

Micro Scale Addressable Superhydrophobic Reserved Batteries Using Nanostructured Materials

Victor Lifton and Steve Simon

mPhase Technologies Inc.
Little Falls, New Jersey 07424

Abstract: This paper presents the details of a novel battery architecture based on superhydrophobic nanostructured materials. Both electrodes of a battery are formed on nanostructured silicon surfaces that are subsequently treated to make them superhydrophobic, effectively separating the liquid electrolyte from the active electrode materials. A phenomenon called electrowetting that promotes electrolyte penetration into the electrode space to initiate an electrochemical reaction is used to activate the battery to provide power on demand. This architecture makes possible an extremely long shelf life, instantaneous ramp-up to full power, and chemistry-independent functionality.

Keywords: Microfluidics; electro-wetting; hydrophobic surfaces, reserved battery; nano structured surfaces

Introduction

For decades, capabilities of semiconductor technology that enables many portable electronic devices have been advancing rapidly, at times doubling every twelve to eighteen months. In the meantime, battery technology has been advancing only 3% to 5% per year and reserve battery capabilities at an even slower rate. Devices containing semiconductor components that require a primary battery or a battery backup have proliferated rapidly in every major national and global economic sector imaginable (e.g., transportation, health, defense, security, energy, and the environment). These devices have forms ranging in size from large-scale computing devices, personal computers, handheld devices, embedded devices, to remote sensors and newly emerging nano-sized devices. Moreover, the applications of these devices have become more and more critical to decision-making, so there is a strong need for a breakthrough technology in the area of battery technology.

mPhase Technologies and its partner Bell Labs have been jointly conducting research over the past two years that demonstrate the control and manipulation of fluids on superhydrophobic surfaces to create power cells by controlling the wetting behavior of an electrolyte on nanostructured electrode surfaces [1]. This research has laid the groundwork for the continued exploration of intelligent nanotechnology power cells (nanobatteries) and has provided a path to the commercialization of the technology for a broad range of market opportunities.

In the current market environment, the proposed

nanobattery architecture would be considered a disruptive technology, a technology that provides a fundamental paradigm shift in battery and power technology. With it, the size, weight, and shelf-life characteristics of batteries could be dramatically enhanced and appropriate chemistries could be chosen for the designs used to power various portable electronic devices, such as sensors and transmitters for sensor networks. Packaging could be more flexible (e.g., shaped or conformal batteries), but could still be designed to work within the requirements of the physical dimensions of existing electronic devices. Batteries would have intelligence; they could potentially activate cells as needed to produce the power output required, thus extending the useful duty cycle of the battery. In a reserve configuration, power could always be available as a backup to the primary source, because the unique architecture of such a battery would produce negligible loss of capacity in a reserved state. Shelf life would be increased dramatically, because the electrolyte would not come in contact with the electrode until activation. For the military, homeland security, and first responders, this feature would be highly desirable, because batteries could be stored for decades without fear of dissipation. Conventional batteries in storage dissipate as much as 10% per year before use, while the nanobattery is projected to last 15 to 20 years. Because of the very small distances within the nanostructures, the time to full-power activation would be reduced, creating a power source for high-performance electronics.

In advanced configurations, the silicon-based architecture of the battery that is currently being developed has the potential to allow the integration of electronic components directly into the manufacturing process of the battery, making it possible to create new classes of tightly integrated devices (e.g., wireless sensors, integrated active radio frequency identification [RFID] tags and lab-on-the-chip systems) for both defense and commercial markets.

Principle of Operation

The proposed battery architecture places our battery into a so-called reserve battery class [2]. The main function of reserve batteries is to provide power when required, while enduring prolonged periods of storage. Such batteries may spend most of their lives in reserve and be activated only for a brief period as backup power sources.

In order to be capable of enduring such a long shelf life, a traditional reserve battery normally has a mechanical separator to keep the electrolyte away from the active

electrode materials. This architecture leads to reduced power density, because inert filler materials, the actuation mechanism, and separators occupy a significant part of the volume of the battery.

Our approach to these deficiencies is to employ novel nanostructured superhydrophobic materials combined with electrowetting to create an architecture that makes it possible to keep the electrolyte and electrode separate from each other and yet to provide significant reduction in the dead volume in the battery.

Nanostructured Superhydrophobic Surfaces

Our development capitalizes on the fundamental work of Krupenkin et. al. on the dynamic tuning and control of fluids on nanostructured surfaces [1]. The surfaces consist of a honey comb structure whose dimensions can vary based on characteristics that may be required to support various battery configurations and activation requirements. For illustrative purposes this example **Figure 1** shows cell structures that are 30 μm wide, 30 μm tall and cell walls 2 μm thick. When treated with an appropriate fluorocarbon polymer, such a surface demonstrates superhydrophobic behavior, distinguishing itself from a regular surface by the substantially higher contact angle (i.e., > 120 degrees versus < 90 degrees) of a liquid on it. When placed on such a surface, a droplet or a larger reservoir of electrolyte stays fixed on the surface of the structure and does not penetrate through the bottom of the honeycomb membrane. Other nano structured surfaces that have been explored were comprised of an array of cylindrical silicon posts with dimensions 7 μm tall, 350 nanometers wide and a pitch between posts of 3 μm .

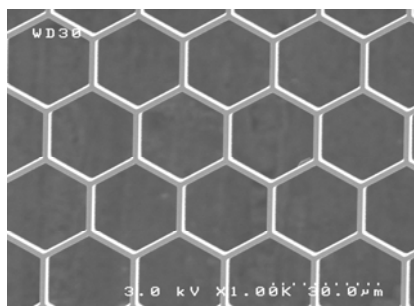


Figure 1.

SEM of Honeycomb membrane structure used to separate electrolyte from electrodes.

Electrowetting makes it possible to change the contact angle of the solid-liquid interface by applying voltage to the liquid. It has been successfully used to create a variety of optical devices (e.g., lenses and diffraction gratings) and is now being combined with nanostructures to create novel batteries and battery architectures with unique characteristics [3-6]. When a pool of electrolyte sits on top

of the honeycomb membrane structure or nanoposts of a nanostructured surface, it can be triggered to penetrate the membrane or the space between the nanoposts and initiate an electrochemical reaction with the active electrode material deposited on the bottom surface of the battery containing the electrodes.

To demonstrate the principle of operation and to fully characterize our battery architecture, we decided to start with a well-known and well-documented battery chemistry that would make quick assessment and comparison possible. For these reasons, we chose a Zn/MnO₂ electrode pair in a ZnCl₂/NH₄Cl electrolyte to be the first proof-of-concept system. The next section describes the advantages that such a battery will have as well as the technical challenges that must be overcome for successful commercialization. **Figure 2** provides a schematic depiction of such a battery, showing two electrodes, electrolyte penetrating the nanopost array, and details of the nanostructure.

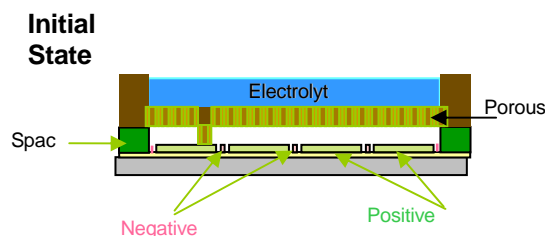


Figure 2.
Cross-section of battery in active state.

Only the essential parts (i.e. the membrane, the electrolyte sitting on top of membrane and Zn and MnO₂ plated into the planar substrate) are shown.

Advantages of a Nanobattery

The advantages of using a nanostructure-based battery architecture are numerous and they give the battery the following unique characteristics:

- A flexible architecture that allows a wide range of liquid chemistries (both aqueous and non-aqueous) to be adapted to fit the design.
- Improved power densities compared to other reserve battery technologies of comparable size. The design of the battery does not require ancillary structures to create physical separators between the electrolyte and the electrodes.
- A long shelf life that is predicted to last over 15 to 20 years.
- A unique architecture design that enables individual addressability of nanocells so they can be selectively activated as required.
- Applicability to primary and reserve battery applications.

- Scalability (i.e., ease of miniaturization).
- Fast ramp-up to full power (i.e., ~ 1 ms).
- Compatibility with semiconductor processing; direct integration into a package with the devices it is powering.
- Inexpensive fabrication by using microelectronic manufacturing techniques.
- Capability to neutralize harmful chemicals at the end of the battery life cycle for safe disposal.

Proof-of-Concept Demonstration

An ability to manipulate and control the electrolyte solution on the electrodes of the battery is the result of our work on organic coatings on the nanostructures that allow a superhydrophobic state to be maintained on some portions of the nanostructures to repel the aqueous electrolyte, while a hydrophilic state is maintained on other portions. This superhydrophobic/hydrophilic transition provides the underlying physics of our design, which allows the contact angle of the electrolyte solution to change from an inactive state, in which the electrolyte has no physical contact with the electrodes, to an active state, in which the electrolyte comes into contact with the electrodes, thus producing voltage in the battery. Although a variety of coatings to render surfaces hydrophobic have been evaluated, the material of choice so far remains a coating of conformal, low-surface-energy fluorocarbon polymer.

In **Figure 3**, Electrolyte is placed on top of the membrane surface. At this stage, electrolyte does not touch the Zn or MnO₂ electrodes therefore, no voltage is generated. Upon application of a trigger pulse, the electrolyte comes into contact with the electrodes, initiating the electrochemical reaction and completing the circuit. The battery is now operational and produces voltage.

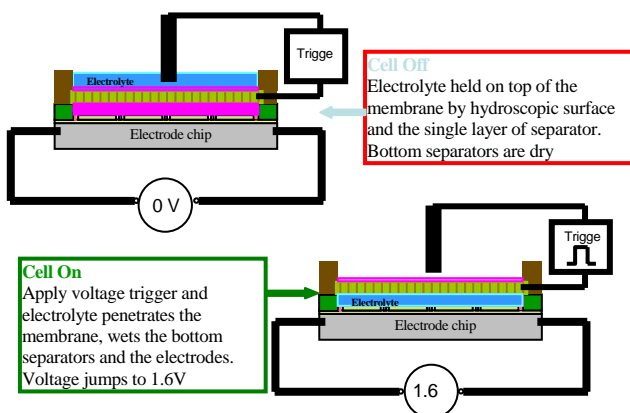
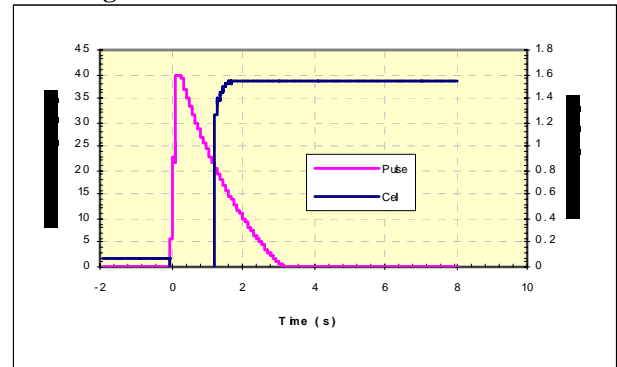


Figure 3.

Battery going from inactive to active on state

A typical battery characterization test configuration is shown in **Figure 4** contains an actual voltage trace of such a test. In the trace, one can clearly see all the features of the proposed system: the dormant state of zero voltage, the trigger by a voltage pulse, and the voltage generated in accordance with thermodynamic predictions (1.6 V).

'Triggering' the cell on – Pulse response and Cell Voltage



Membrane: $d = 20\mu\text{m}$; $h = 20\mu\text{m}$; $t_h = 1\mu\text{m}$, coated with hydrophobic coating.

Figure 4.

On application of a voltage pulse across the membrane for 158 ms the electrolyte penetrates through the membrane to the electrodes and the voltage of the cell rises to 1.6V indicating the cell is active.

Conclusion

In conclusion, we have demonstrated a working reserve-battery prototype based on superhydrophobic nanostructured surfaces. The battery has three characteristic features: (i) an inactive state in which the electrolyte is completely separated from the electrodes by the nanostructures, (ii) battery actuation by a voltage pulse, and (iii) stable voltage generation. We are now in a position to refine and fully characterize the nanobattery to compare it to conventional battery structures. A wide applicability of the proposed architecture to a variety of liquid battery chemistries (for example, Li-based for much higher energy and power density) is expected and is the subject of an ongoing investigation. The proposed architecture is a disruptive technology that represents a fundamental paradigm shift in battery and power technology.

Acknowledgment

The research described in this paper was performed in collaboration with Bell Labs and the New Jersey Nanotechnology Center. The authors wish to acknowledge

the support and contributions provided by all members of the Lucent team.

References

- [1]. T. N. Krupenkin, J. A. Taylor, T. M. Schneider, and S. Yang, "From Rolling Ball to Complete Wetting: The Dynamic Tuning of Liquids on Nanostructures Surfaces," *Langmuir* 20 (2004), 3824–3827.
- [2]. D. Linden and T. B. Reddy (eds.), *Handbook of Batteries*, McGraw-Hill, New York, NY, 2002.
- [3]. F. Cattaneo, K. Baldwin, S. Yang, T. N. Krupenkin, and J. A. Rogers, "Digitally Tunable Microfluidic Optical Fiber Devices," *J. Microelectromech. Syst.* 12 (2003), 907–912.
- [4]. J. Hsieh, P. Mach, F. Cattaneo, Y. Yang, T. N. Krupenkin, K. Baldwin, and J. A. Rogers, "Tunable Microfluidic Optical-Fiber Devices Based on Electrowetting Pumps and Plastic Microchannels," *IEEE Photon. Tech. Lett.* 15 (2003), 81–83.
- [5]. T. N. Krupenkin, S. Yang, and P. Mach, "Tunable Liquid Microlens," *Appl. Phys. Lett.* 82 (2003), 316–318.
- [6]. S. Yang, T. N. Krupenkin, P. Mach, and E. Chandross, "Tunable and Latchable Liquid Microlens with Photopolymerizable Components," *Adv. Mater.* 15:11 (2003), 940–945.