

# SOLUTION PROCESSED MICROBATTERIES FOR ENERGY HARVESTING APPLICATIONS

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## ABSTRACT

In order to meet the need of microbatteries with high areal specific capacities for energy harvesting applications, we developed a solution chemistry and coating process that allows the formation of a microbattery with an in-situ formed separator layer. This microbattery shows a reversible capacity of  $\sim 1$  mAh/cm<sup>2</sup>, far exceeding the capacities of vacuum deposited microbatteries.

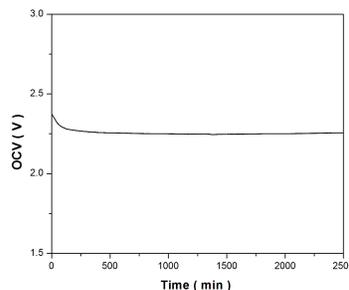
## 1 INTRODUCTION

Energy storage is essential for realizing the full benefit of any energy harvesting systems, such as powering sensors, actuators and short range communications. Minimizing the footprint of energy storage devices can enable compact packaging of integrated systems. Currently, microbatteries are fabricated by sequential deposition of electrode and electrolyte layers with vacuum techniques, such as magnetron sputtering and chemical vapor deposition<sup>1</sup>. In addition to the high costs, these batteries are greatly limited in available form factors. Typically, micrometer thick cathodes and anodes are separated by inorganic separators of similar thickness. The need for high temperature sintering also limits the substrates on which these batteries can be fabricated. An example is the solid state thin film lithium battery composed of a lithium cobalt oxide cathode, a nitrogen doped lithium phosphate electrolyte layer, and a lithium metal anode<sup>2</sup>. The sputtered oxide layer is sintered at high temperature before other layers can be deposited. The area specific capacity is usually around 60  $\mu$ Ah/cm<sup>2</sup> determined by the limited oxide cathode thickness due to the low ion and electron conductivities.

## 2 DESIGN PRINCIPLES, RESULTS, AND DISCUSSION

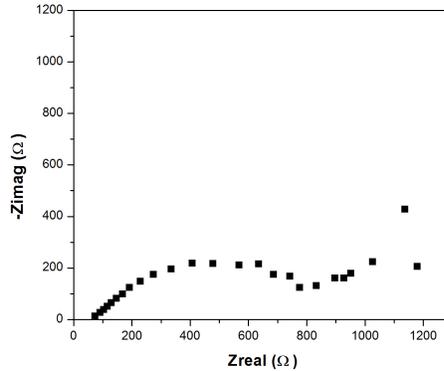
It is highly desirable to fabricate small footprint batteries with a vertical structure similar to those of bulk batteries which consists of high conducting composite cathode and anodes of 10s of  $\mu$ m thick, leading to capacities of  $> 2$  mAh/cm<sup>2</sup>. Unfortunately, the required slurry casting, drying and the need of a porous separator makes it impossible to realize such a structure at small footprints (e.g.,  $< 0.1$  cm<sup>2</sup>).

To overcome these difficulties, we present here a microbattery that can be readily fabricated using solution deposition. A lithium polysulfide based solution is deposited onto a lithium metal surface. The reaction between them creates a solid electrolyte layer in-situ. This eliminates the need for a polymer separator. A carbon slurry mixed with polysulfides is then applied to form the cathode. Controlled removal of the solvents leads to the formation of a microbattery. The chemistry of the battery is similar to that of lithium-sulfur batteries, which have among the highest specific energy (2600 Wh/kg) of known rechargeable batteries<sup>3</sup>.



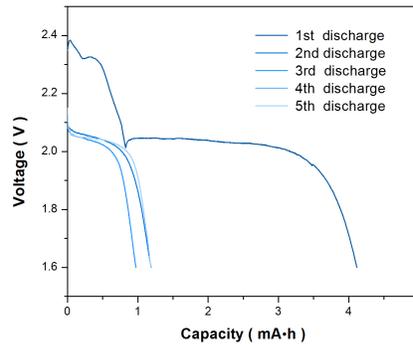
**Figure 1** The microbattery with an in-situ formed electrolyte layer shows stable open circuit voltage.

Figure 1 shows the open circuit voltage profile as a function of time of a microbattery. The value of 2.25 V is consistent with that of a Li-S battery. The long term stability also indicates that the in-situ formed electrolyte is robust and prevents self discharge effectively. The robustness of this layer is essential for forming non-planar interfaces that will be elaborated below.



**Figure 2** Nyquist plot of the microbattery at open circuit voltage.

Figure 2 displays the Nyquist ac impedance plot of the microbattery with an area of  $1 \text{ cm}^2$ . The depressed semi-circle represents the interfacial charge transfer process with a resistance of 820 Ohm. This value is comparable to that of state of the art lithium ion batteries which show a resistance of about 40 Ohm per geometric square centimeter but the actual interfacial area is an order of magnitude higher<sup>4</sup>. This resistance value makes the cell suitable for operation at moderate current densities.



**Figure 3** Discharge profiles of the microbattery during the first five cycles at  $88 \mu\text{A}/\text{cm}^2$

Figure 3 confirms that the battery can cycle reversibly at a modest current density. During the first cycle, the cell delivers a capacity of over  $4 \text{ mAh}/\text{cm}^2$ , a value that is comparable to state of the art lithium-ion batteries. On subsequent cycles, the observed reversible capacity is relatively stable at about  $1 \text{ mAh}/\text{cm}^2$ . The large drop in capacity after the first cycle is quite common in Li-S batteries where the polysulfide migrates between the cathode and the anode, preventing fully charging the cathode to elemental sulfur<sup>3</sup>. Work is in progress to further improve the cycling stability. Nevertheless, the observed reversible capacity of  $1 \text{ mAh}/\text{cm}^2$  far exceeds those achieved with thin film batteries prepared by vacuum deposition.

Due to the solution based process, complex form factors can be fabricated, depending only on the contour of the initial lithium surface. These complex architectures will allow microbatteries to be deposited onto small, irregularly shaped areas, which are often the only available options on integrated circuit boards with minimized packaging.

### 3 CONCLUSIONS

By using a unique sulfide based solution chemistry, a microbattery with an in-situ formed electrolyte layer was fabricated that can undergo reversible cycling. The battery shows a capacity of over 1 mA/cm<sup>2</sup> far exceeding those achievable with solid state microbatteries prepared by vacuum deposition. The current fabrication method of solution processing is simple and potentially inexpensive.

### ACKNOWLEDGEMENTS

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