Supercapacitor Electrodes Based on Three-Dimensional Copper Structures with Precisely Controlled Dimensions

Andac Armutlulu,*^[a] Lawrence A. Bottomley,^[b] Sue Ann Bidstrup Allen,^[c] and Mark G. Allen^[d]

Well-ordered three-dimensional Cu architectures serving as low-resistance current collectors for supercapacitor applications are fabricated by combining microfabrication and electrochemical techniques. These techniques enable the realization of electrodes with precisely controlled characteristic dimensions, including the surface area, thickness of the active material, and interlayer spacing. Highly laminated Cu structures are formed by through-mold electrodeposition of alternating Ni and Cu layers followed by selective electrochemical removal of Ni layers. Underpotential deposition is utilized to precisely measure the electrochemically accessible surface area of the resultant Cu structure. A conformal, thin layer of nickel hydroxide is electrodeposited onto the Cu backbone, forming the supercapacitor electrode. The resulting electrodes exhibit a high specific capacitance value of 733 Fg⁻¹. In cycle testing, the electrodes deliver 94% of their capacitance after over 1000 cycles. The supercapacitor is also shown to deliver 69% of its 5 mV s⁻¹ capacity at rates as high as 25 mV s⁻¹. These results illustrate the benefits of using well-ordered metal architectures as current collectors for advanced electrochemical energy storage applications.

1. Introduction

There is a high demand for energy-storage devices with both high power and energy densities. Numerous studies have focused on the design of materials that enable a simultaneous improvement in both aspects.^[1-6] These studies mainly involve enhancing the power densities of batteries or the energy densities of supercapacitors. Improvements to energy density can be achieved by improved energy-storage materials and/or increasing the percentage of mass or volume in the system devoted to the energy-storage material. Power density, on the other hand, is limited by the transport of ionic and electronic species from one electrode to the other, as well as the reaction kinetics at the electrodes. Multiple factors play vital roles in the energy-transfer rate. Certain factors, such as the diffusivity and conductivity of the system components, are determined by the choice of electrode materials, electrolytes, and operating conditions of the system. Other factors, however, mainly rely

[a] Dr. A. Armutlulu
School of Chemical and Biomolecular Engineering Georgia Institute of Technology
311 Ferst Drive NW, Atlanta, GA 30332 (USA)
E-mail: aarmutlulu3@gatech.edu
[b] Dr. L. A. Bottomley
School of Chemistry and Biochemistry
Georgia Institute of Technology
901 Atlantic Drive, Atlanta, GA 30332 (USA)

[c] Dr. S. A. Bidstrup Allen
 Department of Chemical and Biomolecular Engineering
 University of Pennsylvania
 220 South 33rd Street, Philadelphia, PA 19104 (USA)

 [d] Dr. M. G. Allen
 Department of Electrical and Systems Engineering University of Pennsylvania
 200 South 33rd Street, Philadelphia, PA 19104 (USA) on geometric design choices such as surface area, porosity, active material thickness, and interelectrode distance. Improvements in power density require an optimization process that takes these multiple factors into account.

Ideally, high-power electrochemical devices should possess large electrode surface area and minimum thickness of the active material, in order to maintain their high-power capabilities. The maximization of the surface area per unit mass or volume is important, as it increases the amount of active material located at or near the electrode–electrolyte interface. The active material thickness, on the other hand, sets the diffusion and conduction path lengths for ions and electrons, respectively. These path lengths determine the internal resistance of the system during the charge and discharge processes. Hence, the minimization of these path lengths plays a vital role in the performance of the device.

Examples of approaches to maximize electrode surface area include various structures constructed from metal networks, nanotubes, aerogels, and xerogels.^[7–13] These structures offer complex geometries with extremely high surface area, yet they are mainly fabricated in a non-deterministic way, which limits the control over their critical dimensions, as well as over their uniform reproducibility and scalability.

Herein, we present a method for fabricating and characterizing well-ordered, scalable, and high-surface-area 3D Cu architectures suitable for use as current collectors in electrochemical energy-storage applications. These Cu architectures feature precisely controlled characteristic lengths that address the aforementioned critical factors and ultimately determine the device performance. The method involves robotically assisted sequential electrodeposition of alternating Cu and Ni layers to form a multilayer structure of desired thickness. Performing

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this process under current-controlled conditions enables precise control over the dimensions of individual layers in the multilayer structure. Laminated, high-surface-area Cu architectures are obtained by selective electrochemical etching of sacrificial Ni layers from the multilayer structures. The surface area of the resultant Cu architecture was analyzed by using underpotential deposition (UPD) of thallium (TI). Upon completion of the surface area analysis of the laminated Cu structure through UPD, the conformal electrodeposition of a thin nickel hydroxide [Ni(OH)₂] film onto the backbone is carried out to form the supercapacitor electrode. The electrochemical performance of the supercapacitor electrode, including its capacitance, power capability, and cycling stability is evaluated by using cyclic voltammetry (CV), as well as galvanostatic charge and discharge tests.

2. Results and Discussion

2.1. Fabrication of Multilayer Cu/Ni Structure

The fabrication of a Cu electrode is schematically illustrated in Figure 1. Initially, a photoresist mold was patterned on a Cusputtered glass substrate. It was followed by electroplating of the Cu and Ni layers from their respective baths in an alternating fashion by using an automated robotic process. After the



Figure 1. Fabrication sequence of the multilayer electrode: A) photoresist mold with a pillar array deposited and patterned on Cu-sputtered glass substrate, where the shape of the pillars dictates the geometry of the etching holes; B) robotically assisted sequential electrodeposition of alternating Cu and Ni layers followed by stripping of the photoresist mold; C) deposition and patterning of the second photoresist mold for the anchors and the connection pad; D) electroplating of the Cu anchors and the connection pad followed by the stripping of the mold and the selective electrochemical removal of the Ni layers; E) optical image showing the top view of the resulting multilayer Cu structure.

electrodeposition of 25 Cu/Ni pairs, the initial photoresist mold was stripped by using acetone. A second photoresist film of the same type as the first one was then patterned on the multilayer structure, which served as the mold for the electrodeposition of Cu anchors, as well as the connection pad, onto the specific regions of the multilayer structure. Upon completion of the anchor electrodeposition, the second photoresist layer was removed again through immersion in acetone. Figure 1E demonstrates the resulting structure fabricated on a footprint area of 1×1 cm². Additional details about the fabrication process of the multilayer structures can be found in our previous studies, where the removal of Cu over Ni was performed by means of selective wet etching to realize Ni-based electrodes for battery applications.^[14,15]

The electrodeposition of the Cu and Ni layers was performed under galvanostatic conditions at room temperature. In this way, for a given exposed surface area, we have precise control over the thickness of each individual layer simply by adjusting deposition time and current density. The theoretical surface area of the resultant structure can be estimated by taking into account the footprint area of 1 cm², the number of Cu layers (25), and by removing the area taken up by the etching holes to give a calculated area of 40 cm². The accuracy of the value will be checked by the UPD technique, as described in the corresponding section.

Although the etching holes reduce the electrode surface area by 20%, they play a vital role in mass transport during both the etching and operation steps. In the etching process, the duration for removal of the sacrificial Ni layers is significantly decreased by the incorporation of the etching holes as they minimize the etching depths. In terms of the electrode operation, the holes provide reduced diffusion pathways for the liquid-state ions of the electrolyte, which is essential for high-power applications. The etching holes, along with the anchors supporting the structure, are depicted in Figure 2.

2.2. Selective Electrochemical Dissolution of Ni Layers

Numerous studies concerning the selective electrochemical dissolution of metals have been reported.^[8, 16-18] Most involve



Figure 2. Optical images showing the anchors and the etching holes of the multilayer structure: A) corner of the structure shown in Figure 1E and B) enlarged view of one of the anchors with a successful step coverage inside the etching holes.

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dealloying, where the least noble element in a structure, fabricated as a homogeneous solid-phase solution of two or more metals, is selectively dissolved in an electrolyte, resulting in highly porous interconnected structures. These structures render functional nanoporous materials with high surface-tovolume ratios; yet, they are fabricated in a non-deterministic fashion, which makes it difficult to maintain control over their aforementioned critical dimensions. As described earlier, the focus of the approach presented herein is to develop laminated structures composed of individual layers with controlled thicknesses and geometric surface areas, enabling well-ordered 3D structures following the removal of the sacrificial material.

Cu is thermodynamically more stable than Ni. The standard electrode potential (SEP) for the Ni²⁺/Ni couple, relative to the standard hydrogen electrode (SHE), is reported as -0.25 V, whereas the SEP of Cu²⁺/Cu couple is 0.34 V. Hence, Ni layers are readily and selectively dissolved in acidic solutions when a potential is applied that lies between the redox potentials of Ni²⁺/Ni and Cu²⁺/Cu. Ni, however, undergoes passivation in acidic solutions, complicating the selective dissolution process. The passivation has been revealed to be less effective in the presence of sulfur.^[19,20] Hence, sulfuric acid (H₂SO₄) is the preferred etching solution in this step.

The optimal potential for the selective etching of the Ni layers in H_2SO_4 was determined from the potentiodynamic curves shown in Figure 3. The curves were generated by



Figure 3. Potentiodynamic plots for Ni and Cu in 0.1 M H₂SO₄ solution: A) current responses of the Ni and Cu electrodes after sweeping the potential from -1 to 0.4 V at a scan rate of 5 mV s⁻¹ and B) close-up view of the corrosion potential region showing the difference between Ni and Cu corrosion potentials.

sweeping the potential from a cathodic potential of -1.0 V to 0.4 V in the anodic region at a scan rate of 5 mV s⁻¹. The corrosion potentials for Ni and Cu in this medium were -58 and -18 mV, respectively. To achieve Ni dissolution with infinite selectivity, the applied potential should fall between these two corrosion potentials. Also, to maximize the selective dissolution rate of Ni layers without sacrificing any Cu, the applied potential needs to be just below the corrosion potential of Cu.

(A) Си аnchors (B) 500 µm (С)

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3 µm

Figure 4. SEM images of the multilayer structure: A) tilted view showing the corner of the multilayer Cu structure, B) Cu layers inside the etching hole supported by the anchor following the selective removal of Ni layers, and C) close-up view of the individual Cu layers.

10 µm

Therefore, the optimum potential was found to be -20 mV. Selective etching of the Ni layers was achieved at this potential over a 24 h period. Figure 4 illustrates the scanning electron microscopy (SEM) images of the multilayered Cu structure after the selective removal of the Ni layers. As can be seen in Figure 4, the Cu anchors provide a mechanical support to prevent the Cu layers from collapsing on each other upon complete removal of Ni layers. The anchors also enable an interlayer electronic conduction path.

2.3. Surface Area Characterization of the Cu Backbone

In energy-storage applications, knowledge of the effective electrode surface area (i.e. electrochemically active surface area) is vital to the design and ultimate performance of power devices. It is also well known that the actual surface area of electrodeposited films significantly differs from their physically apparent geometrical surface area, owing to the surface roughness and the morphology of the deposits. Factors such as the composition and aging of the electroplating bath, plating current density, temperature, and choice of substrate to be electroplated can have a substantial effect on the porosity and grain size of the deposited films.^[21-25] For simple geometries such as single-layer thin films, the surface roughness can easily be determined through the usual scanned-probe techniques. However, for our multilayer Cu structure, with a relatively complex 3D architecture, determining the surface roughness can only be achieved for the topmost layer. Although the Brunauer-Emmett-Teller (BET) method is the most widely used technique for determining the surface area of various materials, it has limited utility in complex structures that are composed of electrodes, connection pads, packaging material, and substrate.^[26] Additionally, there are several shortcomings associated with its operating conditions, including the need for a large amount of sample, owing to the lack of sensitivity and relatively high temperature treatment exceeding 100°C for contami-



nant removal, which might cause undesired deformations in the material.^[27] Also, the electrochemically accessible surface area of a solid electrode that is in contact with a liquid electrolyte is generally smaller than the BET surface area.^[28] For these reasons, we preferred UPD over BET as a relatively precise and rapid characterization tool for the surface-area analysis of the fabricated Cu structures.

The utility of UPD for determining the surface area of simple architectures (i.e. thin films) has been demonstrated in the literature.^[27,29-35] However, to the best of our knowledge, this method has not been utilized for the surface-area characterization of rather complex 3D electrodes in the electrochemical energy-storage area. Other applications of UPD include the fabrication of multilayered structures by using electrochemical atomic layer epitaxy and the formation of catalytic surfaces with enhanced activity.^[36-42]

Being a cost-effective and relatively fast technique, UPD enables a precise and reproducible surface modification through the formation of up to a monolayer thickness on the electrode surface.^[43] Deposition of a monolayer through UPD is only possible when there is a potential difference between the bulk deposition and the deposition of the first monolayer on the substrate. For the study reported herein, the deposition of a TI monolayer has been selected as a probe of the effective surface area of the 3D Cu structures.^[44-46] The potential of the 3D structure was set at a value slightly greater than the potential for bulk deposition to form a monolayer of TI. Following the monolayer formation, the applied potential was adjusted to a value anodic of the UPD process to oxidatively strip the TI monolayer from the surface as the amount of charge transferred was being carefully monitored. As the amount of the charge is proportional to the number of TI atoms removed from the electrode surface, the surface area of the electrode can be easily determined.

To validate our application of UPD in determining the electrochemically active electrode surface area, experiments were carried out in a solution made up of 0.5 м Na₂SO₄ and 2.5 mм Tl₂SO₄. A polycrystalline 2D Cu electrode with a known surface area of 0.25 cm² was prepared by using a lift-off process, in which Ti and Cu films were sputtered onto a glass substrate with a patterned photoresist film on the top surface, for which Ti serves as an adhesion promoting layer between Cu and glass. After the removal of the photoresist, the electrode was immersed in the TI-based electrolyte and a CV scan was conducted in a three-electrode-cell configuration, where Pt and Ag/AgCl were utilized as the counter and reference electrodes, respectively. Figure 5 presents a voltammogram of TI on the Cu electrode. A reduction peak associated with TI monolayer formation can be seen at approximately -0.50 V, which is in good agreement with the previously reported value of -0.49 V.^[46] The anodic peak at -0.44 V corresponds to the desorption of the TI from the electrode surface. Bulk deposition, on the other hand, starts after the second cathodic peak at -0.7 V, which has the corresponding anodic dissolution peak at -0.69 V.

Upon completion of the CV tests on the Cu electrode, a Ni electrode was prepared by electroplating a 500 nm-thick Ni

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Figure 5. CV profile of Cu and Ni electrodes in Tl solution: A) comparison of Cu and Ni electrodes and B) enlarged view of the Ni electrode.

film on the aforementioned Cu electrode with the same surface area of 0.25 cm². A voltammogram was obtained on this Ni electrode by using the same TI-based electrolyte. As can be seen in Figure 5, there is no corresponding peak current for the deposition of the TI monolayer on Ni in the given potential range. The significance of this finding is that, if residual Ni is present in the multilayer 3D structure from incomplete etching, it will not interfere with our determination of the effective surface area of Cu. In addition to Cu being nearly four times as conductive as Ni, and thus being more suitable for high-power applications, the lack of an appropriate electrolyte to measure the surface area of Ni through UPD is the other motivation for us to prefer Cu-based multilayer electrodes over their Ni-based counterparts.

To confirm that the UPD of TI on the Cu surface is taking place at the first cathodic peak, chronoamperometric experiments were performed. The potential of the Cu electrode was first set to -0.65 V for 30 s and then increased to -0.4 V. The amount of charge stripped was estimated by integrating the area under chronoamperometric curve and was found to be 111 μ C cm⁻². This value is almost identical to the reported quantity of charge density of 112 μ C cm⁻² necessary to form a TI monolayer on a polycrystalline Cu surface.^[46] Increasing the time for the applied potential of -0.65 V from 30 s to 2 min did not result in any significant change in the stripped charge quantity, indicating that 30 s is sufficient to form a TI monolayer on the polycrystalline Cu surface.

A second validation experiment was sought to determine the change in the effective surface area of the electrode while maintaining its geometric area. To accomplish this, the Cu electrode formed by sputtering, as described in the preceding paragraph, was thickened through electrodeposition of an additional Cu layer, which increases the surface roughness. A 1 µm-thick Cu layer was electroplated onto the sputtered Cu layer under the same conditions as in the fabrication of the multilayer structures. After repeating the UPD procedure, an average total charge of $132 \,\mu\text{C}\,\text{cm}^{-2}$ was obtained. Dividing this value by the theoretical value associated with the TI mon-



Figure 6. Total amount of charge transferred during the stripping of the TI monolayer from the Cu films with various surface areas from 0.25 to 1.25 cm².

olayer on a polycrystalline Cu surface (112 $\mu C\,cm^{-2}$), a surface roughness factor of 1.18 was calculated.

To further confirm that the UPD approach can be utilized to estimate the change in surface area, a calibration plot was prepared, as shown in Figure 6, by employing three more electrodes with varying surface areas of 0.50, 1.00, and 1.25 cm². These electrodes were prepared in the same fashion as the aforementioned one with the surface area of 0.25 cm². The same UPD experiments were conducted with all of the electrodes, and the amount of the total charge stripped from each one was plotted with respect to the surface area of the electrodes. This analysis revealed a clear, linear relationship, supporting the utilization of the UPD approach for the surface area estimation.

Upon carrying out selective dissolution of Ni layers from the multilayer structures in the H_2SO_4 electrolyte, UPD experiments were performed to determine the total surface area of the resulting laminated Cu structure. After three consecutive UPD runs, an average total charge of 5527 μ C was obtained for the anodic dissolution of the TI monolayer. To ensure that all of the sacrificial Ni layers were completely removed, a selective dissolution potential of –20 mV was applied in the H_2SO_4 electrolyte for a further 2 h, which was followed by the UPD experiment. No significant increase in the amount of stripped charge was observed, suggesting that no Ni remained in the structure.

The effective surface area of 49.3 cm² was obtained by dividing the total amount of charge required to strip the TI monolayer from the 3D electrode (5527 μ C) by the charge density required to remove a complete TI monolayer (112 μ C cm⁻²). As mentioned earlier, by design, the total geometric surface area of our 25-layer Cu electrode is 40 cm². If one assumes that the surface roughness factor of 1.18, obtained on the test electrodes used for calibrating the UPD method, is a reliable estimate of the roughness of each layer in our multilayer 3D structure, then the predicted effective surface area becomes 47.2 cm². If this assumption holds, the remaining difference of 2.1 cm² is postulated to result from the surface area of the Cu anchors as well as the sidewalls of each layer.

2.4. Formation of the Supercapacitor Electrode

Supercapacitors are recognized as promising next-generation energy-storage devices and have been widely utilized in various applications ranging from portable electronic devices and autonomous microsystems to electrical vehicles.^[47] In recent years, considerable effort has been devoted to the development of supercapacitors and significant improvements have been achieved through developing new active materials, altering the morphology of the existing materials, and implementing high-surface-area structures that serve as current collectors, utilizing thin films of the existing materials.^[47,48] The approach reported herein addresses the latter strategy, in which the fabricated Cu structures are to serve as current collectors for supercapacitors.

Among numerous electrodepositable transition-metal oxides and hydroxides featuring pseudocapacitive properties, Ni(OH)₂ was selected as a well-studied example of active materials for supercapacitors to confirm the superior performance enabled by 3D structures. Factors including its high theoretical specific capacitance, cost effectiveness, easy synthesis, well-defined electrochemical redox activity, environmentally benign nature, and availability in various morphologies have rendered Ni(OH)₂ a promising candidate for supercapacitor materials.^[7,49-53]

The final step in the fabrication sequence involves the electrodeposition of the active material onto the 3D Cu backbone. A very thin Ni layer was first electrodeposited potentiostatically onto the 3D Cu electrode by using the same bath that was used to electroplate the sacrificial Ni layers. Pulsed cathodic potentials were applied to the Cu backbone with a 10% duty cycle to ensure conformal coating of the electrode. Next, a conformal layer of Ni(OH)₂ was electrodeposited in a similar fashion, in which pulsed cathodic potentials were applied to the electrode in a Ni(NO₃)₂ bath. Note that prior deposition of a thin Ni layer provided better adhesion and, thus, better cycling stability for the Ni(OH)₂ film compared with the direct deposition of Ni(OH)₂ onto the bare Cu backbone. This thin Ni coating also prevents Cu from exposure to the alkaline electrolyte, inhibiting possible side reactions and electrode degradation. The electrodeposition processes for both Ni and Ni(OH)₂ were carried out in a three-electrode cell with Pt and Ag/AgCl as the counter and reference electrodes, respectively.

To confirm that the Ni(OH)₂ film is formed in a conformal fashion on the entire surface of the multilayer structure, a cross section of a layer from the multilayer electrode was exposed following partial immersion of the electrode in concentrated nitric acid solution for less than 5 s. Figure 7 presents the SEM image of the cross-sectional view of a Cu layer with a thin Ni/Ni(OH)₂ film on both sides.

For further electrochemical confirmation of the maximum and conformal surface coverage after each deposition step, CV scans were carried out at a rate of 10 mV s^{-1} in a 1 m KOH solution, using the same three-electrode-cell configuration as before. Figure 8 shows the CV profiles of the blank electrode (Cu only), Ni-coated electrode, and final electrode after Ni(OH)₂ deposition. A significant shift in the anodic and cathodic peaks of the blank Cu electrode following Ni deposition suggests





Figure 7. Cross-sectional view of an individual layer of the multilayer electrode after deposition of the active material.



Figure 8. CV profiles of the multilayer structures in 1 M KOH at 10 mV s^{-1} : A) bare multilayer Cu electrode following the selective removal of the Ni layers, B) Ni-coated multilayer Cu electrode, and C) final electrode after Ni(OH)₂ electrodeposition.

a predominant existence of the Ni coating on the Cu surface. Similarly, Ni(OH)₂ deposition yields a unique CV profile, indicating almost complete surface coverage.

2.5. Performance Characterization of the Electrode

The electrochemical performance of the Ni(OH)₂-coated electrode was evaluated by using a three-electrode system in 1 m KOH solution, in which the Pt and Ag/AgCl electrodes were utilized as counter and reference electrodes, respectively. To characterize the capacitive behavior of the electrode, CV analysis was conducted between potentials of 0.0 and 0.6 V at various scan rates, ranging from 5 to 25 mV s⁻¹, as shown in Figure 9A. The shape of the CV curve indicates a distinguished pseudocapacitive characteristic from pure double-layer capacitance, which ideally would have a rectangular shape. Two clear anodic and cathodic peaks are observed in the voltammogram shown in Figure 9A, which correspond to the reversible, surface Faradaic reactions of Ni(OH)₂ [Eq (1)].^[54]

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$$
 (1)

These peaks exhibit almost perfect symmetry, suggesting an excellent reversibility of the active material.^[53] Increasing the scan rate from 5 to 25 mV s⁻¹ results in the shift of the oxidation and reduction peaks to more positive and negative potential values, respectively. This shift is reflective of the internal resistance of the pseudoactive material.^[50]

The CV profiles were also used to determine the specific capacitance, C_s (Fg⁻¹), of the electrodes by calculating the area under the CV curve, according to Equation (2):

$$C_{\rm s} = [mv(V_{\rm c} - V_{\rm a})]^{-1} \int_{V_{\rm a}}^{V_{\rm c}} I(V) dV$$
⁽²⁾

where m is the total mass of the active material (g), v is the scan rate (mV s⁻¹), V_c is the cathodic potential (V), V_a is the anodic potential (V), and I is the response current as a function of the applied potential (A). The total mass of the deposited active material was measured to be 1.8 mg, which is in accordance with the theoretical value estimated from the current applied during the electrochemical deposition of the Ni(OH)₂. By inserting the total mass of the active material into Equation (2), the specific capacitances of the electrodes were calculated to be 733, 667, 597, 521, and 503 Fg^{-1} at scan rates of 5, 10, 15, 20, and 25 mV s⁻¹, respectively. The specific capacitance, as a function of the scan rate, can be seen in Figure 9B. As the scan rate was increased to 25 mV s⁻¹, the specific capacitance dropped to 503 Fq^{-1} , which is approximately 69% of that at 5 mV s⁻¹. This remarkably high capacity retention is an indication of enhanced high-rate performance when compared to previously reported values in the literature.^[7,49,51,55-57]

In addition to the CV profiles, galvanostatic charge and discharge tests were carried out to calculate the gravimetric capacitance of the electrodes using Equation (3):

$$C_{\rm s} = \frac{l}{mv} \tag{3}$$

Figure 9C demonstrates the charge and discharge curves of the electrode at various current densities. The corresponding specific capacitance values at the discharge rates of 5, 10, 15,



and 20 A g⁻¹ were determined to be 540, 420, 390, and 270 F g⁻¹, respectively. Increasing the current density from 5 to 20 A g⁻¹ results in a decrease in the gravimetric capacitance of approximately 50%.

CV runs were also performed to investigate the long-term stability of the electrode in 1 M KOH electrolyte. Figure 9D illustrates the capacitance retention of the supercapacitor electrode measured at a relatively high scan rate of 20 mV s⁻¹ for over 1000 cycles. The electrode exhibited only around 6% degradation in the capacitance after 1000 cycles at relatively high scan rates. This indicates negligible degradation and a remarkable long-term stability of the electrode, as well as an improved cycle-life performance when compared to previously reported values in the literature.^[7,50,51,55,57–61] A performance comparison of the Ni(OH)₂-based electrodes reported herein and in the literature is shown in Table 1.

As can be seen from Table 1, the best performance in terms of the specific capacitance $(3152 \text{ Fg}^{-1} \text{ at } 4 \text{ Ag}^{-1})$, which is also the highest reported so far, was obtained by the direct electrodeposition of Ni(OH)₂ onto a highly porous 3D Ni foam.^[7] Similar to the structures reported herein, Ni foam serves as a highly conductive backbone possessing an ultrahigh surface area; and its porous nature facilitates access of the electrolyte to

Figure 9. Performance characterization of the multilayer Ni(OH)₂ electrode: A) CV profiles of the Ni(OH)₂ electrode at various scan rates, B) specific capacitance of the Ni(OH)₂ electrode as a function of the scan rate based on the CV profiles, C) galvanostatic charge/discharge curves of the Ni(OH)₂ electrode at various rates, and D) cycle performance of the supercapacitor recorded at a scan rate of 20 mV s⁻¹ for 1000 cycles.



Table 1. Performance comparison of various Ni(OH) ₂ -based electrodes.								
Specific capacity ^[a] [F g ⁻¹]	Specific capacity ^[b] [F g ⁻¹]	Capacitance retention ^[a] [%]	Capacitance retention ^[b] [%]	Cycle life (cycles) [%]	Ref.			
733 (5 mV s ⁻¹) - 1735 (1 mV s ⁻¹) - 1715 (5 mV s ⁻¹) - 2188 (1 mV s ⁻¹) 1953.6 (2 mV s ⁻¹) 1300 (1 mV s ⁻¹) 771 (5 mV s ⁻¹) - - - - - - - - - - - - -	$540 (5 A g^{-1})$ $3152 (4 A g^{-1})$ $-$ $166 (0.5 A g^{-1})$ $1874 (4 A g^{-1})$ $597.4 (0.3 A g^{-1})$ $1868 (20 A g^{-1})$ $-$ $1532 (0.2 A g^{-1})$ $578 (0.5 A g^{-1})$ $1235 (1 A g^{-1})$	$\approx 69 (5-25 \text{ mV s}^{-1})$ $=$ 30 (1-50 mV s^{-1}) $=$ 67 (5-20 mV s^{-1}) $=$ 57 (1-20 mV s^{-1}) $\approx 44 (2-20 mV s^{-1})$ $\approx 68 (1-5 mV s^{-1})$ $\approx 47 (5-20 mV s^{-1})$ $=$ $=$ $=$ $=$ $=$ $=$ $=$ $=$ $=$ $=$	$50 (5-20 \text{ Ag}^{-1})$ $\approx 9 (4-16 \text{ Ag}^{-1})$ $-$ $\approx 67 (0.5-10 \text{ Ag}^{-1})$ $-$ $64 (0.3-5 \text{ Ag}^{-1})$ $72 (20-70 \text{ Ag}^{-1})$ $-$ $\approx 55 (0.2-4 \text{ Ag}^{-1})$ $\approx 76 (0.5-2 \text{ Ag}^{-1})$ $\approx 63 (1-20 \text{ Ag}^{-1})$	≈ 94 (1000) 48 (300) - 65 (1000) ≈ 82 (1000) 93.5 (500) 95 (200) 81 (300) 95.5 (400) 80 (500) 78 (500)	this work [7] [49] [50] [51] [52] [53] [56] [57] [58] [59] [60] [60]			
[a] Based on CV data. [b] Based on galvanostatic charge/discharge data.								

the entire electrode. Interestingly, when the current density was increased to 16 Ag^{-1} , a drastic drop in the specific capacitance was observed (280 Fg^{-1}). This corresponding capacitance retention of approximately 9% is significantly lower than the performance reported in this work (50% at 20 Ag^{-1}). Furthermore, the capacitance of foam-based electrodes dropped with cycling. They were shown to maintain only 52% of their capacitance after 300 cycles; this significant loss was attributed to the Ni(OH)₂ flaking off.^[7] In comparison, the electrodes presented herein maintain approximately 94% of their original capacitance after 1000 cycles (Figure 9D). Therefore, the deterministically engineered high-surface-area electrode presented herein offers substantial improvements in both cycling stability and power delivery over the Ni foam electrode.

3. Conclusions

The work reported herein involves the design, fabrication, and characterization of high-performance Ni(OH)₂ supercapacitor electrodes. These electrodes are based on well-ordered and highly scalable 3D architectures that are composed of laminated, highly conductive Cu backbone structures with a conformally electrodeposited thin film of Ni(OH)₂ as the electrochemically active material. The fabrication process consists of a series of microfabrication technologies and electrochemical techniques. Among the electrochemical methods utilized in this work, UPD was shown to be a simple and reliable tool for precisely determining the surface area of microfabricated 3D Cu architectures. The resulting electrodes offered a relatively high specific capacitance of 733 F g⁻¹ that was determined through a CV scan at a rate of 5 mV s⁻¹. The device demonstrated a remarkable power capability by delivering 69% of its capacitance at a relatively high scan rate of 25 mV s⁻¹. A similarly high capacitance delivery was observed when performing galvanostatic charge and discharge experiments at rates as high as 20 Ag⁻¹. In excess of 1000 CV runs were carried out at 20 mV s⁻¹, and the device showed an outstanding cycling stability with a capacitance retention of 94%. These high energy and power densities have been attributed to the high surface area and minimal internal resistance of the electrode, respectively, both of which are highly desirable features for electrochemical energy-storage systems. Although similar performance improvements were able to be reportedly achieved by utilizing various 3D architectures, including metal foams, nanotubes, and aerogels, these structures generally lack scalability, and the methods to fabricate these structures do not allow precise control over their critical dimensions and, hence, they are not as reproducible. An important and unique feature of the Cu electrodes reported herein, on the other hand, is their scalability, which opens up the possibility of electrodes with higher areal energy densities that can be achieved by simply increasing the number of layers, maintaining the same footprint and without altering the precisely determined characteristic dimensions, such as diffusion and conduction path lengths. Thus, as the amount of stored energy is significantly increased, the high power capability of the electrode is maintained. The highly conductive Cu current collector coated with a thin and conformal active material film minimizes device resistance through its highly conductive backbone and relatively short diffusion pathways. Another advantage of this batch fabrication approach is the ability to fabricate multiple electrodes on a substrate simultaneously, owing to the automated and robotically assisted sequential deposition technique. One final unique feature offered by these versatile Cu backbones is the ability to incorporate other active materials with higher intrinsic capacitances (e.g. RuO₂), thus furthering the increase in energy density.

Experimental Section

Preparation of the Photoresist Mold

A negative-tone photoresist (NR21-20000P, Futurrex) was spincoated on a Ti/Cu-sputtered glass substrate at 1200 rpm for 10 s, leading to an approximate film thickness of 100 μ m. Next, a softbake process was carried out on hot plates at 80 and 150 °C for 10 and 5 min, respectively. Following the pre-exposure bake, the photoresist film was patterned with a chrome mask under UV exposure at 365 nm by a total energy of 5 J. Post-exposure bake was per-



formed on a hot plate at 80 $^{\circ}$ C for 10 min, and then the photoresist was developed in an aqueous tetramethylammonium hydroxide (TMAH) solution (RD6, Futurrex) until all of the unexposed regions of the photoresist dissolve.

Formation of Multilayer Structures

Robotically assisted sequential electroplating of Ni and Cu layers was carried out in their respective plating baths to form multilayer structures. For the electrodeposition of Cu, a commercial plating solution (Clean Earth Cu-Mirror, Grobet) was used, in which highpurity Cu sheets were utilized as counter electrodes. As for the electrodeposition of Ni layers, an all-sulfate Ni bath was used along with a high-purity Ni foil as the counter electrode. The Ni plating bath was prepared by dissolving nickel(II) sulfate hexahydrate (NiSO₄· $6H_2O$, 400 g), boric acid (H₃BO₃, 40 g), and saccharin (3 g) in deionized (DI) water (1 L) with a resistivity of 17.5 M Ω cm. Prior to electrodeposition, both the Cu and Ni foils were degreased by cleaning thoroughly with acetone, methanol, and isopropyl alcohol (IPA), followed by hydrochloric acid (HCI) treatment to remove the oxide layer on the surface. All electroplating processes were carried out at room temperature and at a current density of 10 mA cm⁻². Between the electrodeposition of two consecutive Cu and Ni layers, the substrate was thoroughly rinsed in two separate DI baths to avoid cross-contamination of the plating baths.

Synthesis of the Ni(OH)₂ Film

Electrodeposition of the active material [i.e. $Ni(OH)_2$] was carried out in $Ni(NO_3)_2$ solution (0.2 M) by using a solvent that consisted of 80:20 volume percent (v/o) water and ethanol. A three-electrodecell configuration was prepared, in which a multilayer structure, a Pt sheet and Ag/AgCl were utilized as the working, counter, and reference electrodes, respectively. To ensure conformal deposition of the active material, cathodic potential pulses were applied to the substrate (0.5–1 V) with the help of a potentiostat (WaveDriver 10, Pine Instruments). A rest time of 9 s was provided for mass transfer after each pulse of 1 s for 300 cycles.

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