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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.

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., microsensors, 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 mm 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 °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.