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Development of Techniques for the Fabrication of Micro- and Nano-batteries for Biomedical Applications

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Abstract: Future bio-medical devices with dimensions in the nanoscale region will need independent energy sources to power them. Lithium-ion micro- and nano-batteries are excellent candidates for these power sources. Our proposed nanobattery design ensures that these batteries remain lightweight and safe with fast rechargeable times. We have used femtosecond laser for precision machining. Intense electric fields produced by the laser beam induces electrical breakdown due to avalanche ionization. For femtosecond pulses, this breakdown threshold remains fairly deterministic thereby allowing the use of femtosecond lasers for micro- and nano-machining. The nanobattery consisted of an anode, cathode and separator. The anode was made of graphite or molybdenum oxide while the cathode was made of LiCoO₂. The separator was a Kapton membrane with an array of n x n holes micro- or nano-scale holes machined into it which were then filled with Li-based electrolyte. For biomedical applications these batteries must be packaged with bio compatible polymers. Initiated chemical vapor deposition is an attractive technique where polymeric films are deposited by activating a mixture of gas of monomers and initiators. This solventless technique is substrate independent and should lead to the deposition of biocompatible films that can be used to coat and package electronic devices.

1 INTRODUCTION

As technology progresses there is an increasing demand to shrink biomedical electronic devices to the micro- and nano-scale. These nanoscale biomedical devices will need bio-compatible energy sources to provide power on demand. Thus, development of micro- and nano-batteries is of great interest to the biomedical instrumentation community.

Ideally, a nanobattery is envisioned as a single battery cell with nanoscale dimensions that can be integrated on to a nanodevice. However, given the current status of technology, it is difficult to fabricate a single nanobattery with assured reliable performance. Thus the first logical step to achieve this goal is to develop a macrobattery with an array of micro- or nano-cells. Each cell is itself a battery and they are electrically connected in parallel so that the total power drawn from this device is the sum of power from this array of micro- or nano-cells. Once this battery is fabricated then bio-compatible

coatings need to be developed to package the nanobattery systems so that they may be implanted safely in biological systems.

The nanobattery system developed by our group also has the following advantages. While conventional batteries are typically heavy and this limits their use in a number of applications, nanobatteries are lightweight and hence versatile. Runaway thermal failure is eliminated since each nanocell is electrically isolated from the rest of the nanocells. Also, since the volume of each cell is small, any thermal runaway reaction is contained in a nanocell and will produce limited heat that the battery can easily withstand.

Given their high energy density, Lithium ion (Li⁺) based battery cells have become most accepted. A survey of literature shows that there are numerous papers that describe either the use of very thin films of electrolyte materials to construct battery systems or describe the potential of these films to be used in batteries (Park et al., 2000a); (Park et al., 2000b); (Dudney et al., 2000); (Humble et al., 2003);

(Humble et al., 2001). However, recent papers by number of researchers have described the construction of micro- and nano-batteries with diameters up to 200 nm across and 60 μ m deep (Brazier et al., 2008); (Zhang et al., 2004); (Dewan et al., 2003); (Stephan et al., 2003); (Vorrey and Peters, 2003); (Layson et al., 2003). Individual growth and use of nanoelectrodes using carbon nanotubes were also described (Jogelkar et al., 2004). However, these nanobatteries had some serious drawbacks. The size and arrangement of individual nanocells, which were fabricated porous alumina, varied substantially. Only a small fraction of the cells were electrically active and the outcome was completely stochastic.

We have developed a laser machining technique using a femtosecond laser that allowed us to successfully fabricate array of nanocells in a Kapton membrane. The cells are isolated and are connected, in parallel, by the cathode and anode.

2 EXPERIMENTAL DETAILS

2.1 Development and Construction of the Battery

All materials are susceptible to damage by a focused laser beam when the induced electric field produced by the laser beam is comparable to the Coulomb field an electron sees in the proximity of the atomic nucleus leading to the creation of an avalanche process for the free electrons. This process also occurs in transparent materials which become opaque when the free electron density approaches the critical density for that particular light. It is important to note that this optical breakdown has a non-linear dependence on intensity and this allows for the damage to be restricted to the subdiffraction limit by “thresholding” allowing the fabrication of nanoscale features (Squier et al., 1991); (Jogelkar et al., 2003). Though, optically induced dielectric breakdown scales as $t^{1/2}$, where t is the pulse width for pulse durations longer than 10 ps, the damage threshold remains fairly constant (and deterministic) for shorter pulses (Stuart et al., 1996). For ultra-short pulses, polarization of the beam also plays an important part. For linear polarization, a machined hole becomes a narrow groove in the direction of the polarized beam. This effect was pronounced at low pulse energy close to the threshold of the material (Venkatakrishnan et al., 2002). At low energies, only the central part of the beam has enough energy to ablate the material and thus, in this energy regime,

polarization plays an important part. For laser pulses with a Gaussian spatial beam profile, the diameter D of the ablated area is given by

$$D^2 = 2\omega_0^2 \ln\left(\frac{\varphi_0}{\varphi_{th}}\right) \quad (1)$$

Here ω_0 is the beam radius and φ_0 and φ_{th} are the laser fluence and the threshold modification fluences, respectively. The laser pulse energy E_{pulse} is related to laser fluence by

$$\varphi_0 = \frac{2E_{pulse}}{\pi\omega_0^2} \quad (2)$$

Combining the above two expression, we have

$$D = \sigma \sqrt{\ln\frac{E_{pulse}}{\gamma}} \quad (3)$$

where σ and γ are fitting parameters (γ gives the threshold energy). It is clear by controlling the energy of the laser pulse the diameter of the ablated area can be controlled.

The basic battery design is shown below in Figure 1. The battery consists of three layers. The middle layer is made of Kapton with an $n \times n$ array of micro- or nano-cells machined into it. The bottom and top layers are the two electrodes.

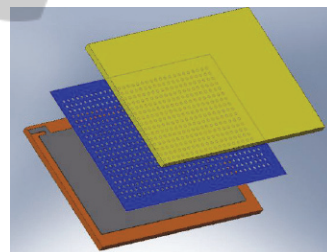


Figure 1: Basic design of a nanobattery. The middle layer is laser-machined Kapton with an $n \times n$ array of nanocells. The top and bottom layers are the electrodes.

In this work, we used commercially available lithium cobalt oxide (LiCoO_2) as the cathode and molybdenum oxide (MoO_2) as an anode. Lithium hexafluorophosphate (LiPF_6) was used as an electrolyte. Details of the construction of these micro- and nano-batteries are given elsewhere (Conner and Mitra, 2011a; 2011b). In addition to the micro- and nano-batteries, control batteries were also constructed. Control batteries had the same electrodes and electrolytes but polyolefin separators were used instead of laser-machined Kapton membrane.

Figure 2 shows the arrangement of micro-cells in a laser-machined Kapton membrane.

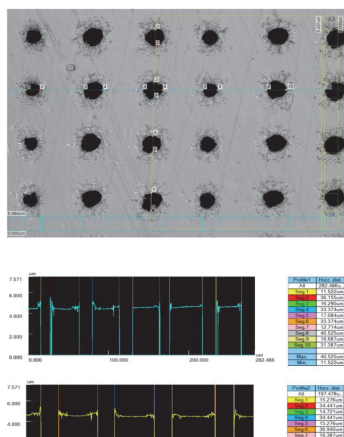


Figure 2: Array of cells machined in a Kapton membrane. A 12 mm thick Kapton membrane was placed on a mask and ablated with the laser. Note the near vertical cell walls.

Once constructed, the current (I) versus potential (V) was tested for these nanobatteries on an electrochemical workstation CHI 660C. The open circuit voltage (V_{oc}) for each battery was measured before each scan. For each battery, the first scan was started from V_{oc} and increased to 4.1 volts. The step size was 0.001 volts and the scan rate was 0.01 volts/s. The potential for subsequent segments would be cycled from 4.1 volts to 2.5 volts. Each battery was cycled five times.

The performance of a micro-battery with Kapton separator and LiCoO_2 and graphite and MoO_3 electrodes were analyzed and compared with the control batteries. The performance of the micro/nanobatteries is superior to the control batteries with polyolefin separators. When a battery is cycled through 2.5 volts and 4.1 volts, a certain amount of charge the cycled charge is given by the enclosed curve. In all cases, the micro-batteries showed superior performance compared to the control batteries. Taking into account the fact that only 58% of the area in micro-batteries are active compared to the control batteries, the performance of micro- and nano-batteries is estimated to be at least better by 40%. This is an important observation for the use of micro- nano-batteries in nanoscale devices for biomedical applications.

2.2 Challenges for Packaging

For use as a bio-medical power supply that can be implanted in a biological system, the nanobatteries need to be packaged in a safe and reliable way. Given the small size of these devices, an attractive packaging method is to use bio-compatible polymer

coatings. It is important to keep the overall size of the system in the nanoscale region.

An attractive method is initiated chemical vapor deposition (iCVD) of polymers. While CVD is a mature technology, application of iCVD for packaging of nanobatteries with polymer films remains at a conceptual stage. In this process, polymers are deposited from vapor phase monomers. The reaction rate is greatly enhanced upon introducing initiator molecules (Baxamusa et al., 2009). Typically, a volatile initiator molecule is mixed with the monomer and activated over a heated filament in a vacuum chamber. iCVD is a one-step film growth method which mimics the free-radical chain growth polymerization. Figure 3 below shows the top view of the iCVD reactor that is under construction in our laboratory.

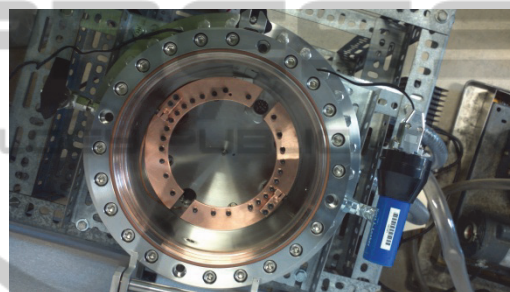


Figure 3: Top view of the iCVD reactor under construction.

The reactor is stainless steel chamber with an array of nickel-chrome filaments. The copper electrodes allow the placing of evenly spaced filaments across the substrate (which sits below the filament). This geometry allows for the even distribution of temperature. The filaments are resistively heated and the temperature of the filaments can be raised to 400 °C. The substrate will be placed about 2.5 cm from the filament array and will be cooled actively to maintain a temperature of 50°C. The monomer and the initiator will be premixed and introduced over the filaments. The initiator molecules will decompose either on the surface of the filaments or in the hot zone near the filament. The iCVD method has several advantages. First, the ability to conformally coat surfaces will allow the coating of nanostructures and objects of irregular shape. Second, the associated temperatures needed for film deposition is low. This will allow deposition on fabricated electron devices like nanoscale batteries and biological systems without causing damage.

Lastly, one can use a variety of commercially available monomers to grow a variety of polymeric

materials. There are a number of candidates for biocompatible and biopassive surfaces. For example, organosilicone coatings are electrically insulating and biopassive.

Poly(trivinyltrimethylcyclotrisiloxane) (PV_3D_3) films have been deposited by using iCVD (O'Shaughnessy et al., 2006); (Murthy et al., 2002). PV_3D_3 has a highly crosslinked structure that makes it insoluble in both polar and non-polar solvents. This makes the structure also very stable. Another possible monomer is Poly (tetrafluoroethylene) (PTFE). It has been found that the rate of deposition of PTFE films is dramatically increased with the addition of perfluorooctane (PFOS) in the gaseous mixture (Baxamusa et al., 2009). PTFE films can be conformally coated. They are also hydrophobic and biocompatible and are used in the medical device industry and hence are expected to be a good candidate material as a nanobattery packaging system.

The iCVD films can be deposited rapidly and the technology is scalable. Hence, iCVD is a very attractive technique for packaging of nanobatteries and any other nanoscale medical devices.

3 CONCLUDING REMARKS

In this work we report the fabrication of micro- and nano-batteries using femtosecond laser machining. Though the first batteries are array of $n \times n$ micro-cells, laser machining is clearly a technology that would allow the fabrication of a single nanobattery. Though the field of nanobatteries is still in its infancy, we have outlined methods that should lead to the fabrication of an array of nanobatteries or even a single nanobattery appropriately packaged in biopassive and biocompatible coatings. This, then, could be the first step to the development of power sources for future nanodevices that can be directly implanted in biological systems.

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