

ELECTRODEPOSITION OF NANO-SIZED ZINC ANODES ON VIRAL TEMPLATES

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Abstract: The development of nanostructured zinc anodes for alkaline batteries utilizing electrodeposition on nickel-coated *Tobacco mosaic virus* (TMV) is reported. Zinc is deposited from a potassium hydroxide (KOH) electrolyte saturated with zinc oxide (ZnO) nanopowder. Microstructural analysis using SEM and Energy Dispersive X-ray Spectroscopy (EDX) verifies the presence of zinc and indicates good uniformity and porosity of the nanostructured electrode. Electrochemical characterization demonstrates appropriate cyclic behavior and capacity in the range of ~ 2.2 to 2.7 mAh/cm² for the first 50 cycles of operation. These results, combined with the processing capabilities of the TMV, enable the development of next-generation all-virus-structured microbatteries.

Keywords: *Tobacco mosaic virus*, nanostructures, anode, batteries

INTRODUCTION

The development of miniaturized autonomous microsystems is highly dependent upon the integration of on-chip efficient power sources that can meet the energy requirements of such applications. These modules must balance the trade-off between small footprint and high capacities and energy densities which are desirable for proper and uninterrupted operation. In the field of Microelectromechanical Systems (MEMS), this issue has been addressed by increasing the reactive surface area of microbatteries in the out-of-plane dimension through the realization of three-dimensional architectures [1-3]. These designs result in higher aerial capacities and energy densities without compromising device footprint.

A very attractive and promising approach in this direction is the development of novel electrodes based on nanostructured materials. Nanosized materials provide higher surface area, shorter distances for charge and mass transfer and improved ion kinetics and accordingly, their utilization in power sources is an actively researched topic [4, 5]. In previous work, our group has used the *Tobacco mosaic virus* (TMV) as a versatile and inexpensive template to synthesize materials for energy related applications [6, 7]. The TMV is a high aspect ratio cylindrical plant virus measuring 300 nm in length with a diameter of 18 nm. Genetic modifications in the virus coat proteins allow the insertion of functional groups that facilitate

attachment of the TMV onto various substrates as well as coating with inorganic materials in electroless solutions. This synthetic pathway has been combined with MEMS fabrication techniques for the realization of a proof-of-concept nickel-zinc microbattery [7] as well as the development of combined bottom-up/top-down biofabrication methods such as photolithographic patterning of coated TMV and assembly onto three dimensional architectures [8].

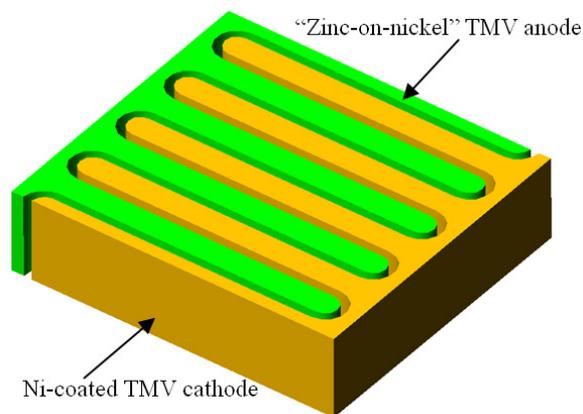


Fig. 1: Schematic showing envisioned three-dimensional nickel-zinc microbattery with two virus-structured electrodes.

The work presented here is motivated by the envisioned next-generation of devices shown in Fig. 1. In this design, three-dimensional microstructures will be fabricated to increase device area and nickel-coated TMV will be selectively assembled on their

surface. The zinc electrode is successively deposited using electroplating on the nickel-coated virus, resulting in an increased surface area device with two virus-structured electrodes. In this paper, the feasibility of structuring a zinc electrode on nanostructured nickel surfaces assembled on planar substrates is investigated.

EXPERIMENTAL

Sample Fabrication

In order to accurately control the electrode surface area on which the virus is assembled, samples are fabricated using lithographic techniques. The process, shown schematically in Fig. 2, begins with the deposition of a 200 nm thick silicon nitride layer using LPCVD on a silicon wafer. Square electrode areas ranging from 0.36 to 1 cm² and connection pads adequately spaced from the active surface are defined using photolithography. Titanium and gold layer (20 and 250 nm) are then e-beam evaporated and serve as the basis for TMV self-assembly. Following this process, the virus is attached to the gold surface and then coated with nickel using the process described in [6, 7]. After nickel plating, the chips are immersed in an acetone bath and ultrasonicated; this results in removal of the coated TMV, metal, and underlying photoresist leaving the virus in the defined areas only.

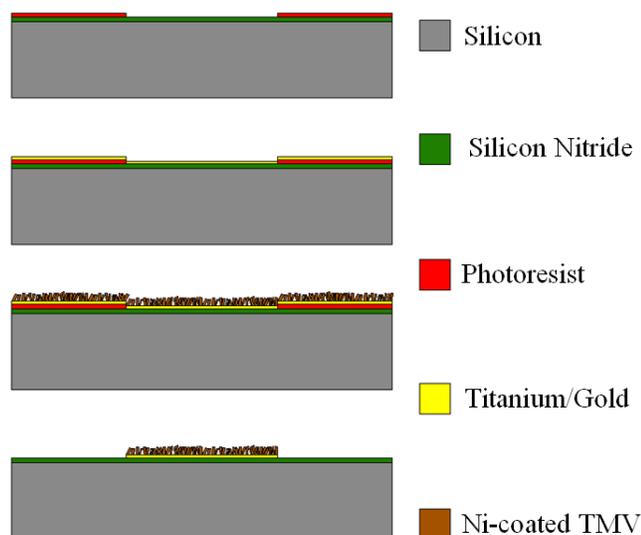


Fig. 2: Cross-sectional schematic of the sample fabrication process flow (before zinc electrodeposition).

The electrolyte used for zinc electrodeposition is composed of potassium hydroxide (KOH) at a concentration of 4 M and zinc oxide nanopowder (size <100 nm) which is diluted in the solution until it becomes saturated. A commercial nickel hydroxide cathode is used a

counter electrode and the nickel-coated TMV chip is the working electrode. Since nickel is a very good catalyst for hydrogen evolution, a two-step electroplating process is used. At first, a high current density of 7 mA/cm² is applied until the potential between the two electrodes stabilizes around 1.8 V. At this point, nucleation of zinc particles begins on the working electrode surface and the current density is decreased to 3-5 mA/cm² to obtain a thinner and more uniform deposit around the nickel-coated TMV. The actual plating time is then varied according to the desired deposition thickness and loading.

Fig. 3 shows an SEM image of a nanostructured electrode where zinc has been deposited on the metal-coated virus surface. The corresponding EDX map verifies the presence of the main elements of interest on the structure. The presence of the oxygen signal is due to the drying process of the chips, which is conducted on a level hotplate in air at ~150°C; this results in partial oxidation of the metallic deposits.

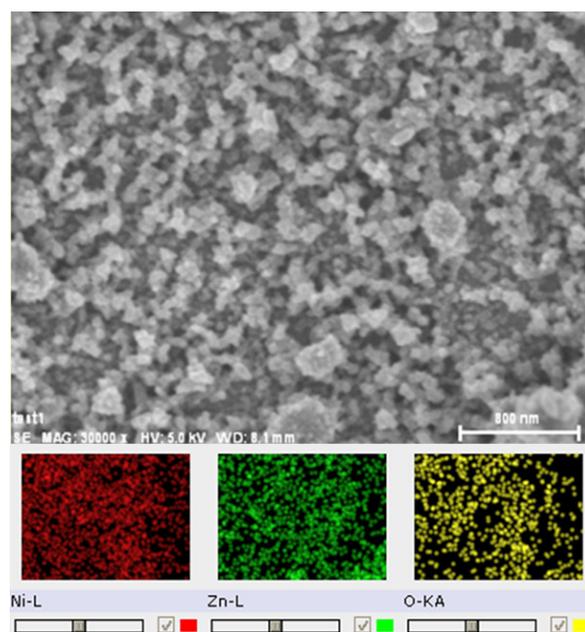


Fig. 3: SEM image of a fabricated nanostructured electrode and corresponding EDX elemental mapping.

Fig. 4 contains close-up view SEM images of samples before and after zinc electrodeposition. It can be observed that by properly controlling the deposition parameters (actual deposition time and current density) the thickness and uniformity of the zinc deposit can be tuned accordingly. Larger clusters than can be seen in Fig. 3 and 4 can be

avoiding by further decreasing the current density. However, due to known problem of zinc dissolution in the alkaline electrolyte [9], to achieve a high capacity, a higher zinc loading is required.

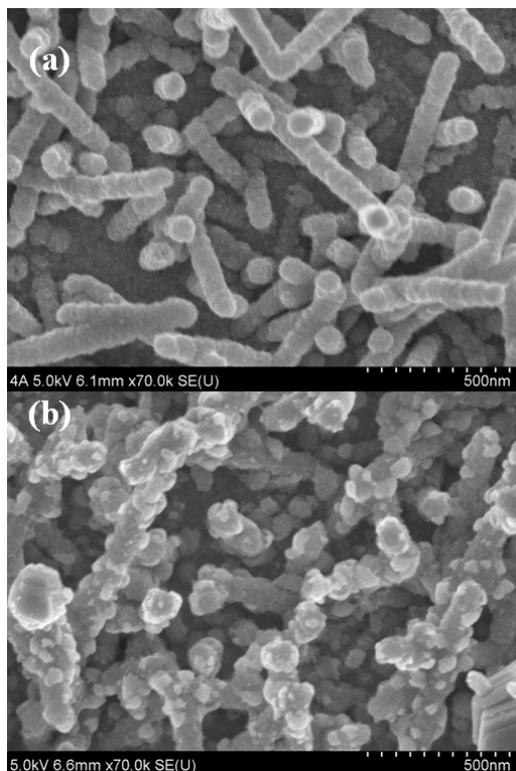


Fig. 4: SEM images of nickel-coated TMV surface before (a) and after (b) zinc electrodeposition.

Testing Set-Up

The performance of the synthesized zinc anodes was evaluated in a nickel-zinc battery configuration to investigate the cycling behavior and cycle stability. The electrolyte was again KOH 4M saturated with ZnO nanopowder, however in this experiment only the “clean” part of the solution was utilized (i.e. solution in which ZnO was completely dissolved). A similar cathode was used as a counter electrode and a zinc strip embedded in separator served as a reference electrode to monitor the potential of the nanostructured anode separately.

In order to minimize additional deposition of zinc which can occur during repeated cycling as the deposit is redistributed on the surface, a sealed container was used. This configuration prevents evaporation of the electrolyte which is necessary to ensure that the solution does not become oversaturated and thus promote excessive deposition. An optical image of the cell employed in this characterization is shown in Fig. 5. A Teflon tube is filled with the electrolyte up to a certain level which is enough to wet the electrodes; a top Teflon capping

manifold bearing wires for electrical connections to the electrodes is inserted inside the tube and held in place with screws around the perimeter, while an o-ring provides proper sealing. The cell is then connected to an Arbin Instruments battery test station which cycles the working-to-counter potential from 1.8 to 1.3 V at a constant current of 2 mA while monitoring the potential between the working and reference electrodes.

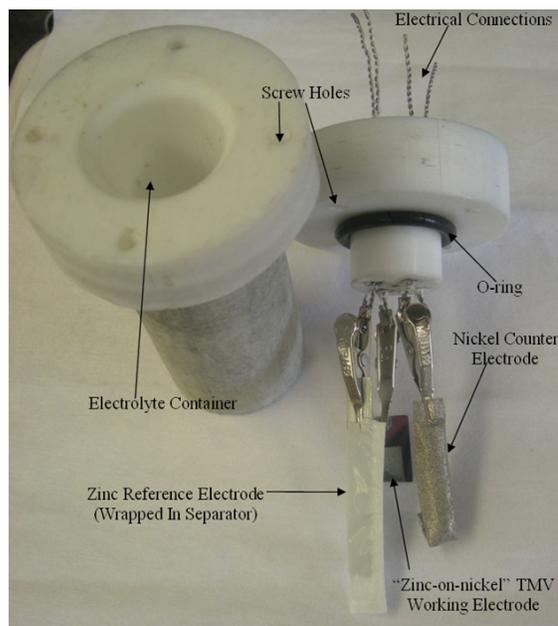


Fig. 5: Optical image showing the cell used for testing.

RESULTS AND DISCUSSION

Fig. 6 is a graph showing a typical charge-discharge cycle of the assembled cell. It can be observed that the capacities for charging and discharging are approximately equal, as indicated by the respective times. This implies appropriate behavior of the cell, since it delivers most of its charge capacity during every cycle.

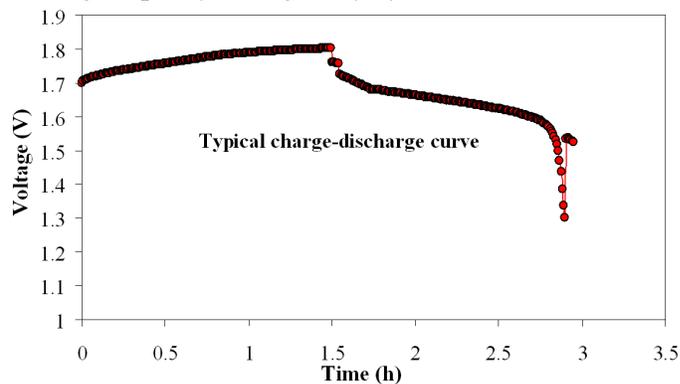


Fig. 6: Typical charge-discharge curve of a TMV sample plated at 5 mA/cm² for 20 minutes and cycled at a rate of 2 mA.

The capacity vs. cycle number graph for the same synthesized surface is shown in Fig. 7. After the first forty nine cycles of operation, the capacity (~2.2 mAh/cm²) has dropped less than 15% from the approximate initial values of 2.6-2.7 mAh/cm², indicating a very good cyclic stability for the virus-structured zinc electrode.

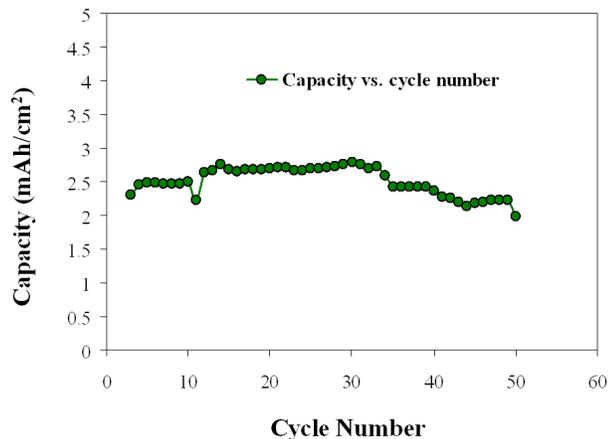


Fig. 7: Capacity vs. cycle number for the same sample.

It should be noted that the capacity in this work is normalized based on the areal footprint of the sample chips and not the mass loading of the zinc active material (gravimetric capacity). While mass loading was measured with a high precision microbalance (± 1 μ g) before and after the electroplating process, additional deposition of zinc is not completely eliminated from the experiments; this implies that precise calculation of the gravimetric capacity cannot be obtained with the electrolyte used, making the areal capacity a more accurate representation of the electrode performance.

CONCLUSION

The development of a nanostructured zinc anode using electrodeposition on a nickel-coated TMV template was presented in this paper. Zinc was deposited using a two-step electroplating process in an electrolyte composed of 4 M KOH saturated with ZnO nanopowder. Variation of the critical deposition parameters (time and current density) allows accurate control of the deposit morphology as indicated by SEM down to tens of nanometers thick layers around the TMV surface. Thicker zinc deposits were electrochemically characterized in an alkaline nickel-zinc battery configuration using a sealed Teflon cell. Results indicate appropriate cycling behavior with symmetric charge/discharge cycles and excellent cyclic stability of the electrode for up to 50 cycles of operation. These results demonstrate the feasibility of expanding the range of available materials that can be

synthesized using the nickel-coated TMV template. Additionally, due to the solution-based nature of electrochemical deposition, the proposed process can be directly expanded from planar to three-dimensional geometries for the realization of increased surface area, high-performance alkaline microbatteries.

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REFERENCES

- [1] Long J W, Dunn B, Rolison D R, White H S, 2004 Three-Dimensional Battery Architectures, *Chem. Rev.*, 104, 4463-4482
- [2] Teixidor G T, Zaouk R B, Park B Y, Madou M J, 2008 Fabrication and characterization of three-dimensional carbon electrodes for lithium ion batteries, *J. Power Sources*, 183, 730-740
- [3] Chamran F, Yeh Y, Min H-S, Dunn B, Kim C-J, 2007 Fabrication of High-Aspect-Ratio Electrode Arrays for Three-Dimensional Microbatteries, *J. Microelectromech. Syst.*, 16, 844-852
- [4] Guo Y-G, Hu J-S, Wan L-J, 2008, Nanostructured materials for electrochemical energy conversion and storage devices, *Adv. Mater.*, 20, 2878-2887
- [5] Rolison D R, Long J W, Lytle J C, Fischer A E, Rhodes C P, McEvoy T M, Bourg M E, Lubers A M, 2009 Multifunctional 3D nanoarchitectures for energy storage and conversion, *Chem. Soc. Rev.*, 28, 226-252
- [6] Royston E, Ghosh A, Kofinas P, Harris M T, Culver J N, 2007, Self-assembly of virus-structured high surface area nanomaterials and their application as battery electrodes, *Langmuir*, 24, 906-912
- [7] Gerasopoulos K, McCarthy M, Royston E, Culver J N, Ghodssi R, 2008, Nanostructured nickel electrodes using the *Tobacco mosaic virus* for microbattery applications, *J. Micromech. Microeng.*, 18, 10
- [8] Gerasopoulos K, McCarthy M, Banerjee P, Fan X, Culver J N, Ghodssi R, 2009, Biofabrication methods for the patterned assembly and synthesis of viral nanotemplates, *Small*, submitted
- [9] McLarnon F R, Cairns E J, 1991, The secondary alkaline zinc electrode, *J. Electrochem. Soc.*, 138, 645-664