# MICROBATTERIES WITH TOBACCO MOSAIC VIRUS TEMPLATED ELECTRODES

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## ABSTRACT

The successful demonstration of a MEMS-fabricated battery incorporating viral nanostructures to increase the effective electrode area is reported in this paper. Nickel-zinc microbatteries with nanostructured cathodes utilizing self-assembly of the Tobacco Mosaic Virus (TMV) have been fabricated and characterized. A novel packaging scheme was created to investigate the effects of TMV coatings as well as microbattery geometry. Addition of the TMV structures increases the reactive surface area by an order of magnitude and enhances the battery performance. The capacity of a TMV modified battery was improved by a factor of six over planar electrode geometries. Appropriate charge-discharge behavior was observed for various designs, showing a twofold increase in capacity for an equivalent decrease in electrode spacing.

## 1. INTRODUCTION

Microbatteries are essential components in miniaturized systems such as smart dust nodes, wireless distributed sensor networks and hybrid power supplies, which require efficient power management for autonomous operation. The overall size of these systems is a limiting factor for the performance of microfabricated batteries. While traditional thin film batteries use planar electrode designs [1,2], MEMS fabrication techniques have been used to create high aspect ratio microstructures to increase the active electrode area. These three-dimensional architectures increase microbattery performance and energy density while maintaining device footprint [3,4].

To further increase available electrode area, the integration of biological structures has also been investigated. Nam *et al* demonstrated nanostructured electrodes for lithium ion batteries using M-13 bacteria virus coatings [5]. Previous work by our collaborators reports the use of genetically modified Tobacco Mosaic Virus (TMV) in the fabrication of nickel electrodes [6]. The current work focuses on integrating these TMV coated electrodes into a novel MEMS-fabricated battery. The TMV nanostructures have been used to increase the surface area of nickel cathodes within a nickel-zinc microbattery system. This is the first demonstration of a MEMS battery incorporating viral nanostructures to increase capacity.

## 2. MATERIALS AND CHEMISTRY

### Tobacco Mosaic Virus

The Tobacco Mosaic Virus (TMV) is a cylindrical high aspect ratio plant virus measuring 300nm long with an outer diameter of 18nm and an inner diameter of 4nm. The TMV is a robust biological platform, showing stability in a range of temperatures (up to 60°C) and pH values (2-10). It has been previously reported that genetically modifying the virus' coat proteins to introduce a cysteine residue facilitates self-assembly and electroless metal deposition [7].

In this work, we use the TMV1cys, an engineered modification of the wild-type virus containing a novel coat protein residue. This allows for self-assembly of the virus onto gold surfaces through thiol-gold interactions. After binding on the substrate, the TMV1cys can be coated with metals (nickel and cobalt) through an electroless deposition technique at room temperature. This technique produces dense, uniform coatings of the viral nanostructures which has been found to increase surface area by an order of magnitude compared to unmodified substrates [6]. Figure 1 shows SEM images of nickel coated gold surfaces with and without viral nanostructures.

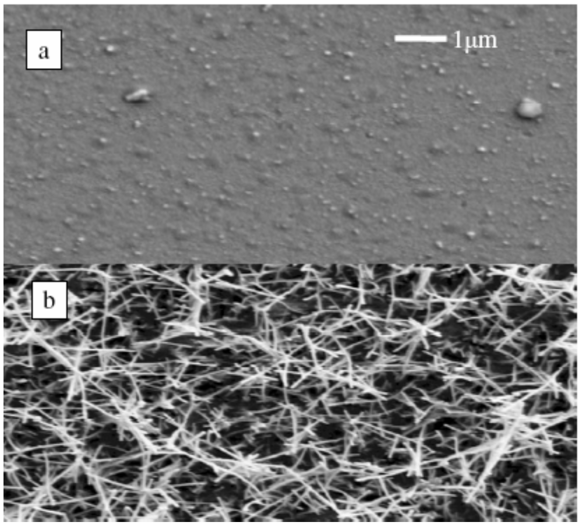

*Figure 1: SEM images of (a) unmodified and (b) TMV modified nickel electrodes.*

**Battery Chemistry**

The microbattery developed in this study uses a nickel-zinc system with a potassium hydroxide (KOH) electrolyte. This is a rechargeable alkaline battery that does not require special separators and can be constructed using standard MEMS fabrication processes. Its rechargeable nature allows it to be used in applications where many charge-discharge cycles are necessary.

Elemental analysis of the nickel coated TMV structures using X-ray spectroscopy shows the presence of nickel oxide (NiO) and nickel hydroxide ($Ni(OH)_2$) on the surface [6]. This implies that two reactions are occurring during battery operation:

$$2NiOOH + Zn + 2H_2O \Leftrightarrow 2Ni(OH)_2 + Zn(OH)_2$$
$$NiO + Zn \Leftrightarrow Ni + ZnO$$

The expected theoretical voltages for these two chemistries are 1.73V and 1.5V respectively.

## 3. DESIGN AND FABRICATION

The microbattery test device is comprised of two electrodes separated by an electrolyte cavity defined in SU-8. An image of a device diced in half and its cross sectional schematic are shown in Fig. 2. The bottom electrode (cathode) consists of nickel coated TMV structures assembled on a gold current collector and the top electrode (anode) is a zinc plate. The electrolyte is introduced via through-holes machined in the zinc.

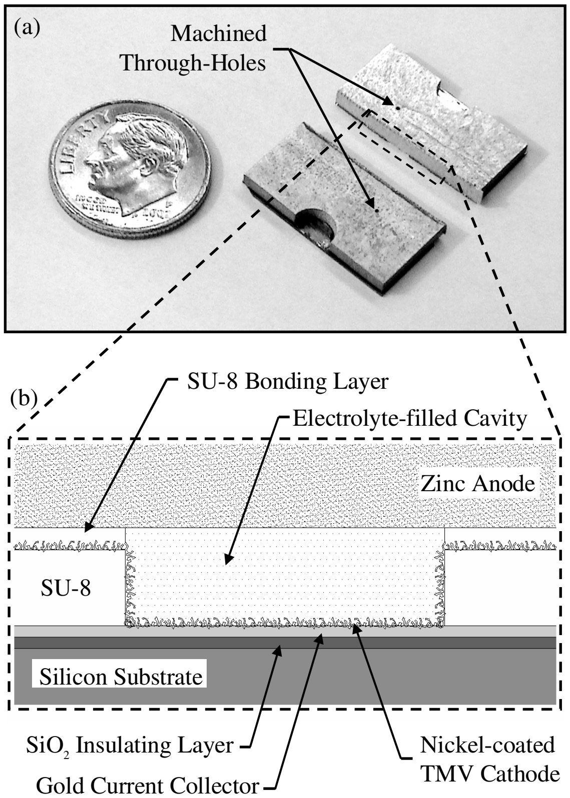

*Figure 2: (a) Photo of a microbattery diced in half and (b) cross sectional schematic.*

The fabrication process begins with the deposition of a 0.5µm LPCVD $SiO_2$ film on a p-type silicon wafer. This dielectric layer is used to isolate the substrate from the cathode. The gold current collector and substrate for TMV assembly is formed by e-beam evaporation of chrome (50nm) and gold (250nm) layers. A single photolithography step is then used to fabricate the SU-8 cavity on the gold film. Using SU-8 50, cavity areas of 0.36cm$^2$ and 0.64cm$^2$ with heights of 55µm and 100µm were created.

After SU-8 lithography, the wafers are diced into individual cathode layers and the fabrication continues at the die level. The nickel electrodes are then formed using the process described in [6]. The silicon die are first immersed in a solution containing 0.11 mg/ml of TMV1cys in sodium phosphate buffer solution and allowed to incubate overnight. The surface of the virus is then activated with a palladium catalyst during a second overnight step. Finally, the nanostructures are coated with nickel in an electroless plating solution.

The bottom electrode is bonded to the zinc plate which acts as the anode. The zinc anode is macroscopically machined with 500µm diameter fluidic ports for electrolyte circulation. Bonding is achieved with an intermediate SU-8 5 layer using a stamp-and-stick procedure. In addition to bonding, this SU-8 layer electrically isolates the two electrodes, since TMV was found to adhere well to SU-8 (Fig. 2b).

## 4. TESTING

The microbatteries were characterized using a potentiostat to investigate their charge-discharge behavior. A novel packaging scheme was created to facilitate testing of the different footprint areas. The device is sandwiched between two plastic components bolted together. The microbattery is placed on a rubber film at the base of the package and then covered with the top piece, containing various fluidic ports. Six rubber o-rings are used for support and sealing, while electrical connections with the potentiostat terminals are made with alligator clips.

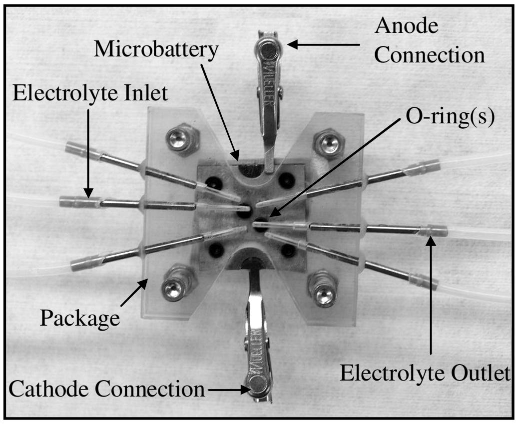

*Figure 3: Photo of a packaged microbattery showing the fluidic and electrical connections.*

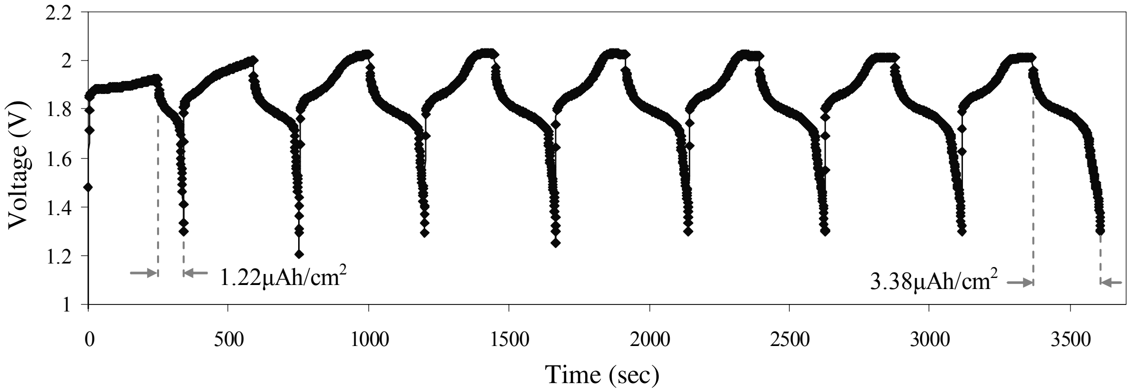

*Figure 4: Charge-discharge curve of a TMV microbattery showing capacity during the first and eighth discharges.*

The electrolyte selected for these experiments was a one molar (1M) KOH solution. This concentration is notably lower than those reported in the open literature, typically 4M to 6M [2,4,8]. It was observed that the zinc plate corrodes rapidly at higher concentrations, limiting testing capabilities.

## 5. RESULTS

### Charge-Discharge Response

Figure 4 shows the charge-discharge curve of a microbattery with a footprint area of $0.64 cm^2$ and an electrode distance of 55μm. The device is discharged at a constant current density of $50 \mu A/cm^2$. During each cycle, more nickel is converted to nickel oxide and nickel oxyhydroxide and the capacity of the battery increases. The first eight cycles of operation are shown in Fig. 4 where the capacity gradually increases from $1.22 \mu Ah/cm^2$ to $3.38 \mu Ah/cm^2$. This particular device operated successfully for more than 30 cycles reaching a capacity of $4.45 \mu Ah/cm^2$. The capacity versus cycle number is plotted in Fig. 5 (device 3) showing a continually increasing capacity until testing was manually stopped.

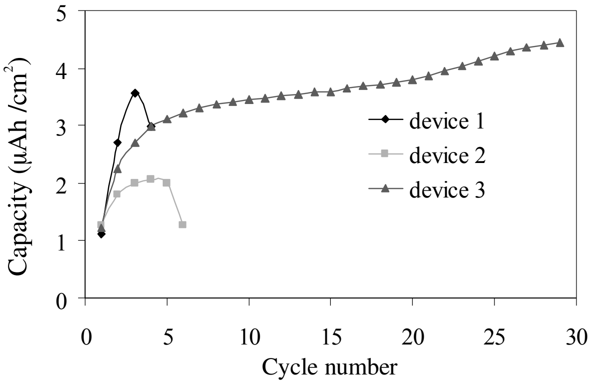

*Figure 5: Capacity versus cycle number for three identical devices with active areas of 0.64cm² and electrode spacings of 55μm.*

Several devices of the same geometry (electrode gap, active area) were tested in an attempt to extract an experimental model of battery performance. Figure 5 shows a plot of capacity versus cycle number for three such devices. While the capacity and behavior are similar for the first few cycles, obvious discrepancies can be seen thereafter. In several of the devices tested (such as devices 1&2 in Fig. 5) the pre-set upper voltage limit of the potentiostat was reached, the charge-discharge behavior became increasingly erratic, and the capacity degraded abruptly. Fabrication imperfections and variations between devices are believed to contribute to this lack of repeatability.

### Effect of TMV Coating

In order to investigate the effect of increased surface area on performance, the capacities of batteries with and without viral nanostructures were compared. Batteries without TMV modified electrodes were fabricated using the same process, but they were not coated with TMV before activation with the palladium catalyst. In this test, the individual cathode layers were pre-charged in a 1M KOH solution against a dummy zinc anode before assembly. The assembled cells were then discharged at a constant rate of 50μA. The graph of the capacities during the initial discharge cycle is shown in Fig. 6. It is observed that the capacity of the TMV modified cell exceeds that of the unmodified one by a factor of six, showing a significant increase in battery performance.

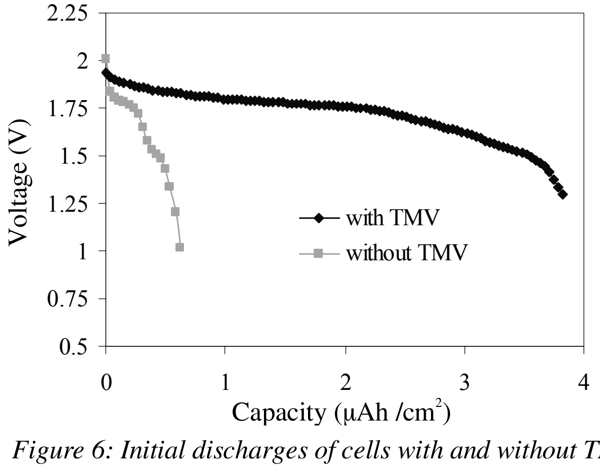

*Figure 6: Initial discharges of cells with and without TMV coatings.*

**Effect of Electrode Gap**

Devices with different cavity heights were tested to investigate the effect of electrode spacing. Figure 7 shows the capacity versus cycle number for electrode spacings of 55µm and 100µm. A decrease in electrode gap by a factor of two produces an approximately equivalent increase in capacity. This is attributed to the decrease in internal resistance within the cell.

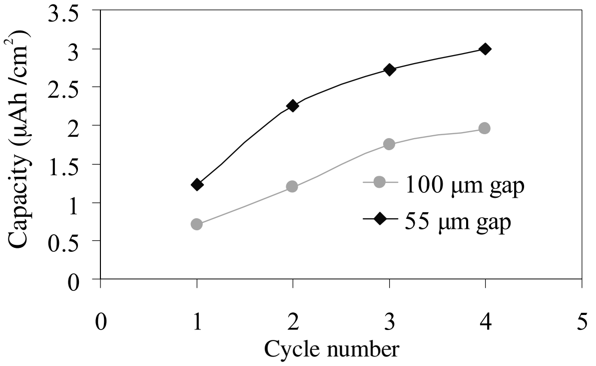

*Figure 7: Graph showing the capacity versus cycle number for devices with different electrode spacings.*

## 6. DISCUSSION

Geometrically identical devices were tested in this work and repeatability was not achieved. This is primarily attributed to the variability in the fabrication process. Die-level fabrication of the cathode layers, differences in zinc surface quality and bonding imperfections are believed to introduce inconsistencies between devices. Future work will focus on developing a batch-fabrication process to mitigate such variations.

Common problems encountered in nickel-zinc batteries are zinc corrosion in the alkaline electrolyte and uneven redistribution of chemical byproducts on the anode, leading to dendrite formation [8]. Rapid zinc degradation was observed in many of the devices tested for this work, preventing the cells from reaching maximum capacity. Examination of the electrode surfaces after testing showed the formation of a substantial passivation layer on the zinc anode. This is attributed to the lower available surface area of the zinc, as compared to the nanostructured nickel electrode. The benefit of the TMV coatings can be fully realized by incorporating high aspect ratio nanostructures on the anode as well as the cathode, increasing the capacity of the cell while reducing the effects of passivation.

## 7. CONCLUSION

This work is the first successful demonstration of a MEMS battery utilizing viral nanostructures. Self-assembly and metallization of the TMV have been integrated with traditional MEMS fabrication technologies. Nickel-zinc microbatteries with TMV nanostructured cathodes have been successfully designed, fabricated and characterized. Appropriate charge-discharge response was demonstrated with a TMV modified device for more than thirty cycles. The initial capacity of these nanostructured batteries was improved by a factor of six compared to cells that did not have viral coatings. Additionally, the effect of electrode spacing on battery performance was investigated. Microbatteries with smaller electrode gaps showed an increased capacity, demonstrating the importance of this parameter. Combined with the simplicity of viral self-assembly, these results show the feasibility of developing compact high-performance microbatteries based on this technology.

## ACKNOWLEDGEMENTS

This work is supported by the Laboratory for Physical Sciences (LPS) at the University of Maryland. The authors would like to thank Professor Peter Kofinas and Mr. Ayan Ghosh for assisting with the data acquisition, Mr. Nathan Siwak for taking SEM images and the staff at LPS and the Maryland Nanocenter for providing access to their clean-room facilities.

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