Dispenser Printed Electrochemical Capacitors for Power Management of Millimeter Scale Lithium Ion Polymer Microbatteries for Wireless Sensors

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Abstract

A direct write dispenser printing system demonstrates a flexible method for integrating electrochemical energy storage components onto an autonomous device. The capacitor's function will be to extend the lifetime of a rechargeable battery by absorbing the high power demands of the electronic device. Electrochemical capacitors based on mesocarbon microbeads suspended in a poly(vinylidene fluoride) polymer binder are printed onto a substrate. The electrolyte is composed of the binder and 1-butyl-3-methylimidazolium tetrafluoroborate, a room temperature ionic liquid. The electrode and electrolyte films are printed successively on top of each other. The gel electrolyte flows and therefore can be printed, but when dried, has enough mechanical strength to support the weight of the top electrode and current collector. It also has a high room temperature ionic conductivity of $10^{-2.798}$ Scm^{-1}, sufficient for high power devices, like wireless sensors. Cyclic voltammetry of the electrolyte showed its electrochemical stability with respect to potential. The capacitors were also galvanostatically cycled and a discharge capacity of $65\pm7.5\mu F$ was calculated.

Keywords: Electrochemical Capacitor, Direct Write, Dispenser Printing, Energy Storage

1 – INTRODUCTION

Electrochemical capacitors with high capacity, long cycle life, and high power delivery capability are recognized as an integral component of energy storage systems for self-sufficient centimeter-scale devices (e.g., wireless sensors, "smart dust"). For devices with limited physical space, finding a microbattery that can meet high energy and power density requirements while maintaining a small form factor poses a considerable challenge. An energy storage system with a microcapacitor placed in parallel with a microbattery has been proposed to best meet these demands [1]. The capacitors are crucial for load leveling the battery in order to preserve its cycle life and capacity. Complete solid-state energy storage components are preferred to avoid any complex packaging processes, leakage, and the possibility of volatile solvents exploding[2] .

Common electrochemical capacitors are fabricated with parallel activated carbon electrodes and an aqueous or organic solvent or polymer as its electrolyte. Both types of electrolytes have limitations that degrade their usefulness in self-sufficient micropower devices. The energy density of capacitors that utilize an aqueous or organic solvent electrolyte is often limited by the electrochemical stability of the electrolyte because the energy stored in a capacitor is proportional to the square of the potential difference that the capacitor is cycled between [3]. Aqueous solvents are typically stable over a narrow 1V potential difference,

while organic solvents are stable in a 1.5-2V range [4]. For polymer electrolyte systems, the power density of a capacitor suffers due to the polymer's low room temperature ionic conductivity. Most applications require the electrolyte ionic conductivity to be greater than 10^{-3} Scm^{-1} [5]. Conventional polymers have ionic conductivities that are orders of magnitude below this. Room temperature ionic liquid (RTIL)-based electrolytes can alleviate both problems because they are stable over wider ranges of potentials (as high as 4V, compared to organic solvents), and their ionic conductivities have been reported to be as high as 60 mS cm^{-1} at room temperature [6]. Furthermore, ionic liquids are non-volatile and therefore safer due to their negligible vapor pressures. Composite gels of a polymer and an ionic liquid can be made to create capacitor electrolytes that are mechanically strong enough to support their own weight and eliminate the need for a containment vessel or separator.

As overall device packaging for autonomous computers approaches the millimeter scale, the volume cost of off chip batteries becomes significant and approaches for on chip manufacturing are an attractive solution for using the device as part of the battery's packaging [7]. Considerations for integrating the micropower system on an electronic device include the need for the process to be conducted at near ambient temperatures (less than 200°C) to avoid damaging any other neighboring chip components, as well as finding a deposition system that

can handle the higher viscosity materials typical of electrochemical systems. We have developed a direct-write process for printing capacitors and batteries that is both low cost and low temperature, and it is capable of printing materials of a wide range of viscosities. The printing system consists of a dispenser controlled by a pneumatic regulator and a 3-axis stage with micron resolution. Thin films are printed via a rapid succession of drops extruded from a dispenser tip. Depending on the material, syringe tip diameter, and extrusion pressure, films with thicknesses of 15-100$\pm$5μm have been printed. The printing pastes usually consist of a powder of an active material that is mixed in a polymer binder and a volatile organic solvent. The relative proportion of active material to binder depends on the application while the organic solvent is used to tailor the viscosity of the paste for specific printed profiles. These pastes are then directly printed in a programmed pattern onto a substrate without the need for lithographic processes.

In this paper, electrodes of MCMB (mesocarbon microbead) in a PVDF [poly(vinylidene fluoride)] polymer binder are printed with a $BMIM^+BF_4^-$ ionic liquid in PVDF gel electrolyte. The capacitors' profiles were characterized and then they were electrochemically tested, and the viability of this deposition process for electrochemical capacitors is discussed. Also, the conductivity of a $BMIM^+BF_4^-$ ionic liquid and PVDF polymer binder composite are measured with respect to temperature and compared to the conductivity of the ionic liquid alone.

2 – EXPERIMENTAL

2.1 - Capacitors
The capacitor electrode paste consists of 65.58 wt% 6-28 μm MCMB (Alumina Trading Co.), 31.84 wt% PVDF (Scientific Polymer Products, Inc.), and 2.58 wt% acetylene black (Alfa Aesar) for enhanced electronic conductivity. The electrolyte consists of a 1:1 weight ratio of PVDF and $BMIM^+BF_4^-$. The amount of NMP added varies according to desired viscosity, and for the electrode paste, is generally twice the weight of all the powder. For the electrode paste with a total powder weight of 8.3862g, 15mL of NMP was added. 4mL of NMP was added to a composite of 5.784g PVDF and 5.784g $BMIM^+BF_4^-$.

The self-standing "sandwich" capacitors are fabricated on stainless steel foil, which serves as the current collector. The foil's surface is roughened with a pre-etch using ferric chloride for 15s for better paste adhesion. A 5mm x 5mm x 30μm$\pm$3μm MCMB electrode film is first printed on the foil. An electrolyte layer of 15$\pm$3μm thickness is then printed on top of the electrode to completely cover it. The final MCMB electrode is then printed above the electrolyte layer with similar dimensions to the bottom electrode. The top electrode's current collector is a stainless steel foil that is clamped on to provide both good contact and some

compression. After each film is printed, they are dried at 50-60°C for 12 hours before printing the next film.

2.2 - Electrochemical Testing
Conductance measurements were made by constructing Swagelok cells with a 1cm^2 area of electrolyte material sandwiched between two stainless steel electrodes. The electrodes are separated by a 256μm spacer? A Solartron SI 1254 four-channel frequency response analyzer was used to measure conductivity between 254-363K through AC impedance measurements at a constant voltage of 5mV. Frequency was altered from 65000 to 10 Hz. The capacitors were characterized for capacity, cycling, and self-discharge behavior, using a wireless galvanostat/potentiostat, "Jonny Galvo" [8] . Cyclic voltammetry (CV) measurements were conducted using a Gamry PC3/300 potentiostat. The voltage was swept at a scan rate of 5mV/s. Cycling and CV tests were conducted on unsealed cells at room temperature.

3 – RESULTS
Measurements comparing the ionic conductivity of $BMIM^+BF_4^-$, with the electrolyte paste of 1:1 wt. PVDF-$BMIM^+BF_4^-$ in Fig. 1 show that at ambient temperatures, the polymer binder does not degrade the conductivity significantly. In fact, at T=298.55K, the electrolyte has a conductivity of $10^{-2.798}$ Scm^{-1}, which meets the requirements discussed before for high power energy storage devices.

Cyclic voltammetry was used to determine the stability of the $BMIM^+BF_4^-$-PVDF electrolyte within the potential range of -2 to 2V at a sweep rate of 5mV/s. Irregularities in the curve shown in Fig. 2 may be due to the presence of water electrolyzing in the system. It is worth noting that water has been shown to reduce the electrochemical stability window of the ionic liquid as well [9].
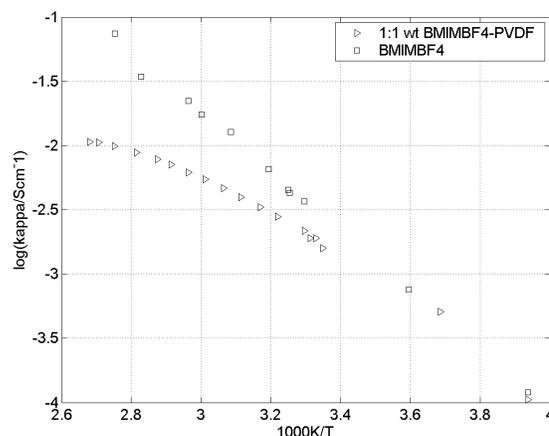

Figure 1 - Conductivity of $BMIM^+BF_4^-$ and 1:1wt PVDF-$BMIM^+BF_4^-$ with respect 1000K/Temperature.

Figure 2 - CV of PVDF-BMIM$^+$BF$_4^-$ at 5mV/s sweep between -2 to 2V. Noise along the graph may be due to the presence of water.

The cells were galvanostatically cycled between 0-2V with 5μA charge and discharge currents. The 47-54th cycles are shown in Fig. 3. The capacitance for charging or discharging can be calculated using Eq. (1):

$$C = \frac{I \cdot \Delta t}{\Delta V} \qquad (1)$$

where C is the capacitance, I is the charge or discharge current, Δt is the time of charge or discharge, and ΔV is the difference in potential difference [10] . For the 52nd cycle shown in Fig. 4, the charge time measured was Δt_{charge}=40$\pm$3s while the discharge time was $\Delta t_{discharge}$=26$\pm$3s. The calculated capacitances are C_{charge}=100$\pm$7.5μF and $C_{discharge}$=65$\pm$7.5μF. The non-linear curves indicate a departure from ideal capacitor behavior, probably due to poor interfacial contacts and other losses to resistance.

4 – DISCUSSION

Dispenser direct write printing is a viable method for fabricating stand-alone electrochemical capacitors. Printing multi-layer stacks of films of varying composition has proven difficult for similar deposition processes because of concerns of mixing between an already printed layer and a wet ink, especially when the layers use a common solvent [11]. Though the electrode and electrolyte layers share a common solvent (NMP), the gel electrolyte's high viscosity allows it to retain structural rigidity and protects the cell from shorting, even under some compression. Furthermore, any mixing at the interfaces of successive films is probably a minimum because of the inability of BMIM$^+$BF4$^-$ to wet and dissolve PVDF without any mechanical agitation. Investigations of how these properties affect the interfacial contact between layers are forthcoming. Since the capacitors are self-standing without being packaged under compression, their performance may be improved by printing thinner electrode and electrolyte layers without shorting.

The electrochemical performance of the capacitors can be greatly improved by using an activated carbon powder with higher surface area while still considering low material costs. The surface area of 6-28 μm MCMB has been reported to be about 1-10m^2/g depending on processing. Osaka et al. have invested activated carbon powders with surface areas as large as 2500m^2/g, and showed that such powders have capacitances that are two orders of magnitude higher [12].

Another property worth improving is the adhesion and contact between the current collector and electrode layers. Electrically conductive metal powders have been successfully printed using other deposition processes [13]. Printing these powders should be compatible with our dispenser system, and would allow us demonstrate a method for depositing complete electrochemical devices
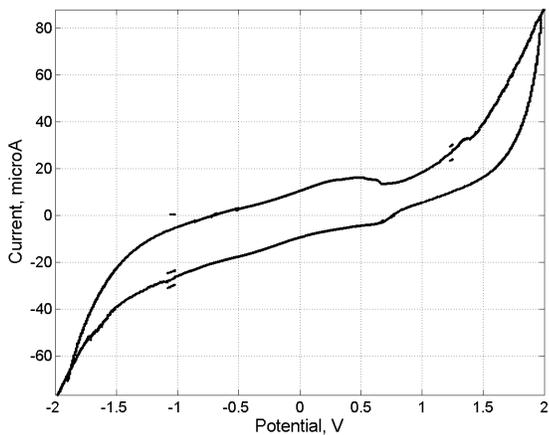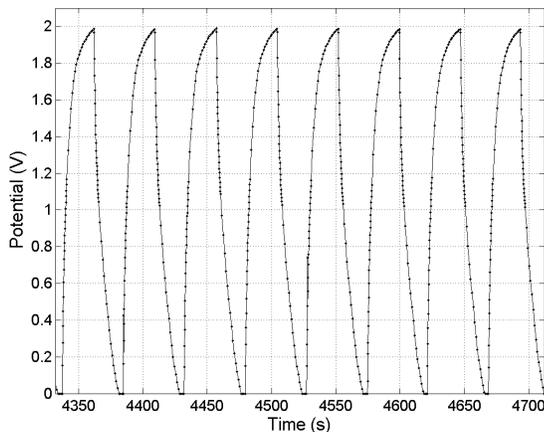

Figure 3 - The 47-54th galvanostatic cycles of the cell between 0-2V with charge and discharge currents of 5 μA.
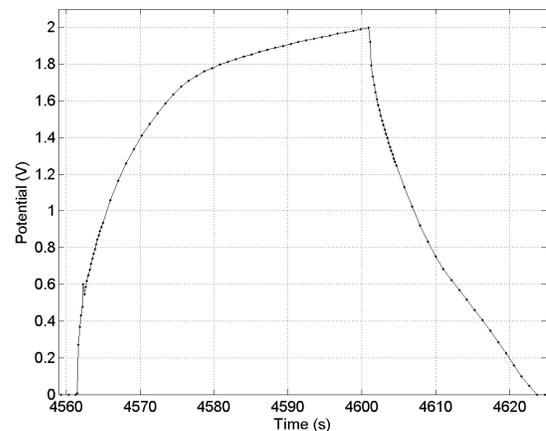

Figure 4 - Change and discharge curve for the 52nd cycle. The cell was charged and discharged at 5 μA.

without the need of any subtractive or lithographic processes.

5 – CONCLUSIONS

A direct-write dispenser printing method for depositing microcapacitors on-chip has been shown to be viable. The capacitor will be able to load-level a battery. This is especially critical for energy and power hungry electronic devices. MCMB powder in PVDF and $BMIM^+BF_4^-$-PVDF gel electrolytes can be deposited sequentially to create a stacked structure. The printed layers were profiled, showing minor surface roughness that is acceptable for good electrochemical performance. Electrochemical characterization of the $BMIM^+BF_4^-$-PVDF electrolyte shows that it is an appropriate choice for wireless sensor and other high power applications. The capacitance calculated can be enhanced drastically by using much higher surface area carbon powder as well as improving the adhesion between printed layers and with current collectors. With further efforts towards creating a fully printed electrochemical device integrated directly on-chip, the prospect of fully autonomous devices becomes even more realizable.

6 – ACKNOLWEDGEMENTS

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