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PNNL-32631

Pushing the Limits of Micro battery Capacity and Energy

February 2022

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
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Abstract

Micro battery with higher energy density will extend the service life of the miniature sensors so that the scientists and engineers could be able to collect more data along with the time in ecological and environmental vectors, such as animal tracking. Within this project, a completely new cell design (Gen2) for micro batteries to further increase their cell capacity and energy is developed. The new cell design directly packages the active material in a hard aluminum case, decreasing the percentage of non-active components. The manufacturing process to improve wetting ability is studied and the trial run is finally given to evaluate the feasibility of the proposed technology. It's found that both the capacity and energy with same battery size could be increased by 30% comparing with Gen1 micro battery technology previously developed by PNNL. The yield of Gen2 micro batteries is still lower due to the high degree of manual operation, especially for drilling process where more precise position control is needed. More effort is still required to improve the capability of automatic manufacturing processes. The new battery technology will support the development of smaller and lighter miniature sensors at PNNL and could potentially contribute to the large-scale manufacturing capabilities of micro batteries in US with reliable performances and long-term shelf life.

Acknowledgments

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Contents

1.0 Introduction

The size of electronic devices has generally decreased while the capabilities and quality of the devices continues to increase as modern electronic components used in such devices are developed and improved upon. Microelectronics have also been developed including miniature transmitters, sensors, and actuators. Numerous types of batteries are used to provide electrical energy to the electrical devices for use in varied applications with different requirements for electrical energy. However, conventional battery configurations are relatively large in size or have insufficient capacity. The reduction in physical size of the battery impacts the capacity and lifetime of the battery, and batteries play a critical role in determining the lifetime of downsized sensors, wearable devices, medical devices, and animal acoustic telemetry transmitters in a few illustrative examples. There are and will continue to be demands for batteries which provide increased energy capacities on a smaller scale for use in microelectronics. [1]

For the past eight years, three types of cylindrical micro batteries have been developed and used to implant to fish tags to study the fish activity.[2,3] The micro batteries (MB) include MB1842, MB3060 and MB47149 (Fig.1). The first two numbers present the diameter of the micro battery, and the rest of the numbers are height of the micro battery. The units of diameter and height are millimeters. For pursing high energy density of the micro battery, carbon monofluride (CFx) and Li metal are used as cathode and anode active materials respectively. A traditional winding process is applied to produce those micro batteries by rolling four layers, including one cathode electrode sheet, two separator sheets and one Li metal anode sheet, into a cylindrical shape. The micro battery produced with this process is defined as generation 1 (Gen1) micro battery.

The micro batteries with Gen1 technology have been successfully supplied to the clients for sensor production and animal studies. However, micro batteries with higher capacity and energy density are required by the clients to allow the study of animal tracking with longer time or juvenile/larva animals. New micro battery technology with higher energy density is therefore urgently required. In this project, a new cell design, denoted as Gen2 technology, in which the battery case is directly packaged with active materials, is developed. The feasibility, prototype, and remaining issues with the new cell design are also studied.

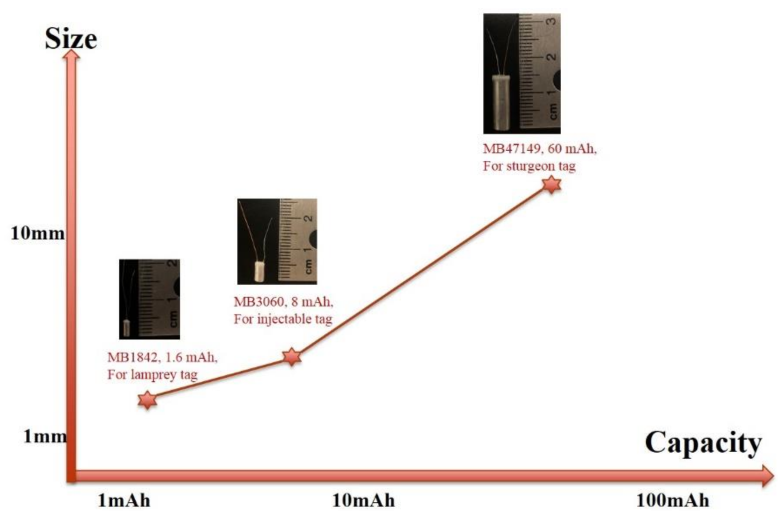


Fig.1 Three types of cylindrical micro batteries (Gen1) developed at PNNL.

2.0 Background, Discussion, and Results

2.1 New cell design (Gen2) to increase the capacity and energy

Gen1 technology utilizes a traditional winding process to produce the Jellyroll (Fig.2a). With Gen1 technology, MB1842 micro battery can deliver a 1.5 mAh of capacity (see Fig.2a bottom). The diameter is 1.8 mm, and the height is 4.2 mm in MB1842 micro battery. In Gen1 technology, many non-active materials have to be involved to support the active materials, like the current collector and binder. Typically, total weight of a MB1842 battery is ca. 23 mg and the cathode electrode (average weight: 3.24 mg) has a 14.1% weight ratio in the whole battery. The cathode materials, composed of CFx/Carbon/PTFE binder with a ratio of 88:7:5, are pressed onto a 77-micron Al mesh. In the cathode electrode, the wt% of Al mesh and PTFE binder are 29% and 3.5% respectively. Replacing non-active Al mesh and PTFE binder with CFx active material will add approximately 1 mg of CFx material that will increase the capacity to at least 2.2 mAh for MB1842, considering CFx has a specific capacity of 700 mAh/g in Gen1 technology.

The idea of Gen2 technology is to reduce the non-active materials, like Al mesh and binder. The cathode materials, which are only composed of CFx and carbon additive are directly filled into a cylinder case (Fig.2b). Li metal anode wrapped by the separator is closely attached inside the wall (Fig. 2b). With this new design, one of the cells delivered 2.5 mAh at 0.1 mA (Fig.2b bottom), a capacity increase of almost greater than 60%, indicating the potential feasibility of the Gen2 technology. Note that, in this project, we focus on increasing the capacity and energy of MB1842 micro battery as 1) requirements from the clients and 2) Gen2 technology favors smaller size (shorter diffusion path for electron and lithium ions). In the discharge curves in Fig.2b, the sudden voltage drop at 1.1 mAh may be caused by the wetting issue. More effort is required to smooth the discharge curve of the Gen2 battery.

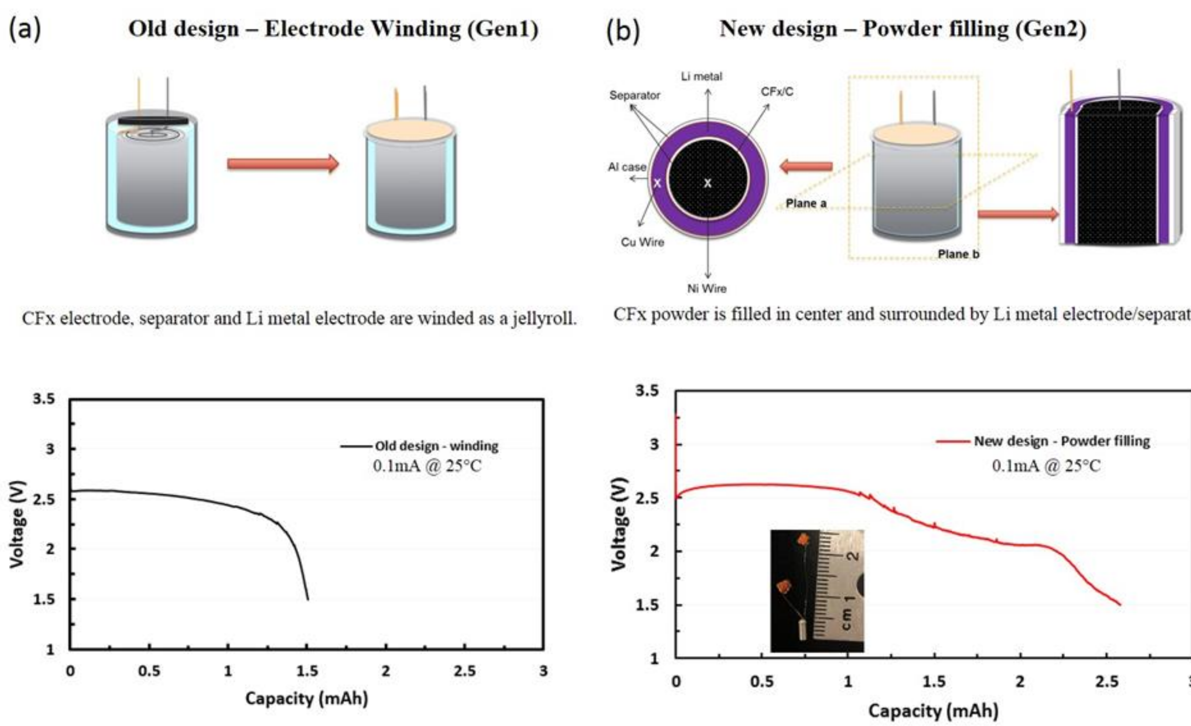
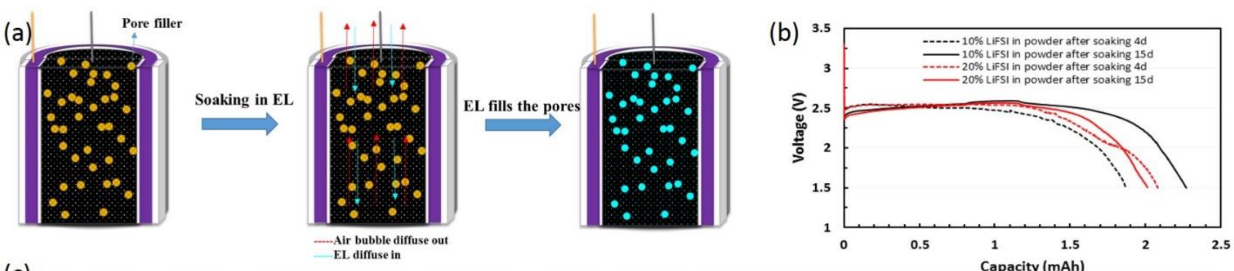


Fig.2 Cell structure and cell performance of Lamprey micro batteries (MB1842) with a) old design (Gen1) and b) new design (Gen2).

2.2 Pore filler to improve the wetting ability

Gen2 technology has potential to increase the capacity and energy of MB1842. However, as seen in Fig.2b, the voltage of MB1842 after discharged to 1.1 mAh decreases fast and won't be good for a steady operation and signal strength of fish tag. The voltage decrease suggests a higher polarization of a physical/electrochemical process in the battery, probably from the lack of electrolyte and limited swelling room for CFx cathode as there is less porosity in the compact design. One proposed solution to improve wetting of the CFx cathode is mixing a pore filler with the CFx/carbon powder. Pore filler is previously mixed with the CFx/carbon powder, and the mixed powder is then filled into the cylindrical case followed with a soaking process in electrolyte. The pores are created after the pore filler dissolved (Fig.3a), and a good pore filler is not expected to affect the cell performance. Here, 10% or 20% LiFSI was used as pore filler. LiFSI is the lithium salt in the electrolyte and not harmful for the cell performance. As shown in Fig.3b, with prolonged soaking time in electrolyte (at least 2 weeks), the voltage decrease is expected to be similar as Gen1 micro battery (Fig.1a), but the capacity unfortunately decreases to 2-2.3 mAh as some cathode active material is replaced by the non-active the pore filler (Fig.3b). Five fish tags have been tested with as-prepared Gen2 MB1842 micro battery by tag group at PNNL. Three fish tags with battery#2, #3 and #4, have a tag life of 4.9, 4.8 and 5.3 days respectively. It's 29-43% increase for the tag life comparing with 3.7 days in Gen1 micro battery, further indicating the feasibility of the Gen2 technology. However, the results are not consistent; the life of battery#1 and #5 are below the 3.7-day lifetime of Gen1 micro batteries. Besides, long soaking time is not good for large-scale production of micro batteries, another solution must be taken into account.



(c)

Battery ID	Tag ID	PRI (Second)	Test location	Tag activation date	Tag dead date	Tag life (days)	Note
1	G72256839	0.5	LSL2 bucket scanner	1/14/19 16:35	1/18/19 4:48	3.5	Tested in bucket scanner
2	G72FEDC11	0.5	LSL2 bucket scanner	1/14/19 16:55	1/19/19 14:47	4.9	Tested in bucket scanner
3	G721234	0.5	Lamprey Production Drawer	1/15/19 18:00	1/20/19 12:00	4.8	Estimated tag life. Tested in drawer. Tag was checked only once a day.
4	G725678	0.5	Lamprey Production Drawer	1/15/19 18:00	1/21/19 1:00	5.3	Estimated tag life. Tested in drawer. Tag was checked only once a day.
5	G72ABCD	0.5	Lamprey Production Drawer	1/15/19 18:00	1/18/19 18:00	3.0	Estimated tag life. Tested in drawer. Tag was checked only once a day.

Fig.3 a) Schematic of proposed first solution to create more pores in Gen2 micro battery and b) cell performance from this solution, 10% or 20% LiFSI was used as pore filler. c) Tag life test of 5 as-prepared Gen2 MB1842 micro batteries.

2.3 Central tunnel design to improve the wetting ability

A good cell design for Gen2 technology should consider CFx loading, wetting ability of CFx cathode and room for cathode swelling. The simpleness of the process should also be considered. With the absence of Al mesh and binder in Gen2 micro battery, higher CFx loading (ca.3.6 mg) is easily attainable. A tunnel created by drilling a hole at the center of the cathode electrode enables the easier wetting of electrode, more storing of electrolytes and more room for cathode swelling (Fig. 4). The improvement on wetting also decreases the manufacturing time of micro batteries. The current diameter of the hole is 0.3 mm and still needs to be optimized to balance the CFx loading and reserved room for wetting and swelling. The soaking time in electrolyte by this method is decreased to 8 hours, and thus feasible for production.

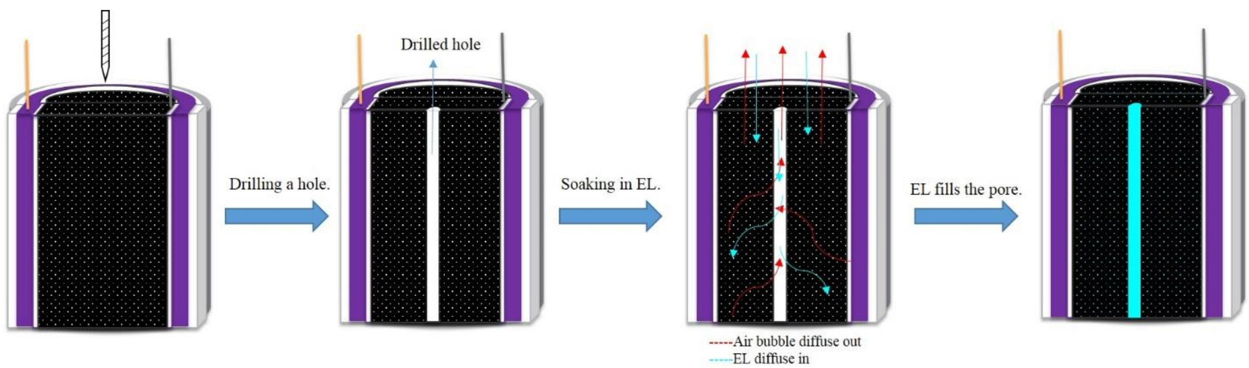


Fig.4 Schematic of proposed second solution to create more pores in Gen2 micro battery.

A typical manufacturing procedure with this central tunnel design to produce Gen2 micro battery (MB1842) can be found in Fig.5 and Fig.6. Some typical procedures include: 1) Li metal sealed in a polyethylene (PE) separator bag. PE separator is applied as it has preferred mechanical strength at both TD and MD directions; 2) Fill/press the CFx/C powder into the cylindrical case and 3) Drill a hole at center of the cathode electrode. These three steps contribute most to the total yield and consistency of the micro battery production. Note that, manual drilling with a tiny drilling bit is performed (Fig.6), and this manual process would cause issues with consistency described in section 2.5.

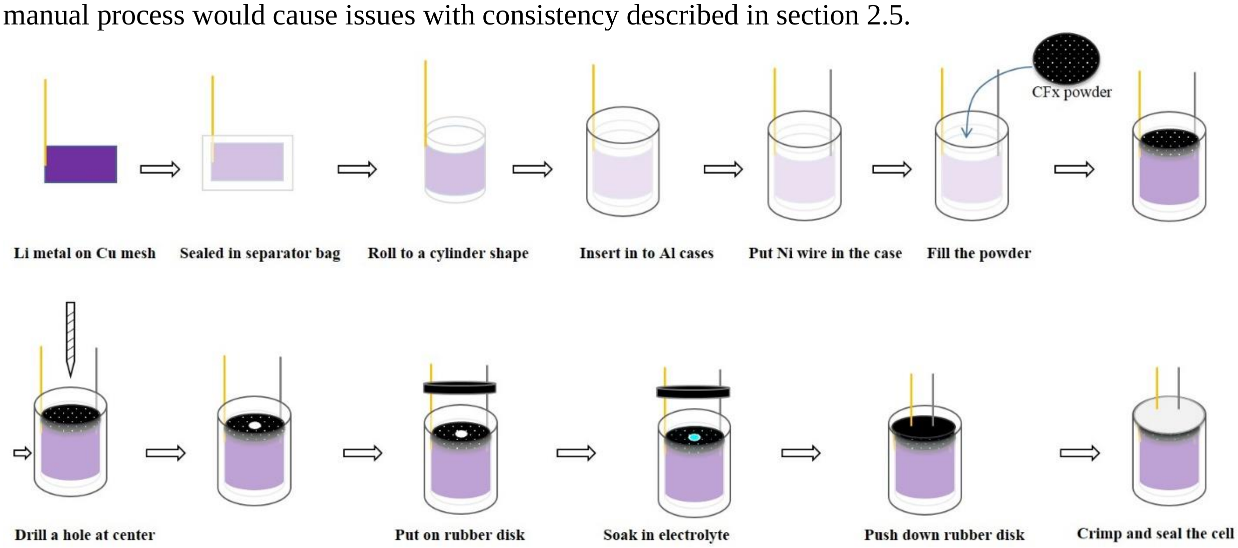


Fig.5 Schematic of a typical procedure for producing Gen2 micro battery (MB1842).

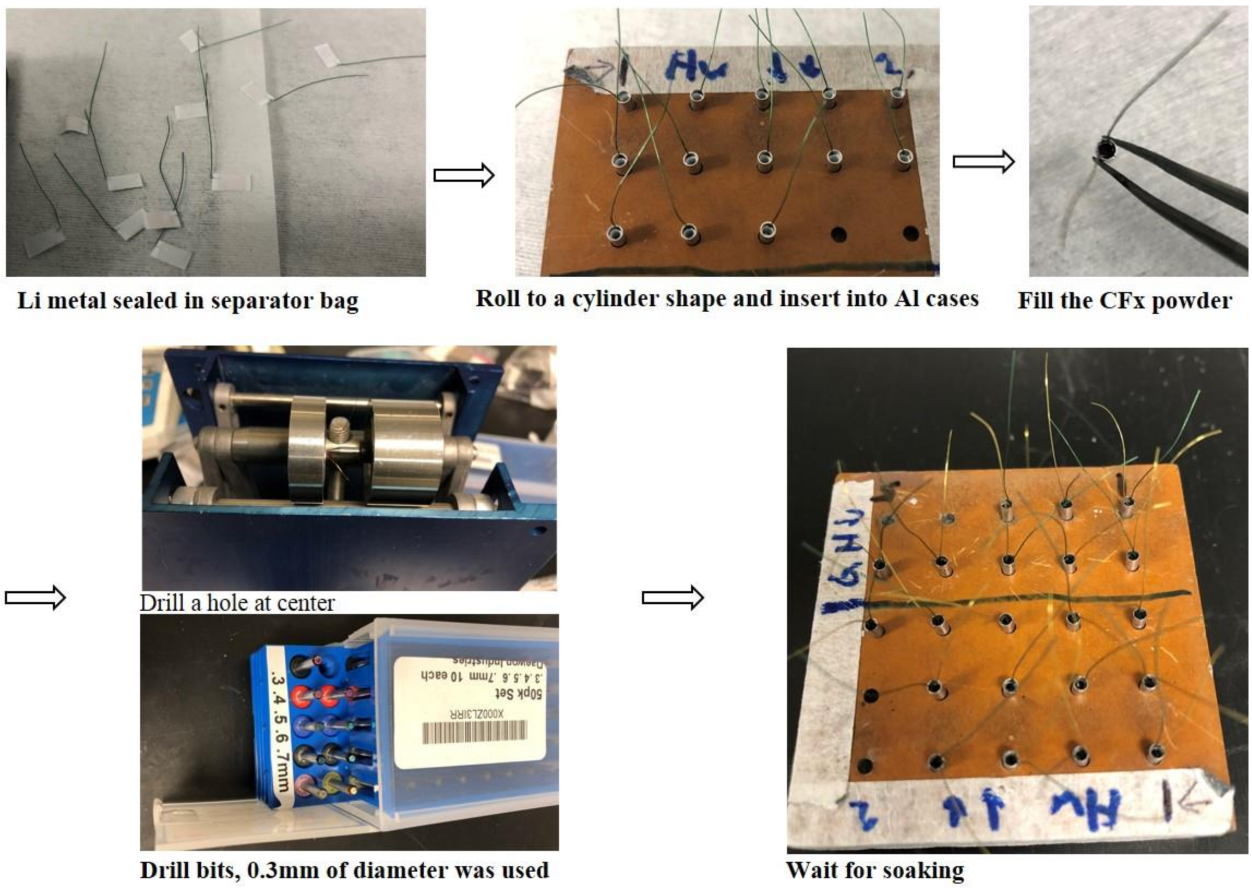


Fig.6 Digital photos of some typical procedures in Fig.5.

After the procedure was performed several times, a recent batch of eight MB1842 displays more consistent results. EIS impedance tests were carried out to characterize the impedance performance of Gen1 and Gen2 micro batteries. In a typical EIS test, a Nyquist plot is normally used to analyze the impedance behavior of interested battery. As shown in Fig.7a, R1, the first intercept on Z' axis, presents the ohm impedance of battery, including contact resistance, electron diffusion in electrode and lithium ions diffusion in electrodes, electrolyte and separator. R2 includes both SEI film resistance and charge transfer reaction resistance of cathode and anode electrodes. The slope at lower frequency implicates the difficulty of Li^+ diffusion in solid electrodes and is believed to easily diffuse in solid electrodes for Li^+ if it's close to 1.

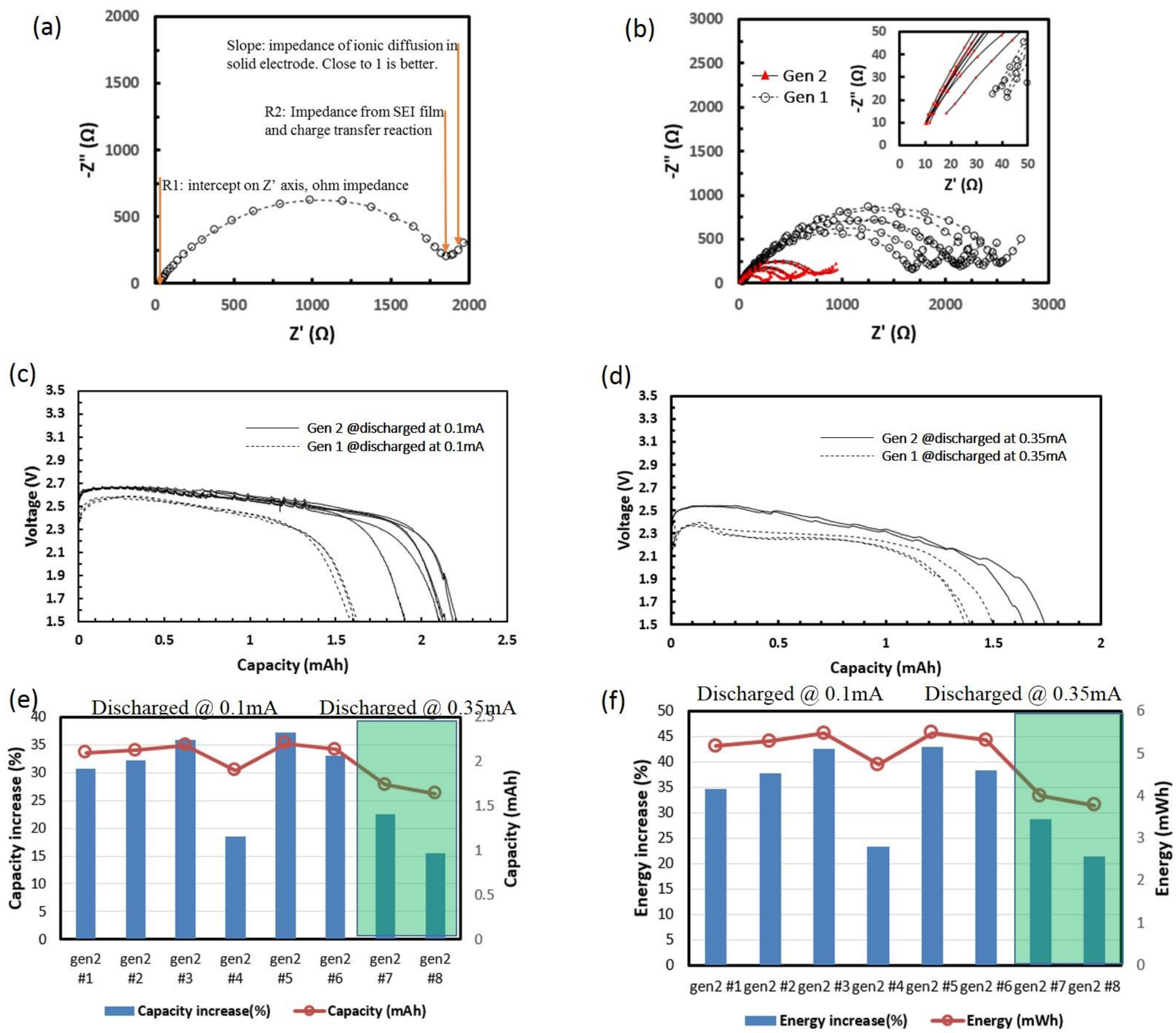


Fig.7 a) Schematic to present three key parameters in a Nyquist plot by EIS impedance. b) The Nyquist plot of the six fresh Gen1 micro battery and as-prepared eight fresh Gen2 micro battery (MB1842), circle with dash line is Gen1 micro battery. EIS test was performed with 5 mV and 100 kHz-1 Hz. c) Cell performance of Gen1 and Gen2 batteries discharging at 0.1 mA and d) 0.35 mA, real line is discharging curve of Gen2 battery while dash line for Gen1 battery. e) Capacity increase and f) energy increase analysis is also summarized.

With the newly developed Gen2 procedure, both the R1 and R2 are decreased for the more compact design in Gen2 micro battery. R1 of six as-prepared Gen2 MB1842 micro batteries range from 10 to 20 ohm while 30-40 ohm for the Gen1 MB1842 micro batteries. R2 of these six Gen2 MB1842 micro batteries range from 200 to 800 ohm, lower than 1500-3000 ohm for the Gen1 MB1842 micro batteries (Fig.7b). However, the slope of Gen2 micro batteries deviates from 1 more than Gen1 micro batteries, indicating a more difficult Li^+ diffusion in solid electrodes. Five out of six MB1842 micro batteries consistently deliver 2.1-2.2 mAh of capacity discharging at 0.1 mA. They exhibit a 30-40% capacity increase when comparied with 1.6 mAh for Gen1 micro batteries (Fig.7c and 7e) and 35-45% for energy increase (Fig.7f) contributed by the higher discharge voltage platform. At 0.35 mA of discharging current, the capacity increase is 15-25% and 20-30% for the energy increase. Here, the cell test at 0.1 mA is used to test how much capacity and energy the micro batteries have while 0.35 mA is required as the maximum current present in the fish tag (Lamprey). With increasing current, the limited discharge capability of the Gen2 is seen due to slower dynamics of lithium ions diffusion in the cathode. The Gen2 micro battery technology is preferable to small battery and application with small discharge current. The new process enables a faster production and more consistent result comparing with previous design for Gen2 micro battery in Fig.3a.

2.4 Gen2 micro battery technology: trial run

According to the previous results from last batch (Fig.7b-7d), a trial run with more samples was conducted to evaluate the procedure. In Fig.8, the production data of 52 Gen2 MB1842 micro batteries have been recorded along with the procedure. It can be seen that most of the cells have a 4.3 mg of CFx/C loading (CFx:C=90:10, the carbon additive includes Super P, CNT and CNF), 3.2-3.3V of OCV, 10-20 ohm of R1 and 600-800 ohm of R2, 2.1 mAh@0.1 mA and 1.7 mAh@0.35 mA of capacity and 5.0 mWh @0.1 mA and 4.0 mWh@0.35 mA of energy. The slight fluctuation indicates the consistency of the production still needs to be improved in the future.

The capacity increase, energy increase and yield analysis of this trial run has been summarized in Fig.9. At 0.1 mA of discharging current, the yield of capacity increase >20% is 81.8% and 45.5% for capacity increase >30%, the yield of energy increase >20% is 87.9% and 54.5% for energy increase >30%. It has a relatively good yield if the increase rate is set above 20%, but the yield drops for increase rate above 30%. The process still needs to be optimized to get consistent micro batteries and better yield for increase rate above 30%. At 0.35 mA discharging current, the yield above 30% of increase rate drops fast, 10.5% for >30% capacity increase and 31.6% for >30% energy increase. Currently, it's not known why the yield drops fast at higher discharge rates, probably from the Li^+ diffusion in solid electrodes as implicated from the slope deviating far away from 1 in Fig.10b, the true reason is still not clear and needs to be determined in the future. It's noted that the drilling process is operated by hand, and as a result, the hole is not always at center of cathode electrode which may cause the issue on diffusion dynamic and consistency.

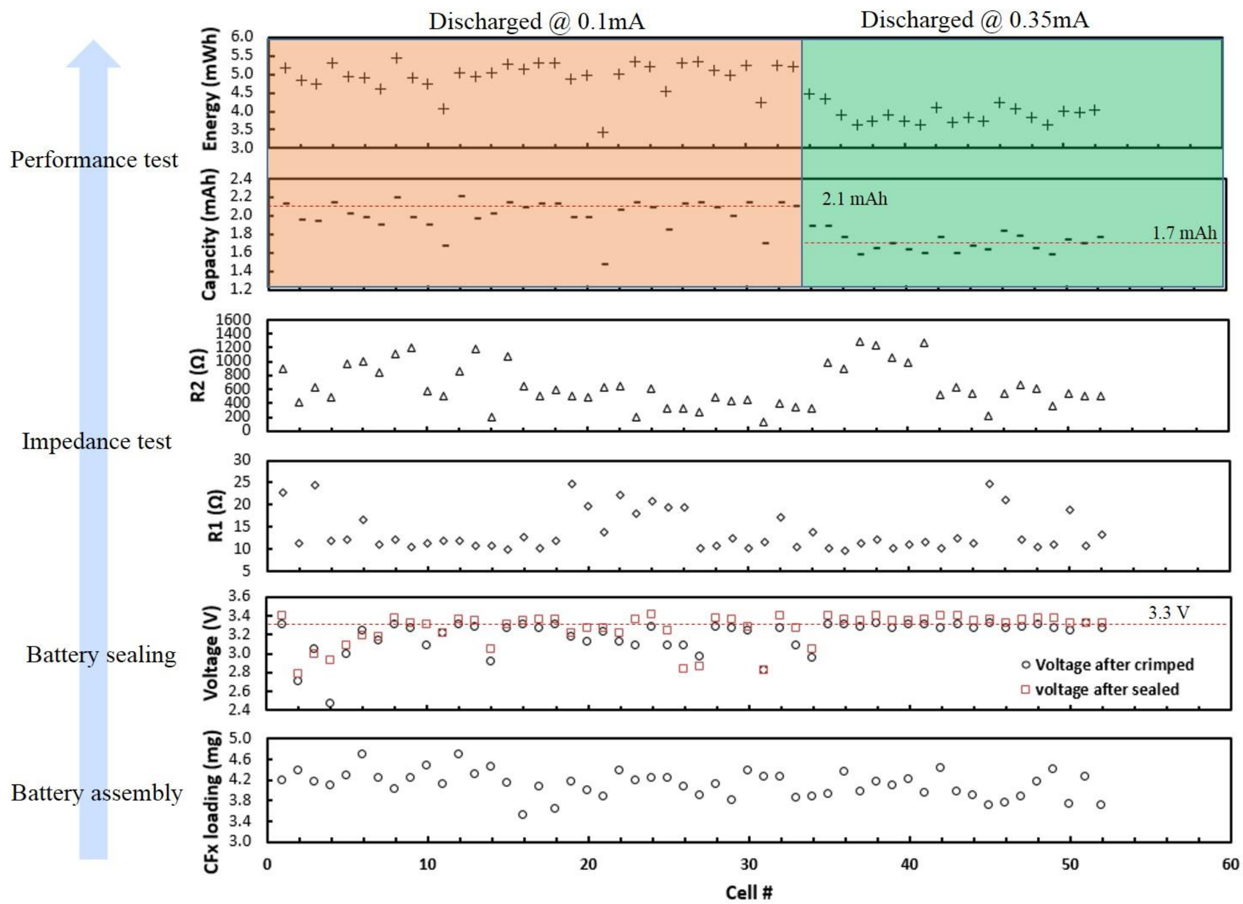
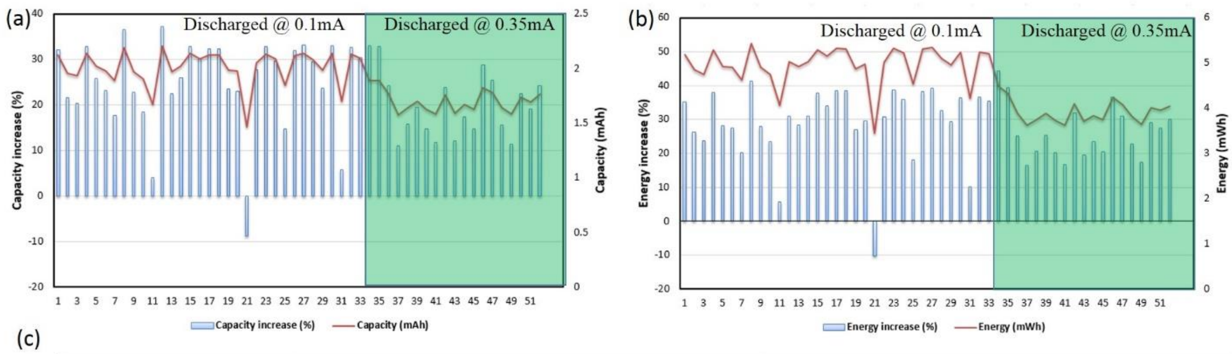


Fig.8 Production data of 1st trial run along with the procedure, including 52 MB1842 micro batteries, 33 cells are discharged at 0.1 mA and 0.35 mA for 19 cells.



(c)

Increase rate	Yield (discharged, 33 cells) at 0.1 mA		Yield (discharged at 0.35 mA, 19 cells)	
	Numbers of cell meet the rate	Yield	Numbers of cell meet the rate	Yield
Capacity >20%	27	81.8%	8	42.1%
Capacity >30%	15	45.5%	2	10.5%
Energy >20%	29	87.9%	15	78.9%
Energy >30%	18	54.5%	6	31.6%

Fig.9 a) Capacity increase, b) energy increase and c) yield analysis for trial run in Fig.8.

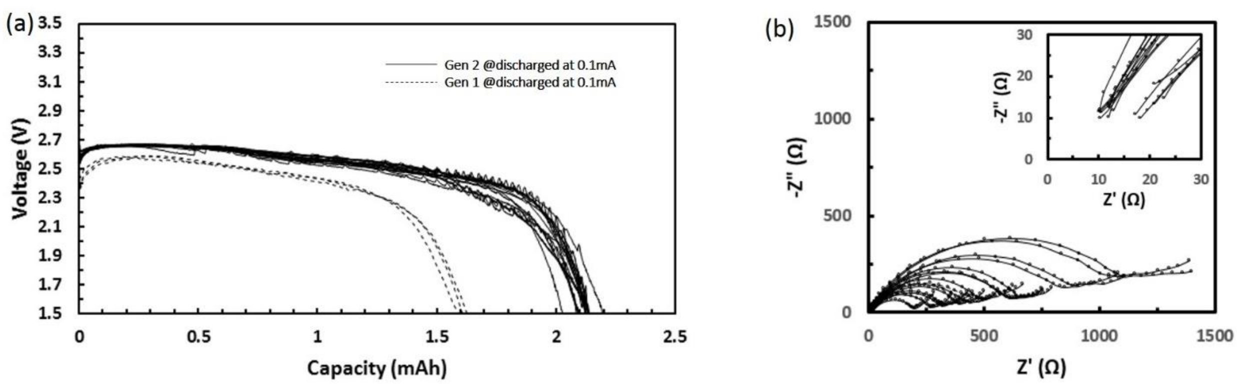


Fig.10 a) Cell performance discharged at 0.1mA and b) Nyquist plot of 15 MB1842 micro batteries with >30% capacity increase rate in Fig.8c.

2.5 Gen2 micro battery technology: issues

As the experience from production in the trial run, the most difficult and uncontrolled process is drilling the hole at the center of the cathode electrode due to the poor alignment between the drill bit and cylindrical case. It's more serious with manual operation. Three tiny drilling bits were broken as the alignment problems persisted during the trial run for 52 cells. Fig.11 shows the home-made drilling/alignment tools for drilling the holes at the center of the cathode during the trial run.

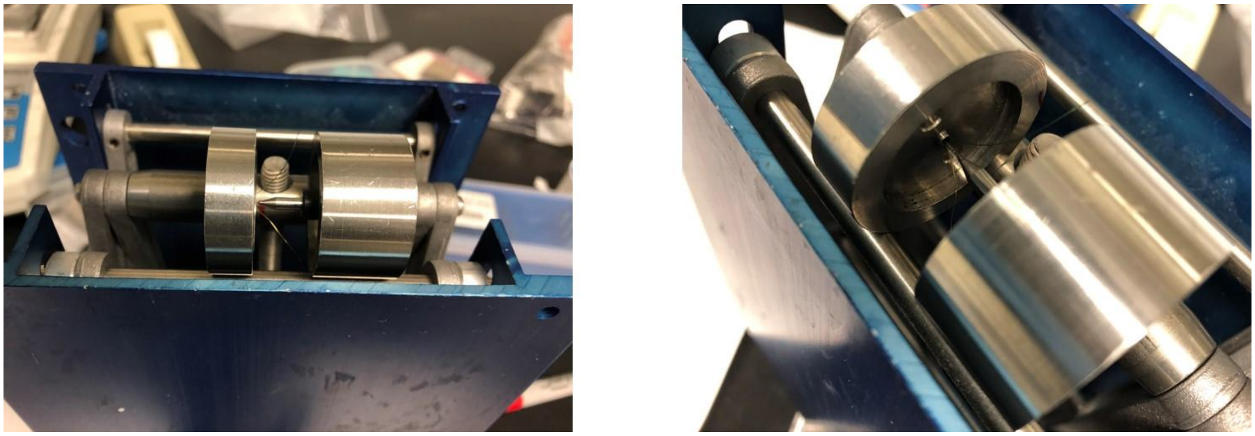


Fig.11 Home-made alignment tools (includes a lift table or lab jack, top and bottom crimping die) for drilling a hole at the center of the cathode.

It can be seen with statistical data on the position distribution of the drilled hole in 52 cells, shown in Fig.12, the hole is not always located at center. It might cause the uneven current distribution and longer diffusion path in some directions. Most of the holes are close to the separator and thus presents higher risk for large self-discharge rate, even short if the separator gets drilled/scratched. It's believed that the consistency and yield of the Gen2 micro battery production will be greatly improved if an automatic alignment/drill tools is developed and applied. It's also noted that all the capacity test of Gen2 micro batteries above were carried out after one hour's rest after sealed. So, the self-discharge rate relating to the shelf life is not studied at this time, and it also needs to be investigated in the future.

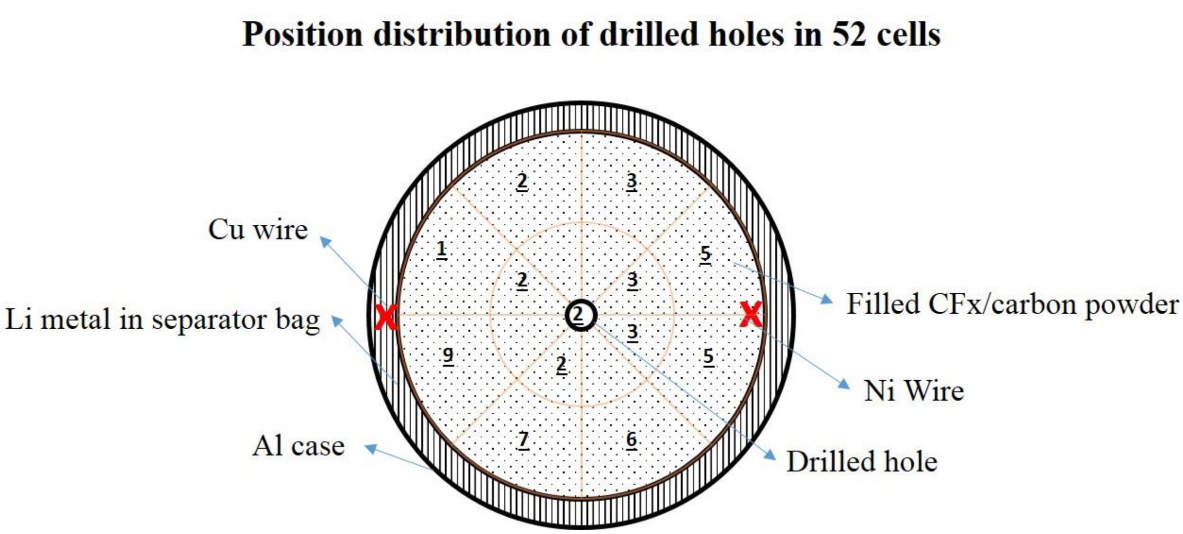


Fig.12 Statistics of the position distribution of the drilled holes in 52 cells during the trial run. Number is the number of cells with drilled hole located in this area.

2.6 Summary

Gen2 micro battery technology has the potential to increase the capacity and energy of the micro battery (MB1842) by removing non-active materials, like Al mesh and PTFE binder. Central tunnel design by drilling a hole at center of the cathode enables a faster-wetting time and leaves more room for cathode swelling. At 0.1 mA of discharging current, a trial run with the recommended procedure shows that at least 80% of the yield can achieve >20% capacity increase and >20% energy increase. If the increase rate is >30%, the yield drops to ca. 50%. At higher discharging current, 0.35 mA, the yield drops fast. The reason behind is not clear and needs to be figured out in the near future. For the uneven distribution of the drilled holes, an auto alignment/drill tool urgently needs to be developed to improve the consistency and yield of Gen2 micro battery production. The Gen2 micro battery technology developed in this project has been followed and continuously developed in a DOE project: 76491 - American Shad Tag Development.

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