FACILE BATCH MODE PROCESS FOR HIGH CAPACITY RECHARGEABLE NICKEL-ZINC MICROBATTERIES

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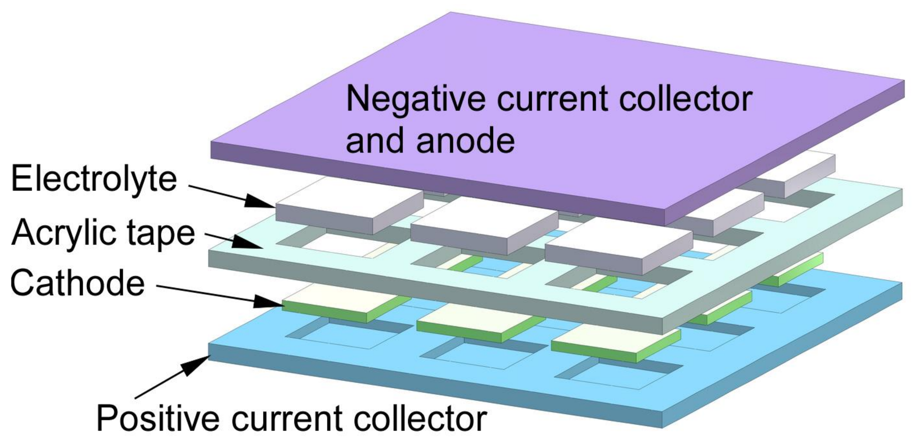
Summary: Battery miniaturization is necessary to keep pace with the advances in microsystem technologies. The size of the microsystem is often determined by the size of its power source, which is typically the largest component in the microsystem. There is a demand for high performance miniature power sources which could enable new microsystems, particularly autonomous microsystems. Such microsystems need rechargeable batteries that have dimensions on the scale of 1–10 mm³. Although Li-ion batteries are appealing in terms of capacity, cyclability, and high-temperature performance, Ni-Zn batteries have certain benefits like high power density [1] while still providing good cyclability. Additionally, Ni-Zn batteries utilize low-cost materials that are easy to handle and are more environmentally benign.

This work presents a facile approach for batch mode fabrication of millimeter-scale Ni-Zn batteries that is facilitated by unconventional structural materials and fabrication options [2] . Micro electrodischarge machining (µEDM) is used to define arrays of cavities in foils of Ni and Zn. The cathode and electrolyte materials are incorporated using a self-aligned damascene method. The fabricated batteries have a footprint of 2.2 × 2.2 mm², a nominal voltage of 1.7 V, and a typical capacity of ≈63 µAh. These batteries provide sufficient power and energy density for mm-scale autonomous microsystems that are being actively developed for health and wellness, as well as environmental applications. The fabrication process can be scaled to manufacture large arrays of microbatteries.

1 Concept and Design

- Cathode: Nickel oxyhydroxide (NiOOH)
- Positive current collector: Ni foil
- Anode and negative current collector: Zn foil
- Electrolyte: Polymer gel electrolyte

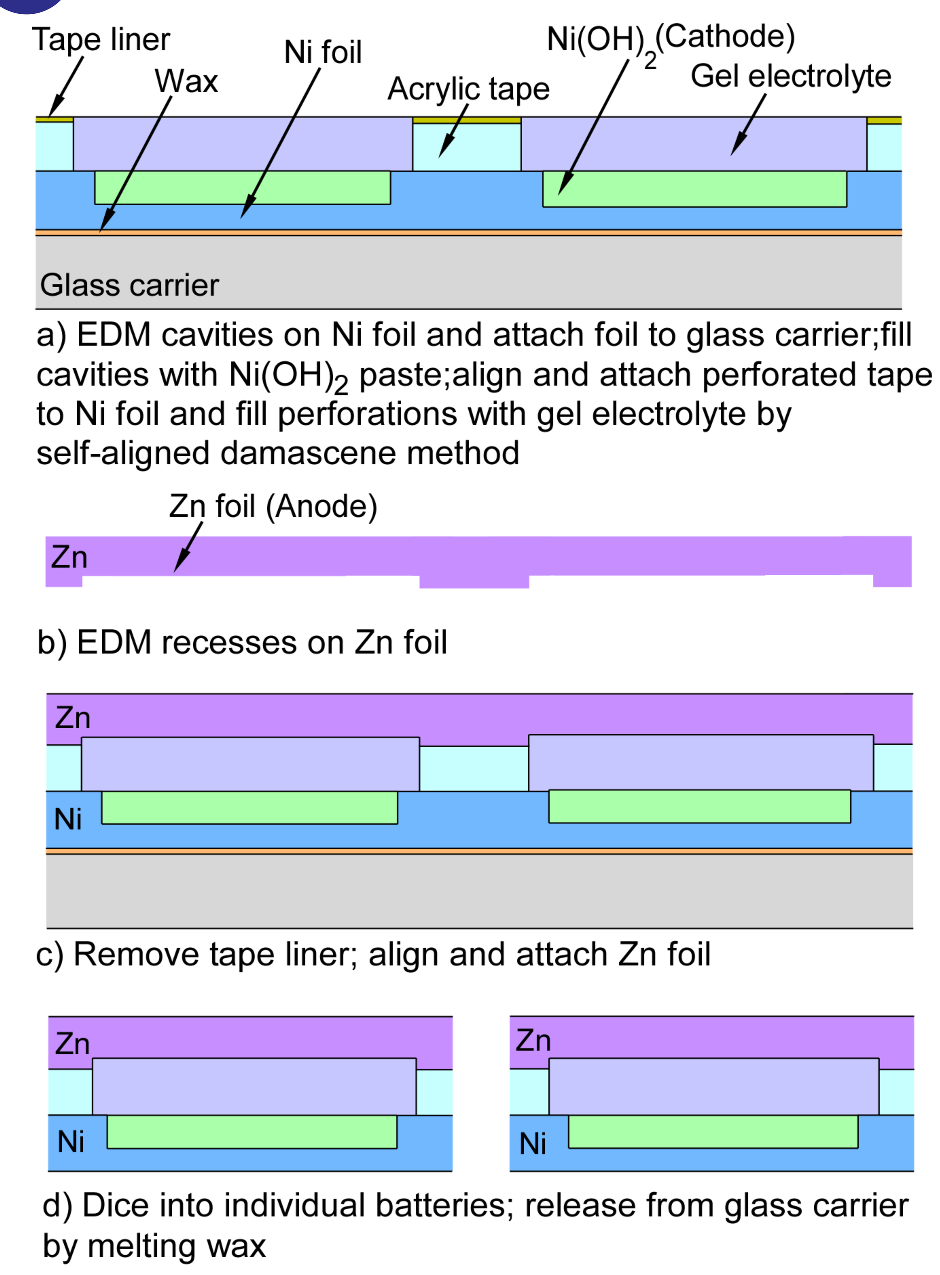


Design of the microbattery for batch mode fabrication in an array (3 × 3 array illustrated)

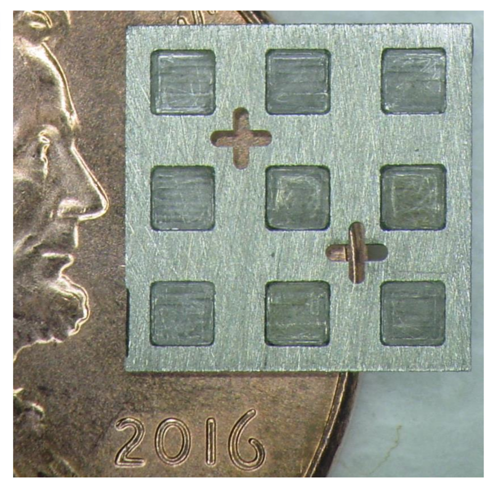
- Electrochemical reactions:

Discharge	Cathode	$2NiOOH + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$
	Anode	$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$
	Overall	$2NiOOH + 2H_2O + Zn \rightarrow 2Ni(OH)_2 + Zn(OH)_2$
Charge	Overall	$2Ni(OH)_2 + Zn(OH)_2 \rightarrow 2NiOOH + 2H_2O + Zn$

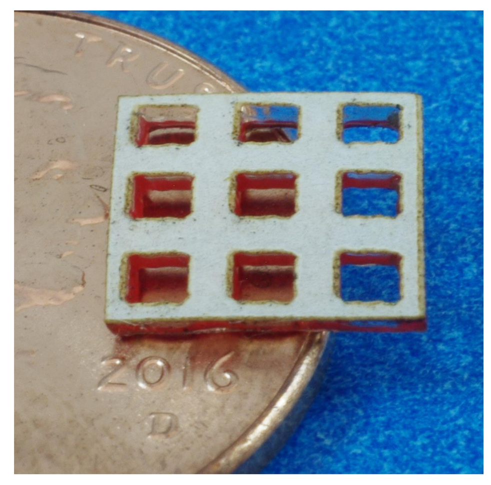
2 Fabrication



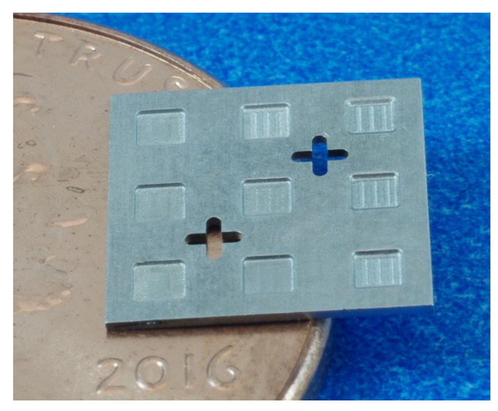
Fabrication process flow



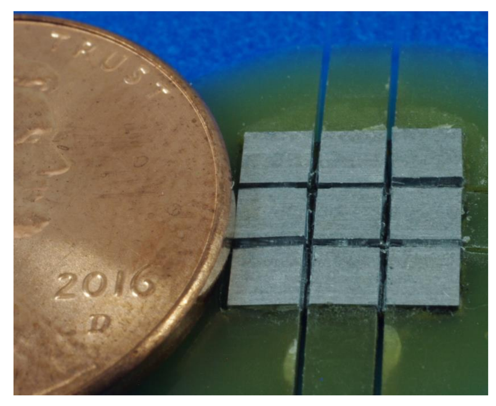
µEDM cavities (150 µm deep) in Ni foil (250 µm thick)



Perforations in acrylic tape (250 µm thick) cut by laser



µEDM recesses (150 µm deep) in Zn foil (250 µm thick)



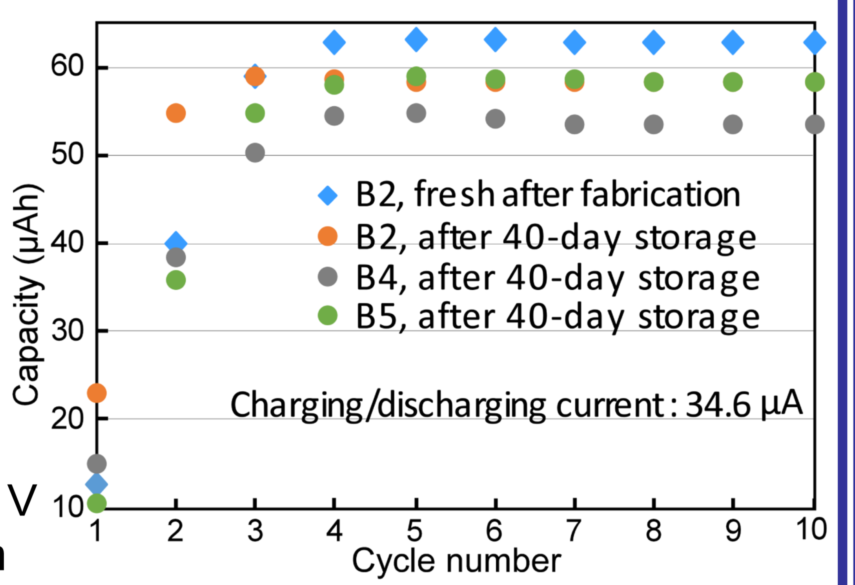
A 3 × 3 array of fabricated microbatteries after singulation

Fabrication results

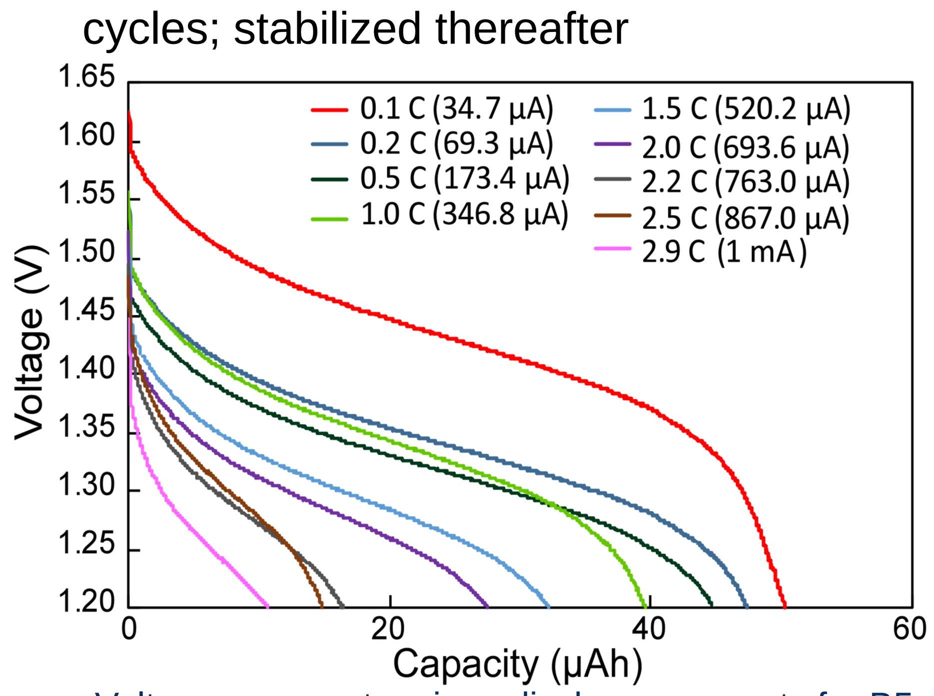
- Cathode paste: $Ni(OH)_2$ powder (active material), cobalt powder (conductive material) and polyvinyl alcohol (binder solution), 10:1:6 by weight [3]
- Polymer gel electrolyte: Polyacrylic acid in 8 M KOH aqueous electrolyte, 1:200 and stir until a homogenous gel forms [4]
- Self-aligned damascene method: spread paste/gel on foil/tape surface and drive squeegee across foil/tape surface to fill cavities with paste/gel
- Acrylic adhesive tape: patterned using high throughput, low power laser; used as insulating middle layer and the battery sidewall
- Zn foil recesses: reduce overflow of electrolyte during attachment

3 Experimental Results

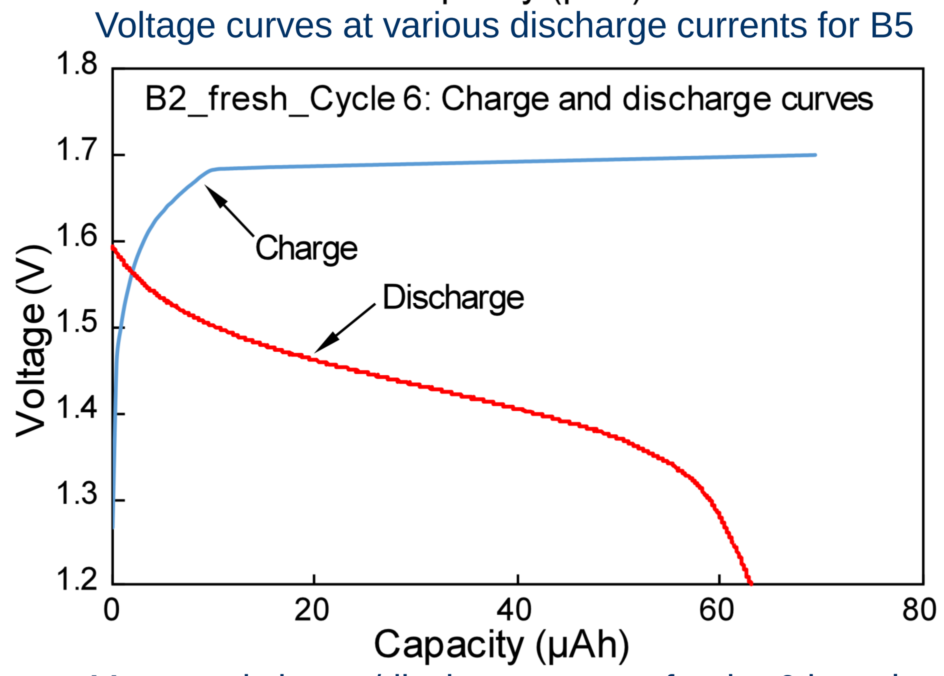
- Batteries tested using constant current in charging/discharging
- Nine batteries from a fabricated 3 × 3 array assigned battery ID B1-9
- Batteries charged and discharged for ≥10 cycles at charge/discharge rates of 0.1 C (10% of calculated theoretical capacity per hour i.e. 34.6 µA based on theoretical capacity of 346 µAh
- Charge time: 2 hours; discharge cut-off voltage: 1.2 V
- Formation reaction (oxidation of $Ni(OH)_2$ to NiOOH) during initial 3 charge/discharge cycles; stabilized thereafter



Measured capacity by cycle number for three different battery samples



Voltage curves at various discharge currents for B5



Measured charge/discharge curves for the 6th cycle of B2 tested immediately after fabrication

- B2 tested immediately after fabrication: maximum capacity of 63.16 µAh, corresponding to an energy density of 1.31 mAh/cm²
- Superior energy density attributable to structural design and material choices. In particular, dimensions and material choices of cathode and electrolyte [5,6] are significant contributing factors
- B2 capacity reduced by <7% after 40 days of storage
- Capacity of B4 and B5 after 40 days storage comparable to B2 after storage
- Multiple discharges for B5 from with increasing current from 34.7 µA to 1 mA
- B5 continuous discharge time at 1 mA: ≈38 seconds; maximum power: 1.45 mW; average power density: 26.88 mW/cm², sufficient to power many autonomous microsystems [6]

Battery specifications

Chemistry	Nickel-zinc
Overall size	2.2 × 2.2 × 0.75 mm³
Active material area	1.96 mm²
Nominal voltage	1.7 V
Measured capacity	≤63.16 µAh
Energy density	≤1.31 mAh/cm²
Max. discharge current tested	1 mA
Maximum power @1 mA	1.45 mW
Average power density @1 mA	26.88 mW/cm²

Process benefits

(i) Ni, Zn and acrylic tape: commercially available
(ii) Electrolyte: oxygen-free environment not required
(iii) Zn foil: both anode and negative current collector
(iv) Self-aligned damascene method: no need of specialized equipment

Comparison of this work with other published work on Ni-Zn batteries in literature

Work	Typical process used	Cell area (cm²)	Capacity density (normalized by cell area) (mAh/cm²)
This work	Self-aligned damascene method	0.048	1.31
3-D Ni-Zn microbatteries [1]	Micromolding of high aspect ratio electrodes using DRIE-etched holes in Si substrate; electroplating of electrode materials.	0.25	0.0025
Microscopic Ni-Zn batteries [7]	Electron beam evaporation; electroplating and photolithography patterning of current collectors.	0.02	0.389
Ni-Zn battery with polymer hydrogel electrolyte [5]	Electrodeposition; not batch mode	Macro-scale battery	
Ni-Zn battery with hybrid hydrogel electrolyte [6]	Paste electrodes; not batch mode	Macro-scale battery	

References

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Acknowledgements

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