



Model-assisted development of microfabricated 3D Ni(OH)₂ electrodes with rapid charging capabilities

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HIGHLIGHTS

- A 3D multilayer Ni(OH)₂ cathode is fabricated by microfabrication technologies.
- The laminated electrodes exhibit 50% capacity retention at 150C charge rate.
- Electrodes with areal capacities as high as 2.43 mAh cm⁻² are realized.
- Remarkable cycling ability at high rates for more than 80 cycles is demonstrated.
- A model is developed to characterize and optimize performance of the electrodes.

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ABSTRACT

Three-dimensional (3D) nickel hydroxide electrodes based on well-ordered and laminated structures are prepared via an electrochemical route combined with microfabrication technologies. The electrodes exhibit enhanced rate capabilities owing to their large surface area and reduced diffusion and conduction path lengths for the charge transfer. Highly laminated electrodes enable areal capacities as high as 2.43 mAh cm⁻². When charged at fast rates of 150C, the electrodes are able to deliver more than 50% of their initial capacity. The electrochemical performance of the fabricated electrodes is predicted with close approximation by means of a mathematical model developed by employing fundamental mass transport and reaction kinetics principles. This model is then used to optimize the characteristic dimensions of the electrodes and make projections of performance for various energy and power needs.

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1. Introduction

Energy storage devices with both high power and energy densities have garnered increasing attention over the past two decades, particularly due to the widespread development of portable

electronic equipment, requiring on-board power sources and demanding more energy with increased versatility. Technological advancements in the electronic device industry in both macroscale (e.g., smart phones, tablets, drones) and microscale (e.g., micro-sensors, microactuators) have been much more rapid than that of compatible and suitably sized power source technologies. Except under the condition that a new battery chemistry with significantly higher energy density than the current systems is established, longer operation times can only be realized by increasing the mass of the electrochemically active material existing in the battery cell, which would add to the total weight of the device, and thus, become incompatible with the current shrinking trend of the portable devices. However, improvements in the rate of energy

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transfer, i.e. the power, with a minimum forfeit in the capacity, would aid in the development of batteries with rapid charging capabilities, which can be considered as a potential solution to the increasing demand for on-board energy storage systems.

Recently, several studies have focused on the development of materials that realize batteries with improved power densities, and thus, rapid charging and discharging capabilities [1–5]. The power density of these batteries primarily depends on the rate of the intra- and inter-electrode transport of ionic and electronic species. The factors affecting the transport rate of these species can be classified in two main categories: (i) intrinsic factors, such as diffusivity and conductivity of the system elements, which are primarily determined by the choice of electrode materials, electrolytes, and operating conditions (e.g., temperature); (ii) extrinsic factors, such as surface area, thickness of the electrochemically active material, and separation distance between the electrodes, which mainly rely on the geometric design of the system. All of these factors can be subjected to an optimization in order to design a system with maximum power density with minimum compromise to the energy capacity. Large electrode surface area is essential for high-power applications, since it increases the amount of active material in contact with the electrolyte, and thus, the number of potential sites for the redox reactions. On the other hand, the thickness of the active material on the current collector determines the path lengths for the diffusion and conduction of the ionic and electronic species, respectively. Since the rapid transport of these species is vital for high power applications, the minimization of the transport path lengths is also crucial.

Some of the recent approaches to achieve high-surface-area electrodes suitable for high-power applications involve a variety of structures in the form of metal foams, nanorods, nanotubes, aerogels, and xerogels [3,6–14]. These structures indeed feature rather complex three-dimensional (3D) architectures exhibiting extremely high surface area; yet, they are primarily based on non-deterministic synthesis techniques which limit the control over their aforementioned critical dimensions affecting the power performance of the battery, as well as over their scalability and reproducibility in a uniform fashion.

The study reported herein involves rationally designed and deterministically engineered 3D structures with nearly precise control over the dimensions that address the aforementioned critical factors affecting the high-power capability and ultimately determine the performance of the electrochemical system. A series of fabrication methods encompassing electrochemical techniques and microfabrication technologies have been utilized for the formation and characterization of the scalable, well-ordered, and high-surface-area 3D architectures that can be potentially used as high-power electrodes in a variety of applications, ranging from autonomous microsystems to macroscale portable electronics. Ni(OH)_2 , one of the most well-studied active material in secondary (i.e., rechargeable) battery systems [15], was chosen in this study as the energy storage material.

Besides its numerous attractive properties including its high specific capacity, ease of handling, cost-effectiveness, environmentally benign nature, and well-defined redox activity, Zhang et al. recently reported that electrodeposited Ni(OH)_2 is a suitable candidate for high-power applications [3]. However, for the efficient utilization of Ni(OH)_2 at high charge and discharge rates, the resistance of the material originating from the diffusion of protons within the lattices, as well as from its low electronic conductivity needs to be minimized [16]. For this purpose, nanostructured Ni(OH)_2 featuring a variety of morphologies including nanosheets, nanoribbons, nanotubes, and nanowires has been realized [9,17–23]. Although these materials were able to retain their improved specific capacitance under operation conditions that

involve high charge and discharge rates, they are typically synthesized in powder form. As a result, the incorporation of the active material into the 3D electrode architecture in a homogeneous fashion becomes rather challenging. Furthermore, in order to enhance the adhesion of the active material particles to the high surface area current collectors, additional materials with adhesive properties (e.g., organic binders) need to be utilized. The presence of such compounds in the electrode is not favorable, since they cause relatively poorer contacts between the current collector and the active material particles, which would lead to increased internal resistance, and in turn, reduced performance. Hence, a feasible approach would require a direct growth of the active material on the 3D current collector. We have adopted electrodeposition, a method that is also compatible with the rest of the electrode fabrication process, to form the Ni(OH)_2 layer on a well-ordered multilayer Ni backbone.

Well-defined geometry of the electrodes furthermore allowed easier implementation of the mathematical models for the optimization of their characteristic dimensions, as well as for performance projections. A two-dimensional (2D) mathematical model has been developed in COMSOL 5.2 by employing fundamental mass transport and reaction kinetics principles. Although mathematical models based on porous electrode theory have already been proposed for conventional NiCd and NiMH batteries [24,25], the model developed in the current study is pertinent to the deterministically engineered 3D structure mentioned herein.

2. Experimental

2.1. Electrode fabrication: overview

The electrodes are based on the anchor-supported lateral high-aspect-ratio structures whose fabrication process was schematically illustrated in Fig. 1. In summary, a photoresist mold was patterned and developed on a metalized glass substrate. Next, alternating Ni and Cu layers were deposited by electroplating in a well-controlled and systematic fashion using an automated robotic plating setup. Following the electroplating of the multilayer structure, the photoresist mold was stripped, and a second photoresist film was formed, which served as the mold for electroplating of thick Ni anchors on specific regions of the sidewalls of the multilayer structures. Thereafter, sacrificial Cu layers were selectively etched resulting in a high-surface-area multilayer Ni backbone. Finally, Ni(OH)_2 was electrodeposited onto the Ni backbone in a conformal fashion.

2.1.1. Deposition of the photoresist mold

A negative-tone photoresist (AZ 125 nXT, AZ Electronic Materials) with an approximate thickness of 0.5 μm was uniformly poured onto a Ti/Cu-sputtered glass substrate with a square footprint and then spin-coated at 100 rpm for 60s. After a soft baking process at 105 $^{\circ}\text{C}$ for 14 h, the sample is cooled for 2 h at room temperature, which is followed by the UV exposure at 365 nm through a hard-contact mask. The total energy dose of the UV exposure was set to 60 J cm^{-2} . Thereafter, the photoresist was developed in a tetramethylammonium hydroxide (TMAH)-based developer (AZ 300 MIF, AZ Electronic Materials) for 45min. Following the development process, the sample was thoroughly rinsed in DI water and then dried at room temperature. Prior to the sequential electroplating process, the photoresist mold was treated with reactive-ion etching (RIE) oxygen plasma (Plasma-Therm) at 200 W for 1 min, which was found improve the wettability of the mold surface and thus, improve the electroplating quality.

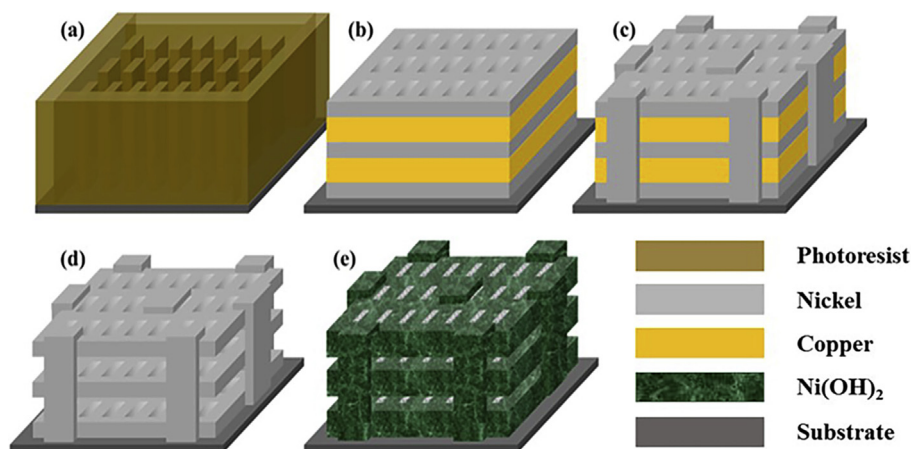


Fig. 1. Schematic illustration of the fabrication process for the $\text{Ni}(\text{OH})_2$ -based electrodes: (a) Deposition of UV-patterned photoresist mold onto a metalized glass substrate, (b) robot-assisted electroplating of alternating Ni and Cu layers followed by the removal of the photoresist, (c) electroplating of the Ni anchors through a second photoresist mold, (d) selective etching of the sacrificial Cu layers, and (e) electrodeposition of the $\text{Ni}(\text{OH})_2$ onto the multilayer Ni backbone.

2.1.2. Formation of highly laminated Ni backbone

Sequential electroplating of Ni and Cu layers was performed galvanostatically using an automated robotic plating setup. An all-sulfate Ni bath with a high-purity Ni foil as the counter electrode was used for the electroplating of Ni layers. The bath was prepared by dissolving nickel (II) sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 400 g), boric acid (H_3BO_3 , 40 g), and saccharin (3.0 g) in 1 L of deionized (DI) water with a resistivity of $18\text{M}\Omega\cdot\text{cm}$. All chemicals were used as received without any further pretreatment throughout the fabrication process. A commercial plating solution (Clean Earth Cu-Mirror, Grobet), along with a high-purity Cu foil, was used for the electroplating of Cu layers. Both Ni and Cu foils were degreased by cleaning thoroughly with acetone, methanol, and isopropyl alcohol. The current density was set to 10 mA cm^{-2} for both Ni and Cu electroplating, and the whole process was carried out at room temperature. To avoid the cross-contamination of the plating solutions, the substrate was immersed in two separate DI water baths between the electroplating of two consecutive Ni and Cu layers. Upon completion of the sequential electroplating process, the photoresist mold was stripped in dimethyl sulfoxide (DMSO) at 80°C with the assistance of ultrasound sonication. A second photoresist deposition process followed by Ni electroplating was conducted for the formation of Ni anchors on specific sites of the laminated structure. In the last step, the sacrificial removal of the Cu layers was performed in an etchant prepared by mixing 50 g of copper sulfate (CuSO_4) with 500 ml of ammonium hydroxide (NH_4OH). SEM images demonstrate the successful removal of the Cu layers (Supplementary Fig. 1). Due to the presence of the anchors, the remaining Ni layers did not collapse after removal of the copper.

2.1.3. Deposition of $\text{Ni}(\text{OH})_2$

A two-electrode cell configuration was used for the galvanostatic electrodeposition of the $\text{Ni}(\text{OH})_2$ layer in a 0.2 M nickel nitrate ($\text{Ni}(\text{NO}_3)_2$) solution, where the laminated Ni structure and a Pt mesh were utilized as the working and counter electrodes, respectively. To ensure a conformal coating of the Ni backbone, cathodic currents were applied in pulses (1s on/9s off) by using a potentiostat (PowerLab 2/20, ADInstruments). X-ray photoelectron spectroscopy (XPS) was utilized for the analysis of chemical states of Ni and O in the electrodeposited active material (Thermo K-Alpha XPS). Ni 2p and O 1s XPS spectra of $\text{Ni}(\text{OH})_2$ films are provided in Supplementary Fig. 2. In the case of Ni 2p spectrum, the

peak at 855.5 eV might be associated with Ni $2p_{3/2}$ of $\text{Ni}(\text{OH})_2$ [26,27]. On the other side, the peak at 531.2 eV found in the O 1s spectrum can be assigned to OH^- derived from $\text{Ni}(\text{OH})_2$ [26].

2.2. Performance characterization of the electrodes

A multilayer $\text{Ni}(\text{OH})_2/\text{Ni}$ structure composed of 100 layers was prepared by using methods described in section 2.1. For characterization of the $\text{Ni}(\text{OH})_2$ electrodes, a three-electrode-cell configuration was prepared, where a platinum mesh and an Ag/AgCl electrode were utilized as the counter and reference electrodes, respectively. All of the charging/discharging experiments were conducted galvanostatically at various rates ranging from 1C to 150C in 6 M KOH electrolyte with the help of a potentiostat (WaveDriver 10, Pine Instruments). Here a x C rate means that the charge/discharge current will charge/discharge the entire battery in x^{-1} hours.

3. Mathematical modeling of the electrodes and diffusion coefficient measurement

A mathematical model relying on fundamental mass transport and reaction kinetics principles has been developed to optimize the characteristic dimensions of the multilayer electrodes suitable for high-power batteries.

The model was built using COMSOL 5.2. Since a 2D model is able to capture most of the essential features of the multilayer structure, we chose to model in 2D instead of 3D to avoid the much more time-consuming 3D computations. A repeating unit of the multilayer electrode, whose top view is shown in Fig. 2(a), was studied. 2D geometry of the side view of the repeating unit is illustrated in Fig. 2(b). Note that a 30-layer structure is shown for clarity of individual layers; more layers can easily be incorporated in the actual model. Width L corresponds to the distance between the adjacent etching holes (i.e., from point a to b in Fig. 2(a)). The lower limit of this width was determined by the design of the lithographic photomask that was used during the photolithography process, and its flexibility was limited due to constraints pertaining to the fabrication of the photoresist mold (i.e., AZ 125 nXT) prior to the automated electroplating process. Designs that have densely packed etching holes, i.e., $L \ll 300\text{ }\mu\text{m}$, require a dense packing of the photoresist pillars, which complicates the fabrication process. Therefore, an experimentally fabricated structure with a pillar size

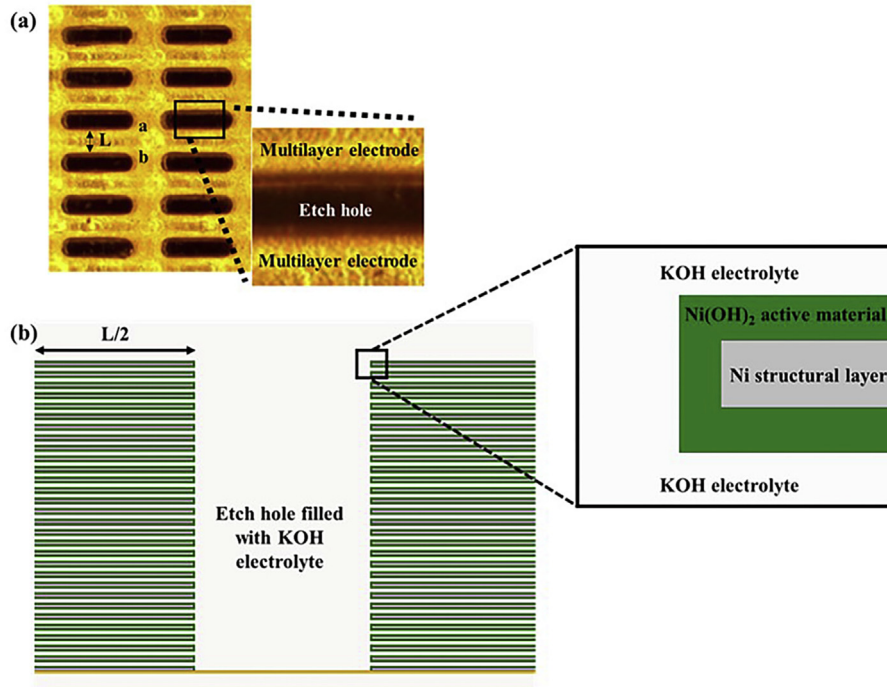
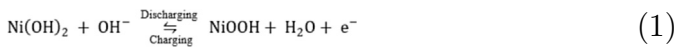


Fig. 2. (a) Optical images showing a section from the top view of the fabricated multilayer electrode along with its etching holes, (b) schematic illustration showing the cross-section of the multilayer electrode for the COMSOL tertiary current distribution interface, with the inset showing a single layer.

of $150 \times 600 \mu\text{m}^2$ and a spacing L of $300 \mu\text{m}$ was selected for the modeling purposes.

The tertiary current distribution interface in COMSOL 5.2, which takes into account the effect of variations in electrolyte composition and ionic strength on the charging and discharging process, was used to calculate the ion concentration distribution in both the liquid and solid phases. The COMSOL partial differential equation interface was used to model the proton diffusion within the $\text{Ni}(\text{OH})_2$ active material. In addition, although the electrochemical characterizations in the experimental work were carried out in a three-electrode set-up, where Pt electrode and Ag/AgCl electrode served as the counter electrode and the reference electrode, respectively, the model assumed a two-electrode configuration for simplicity in modeling. This in principle should not affect performance predictions of the $\text{Ni}(\text{OH})_2$ multilayer half cell, which is the main focus of this study.

$\text{Ni}(\text{OH})_2$ chemistry exhibits a reversible charge storage redox mechanism in which it converts to nickel oxyhydroxide (NiOOH) via diffusion of protons through its solid state lattices. The electrochemical reactions occurring at the $\text{Ni}(\text{OH})_2$ cathode/electrolyte interface are given by:



The Zn counter electrode reactions are as follows:



Proton diffusion to and from the bulk of the active material

enables Reaction (1) to continue at the interface. Reaction (2) refers to the oxygen evolution side reaction during electrode over-charging. Inclusion of this reaction mechanism is necessary because it is fueled by part of the current used to charge the electrode, thus decreasing capacity retention [28,29]. Reaction (3) refers to the zinc reaction at the anode. Since the focus of this study is on performance of the $\text{Ni}(\text{OH})_2$ cathode, concentration of $\text{Zn}(\text{OH})_4^{2-}$ and its conversion to ZnO were not taken into account in the model.

Note that although the OH^- ions are produced from the zinc reaction at the anode during charging, which may potentially deviate from the actual three-electrode scenario, the simulation results, which focused on capacity retention of the $\text{Ni}(\text{OH})_2$ cathode, should still be valid as long as the cathode is set sufficiently far away from the Zn counter electrode, such that semi-infinite condition for the potassium hydroxide (KOH) electrolyte diffusion is satisfied.

The reaction rates for the electrochemical reactions involved in NiZn cell can be described by Equations (5)–(8), using either Butler-Volmer equations or the anodic Tafel equation with respect to a specific reference state [24,25,28–30]:

$$i_{loc,1} = i_{01,ref} \left(\left(\frac{C_{OH}}{C_{OH,ref}} \right) \left(\frac{C_H}{C_{H,ref}} \right) \exp(\alpha_{a1} F \eta_1 / RT) - \left(\frac{C_{H,max} - C_H}{C_{H,max} - C_{H,ref}} \right) \exp(-\alpha_{c1} F \eta_1 / RT) \right) \quad (5)$$

$$i_{loc,2} = i_{02,ref} \left(\frac{C_{OH}}{C_{OH,ref}} \right)^2 \exp(\eta_2 / b_{oer}) \quad (6)$$

$$i_{loc,3} = i_{03,ref} (\exp(\alpha_{a3} F \eta_3 / RT) - \exp(-\alpha_{c3} F \eta_3 / RT)) \quad (7)$$

$$i_{loc,4} = i_{04,ref} \left(\left(C_{OH} / C_{OH,ref} \right)^2 \exp(\alpha_{a4} F \eta_4 / RT) - \left(C_{O_2} / C_{O_2,ref} \right) \exp(-\alpha_{c4} F \eta_4 / RT) \right) \quad (8)$$

The local reaction rates of Reaction (1), Reaction (2), Reaction (3), and Reaction (4) are given as $i_{loc,1}$, $i_{loc,2}$, $i_{loc,3}$, and $i_{loc,4}$, respectively. C_m [mol cm⁻³] and $C_{m,ref}$ [mol cm⁻³] denote the local concentration and the reference concentration of the corresponding species m , respectively. In Equation (5), $C_{H,max}$ [mol cm⁻³] is the proton concentration of Ni(OH)₂ in a fully discharged state, calculated by dividing the density of Ni(OH)₂ (3.55 g cm⁻³) by its molecular weight (92.71 g mol⁻¹), yielding 0.0383 mol cm⁻³. Note that the volumetric change of the active material owing to the difference between the density of the charged and discharged state, was neglected. $i_{0j,ref}$ is the exchange current density evaluated at the reference conditions (where $C_H = C_{H,ref}$, $C_{OH} = C_{OH,ref}$, and $C_{O_2} = C_{O_2,ref}$); b_{oer} [V] is the Tafel slope for oxygen evolution reaction at the cathode; α_{aj} and α_{cj} are the anodic and cathodic charge transfer numbers of j th reaction, respectively. Note that $i_{04,ref}$, α_{a4} , and α_{c4} on Zn were assumed to be the same as those on Cd; these parameters had minimal effects on capacity retention calculations of the nickel hydroxide cathode. F [C mol⁻¹] is the Faraday's constant; R [J mol⁻¹ K⁻¹] is the gas constant, and T [K] is the absolute temperature. The over-potential η_j [V] is defined by:

$$\eta_j = \phi_s - \phi_l - U_{j,ref} \quad (9)$$

where ϕ_s [V] is the electric potential of the solid phase; ϕ_l [V] is the electrolyte potential; $U_{j,ref}$ [V] is the equilibrium potential at the reference condition.

Within the active material, the diffusion of the protons is dictated by Fick's second law:

$$\frac{\partial C_H}{\partial t} = D_H \nabla^2 C_H \quad (10)$$

where D_H [cm² s⁻¹] is the proton diffusion coefficient. For the purposes of this model, the charging is assumed to take place under isothermal conditions at room temperature. Previous studies by Paxton and Newman [31], and more recently by Gu et al. [25] indicate that the diffusion coefficient value can be approximated as a constant for diffusion lengths smaller than 3 μ m, which is also the case in the present study. Thus, despite the fact that the diffusion coefficient of the protons depends on the state of charge (SOC) of the active material [32], a constant value is assumed for D_H throughout charging of the electrode. A wide range of values from 10⁻¹² to 10⁻⁸ [cm² s⁻¹] have been reported for the Ni(OH)₂-based electrodes, which, in addition to SOC, reportedly are also dependent on the synthesis methods and measurement techniques [31,33,34].

Herein, we measured the average diffusion coefficient of our electrodeposited active material over all states of charge by utilizing cyclic voltammetry (CV), which was shown to yield reliable results in other studies [35–38]. A three-electrode cell configuration was used for diffusion coefficient measurement. Freshly electrodeposited Ni(OH)₂ on a Ni foil was used as the working electrode, a large Ni sheet as the counter electrode, and a Hg/HgO electrode (6 M KOH) as the reference. A 6 M KOH solution was used as the electrolyte. The scan range was 0–0.6 V relative to the reference electrode. Scan rates of 2 mV s⁻¹, 4 mV s⁻¹, 6 mV s⁻¹, 8 mV s⁻¹, 10 mV s⁻¹, 15 mV s⁻¹, and 20 mV s⁻¹ were used. All measurements were performed at room temperature using a potentiostat (Ref 600, Gamry).

For an irreversible electrochemical reaction, assuming semi-infinite diffusion holds true for the time scale of the experiment, the peak current from the CV curve can be related to D_H as follows [36]:

$$I_p = 2.99 \cdot 10^5 \cdot n \cdot (\alpha \cdot n_\alpha)^{0.5} \cdot S \cdot C_{H,0} \cdot v^{0.5} \cdot D_H^{0.5} \quad (11)$$

where I_p [A] is the peak current, n is the number of electrons transferred, α is the transfer coefficient with n_α being the apparent number of electrons transferred, S [cm²] is the surface area of the electrode (cm²), $C_{H,0}$ [mol cm⁻³] is the initial proton concentration within the active material (i.e. $C_{H,max}$ [mol cm⁻³]), and v [V s⁻¹] is the potential scan rate. Here, $n = 1$, and the $\alpha \cdot n_\alpha$ value of 1.5 was assumed [36]. In addition, the geometrical area of the electrode was used for S . Based on Equation (11), the slope of I_p vs. $v^{0.5}$ from cyclic voltammograms can be used to determine D_H .

At the active material-electrolyte interface (at $x = \delta$), the proton flux is proportional to the nickel hydroxide reaction rate (Reaction (1)). At the interface of the active material and the Ni current collector (at $x = 0$), since no mass transfer is taking place, the flux equals zero. Taking these assumptions into account, the initial and boundary conditions for the model can be written as:

At $x = \delta$:

$$D_H \frac{\partial C_H}{\partial x} = -i_{loc,1} / F \quad (12)$$

At $x = 0$:

$$D_H \frac{\partial C_H}{\partial x} = 0 \quad (13)$$

At $t = 0$

$$C_H = C_{H,max} \quad (14)$$

The electron conduction within all solid phases is given by Ohm's law and the conservation of current:

$$i_s = -\sigma_s \nabla \phi_s \quad (15)$$

$$\nabla \cdot i_s = 0 \quad (16)$$

where i_s [A cm⁻²] is the local current density within the solid phase; σ_s [S cm⁻¹] is the electrical conductivity of the solid; ϕ_s [V] is the electric potential in the solid phase.

The transport of the ionic species within the liquid electrolyte is dictated by the Nernst-Planck equation:

$$\frac{\partial C_m}{\partial t} = \nabla \cdot ((D_m \nabla C_m) + z_m u_m F C_m \nabla \phi_l) \quad (17)$$

$$i_l = F \sum_m z_m (-D_m \nabla C_m - z_m u_m F C_m \nabla \phi_l) \quad (18)$$

$$u_m = D_m / (k_B T) \quad (19)$$

where $m = K^+$ and OH^- ; i_l [A cm⁻²] is the local current in the KOH electrolyte; ϕ_l [V] is the electrolyte potential; D_m [cm² s⁻¹] is the diffusion coefficient of ionic species within the KOH electrolyte; z_m is the charge number of the ionic species; u_m [s kg⁻¹] is the mobility of the charge species; k_B [J K⁻¹] is the Boltzmann's constant. In Equations (17) and (18), the interactions between KOH solutes are

neglected, and thus the activity gradients are assumed to be equal to the concentration gradients. In addition, natural convection due to local electrolyte density variations is ignored in this model.

Electro-neutrality is assumed to be maintained throughout the solution at all times:

$$\sum_m z_m C_m = 0 \quad (20)$$

The capacity retention τ of the electrode at a given charge rate is defined as:

$$\tau = \int (\oint i_{loc,1} dS) dt / (FC_{H,max} V) \quad (21)$$

where t [s] is the charge time; S [cm²] is the electrode active area; V [cm³] is the volume of the active material. The integration is first performed over the entire electrode/electrolyte interface and then over time.

4. Results and discussions

4.1. Characterization of the fabricated electrodes

We previously demonstrated that battery electrodes based on these multilayer structures were capable of retaining a large portion of their capacities when undergoing rapid charging and discharging [39]. However, such high power rates would only be practically meaningful if a long-term sustainability can be demonstrated as well.

Discharge profiles of a 100-layer electrode with respect to its capacity are presented in Fig. 3(a). Respective charge and discharge rates of 20C and 10C are applied for over 80 cycles, and profiles of six of these cycles are plotted. These profiles are in good agreement with those of Ni(OH)₂ electrodes reported previously in the literature [3,40]. The measured capacity of 2.43 mAh cm⁻² after the 30th cycle is found to drop to 2.02 mAh cm⁻² after the 80th cycle, which corresponds to a significant capacity retention of 83% even at these high charge and discharge rates.

The cycling performance of the 100-layer electrode is also assessed by varying charging rates. For a constant discharge rate of

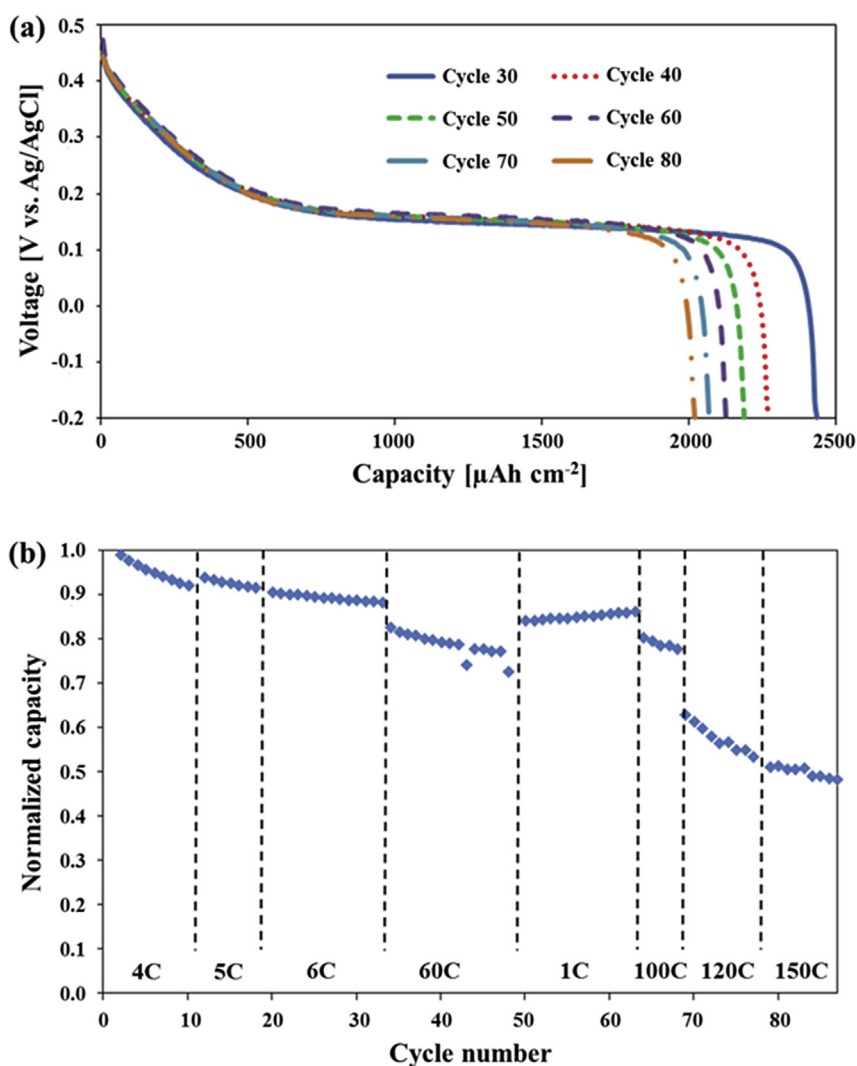


Fig. 3. Performance characterization of the fabricated electrodes: (a) discharge profiles of a 100-layer electrode charged at 20C and discharged at 10C for over 80 cycles, (b) normalized capacity of a 100-layer electrode charged at various rates (1–150C) and discharged at a constant rate of 4C for over 80 cycles.

4C, the electrode is charged at 8 different rates, as shown in Fig. 3(b). More than 80 charge and discharge cycles are conducted, and outstanding capacity retention is observed even at extremely high charging rates greater than 60C. At a charging rate of 150C (i.e., a total charging time of 24 s), the electrode is able to deliver approximately 50% of its 4C capacity, which confirms the high-power capability of this multilayer electrode device. The realization of such high-power capability can be attributed to a thin and conformal active material coating on each Ni layer, which reduces the diffusion and conduction path lengths for the solid-state ions and electrons, respectively. In addition, the high electronic conductivity of Ni backbone minimizes resistance for the transfer of electrons to and from the active material. Note that the normalized capacity at 1C after 50 charge and discharge cycles is slightly lower than that at 6C after 20 cycles may stem from the loss of some active material due to pulverization during the harsh operating conditions (i.e., 60C charge rate for 15 cycles) [41].

This high cycling stability is also an indication of mechanical stability and integrity of the electrodeposited $\text{Ni}(\text{OH})_2$ films on the multilayer Ni backbone, which are further confirmed by the high-resolution SEM images shown in Fig. 4. Although some cracks are observed in Fig. 4(a), the film remains mostly intact due to the good adhesion between the Ni backbone and the active material, even at these high charge and discharge rates.

The capability of depositing $\text{Ni}(\text{OH})_2$ onto relatively complex 3D architectures in a conformal fashion is shown in Fig. 4(b). The bottommost layer of the multilayer electrode is carefully separated using a piece of tape adhered to the electrode. The SEM image of the separated layer demonstrates that the $\text{Ni}(\text{OH})_2$ film is able to preserve its conformal coating not only on the sidewalls, but also on the inner regions of the Ni layers.

It is noted that some portions of the Ni current collector underneath the $\text{Ni}(\text{OH})_2$ film are exposed due to the cracks that form in the active material following the harsh charge/discharge conditions. Therefore, it is important to determine whether the exposed regions of the Ni backbone contribute to the performance of the electrode because of the $\text{Ni}(\text{OH})_2$ formation during the charging (i.e., anodizing) steps, especially at high rates. Anodic oxidation of Ni is known to result in the growth of a $\text{Ni}(\text{OH})_2$ film. However, due to the self-limiting nature of the growth of hydroxide layer, the resulting film would be expected to be of relatively insignificant thickness ($\sim 1\text{--}2\text{ nm}$) unless specific techniques, such as periodic square-wave potentials at high frequencies, are applied [42]. As a result, a negligible contribution is expected from anodically grown $\text{Ni}(\text{OH})_2$ film. To further confirm this experimentally, a blank multilayer Ni structure is tested prior to deposition of $\text{Ni}(\text{OH})_2$ under the same charge and discharge conditions. The measured

capacity of the blank electrode is less than 1% of what is obtained from the $\text{Ni}(\text{OH})_2$ -coated electrode.

4.2. Modeling of the fabricated electrodes

To determine whether the model can successfully predict the performance of the fabricated electrodes, capacity retention calculations (Equation (21)) are performed using the model described earlier, based on experimental dimensions of the aforementioned 100-layer structure: $1\text{ }\mu\text{m}$ for active material thickness, $2\text{ }\mu\text{m}$ for interlayer spacing, and $1.5\text{ }\mu\text{m}$ for Ni structural layer. The mathematical model requires a number of physical properties. These parameters are found from existing literature and listed in Table 1 below.

As can be seen in Fig. 5, theoretical results obtained from the model agree with the experimental results. This agreement between the experimental and the modeling results indicates that the model can be employed to optimize the design of multilayer electrodes for rapid charge and discharge power applications.

Note that, as mentioned previously, a key model input parameter is the diffusion coefficient of protons within the $\text{Ni}(\text{OH})_2$ active material, D_H . In the model, a best-fit value of $3.4 \times 10^{-10}\text{ cm}^2\text{ s}^{-1}$ is used for D_H . Repeated cyclic voltammetry measurements show that the experimental diffusion coefficient value ranges from $2 \times 10^{-10}\text{ cm}^2\text{ s}^{-1}$ to $3 \times 10^{-10}\text{ cm}^2\text{ s}^{-1}$. A sample experimental cyclic voltammogram of the $\text{Ni}(\text{OH})_2$ electrode is shown in Supplementary Fig. 3(a), and the corresponding relationship between I_p and $v^{0.5}$ is shown in Supplementary Fig. 3(b). Since the best-fit value from the mathematical model is close to the experimentally measured value and a constant average diffusion coefficient could be used as previous studies suggest, we are justified in using the best-fit value for the model.

4.3. Design of the electrodes

One of the main premises of this study is the ability to control the characteristic dimensions, such as the surface area and the active material thickness, of the fabricated electrodes. Therefore, efforts are directed towards finding the optimal electrode dimensions that would lead to enhanced power performance. As mentioned previously, maximization of the surface area, along with the minimization of the diffusion and conduction path lengths, would lead to electrodes with high capacity and rapid charging capabilities. In the multilayer fabrication approach, the surface area maximization can simply be achieved by increasing the number of layers, as well as by decreasing the interlayer spacing and Ni structural layer thickness. Thus, two geometrical parameters are

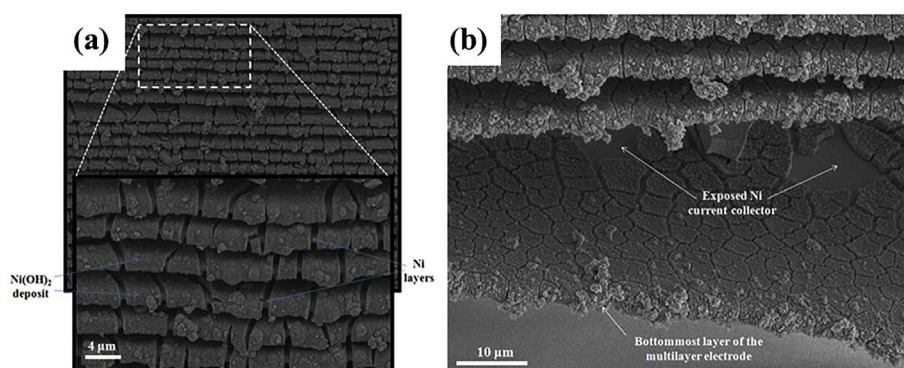


Fig. 4. SEM images of the multilayer electrode following the cyclic performance tests: (a) side view of the electrode, (b) the bottommost layer separated from the rest of the multilayer electrode to confirm integrity and conformal coating of the active material after cyclic performance tests.

Table 1

Values of physical parameters.

Parameter	Value	Unit	Source
D_{OH}	3×10^{-5}	$\text{cm}^2 \text{s}^{-1}$	[43,44]
D_{O_2}	1×10^{-3}	$\text{cm}^2 \text{s}^{-1}$	[24]
D_H	3.4×10^{-10}	$\text{cm}^2 \text{s}^{-1}$	Best-fit from the model
$i_{01,ref}$	1.04×10^{-4}	A cm^{-2}	[31]
$i_{02,ref}$	1×10^{-11}	A cm^{-2}	[24]
$i_{03,ref}$	1.75×10^{-2}	A cm^{-2}	[30]
$i_{04,ref}$	1×10^{-14}	A cm^{-2}	[24]
$C_{OH,ref}$	6×10^{-3}	mol cm^{-3}	
$C_{O_2,ref}$	10^{-7}	mol cm^{-3}	[24]
$C_{H,ref}$	$0.5 C_{H,max}$	mol cm^{-3}	[24]
$C_{H,max}$	3.83×10^{-2}	mol cm^{-3}	[25]
b_{oer}	0.018	V	[28]
$U_{1,ref}$	0.427	V vs. Hg/HgO	[24]
$U_{2,ref}$	0.3027	V vs. Hg/HgO	[24]
$U_{3,ref}$	-1.38	V vs. Hg/HgO	[45]
$U_{4,ref}$	0.3027	V vs. Hg/HgO	[24]
α_{a1}	0.5	1	[24]
α_{c1}	0.5	1	[24]
α_{a3}	0.5	1	[30]
α_{c3}	0.5	1	[30]
α_{a4}	1.5	1	[24]
α_{c4}	0.5	1	[24]
σ_{Ni}	1.38×10^5	S cm^{-1}	[46]
$\sigma_{Ni(OH)_2}$	$0.1185 \exp(-8.459 (C_H/C_{H,max})^4)$	S cm^{-1}	[47]
σ_{Zn}	1.66×10^5	S cm^{-1}	[46]

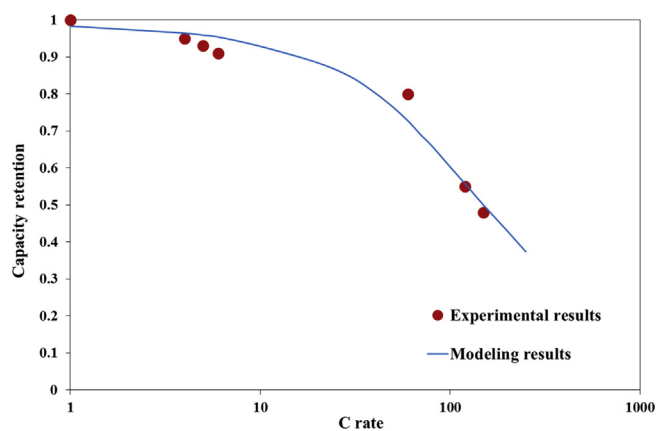


Fig. 5. Experimental vs. model capacity retention of a 100-layer electrode with 1.5 μm Ni structural layer, 1 μm Ni(OH)₂ on each side of a single Ni layer, and 2 μm interlayer spacing at various charge rates.

considered in this optimization study in order to maximize the surface area: the interlayer spacing between two active material layers and the thickness of the Ni structural layer. However, the minimization of the diffusion and conduction paths, which enables high charge rates, has to be achieved at the expense of energy density, due to decreased active material thickness relative to the thickness of the Ni structural layer. Consequently, the active material thickness used for the multilayer structure depends on the specific application scenario.

Fig. 6 shows the relationship between energy/power density and interlayer spacing for a fixed total height of 218 μm , the active material thickness, the Ni structural layer thickness, and the charge rate. The total height is fixed in this optimization study to reflect the fabrication constraint due to maximum height that can be achieved by the photoresist mold experimentally, which is about 300 μm . Values higher than 218 μm are not used due to significant computational loads. Also note since we mainly focus on cathode optimization in the current study and the anode is assumed to be in

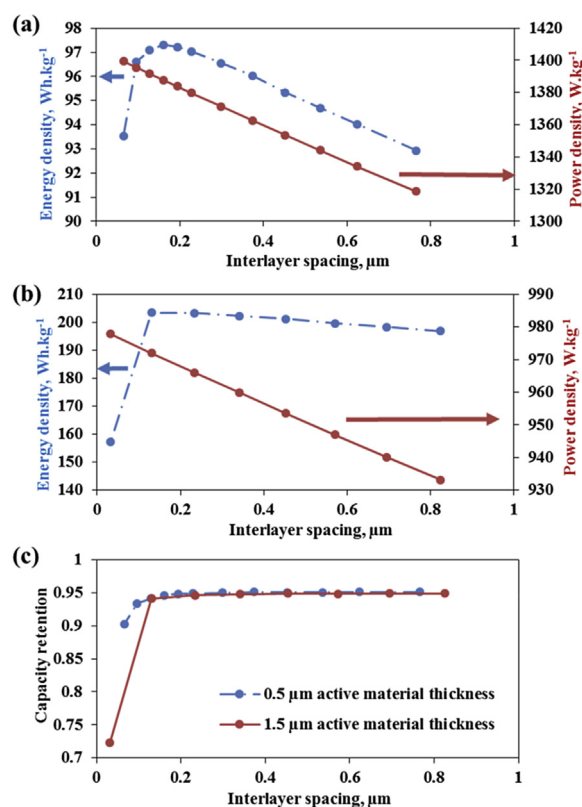


Fig. 6. Gravimetric energy and power densities as a function of interlayer spacing for an electrode with 218 μm total height and 1.5 μm Ni thickness: (a) 0.5- μm -thick active material at 13.5C, (b) 1.5- μm -thick active material at 4.5C. (c) capacity retention as a function of interlayer spacing for electrodes with 0.5 μm and 1.5 μm thick active material, 13.5 C and 4.5 C charge rates respectively, 218 μm total height, and 1.5 μm Ni thickness.

great excess, the energy and power densities are calculated based only on the cathode structure (including the mass and the volume

of the Ni current collector, the active material, and the electrolyte within the cathode structure). It can be seen from Fig. 6(a) and (b) that when interlayer spacing is greater than 0.2 μm , both energy and power densities decrease as interlayer spacing increases, as a result of decreased number of layers. However, when the interlayer spacing decreases below 0.2 μm , as can be seen in Fig. 6(c), capacity retention decreases dramatically below 95%, likely because the amount of electrolyte (i.e., KOH) in between two active material layers, especially for the layers in the middle of the structure, becomes insufficient to support the electrochemical reaction as the interlayer spacing narrows (See Supplementary Fig. 4(a)). This causes a decrease in the active material utilization (See Supplementary Fig. 4(b)) and thus energy density. In addition, through extrapolation, gravimetric power density improves marginally below 0.2 μm for all active material thicknesses shown. Hence, an interlayer spacing of 0.2 μm is set to be the optimal value.

During charging of the electrode, protons diffuse from the bulk of the active material (i.e., $\text{Ni}(\text{OH})_2$) to the electrode/electrolyte interface, resulting in a concentration gradient that forms within the active material film. As the charge rate increases, the concentration gradient for the protons increases. At sufficiently high charge rates, it may not be possible for the protons to diffuse away from the active material in a desired duration of time due to limited proton diffusion rates and earlier onset of the oxygen evolution reaction. Fig. 7(a) shows the concentration profile of protons across the active material film at the end of the charging process. It can be clearly seen from Fig. 7(a) that for a $\text{Ni}(\text{OH})_2$ film thickness of 1 μm , a negligible concentration profile forms across the active material at 1C, indicating that it is possible to almost fully charge the electrode at this rate. As the charge rate increases, there is a gradual increase in the amount of protons at the current collector/ $\text{Ni}(\text{OH})_2$ interface, which are not able to be delivered to the electrolyte. With

a charge rate of 120C, about 30% of the protons cannot be transported to the electrolyte in 30 s.

Thus, we can conclude that for each active material thickness, there is a maximum C rate, say x C, for the active material to be fully (or almost fully, i.e., 95%) charged within x^{-1} hours. Fig. 7(b) shows the relationship between this maximum charge rate and the active material thickness. As expected, the maximum charge rate that allows at least 95% capacity retention decreases with the active material thickness due to increased diffusion lengths. Hence, we can clearly observe the tradeoff between energy density and power density for the $\text{Ni}(\text{OH})_2$ electrode, and in fabrication we can choose the active material thickness depending on whether energy density or power density is deemed more important in the actual application scenario.

The impact of the active material thickness, as well as the Ni structural layer thickness, on both the energy and power density of the electrodes is shown in Supplementary Fig. 5. Note that all data points are generated using an optimal interlayer spacing of 0.2 μm . Corresponding power density on the y-axis represents the maximum power that could be obtained for a certain active material thickness, with minimal loss in energy density, i.e. 95% capacity retention. We can see that a thinner $\text{Ni}(\text{OH})_2$ layer improves the power performance but at the expense of the storable energy. The gravimetric density is more important for macroscale applications where the mass of the power source is usually the limiting factor (e.g., cell phones), whereas the volumetric density is generally the main concern for applications with limited space (e.g., microsensors and microactuators). Note that for the power and energy density calculations, the charging potential of the electrode is assumed to be constant and equal to 1.8 V. In addition, as expected, a thinner Ni structural layer improves the power and energy densities regardless of the active material thickness.

In Fig. 8, we construct Ragone plots of the micro-fabricated multilayer electrode by plotting the projected power density on the y-axis and the projected energy density on the x-axis, parametrized by the Ni structural thickness. For each Ni current collector thickness, energy densities for active material thickness ranging from 0.4 μm to 1.5 μm at an interval of 0.1 μm are calculated. Again all data points are generated using an optimal interlayer spacing of 0.2 μm , and corresponding power density on the y-axis represents the maximum power that could be obtained with 95% capacity retention. We also incorporate the performance of the experimentally fabricated structure on the plot. Based on the projections, it can be seen that on both gravimetric and volumetric basis, by reducing the interlayer spacing from 2 μm to 0.2 μm and Ni structural layer thickness from 1.5 μm to 0.5 μm , we can double the energy density and increase the power density by almost one order of magnitude, in comparison with experimental performance.

However, we must realize that the surface area maximization can be limited by fabrication constraints, including the total height of the electrode (i.e., achievable photoresist mold thickness) and the minimum allowed thickness for individual Ni layers to remain mechanically intact. Even though electroplating would allow formation of Ni and Cu layers on the nanometer scale [48,49], Ni structural layers should possess a certain thickness in order to sustain mechanical integrity of the electrodes for the rest of the fabrication process, which involves etching of the Cu layers, a relatively harsh protocol, and deposition of the active material. Furthermore, utilizing very thin Cu layers is found to complicate the deposition of the active material. Even under pulse plating conditions with very long off times, the channels are observed to be clogged owing to the non-uniform and excess deposition of $\text{Ni}(\text{OH})_2$ onto the sidewalls of the multilayer Ni backbone. Thus, new fabrication schemes need to be devised in order to achieve multilayer electrodes with optimized dimensions. Nonetheless, the

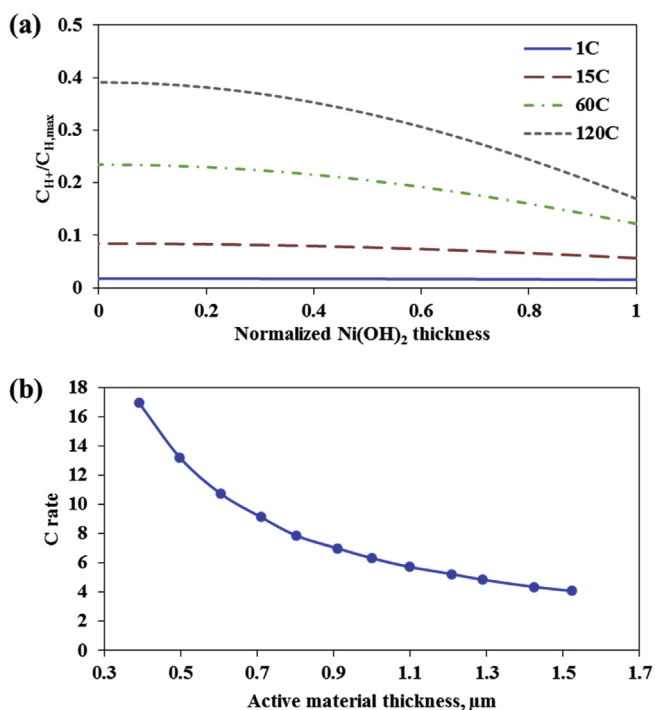


Fig. 7. (a) Concentration profiles of H^+ across the active material thickness at the end of the charging process at different C rates, at the middle layer of a 10-layer structure. Normalized thickness values of 0 and 1 refer to Ni current collector/ $\text{Ni}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2/\text{KOH}$ electrolyte interfaces, respectively, and (b) Maximum charge rate that allows 95% capacity retention of different active material thickness. Structure dimensions: 1.5 μm Ni thickness, 0.2 μm interlayer spacing, 218 μm total height.

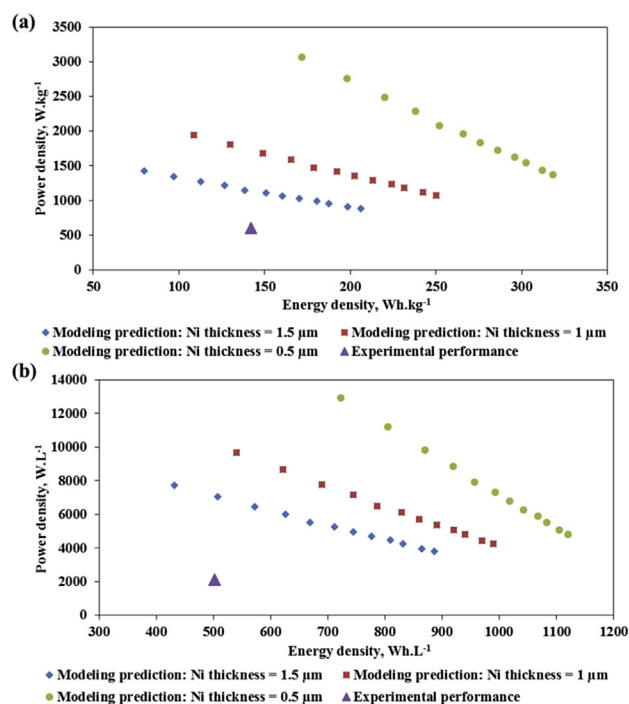


Fig. 8. For a 218 μm tall structure with 0.2 μm interlayer spacing, theoretical power density of the electrodes is plotted as a function of theoretical energy density, parametrized by the Ni current collector layer thickness; comparison is made with experimental performance on: (a) gravimetric basis, (b) volumetric basis. For each Ni current collector thickness, the individual data points represent active material thicknesses ranging from 0.4 μm to 1.5 μm, with an interval of 0.1 μm.

optimization studies have shown that the application of this multilayer structure could lead to batteries with significantly enhanced performance in terms of both energy and power densities.

5. Conclusions

We have demonstrated highly scalable and well-ordered microfabricated 3D Ni(OH)₂ electrodes with rapid charging capabilities. These electrodes are based on multilayer microstructure concept with precisely controlled dimensions, which is able to address several aspects of battery dynamics that are essential for enhanced performance. First, highly laminated Ni layers enable high surface area that is essential for high-power electrodes. Second, the realization of a thin and conformal active material coating on each Ni layer reduces the diffusion and conduction path lengths for the solid-state ions and electrons, respectively. Hence, the power-limiting effect originating from the low ionic conductivity of Ni(OH)₂ is significantly mitigated. Finally, the mechanically stable and electrochemically inert Ni backbone serves as the current collector. The high electronic conductivity of Ni minimizes resistance for the transfer of electrons to and from the active material. Electrodes with areal capacities as high as 2.43 mAh cm⁻² are realized, which simultaneously feature remarkable cycling stability when charged and discharged at high rates for more than 80 cycles. We are also able to fabricate electrodes that deliver more than 50% of their capacities when charged at an ultrafast rate of 150C. Moreover, a mathematical model has been developed, which is shown to successfully predict the electrochemical performance of the fabricated multilayer electrodes. Depending on the energy and power needs, these models open up the possibility for the realization of deterministically engineered electrodes for both micro- and macro-scale applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2017.05.017>.

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