AMO R2R Advanced Materials Manufacturing (AMM) Consortium and Structured Electrodes for Lithium-Ion Batteries

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Extended Abstract:
Oak Ridge National Laboratory (ORNL) is leading the Department of Energy (DOE) Advanced Manufacturing Office (AMO) Roll-to-Roll (R2R) Advanced Materials Manufacturing (AMM) Consortium with national laboratory partners Lawrence Berkeley National Laboratory (LBNL), Argonne National Laboratory (ANL), and the National Renewable Energy Laboratory (NREL) and industry partner Eastman Kodak. The goal of the AMO R2R AMM Consortium is to broadly disseminate materials, processing science, and advanced technologies to industry in R2R manufacturing. This multi-laboratory/industry partnership is enabling advanced R2R manufacturing R&D to demonstrate a new materials genomic approach to optimization of process parameters for finding new transformational improvements in manufacturing technologies enabling "green" energy applications. Cost effective and energy efficient R2R manufacturing technologies will enable new energy efficient devices and products reducing our nation's energy consumption and greenhouse gas emissions.

ORNL, ANL, LBNL, NREL, and Eastman Business Park are broadly disseminating materials, process science, and advanced technologies to industry in the R2R manufacturing space. During the past 2.5 years, the four-lab Consortium has successfully demonstrated combined capabilities for rapid clean energy manufacturing development. The first demonstration topic was on lithium ion battery manufacturing, and newer topics include membranes for water purification and R2R technology for flexible devices (batteries, fuel cells, window and electronic films, and photovoltaics). Batch processing and part discretization are being replaced where possible with a broad R2R approach, and device validation is being completed using data gathered during processing where optimization and QC is done "on the fly". This Consortium creates a national critical team of experts covering all needed aspects from materials genome modeling and simulation through powder materials synthesis, slurry formulation and scale-up, pilot deposition and curing process development, non-destructive process evaluation, big data analytics and validation, to full scale production of roll-goods. This new approach is enabling up to an order of magnitude shorter process development cycles, bringing the time from 20 years down to 2 years with the pathway for initial commercialization within months of that.

DOE cost targets for advanced energy storage and conversion applications will not be met without significant and timely advancements in R2R manufacturing. Required R2R advances include adaptation of existing processing methods and development of novel methods, and have the potential to significantly impact U.S. manufacturing sector recovery, environmental security, energy security, and sustainable transportation adoption. *Economies of scale through increased manufacturing volumes based on traditional assembly and processing methods will not suffice.* For example, current **baseline technology** cell costs in the lithium-ion battery industry are about 2.5× the $100-125/kWh ultimate target of the DOE Vehicle Technologies Office (VTO). In order to reach the target of a 2.5× increase in performance to 500 Wh/kg, novel R2R processing technologies will be required. Furthermore, polymer electrolyte fuel cell stacks currently cost almost 10× in low volumes compared to the ultimate cost DOE Fuel Cell Technologies Office (FCTO) target of $30/kW. Other examples of DOE EERE funded technologies that have a similar cost-target issue are chemical-process industry membranes, window films, PV films, and electronic films. The DOE Advanced Manufacturing Office (AMO) is poised to assist in reaching low $/m² costs of these various critical energy related applications through addressing R2R manufacturing problems common to each application. The Consortium is employing a four-point strategy to address these gaps:

1. Implement high-speed, low-cost (operating and capital) methods for reaching ultimate cost targets;
2. Develop in-line metrology and non-destructive evaluation (NDE) to enable closed-loop feedback control of R2R processes;
3. Link processing parameters and defects to device performance;
4. Develop optimized designs (layering, gradients, patterning, etc.) layering approaches common to many existing and emerging applications.

The Consortium is focusing on two technology areas: Membranes and flexible devices – membranes for chemical separation applications such as water purification and desalination and flexible energy-device applications such as batteries, fuel cells, PV films, window films, and electronic films. Big data analysis, data mining, and other data analytics technologies are being utilized to perform predictive modeling and simulation, optimize processing conditions for performance, and develop closed-loop intelligent feedback systems for high-yield low-cost production.

Some examples of specific problems that the AMM Consortium are addressing are: the impact of new and existing raw material morphology and structure on processibility; reduction in process energy usage, for example by transitioning from batch to continuous processes; multilayer coatings and 3-D patterning of active layers; energetic curing of dispersions at high-speed; linking of pre-pilot processing (10s to 100s of feet) experiments to pilot-scale processing (thousands to millions of feet); impact of process parameter variation on device performance and durability; and in-line coating metrology for developing feedback loops to the deposition step. The information gained by improving R2R manufacturing capabilities in one application is providing understanding that will be leveraged with other applications. Therefore, the accomplishments of this AMO Consortium benefits the entirety of EERE by advancing broadly applicable methods as opposed to a product-specific manufacturing process.

A key example of this Consortium effort is electrode structuring (in particular for lithium-ion cells) through particle size optimization and layer structuring. When a simple particle-size modification was made and combined with a thick (4 mAh/cm²) bilayer approach, substantial improvements were realized in rated capacity at 2C discharge rates, which enabled simultaneous high energy and power density. This technology could also be beneficial for the new VTO extreme fast charging (XFC) goal of 10-15 min. Figure 1 shows two examples (2×7 combinations) of the total matrix of samples tested (7 different anodes paired with 7 different cathodes) for rate performance. Two baseline configurations for both the anode and cathode were used consisting of all large and all small particle sizes. The results for the best and worst anode/cathode combinations are shown in Figure 2. These two groups begin to separate at 1C and show significant capacity differences at 2C and 3C, with the best anode/cathode combination (Dual-pass cathode with large particles on bottom/Dual-pass anode with small particles on bottom) reaching 59% of original capacity at 2C and the worst anode/cathode combination (All large particle cathode/Single-pass anode with large particles on bottom) only reaching 25%. These results demonstrate that the rate performance at high C rates can be substantially improved by pairing specific structured anodes and
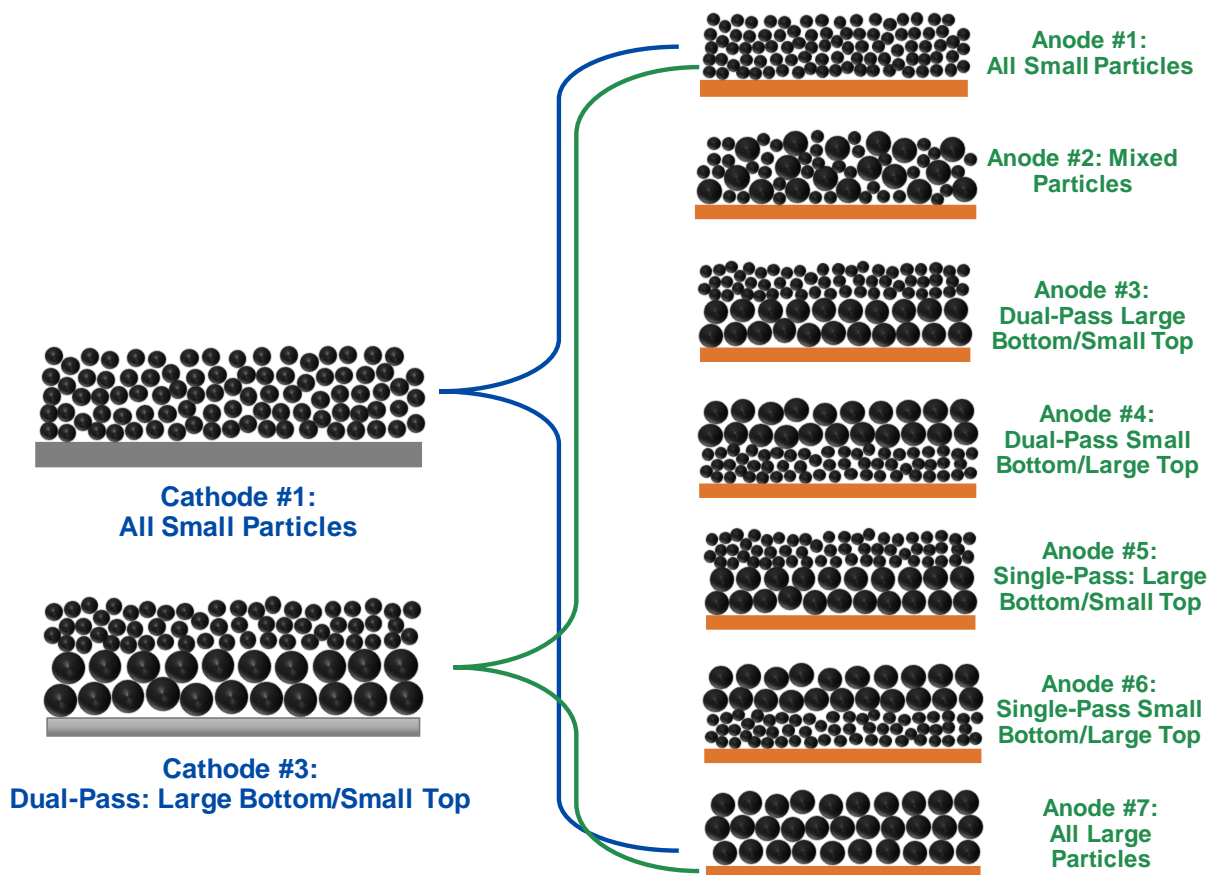
Figure 1. Fourteen of the 49 total configurations evaluated in the lithium-ion structured electrode architecture study. A 2×2 matrix of baselines was used consisting of all small and all large particles at both the anode and cathode.

cathodes together. While it is difficult to determine a distinct pattern for the anodes among these two groups, a clear trend can be observed for the cathodes. The best performing cathodes are #1 (All small particles) and #3 (Dual-pass with large particles on bottom), while the worst performing cathodes are #7 (All large particles), #4 (Dual-Pass with small particles on bottom), and #6 (Single-Pass with small particles on bottom).

Although the rate performance seems to be more dependent on the cathode than the anode, the choice of anode for a particular cathode is still very important. For example, cells made with cathode #3 (Dual-pass with large particles on bottom) and anode #4 (Dual-Pass with small particles on bottom) achieved 59% of their original capacity at 2C, whereas cells made with cathode #3 and anode #5 (Single-Pass with large particles on bottom) reached only 44% of their original capacity at 2C. Overall, these results demonstrate that the performance at high C rates can be substantially improved by structuring the cathode and anode. While the cathode seems to have more of an impact on overall cell performance, the choice of anode is also critical.

In an effort to examine the durability under long-term cycling of some of the best and worst performing electrodes, sixteen structured anode/cathode combinations were chosen for cycle life testing in single-layer pouch cells based on the ORNL rate performance results and Argonne National Laboratory coin cell cycle life results. For each combination, three cells were tested at C/2 charge, C/2 discharge, and three cells were tested at C/2 charge, 2C discharge (since this is the C rate where we began to see significant capacity differences in the rate performance data).

Best and Worst Anode/Cathode Combinations

% of Original Capacity vs C Rate

Best
C3: Dual-Pass Large Bottom /
A4: Dual-Pass Small Bottom

Worst
C7: All Large/
A5: Single-Pass Large Bottom

Best 8
- C1: All Small/ A2: Mixed
- C1: All Small / A3: Dual-Pass Large Bottom
- C1: All Small / A4: Dual-Pass Small Bottom
- C1: All Small / A7: All Large
- C3: Dual-Pass Large Bottom / A2: Mixed
- C3: Dual-Pass Large Bottom / A3: Dual-Pass Large Bottom
- C3: Dual-Pass Large Bottom / A4: Dual-Pass Small Bottom
- C3: Dual-Pass Large Bottom / A6: Single-Pass Small Bottom

Worst 8
- C7: All Large / A1: All Small
- C7: All Large / A5: Single-Pass Large Bottom
- C7: All Large / A6: Single-Pass Small Bottom
- C4: Dual-Pass Small Bottom / A5: Single-Pass Large Bottom
- C4: Dual-Pass Small Bottom / A7: All Large
- C6: Single-Pass Small Bottom / A5: Single-Pass Large Bottom
- C6: Single-Pass Small Bottom / A6: Single-Pass Small Bottom
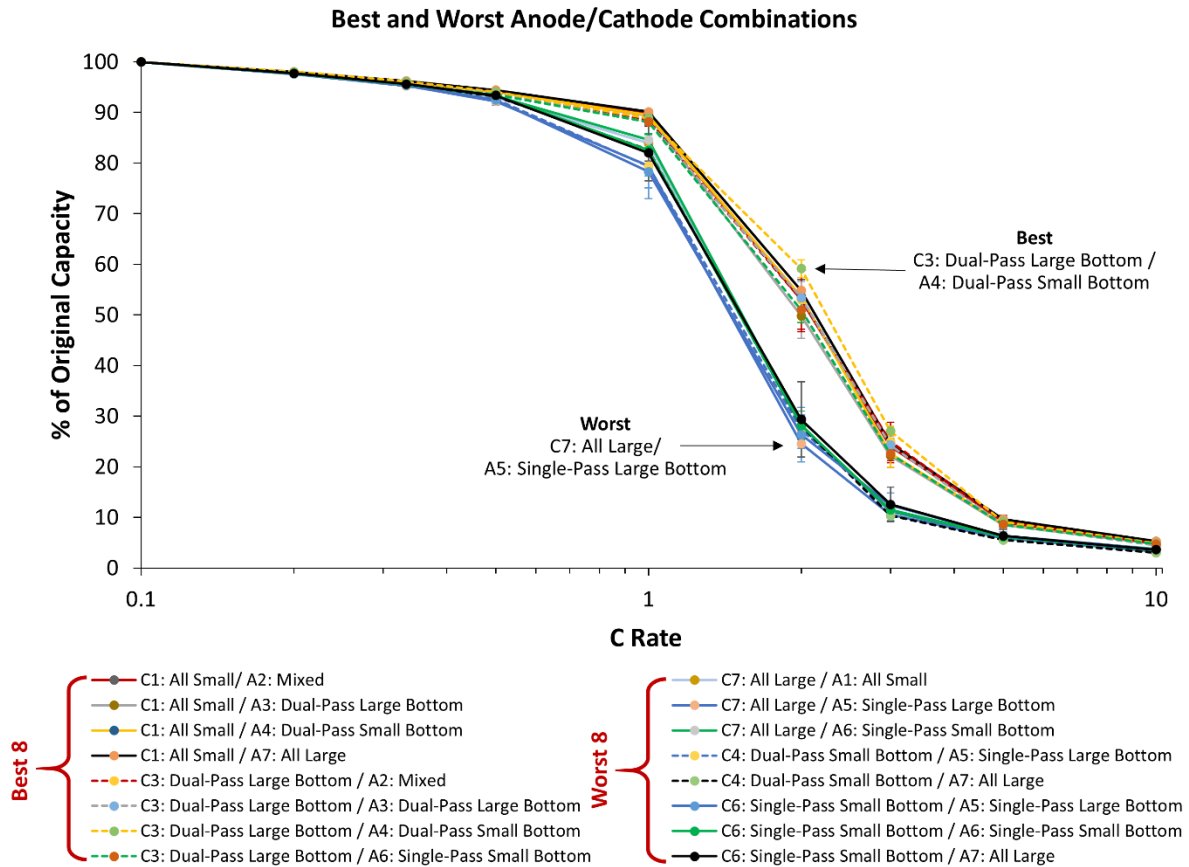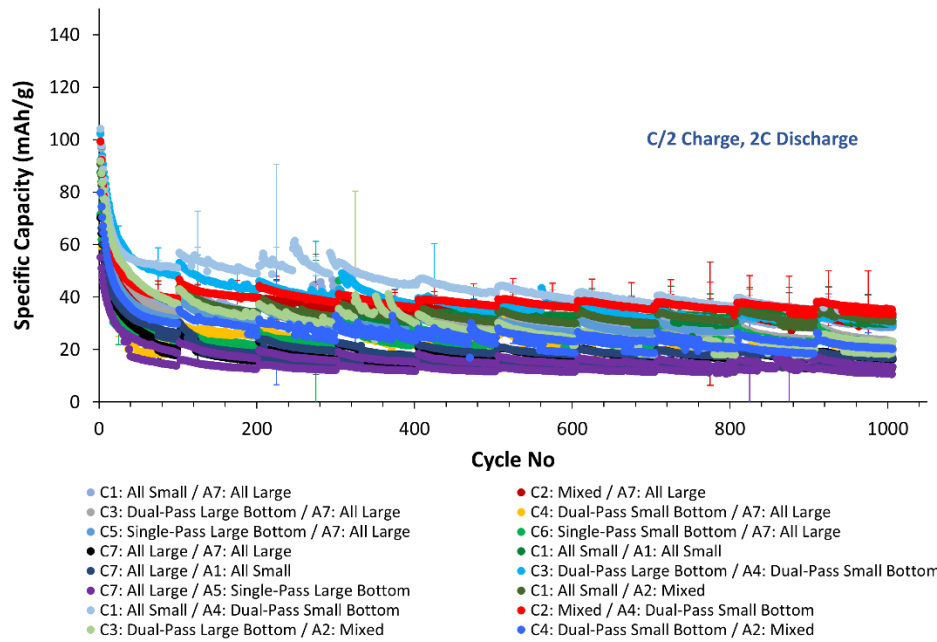- C6: Single-Pass Small Bottom / A7: All Large

Figure 2. Comparison of the discharge rate performance of single-layer pouch cells made with the best and worst anode/cathode combinations. Each data point is an average of three pouch cells, with the initial capacity taken as the capacity at a discharge rate of C/10. The error bars represent the standard deviation at each C rate. All cells were filled with 1.2 M LiPF$_6$ in 3:7 wt% EC/EMC electrolyte.

Cells cycled at C/2 charge, 2C discharge completed 1000 cycles, and the results are shown below in Figure 3 (the last 100 cycles are shown in Figure 3b for clarity). All of the cells show significant capacity loss in the first 100 cycles, but after this point the capacity fade is relatively minor. The capacities ranged from 35 mAh/g for the C2: Mixed / C4: Dual-Pass Small Bottom combination down to 12 mAh/g for the C7: All large / A5: Single-Pass Large Bottom combination. Combinations that are good for rate performance were not necessarily expected to be good for cycle life, but the same trends generally held for both data sets. Cells made with small particle cathodes (C1) or two-layer cathodes with large particles on the bottom (C3) generally performed better, while cells made with large particle cathodes (C7) or two-layer cathodes with small particles on the bottom (C4 & C6) generally performed worse. However, a notable difference between the two data sets comes from cells made with the mixed particle cathode (C2). When paired with the appropriate anode (A4 Dual-pass with small particles on bottom), this combination exhibited the highest capacity after 1000 cycles at 2C (~35% retention). However, the 2C capacity retention from the rate performance tests (46%) was not one of the best. It is important to note that even though this top cell combination only reaches 35 mAh/g after 1000 cycles (there is definite room for improvement), these results demonstrate that particle size and cell architecture do make a difference for high-rate cycle life performance (see Figure 3).

a)

Cycle Life Comparison (2C Discharge)

C/2 Charge, 2C Discharge

- C1: All Small / A7: All Large
- C2: Mixed / A7: All Large
- C3: Dual-Pass Large Bottom / A7: All Large
- C4: Dual-Pass Small Bottom / A7: All Large
- C5: Single-Pass Large Bottom / A7: All Large
- C6: Single-Pass Small Bottom / A7: All Large
- C7: All Large / A7: All Large
- C1: All Small / A1: All Small
- C7: All Large / A1: All Small
- C3: Dual-Pass Large Bottom / A4: Dual-Pass Small Bottom
- C7: All Large / A5: Single-Pass Large Bottom
- C1: All Small / A2: Mixed
- C1: All Small / A4: Dual-Pass Small Bottom
- C2: Mixed / A4: Dual-Pass Small Bottom
- C3: Dual-Pass Large Bottom / A2: Mixed
- C4: Dual-Pass Small Bottom / A2: Mixed

b)

Cycle Life Comparison (2C Discharge)

C/2 Charge, 2C Discharge

- C1: All Small / A7: All Large
- C2: Mixed / A7: All Large
- C3: Dual-Pass Large Bottom / A7: All Large
- C4: Dual-Pass Small Bottom / A7: All Large
- C5: Single-Pass Large Bottom / A7: All Large
- C6: Single-Pass Small Bottom / A7: All Large
- C7: All Large / A7: All Large
- C1: All Small / A1: All Small
- C7: All Large / A1: All Small
- C3: Dual-Pass Large Bottom / A4: Dual-Pass Small Bottom
- C7: All Large / A5: Single-Pass Large Bottom
- C1: All Small / A2: Mixed
- C1: All Small / A4: Dual-Pass Small Bottom
- C2: Mixed / A4: Dual-Pass Small Bottom
- C3: Dual-Pass Large Bottom / A2: Mixed
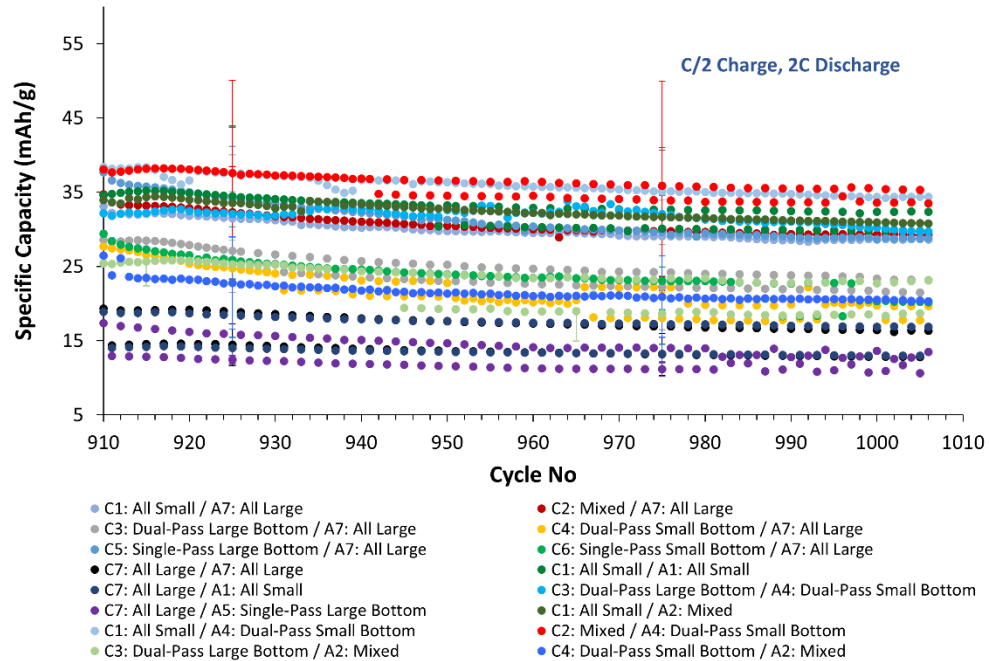- C4: Dual-Pass Small Bottom / A2: Mixed

Figure 3. Cycle life performance of single-layer pouch cells made with selected anode/cathode combinations. Charge C/2, discharge 2C. a) 1000 cycles; b) Last 100 cycles shown for clarity. HPPC was performed every 100 cycles. Data is an average of 3 cells for each combination, and each error bar is an average of the standard deviation for those 50 cycles.

Cells cycled at C/2 charge, C/2 discharge have not yet completed 1000 cycles, but the results thus far are shown in Figure 4. The same trends can be observed in this slower cycling data as in the faster 2C cycling data. Again, the best-performing cells are generally those made with small particle cathodes (C1) or two-layer cathodes with large particles on the bottom (C3), while the worst-performing cells are generally made with large particle cathodes (C7) or two-layer cathodes with small particles on the bottom (C4 & C6). As with the high-rate cycling data, cells made with a mixed particle cathode (C2) and a two-layer anode with small particles on the bottom (A4) show the best capacity retention (~90%) after 300 cycles. Conversely, cells made with a large particle cathode (C7) and a small particle anode (A1) show the worst capacity retention after 400 cycles (~35%) (although the cell-to-cell variation for this combination is quite high). Overall, many of the cell combinations demonstrate excellent capacity retention after 300-500 cycles, but there are clear differences between them, confirming that particle size and electrode structure can be tuned to improve cycle life (see Figure 4).
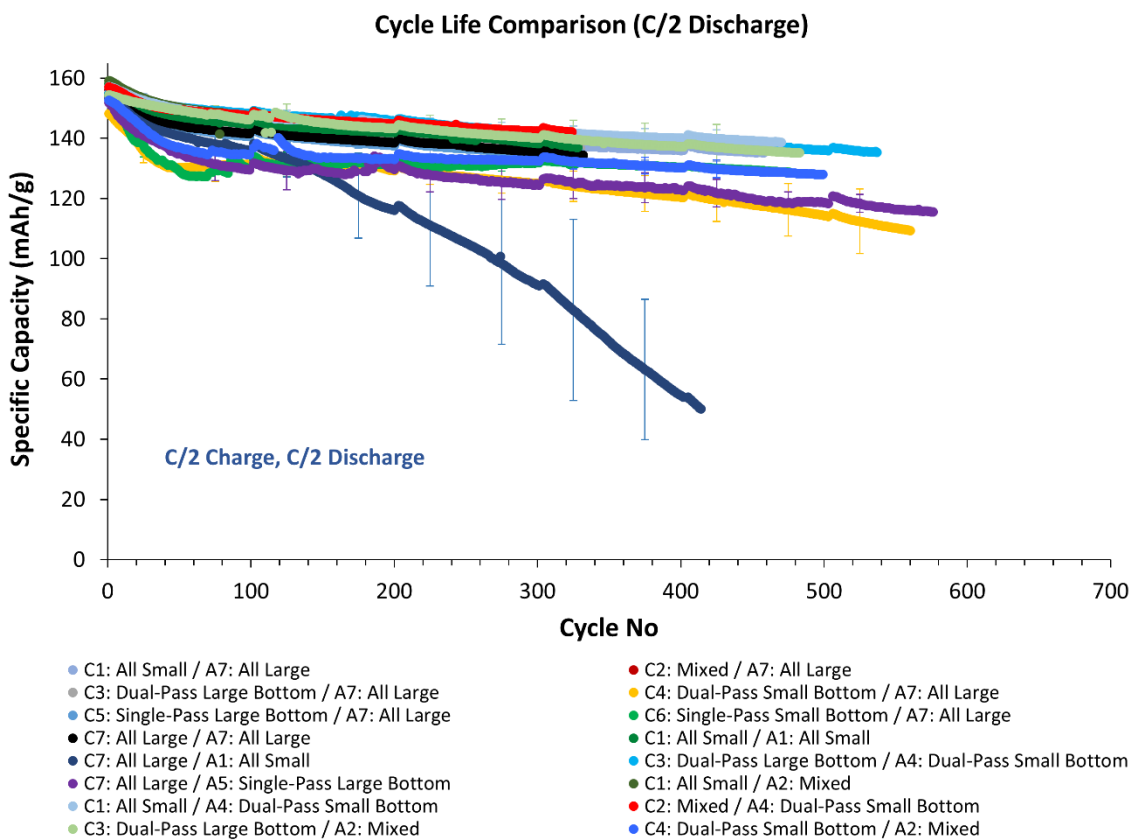

Figure 4. Cycle life performance of single-layer pouch cells made with selected anode/cathode combinations. Charge C/2, discharge C/2. HPPC was performed every 100 cycles. Data is an average of 3 cells for each combination, and each error bar is an average of the standard deviation for those 50 cycles.