FABRICATION OF MICRO-ACTUATED GALVANIC CELLS AS POWER ON DEMAND FOR LAB ON A CHIP APPLICATIONS BY MEANS OF NOVEL PCB/MEMS TECHNOLOGY

Cardenas-Valencia, A. M., cardenas@marine.usf.edu Fries, D. P., dfries@marine.usf.edu, Steimle, G., gsteimle@marine.usf.edu, Broadbent, H., heather@marine.usf.edu, Langebrake, L. C. llange@marine.usf.edu, Benson, R. F., rbenson@marine.usf.edu

University of South Florida, Center for Ocean Technology, 140 Seventh Ave S.
St. Petersburg, FL, USA, 33701

ABSTRACT

A novel copper-clad liquid crystal polymer material is proposed as a basic material for the construction of galvanic cells. Copper is an ideal material that allows not only the formation of conductor patterns in the material but also can be electroplated selectively with a wide variety of metals to create heterogeneous systems. The use of a novel mask-less patterning system described herein opens up the opportunity for micro fabrication of different microstructures that can be layered to form complex two and potentially three-dimensional micro fluidic networks. Achieving the photo-imprinting by the use of a novel mask-less system not only reduces the cost but also allows for ease and flexibility in making systems and is ideal for research and development environments. In this paper micro galvanic cells actuated by means of fluidic actuators have been designed and constructed. The electrochemical galvanic cells used as power source examples are a Daniell's (Copper-Zinc) electrochemical battery, and an aluminum-air galvanic system. The choice for the electrochemical systems is discussed and some preliminary results are presented to show the levels of energy available. In addition, the basic concept of an electrically induced expansion mechanism for circuit activation on demand is described. Lastly, the mechanics of the suggested actuation mechanism are discussed.

INTRODUCTION

High power to small size energy sources have become a topic of intense research. Both, consumer technology, (from toys to cell phones and lap top computers), and research technology used in portable instrumentation (sensors, biomedical diagnosis and operational devices) push for scaling down reliable power devices. Numerous novel devices are emerging related to the development of micro electro-mechanical systems, MEMS. Analytical systems, sensors and mechanical devices are undergoing size reduction to micro-scales, and in many cases these systems are more efficient than macro-scale equipment. One of the accepted advantages of MEMS instruments is the low power consumption. The use of peripheral energy devices to power MEMS and other systems currently hinders their application range.

A further limitation to the rapid development of miniature power sources is that designing power systems is challenging since power requirements can vary considerable depending on the application under consideration. Existing small energy sources vary widely in design and in their principles of operation. Scavenger mechanisms, thermal engines, fuel cells, and chemical batteries are some of the current power systems under study (Koeneman, P. B.,1997; Pescovitz, D. 2002).

A review on current research on scavenger energy was compiled by Roundy (2002). The volumetric power density is relatively small, but according to Roundy (2002) is enough to power small wireless computing devices. These systems provide a continuous way to transform events present in certain environmental conditions into useful energy. They are attractive since the energy is available while the conditions to harvest are present, however these systems have to be designed for specific operation conditions.

Much attention has been focused on micro-turbines and combustion driven power generation mechanisms. The efficiency of these devices is normally low. Muller and Frechette, 2002 reported, efficiencies in Brayton and Rankine cycles of 1-10 %. However, thermal engines theoretically have high energy densities. The power per unit mass, increases with the inverse of their characteristic dimension. In fact, their energy density compared to

batteries is higher. Most of these devices however, are still in their proof of concept stages.

Some of the systems mentioned above, are well suited for certain applications, but may be impractical for others. Electrochemical batteries present a competitive portable system solution. Their volumetric power density has continually increased and led to the development of the battery industry. Long life electrochemical batteries and miniaturization would seem almost contradictory. However, for a fixed energy requirement during a specific amount of time, they are still an attractive option The power generated within an electrochemical cell is proportional to the area of the electrodes, making the scaling down of batteries simple. Modifications can be made in a battery system solely in the area of the electrodes to obtain a different current intensity out-put. Furthermore, it is known that micro-fabrication provides a fabrication route to enhance the area/volume ratio, naturally micro-fabrication techniques are necessary when developing power MEMS.

Different galvanic cells mechanisms have been used for powering MEMS (Pescovitz,, 2002). It is commonly known that these systems degenerate over time. Battery leakage and ionic diffusion effects cause such degeneration, (Dyer, 1999). This has been addressed somewhat by using on-demand actuated batteries, (Cardenas-Valencia et al., in press). We have concentrated on the development of micro-batteries as short-term use, high power per unit volume delivery systems. Specifically small on-demand galvanic cells for powering MEMS devices have been micro-fabricated. In this paper we present two examples of galvanic actuated micro-batteries and a simple way to manufacture the batteries. The conjunction of the on-demand concept and the feasibility of easy micro-fabrication could potentially make the micro batteries an attractive option to power MEMS systems. Long storage lifetimes for reserve batteries are needed for powering real systems in the field and even implanted biomedical MEMS scale devices.

The novelty of our MEMS scale cells is composed by two elements. First the processes used for the fabrication are commonly used in printed circuit board technology. Recently, the use of traditional PCB technology materials has appeared in the micro-fabrication arena and several micro-fabricated devices using these materials have been reported (Merkel et al, 1998; Nguyen and Huang, 2001). Additionally, the moisture resistance properties of emerging PCB substrates used here, have allowed them to become the materials of increased interest for packaging and enclosure of MEMS devices (Yang, 2002). Specifically, a copper cladded liquid crystal polymer,(LCP) printed material was selected as the basic construction material for our power packages We have chosen to use a LCP-Cu flex-circuit format to permits designs for potential conformal power sources and for multiple laminated cells for increased power generation An added elements is that copper processing (etching, plating, etc.) is well documented, and makes the conforming systems more producible

This paper also presents the photo fabrication technique that we have used to create the microarcitectures. We have employed a novel micron-scaled resolution, maskless photoimaging tool that permits the creation of small, arbitrary features. This microdevice printer is useful for constructing fluidic channels, devices, structures and packages, utilizing any photoimageable or photoreactive material that can be applied towards fabrication of integrated microfluidic-based systems (Hand, 2002). The use of this rewriteable electronic pattern generator enables a less complex fabrication scheme for making the heterogenous cells when compared to standard micro-fabrication.

Proposed electro-chemical & actuation systems

The major advantages of the micro cell concept presented are the switch on demand of power, and the highly producible laminate system design. Herein, we describe two micro-actuated on demand batteries that have been known for relatively long time and are well studied. One is an aluminum-air cell and the other is a copper-zinc battery.

Aluminum-Air battery. The major advantage of this cell system stems from the high energy density. Under standard conditions a reversible energy of 25.1 kJ/g or 67.8 kJ/cc at the anode in strong alkali media is available. The overall desired electro-chemical reaction in alkali media is:

$$4Al_{(s)}+3O_{2(g)}+6H_2O_{(l)} \rightarrow 4Al(OH)_{3(s)} \quad (1)$$

In practice as the cell discharges polarization effects appear. These effects are due to the presence of competitive reactions, which depend on the cell configuration/ dimensions, reagents and the proportions at which they are introduced. For instance, one of the known side reactions that compete with the desired electrochemical reaction is:

$$2Al_{(s)} + 3H_2O \rightarrow 2Al(OH)_{3(s)} + 3H_{2\,(g)} \quad (2)$$

Furthermore, the formation of insoluble aluminum hydroxide leads to deposition on the surfaces of the cell. While these effects are problems for the macro-cells, the micro-cell offers an advantage for the aluminum-air battery where the battery is intended to be short-lived and supply a specific amount of energy. A new and fresh battery is actuated for each instance energy is needed. The actuation of the battery by movement of the electrolyte becomes an important feature of the aluminum-air micro-battery. The actuation used for the Aluminum cell relies on the thermal expansion of a working fluid that pushes a discrete amount of electrolyte, into the reacting chamber. The concept of this micro-fluidic cell was presented previously, (Cardenas-Valencia, in press). Herein the micro-fluidic actuation has been modified for easier filling.

The main concept presented here is a galvanic aluminum anode cell actuated with low power micro-fluidics. The chemistry and construction of this type of system avoids challenges that have retarded the development of a reliable commercial Al/air macro-battery. A complete description of these challenges can be found elsewhere (Li and Bjerrum, 2002; Licht, 1998).

Copper-Zinc battery. This battery is commonly known as the Daniell's battery in recognition of its inventor. The Daniell's battery was one of the first electrochemical systems with commercial success (Morris and Arena, 1993). It was extensively used in England and the United States as the main power source for intercontinental telegraphic systems, in which, while reliability was necessary, high current intensities were not needed. The overall reaction in this case is:

$$Zn_{(s)} + CuSO_{4\,(aq)} \rightarrow Cu_{(s)} + ZnSO_{4\,(aq)} \quad (3)$$

Notice in this case, that all chemicals involved are non-gaseous, which reduces polarization effects. At 25 ^{o} C when the concentration of Copper and Zinc ions are equal to 1.0 M, the Cu oxidizes the Zn easily producing areversible potential of 1.10 V. The reversible energy at standard conditions is 3.25 kJ/g of Zinc. Even though, the energy supplied with this electro-chemical cell is not impressive, it was chosen for this project because it constitutes a simple and direct way to implement a cell using Copper-clad LCP material. For this battery two compartments are necessary: One of them with a Zinc anode and the other with a Copper cathode. Each electrode compartment will be in the presence of solutions of the metal salts under consideration. They can be in contact through a porous membrane. In order to reduce the liquid junction potential, an agar salt bridge is normally used. Potassium chloride, KCl is the material of choice, due to its ionic transport properties (Atkins, 1990). We have decided to use a polyacrylamide swellable polymer that upon the release of the KCl solution, will close the cell circuit. In this case, the thermal pneumatic actuation used for the aluminum cell will be used to "wet" the polymeric material. This material will swell to bring the two compartments together.

MICROACTUATED CELLS

Design considerations

In this section, we describe the actuation mechanism chosen to initiate the batteries. This actuation mechanism sometimes referred to as thermo-pneumatic, has been successfully used before. It was chosen due to its dispensing resolution with adequate pressures for fluid flow into polymeric micro-channels (Maghribi et al, 2001). A resistance heater is used for heating the working fluid, a high thermal expansion liquid. This actuation liquid is a water immiscible (to avoid use of membranes, and simplify the design), high temperature coefficient of expansion, and low heat capacity fluid. A popular 3M fluoro-compound, FC-77 used in thermal management applications, was chosen for his purpose (3M Specialty fluids, 1998). The working fluid is in one reservoir contiguous to another in which the electrolyte rests. During the process of heating, the fluid expands pushing the electrolyte solution. The electrolyte will then enter the last reservoir completing the micro-fluidic actuation. Since the performance of such a micro-fluidic actuated cell is dependent on the energy required to move a certain amount of fluid into the galvanic reservoir, the heating mechanism had to be optimized. The optimization of the power was achieved by using an efficient resistance heater, whose design was reported by Cardenas-Valencia et al (2003).

MICROFABRICATION

Fabrication of a micro fluidic cell has been described by Cardenas-Valencia et al (2002). Poly(dimethyl-siloxane), PDMS (Sylgard^{TM} resin, acquired from Essex) is one of the main constituent materials for both cells. The bottom layer of the cell (figure 1) was formed by embedding the Copper-LCP resistor in a PDMS block. The block was formed by casting the piece in a Teflon^{TM}-machined mold. The top layer was fabricated by etching soft glass slides (Corning Glass) after a layer of photo-resist was applied and baked. The glass etch used was a HF 5:1 solution (Kepro Circuit Systems). Two injection ports were drilled using a 0.127 mm diameter diamond tip drill. The two layers, shown in figure 1, are then glued by polymerizing in situ PDMS resin applied between them. The next step for the cell micro-fabrication is the filling of the reservoirs. Micro-pipettes (Fisher Scientific) were used to fill the micro-fluidic reservoirs. The A-reservoir illustrated in figure 1, is filled with the working liquid and subsequently, reservoir B with electrolyte solution. A final layer was glued in the top layer sealing the cell. The final layer was prepared by spinning at 1500 rpm a small amount of resin on a glass slide. In all cases the PDMS layers were cured at 120 ^{o} C during 30 minutes.

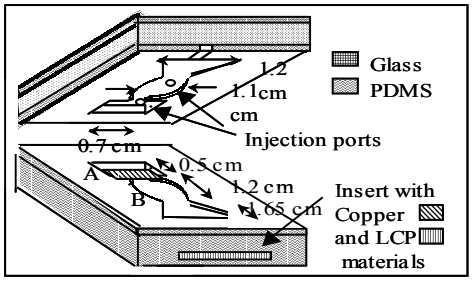

Figure 1. Isometric view of the micro-fluidic cell

Masking is one of the essential steps in micro-fabrication. Detailed processes for mask fabrication can be found elsewhere, (Gad-el-Hak, 2001) and it is commonly accepted that this process constitutes one of the most expensive and time-consuming tasks associated with the manufacturing of micro-devices.

Mask-less Lithography. The exposure system model SF-100 is a drop-in replacement for standard exposure methods. The mask-less photolithography system was acquired from Intelligent Micro Patterning LLC, (St. Petersburg, Fla.). The system contains the optics, light source, and integrated electronic components used to directly generate aerial projected patterns for the exposure of photo-sensitive materials (Hand 2001). The system is presented schematically in figure 2. The "artwork" or photo-image design is generated in a computer using any available drawing software. The artwork pattern is then transferred to the substrate surface to expose the photosensitive material for the pattern transfer step. In this manner, quick and inexpensive patterning of different materials on other substrates can be achieved. The lines in figure 2 represent the image being transferred to the substrate. A microscope is used for substrate alignment with the pattern. The alignment is controlled through a computer controlled multi-axis stage that offers 35nm step sizes.

A 13 μm copper-0.002" PCB Zyvex-flex-circuit material, (Rogers Corp.) in which the substrate is a liquid crystal polymer (LCP), has been chosen to manufacture the resistance heaters. They were tin plated to protect the copper from oxidation. The electro-less tin-plating solution (Kepro-Circuit Systems) was used at ambient temperature. The process flow for the micro-fabrication of resistors that will be used as heating devices was described in Cardenas-Valencia et al. (2003). The materials used for photo-imprinting the copper-LCP PC board materials were photo-resist SC1827, (Shipley) applied by spinning at 1500 rpm and cured on a hot plate at 115 ^{o} C for 5 minutes. The photo-resist was exposed for 9 seconds in the photolithography system described above. The photo-resist was developed at ambient temperature by immersing it in a 453 micro-posit developer (Shipley) under sonication for about 3 minutes. The copper etching material was a ferric chloride solution used at 110 ^{o}C. For the zinc-copper battery forming layers, we have used double sided Copper-clad liquid crystal polymer (3M). The patterning of the resistor and the reservoirs for the catholyte and anolyte soilutions was carried out as described above. The LCP material is etched using a saturated solution of KOH (Fisher Scientific) at 98 ^{o}C. The zinc electro-platting on the Copper was done in an acid zinc chloride bath with a Pro-Craft electroplater (Model 45.506G) operated at 0.5 amps and using a stainless steel electrode. The plating time for the preliminary batteries electrodes was approximately 10 minutes. A general process flow for this case is presented in figure 3.

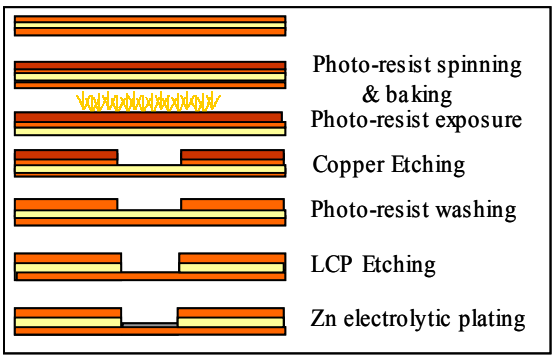

Figure 2. Process flow for a double sided copper LCP material.

Al-air micro-actuated cells

The layering of the different layer formed the reservoirs and the channeling required for the microfluidic actuation. The triangular reservoir in figure 1 constituted the electro-chemical reservoir. Upon micro-flow initiation the electrolyte will enter the galvanic reservoir in which the aluminum anode and a commercial oxygen cathode material are located. The electrolyte then allows the electrical contact between the two electrodes and energy is provided as the electrochemical reaction takes place.

The adhesive PDMS layer serves also to hold the electrodes in place which in this case are aluminum and a Porous oxygen catalytic cathode. Aluminum foil was the anode (0.004 in) thickness, (Alcoa Technical Center). The cathode material was a commercial composite air cathode (AC65 Air cathode - Alupower Inc.). The liquid to be actuated in this case is electrolyte aqueous solution of KOH reagent grade (Fisher Scientific). Two concentrations of this electrolyte were prepared, 1 and 9 M. Figure 3 shows a planar view of the top of the micro-fabricated electro-galvanic cell and several cuts of the planar faces. Resulting dimensions are given in centimeters.

Zinc-Copper battery. Poly(acrylamide) bridging actuation.

The actuation of the cell is based on a gelled poly (acrylamide). This polymeric material has the capacity of swelling and contracting upon applied external stimulus. There have been different studies in which the swelling is due to different factors. A crucial advantage of this polymeric material is its extended use as a concentrator, and release agent. Hoffman et al (1999) have patterned this material and recognized the potential as micro-actuators. It is also known that the material can be bonded to glass surfaces. Our initial testing was based on the works of Saitoh et al (2002).

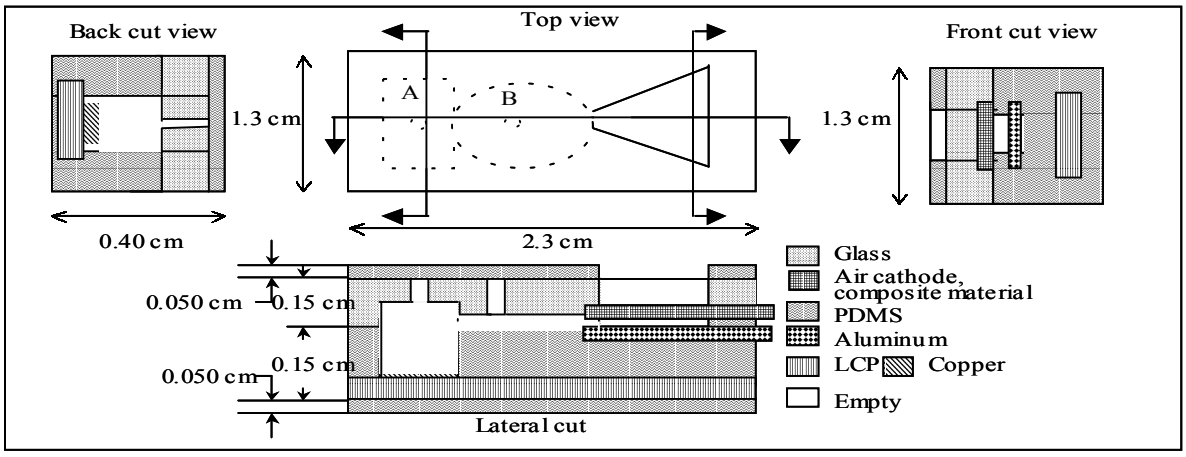

Figure 3. Constituent layers and dimensions of the micro-fluidic actuated Al-air cell constructed (Not at scale)

Several mechanisms have been proposed for the actuation of the acrylamide gels. Because they respond to the addition of solutions, electric and thermo actuation are attractive options under study. (Beebe et al, 2000). However, we have decided to use the swelling due to the injection of an aqueous solution. It has been shown by various researchers that the degree of swelling can be modified by the use of different saline concentrations. Lobo et al. (2001), specifically used KCl, a salt that is commonly used as a component in salt bridge studies due to their ionic transport behavior when dissociated. This solution delivery will be accomplished then in a similar manner as the actuation described for the Al-air cell. For the synthesis, we have decided to use the recipe given by Saitoh et al (2002).

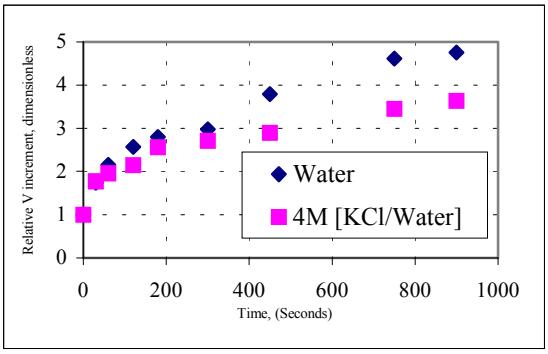

Figure 4. Meaured volumetric increments vs time of poly(acrylamide) swollen with two solvents.

We have tested the swelling of a 2 % cross-linked poly(acrylamide), by bonding the synthesized poly(acrylamide) in a capillary glass tube (Fisher Scientific). Specifics on the synthesis and the actuation will be reported elsewhere. Herein, we report the swelling actuation with water and a 4 M KCl aqueous solution. The volume of poly(acrylamide) and KCl solution added were approximately 200 micro-liters in a 2 mm diameter capillary glass tube. Figure 4 reveals that a volume increment of twice the original size can be achieved at around 40 seconds upon the KCl aqueous solution addition.

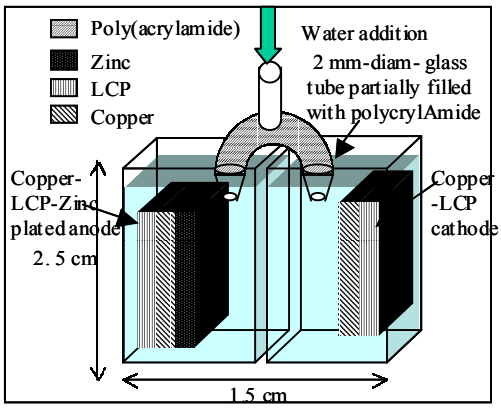

Figure 5. Miniactuated test cell for testing the power density and the energy available upon actuation for a Zinc-Copper battery, with poly(acrylamide) bridge.

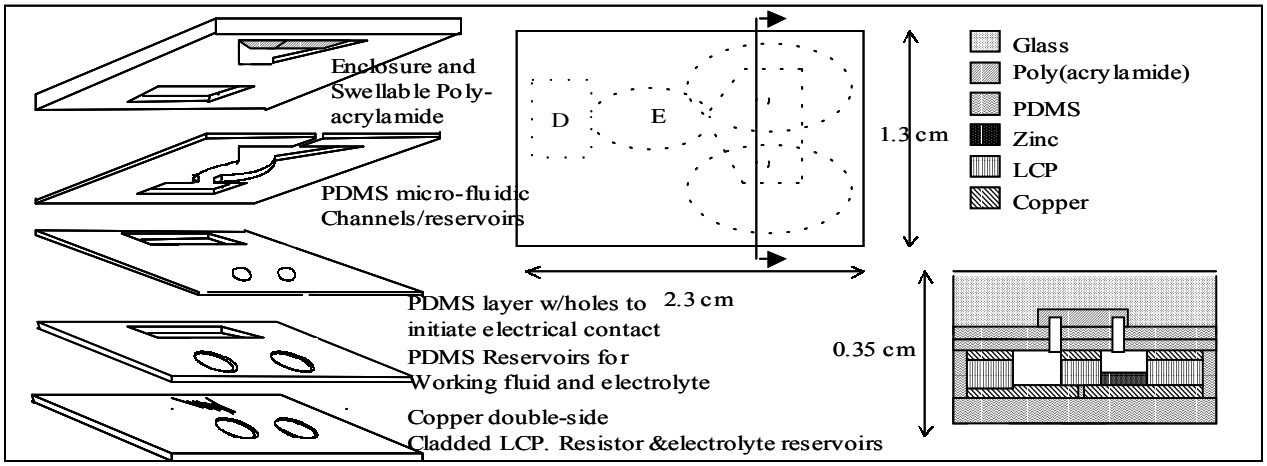

Figure 6. Conceptual design of a Zinc-Copper micro-fabricated battery, showing the designed dimensions (Not at scale)

The integration of the conceptual cell presented in fig 6 is in process. The PDMS layers could be replaced with fluidic LCP layers and laminated together. The electrochemical performance of this system is based on the use of a system like the one presented in figure 5.

The micro-fabricated reservoir bottoms were formed of the required metals to form a galvanic cell, one for the cathode (Copper) and the catholyte (1 M Copper sulfate solution) and another one for the anode (Zinc electroplated on the Copper) with the respective anolyte (1 M Zinc sulfate) solution. The actuation mechanism to bring the cathode and anode in ionic contact in this cell consists of a gelled polymeric material made of polyacrylamide acting as a salt bridge. Polymeric salt bridge fabrication is occurring presently. In this form, the long battery shelf life is achieved by having these compartments separate. The polymer is patterned in the channel but is not in initial contact with the electrolyte, but upon first actuation with the addition of liquid induces swelling in the polymer completing the electrical circuit. The actuation mechanism will be controlled through the polymeric composition, the concentration and type of solution to be pushed into the polymer, and the primary actuation mechanism.

EXPERIMENTAL PROTOCOL

The net cell energy out-put is given by the following expression;

$$\text{Energy}_{\text{Net}} = \text{Energy}_{\text{out}} - \text{Energy for actuation}_{\text{in}} \qquad (4)$$

The required energy to initiate the cell, Energy for actuation$_{in}$, was optimized by applying a voltage that maximizes the heating efficiency input into the system, (Cardenas-Valencia et al, 2003). It is well known that the performance of an electro-chemical cell depends on the power that is withdrawn from it (Atkins 1990). As more current is drawn from a cell, over-potentials (either due to local concentration gradients or to the hindered ionic transport due to gas release), reduce the effective voltage produced. The polarization curve depends on the physical configuration of the cell and on the chemicals and their concentrations used. This relationship is a unique to each cell and characterizes its performance. The micro galvanic cell has been characterized using this criterion. Various micro-cells were fabricated and their output voltage was recorded as function of time when subjected to different resistive loads. Measurements with each load were performed subsequently at least 5 times. Voltages and current intensities applied were measured and recorded over time by means of a Fluke-189 multi-meter. Both electrical energies were calculated as follows;

$$E = \int_{t_1}^{t_2} \text{Power} \; dt \qquad (5)$$

RESULTS & DISCUSSION

An electrical power input of 0.063 Watts, was used to heat the working fluid. The resistor/voltage utilized was optimized for minimal power actuation (Cardenas-Valencia, 2003) .The amount of energy utilized to fully fill the cell in figure 1 was approximately 3 Joules. In Figure 7 we present micrographs of the fluidic actuation as it fills the triangular electro-galvanic reservoir.

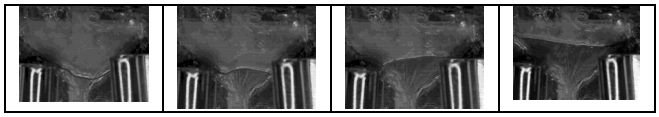

Figure 7. Micro fluidic actuation successive photographs taken at t= 1, 8 15 and 23 seconds

Electro-chemical Performance.

Figures 8 and 10 reveal the voltage available with the corresponding current intensity per unit area for the Al-air and Copper-Zinc batteries, respectively. Figures 9 and 11 show the area power density vs the current intensity superficial density for these systems.

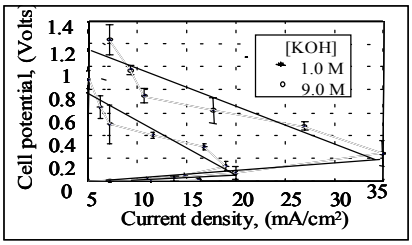

Figure 8. Polarization Curve for the Aluminum-Air micro-fabricated battery with two different electrolytes

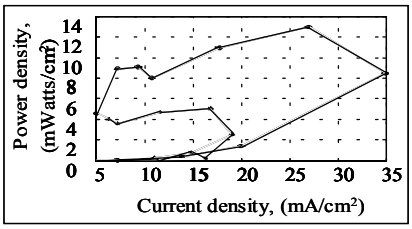

Figure 9. Area power density vs Current density for Aluminum-air cell using two different electrolytes

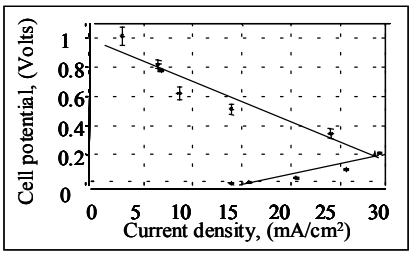

Figure 10. Polarization curve for the Copper-Zinc fabricated battery

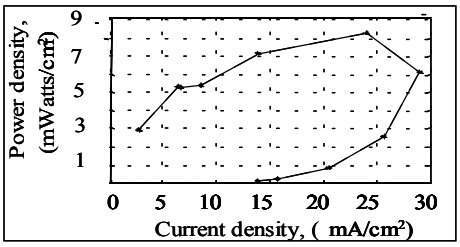

Figure 11. Area power density vs Current density for the Copper-Zinc cell using two different electrolytes

The cell characterization through the data in figures 8-11 determines the optimal load rate (at which the power density is highest). The active cell area, and the load imposed on the cell determine the current available, thus specifying the energy available. By imposing the optimal loading on the cell we computed the cumulative energy (equation 5) using trapezoidal integration. The cumulative energy represented the $Energy_{out}$ in equation 4. By using the dimensions on the cells presented in figures 3 and 6, volumetric power densities can be calculated. Table 1 summarizes the net volumetric power densities, (equation 4) for the electrochemical systems described herein.

Table 1. Comparison of power densities and energy delivered at short times for the described and other electrochemical systems.

System	Energy $_{Net}$ Delivered (Joules)	Time elapsed (minutes)	Power density (mW/cm^3)	Reference
Al-Air micro-cell	1.0	5	2.5	This work
Copper-Zinc Micro-cell	0.84	8	1.6	This work
Non rechargeable Lithium battery	0.03	5	0.090	Compilation by Roundy et al, 2002
	$2.84x10^3$	(1 Year)	0.090	

CONCLUSIONS & FINAL CONSIDERATIONS

It has been shown that electro-chemical cells represent a simple concept that can be readily micro-fabricated. It is been demonstrated that the manufacture of the MEMS power devices in a PCB format is simple and direct. In the cells presented, the open voltage of the micro-battery approximated the theoretical 1.10 V for the Daniell Battery and 1.9 V for the Aluminum-air galvanic cell. In these cells, the life of the battery could potentially be regulated by the amount of Zinc electroplated in one of the compartments (Daniell), or the amount of aluminum anode (Al-air) available to electrochemically react. We have practically measured power and energy levels attainable in examples of micro-fabricated cells. Based on the dimensions of the illustrated cells in figures 3 and 6, volumetric power densities have been calculated. The batteries have proven to poses a high power density with superior energy storage capability for short delivery times. Superior power volumetric density values could be achieved by reducing the dimensions of the cell. The demonstrated energy levels and delivery time frames suggests that these devices could potentially be used for certain fieldable and implantable applications in power MEMS systems.

It is worth to point out that, low columbic efficiencies based on the weight of aluminum consumed in the 9 M KOH electrolyte have been measured. However the energy released was faster, constituting a higher volume power density. The electrochemical system efficiency should be taken into account when calculating power density per unit mass. Currently, our group is working on higher efficiency aluminum anode chemistries that will be miniaturized, producing systems with high efficiency and high power densities both, per unit volume and per unitary mass unit.

The simplicity of the reported micro cells allows for easily configurable designs, both planar and conforming and the potential for generation of devices with customized energy densities through laminate stacking. These devices show potential for eventual use in general or specialized MEMS applications.

ACKNOWLEDGMENTS

Distribution Statement 'A', Approved for Public Release-Distribution Unlimited. The financial support for this project, provided by the U.S. Army, Space and Missile Defense command to the University of South Florida through grant DASG60-00-C-0089 is gratefully acknowledged. We also would like to thank Dr. Donald Smith of Alcoa Technical Center for the free high purity Aluminum samples that kindly sent to us.
Dr. Cardenas-Valencia would like to continue acknowledging financial support of CONACYT and the University of Guadalajara, in Mexico for the scholarships granted for the completion of his doctoral studies.

REFERENCES

3M Specialty materials. 2000, FC-77 ™ Electronic Liquid, Product Information,St. Paul, MN. pp. 1-4.

Atkins, P. W., 1990, in Physical Chemistry. W. H. Freeman and Company, New York, NY, pp. 907-930

Beebe, D. J., Moore, J. S., Bauer, J. M. Yu, Q., Liu, R. H., Devadoss, C. and Jo, B.-H., 2000, Nature, Vol. 404, pp. 588.

Cardenas-Valencia, A. M., Challa, V. R., Fries, D. P., Langebrake, L. C., Benson, R. F., Bhansali, S., A Microfluidic Galvanic Cell as an On-line Chip Power Source, *Sens. and Act. B.,* in press.

Cardenas-Valencia, A. M., Fries, D. P., Langebrake, L. C., Benson, R. F., Rapid Design, Fabrication and Optimization of a Single Event of a Thermo-pneumatic microactuation for the Delivery of Minute Amounts of Liquids, *to be presented at the Proc. First International Conference on Microchannels and Minichannels,* April 21-23, 2003, Rochester, NY.

Dyer, C. K., 1999, Replacing the Battery in Portable Electronics, *Sci. Am.*, Vol. 281 No. 1 pp. 88 - 93.

Gad-el-Hak, M. 2001, *The MEMS Handbook*, CRC Press. Series for Mechanical Engineering.

Hand, A., 2001, Start-up Company Exploits Maskless Photolithography Technique, *Sem. Int.,* Vol. 24 No 9, pp. 44

Hoffman, J., Plötner, M., Kuckling, D., and Fischer W-J., 1999, Photopatterning of thermally sensitive hydrogels useful for microactuators, Sens. and Act: A, Vol. 77, pp. 139-144.

Koeneman, P. B., Ilene, J.B, Wood, K. L., 1997, Feasibility of micro power supplies for MEMS, *J. Micro-electr.-mech. Syst*., Vol. 6 No. 4.

Li, Q., and Bjerrum N. J., 2002, " Aluminum as anode for energy storage and conversion: A review" J. Power Sources, in press.

Licht, S., 1998 " Novel aluminum batteries: a step towards derivation of superbatteries" *Coll. Surf. A*, Vol. 134, No 1-2, pp. 241-248.

Lobo, V. M. M., Valente A. J. M., Polishchuk, A. Y. and Geuskens, G., 2001, Transport of non-associated electrolytes in acrylamide hydrogels, *J. Mol. Liq.* 94, pp. 179-192.

Maghribi, M. N., Krulevitch, P., and Hamilton, J. K., 2001, Microsyringe arrays in Poly(dimethylsiloxane), *Proc. Of the μTAS 2001 Symposium*, Monterey, CA, pp.165-166.

Merkel, T., Graeber, M., and Pagel, L., 1998 A new technology for fluidic Microsystems based on PCB technology, *Sens. and Act.*, Vol. 77, pp. 98-105.

Nguyen, N., and Huang, X, 2001, Miniature valve less pumps based on printed circuit board technique, *Sens. and Act: A*, Vol. 88, pp. 104-111.

Morris, H., and Arena, S., 1993, Oxidation-reduction, in Foundations of College Chemistry, Brooks/Cole Publishing Co., Pacific Grove, CA, pp. 430-454.

Muller, N., and Frechette, L. G., 2002, Performance Analysis of Brayton and Rankine Cycle Microsystems for Portable Power Generation, *Proc. ASME International Mechanical Engineering Congress and Exposition, IMECE 2002,* New Orleans, LA, Vol. 2, IMECE2002-39628.

Pescovitz, D., 2002, The Power of Small Tech, *Small times.* Jan/Feb 2002, pp. 21-31.

Roundy, S., Wright, P. K., and Pister, K. S. J., 2002, Micro-electrostatic Vibration-to-electricity Converters, *Proc. ASME International Mechanical Engineering Congress and Exposition, IMECE 2002,* New Orleans, LA, Vol. 2, IMECE2002-39309.

Saitoh, T., Suzuki, Y., and Hiraide, M., 2002, Preparation on Poly(N-isopropylacrylamide)-Modified Glass Surface for Flow Control in Microfluidics, *Anal. Sci.*, Vol. 18, pp 203-205.

R. Yang, Liquid Crystal Polymers, Advanced Packaging Magazine, March 2002,. 17-22.