Pacific Northwest
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PNNL-34875

Rechargeable Micro-Batteries

September 2023

Bingbin Wu
Kevin Baar
Jun Lu
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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

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Abstract

The quest for efficient power sources for small sensors has led to a growing interest in rechargeable micro-batteries, offering the potential to harness energy from various sources for extended periods. This project delves into a multifaceted project aimed at enhancing the performance and viability of rechargeable micro-batteries in this context. The Pacific Northwest National Laboratory (PNNL) has leveraged its expertise in primary micro-battery development, evolving into a software-driven approach for designing cylindrical micro-batteries. This project addresses the cycle life issue through innovative cell design, electrode optimization, and electrolyte refinement. A case study of the MB1842 rechargeable micro-battery demonstrates the promising outcomes of these advancements, showcasing a capacity of 0.32 mAh at ~1C (0.35 mA) and remarkable cycle performance, extending the cycle life to 510-570 cycles at 80% end-of-life (EOL), 710-760 cycles at 70% EOL and 840-940 cycles at 60% EOL, thereby ensuring a service life of 10 years for these rechargeable micro-batteries. This endeavor represents a significant stride towards unlocking the full potential of rechargeable micro-batteries, paving the way for their widespread application in small sensor technologies. The outcome from this project also successfully supports the award of a new project: 80621 - Self-Powered Modular Acoustic Telemetry System with Sensing.

Summary

This project has achieved its objectives by successfully delivering over 500 cycles at 80% of the end-of-life (EOL) capacity for rechargeable micro-batteries. The primary strategies employed to realize this milestone encompass improved cell design, electrode optimization, and electrolyte refinement. The successful outcomes of this project have paved the way for securing funding for a new project (80621 - Self-Powered Modular Acoustic Telemetry System with Sensing), further strengthening PNNL's leadership in the field of micro-batteries and miniature sensor technologies.

Acknowledgments

This research was supported by the **I3T Strategic Investments**, under the Laboratory Directed Research and Development (LDRD) Program at Pacific Northwest National Laboratory (PNNL). PNNL is a multi-program national laboratory operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830.

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1.0 Introduction

For small sensors, the use of rechargeable micro-batteries can offer significant advantages, allowing the efficient utilization of energy harvested from the environment. Rechargeable micro-batteries, with a volume of less than 0.1 cm^3, have garnered increased attention thanks to advancements in micro- and nano-electromechanical systems (MEMS/NEMS) technology. These batteries find applications in microsensors, micromachines, and implantable medical devices. One promising technology in this domain is the thin-film, all-solid-state battery, characterized by its ultra-thin profile (thickness < 10µm). However, while these batteries excel in terms of rechargeability, their capacity and power output still fall short of meeting the demands of modern sensors. Thicker film all-solid-state batteries can provide greater energy storage due to a larger quantity of active materials, but they continue to face challenges in terms of power output and mechanical robustness. Recent innovations in the fabrication of rechargeable micro-batteries, incorporating 3D micro-architecture electrodes, have shown promise by offering both higher energy density and power density. Nevertheless, these batteries are constrained by concerns related to manufacturing cost, shelf life, and cycle longevity, limiting their potential for widespread commercialization.[1]

Since 2012, the Pacific Northwest National Laboratory (PNNL) has achieved successful developments in cylindrical-shape primary Li/CFx micro-batteries of various sizes. [2,3] Building upon our knowledge and experience with primary micro-batteries, we have developed specialized software for cylindrical battery design as part of a previous I3T LDRD project (see Figure 1). This software encompasses primary micro-battery design with machine learning integration, secondary micro-battery design involving novel electrode configurations, and the design of 18650/21700/xxxxx lithium-ion batteries, informed by insights gained from commercial battery electrode designs. This software streamlines the process of designing rechargeable micro-batteries to meet specific size requirements, while also providing essential electrode parameters for manufacturing.

Furthermore, our innovative electrode design allows us to create rechargeable micro-batteries with a height of less than 4mm, pushing the boundaries of current winding technology in commercial lithium-ion batteries. Our proposed solution involves an anode electrode sheet coupled with a small piece of Li metal film that acts as a lithium source, paired with a lithium-free cathode electrode sheet within the rechargeable micro-battery. Upon electrolyte injection, the Li metal automatically migrates to the anode, achieving full lithiation. Notably, there is no need for a battery formation process in this approach. Even in cases where misalignment of the anode and cathode electrode sheets occurs during the winding process or when the anode sheet is smaller than the cathode sheet, Li metal deposition issues are eliminated. This enables the production of shorter rechargeable micro-batteries with uniform electrode sizes.

As depicted in Figure 2, our exemplar rechargeable micro-battery, MB1842, featuring the novel electrode design, exhibits a capacity of 0.32 mAh at 0.8C (0.35mA of current), which is applicable in devices like eel/lamprey acoustic transmitters. This battery has been cycled 130 times at 80% of its end-of-life (EOL) capacity and 200 times at 60% of EOL. To achieve a service life of 10 years, we recognize the need to enhance the cycle life, aiming for at least 500 cycles. Achieving this requirement will necessitate continuous efforts focused on refining the cell structure and optimizing the manufacturing process. This project endeavors to attain this objective through enhanced cell design, electrode optimization, and electrolyte refinement.

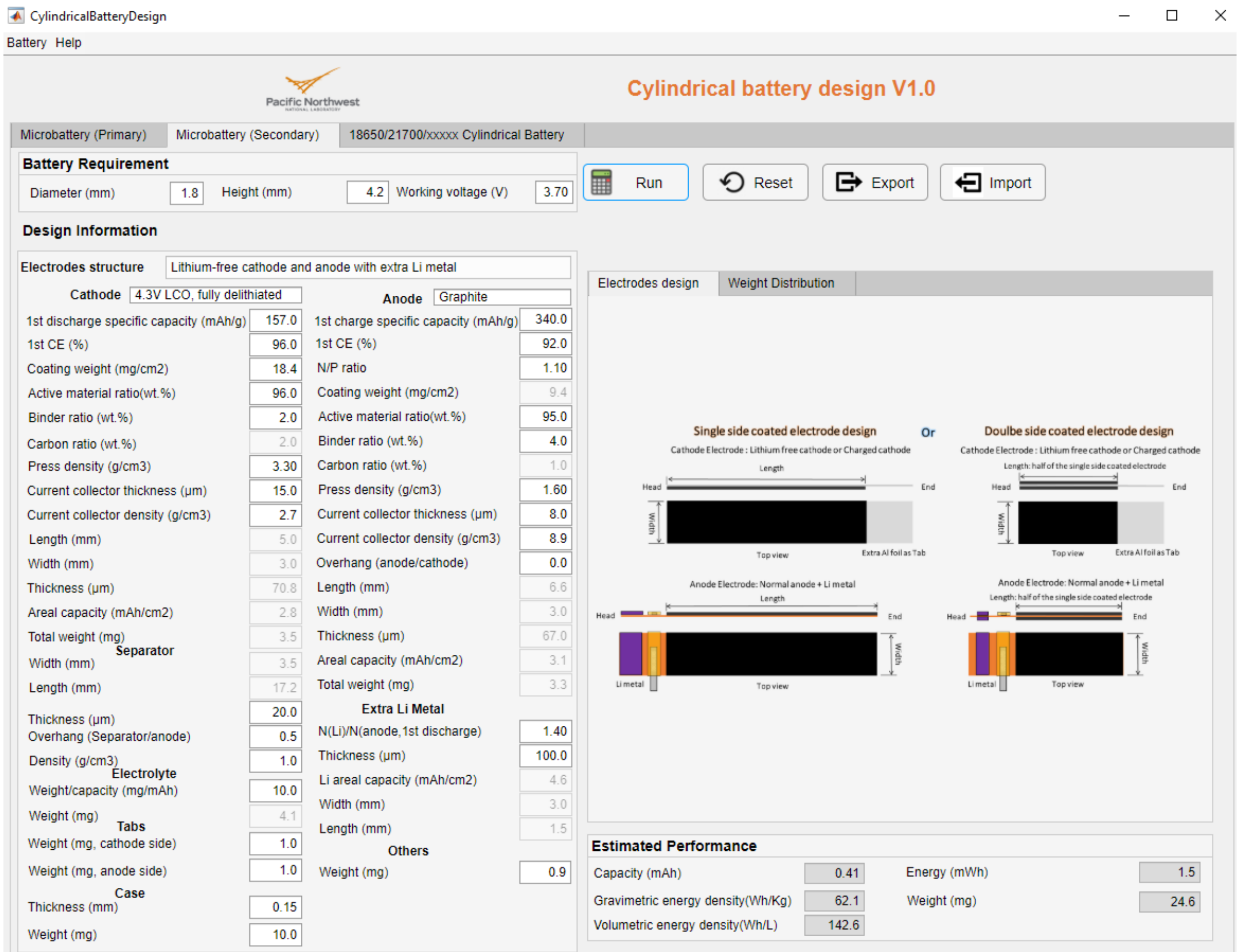

Figure 1. Software for cylindrical battery design. Cylindrical batteries include primary micro-battery, rechargeable micro-battery and 18650/21700/xxxxx lithium-ion batteries.

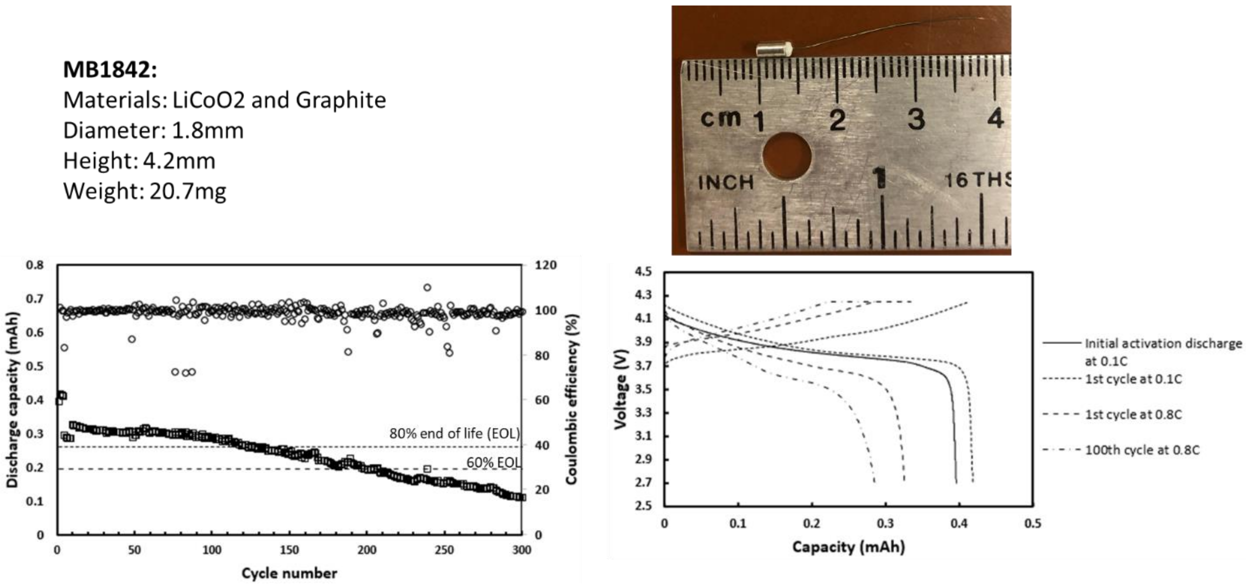

Fig.2 Battery performance of the exampled rechargeable micro-battery.

2.0 Section: Results and Discussions

To extend the cycle life of rechargeable micro-batteries, as demonstrated with PNNL's innovative electrode design, a comprehensive approach is undertaken. This includes customized cell design, electrode optimization, and electrolyte refinement, all geared toward achieving the ambitious target of over 500 cycles at 80% of the end-of-life (EOL) capacity. The MB1842 cylindrical cell serves as an illustrative example, featuring a diameter of 1.8 mm and a height of 4.2 mm.

2.1 Cell design

As depicted in Figure 2, the previously showcased rechargeable MB1842 exhibited a cycle life of 130 cycles at 80% of its end-of-life (EOL) capacity. This cell featured a positive electrode composed of delithiated $LiCoO_2$ (LCO), with dimensions measuring 3.0 mm (width) by 5 mm (length). Notably, the electrode boasted a coating weight of 18.4 mg/cm², resulting in an impressive areal capacity of 2.8 mAh/cm². This electrode closely resembled those employed in larger cells. However, transitioning to smaller cell sizes, akin to grains of rice, introduces significant challenges. The battery experiences substantial stress due to the pronounced curvature in the Jellyroll, which may lead to damage, such as micro-cracks, during the winding process. To address this formidable challenge, the utilization of thinner electrodes with reduced material loading emerges as a viable solution, effectively mitigating the stress within the Jellyroll structure.

In Figure 3, we introduce a redesigned cell featuring lightweight electrodes as part of our ongoing efforts to enhance rechargeable micro-battery performance. Notably, the coating weight of the LCO (Lithium Cobalt Oxide) electrode has been significantly reduced to 7 mg/cm², corresponding to an impressive areal capacity of 1 mAh/cm². This crucial adjustment substantially bolsters the cell's resilience, making it more tolerant of the significant curvature inherent in small-sized cells. To ensure that the cell retains its capacity, the length of the electrode has been tripled, compensating for the lower coating weight. This extended electrode length ensures that the cell can consistently deliver a capacity ranging from 0.3 to 0.4 mAh, thereby meeting the performance criteria. Maintaining a consistent N/P (Negative/Positive) ratio of 1.1, we have adjusted the graphite anode, reducing its coating weight to 3.4 mg/cm² while extending its dimensions to 3 mm (width) by 16 mm (length). Both the LCO and graphite electrodes have been single-side coated due to their reduced coating weights. The manufacturing process commenced with the delithiation of the LCO in an Li/LCO pouch-type half-cell. To facilitate the lithiation of the graphite electrodes, an additional Li foil, measuring 100 microns in thickness and 3 mm (width) by 1.5 mm (length), was affixed to the Cu (Copper) foil. It is worth noting that the weight ratio of active materials, including LCO and graphite, remains relatively small, accounting for only 11% and 6%, respectively, in contrast to the more substantial proportion occupied by the cell housing, which accounts for 36% (Figure 4). These modifications collectively contribute to the improved performance and cycle life of our rechargeable micro-batteries, bringing us closer to our goal of over 500 cycles at 80% of the end-of-life (EOL) capacity.

Battery dimension						
	Diameter (mm)	1.8				
	Height (mm)	4.2				
	Working voltage (V)	3.7				
Cathode	4.3V LCO, fully delithiated			Anode	Graphite	
	1st discharge specific capacity (mAh/g)	157			1st charge specific capacity (mAh/g)	340
	1st CE (%)	96			1st CE (%)	92
	Coating weight (mg/cm2)	7			N/P ratio	1.05
	Active material ratio(wt.%)	95			Coating weight (mg/cm2)	3.4
	Binder ratio (wt.%)	2			Active material ratio(wt.%)	95
	Carbon ratio (wt.%)	3			Binder ratio (wt.%)	4
	Press density (g/cm3)	3.8			Carbon ratio (wt.%)	1
	Current collector thickness (µm)	15			Press density (g/cm3)	1.6
	Current collector density (g/cm3)	2.7			Current collector thickness (µm)	8
	Length (mm)	13.9			Current collector density (g/cm3)	8.94
	Width (mm)	3			Overhang (anode/cathode)	0
	Thickness (µm)	33.4			Length (mm)	15.7
	Area capacity (mAh/cm2)	1			Width (mm)	3
	Total weight (mg)	4.7			Thickness (µm)	29.2
Seperator	Width (mm)	3.5			Areal capacity (mAh/cm2)	1.1
	Length (mm)	35.3			Total weight (mg)	5
	Thickness (µm)	9		Extra Li	NLi/Nanode(1st discharge)	1.4
	Overhang (Sep/anode)	0.5			Thickness (µm)	100
	Density (g/cm3)	1			Li areal capacity (mAh/cm2)	1.7
	Weight/capacity (mg/mAh)	10			Width (mm)	3
	Weight (mg)	4.3			Length (mm)	1.3
Tabs	Weight (mg, cathode side)	1		Others	Weight (mg)	0.86
	Weight (mg, anode side)	0.99				
Case	Thickness (mm)	0.15		Weight distribution		
	Weight (mg)	10		Cathode	Cathode electrode	2.91
					Cathode current collector	1.8
	Capacity (µAh)	433.8			Cathode tab	1
	Energy (µWh)	1605.1		Anode	Anode electrode	1.6
	Weight (mg)	27.6			Anode tab	0.99
	Gravimetric energy density (Wh/kg)	58.1			Anode current collector	3.36
	Volumetric energy density (Wh/L)	150.2			Extra Li	0.2
				Separator	PP/PE Separator	0.56
				Electrolyte	Electroltye	4.34
					Al Case	10
					Others	0.86
					Total weight	27.61

Figure 3. Cell design with thin electrodes provided by in-house developed software as showed in Figure 1.

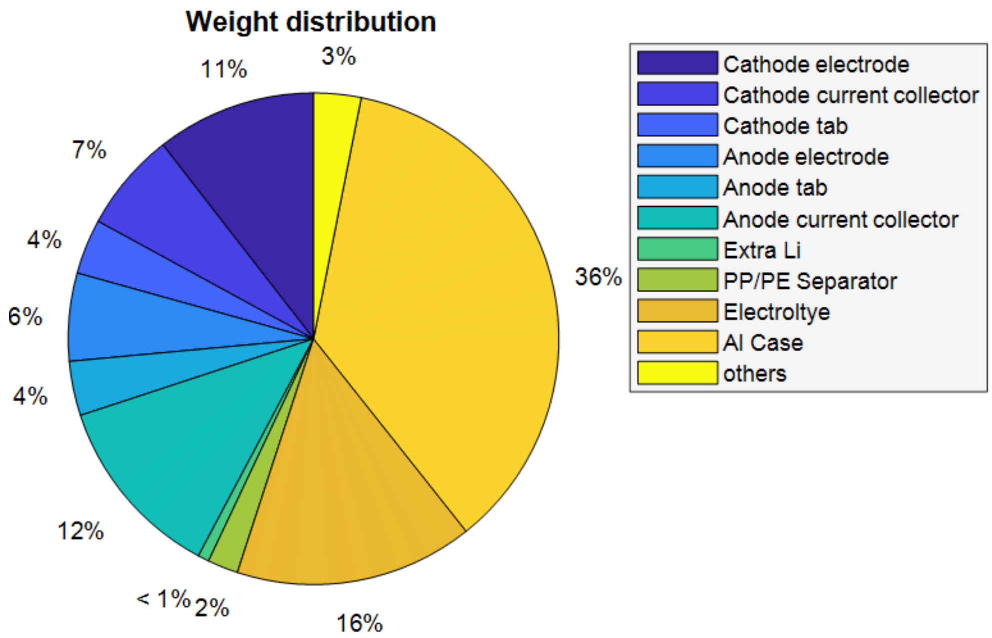

Figure 4. Weight distribution of the rechargeable micro battery designed in Figure 3.

2.2 Electrodes optimization

The electrodes within rechargeable micro-batteries are critical components composed of active materials, conductive carbon additives, and a polymer binder. The even distribution of these materials within the electrodes plays a pivotal role in determining the cell's internal impedance and cycling stability. Moreover, as we scale down the size of the cell, the significance of flexibility in the cylindrical Jellyroll structure during the winding manufacturing process becomes increasingly pronounced. This flexibility directly influences the dimensional stability of the electrodes, especially when dealing with the substantial curvature inherent in smaller cells.

Single-walled carbon nanotubes (SWCNTs) emerge as remarkable materials in this context. SWCNTs are highly conductive one-dimensional carbon structures that have found applications in next-generation silicon-based high-energy-density lithium-ion batteries. Their extended nanotube structure contributes not only to enhanced flexibility but also to improved electron conductivity, particularly beneficial for silicon anodes, which undergo significant swelling during the galvanic charge/discharge process. To enhance the flexibility and strength of the cathode and anode electrodes in micro batteries, we have strategically incorporated SWCNTs into the electrode composition, alongside the active materials and binder. As illustrated in Figure 5, both the Lithium Cobalt Oxide (LCO) and graphite particles measure between 10-20 microns in size. Notably, the LCO used here is single crystal, a departure from the more common polycrystalline LCO in most state-of-the-art lithium-ion batteries. This choice is driven by its proven cyclic stability over prolonged cycling in industry.

Furthermore, careful attention has been paid to ensure the even distribution of carbon black and SWCNTs surrounding the active material particles within the electrodes. This meticulous electrode design, optimized with SWCNTs, has significantly improved flexibility during the winding process of rechargeable micro-batteries. These enhancements underscore the critical role of SWCNTs in achieving our project's goals of delivering over 500 cycles at 80% of the end-of-life (EOL) capacity. The meticulous design and integration of SWCNTs into the electrodes not only bolster cycling stability but also pave the way for more reliable and efficient micro-battery technology, poised to meet the demands of an array of small-scale applications.

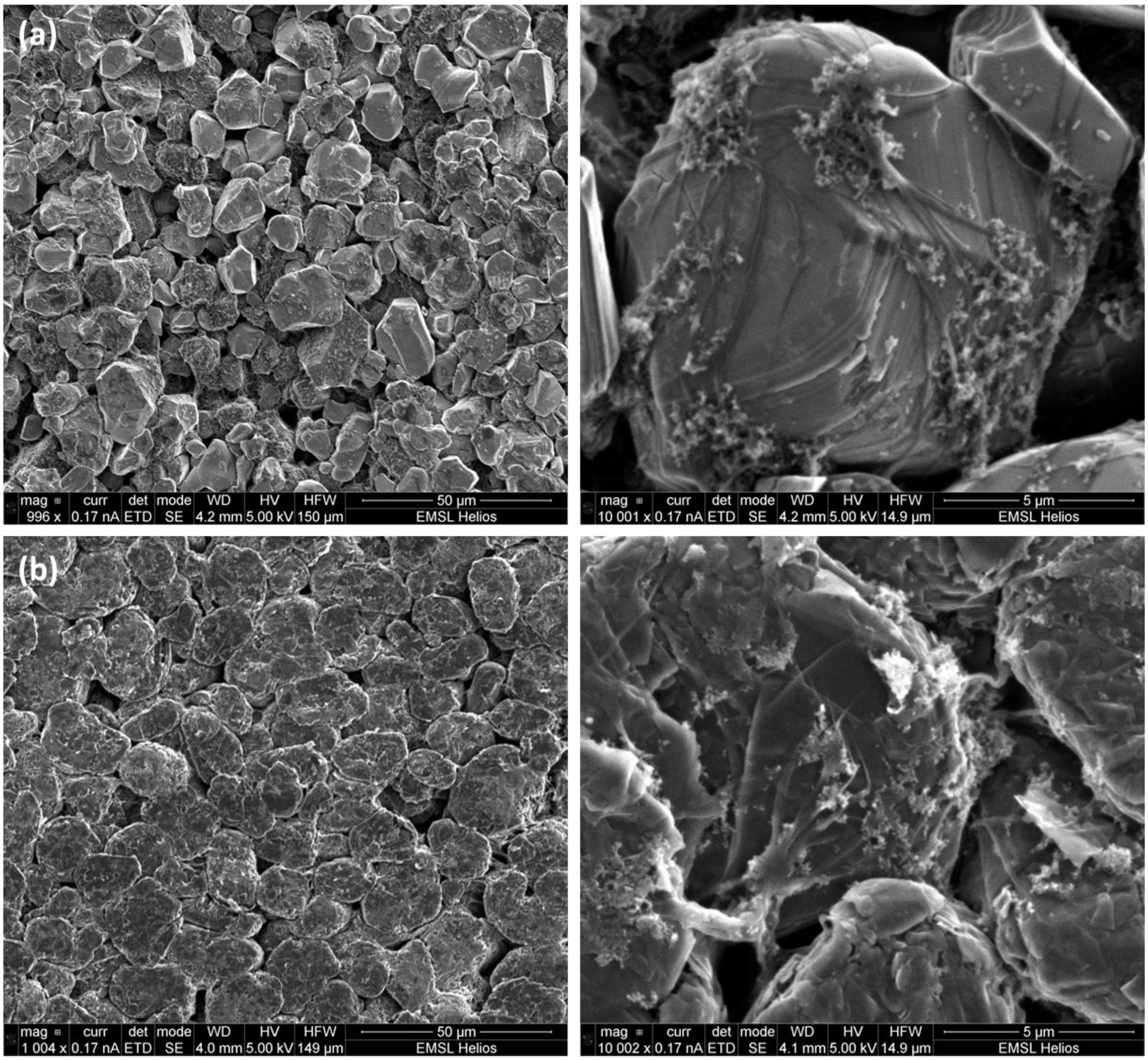

Figure 5. SCNT modified (a) LCO electrode and (b) graphite electrode.

2.3 Electrolyte optimization

With our meticulously optimized cell design featuring thin electrodes and SWCNT-modified cathode/anode electrodes, our rechargeable micro-batteries, operating in a traditional carbonate electrolyte, have achieved remarkable cycling performance. As showed in Figure 6 (black), the battery now demonstrates a cycle life of 513 cycles at 80% of its end-of-life (EOL) capacity, extending to 715 cycles at 70% EOL and an impressive 844 cycles at 60% EOL. Even after enduring a rigorous 2500 cycles, these batteries refuse to fade away completely; they retain approximately 6% of their initial capacity, exemplifying their robustness and longevity. The cumulative capacity at 80% EOL reaches an impressive ~130 mAh. Translated into practical terms, this equates to an approximate service life of 8 years, considering a scenario with lamprey tags transmitting data at a 5-second ping rate for 30 days. Furthermore, by running the cells down to 60% EOL, we can anticipate a service life of over 10 years. The traditional carbonate electrolyte, referred to as EL1, comprises a composition of 1.0 M $LiPF_6$ in EC/DEC/EMC (1/1/1, volume ratio), enriched with 1 wt.% VC (vinylene carbonate) and 1 wt.% FEC (fluroethylene carbonate). This electrolyte formulation has delivered results that unequivocally align with the objectives of this project, thereby reinforcing the effectiveness of our thin cell design and SWCNT-modified electrode strategies, as elaborated in Sections 2.1 and 2.2. In summary, our project has achieved an exceptional milestone in the realm of rechargeable micro-batteries, showcasing their ability to not only meet but surpass cycle life expectations. The combination of innovative cell design and advanced electrode modifications promises to revolutionize micro-battery technology, making it a robust and long-lasting power source for diverse small-scale applications.

Moreover, by introducing a new electrolyte formulation, denoted as EL2 (Figure 6 in red), we have achieved a remarkable extension in cycle life. EL2 composed of LiFSI, DME and TTE with a molar ratio of 1:1.2:3. The rechargeable micro-battery now demonstrates an impressive performance, reaching 575 cycles at 80% of their end-of-life (EOL) capacity, extending further to 761 cycles at 70% EOL and an astonishing 943 cycles at 60% EOL. This substantial improvement in cycle life is primarily attributed to the enhanced cycling stability of graphite/LCO rechargeable micro-batteries, facilitated by the improved stability of the CEI (Cathode Electrolyte Interface) and SEI (Solid Electrolyte Interface) layers. Even after enduring a strenuous 2500 cycles, the cell maintains approximately 10% of their initial capacity, a testament to their superior cycling performance when compared to the traditional carbonate electrolyte EL1.

It's noteworthy that the rechargeable micro-battery developed in this project features a unique design with only one lid, as depicted in Figure 6 (inset). In this configuration, the lid serves as the negative end, while the cell housing itself acts as the positive end, further optimizing the cell's performance and packaging efficiency.

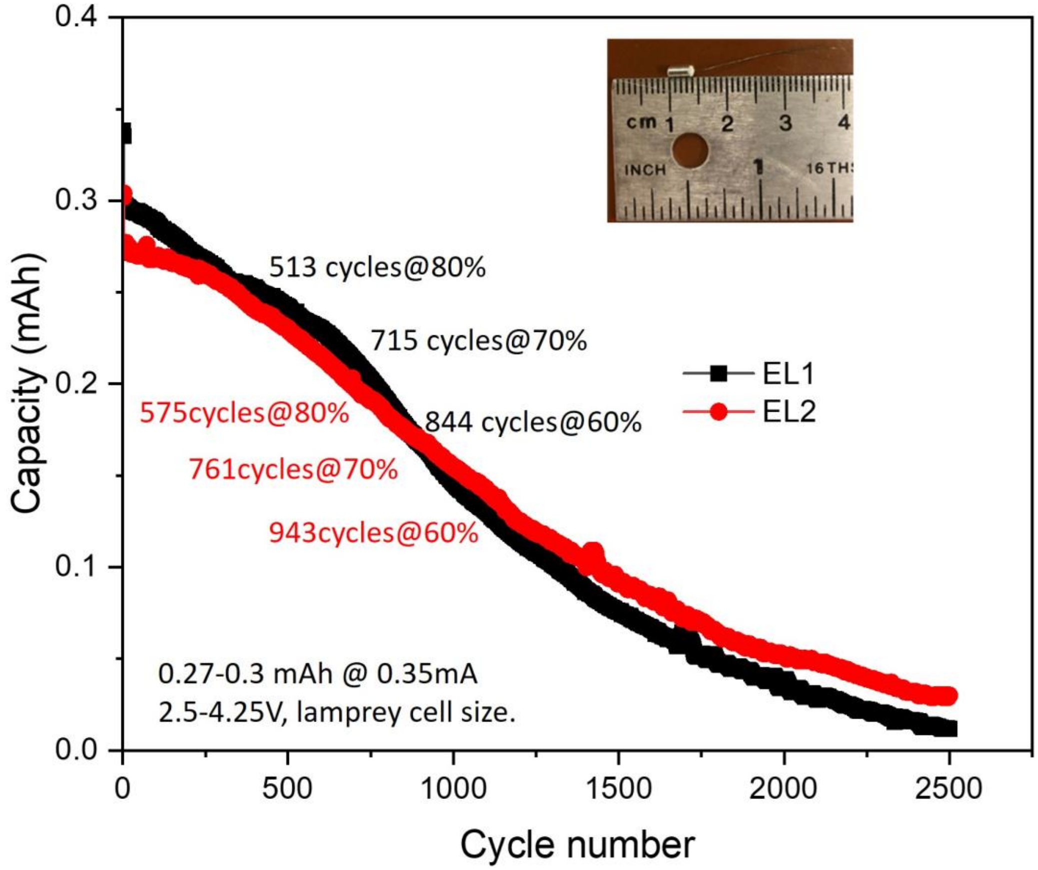

Figure 6. Galvanically charge/discharge cycling of rechargeable micro batteries MB1842 with two electrolytes. Two cycles at 0.05 mA and 0.35 mA (~1C) for the cycling. Working voltage: 2.5-4.25 V. the cell tested at room temperature. Inset picture: as-developed rechargeable micro battery MB1842.

Having achieved the requisite electrical performance and perfected the manufacturing process, we proceeded to evaluate the charging behavior of a rechargeable MB1842 micro-battery. This assessment was carried out using mimic circuits designed to replicate the conditions of a self-power tag. Typically, self-power tags are unable to supply sufficient current to charge a micro battery, particularly if the internal resistance of the micro battery is excessive. To address this, we employed a demonstration circuit (Figure 7) engineered to generate a current as minuscule as possible, mimicking the conditions of a self-power tag.

As illustrated in Figure 8, the rechargeable micro-batteries, charged at a rate of 4.4 µA using the demo circuit, delivered a capacity of 0.36 mAh, akin to the results in Figure 6. This outcome underscores the minimal internal resistance of the battery, a consequence of our thin electrode design and SWCNT-modified electrodes. Impressively, even when charged at a lower current of 1.6 µA, the battery still delivered 0.24 mAh of capacity, equivalent to approximately 67% of its initial capacity.

In summary, this project has achieved a significant milestone by successfully developing rechargeable micro-batteries that meet or exceed the stringent requirements typically seen in commercial cylindrical batteries, with a cycle life exceeding 500 cycles at 80% of the end-of-life (EOL) capacity. Nevertheless, there remain areas to explore and refine, particularly regarding manufacturing process consistency and shelf life. These aspects warrant further study before the as-developed rechargeable micro-battery can transition to the final market, ensuring its reliability and longevity in real-world applications.

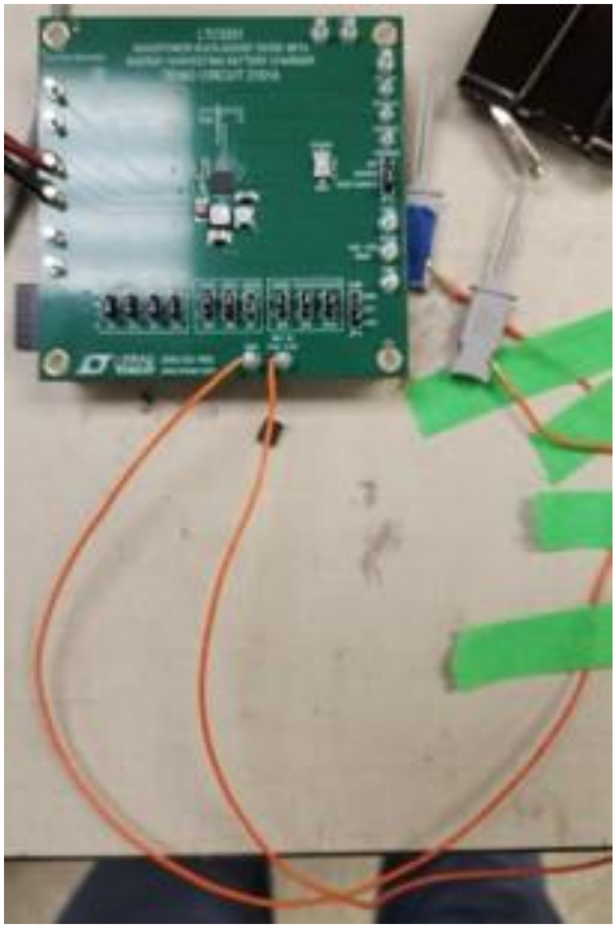

Figure 7. Demo circuits to charge the as-developed micro battery.

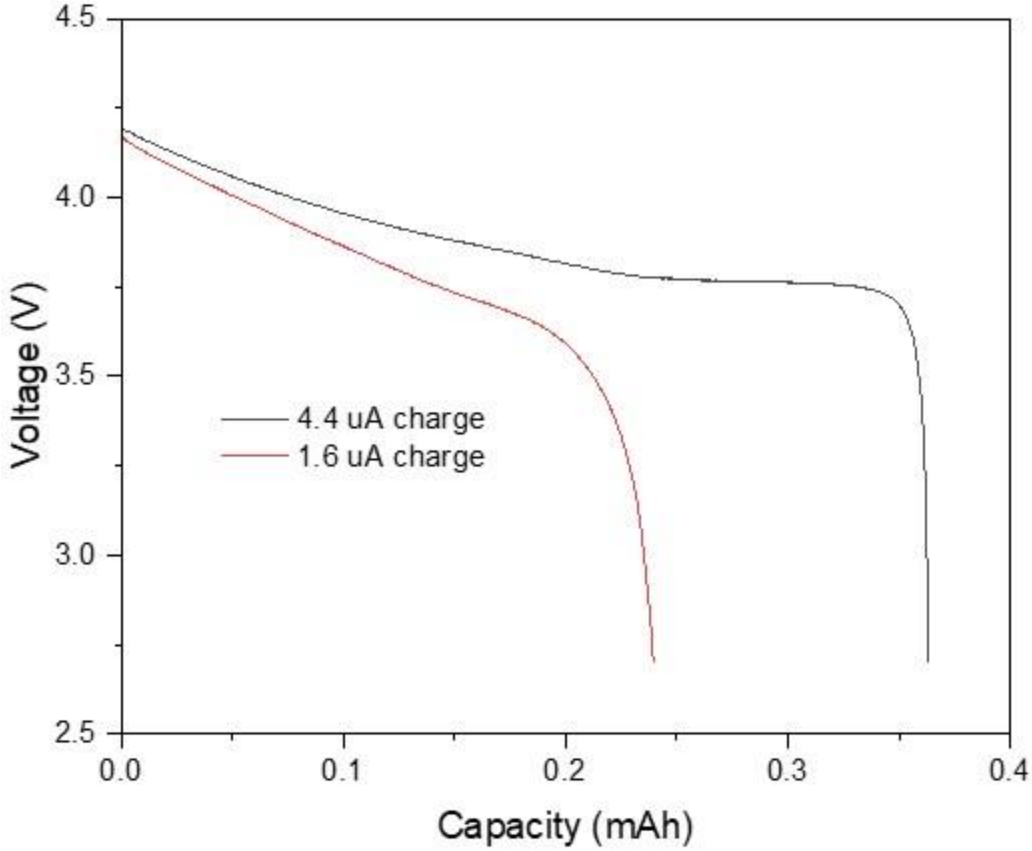

Figure 8. The discharge behavior after charged with demo curcuits (Figure 7) at 4.4 µA (black) and 1.6 µA (red). Discharge current: 0.05 mA.

3.0 References

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