**Copper-Plated Paper** 



# **Copper-Plated Paper for High-Performance Lithium-Ion Batteries**

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Paper is emerging as a promising flexible, high surface-area substrate for various new applications such as printed electronics, energy storage, and paper-based diagnostics. Many applications, however, require paper that reaches metallic conductivity levels, ideally at low cost. Here, an aqueous electroless copper-plating method is presented, which forms a conducting thin film of fused copper nanoparticles on the surface of the cellulose fibers. This paper can be used as a current collector for anodes of lithium-ion batteries. Owing to the porous structure and the large surface area of cellulose fibers, the copper-plated paper-based half-cell of the lithium-ion battery exhibits excellent rate performance and cycling stability, and even outperforms commercially available planar copper foil-based anode at ultrahigh charge/discharge rates of 100 C and 200 C. This mechanically robust metallic-paper composite has promising applications as the current collector for light-weight, flexible, and foldable paper-based 3D Li-ion battery anodes.

Paper products constitute the largest use of cellulose rich fibers from trees by volume.<sup>[1,2]</sup> As a substrate, paper has four interesting properties<sup>[3–5]</sup>: i) it is flexible and mechanically robust; ii) its surface can be patterned using numerous printing techniques; iii) it may be formed into different shapes and structures through folding, cutting, and stacking; iv) it has a fibrous texture where the fibers also have a hierarchical nano-sized fibrillar structure with a large specific surface area that can be chemically modified to bind numerous materials (such as biomolecules and nanomaterials). Paper can also carry and transport liquids through spontaneous wicking and capillarity.

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Thanks to all these properties, paper has shown potential in a number of applications such as printed electronics,<sup>[4,6]</sup> paper microfluidics,<sup>[7,8]</sup> and energy storage devices.<sup>[9,10]</sup> Its full potential in these applications is, however, limited by the electrically insulating nature of the cellulose fiber (e.g., in electrochemical energy storage where high electronic conductivity is usually required).<sup>[9,11]</sup> One common method of endowing paper with electronic conductivity is to decorate the cellulose fibers with organic conductors such as poly(3,4-ethylenedioxythiophene)-(PEDOT:PSS),<sup>[12]</sup> poly(styrenesulfonate) polyaniline (PANI),<sup>[13]</sup> carbon nanotubes (CNTs),<sup>[14]</sup> or graphene.<sup>[15]</sup> These conductive materials can be coated onto cellulose fibers by simply dipping or soaking

paper into the dispersions of the conductive materials or their corresponding precursors.<sup>[16,17]</sup> Alternatively, these dispersions can be filtered through the paper to absorb the materials into the cellulose fibers.<sup>[18,19]</sup> Typically, a conformal conductive coating is deposited on the cellulose fibers. These coatings preserve the mechanical flexibility of both the fibers and the paper.<sup>[20]</sup> The shortcoming of organic electronic inks is, however, their relatively low conductivity. Worfolk et al. reported the highest conductivity of PEDOT:PSS thin films as 4600 S cm<sup>-1</sup> with a sheet resistance of 17  $\Omega \Box^{-1,[21]}$  (typical conductivity of PEDOT:PSS is around 1000 S cm<sup>-1</sup>)<sup>[4,22]</sup> which still falls short by orders of magnitude for applications that require low resistance, and high currents such as printed circuit boards.<sup>[6]</sup> Since most of these polymers are p-type semiconductors, which lose their conductivity at a reducing current,<sup>[23]</sup> their use as current collectors for electrochemical energy storage is bound to be limited. CNTs are an alternative to conducting polymers used to make electronically conductive paper. Hu et al. reported CNTcoated paper with a sheet resistance of  $\approx 10 \Omega \square^{-1}$  and explored its potential as a lightweight current collector for lithium-ion batteries.<sup>[24]</sup> That is, to the best of our knowledge, the lowest sheet resistance obtained with organic electronic materials on paper.

In contrast, metals such as silver  $(6.30 \times 10^5 \text{ S cm}^{-1})$  or copper  $(5.96 \times 10^5 \text{ S cm}^{-1})$  form thin films with a sheet resistance up to 3 orders of magnitude lower than that of organic conductors.<sup>[11,24,25]</sup> Copper (Cu) is particularly attractive for paper electronics<sup>[26]</sup> because it has extremely low resistivity and relatively low cost compared to organic conductors or silver



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**Figure 1.** Copper-plating and glycerol treatment. a) Schematic illustration of the paper copper-plating process. Microscopic and SEM images at different magnifications of b) the bare paper, c) the copper-plated paper before glycerol treatment, and d) after glycerol treatment.

(see Table S1, Supporting Information). Cu can be printed – and therefore patterned – on paper substrates from ink nanodispersions.<sup>[25]</sup> The Cu coating obtained from the latter method is, however, limited to the outer surface, which leaves the majority of the inner area of the fiber insulating. This is attributed to the large size of ink particles, which prevents penetration into the fiber bulk and, hence, the paper.<sup>[27]</sup> In addition, printing Cu generally requires a sintering step to fuse the particles and make the patterns conducting.<sup>[28,29]</sup> This post-treatment significantly increases the energy expenditure of production as well as limits the potential substrates to thermally insensitive ones.<sup>[30]</sup> Alternatively, metals are sputtered<sup>[31]</sup> and evaporated onto paper.<sup>[32]</sup> All of these methods, however, fail to optimally utilize the internal bulk structure of paper, or access the internal structure of the fibers.

In this work, we present an electroless Cu-plating method where we coat a thin layer (~370 nm) of interconnected Cu nanoparticles on cellulose fibers. The plating process involves soaking the paper in a precursor solution and then in glycerol. This facile process endows the resulting Cu-plated paper (CPP) with a metallic-like conductivity (960 ± 150 S cm<sup>-1</sup>) even at low Cu volumetric fractions (1.6%). This CPP exhibits extremely low sheet resistance of 72 ± 12 m $\Omega$   $\Box^{-1}$ , which is up to 3 orders of magnitude lower than what may be achieved using organic electronic inks,<sup>[21]</sup> carbon nanomaterials,<sup>[33,34]</sup> or inkjet-printed copper (0.1–2  $\Omega$   $\Box^{-1}$ ).<sup>[35–37]</sup> Our Cu-plating process maintains the high porosity intrinsic to paper. We exploit this unique property to demonstrate paper-based 3D Li-ion battery (LIB) anodes

with excellent cycling stability and stable rate performance even at ultra-high charge/discharge rates (100 C and 200 C).

We coated a Whatman chromatography paper with interconnected Cu nanoparticles using a chemical deposition method (shown schematically in **Figure 1**a). We chose this type of paper as our model substrate because of its high cellulose purity and high specific surface-area structure (see Figure 1b), which facilitates liquid transport inside the paper. This paper is also standardized, which is helpful for consistency and repetition of the experiments. Whatman paper can, however, be easily replaced with other papers for large-scale production of CPP. The reaction route of the electroless Cu plating is shown in Equation (1). Dimethylamineborane (DMAB) reduces the copper precursor, namely Cu (II) chloride, into copper in situ.

$$4(CH_3)_2 \text{ NHBH}_3 + 12CuEDTA^{2-} + 9OH^- \rightarrow HB_4O_7^-$$
  
+12Cu+4(CH\_3), NH\_2^+ + 12HEDTA^{3-} + 2H\_2O (1)

Boric acid acts as a buffering agent to stabilize the pH during the reduction.<sup>[38]</sup> Ethylenediaminetetraacetic acid (EDTA) acts as a coupling reagent to modulate the reaction rate and to maintain a homogeneous distribution of Cu<sup>2+</sup> ion over the surface of paper fibers.

After the Cu plating, we placed the CPP in a glycerol bath at 180  $^{\circ}$ C for 30 min to reduce any excessive copper oxides, as follows:



$$Cu_2O + 2 \xrightarrow{HO} \xrightarrow{OH} \rightarrow 2 Cu + 2 \xrightarrow{HO} \xrightarrow{O} \xrightarrow{OH} + H_2O$$
(2)

More importantly, this glycerol treatment sinters the Cu particles.<sup>[39]</sup> During the latter step, the paper turned from brownish red, a color characteristic of copper oxides, into reddish-orange, characteristic of Cu (Figure S1, Supporting Information). Figure S2 in the Supporting Information shows a comparison of the X-ray diffraction (XRD) patterns of the CPP before and after glycerol treatment. Before the glycerol treatment, there were trace amounts of cuprous oxide in the CPP. Only characteristic diffraction peaks of crystalline Cu remained in the pattern after the treatment, which is evidence of the effectiveness of the glycerol bath at reducing impurities. Moreover, the glycerol treatment sintered the Cu particles and formed a uniform Cu film on the fiber surface (see Figure 1c,d). The sintering also happens at the junctions between fibers, which increases the conductivity further.

We measured the thickness of the CPP to be 147  $\pm$  8 µm (that of the unmodified bare paper was  $144 \pm 5 \mu m$ ). The thickness of the copper layer was  $370 \pm 190$  nm, statistically collected from several scanning electron microscopy (SEM) images. The relatively large deviation was a result of the big grain size of the Cu particles and the thicker layer at the joints of cellulose fibers. The weight of the deposited Cu was 2.2 mg cm<sup>-2</sup>, corresponding to a total volume fraction of 1.6% Cu in the CPP. We note that this weight is only one-fifth of the weight of a standard Cu foil for battery (11 µm in thickness). The optical microscopy and SEM micrographs in Figure 1b-d clearly indicate that the CPP retains the porous structure of the paper with a thin continuous cladding of Cu on the cellulose fibers. We also observed the Cu layer wrapping around a single cellulose fiber (shown in Figure S3, Supporting Information). From SEM with energy-dispersive X-ray spectroscopy (EDX) element mapping, we observe that the Cu is distributed in the bulk of the paper and interconnected, even inside the paper (see Figure S4, Supporting Information). These results suggest that we managed to plate Cu inside the bulk of the paper and, hence, utilized its inner surface area.

The conductivity of the glycerol-treated CPP is 960 ± 150 S cm<sup>-1</sup> (that of CPP without glycerol treatment is 548 S cm<sup>-1</sup>). We divide the conductivity value by the volume fraction (1.6%), which gives a conductivity of  $6.0 \times 10^4$  S cm<sup>-1</sup> for the Cu phase of our composite. This value is barely one order of magnitude lower than the conductivity of a crystal-line slab of Cu at 20 °C ( $5.9 \times 10^5$  S cm<sup>-1</sup>), which is remarkable considering the random structure of the paper substrate. We calculated the effective surface area of the Cu in CPP from its sheet resistance ( $72 \pm 12 \text{ m}\Omega \square^{-1}$ ) as 9 times the projected 2D area of paper (see Experimental Section). This large surface area of Cu stems from the porous structure of the bare paper and indicates a 3D interconnected conducting cladding around the cellulose fibers.

The low-resistance CPP retains the porosity and high surface area of the paper, and acts as a 3D scaffold for electronic devices. This feature is advantageous for energy storage systems, e.g., LIB current collectors. An ideal current collector should have negligible resistance, high surface area, short and efficient conducting pathways from the active battery material to the current collector, and a surface onto which the active material can be deposited easily (e.g., printed). As our CPP ticks all these boxes, we set out to make a high-performance anode using the CPP as both the current collector and the supporting substrate. We fabricated LIB anodes (see Figure 2a) by covering the CPP with a slurry, which contains lithium titanate (LTO) nanoparticles (0.22 mg cm<sup>-2</sup>) as the lithium intercalating material, multi-wall carbon nanotubes (MWCNTs) as the electron conductor, and cellulose nanofibrils (CNF) as binder. The slurry was able to penetrate into the porous CPP and formed a film around the conductive fibers. From the SEM images in Figure 2b, we observed evenly distributed cubic LTO nanoparticles on the surface of the Cu coating on the paper. We then assembled a half-cell battery by packaging the CPP-based anode together with a piece of lithium foil (Figure 2a). As a control, we also used a commercially available Cu foil (11  $\mu$ m thick, with a sheet resistance of 1.5 m $\Omega$   $\Box^{-1}$ ) as current collector and fabricated a half-cell battery using the same slurry composition and device structure.

We performed cyclic voltammetry (CV, Figure S5, Supporting Information) at a scan rate of 0.1 mV s<sup>-1</sup> to evaluate the CPP-based LIB. The CPP- and Cu foil-based electrodes showed a similar CV behavior. We observed an anodic peak current of 0.32 A  $g^{-1}$  at 1.69 V (vs Li/Li<sup>+</sup>) and a cathodic peak current of 0.29 A g<sup>-1</sup> at 1.46 V for the CPP-based electrode. The Cu foilbased electrode showed a peak anodic current of 0.52 A  $g^{-1}$ at 1.67 V and a peak cathodic current of 0.49 A  $g^{-1}$  at 1.47 V. The anode assembled on CPP had lower currents and a wider separation of the peak potentials than the Cu foil-based anode. The anodic and cathodic peak currents of each anode were not identical, which may be attributed to some irreversible reactions happening to the anodes.<sup>[40]</sup> At a cycling rate of C/10, the CPP-based anode showed a specific capacity of 125 mAh g<sup>-1</sup> (Figure 2c) while the anode on Cu foil showed a capacity of 156 mAh g<sup>-1</sup> (Figure S6a, Supporting Information). These specific capacities are both lower than 175 mAh g<sup>-1</sup>, which is the theoretical capacity of LTO (likely due to inefficient use of the active sites of LTO, or as a result of a less tightly packed configuration of the pouch cells).

We tested the rate performance of the CPP-based anode at various charge/discharge current densities, ranging from C/10 to 200 C (Figure 2c,d). The half-cell worked over this entire C-rate range. After the first 15 cycles at C/10 and C/2, the anode exhibited stable and reversible capacities. For all the cycles (except the starting cycle of each C-rate), the coulombic efficiency was in the range of  $100 \pm 1\%$ . We derived the specific capacity as 108 mAh g<sup>-1</sup> at 1 C with almost no loss in capacity after 55 cycles at various charge/discharge C-rates, ranging from C/10 to 200 C. This result clearly indicates the high rate capability of the CPP-based anode.

We evaluated the stability of the CPP-based electrode by cycling at 1 C for 100 cycles. During these cycles, the anode exhibited highly stable charge/discharge behavior with nearly identical profiles (Figure 2e). Moreover, the half-cell retained 98% of its initial capacity after 100 cycling with coulombic efficiency of nearly 100% (Figure 2e,f).

As shown in **Figure 3**, we were able to repeatedly and stably charge and discharge the CPP-based anode at 100 C and 200 C.







**Figure 2.** Configuration and performance of the CPP-based half-cell. a) Schematic illustration of the configuration of the copper-plated paper-based half-cell. b) SEM images of the paper-based anode. Electrochemical performance of the paper-based anode for LIB: c) charge/discharge profiles at different C-rates, d) rate performance, e) charge/discharge profiles at 1st, 10th, 50th, and 100th cycles at 1 C, and f) cycling performance at 1 C.

In contrast, the discharge behavior of the Cu foil-based anode ranged from a slight (at 20 C) to a pronounced distortion (at 50 C), indicating an unstable insertion of  $Li^+$  (Figure S6a,b, Supporting Information). When the C-rate increased to 100 C

or 200 C, the half-cell based on Cu foil started malfunctioning to the point where the charge/discharge displayed erratic behavior (Figure 3d; Figure S6a,b, Supporting Information). To the best of our knowledge, our work is the first investigation presenting







Figure 3. Comparison between the copper-plated paper and Cu foil as current collector for LIB anodes. a,b) Schematic illustration showing the differences of electron and ion transport between the paper-based anode and the Cu foil-based anode. The 10 charge/discharge cycles of c) the CPP and d) the Cu foil-based anode at 100 C and 200 C. EIS spectra change of e) the CPP and f) the Cu foil-based anode after 100 cycles of charge/discharge at 1 C.

an LIB anode, based on a commercially available LTO, that can be cycled at 100 C and 200  $\rm C.^{[40-42]}$ 

These results demonstrate that the performance of the LIB half-cell benefits from the porous, conducting architecture of the CPP. We propose three reasons for the high charging rate performance. i) Compared to bulk copper foil, the CPP structure increases the effective conducting surface area by 9 times with minimum amount of Cu. ii) The interconnected structure of the CPP enables electron transport in all directions: both around the fiber, and between the fibers. A Cu foil, however, only allows electron conduction inside its bulk as schematically shown in Figure 3a,b. iii) The pores of the paper and the interior structure of cellulose fibers also enable ion transport in all directions around the electrolyte-soaked fibers. As a result,

the CPP provides more evenly distributed electron/ion transport pathways and mitigates the electrical loading per area of conducting surface, which makes high C-rate charge/discharge possible when large currents are applied.

To further understand the dynamics of the CPP based batteries, we performed electrochemical impedance spectroscopy (EIS). The charge transfer resistance of CPP-based electrode, indicated by the diameter of the hemisphere at the high- to medium-frequency region of the EIS spectra, was higher than that of Cu foil-based electrode. This effect is due to the extended surface area of the CPP (Figure 3e,f), which provides more active sites. After 100 cycles of charge/discharge, the charge transfer resistance decreased because of the improved wetting of the electrolyte into the porous structure of the paper-based electrode, which enhanced the ion transportation across the interfaces between the fibers of the electrode. In addition to the ionic transport between the fibers, the interior structure of the cellulose fibers in paper also acts as efficient pathways for ionic transport.<sup>[43]</sup> We obtained lower diffusion resistance for the (ionically transporting) CPP-based electrode, which is indicated by the steeper tail at the low-frequency region in the EIS spectra. The CPP-based electrode also showed lower intrinsic resistance in the high-frequency region than the Cu foil-based electrode (i.e., the real component of the impedance at 200 kHz was 3.3  $\Omega$  for the CPP electrode, lower than the Cu foil's 4.9  $\Omega$ ; see insets in Figure 3e,f). The lower intrinsic resistance enabled an improved rate capability.

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In summary, the excellent rate capability of the CPP-based half-cell outperforms conventional Cu foil-based electrodes and enables the possibility of charging/discharging the half-cell within 36 and 18 s, respectively, which is significantly shorter than typical charge/discharge time required for LIBs.

To demonstrate the flexibility of the CPP-based electrode, we tested the effect of rolling and folding on the electrochemical performance. This was achieved by characterizing the half-cell while rolling the battery around a cylindrical vial with a diameter of 1.5 cm (**Figure 4**a,b), and folding the half-cell by 180° (Figure 4c,d). The half-cell exhibited a capacity of 107 mAh g<sup>-1</sup> (when rolled) and 99 mAh g<sup>-1</sup> (when folded), at 1 C, which is slightly lower than the capacity measured when the half-cell is unbent. Furthermore, it maintained its ultra-high rate capability at 100 C and 200 C, and cycling stability. Both the rolled and folded devices retained more than 99% of the specific

capacity after 50 cycles of charge/discharge at 1 C. The performances of the rolled and folded anode were nearly identical to the performances of the unbent anode, indicating excellent mechanical stability of the CPP as current collector for anode of LIB.

We developed a method for electrolessly plating Cu on cellulose paper. Our process deposits a thin, conformal layer of fused Cu nanoparticles around the fibers of the paper. On the one hand, CPP offers several advantages: i) for a cellulose composite, it has a high conductivity of 960 ± 150 S cm<sup>-1</sup> and very low sheet resistance of 72 ± 12 m $\Omega$   $\Box^{-1}$ ; ii) its production process is compatible with large-scale printing/cutting; iii) it is mechanically robust and does not lose its conductivity upon rolling, folding, or even creasing; iv) it retains the porous structure of the paper substrate providing a surface area up to one order of magnitude that of the 2D area of paper. On the other hand, the Cu-plating process is time consuming (72–96 h). Further optimization, such as adjusting the reaction temperature, may mitigate this issue.

We exploited the high surface area of the electrically conducting CPP to assemble and characterize paper-based LIB anodes. These flexible anodes exhibited excellent rate performance and good cycling stability, especially at ultra-high charge/discharge rates (100–200 C), where they even outperformed Cu foils, which are widely used in commercial LIBs.

The demonstrated CPPs is potentially useful in many other areas such as water/air cleaning,<sup>[44,45]</sup> heat sink,<sup>[46]</sup> electrochemical sensors,<sup>[47]</sup> and paper microfluidics,<sup>[48]</sup> where porous structure would enhance the performance of Cu substrates.



Figure 4. Battery performances while bending. a) A photograph showing the rolled Cu-plated paper-based half-cell lighting up a LED and b) the corresponding rate performance. c) A photograph showing the half-cell lighting up a LED while folded and d) the corresponding rate performance.





## **Experimental Section**

Cu Plating and Glycerol Treatment: We dissolved  $250 \times 10^{-3}$  M EDTA,  $250 \times 10^{-3}$  M Cu (II) chloride, and 0.5 m boric acid in water and adjusted pH to 7.0 with sodium hydrate. We stored the solution at 4 °C, and added 0.5 m DMAB into the solution just before use.

We soaked the cellulose paper in the solution and carried out the reaction at 4  $^{\circ}$ C until the blue solution turned colorless (generally the reaction took 3-4 days). The CPP was then washed thoroughly with ultrapure water and vacuum dried at room temperature.

We immersed the CPP into glycerol and heated up to 180  $^\circ C$  for 30 min. Then we washed the CPP with ethanol and dried it with nitrogen gas.

Square Resistance Measurement and Conductivity Calculations: We used a Keithley 2401 sourcemeter to carry out the conductivity/resistance measurement with a four-probe connection. We measured the length and width of the CPP with a digital caliper, and the thickness with a Mitutoyo Absolute thickness gauge at room temperature and a relative humidity of 50%. We measured the resistance of the sample and calculated the conductivity ( $\sigma_c$ ) as follows:

$$\sigma_c = \frac{L}{R \times W \times t_c} \tag{3}$$

where *R* is the resistance measured; *W* is the width of the sample;  $t_c$  is the thickness of the composite; and *L* is the length of the measured area.

We calculated the sheet resistance  $(R_s)$  of the CPP as follows:

$$R_s = \frac{R \times W}{L} \tag{4}$$

We calculated the effective thickness  $(t_e)$  of Cu thin layer as follows:

$$t_e = \frac{1}{R_s \times \sigma_{Cu}} \tag{5}$$

where  $\sigma_{Cu}$  is the conductivity of pure copper,  $5.96\times 10^5$  S cm^-1. We do this calculation based on the following hypothesis: i) the effective Cu is the pure Cu, which contributed to the conductivity; ii) the sheet resistance is independent from surface flatness.

We calculated the effective conducting surface area ( $S_{\rm e})$  of the CPP as follows:

$$S_e = \frac{m/\rho}{t_e} \tag{6}$$

where *m* is the weight of the deposited Cu;  $\rho$  is the density of pure Cu (8.96 g cm<sup>-3</sup>); and  $t_e$  is the effective thickness of Cu calculated on the basis of sheet resistance with Equation (5).

Battery Assembly and Electrochemical Measurements: We casted a slurry of which the dry content consists of LTO (80 wt%), MWCNT (10 wt%), and CNF (10 wt%) onto the CPP and the Cu foil with mass loading of LTO of 0.22 mg cm<sup>-2</sup>. We packaged the as-prepared anode with a piece of lithium foil as the counter electrode and a polyethylene (PE) separator into a pouch cell containing 1.0 M LiPF<sub>6</sub> in EC/DEC = 50/50 v/v as the electrolyte inside a glovebox (MBraun Labstar, with both moisture and oxygen levels less than 1 ppm).

We performed the electrochemical characterizations of the CPP as a current collector for anode of LIB with a BioLogic VSP potentiostat/galvanostat using two-electrode configuration. We conducted the characterizations in the sequence of CV, rate performance, and cycling stability. In each of the charge/discharge cycles, we discharged the half-cell first and then charged it. For different C-rates, we took 1 C as 175 mA  $g^{-1}$  for LTO. We calculated the Coloumbic efficiency (CE) as follows:

$$CE = \frac{C_{Charge}}{C_{Discharge}} \times 100\%$$

where  $C_{\text{Charge}}$  is the specific capacity of charging and  $C_{\text{Discharge}}$  is the specific capacity of discharging in the same cycle.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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#### **Conflict of Interest**

The authors declare no conflict of interest.

#### Keywords

copper-plating, lithium-ion batteries, paper

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