

Facile 3D Metal Electrode Fabrication for Energy Applications via Inkjet Printing and Shape Memory Polymer

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Abstract. This paper reports on a simple 3D metal electrode fabrication technique via inkjet printing onto a thermally contracting shape memory polymer (SMP) substrate. Inkjet printing allows for the direct patterning of structures from metal nanoparticle bearing liquid inks. After deposition, these inks require thermal curing steps to render a stable conductive film. By printing onto a SMP substrate, the metal nanoparticle ink can be cured and substrate shrunk simultaneously to create 3D metal microstructures, forming a large surface area topology well suited for energy applications. Polystyrene SMP shrinkage was characterized in a laboratory oven from 150-240°C, resulting in a size reduction of 1.97-2.58. Silver nanoparticle ink was patterned into electrodes, shrunk, and the topology characterized using scanning electron microscopy. Zinc-Silver Oxide microbatteries were fabricated to demonstrate the 3D electrodes compared to planar references. Characterization was performed using 10M potassium hydroxide electrolyte solution doped with zinc oxide (57g/L). After a 300s oxidation at 3Vdc, the 3D electrode battery demonstrated a 125% increased capacity over the reference cell. Reference cells degraded with longer oxidations, but the 3D electrodes were fully oxidized for 4 hours, and exhibited a capacity of 5.5mA-hr/cm² with stable metal performance.

1. Introduction

The current trend towards powerful and compact low-cost portable electronic devices has created a great need for higher performance power sources. To overcome the limits of existing technologies, development of both novel chemistries and device design are being explored. Innovations in metal electrode design have been of great interest to boost the performance, lifetime, and reliability of power generating devices including fuel cells and batteries [1]. Increasing the surface area of device electrodes to increase energy density is one popular strategy employed to boost performance including porous [2] and microfabricated structures [3]. These fabrication strategies show promising performance gains, but the techniques often require complex or time-consuming process steps, making them sub-optimal for low-cost device fabrication. To meet consumer demand for complex portable electronics, further development of high-performance low-cost power sources is paramount, necessitating the development of alternative fabrication techniques.



Inkjet printing is a promising form of additive microfabrication that allows for the direct patterning of structures from metal nanoparticle bearing liquid inks. After deposition, these inks typically require a thermal curing step to drive off the carrier solvents and render a conductive film via nanoparticle sintering [4]. As metal is selectively deposited, material waste and its associated cost can be minimized. Further, this metallization technique is compatible with large area and roll-to-roll substrate processing and can be performed at relatively low-temperatures and at atmospheric pressure, allowing the use of low-cost polymeric substrate materials. Inkjet printing has been employed to fabricate zinc-silver oxide batteries by forming arrays of silver pillars onto device electrodes to increase electrode surface area, however these pillars require time and precision to produce [5].

Shape memory polymers (SMP) are a class of material that undergoes a geometric transformation upon the application of a stimulus. Both polystyrene and polyolefin are two commercially available thermoplastics that can be manufactured to undergo a large anisotropic shape change to shrink its lateral dimensions upon the application of heat above its glass transition temperature but below its melting temperature [6]. Heat-shrink tubing to insulate electronic wiring connections is one popular application of the material. Thermally contracting SMP substrates have previously been explored for microfluidic device fabrication [7]. Upon SMP contraction, patterned areas thicken to form 3D micromold structures. Additionally, SMP substrates have previously been explored for generating wrinkle patterns in sputtered metal films [8]. Substrate contraction led to buckling of the metal thin films under the large compressive stresses to form 3D topologies. By combining inkjet printed metals with SMP contraction, a simple 3D metal electrode fabrication technique can be realized.

In this paper we combine inkjet printed silver and polystyrene shape memory polymer to realize electrode structures for microfabricated batteries. Shrinking the substrate after deposition allows one to overcome the fundamental resolution of the inkjet deposition system to yield high-resolution metal patterns in a single process. After process characterization, the resulting films are studied using scanning electron microscopy. The fabrication process is then used to realize zinc-silver oxide (Zn-AgO) microbatteries that exhibit improved performance over conventional planar thin-film devices. This work represents the first exploration of inkjet-printed metal films on SMP substrates and its application as three-dimensional Zn-AgO microbattery electrodes, demonstrating the suitability of the technique for energy applications.

2. Experimental

Low-cost consumer-grade polystyrene SMP substrate (MagicShrink) was selected for this study. As-received substrate sheets were cut into samples, rinsed in ethanol, and dried with compressed air prior to use. A commercial research-grade inkjet deposition system (Fujifilm Dimatix DMP-2831) equipped with 10pl nozzles was employed in this work using 50nm diameter silver (Ag) nanoparticle ink (ANP DGP-40LT-15C). All deposition occurred with a substrate temperature of 60°C using a nine-step interlacing technique detailed elsewhere [9]. After patterning, all nanoparticle films were placed onto a 6mm aluminium plate in a preheated laboratory oven above 150°C for 10 minutes to induce sintering and generate coherent conductive metal geometries.

Shape memory polymer behaviour was characterized by patterning nominally 3 mm by 3 mm pads onto clean substrates. The as-printed geometries were then measured using optical microscopy (Mitutoyo), before being loaded into a preheated laboratory oven. The temperature was varied from 150 to 240°C for a duration of 10 minutes and then the samples removed and allowed to cool to room temperature. The resulting samples were then measured using optical microscopy and the size reduction factor computed. Finally, a scanning electron microscope (Hitachi S-3400) was employed to characterize the topology of the inkjet printed silver on the contracted SMP substrates.

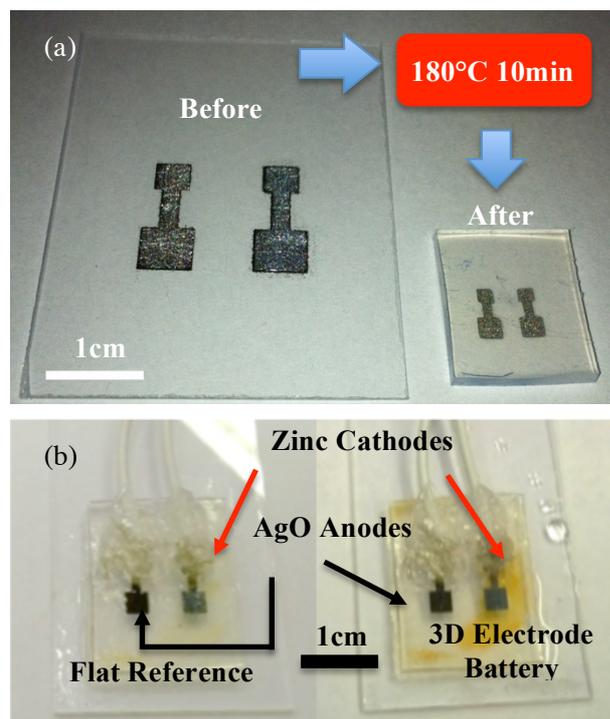


Figure 1. (a) As-printed (left) and post-heated (right) inkjet printed silver electrodes. (b) Packaged batteries after functionalization in KOH with ZnO. Black silver oxide is apparent.

Zn-AgO microbattery electrodes were fabricated by printing oversized pairs of silver electrodes onto SMP to yield an area of 3mm by 3mm after substrate contraction. 3mm by 3mm electrode pairs were also printed onto SMP substrates previously shrunk at 180°C for 10 minutes to serve as reference devices. After metal deposition, all substrates were placed in a laboratory oven at 180°C for 10 minutes to contract the substrates and sinter the Ag film. Devices were then connected to lead wires using silver epoxy (Chemtronics CW2400) and encapsulated in two-part epoxy, leaving only the square electrodes exposed. A 10M potassium hydroxide (KOH) solution doped with dissolved zinc oxide (ZnO) powder (57g/L) was selected for the battery electrolyte, and has been used previously [5]. Characterization was performed using an electrochemical workstation (CHI660E). A constant electric potential (3V) was applied across the printed Ag pads, resulting in the oxidation of the positive electrode and zinc (Zn) electrodeposition on the negative electrode to form a galvanic cell. All cells were tested in a two-electrode configuration using a 5mV/s scan rate. Measurements were performed on both 3D and planar electrode cells serving as a reference. After packaging, the resulting electrodes were characterized via optical microscopy to allow for data normalization based on true electrode area.

3. Results and Discussion

Figure 1(a) illustrates the response of shape memory polymer to the application of 180°C for 10 minutes. While the lateral dimension decrease, the substrate thickness increases proportionally. Printed silver appears dull after substrate contraction but exhibits excellent surface adhesion using a scotch-tape test. Scanning electron micrographs of samples after substrate contraction (Figure 2) reveal a highly textured 3D topology. The substrate contraction exerts large compressive stresses on the overlying patterned material, resulting in buckling of the printed Ag film. Out-of-plane buckling and ripples were observed in all features with large areas of metal exhibiting complex surface topology with crumpling and rosette-like shapes. The electrical resistance of the printed silver after SMP

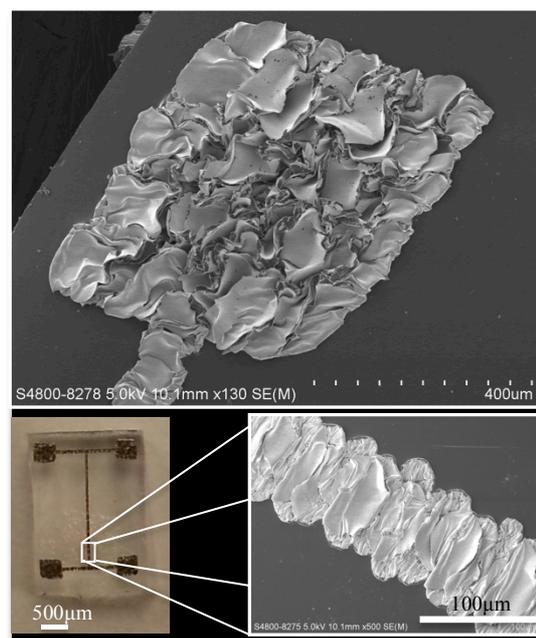


Figure 2. Scanning electron micrographs reveal the 3D topology and large surface area of the buckled printed silver after SMP substrate contraction (180°C for 10 minutes) for a pad (top) and a line (lower-right) on a bridge test structure (optical – lower-left).

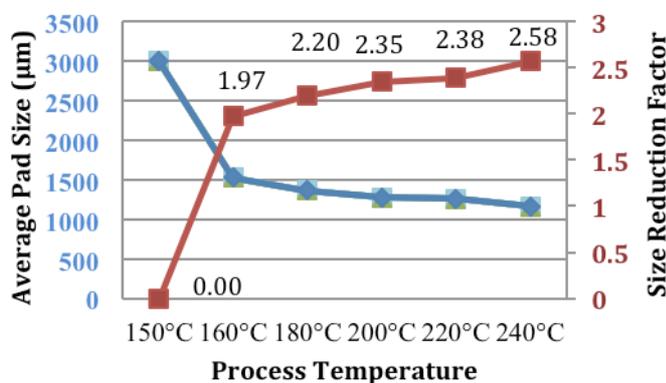


Figure 3. Average pad size (blue) and size reduction factor (red) for 10 samples at each temperature point after a 10-minute oven bake.

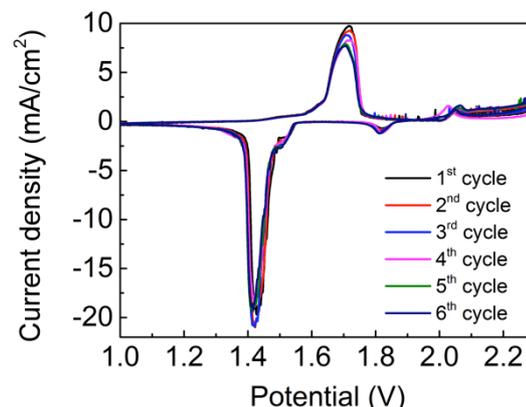


Figure 4. Cyclic voltammograms of the printed 3D silver electrodes on SMP for 6 cycles in 10M KOH electrolyte doped with ZnO (57g/L).

contraction was found to increase by a factor of 4 compared to silver films printed onto pre-shrunk SMP substrates. The average pad size of 3mm by 3mm pads and the corresponding size reduction factor is shown in Figure 3 after a 10-minute oven process for 10 samples at each temperature (error bars shown). The SMP manufacturer recommends a 160°C process temperature, and measurements were carried up to 240°C, showing an increase in SMP contraction with increasing process temperature with low variability. Above 240°C the melting point of polystyrene was reached.

Microbatteries were fabricated on both unshrunk and pre-shrunk SMP substrates, packaged, and functionalized in ZnO doped KOH as shown in Figure 1(b). Black silver oxide was apparent on functionalized microbatteries. During device functionalization, it was found that the planar reference battery electrodes delaminated from the substrate for silver oxidation/zinc electrodeposition times greater than 300s. Similar behaviour has been observed for other printed batteries and is surmised to be due to stress induced during this process [5]. However, no film delamination was observed for 3D electrodes, allowing oxidation/electrodeposition to continue for 4 hours. Enhanced metal/SMP adhesion has previously been observed for gold and should be investigated further for printed materials [8]. Cyclic voltammetry (scan rate: 5mV/s) was then used to characterize the reduction and oxidation regimes of the battery cell over six consecutive cycles of the 3D electrodes as shown in Figure 4. A strong anodic peak was observed at 1.73V with a second smaller peak at 2.05V, which correspond to the formation of monovalent and divalent silver oxide on battery anode. Upon

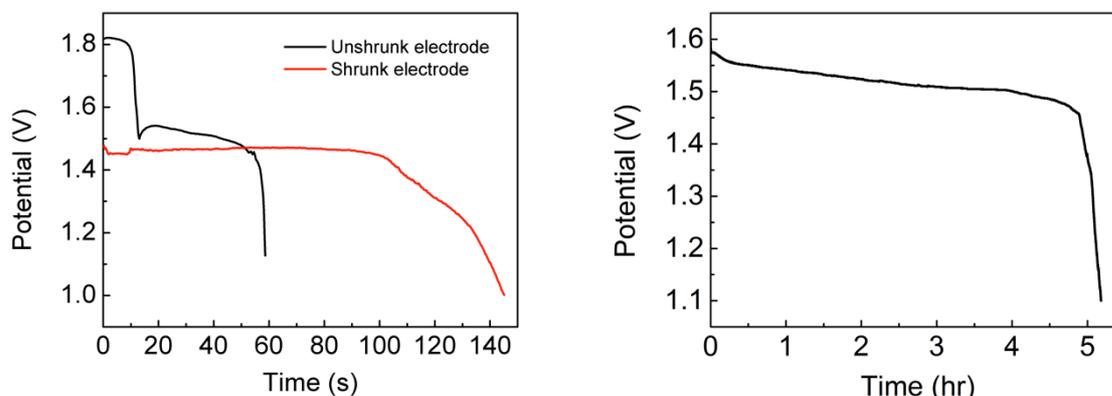


Figure 5. Discharge curves at a constant current of 1.1mA/cm², for (left) samples oxidized for 300s, the maximum for the reference sample, (right) and a 3D electrode battery, oxidized for 4 hours.

reversing the scan voltage direction (decreasing), a slight cathodic peak is observed at 1.81V and a strong peak at 1.42V. Over six cycles, the response of all peaks but that at 1.81V decrease in magnitude, suggesting a change in silver oxide stability over time. The microbatteries were then discharged at 1.1mA/cm² to test battery performance as illustrated in Figure 5. For 3D electrodes oxidized for 300 seconds to allow comparison with the reference cells, the 3D cells exhibited a 125% increase in capacity. As the original electrode size was 120% larger before shrinking, the performance increase scales with electrode surface area. A 3D electrode microbattery was then discharged after a 4-hour oxidation/electrodeposition step, and exhibited an improved capacity of 5.5mA-hr/cm² while the underlying metal film did not show signs of delamination from the substrate.

The simple microbattery geometry used in this initial investigation has validated the concept of using inkjet printed silver on shape memory polymer as a simple method to create 3D electrodes to boost performance and stability over planar thin-film electrodes. Further study is needed to optimize the battery design using a more practical configuration such as interdigitated electrodes. The electrolyte solution ultimately degraded our packaging materials, necessitating the development of alternatives.

4. Conclusion

The use of inkjet printed silver on thermally contracting shape memory polymer to form 3D metal electrodes for energy applications has been demonstrated and validated through the realization of a Zn-AgO microbatteries. The size reduction factor of SMP films was found to be highly repeatable at multiple process temperatures, while creating 3D metal topologies. Zn-AgO microbatteries with 3D electrodes demonstrated greater capacity and better metal adhesion compared to the planar references tested. Using low-cost shape memory polymer and inkjet printed metal to more than double the electrode surface area in a simple fabrication process has the potential to improve electrode performance for energy application.

5. Acknowledgement

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