Cu in the electroless plating system, the Cu^{2+} concentration is an important factor in regulating electroless plating. As a result, a series of Cu^{2+} concentration experiments were conducted to examine its effect on Cu morphology and its Mg electrochemical behavior.

In Figure 6, the morphology of the Cu coating at $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentrations from 0.75 to 2.0 g/L is shown in Figure 6a-f, and the half-cell electrochemical data are presented in Figure 5g. Figure 6h shows the mass of the Cu coating under different conditions. Clearly, as the concentration increases, the mass increases.

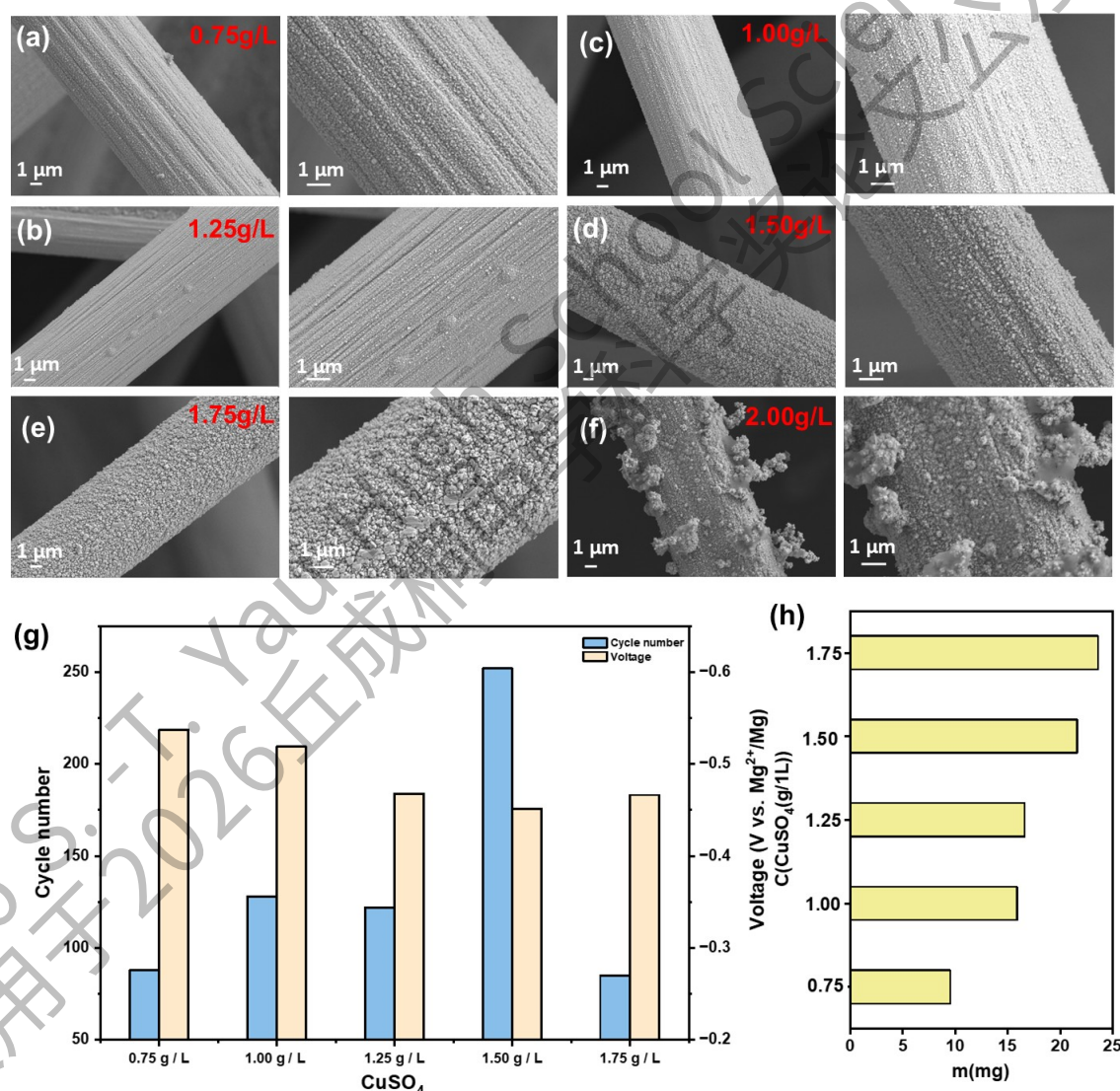


Figure 6. (a)-(f) The SEM images of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentration-ranging samples, (g) Half-cell electrochemical data of the samples, (h) The mass of the coating under different concentrations.

At low Cu^{2+} concentrations, the particles are small in size. With increasing Cu^{2+} concentration, the enhanced free Cu^{2+} promoted the growth and interconnection of Cu deposits, leading to a denser and smoother coating. However, excessive $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentration (2.00 g/L) accelerated Cu growth and induced intense particle aggregation, also leading to bath deactivation, as shown in Figure 6f. The sample of 1.00 g/L seems to be optimal, with refined grains and a uniform surface.

According to the electrochemical performance in Figure 6g, however, the sample prepared with 1.50 g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ exhibited the best electrochemical performance, with the longest cycle number and the least negative initial nucleation potential.

3.1.4 Influence of the reducing agent concentration

Dimethylamine-borane (DMAB) is the reducing agent of the plating system, controlling the process of Cu^{2+} being reduced to Cu and deposited. A series of DMAB concentration experiments were executed to examine its effect on Cu morphology and the Mg electrochemical behavior.

In Figure 7, the morphologies of the Cu coatings obtained at DMAB concentrations from 0.2 to 2.0 g/L are shown in Figure 7a-j, and the corresponding half-cell electrochemical data are presented in Figure 7k. Figure 7l shows the mass of the copper coating under different conditions. The mass increases as the concentration increases.

At low DMAB concentrations, the insufficient reduction capability resulted in limited Cu deposition, leading to sparse Cu particles and incomplete surface coverage, revealing the dark carbon fiber paper underneath. With increasing DMAB concentration, the enhanced reduction of Cu^{2+} promoted the growth of Cu deposits, accompanied by an increase in Cu loading. As shown in the morphology (Figure 7a-j), the samples from 0.8 g/L to 1.2 g/L all have preferable morphology, owing to a uniform surface, connected particles, and refined grains.

Based on the electrochemical data (Figure 7k), it is obvious that the sample prepared with 1.2 g/L DMAB exhibited the best electrochemical performance, with the longest cycle number and the least negative initial nucleation potential. This reveals the defect in estimating based on morphology.

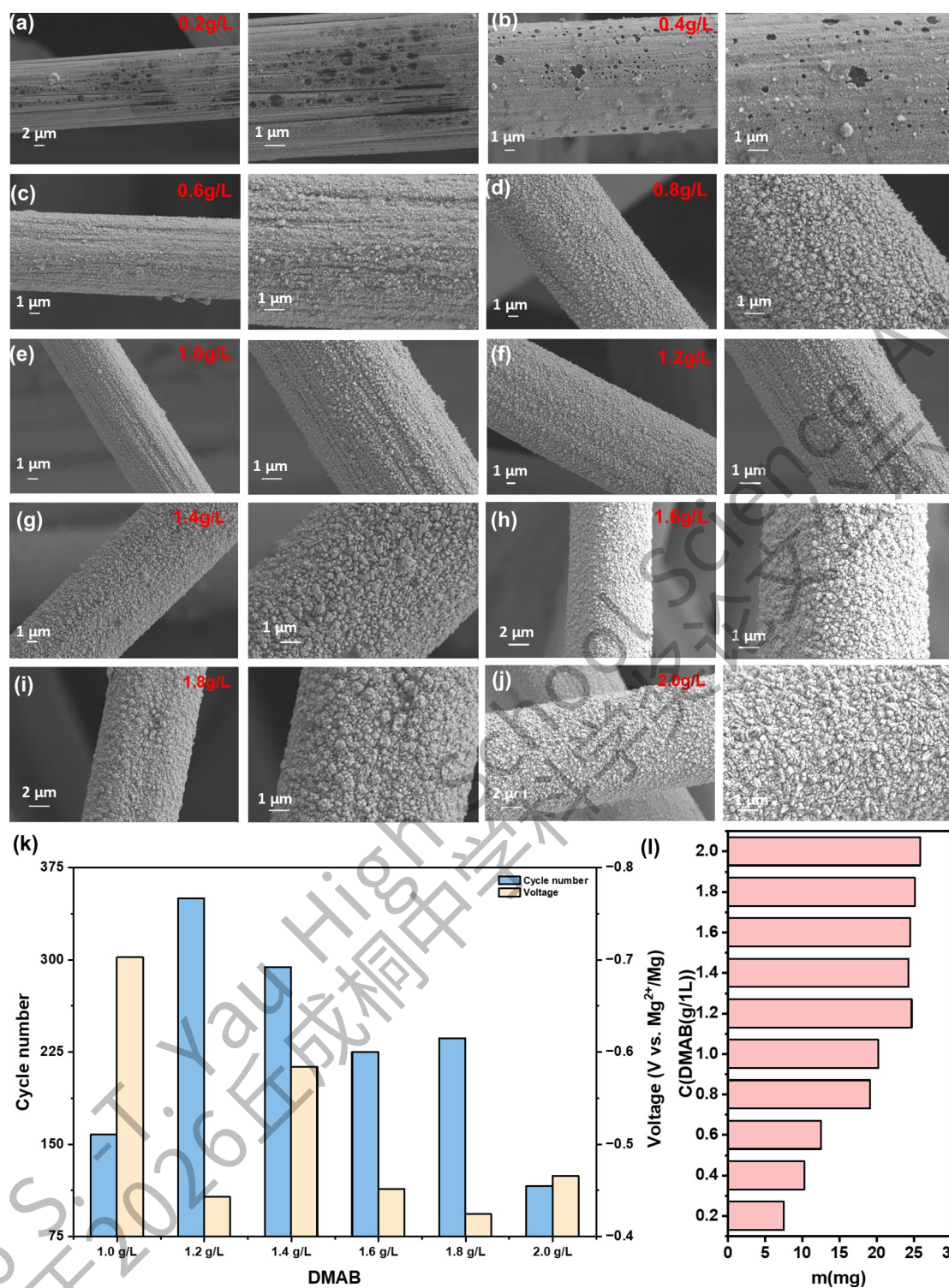


Figure 7. (a)-(j) The SEM images of reducing agent concentration-ranging samples, (k) Half-cell electrochemical data of the samples, (l) The mass of the coating under different concentrations.

3.1.5 Influence of additives

To further control the electroless plating process and improve the electrochemical performance, additives are introduced into the plating bath to regulate the Cu

morphology and optimize the current collector. Cytosine and ethanol are applied to the system, producing half-cells with less negative initial nucleation potential and higher CE.

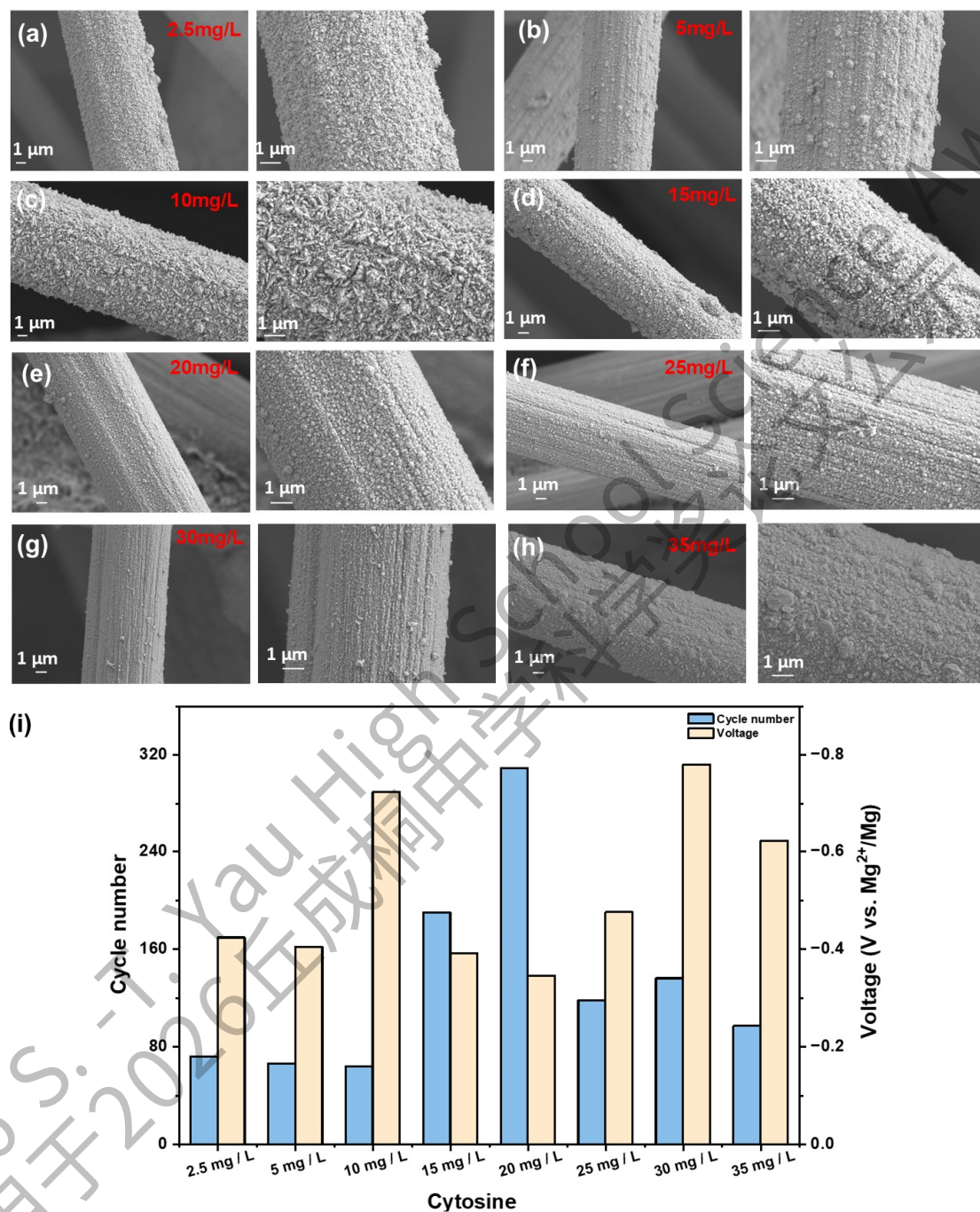


Figure 8. (a)-(h) The SEM images of cytosine concentration-ranging samples, (i) Half-cell electrochemical data of the samples.

In Figure 8, the morphologies of the Cu coatings obtained at cytosine concentrations from 2.5 mg/L to 35 mg/L are shown in Figure 8a-h, and the half-cell

electrochemical data are presented in Figure 8i.

Cytosine can regulate the reaction rate and produce different morphologies. The particles show a tendency to decrease in size overall. According to the morphology (Figure 8a-h), the 20 mg/L and 25 mg/L samples are alike: they both have small particles and a uniform surface, seemingly the optimal morphology.

According to the half-cell data, the sample with a concentration of 20 mg/L exhibits the best electrochemical performance, with the longest cycle number (309) and the least negative initial nucleation potential (-0.3452 V). The 25 mg/L sample's electrochemical data is poor.

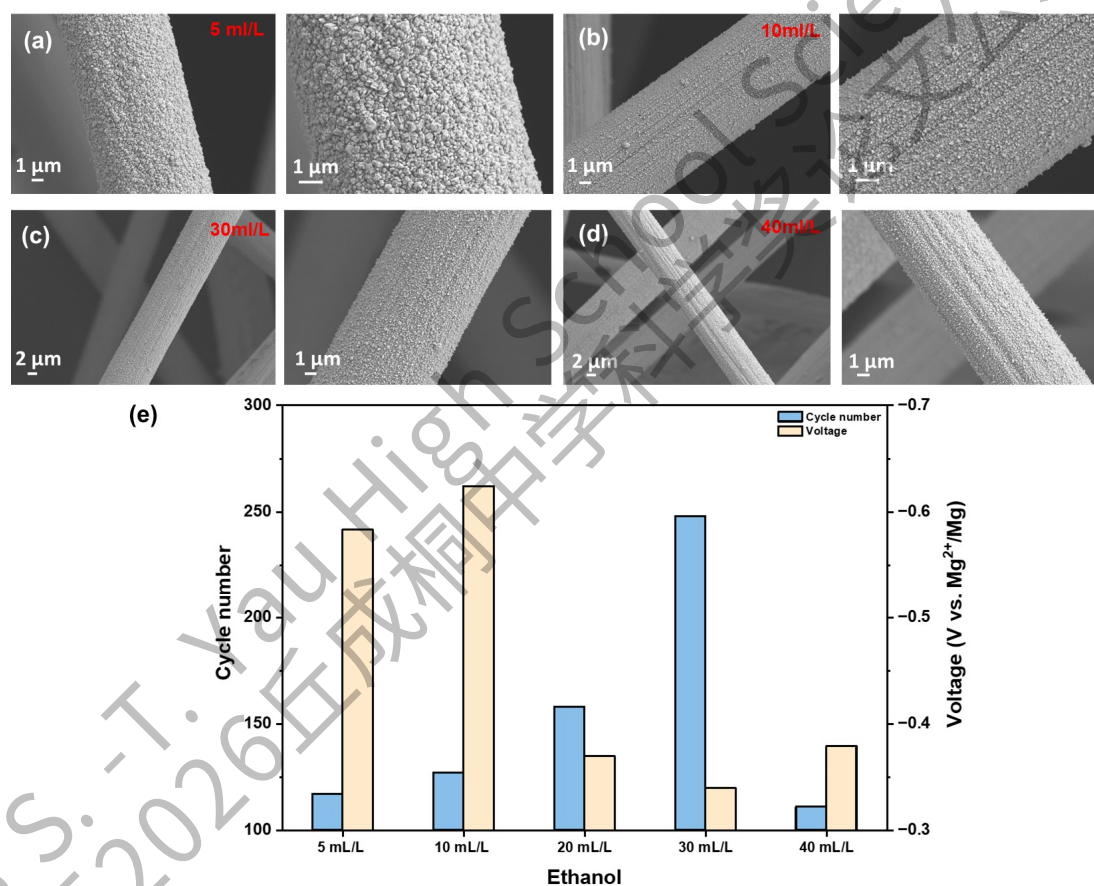


Figure 9. (a)-(d) The SEM of ethanol concentration-ranging samples, (e) Half-cell electrochemical data of the samples.

The morphology of the Cu coating containing ethanol from 5 mL/L to 40 mL/L is shown in Figure 9a-d, while the half-cell electrochemical data are shown in Figure 9e.

The effect of ethanol concentration on Cu deposition morphology and the

electrochemical performance was examined. As the concentration increases, the grains are more refined. According to the morphology (Figure 9a-d), both 30 ml/L and 40 ml/L have favorable morphology, owning a uniform, refined grain size and smooth coating.

Based on the electrochemical data, however, the 30 ml/L is the optimal sample, with the longest cycle life and the smallest negative initial nucleation potential. The 40 ml/L sample has extremely poor performance.

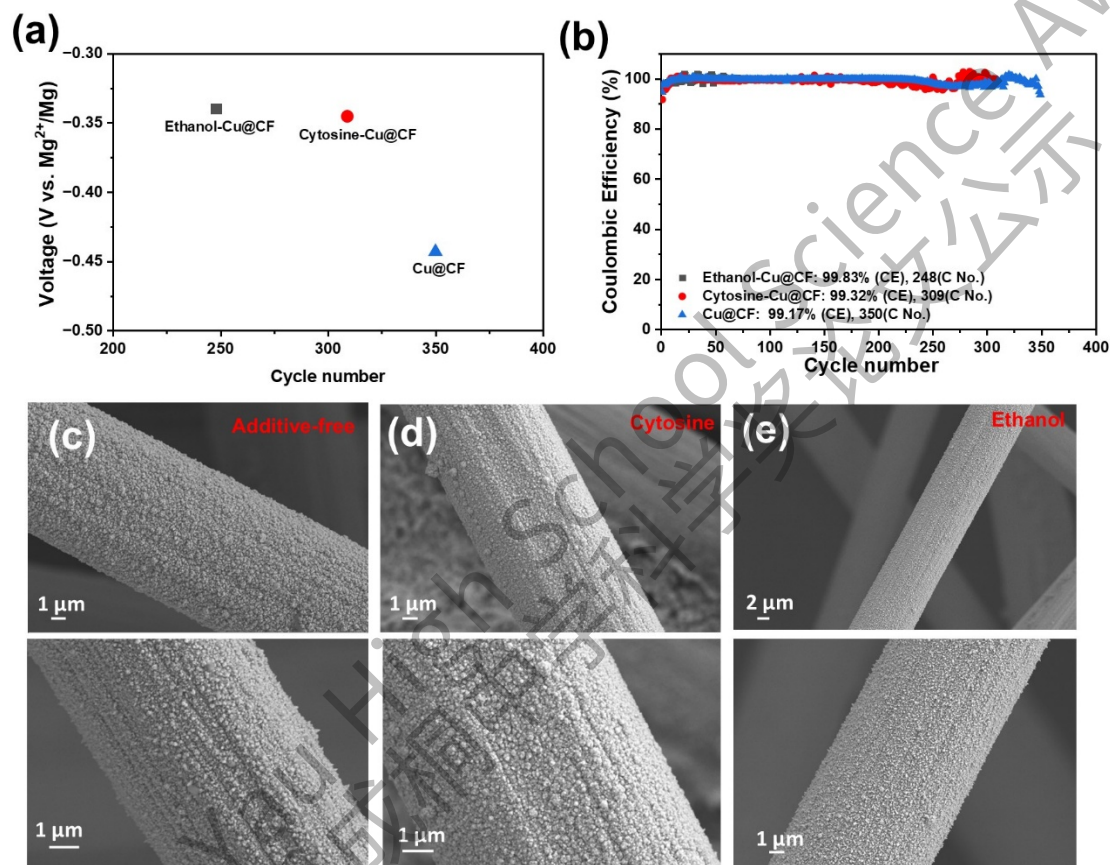


Figure 10. (a) Mg initial nucleation potentials vs. cycle number of ethanol-Cu@CF, cytosine-Cu@CF, and Cu@CF, (b) CE of Mg plating/stripping on different Cu@CF electrodes, (c)-(e) SEM images of additive-free Cu@CF, cytosine-Cu@CF, and ethanol-Cu@CF.

Figure 10 shows that both the ethanol- and cytosine-modified samples exhibit a higher CE and a less negative initial nucleation potential, demonstrating that these additives can partly enhance the electrochemical performance of Cu@CF, particularly by lowering the. The Cu coatings obtained with the additives are smoother and refined.

However, although the Cu@CF 3D current collector prepared using additives in the electroless plating solution system reduced the initial nucleation potential during

the Mg deposition process, it did not improve the battery's cycling performance. This may be because the Cu@CF current collector prepared using this plating system can only optimize the surface morphology of the copper deposit and regulate the initial nucleation behavior of magnesium deposition at the electrode/electrolyte interface, but cannot suppress the ongoing side reactions between magnesium metal and the electrolyte. In addition, the introduction of additives into the plating solution may alter the crystal structure of the copper deposit, thereby causing dendrite growth during the magnesium deposition process and further promoting electrode structural degradation during long-cycle run.²⁵

3.1.6 Electrochemical Performance of the Optimized Cu@CF

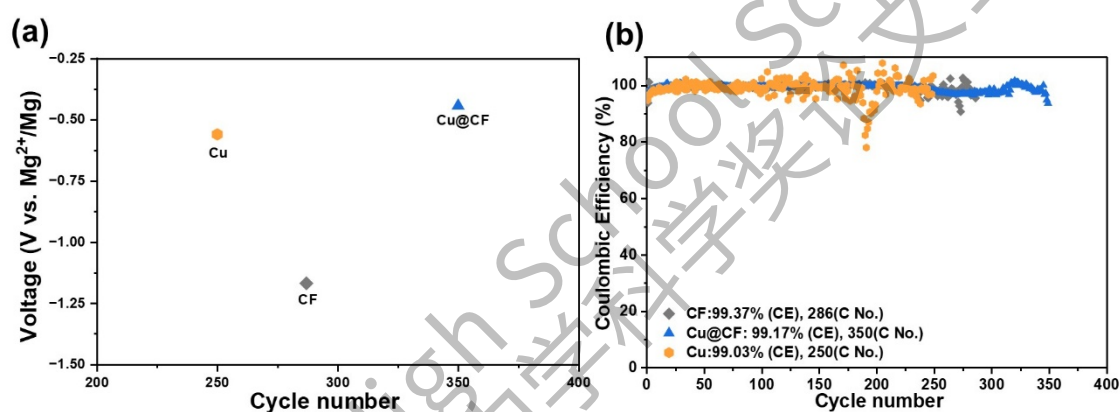


Figure 11. (a) Comparison of the initial Mg nucleation potential and cycle number of CF, Cu, and Cu@CF. (b) Coulombic efficiency during Mg plating/stripping cycling.

The ideal conditions for electroless plating are achieved with 1.5 g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 1.2 g/L DMAB, a temperature of 50°C, and a deposition time of 25-30 min. The optimal Cu@CF 3D current collector is fabricated by electroless plating under these conditions.

In half-cell tests, we evaluated the cycling CE of Cu@CF, CF, and Cu current collectors at 4.0 mA cm^{-2} . The Cu@CF 3D current collector exhibited significantly superior electrochemical performance compared to the CF current collector and the Cu current collector, as evidenced by a markedly reduced initial nucleation potential and a substantially prolonged cycle life.

The initial nucleation potential of Cu@CF improved by 62% compared to the CF current collector (from -1.168 V to -0.443 V) and by 21% compared to the Cu current

collector (from -0.560 V to -0.443 V). The notable decrease in initial nucleation potential suggests that the electroless copper plating process has significantly improved the magnesiophilicity of the carbon fiber paper surface. This reduction lowers the energy barrier for magnesium deposition, facilitating a more uniform and compact magnesium layer.

Moreover, the cycle life of Cu@CF increased by 22% compared to the CF 3D current collector (from 286 cycles to 350 cycles) and by 25% compared to the Cu current collector (from 250 cycles to 350 cycles). The significant enhancement in cycle life indicates that the Cu@CF 3D current collector can effectively sustain structural stability during repeated deposition and stripping processes, curtail side reactions and dendrite growth, thus ensuring the long-term stability of the half-cell.

3.2 Discussion

Considering the results above, the discrepancy between morphology and electrochemical data further demonstrates that a sample's electrochemical performance cannot be decided by relying on its morphology. A coating with an apparently favorable morphology may not necessarily exhibit superior electrochemical performance, while a coating with excellent electrochemical performance may not always possess an ideal surface morphology. This is because SEM fails to characterize some microstructures, like the interparticle gaps or the defects within particles. Also, it's hard to choose the optimal surface when two samples are both uniform, with only particle sizes different. Furthermore, morphology only characterizes the static structural features of the coating and can't reflect the dynamic process during actual electrochemical deposition.

For the plating time series, both the 30 min and 50 min samples exhibited favorable surface morphologies. However, the 30 min sample showed excellent electrochemical performance, whereas the 50 min sample performed poorly. This could be due to their different particle sizes. Excessive Cu particle growth may reduce favorable Mg nucleation sites, enlarge interparticle gaps, and promote particle coarsening and agglomeration, resulting in poorer Mg deposition behavior. For the temperature theories,

both the 30°C and 50°C samples seem to be favorable, with small particle size and a compact and uniform surface. However, the 30°C sample exhibits poor electrochemical performance, which could be attributed to the insufficient growth of Cu under slow kinetics, which leads to interparticle gaps that SEM can't detect. The 50°C sample is proven to be the best. A similar observation applies to the sample of Cu^{2+} concentration. The 1.00 g/L sample has small and compact particles and a smooth surface, but the unconnected gaps between particles deteriorate its electrochemical performance. For DMAB concentration, it's hard to choose the best morphology from 0.8 g/L to 1.2 g/L since they resemble each other. However, only the 1.2 g/L sample exhibits outstanding electrochemical performance. This reflects the limitation of SEM characterization: SEM cannot fully reveal the internal microstructure of these smaller particles. The dynamic behavior during Mg deposition is out of consideration either, which explains the discrepancy between the morphology and the electrochemical performance. The cytosine and ethanol samples both have two samples prepared at similar concentrations that exhibited similarly favorable morphologies, but their electrochemical performances differed significantly. These could again be explained by the internal microstructure and the dynamic processes that are not detected.

In addition to the evaluation of the optimized results, several distinctions can be observed among the different plating conditions. Although both high temperature and prolonged plating time produced relatively large Cu particles, the high-temperature samples exhibited much better electrochemical performance, whereas extended plating times resulted in poor cycling stability. A similar contrast was observed for low CuSO_4 and low DMAB concentrations: both showed poor electrochemical performance, but the low CuSO_4 sample maintained a relatively uniform and fine-grained coating, while the low DMAB sample exhibited incomplete and highly nonuniform deposition. Another distinction appeared in samples with small grains. Although fine particles are often considered favorable, the low CuSO_4 samples with small grains still showed poor electrochemical performance, whereas additive-modified samples with similarly refined grains exhibited significantly improved electrochemical behavior. These

observations indicate that similar apparent morphologies can correspond to markedly different electrochemical performances, and that surface morphology alone is insufficient to evaluate the quality of the current collector.

The mechanism of the additives is discussed here. Cytosine works differently at different concentrations. At low cytosine concentrations, the Cu coating displayed a dense but rough morphology. This is because, at low concentration, cytosine increases the reaction rate by facilitating interfacial electron transfer through its delocalized π -electron system, promoting the reduction of Cu^{2+} to Cu.²⁶ With increasing cytosine concentration, cytosine acts as a refining agent²⁷: the Cu particles became more uniformly distributed and refined. This could be attributed to the coordination interaction between cytosine and Cu species. The N and O atoms in cytosine provide available lone-pair electrons that can interact with Cu^{2+} through coordination, thereby modifying the local Cu^{2+} coordination environment and reducing the excessive reduction rate of Cu species.^{28,29} Further raising cytosine concentration leads to nonuniform morphology because, by covering the copper surface, the excessive cytosine reduces the availability of active Cu species and decreases the effective nucleation density, causing newly reduced Cu atoms to preferentially deposit onto existing Cu nuclei instead of generating new ones.^{26,27}

Ethanol may improve the electroless Cu deposition by modifying the interfacial wetting behavior of the plating solution on the carbon fiber substrate. Owing to its lower surface tension compared with water, ethanol can facilitate the penetration of the plating solution into the internal pores of the CF framework and improve the accessibility of Cu species to the fiber surface.³⁰ The particles are more refined after its modification. In addition, alcohol-containing additives have been reported to influence Cu nucleation and growth kinetics through interfacial adsorption.³¹ These effects may promote more homogeneous Cu nucleation, thereby providing more activated sites for Mg deposition.

The additives may regulate Cu nucleation and growth by suppressing excessive local deposition, leading to a more uniform and continuous Cu coating. Such a regulated surface provides more uniformly distributed active sites for Mg nucleation and

promotes homogeneous electron and Mg^{2+} transport across the electrode. Moreover, the additives could change the surface structure and interfacial properties of Cu, further lowering the energy barrier for heterogeneous Mg nucleation. The particles are more refined after modification, thus providing increase density of active Mg nucleation sites. This is consistent with the significantly reduced Mg nucleation after additive incorporation. The magnesiophilicity is improved significantly.

These results suggest that the estimation of a current collector should rely on electrochemical performance rather than the SEM characterization of the morphology, since the undetectable microstructures and the dynamic Mg deposition process could not be reflected in the morphology. The introduction of additives can improve the magnesiophilicity of the Cu@CF with Mg metal, but further optimization is required to extend the half-cell's cycle life.

These results further highlight a broader issue in the theoretical evaluation of magnesiophilicity. Because Mg nucleation and deposition are decided by multiple thermodynamic and kinetic factors, static descriptors such as adsorption energy alone may not accurately predict the actual electrochemical behavior. Even static morphology is insufficient in reflecting the electrochemical performance. Therefore, we propose that magnesiophilicity should be evaluated directly through electrochemical measurements, with the Mg initial nucleation potential serving as an experimental indicator of Mg affinity and cycling stability reflecting the reversibility of Mg plating/stripping.

3.3 The full-cell Electrochemical Performance of Optimized Cu@CF

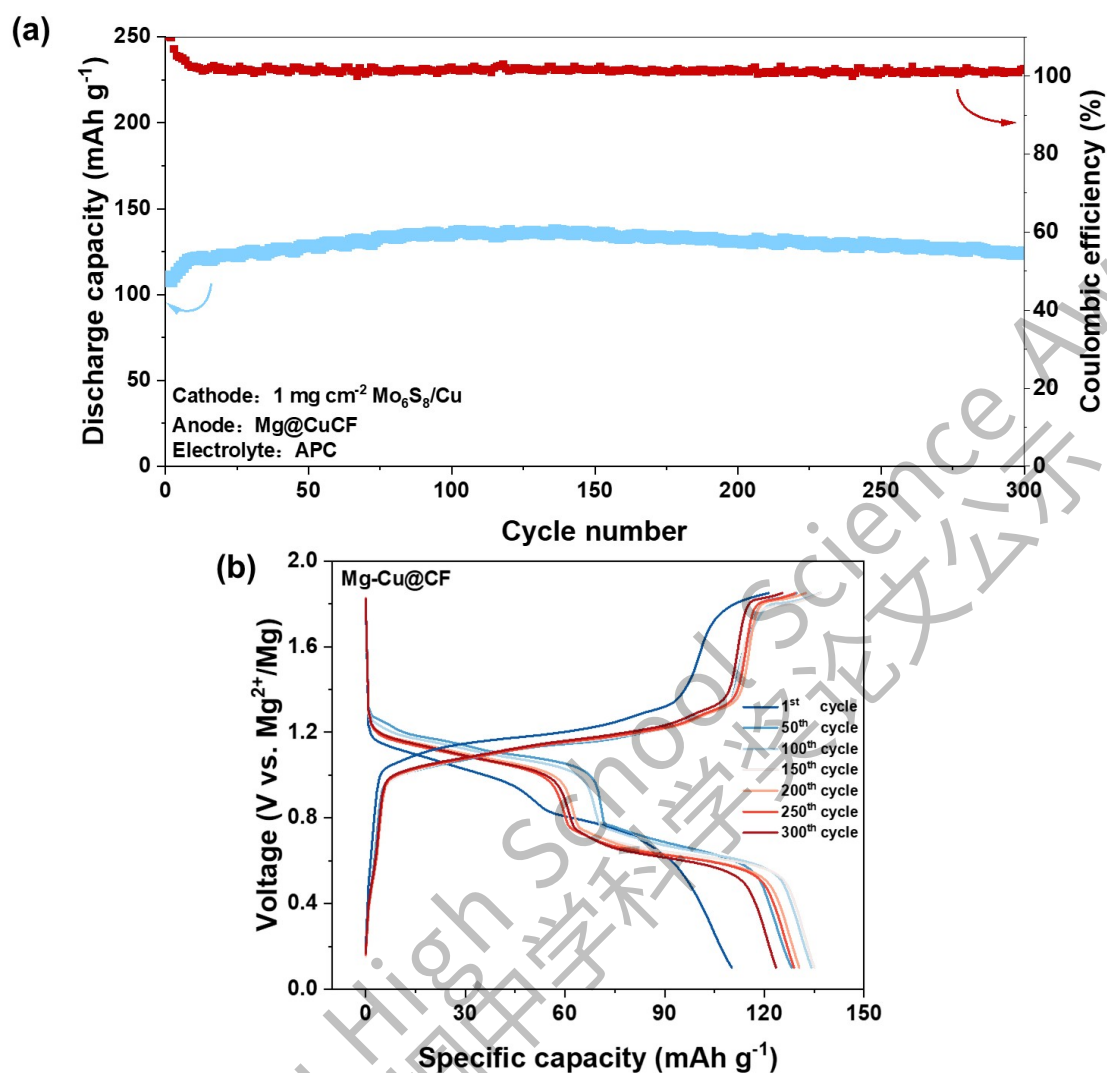


Figure 12. (a) Cycling performance of the Mg@Cu@CF||Mo₆S₈ full cell. (b) Galvanostatic charge–discharge profiles of the Mg@Cu@CF||Mo₆S₈ full cell at selected cycles.

To further evaluate the practical applicability of the optimized Cu@CF, a full cell was assembled using Mg@Cu@CF as the anode and Mo₆S₈ supported on Cu as the cathode, with an active-material loading of approximately 1 mg cm⁻². The cell was cycled at a current density of 100 mA g⁻¹, calculated based on the mass of Mo₆S₈. As shown in Figure 10, the full cell retained approximately 94% of its initial specific discharge capacity after 314 cycles, possessing an outstanding performance. The specific discharge capacity of the Cu@CF-based cell was 127.30 mAh g⁻¹, close to its theoretical capacity. After activation, the charge/discharge curve from the 50th to the 300th cycle largely overlaps, while the characteristic voltage plateaus associated with

Mg²⁺ insertion and de-insertion in Mo₆S₈ are well preserved. The limited change in voltage hysteresis during prolonged cycling indicates relatively stable electrochemical polarization.

The above results confirm that the optimized Cu@CF enables highly reversible Mg plating/stripping and serves as a stable host for Mg metal anodes during prolonged cycling.

4. Conclusion

In this work, a three-dimensional Cu@CF current collector was fabricated by electroless copper plating on carbon fiber paper for rechargeable magnesium batteries. An evaluation method for magnesiophilicity based on the electrochemical performance of the half-cell was established instead of using traditional DFT calculations. The initial nucleation potential is measured to reflect the magnesiophilicity, while the cycle number is used to reflect the stability of the cell. During the optimization, the effects of plating temperature, deposition time, CuSO₄ concentration, DMAB concentration, and additives on the Cu coating and electrochemical performance were systematically investigated, showing a discrepancy between the electrochemical performance and the morphology. This further highlights the significance of estimation through electrochemical performance.

The optimized Cu@CF exhibited improved Mg plating/stripping behavior and prolonged cycling stability. In full-cell tests with a Mo₆S₈ cathode, the optimized Cu@CF-based cell retained approximately 94% of its initial specific discharge capacity after 300 cycles at 0.8C, delivering a specific discharge capacity of approximately 127 mAh g⁻¹. Overall, this work demonstrates the potential of electroless-plated Cu@CF as an advanced 3D current collector and highlights the importance of directly incorporating electrochemical performance into current collector optimization.

5. Methods

5.1 Fabrication of Cu@CF 3D current collector

(1) CF substrate modifications

Commercial carbon fiber paper (CF) was first treated with plasma for 5 min to activate its surface. The plasma-treated CF was then immersed in a functionalization solution containing 20% (v/v) γ -aminopropyltriethoxysilane (KH550) for 15 min, followed by rinsing with distilled water to remove excess KH550. Subsequently, the functionalized CF was immersed in a sensitization solution containing 10 g L⁻¹ SnCl₂·2H₂O and 50 mL L⁻¹ of 37% HCl for 15 min to adsorb Sn²⁺ species onto the surface. After sensitization, the CF was rinsed with distilled water to remove residual sensitization solution. The sensitized CF was then activated by immersion in a solution containing 0.001 g L⁻¹ PdCl₂ and 50 mL L⁻¹ of 37% HCl for 15 min. Finally, the activated CF was thoroughly rinsed with distilled water to remove residual activation solution.

(2) Preparation of Cu@CF 3D current collector by electroless copper plating

Under the optimized conditions, the treated CF was immersed in an electroless copper plating bath at 50°C for 30 minutes. The bath contained copper (II) sulfate pentahydrate (CuSO₄·5H₂O, 0.006 mol L⁻¹), ethylenediaminetetraacetic acid disodium salt (EDTA, 0.006 mol L⁻¹), triethanolamine (TEA, 0.076 mol L⁻¹), and dimethylamine-borane (DMAB, 0.02 mol L⁻¹) as the reducing agent. Before immersion of the CC, either ethanol (30 mL L⁻¹) or cytosine (180 μ M) was added to the plating bath as an additive. After plating, the CF was rinsed with distilled water and ethanol to remove residues and dried.

To optimize the electroless plating conditions, the CuSO₄·5H₂O concentration, DMAB concentration, plating temperature, and plating time were systematically varied over the ranges of 0.003-0.008 mol L⁻¹, 0.003-0.034 mol L⁻¹, 20-70°C, and 20-60 min, respectively. At the same time, the other parameters were kept constant. To optimize the additive concentration, the cytosine concentration was varied from 22.5 to 315 μ mol L⁻¹, while the ethanol concentration was varied from 5 to 40 mL L⁻¹.

5.2 Characterization

The morphologies of Mg deposits and copper coating were analyzed using scanning electron microscopy (SEM, Hitachi S-4800). The structural properties of the samples were examined by X-ray diffraction (XRD, PANalytical X-Pert3 Powder) with a scanning range of 5-85° (2 θ) at a speed of 10° min⁻¹.

5.3 Electrochemical measurements

CR2032-type coin cells were assembled in an Ar-filled glove box (O₂ and H₂O < 0.1 ppm) to evaluate electrochemical properties. For half-cell tests, Cu@CF, CC, and Cu (19 mm diameter discs) were used as cathodes, while Mg foils (1 × 1 cm², 50 μ m thick) served as anodes. Separators included one layer of glass fiber (Whatman GF/D), with APC solution (0.4 M (MgPhCl)₂-AlCl₃ in THF, DodoChem Co., Ltd., China) as the electrolyte. The electrolyte volume was 200 μ L for glass fiber separators. The half cells were tested at a current density of 4 mA cm⁻² and an areal capacity of 4 mAh cm⁻². For full-cell tests, Mo₆S₈ cathodes with an active material loading of approximately 1 mg cm⁻² on Cu current collectors were paired with Mg@Cu@CF anodes. One layer of glass fiber separator (Whatman GF/D) and 200 μ L of APC electrolyte were used. The full cells were tested at a current density of 100 mA g⁻¹.

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致谢:

自从初中学习物理,我就经常接触电池,但是它大多只是作为电路中的一个元器件,从未真正学过它的内部机理,这让我感到十分好奇。到了高中,我开始系统学习化学,了解到物理化学这个领域,第一次认识了电池内部的微观结构,它让我觉得是一个极其动态和精密的体系,我非常感兴趣。同时,家中也有特斯拉电动车,冬天的时候掉电很快且续航不完美,确实带来了一些困扰。我也经常在新闻上看到电池起火爆炸伤人事件,总是心有余悸。于是,经过一番尝试,我联系了北京大学的李琦老师,有幸进入其课题组进行为期约半年的实验,进行镁电池负极集流体的研究,希望参与到电池迭代的技术洪流中,发展更安全更高效且对我国有优势的电池。

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该课题是基于我本身对于电池的兴趣,在我阅读该课题组文献与电池领域文献后与李琦老师探讨后形成的。整个实验,数据分析和论文由我一人完成。其中部分表征和测试由李琦老师课题组的周剑老师和陆林亚师姐辅助完成。由于不能自己操作扫描电子显微镜,周剑老师帮我进行了 SEM 表征,陆林亚师姐指导我组装电池并协助我进行电化学测试。在实验中,我确实遇到了困难,如不熟悉实验操作,不会使用等离子体处理器等,周剑老师带我熟悉实验环节并为我答疑,陆林亚师姐教我电化学方面的各种操作。

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本论文使用 ChatGPT 大模型进行文献的部分检索,使用 Plus 版本。使用范围为语言润色和翻译,对于学科基础问题的解答和论文修改建议的提出。论文主体部分和思路框架均未使用 AI。使用时间请见其他材料的 AI 部分,在论文修改时使用了。