

Novel Si Anode and High Ni NCM Cathode for High Energy Applications

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Abstract

Rechargeable Li-ion batteries play an increasingly critical role to enable energy mobility and support various new high energy and power applications. However, commercial Li-ion batteries based on intercalation chemistry are approaching the expected specific energy plateau around 300 Wh/kg, beyond which new active materials are very likely needed. To overcome this limitation, an engineered Si/carbon composite with reversible capacity >1900 mAh/g was sourced and evaluated to benchmark against a graphite/SiO_x control on the anode side. The graphite/SiO_x system has a reversible capacity of over 630 mAh/g. Preliminary tests, based on single layered pouch cells, demonstrated comparable first coulombic efficiency and cell capacity between them. However, the engineered Si/carbon outperformed the graphite/SiO_x in long-term cycle life by a significant margin of 50%. Separately, single-crystal nickel cobalt manganese oxide (NCM) with 80% nickel content and cobalt free nickel manganese aluminum oxide (NMA) with 90+% nickel were tested to assess rate performance and cyclability. Combining the Si/carbon anode and high nickel oxide cathode, perspective of the next generation cell design that can reach 350 Wh/kg is provided.

Keywords

Si anode; NCM cathode; Li-ion batteries; high energy.

Introduction

Lithium-ion chemistry based rechargeable batteries continue to gain widespread adoption in many applications since its inception in the 1990s by Sony Corporation [1-2], which was built with lithium cobalt oxide (LiCoO₂) cathode and carbonaceous anode. Early commercial demonstration of both energy and life by Li-ion batteries prompts more research and development effort globally to search for new battery materials which operate on reversible intercalation principles [3-4]. This technology push leads to the invention of a wide variety of advanced cathode materials including lithium iron phosphate (LiFePO₄), nickel cobalt aluminum oxide (NCA), nickel cobalt manganese oxides (NCM) and graphitic carbon anodes like artificial and natural graphites, mesocarbon microbeads (MCMB), hard and soft carbons, silicon and SiO_x [5-8]. Consequently, cell level energy density continued to progress fairly well by incorporating high-capacity active materials, from around 100 Wh/kg

initially to 300 Wh/kg and beyond nowadays [9]. Li-ion batteries powered vehicles, a transportation game-changer once viewed as impractical, which finally became a reality and legitimate replacement of combustion engine powered incumbents [10]. However, the needs to address range anxiety and battery charging time continue to challenge battery manufactures even when the cell energy density records keep getting smashed in a matter of days. Some key technological drivers behind this fast-paced Li-ion battery landscape are high nickel ($\geq 80\%$) mixed metal oxides, lithium (Li) rich and manganese rich layered cathodes, Li doped SiO_x, and high capacity engineered Si anodes [7, 8]. Integration of afore-mentioned battery materials into new designs and products is expected to further raise cell energy density to higher levels thereby pave the way for high energy applications [11].

Commercial demands for Li-ion batteries will continue to drive the trend in battery development and manufacturing, but this also presents opportunities for defense, space and aviation industries to evaluate and adopt some off-the-shelf solutions. Against this background, we selectively sourced a few novel battery materials including single crystal NCM 811, cobalt free NMA cathode and a high capacity engineered silicon/carbon composite. We designed these materials into EaglePicher's Li-ion battery platform technology and benchmarked against internal control to assess the feasibility of leveraging those commercial grades for cells, targeting 300 Wh/Kg or higher specific energy. A few conclusions were drawn based on preliminary cell assembly process and performance testing data.

Experimental Section

Materials: New materials involved in this study were sourced from U.S. domestic battery materials suppliers. The cathode raw materials consist of a single-crystal (SC NCM 811) with D₅₀ around 2.5 μm and a cobalt-free NMA with > 90 % nickel. The anode is a highly engineered silicon/carbon composite material with D₅₀ around 8.5 μm . Control materials used in this study are commercial grade NCM 811 cathode and SiO_x/graphite composite anode. All materials were inspected against material certificate of analysis (COA) and used as-received without further purification.

Electrode fabrication: Cathode and anode electrodes with single sided coating were prepared following EaglePicher's standard R&D scale mixing and coating procedures. A batch

with prescribed amounts of active material was blended with conductive carbon, followed by the introduction of binder solution, and solvent. A homogenous slurry was obtained after mixing up to 2000 rpm for 5~10 minutes by a THINKY mixer. The slurry was then coated on thin aluminum (Al) cathode or copper (Cu) anode foils using a doctor blade thin film applicator, and dried at 100°C (212°F) to remove liquid. The resulting electrodes were further pressed to obtain desired electrode thickness and porosity.

Cell assembly: CR2032 coin cells were made for cathode and anode half-cell testing, respectively and Li metal foil of 100 μm thick was used as counter electrode. Single layer pouch (SLP) cells with 70 mm (height) x 55 mm (width) were assembled for full cell performance evaluation. A common poly olefin separator of 16 μm (Celgard, H2512), and an organic carbonates-based electrolyte containing 1.0 M lithium hexafluorophosphate (LiPF₆) and other additives were used to build and activate both coin and SLP cells.

Cell testing: Both coin and SLP cells were formed prior to subsequent rate and cycle life tests, detailed formation and performance testing procedures are outlined in Table 1. Coin cells were tested without compression, whereas SLP cells were under 10 psi compression during the course of formation and testing. An Arbin tester with 48 channels was used and all cells were placed in an incubator with temperature controlled at 25±2°C.

Table 1. Cell formation and testing procedures

Step	Cell	Voltage range	Description
Formation	Cathode half cell	4.3-3.0V	CCCV, +C/10, -C/10
	Anode half cell	1.5-0.05V	CCCV, +C/10, -C/10
	SLP	4.2-2.5V	CCCV, +C/10, -C/10
Rate capability	Half cell	4.2-2.5V (cathode)	CCCV, various discharge rates
	Full cell	4.2-2.5V (anode)	
Cycle life	Both SLPs	4.2-2.5V	CCCV, +C/2, -C/2

Results and Discussion

Electrochemical properties of the engineered silicon/carbon composite were investigated to gain insight into specific reversible capacity, as shown in Figure 1. The first discharge capacity (FDC) of the engineered silicon/carbon composite was 1968 mAh/g, significantly higher than that of the control SiO_x at 1382 mAh/g. Interestingly, the first charge capacity (FCC) of the engineered silicon/carbon composite was also proportionally higher than that of the control, resulting in a high first coulombic efficiency (FCE) for both materials at

about 88% to 91%. It is worth mentioning that such high coulombic efficiency for silicon anode is rare and quite attractive, as it offers a viable path to reach higher cell capacity and energy.

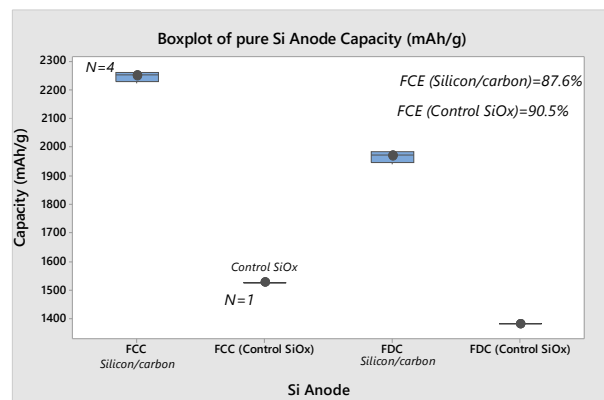


Figure 1 The first charge and discharge capacity comparison of Si anode half-cells

Discharge rate capability of the engineered silicon/carbon was also fairly comparable to the control, as illustrated in Figure 2. The engineered silicon/carbon was mixed with a control graphite which was used for the SiO_x control group. SLP cells at 95 mAh with anode specific capacity of 630 mAh/g were assembled to evaluate rate performance. These cells were charged at C/5 constant current to 4.2V, followed by a taper charge to C/10 current cutoff. Under various discharge rates ranging from C/5 up to 3C, both materials exhibited similar discharge capacity. Since both electrodes were prepared using the same recipe, identical coat weight target and press density thus porosity, the rate capability revealed in Figure 2, could be mainly dedicated by the active material. It is therefore reasonable to conclude that the high-capacity engineered silicon should deliver similar rate performance to that of the control.

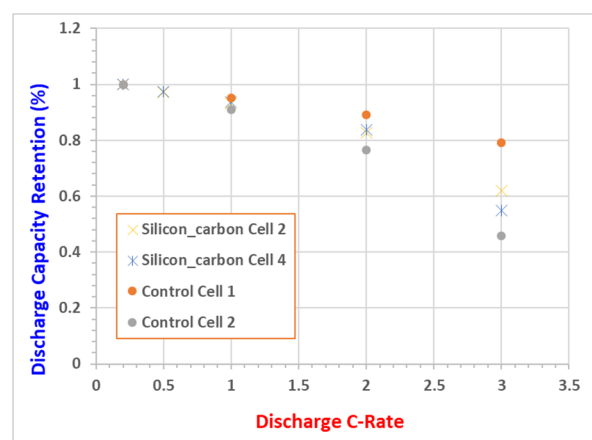


Figure 2 Rate capability comparison of Si anode SLP cells

Long-term cycling stability is always a concern for silicon-based anodes, especially for those with high specific capacities [12]. To assess this critical performance metric, SLP cells, similar to those for rate capability test, were built

by pairing a common control cathode with the engineered silicon/carbon blended with graphite and SiOx/graphite control anodes, respectively. According to Figure 3, the silicon/carbon composite based SLPs displayed noticeably better capacity retention than the control group, maintaining >83% after 300 cycles. One of the better performing silicon/carbon SLPs approached 600 cycles with 85% capacity retention. Based on the capacity decay trajectory, it could potentially reach 800 cycles to end-of-life (EOL) barring any catastrophic failure modes. This result is quite appealing for high-energy cells, as high specific capacity anodes enable thinner anodes, thus fast charge capability without sacrificing cell energy [13-14].

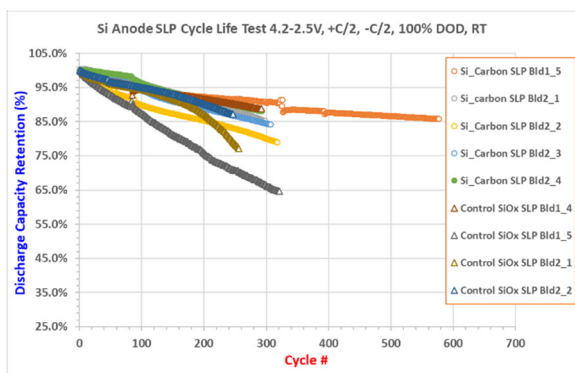


Figure 3 Cycle life of novel silicon/carbon anode vs. control SiOx

Cathode half-cell comparison between SC NCM 811 and control NCM 811 is shown in Figure 4. Average FDC of the SC NCM 811 is about 214 mAh/g, approximately 10 mAh/g higher than that of the control group. Statistically, the range and standard deviation for both groups are quite similar, but sample size of the control group is slightly larger. The first coulombic efficiency (FCE) for the SC NCM 811 is about 87.9% on average, lower than that of the control group of 90.7%. The difference is mainly due to cathode active materials, mostly related to exact nickel content with minor influence from particle morphology since the control group is a conventional polycrystal cathode with secondary particle aggregates around 20 μm, nearly 10 times larger than that of the SC NCM 811.

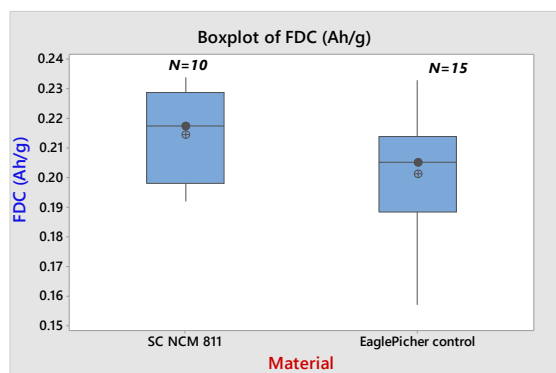


Figure 4. First discharge capacity comparison of cathode half-cells

Compared to the polycrystal counterparts, a main drawback for SC cathode materials is rate capacity owing to the single crystal nature, thus larger primary particle size. However, as shown in Figure 5, this is surprisingly not the case for SC NCM 811, which demonstrated quite comparable discharge rate capacity on par with the control group up to 10C, with rapid capacity reduction beyond 2C discharge rate and down to 40~50% capacity at 4C for both materials.

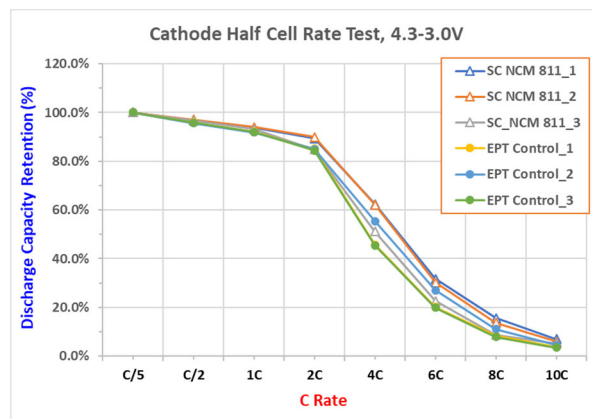


Figure 5 Rate capability comparison of cathode half-cells

SLP cells with reversible capacity around 95 mAh were built to further evaluate the SC NCM 811 cathode in a full cell paired with control SiOx/graphite composite anode. An average FCE of 87.8% was observed, quite close to the control group of 88.0%, this implies that the SC NCM 811 cathode is comparable to the polycrystal control cathode in meeting cell capacity and energy design metrics. Post formation cells were also tested to assess long-term cyclability, as illustrated in Figure 6. Preliminary cycle-life data shows that cells built with the SC NCM 811 cathode fade quicker than control cells in the first 50 cycles, however it is premature to draw any conclusions as more cycle numbers are likely needed.

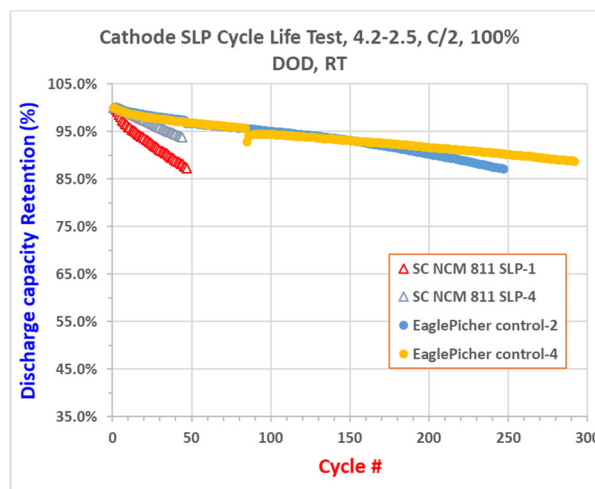


Figure 6 Cycle life of SC NCM 811 vs. control

In addition to the SC NCM 811 cathode, a cobalt-free NMA cathode was being evaluated following exactly the same

screening protocol. This NMA material contains >90% nickel and is capable of delivering 230 mAh/g reversible capacity and long-term cycle life. Experiments are currently underway to confirm those claims using cells fabricated by EaglePicher.

Our aforementioned high-energy control chemistry demonstrated 300 Wh/kg specific energy in a pouch cell with over 10 Ah cell capacity. More effort is also being undertaken to reach 350 Wh/kg and beyond. With the addition of high-capacity active materials such as the silicon/carbon composite anode, SC NCM 811 and >90% nickel NMA, we can potentially obtain 350 Wh/kg specific energy based on cell modeling and energy predication.

Conclusions

Novel silicon/carbon composite and single-crystal NCM 811 and NMA cathode materials were evaluated for high-energy applications, they demonstrated comparable performances against control chemistry including coulombic efficiency and rate capability. The silicon/carbon composite outperformed control in long-term cycling. Those materials are expected to enable high cell specific energy at 350 Wh/kg and beyond.

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References

1. T.B. Reddy (ed.), *Linden's handbook of Batteries 4th Edition*. pp. 26.1-26.4, McGraw-Hill, 2010.
2. M. S. Whittingham. Lithium Batteries and Cathode Materials. *Chem. Rev.*, 104, 4271-4301, 2004.
3. F.J. Gunter and N. Wassiliadis, State of the Art of Lithium Ion Pouch Cells in Automotive Applications: Cell Teardown and Characterization. *J. Electrochem. Soc.*, 169, 030515, 2022.
4. M. S. Whittingham, Electrical Energy Storage and Intercalation Chemistry. *Science*, Vol 192, 4244, 1126-27, 1976.
5. J. B. Goodenough and K.S. Park, The Li-Ion Rechargeable Battery: A Perspective. *J. Am. Chem. Soc.*, Vol. 135, No. 4, 1167-1176, 2013.
6. J. T. Frith, M. J. Lacey and U. Ulissi, A non-academic perspective on the future of Lithium-based batteries. *Nat. Commun.*, 14, 420, pp. 1-17, 2023.
7. A. Manthiram, A reflection on lithium-ion battery cathode chemistry. *Nat. Commun.*, 11, 1550, pp.1-9, 2020.
8. M. N. Obrovac and V. L. Chevrier, Alloy Negative Electrodes for Li-Ion Batteries. *Chem. Rev.* 114, 11444-11502, 2014.
9. Q. Li, Y. Yang, X.Q. Yu and H. Li, A 700W·h·Kg⁻¹ Rechargeable Pouch Type Lithium Batteries. *Chinese Phys. Lett.*, Vol 40, No. 4, 48201-48206, 2023.
10. Li-Bridge Industry Report: *Building a Robust and Resilient U.S. Lithium Battery Supply Chain*. www.anl.gov/access/reference/libridge-industry-report
11. M. J. Lain, J. Brandon and E. Kendrick, Design Strategies for High Power vs. High Energy Lithium Ion Cells. *Batteries*, Vol 5, No. 4, 64, 2019.
12. Y. Jin, B. Zhu, Z. Lu, N. Liu and J. Zhu, Challenges and Recent Progress in the Development of Si Anodes for Lithium-Ion Battery. *Adv. Energy. Mater.*, 7, pp. 1700715-1700732, 2017.
13. Z. Yang, S. E. Trask, X. Wu and B. J. Ingram, Effect of Si Content on Extreme Fast Charging Behavior in Silicon-Graphite Composite Anodes. *Batteries*, Vol 9, No.2, 138, 2023.
14. M. Weiss, R. Ruess, J. Kasnatscheew, *et. al.*, Fast Charging of Lithium-Ion Batteries: A Review of Materials Aspects. *Adv. Energy. Mater.*, 11, pp. 2101126-2101163, 2021.