

# HIGHLY STABLE NANOSTRUCTURED Ni/TiO<sub>2</sub> ANODES ON BIOLOGICAL TEMPLATES

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**Abstract:** This paper reports on the development of nanostructured TiO<sub>2</sub> anodes synthesized using *Tobacco mosaic virus* (TMV) biotemplates. The electrode is formed in a core/shell configuration where chemically deposited nickel on the TMV provides a conducting core and the three-dimensional shape for the deposition of the active material using ALD. The nanomaterials are directly assembled on the substrate thus eliminating the requirement for binders and conductive additives used in electrode fabrication. As a result, this nanocomposite anode shows high rate capability and excellent stability (~1,000 cycles) while outperforming thin film electrode geometries. Combined with the patterning capabilities of the TMV, this technology can be used for the fabrication of high performance microbatteries.

**Keywords:** TMV, Li-ion batteries, nanomaterials, biotemplates

## INTRODUCTION

One of the current limitations in the downscaling of microsystems such as wireless sensor networks is the large size of the battery that is required to meet their power requirements. Next-generation microbatteries need to occupy a small footprint while having high electrochemically active surface area and high energy and power densities. Nanostructured materials are a promising solution due to enhanced properties such as reduced distances for ion diffusion, structural stability as well as larger electrode/electrolyte contact area [1].

In addition to the various conventional methods for the fabrication of nanomaterials, the use of biological templates for the synthesis of functional surfaces has attracted significant attention. This route offers added benefits such as simplicity, low-cost and surface tunability [2]. Work by Nam *et al* and Lee *et al* who synthesized Li-ion battery electrodes using M-13 bacteriophage viruses [3, 4] as well as Kim *et al* who fabricated hollow nanotubes with sacrificial peptides [5] are typical examples of energy related applications. These methods however are based on traditional ink-casting technology for the electrode synthesis and cannot be easily combined with microfabrication for the development of MEMS battery devices.

The method that is presented in this work is an alternative technique that utilizes TMV biotemplates that can directly self-assemble onto current collectors. Previously, metalized viruses have been used by our group to synthesize nickel nanorods which have been used in nickel-zinc microbatteries [6]. Here, the nickel-coated TMV is combined with Atomic Layer Deposition (ALD) of TiO<sub>2</sub> to form core/shell nanostructured anodes for Li-ion batteries. TiO<sub>2</sub> has a Li<sup>+</sup> insertion/deinsertion potential higher than that of

graphite which reduces the power density but at the same time results in cells with increased safety and stability. Nickel-coated TMV can be directly attached onto gold-coated substrates thus forming a three-dimensional current collector that allows conformal deposition of the active material and enhances the rate capability. This property, combined with the photolithographic patterning capabilities of the TMV that have been presented previously, make this approach useful for the fabrication of microfabricated batteries.

## ELECTRODE DEVELOPMENT

### Fabrication

The nanostructured electrodes were synthesized onto stainless steel discs with a 15 mm diameter where a gold film was sputtered to promote TMV self-assembly. After incubation of the substrates in TMV containing solutions, the viruses were activated with a palladium catalyst and then coated with nickel in an electroless plating bath as previously described [6]. Approximately 20 nm of TiO<sub>2</sub> was successively deposited in a Beneq TFS-500 ALD reactor at 150°C using Tetrakis dimethyl amido titanium and water as precursors at a rate of 0.55 nm/cycle. Finally, the nanocomposite was annealed at 450°C in air for three hours to form anatase phase. For comparison, TiO<sub>2</sub> thin films of similar thickness were directly deposited on the steel substrate. The mass of the active material was measured with a high precision microbalance by weighing the discs before and after the ALD process.

### Structural Characterization

The nanostructure of the electrode was investigated using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD). Fig. 1a shows an SEM

image obtained from annealed samples while Fig. 1b is a cross-section TEM image of a coated viral nanorod mechanically removed from the substrate. The SEM picture shows that even after the intense heat treatment the electrode maintains its three-dimensional nanostructure while the TEM image clearly illustrates the distinct layer structure as well as the conformality and thickness control that were achieved with the ALD process.

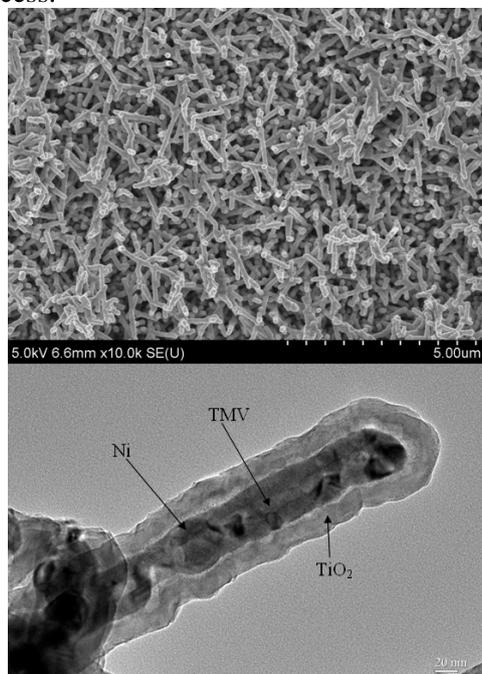


Fig. 1: (a) SEM image of the electrode on the stainless steel and (b) cross-section TEM image of an individual viral template showing the Ni and TiO<sub>2</sub> layer (~20nm).

The effect of annealing the electrode was examined using XRD on annealed and control samples (nickel-coated TMV only and as-deposited nanocomposites). The results are illustrated in Fig. 2 where it can be seen that the anatase peak is observed only in the annealed samples. Other peaks are due to the stainless steel, the nickel core as well as some nickel oxide that has formed during the deposition and annealing steps.

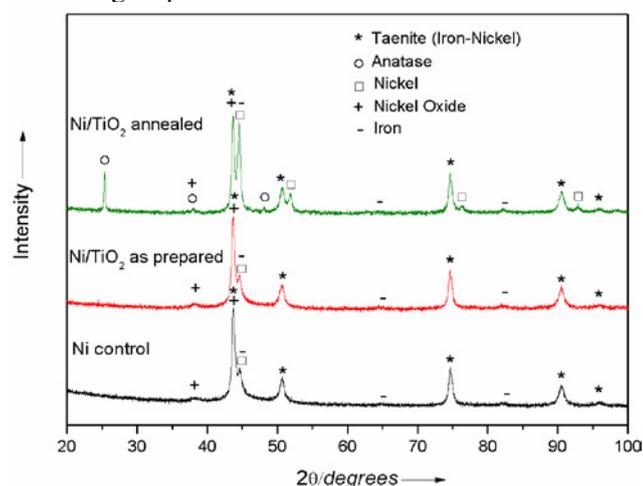


Fig. 2: XRD data of annealed, as prepared and Ni-control samples.

## ELECTROCHEMICAL TESTING

The electrochemical performance of electrodes with and without TMV was characterized in coin-cell configurations using lithium foil as a counter electrode. A cyclic voltammetry (CV) scan obtained in the range of 1-2.6 V at a rate of 0.5 mV/s is shown in Fig. 3. Distinct cathodic/anodic peaks centered around 1.68 V and 2.17 V respectively are observed for both electrodes. These peaks have a two order of magnitude larger height for the TMV electrode, which is attributed to the higher surface area compared to the thin film.

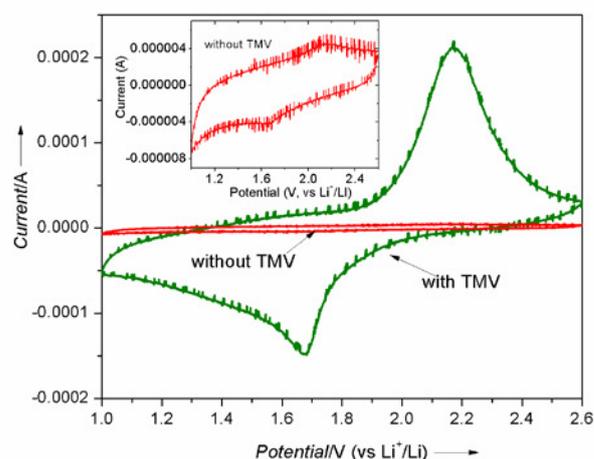


Fig. 3: CV scans at 0.5 mV/s for electrodes with and without TMV.

Galvanostatic charge/discharge cycling was used to evaluate the capacity and cycle life of the electrodes. A characteristic charge/discharge curve is shown in Fig. 4. In accordance with the CV data two plateaus are observed during discharge (Li<sup>+</sup> insertion) and charge (Li<sup>+</sup> extraction). These plateaus appear at higher/lower potentials respectively due to the lower current density used in the galvanostatic test which results in lower overpotentials. Within the first 650 cycles of operation, the capacity drops from 223 mAh/g in the 2<sup>nd</sup> to 185 mAh/g in the 650<sup>th</sup> cycle, indicating an average fading of only 0.026% per cycle.

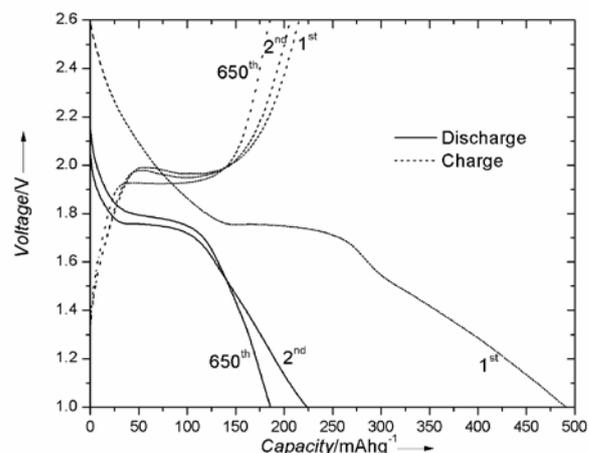


Fig. 4: Charge/discharge curves for TMV modified anodes at a current density of 147 mA/g.

Fig. 4 shows that there is a high irreversible capacity obtained in the first cycle. This is attributed to

a side reaction that converts NiO present in the core to Ni; this reaction is not reversible in the 1-2.6 V range [7]. A series of control experiments was performed to investigate this assumption. Fig. 5 shows CV scans of a nanostructured Ni/TiO<sub>2</sub> nanocomposite and a control sample without TiO<sub>2</sub> (Ni-coated TMV only). It can be seen that while a cathodic peak is observed for the control sample during the first cycle, it is absent from the second scan; no anodic peaks are observed in either cycle in the scan range that is used. Similar results were acquired from the galvanostatic cycling of these two samples (data not shown), indicating the role of this side reaction to the irreversible capacity.

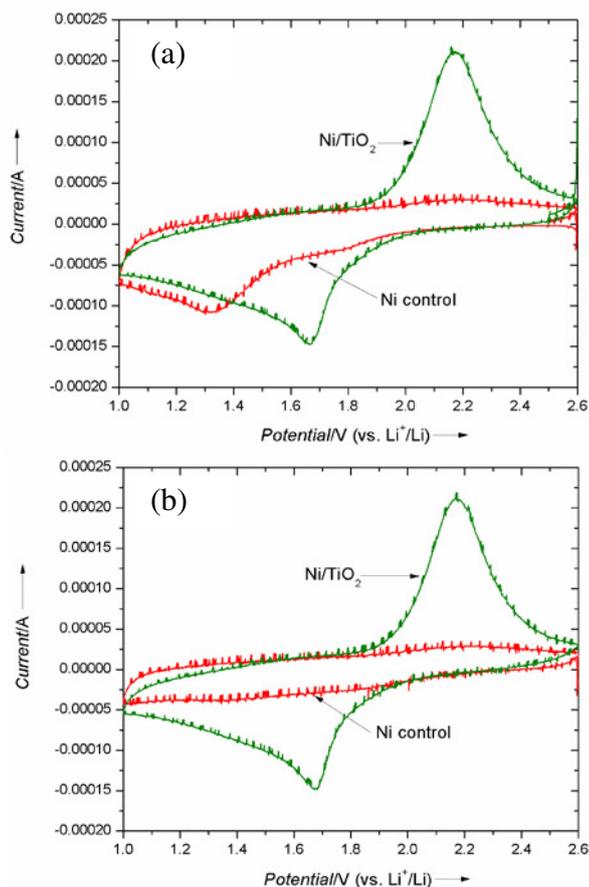


Fig. 5: CV scans at 0.5 mV/s during the first (a) and second (b) cycle for a Ni/TiO<sub>2</sub> nanocomposite and a Ni control sample on TMV templates.

The cyclic stability and capacity of electrodes with and without TMV was investigated at different current rates ranging from 147 mA/g to 500 mA/g. The results are shown in Fig. 6. It can be observed that the virus-modified electrodes outperform planar thin films cycled at 147 mA/g even at the highest current rates. It should be noted that testing for the planar anodes was manually stopped after ~ 230 cycles due to their inferior performance. In addition to the high capacity, the stability of the electrodes is remarkable, achieving values up to approximately 1000 cycles. Morphological examination of the electrode tested at 500 mA/g after 850 cycles was performed using SEM. The respected image is shown in Fig. 7, where no structural degradation is observed for the

nanocomposite and the viral nanorods maintain their three-dimensional nanostructure. These results highlight the importance of the proposed electrode: the robust metalized TMV template, which maintains its structural integrity after rigorous cycling, and the small volume expansion of TiO<sub>2</sub> that enables stable and reliable cycle-life operation create a unique anode with improved electrochemical performance.

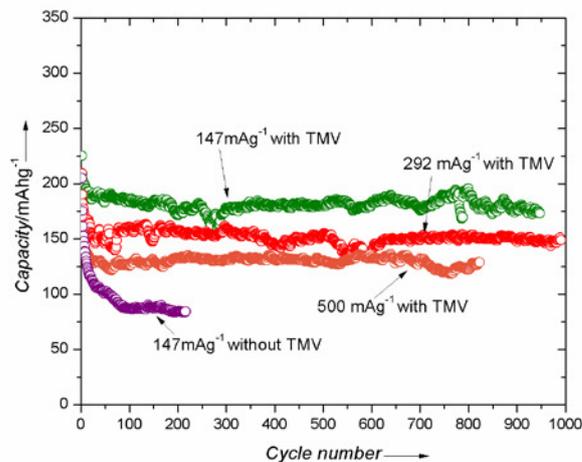


Fig. 6: Capacity vs. cycle number for electrodes with and without TMV.

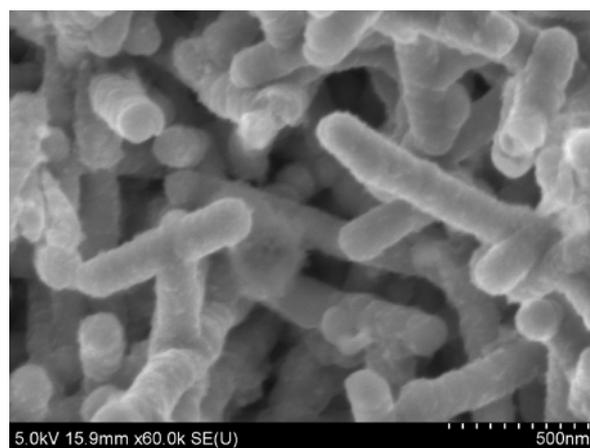


Fig. 7: SEM image of the electrode tested at 500 mA/g after 850 cycles of operation.

Finally, the rate capability of the electrodes was investigated. In this experiment, the cycling current was varied from 50 mA/g to 600 mA/g in increments of 5 cycles. The results are shown in Fig. 8. The TMV-modified anodes deliver almost two times higher capacity compared to the planar thin film. At the rates of 300 and 600 mA/g in particular (which correspond to approximately 7.5C, i.e. charge/discharge of the battery in ~ 1/7.5 hours) the capacity for the nanostructured anode is more than three times higher. This is attributed to the existence of the conductive nickel core and the faster ion kinetics that can be achieved with the nanostructured anode and allow rapid charge/discharge even at very high current densities.

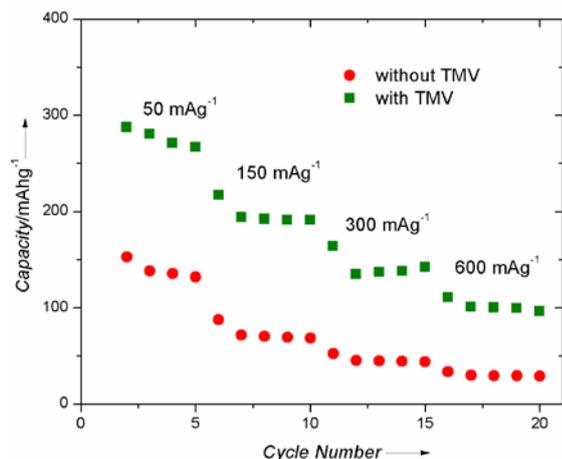


Fig. 8: Rate capability data for electrodes with and without TMV.

## CONCLUSION

In summary, a nanostructured Ni/TiO<sub>2</sub> composite anode using the *Tobacco mosaic virus* was demonstrated. The rigid rod structure of the TMV allows formation of self-assembled, three-dimensional nickel nanonetworks which can be attached directly onto current collectors. ALD was used to create a uniform TiO<sub>2</sub> shell around the metalized viruses. The viral self-assembly eliminated the requirement for traditional ink-casting technologies that are based on binders and other additives and enabled exceptional cyclic stability. Comparison with thin film electrodes demonstrated improved capabilities and reaction kinetics. The synthesis of the virus nanorods is simple and versatile as it can be expanded to several active surfaces and it can readily be incorporated into batch nanofabrication processes.

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