MICRO-ACTUATED ALUMINUM GALVANIC AND SEMI-FUEL CELLS FOR POWERING REMOTE LAB-ON-A-CHIP APPLICATIONS

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ABSTRACT

The fabrication and performance of novel aluminum anode galvanic cells, (including air semi-fuel cells), are presented and compared. The cells are switched on demand by means of two types of low-power-optimized micro-fluidic actuation.

Keywords: Micro-fluidic actuation, aluminum-oxygen semi-fuel & galvanic cells

1. INTRODUCTION

The growing applications of MEMS devices, especially in remote arenas have motivated the development of micro-powering devices. Scavenger energy systems, combustion engines and fuel cells have appeared as candidates to power MEMS [1]. MEMS micro-fabrication techniques allow for reduction of uni-dimensional structures, rendering the possibility for building and designing flat batteries (electrochemical battery tapes) that can be stacked to satisfy higher energy demands, providing means for high specific energy available that can suffice remote powering of MEMS systems. We have combined our efforts to improve aluminum electro-chemistries with novel microfabrication techniques to develop aluminum-air semi fuel and galvanic micro-cells. Battery time degradation is overcome and long on-the-shelf life is rendered to the cells by keeping the electrolyte separate from the reaction chamber. Micro-flow initiation on demand allows the ion contact between two electrodes and energy is provided as the electrochemical reaction takes place. The energy-on-demand concept, using microfluidics in aluminum semi-fuel cells was presented in the past, [2,3] Previous fabrication combined the use of an elastomer resin that served to glue and encased the layers. Here, novel micro-fabrication techniques, improvements in the micro-fluidic actuation and new higher energy output aluminum chemistries are presented.

2. MICROFLUIDIC ACTUATION AND ALUMINUM-O2 CHEMISTRIES

The first actuation mechanism used is a thermo-pneumatic actuation, in which the thermal expansion of a working fluid pushes a discrete amount of electrolyte into the reacting chamber. Good liquid delivery resolution, and large pressure heads were achieved [4] The micro-fluidic channel was placed above the reservoir illustrated in figure



Figure 1. Iso metric view of the LCP layers that form the microfluidic mechanisms tested. Picture inserts show the resistor (left) and electrodes (right) fabricated with copper cladded LCP.

above the reservoir illustrated in figure 3. Even with optimized cycles of design the

energy required to push 5 μ L of liquid was in the order of 3 J. The energy input has been reduced by fabricating a freestanding resistor, as shown in figure 2. The immersion of the resistor in the working fluid FC-77 (3M Corp.) reduced the heat losses, increasing the heating efficiency to about 10% of reported in the past [4].

Table 1. Micro-fluidic actuation characteristics forA 5 micro-litters liquid delivery into a micro-channel

Mechanism	Time for total delivery (secs)	Energy Input (Joules)	
Therm epneumatic	30	3.3	
KCl Electroly sis	4	0.2	

Micro-pumping relying on aqueous solution electrolysis has been reported in the past [5]. This micro-fluidic actuation has been designed in a simple cell and is presented in figure 1. In this case, the fluidic channel was stacked below the bottom layer,

since the bubbles generated from the gold plated copper electrodes tend to rise above the electrodes. The electrolysis reaction to achieve the phase change that in turn generates the pressure to pump the liquid is: $2K_{(aq)}^++2Cl_{(aq)}^-+2H_2O\rightarrow 2K_{(aq)}^{-1}+2OH_{(aq)}^{-1}+Cl_{2(g)}^{-1}+H_{2(g)}^{-1}$

Table 1 summarizes the micro-fluidic actuation characteristics pertinent to the energetic requirements of the cell. Details on the micro-actuation will be presented elsewhere.

Table 2. Summary of the reactions for the Al systems studied for power-MEMS devices

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	AlAir Semi-fuel Cell	Al H ₂ 0 ₂ Cell	Aluminum Na2O2- Cell	
Electrolyte	9M KOH	1 M KOH	1M KCl	
Cathode	1/2O _{2(g)} +H ₂ O+2e ⁻ -2OH ⁻¹	$H_2O_{2(aq)}+OH_{(aq)}^{-1}+2e^-\rightarrow 3OH_{(aq)}^{-1}$	$Na_2O_{2(s)}+2H_2O_{(l)}+2e^{-}\rightarrow 2Na_{(aq)}^{+1}+4OH_{(aq)}^{-1}$	
Overall	4Al(s)+4OH (aq) -1+O2(g)+6H2O	2Al _(s) +3H ₂ O _{2(aq)} +2OH _(aq) ⁻¹	$2Al_{(s)}+3Na_2O_{2(s)}+6H_2O \rightarrow$	
(E°,V)	\rightarrow 4Al(OH)(aq) ⁻¹ (2.75)	\rightarrow 2Al(OH) _{4(aq)} ⁻¹ (3.2)	$2NaAl(OH)_{4(aq)}+4NaOH_{(aq)}$ (3.2)	

Even though competitive reactions have hindered the development of commercial aluminum electrochemical batteries; environmentally friendliness, high energy density, and low cost are advantageous features of these cells [6,7]. Since polarization effects of an electrochemical cell depend on the cell configuration and dimensions, reagents and the proportions at which they are introduced [2,8], the results in with three chemistries of the micro-cell are compared herein: Aluminum-air semi-fuel, Aluminum-Hydrogen peroxide in alkali media, and a patented novel chemistry using the pair Aluminum-sodium peroxide in aluminum cells [8]. The chemical reactions, and the electrolyte solution used are summarized in table 2. Especially advantageous is the use of the solid alkali metal peroxide, since this chemistry allows the use of KCl as both electrolyte and working liquid thereby simplifying the cell design.

3. NOVEL PCB/MEMS MICROFABRICATION: MATERIALS & REAGENTS

A ZyvexTM copper cladded (13 µm thick) liquid crystal polymer, LCP (50µm



Figure 2a. Iso metric view of the LCP comprising layers of Al cells. b, c. Assembled microbatteries showing fabricated devices (dimensions mm). d. Lateral view of an electrochemical chamber cut

thick) (Rogers Corp.) was used to fabricate the layers that comprise the micro-actuated batteries. Advantages on LCP use for micro-fluidic devices are well documented [9,10]. The exposure system: a SF-100 (Intelligent Micro Patterning St Petersburg FL) allows, without the use of masks patterning of standard photo-resist resins. LCP-Cu material used in conjunction with the SF100 system has been exploited widely by Fries et al [11] and has allowed for the design and fabrication of various micro-fluidic devices [4]. Complete process flows for the layers micro-machining, as well as the chemical and materials used can be found elsewhere [2,4,10]. For the novel chemistries reported here, the sodium peroxide (Sigma Aldrich), was previously powdered, pressed, and placed above the cathodic mesh. KCl and KOH (Fisher Scientific), were used as received to prepare the electrolyte solutions. The complete cell is a multi layer stack of three thin layers with cavities (Figure 1), which are aligned and bonded by pressing them at 25 psig and 259 °C during 20 minutes. The middle layer contains the required micro-fluidic path. In it, the rectangular shape reservoir hosts the working fluid, the oval contains the electrolyte and the triangular is the reacting chamber. The other layers are used as spacers and to keep the thin electrodes in place. Etched 50 µm aluminum foil was used as the anode, a commercial air cathode (Alupower) was used for the air semi-fuel cell and a platinum plated stainless steel mesh (Newark Co.) for the other batteries. The new LCP battery design has reduced the total cell volume. For instance, in the aluminum-air cell the volume reduced from 1.3 cm³ to 36 mm³. Figure 2 presents pictures of the microfabricated layers



4. RESULTS AND CONCLUSIONS

Figure 4. Electro-chemical characteristics of the Aluminum anode cells with different oxidizers in the cathodic region.

The performance of the micro-galvanic cells is reported in figure 4. The error bars for the voltage were calculated by doubling the calculated standard deviation of measurements; replicated the power, they were calculated using error analysis, propagation representing 95 а % confidence in the data if the variability is normally distributed. The net

energy available (Output energy

minus energy input for actuation), as well as other battery characteristics are summarized in table 3 for the three chemistries, presented here. A macro zinc-air battery power density reported by Sintef [12] is 240 mW/cm³. This value is higher than that of Al-air

cell reported in table 3, since the net energy considers the actuation energy, (thermopneumatic). However, it was demonstrated before that our Al-air chemistry provided higher energy when compared to a commercial zinc-air button cell [3]. The reduction of the required energy for the actuation reported in here, has significantly improved the cells performance (Table 3).

Table 3. Power densities & energy delivered at short times for	•
the describedelectrochemical systems.	

Actuation mechanism	Cell/ Batery	Operational time, (sec)	Power density (mW/cm³)	Net Energy (Joules)
Thermo-pneumatic	Al-air	300	94	1
Thermo-pneumatic	Al-H2 02	300	200	5
Electro-chemical	Al-Na,O,	300	717	8.5

The major advantages of the micro cell concept presented are the ability to switch actuation as required, the high power density available and the reproducible laminate system design. The

simple versatile design allows for easy modification of the cell dimensions and the chemistries utilized in order to satisfy specific energetic demands.

ACKNOLEDGEMENTS

Financial support, provided by the U.S. Army, Space and Missile Defense command through grant DASG6000C0089 is gratefully acknowledged.

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