Isostatic Pressing of Multilayer Pouch Cells and its Implications for Battery Manufacturing

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KEYWORDS: isostatic pressing, multilayer, pouch cell, processing, solid-state battery

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Summary

We report a comprehensive investigation into the impact of isostatic pressure (ISP) processing on multi-layer pouch cells. The study compares baseline electrodes fabricated using conventional manufacturing processes with isostatically pressed counterparts under varying conditions. Extensive characterization is carried out to assess the differences between baseline cells and those that underwent the isostatic pressing process. The electrochemical performance of the isostatically pressed cathodes was evaluated through impedance spectroscopy and galvanostatic charge-discharge tests. The results indicated that ISP led to notable improvements in porosity, adhesion, and rate performance compared to the baseline cathodes. This work elucidates the microstructural changes induced by ISP in lithium-ion battery cathodes and highlights the technology's promise for advancing battery manufacturing. The findings contribute to a better understanding of how ISP can be effectively integrated into cell assembly, fostering the development of more efficient and scalable battery manufacturing techniques for current Li-ion as well as for solid-state batteries.

Introduction

Lithium-ion batteries (Li-ion) have revolutionized the energy storage landscape, powering a wide range of applications, including portable electronics, electric vehicles, and grid-level energy storage[1-4]. The manufacturing process of these systems plays a crucial role in determining the performance, safety, and cost of Li-ion batteries[5]. Conventionally, Li-ion battery manufacturing involves several key steps, including electrode fabrication, electrolyte preparation, cell assembly, and formation/aging[6]. Electrode fabrication typically involves processes like slurry coating, and calendaring where active materials are mixed with binders and conductive additives to form electrode layers[7]. The calendaring process helps to achieve the desired electrode thickness, density, and porosity. After electrode fabrication, the cell assembly stage involves stacking the electrodes, separator, and electrolyte, followed by sealing the battery in a pouch can, or cylindrical format. Finally, the formation/aging process involves subjecting the cells to controlled charging and discharging cycles to stabilize their initial performance[8].

Solid-state battery manufacturing, on the other hand, represents a new frontier in energy storage technology[9]. Unlike conventional Li-ion batteries, which use liquid electrolytes, solid-state batteries employ solid electrolytes, which offer advantages such as enhanced safety, higher energy density, and wider operating temperature ranges[10]. The manufacturing process for solid-state batteries differs from that of Li-ion batteries, with additional steps such as solid electrolyte synthesis, electrode-electrolyte integration, and solid-state interface optimization[11-15]. While both Li-ion and solid-state battery manufacturing processes share certain similarities, such as electrode fabrication and cell assembly, the integration of solid electrolytes in solid-state battery manufacturing introduces unique challenges[16,17]. These challenges include achieving efficient and uniform solid-state electrolyte deposition, optimizing the solid-state interfaces for low interfacial resistance, and ensuring compatibility between electrode materials and solid electrolytes[18].

Isostatic pressure (ISP) is a scalable, manufacturing process that yields a high degree of control over local feature properties[19]. Isostatic pressing is a manufacturing process that involves applying uniform pressure to a material in all directions. There are different types of isostatic pressing, including hot isostatic pressing (HIP), warm isostatic pressing (WIP), and cold isostatic pressing (CIP). A recent perspective by our team showcased that this approach has been sporadically used

for solid-state battery fabrication and integration while it has hitherto not been leveraged in conventional Li-ion battery manufacturing[19]. ISP offers the potential to overcome the limitations of traditional manufacturing processes by providing precise control over critical parameters such as electrode density, thickness, and porosity. Specifically, for the battery assembly and integration cold isostatic pressing and warm isostatic pressing are two key available modes. Warm isostatic pressing (WIP) is a similar process to HIP but with lower temperature and pressure. WIP is typically performed at temperatures ranging up to 200 °C, which allows for densification of materials without altering their microstructure. Cold isostatic pressing (CIP) involves applying pressure to a material at room temperature, which causes the material to deform plastically and become denser. The pressure in CIP is typically between 100 MPa to 700 MPa, which is lower than the pressure used in HIP and WIP. In recent literature, the role and need of isostatic pressing for processing and integration of solid-state batteries is clearly highlighted[9]. ISP of cathode films was shown to increase the volumetric energy density as well as cycling performance at high rates for LFP based materials[20]. Lee et al. demonstrated a solid-state pouch cell with an Ag-C interlayer processed with WIP that exhibited high energy density (>900 Wh kg^{-1}), stable coulombic efficiencies (>99.8%) as well as long cycle life (1000 cycles)[21]. Fiedler et al. used dry processing approach for composite cathode and separator fabrication along with ISP for integration in S-based solid state pouch cells yielding good cycling and rate performance[22]. For solid electrolytes itself, isostatic pressing has shown to improve density and transport properties leading to improved electrochemical performances[14,23-29].

Overall, ISP has seen a steady growth in being employed for solid-state battery manufacturing for proof-of-principle demonstrations with single-layer cells. However, the impact of ISP on multi-layer pouch cells, which are commonly used in batteries, remains unexplored. Specifically, the questions of pressure distribution, structural and microstructural changes, as well as the impact of ISP on electrochemical performance are not answered. This paper aims to address this research gap by evaluating the impact of isostatic pressure on multi-layer pouch cells, focusing on conventional Li-ion battery technology. Specifically, we employ dummy pouch cells with conventional lithium-ion battery materials to carry out this study. The investigation delves into several pressure-temperature dependencies to identify the optimized ISP conditions for achieving desired effects on pouch cells ranging from 2 layers to 40 layers. By assessing the performance,

cycle life, and capacity of ISP-processed multi-layer pouch cells, we aim to quantify the benefits and limitations of this technology in enhancing battery performance and reliability.

Furthermore, this study acknowledges the broader implications of ISP in the context of solid-state battery manufacturing. The insights gained from evaluating ISP in conventional Li-ion battery materials can potentially inform the development and optimization of solid-state battery fabrication processes. This highlights the dual significance of the research, as it contributes to the advancement of both conventional and solid-state battery technologies. This paper presents an in-depth investigation into the impact of isostatic pressure on multi-layer pouch cells, shedding light on its potential to improve the performance and reliability of Li-ion batteries. The findings from this study will contribute to the ongoing efforts to optimize battery manufacturing processes, ultimately facilitating the widespread adoption of Li-ion batteries in various applications, including solid-state battery technologies.

Results and Discussion

Isostatically pressed dummy pouch cells were extracted and examined in a dry room at the Department of Energy's Battery Manufacturing Facility at Oak Ridge National Laboratory. It was observed that the vacuum seal of the pouch cell itself along with the double-bagging approach used to isolate the pouch cell from the isostatic pressing fluid (oil) was extremely effective. All pouch cells were extracted from the plastic sealing bags without any contamination. On extracting the individual layers within the pouch cells, several notable differences were observed compared to the stacks found in conventional pouch cells. After isostatic pressing, the trilayer assembly of cathode-separator-anode had become rigid and could be handled as a single unit. In contrast, without the addition of electrolyte, electrostatic interaction between the separator and the electrodes makes this assembly typically difficult to handle. In addition, strong texturing of the current collector was observed with the isostatically pressed pouch cells (Fig. 1a). This texturing is imprinted on the current collector from the plastic sealing bag used for encapsulating the pouch cells. Further, adhesion of the separator to the cathode was observed wherein some mechanical effort was required to take the two layers apart (Fig. 1a). Without isostatic pressing, there is typically no adhesion between these two layers even after undergoing the vacuum sealing process.

One major impact of isostatic pressing is in the compaction and densification of materials. To assess the impact of the ISP process on film compaction, we assessed the thickness of the individual cathode and anode layers from all the pouch cells (Fig. 1B). The individual layers of the single- and multi-layer isostatically pressed pouch cells were extracted from the packaging. Subsequently, the individual layer thicknesses were measured using a micrometer. The raw thicknesses of the individual layers are reported in Fig. S2. For single-layer cells, up to five measurements of the thickness of the cathode and anode were taken to estimate the average thickness of the film. For multi-layer cells, the thickness was measured similarly across each of the layers and the average was reported for the cell. We observe that a ~20-30% reduction in thickness is observed for the cathode films while a 30-50% reduction was observed for the anode films. We interpret this results in a two-fold fashion. First reason for higher compaction could be arising from the higher initial porosity of the anode layers. Secondly, the materials of the anode (graphite, binder) have lower mechanical properties (viz. modulus, strength) that lead to higher densification at the pressures applied. The raw thickness values for all the electrodes are reported in Fig. S2. This essentially indicates a high level of calendaring of these electrode films with very low anticipated porosity (<15%). It should be noted that even with this high degree of calendaring, the structural integrity of the current collector was not compromised. In conventional processing, very high calendaring pressures tend to rupture and destroy the current collector films. This is a key result indicating that ISP processing can aid significantly in streamlining the battery manufacturing process. For conventional lithium-ion batteries, we anticipate that it can replace the calendaring step with the added advantage of increasing electrolyte wetting and reducing the time for formation and aging cycle which is a current bottleneck for lithium ion battery processing. For solid-state batteries, coupling the integration of cells and calendaring into a single step will offer several techno-economic benefits. The maximum compaction for the electrode films is observed for the single layer pouch cells pressed at 414 MPa, and room temperature. Warm isostatic pressing at 90 °C and 120 MPa for single layer pouch cell affords slightly higher compaction compared to the pouch cell pressed at room temperature at the same pressure. For multi-layer pouch cells, it is seen that increasing the number of layers within the cell leads to a slightly better compaction of the layers. We anticipate that strong interactions between the layers and pouch cell material lead

to this slight increase. Within multi-layer cells, layer-to-layer variation is low and can be correlated back to variation in the feedstock electrodes used (Fig. 1C).

Isostatic pressing is typically employed industrially with solid components wherein the pressure distribution assessment is only carried out on the outer surface of the part. Due to the fundamentals of operation, the pressure on the outer surface of ISP parts is uniform. However, with battery cells, it is necessary to understand the distribution of pressures within the different layers of the cell itself. So far, no studies have investigated the internal pressure distribution in multi-layered components exposed to ISP conditions. Employing a pressure-sensing film within the construction of the dummy cell, we enable a direct, in-situ measurement of pressure distribution as a function of the isostatic pressing conditions. For the single-layer pouch cells, the optical images for the pressure films from within the pouch cells are shown in Fig. 2A-C. These pressure films were originally white and after pressure turned pink. Differences in shades of color indicate variations in pressure within the films. For all the single-layer films, no variations were detected visually. To assess the multi-layer films, we are plotting the intensity profile (0-255) across the different layers of the cells (Fig. 2D-G). The raw images of the pressure films for all the multi-layer pouch cells are shown in Fig. S3-S6. Across the layers, the intensity profiles remain consistent – with some notable exceptions. It is observed that the first layer always has a lighter shade, indicating a lower effective pressure on that film. The exact reason for this behavior is not understood – but we anticipate this can be mitigated through the design of fixtures to hold the cells within the ISP system. Other than that, the pressure distribution is exceptionally uniform for all the multi-layer pouch cells. This is the first time that the pressure distribution for multi-layer cells has been showcased and the results showcase the ISP can be effectively used to distribute pressure uniformly over large pouch cells.

The microstructure and morphology of the baseline cathode and isostatically pressed cathodes in three different conditions were examined using scanning electron microscopy (Fig. 3). Cross-sectional and top-down SEM images were acquired to gain insight into the electrode's structural characteristics. The baseline cathode, which underwent conventional coating and calendaring processes exhibited a typical morphology, and the presence of pores was evident within the structure (Fig. 3A,E). In contrast, the isostatically pressed cathodes in the three different conditions

revealed a much denser microstructure consistent with the reduction in thickness for these conditions. The cross-sectional SEM images clearly show improved electrode density and enhanced interparticle contact within the active material. It is noteworthy that even at very high isostatic pressures, the cathode particles observed in the top-down images do not show any signs of microstructural deterioration/cracking. The presence of darker features on top of the cathode isostatically pressed at 414 MPa (Fig. 3H) could likely correspond to a trace separator that might have adhered to these particles that underwent degradation under the electron beam. Similarly, the baseline and isostatically pressed anodes were examined by SEM (Fig. S7). Isostatically pressed anodes show similar densification behavior as observed for the cathode films. Similar to the cathode films, no structural damage to the anode particles was observed on the surface of the anode films. To further assess the microstructural evolution, we carried out FIB-SEM tomography of the baseline and isostatically pressed electrodes.

FIB-SEM images of baseline and isostatically pressed cathodes are shown in Fig. 4A-D. Supporting information also contains video files that show cross-sectional FIB-SEM tomography images for these systems (See SI). It is worth noticing that the area of interest covers the entire thickness of the cathode, and consists of active material, carbon-binder matrix, pores, and Al current collector. When the cathode was pressed isostatically under 120 MPa at room temperature, particle crushing along with some microcracks can be observed (pointed region in Fig. 4B). Deformation of the current collector is also evident at the interface of the particle and the aluminum foil, which could be due to the isostatic pressing. By increasing the temperature to 90 °C while maintaining the same pressure (120 MPa, Fig. 4C), similar phenomena such as crushed particles and deformed current collector can be seen.

However, when the isostatic pressing pressure was increased to 414 MPa at room temperature, significantly increased particle-current collector contact became visible with no gaps in between (Fig. 4D). It is likely due to some welding effect because of the higher pressing pressure, which can also explain the ultra-strong adhesion that was observed in peeling test (Fig. 5). Pore size and pore volume information was obtained from subsequent Image processing (Fig. 4E). Notably, isostatic pressing leads to decreased pore size and porosity values within the cathode in comparison with the baseline sample, even though microcracks are presented and being considered as pores.

Meanwhile, applying high temperature during isostatic pressing can further decrease the porosity, but cannot trigger welding effects until a certain high pressing pressure is realized (414 MPa). Particle cracking observed with high isostatic pressures can potentially be a challenge for long-term stability. Optimizing the time-temperature-pressure conditions for isostatic pressing should provide an avenue to mitigate the severity of the particle cracking observed. However, control experiments to achieve equivalent degree of compaction through traditional calendaring process with identical baseline electrodes yields significant damage to the integrity of the punched cathode films (Fig. S8). We employed single- and multi-pass approaches to achieve identical level of compaction achieved from ISP processes and it was clearly observed that the cathode films cannot sustain this processing approach. Both surface as well as cross-sectional images from these calendered electrodes show significant damage to the cathode particle structure (Fig. S9, S10). The current collectors on these calendered electrodes also show significant damage through rupture and cracking (Fig. S11). In contrast, the ISP processed electrodes, for single layer as well as multi-layer pouches resulted in excellent condition of the electrode films (Fig. 1A (inset), S12) with no damage to the integrity of the films. This presents a unique advantage of the isostatic pressing approach to achieve a high degree of compaction of electrode films compared to conventional calendering approaches.

The adhesion strength measurement studies revealed that ISP processed cathodes have at least an order of magnitude higher adhesion strength with current collectors when compared to the adhesion strength of conventionally processed cathodes (Fig. 5). The adhesion strengths were measured by using a peel tester (explained in the experimental section, see supporting information for video of the peel test). During adhesion strength measurements, it was observed that ISP processed cathode layer was so strongly adhered with the current collector that instead of peeling the cathode layer, the double-sided tape was peeled off the steel plate (Fig. 5C). Therefore, in reality, we could only measure the adhesion strength of double-sided tape with the steel plate, and the adhesion strength of ISP processed cathode was beyond the strength of double-sided tape adhesion strength with steel plate. However, in case of conventionally processed cathode, a clean peeling of cathode layer form the current collector was observed (Fig. 5B). We could not measure the exact adhesion strength of ISP processed cathodes with the current collector due to experimental limitations. However, it can be confidently stated that ISP processed cathodes have

at least an order of magnitude higher adhesion strength with the current collector than those of the conventionally processed electrodes. The higher adhesion strength is highly sought after because it lowers the chances of the cathode peeling off from the current collector during long-term cycling.

The preservation of the crystal structure of the cathode and anode during processing is of paramount importance in ensuring the integrity and performance of the energy storage system. The crystal structure, particularly of the NMC cathode, plays a pivotal role in dictating the electrochemical properties and overall efficiency of the battery. Any deviation from the ideal crystal arrangement can have profound implications on the cell's capacity, cycling stability, and rate capability. Therefore, maintaining the crystal structure during processing, such as isostatic pressing, is critical for the successful performance of pouch cell batteries. In our study, we investigated the impact of isostatic pressing on the crystal structure of NMC cathodes within both single-layer and multi-layer pouch cells (Fig. 6, S13). Our X-ray diffraction (XRD) results reveal that, across the range of pressures tested, the crystal structure of the NMC cathode remains remarkably stable. This is true even for the cell processed at higher temperature of 90 °C (Fig. S13). This observation is significant as it suggests that the applied pressures do not induce structural changes in the cathode material, thereby preserving its electrochemical functionality. However, our analysis also unveiled changes in the intensity of XRD peaks, implying potential alterations in the orientation of crystal domains within the cathode (Fig. 6d). The variation in intensity could signify a preferential orientation of crystal planes under the influence of isostatic pressing. Understanding the mechanism behind such preferential orientation is crucial, as it can influence the overall electrochemical performance of the pouch cell. Indeed, recent work on understanding CEI for single crystal cathode particles in SSBs showed that certain facets of cathode show much higher stability compared to other facets highlighting the need for preferential orientation[30]. Further, even with metal anode systems, orientation of the Li metal is shown to impact reversibility of the plating and stripping greatly[31]. These findings open the door to further investigations aimed at elucidating the orientation mechanisms in detail. To comprehensively assess the impact of isostatic pressing on the orientation of crystal domains within the NMC cathode, future research endeavors should delve into more detailed analyses, such as electron microscopy and additional crystallographic techniques. This will enable a thorough understanding

of the interplay between applied pressures and crystallographic orientation, facilitating the optimization of manufacturing processes for enhanced pouch cell performance.

Impedance spectroscopy for the coin cells assembled from the baseline electrodes as well as the isostatically pressed samples are shown in Fig. 7. The as-assembled cells all show similar profiles with a semi-circular feature followed by a diffusion tail. The isostatically pressed samples showed a slightly lower total cell resistance compared to the baseline electrode. Similarly, after the formation cycle, the isostatically pressed films show much lower interfacial resistance. Detailed analysis of the impedance spectra and fitting is shown in Fig. S14-S15 and the equivalent circuit used is described in the supplementary information. The obtained individual resistance components are compared in Table 2 for each cell for the four different processing conditions. At least two cells were evaluated for the electrode of each processing condition. It is discernible from Table 1 that the magnitude of Ohmic and interfacial cell resistances are quite low both before and after formation cycles. It should be noted that Ohmic and interfacial resistances of baseline cells are much higher compared to the isostatic processing electrodes after the formation cycle. Note that the R2 value is gradually decreased from baseline to 414 MPa RT samples (Table 2). The R3 value is reduced significantly compared to the baseline cell, however, the obtained data are not changed chronologically. This might be due to the insignificantly low value which is within the error margin of the fitting parameters. The lower interfacial resistance with isostatically pressed electrodes could arise from several reasons – large electrode surface area due to cracking, potentially homogeneous contact with SEI film compared to baseline electrodes, or even due to improved wetting with the liquid electrolyte. Further work needs to be carried out to assess the origin of the improved interfacial resistance.

The formation cycles for all the systems show similar behavior and coulombic efficiencies in the initial cycles (Fig. S16). The full cells were cycled under nominal C/3-C/3 conditions at 30 °C. Overall, the isostatically pressed samples performed at par with the baseline materials (Fig. 8). After 100 cycles, the baseline materials show a retention of 83%. The cells formed from the dummy cells isostatically pressed at 120 MPa, RT condition, 120 MPa, 90 °C, and 414 MPa, RT conditions similarly show retentions of 80%, 85%, and 85% respectively. The polarization curves from these cells (Fig. S17) show typical profiles as expected from NMC-graphite systems. For the cells made from multi-layered dummy cells, the results are similar in terms of capacity retention

across all the cells tested (Fig. 9). On average, the cells from the four-layer dummy cell showed around ~87% retention, 10-layer cell showed around 85%, 20-layer cell showed around 81%, and 40-layer cell showed around 86% retention. It should be noted that the electrochemical performance of these isostatically pressed samples was tested over multiple coin cells which showed similar performance.

A key benefit from the increased calendaring afforded by the isostatic pressing is potentially in improving the power performance of the cells. This was verified by evaluating the rate performance at C/3, 1C and 3C for the baseline electrode and the cell isostatically pressed at 414 MPa, RT (Fig. 10, S15). At C/3 the baseline electrode and the isostatically pressed electrode show similar performance as already showcased earlier in Fig. 8. However, on increasing the rate to 1C, we see a clear improvement in the capacity attained as well as the retention for the isostatically pressed samples compared to the baseline material. At 1C, the isostatically pressed sample showed 5% higher capacity after 25 cycles and at 3C, showed 10% higher capacity after 25 cycles. This is consistent with the impedance results which showed lower interfacial resistance for the isostatically pressed samples. In general, we think ISP processed materials behave at par with baseline materials. The small window of improvement observed in the rate capabilities could potentially arise from higher densification or from particle breakdown. These results clearly indicate the benefit of isostatic pressing in improving rate-performance of lithium-ion batteries.

Limitations of the Present Study and Implications for Battery Manufacturing

The present study looks at evaluation of current lithium-ion battery materials and the impact of ISP processing on the same. While the results are broadly applicable to solid-state battery systems there a few important caveats that need to be highlighted. Firstly, we note the limited pressure and temperature settings employed in this study. The pressures selected here represent the nominal as well as the outer bounds of the equipment capabilities with CIP and WIP instruments. Our aim was to investigate these metrics as the baseline to assess the impact of ISP on battery materials. It is imperative that a time-temperature-pressure optimization be carried out for a specific chemistry under scrutiny to maximize densification while mitigating detrimental impacts like particle cracking. Further, we do believe that lowering pressures, as well as modifying holding times can help with mitigating particle cracking specifically for the system that we investigated. Solid-state batteries will eventually have composite cathodes, metal or metal alloy anodes as well as solid

separators which might be ceramic or hybrid or amorphous in nature. Mechanical properties of solid ion conductor additives in the cathode are expected to modify the resultant microstructures of the composite cathodes. However, we can safely predict the relative orders of densification using our study as a baseline. Further, initial results with isostatic pressing of Li metal indicates that below a threshold thickness, creep is negligible which is consistent with the knowledge in the literature. These results indicate that ISP processing and metal anode thicknesses will need to be carefully tailored to avoid shorting through creep-like phenomena. Finally, we acknowledge that ISP by definition is a batch process. However, we believe that this process can neatly dovetail with the current manufacturing line-up in the integration and formation steps. Currently, the formation and aging steps in the lithium-ion battery manufacturing process are the greatest bottleneck in terms of time and materials due to extended holds required for adequate wetting as well as finite number of cycling channels available for formation. We believe that integrating ISP into the process chain at this stage will be ideal for maintaining the production throughput in manufacturing plants. In addition, solid-state batteries, in principle, can be bipolarly stacked – leading to the concept of "Cell-to-pack" decreasing the number of cells that need to be processed. Also, formation cycles are likely to be less intensive in SSBs due to Li metal anode concept. Overall, there is still a lot of questions to be answered with regards to production line integration – but we firmly believe that there are techno-economic benefits to integrate ISP within the processing chain.

The impact of isostatic pressing was studied extensively with dummy multi-layer pouch cells. Subsequently, the electrodes from the isostatically pressed pouches were extracted and compared to the baseline electrodes using extensive morphological as well as electrochemical testing. Pressure distributions across the multilayer films is established to be extremely uniform even for pouch cells containing up to 40 individual layers. This emphasizes the scalability of the ISP process for large form-factor cells. Morphological characterization suggests that some structural damage does occur to the cathode particles after ISP processing, however, it does not adversely impact the performance. Peel tests for adhesion indicates that the ISP processed samples achieve an order of magnitude higher bonding of the cathode coating to current collector compared to baseline materials. The isostatically pressed samples retain identical electrochemical performance at nominal C-rate cycling conditions of C/3. At higher rates, a slight improvement in the retention and capacity are observed for the isostatically pressed material due to improved calendaring of the

electrodes. While we believe that the ISP calendaring technology would be ideal for single crystal NMC electrodes, our future endeavors will focus on optimizing ISP pressing conditions to avoid particles cracking across all types of cathodes. The findings of this research open new avenues for the development of innovative and scalable battery manufacturing techniques. ISP emerges as a promising technology to address the challenges associated with conventional manufacturing processes, such as porosity control and electrode density optimization as well as for use in solid-state battery manufacturing.

Experimental Methods

Resource availability

Lead contact:

Further information and requests for additional details should be directed to and will be fulfilled by the lead contact, Marm Dixit (dixitmb@ornl.gov).

Materials availability:

Information on any data and materials used in this study are available from the lead contact upon reasonable request.

Data and code availability:

No code was used for this study. All data is reported within the manuscript of supporting information.

The process flow and experimental pathway followed for this work is schematically shown in Fig. S1a. Dummy cells were manufactured at the Battery Manufacturing Facility at ORNL and subsequently subjected to various ISP protocols. After this, the dummy cells were disassembled, individual layers extracted, and subsequent testing carried out on these extracted films.

Fabrication of the Dummy Pouch Cells

The cathode material used was a polycrystalline NMC622 that was sourced from Targray. Graphite used for this study was SLC1520T, sourced from superior graphite. The separator material employed was Celgard 2325 which was 25 μm thick. Commercial NMC622 and graphite material were used without any further treatment. Cathode slurries were prepared using N-methylpyrrolidone (NMP). The NMP-processed slurry consisted of 90 wt.% NMC cathode active

material, 5 wt.% carbon black, and 5 wt.% polyvinylidene difluoride (PVDF) binder. The anode slurry was prepared by combining 92 wt.% graphite, 6 wt.% PVDF, and 2 wt.% carbon black. To coat the electrodes, a pilot-scale slot-die coater (Frontier) was used. Cathodes were coated onto aluminum foil at loadings ranging from 11.3 to 11.6 mg/cm^2, while anodes were coated onto copper foil at a loading of 7.5 mg/cm^2. All electrodes underwent calendering to achieve a porosity of approximately 35%. Finally, secondary drying was performed either at 115 °C (for NMP-processed) in a vacuum oven before cell assembly. Single- and multi-layer pouch cells were assembled in a dry room with ~0.3% relative humidity. For all cells, Celgard 2325 was used as the separator material. A pressure-sensing film with the range of 7100 to 18500 PSI (49 to 127 MPa) was placed between each layer of the dummy cell. No liquid electrolyte was introduced into the cell before sealing them. Cells with 2 layers (anode and cathode), 4 layers (2x anode and cathode), 10 layers (5x anode and cathode), 20 layers (10x anode and cathode), and 40 layers (20x anode and cathode) were assembled in this fashion.

The typical use of these pressure films is to create an instant, permanent image of pressure variation. These are very commonly used to measure pressing forces in bolted joints, welding fixtures, and jigs. The differences in intensity of the film color depicts the range of pressure observed (Fig. S1b). Overall, the aim of the pressure film images extracted from the single- and multi- layer stacks was to identify if there are pressure pinch points observed after ISP treatment. To simplify the visualization with multi-layer stacks, the intensity average of the electrode film was evaluated using a custom MATLAB routine.

Isostatic Pressing Protocol

CIP and WIP of the assembled dummy pouch cells were carried out using a Quintus laboratory WIP system. The pouch cells were double-bagged and vacuum-sealed in plastic bags before the ISP treatment. The protocols employed for the different pouch cells are detailed in Table 2. For all cycles, the samples were loaded to the maximum pressure value, and held for 5 minutes, followed by a slow pressure release. For the cell processed at 90 °C, the temperature of the chamber was raised to the target value before pressurization. The sealed samples were subsequently opened in the dry room for subsequent characterization.

Fabrication of Coin Cells and Electrochemical Testing

Electrodes to make coin cells were extracted from the baseline electrode foils (no ISP treatment) as well as those extracted from the dummy cells that underwent various ISP processing. For multi-layer cells, representative electrodes from 1st, the middle, and the last layer were punched. The cathode and anode were punched to a diameter of 14 and 16 mm respectively. Full coin cells were assembled in an argon-filled glove box by pairing the cathodes with the corresponding pressed anode. For all cells, Celgard 2325 was used as the separator material, and 1.2 M $LiPF_6$ in 3:7 wt.% ethylene carbonate/ethyl methyl carbonate was used as the electrolyte. To aid in the comparison of data, an equal quantity of 100 µl electrolyte was added to each coin cell. Full coin cells were cycled between 3 V and 4.2 V vs. Li/Li+. Three formation cycles were performed for each cell (C/10 charge, C/10 discharge) before cycle life testing. Cycle life testing was performed by charging and discharging at C/3 for 100 cycles. All tests were conducted in an environmental chamber (Espec) at 30 °C using a Maccor battery cycler (Series 4000).

Characterization

The SEM images of the extracted electrodes were taken on a ThermoFisher Scios 2 FIB-SEM instrument. X-ray diffraction (XRD) patterns of the extracted cathode materials were collected using a Panalytical Empyrean Diffractometer employing Cu Kα radiation at 45 kV and 40 mA conditions. The data were collected at room temperature over the 2θ angle range of 30 to 60° with a step size of 0.01°. FIB-SEM images of the processed and baseline cathodes were collected using the Scios2 FIB-SEM instrument. Subsequent data analysis on the collected 3D stack was carried out using Avizo and custom MATLAB routines. The adhesion strength was evaluated using a peel tester (Mecmesin-Friction Peel Tear) equipped with a 100N module. Figure SX provides a visual depiction of the peel test setup, including a digital photo of the equipment and a zoomed-in image highlighting the different components involved. To measure the adhesion strength, 2.0 cm wide strips of cathodes were cut. A 2.4 cm wide double-sided tape (3M) was placed on the steel plate of the peel tester. The cathode strip was then attached to this double-sided tape, ensuring that the cathode side adhered to the tape while the current collector side faced upwards. A 25-pound weight was applied to the affixed cathode for 1.0 minutes. Subsequently, the metal plate with the attached cathode was securely fastened to the peel tester, and a 2.0 cm wide single-sided tape was adhered to the current collector of the cathode. The single-sided tape was then pulled using a 100N module.

Acknowledgements

This research is conducted at Oak Ridge National Laboratory, managed by UT Battelle, LLC, for the U.S. Department of Energy (DOE) under contract DE-AC05-00OR22725. M.D. was also supported by Alvin M. Weinberg Fellowship at the Oak Ridge National Laboratory. The work was sponsored by Laboratory Directed Research and Development (LDRD) Program at Oak Ridge National Laboratory. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government. DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan. http://energy.gov/downloads/doe-public-access-plan.

Author Contributions

Marm Dixit: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing

Chad Beamer: Formal Analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing

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Declaration of Interests

The authors declare no competing financial interest.

Supplemental information

Supplemental information can be found online at XXXXX.

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Figure Legends:

Figure 1. Isostatic pressing of multilayer pouch cells. (A) Schematic diagram showing the motivation of our study: a pouch cell isostatic pressing, and the dummy cell generated for this study. Texturing of the current collector surface as well as the adhesion of the separator to the cathode are observed from disassembled dummy cells. (B) Normalized changes in thickness compared to the baseline cathode and anode films with different isostatic pressing conditions and pouch cell configurations. (C) The thickness of individual layers of cathode and anode films was observed in multi-layer pouch cells. The symbols represent electrodes extracted from either 4 layer (▼), 10 layer (▲), 20 layer (●) or 40 layer (■) pouch cell stacks. See also Figure S2.

Figure 2. Analysis of pressure distribution. Optical images of the pressure films placed inside the dummy pouch cells that underwent isostatic pressing at (A) 120 MPa, room temperature, (B) 120 MPa, 90 °C, and (C) 414 MPa, room temperature conditions. Intensity profile calculated over the optical image for (D) 4-layer, (E) 10 layers, (F) 20 layers, and (G) 40 layer multi-layer pouch cells.

These cells were all isostatically pressed at 120 MPa, room temperature conditions. See also Figure S3-S6.

Figure 3. Morphology analysis of the cathode films. Scanning electron microscopy images of cross-sectional and planar views of (A,E) baseline cathode material and the cathode films extracted from single layer pouch cells isostatically pressed at (B,F) 120 MPa, room temperature, (C,G) 120 MPa, 90 °C, and (D,H) 414 MPa, room temperature conditions. All the scale bars in the images are 50 μm. See also Figure S7.

Figure 4. Cross-sectional microstructure and porosity analysis of cathodes. FIB-SEM cross sections of the (A) baseline, (B) 120 MPa, RT, (C) 120 MPa, 90 °C, and (D) 414 MPa, RT processed cathode films. (E) Porosity and pore-size distributions of the baseline and ISP processed cathode films estimated from the FIB-SEM tomography datasets. See also Figure S8-S12.

Figure 5. Adhesion measurements of cathode films. (A) Force-distance measurement from the adhesion test carried out for the basline and the ISP processed material. The ISP conditions for the cathode used for this test was 120 MPa, RT. Note that the highest force achieved by the ISP material does not indicate the adhesion of the coating but the tape to the Al backing plate. Optical image of the (B) baseline and (C) ISP processed cathode after the peel testing.

Figure 6. Structural analysis of cathode films. XRD patterns of (A) baseline cathode, and cathode processed in a single layer pouch cell with 120 MPa, RT and 414 MPa, RT conditions. XRD patterns from cathode films extracted from (B) 2 Layer and 4 Layer, (C) 10 layer and 20 layer, and (D) 40 layer pouch cells. These pouch cells were isostatically pressed at 120 MPa, RT conditions. From multi-layer cells, the cathode films were extracted to represent the complete film stack.

Figure 7. Impedance analysis of coin cells assembled from baseline and ISP processed electrodes. Impedance spectra of the as-assembled and formation cycled full cells fabricated with cathode and anode films from the (A, E) baseline material and the ones extracted from the dummy pouch cells that underwent isostatic pressing at (B, F) 120 MPa, room temperature, (C, G) 120 MPa, 90 °C, and (D, H) 414 MPa, room temperature conditions. See also Figure S13.

Figure 8. Electrochemical performance of coin cells assembled from baseline and single-layer, ISP processed electrodes. Cycling performance of cells fabricated with cathode and anode films from the (A) baseline material and the ones extracted from the dummy pouch cells that underwent isostatic pressing at (B) 120 MPa, room temperature, (C) 120 MPa, 90 °C, and (D) 414 MPa, room temperature conditions. The cycling was carried out with a C/3-C/3 protocol at 30 °C. See Figure also S14-S15.

Figure 9. Electrochemical performance of coin cells assembled from multi-layer, ISP processed electrodes. Cycling performance of cells fabricated with cathode and anode films extracted from the (A) first and second layers of the 4-layer dummy cell, (B) first, fifth and tenth layer of the 10-layer dummy cell, (C) first, tenth, and twentieth layers of the 20-layer dummy cell, and (D) first, twentieth and fortieth layer of the 40-layer dummy cell. The multilayer cells were all isostatically processed at 120 MPa, room temperature. The cycling was carried out with a C/3-C/3 protocol at 30 °C. See Figure also S16-S17.

Figure 10. Rate Performance Studies**.** Discharge rate performance of the baseline electrodes and the electrodes extracted from the ISP processed dummy cell at 414 MPa, RT. The cells are tested C/3, 1C, and 3C for 25 cycles at each C-rate. See also Figure S18.

Tables:

Table 1. Comparison of individual resistance components for all four different types of samples

	Before formation cycling			After formation cycling		
Conditions	R1/Ω	R2/Ω	R3/Ω	R1/Ω	R2/Ω	R3/Ω
Baseline	5.1350	8.3560	4.0000	5.4810	6.4590	8.1720
120 MPa RT	3.9040	1.2670	1.7880	2.0510	4.1360	0.99620
120 MPa 90^{o}C	5.3760	2.0000	5.4300	2.7810	3.5720	2.0810
414 MPa RT	3.1870	2.5120	1.3640	2.6080	1.3480	2.3880

Table 2. Conditions for isostatic pressing for dummy pouch cells

Pouch	**Pressure, MPa (KSI)**	**Temperature (°C)**	**Time (min)**	**Medium**
2 Layer	120 (17.4)	RT	5	Oil
2 Layer	414 (60)	RT	5	Oil
2 Layer	120 (17.4)	90 (194F)	5	Oil
4 Layer	120 (17.4)	RT	5	Oil
10 Layer	120 (17.4)	RT	5	Oil
20 Layer	120 (17.4)	RT	5	Oil
40 Layer	120 (17.4)	RT	5	Oil

Supplemental Video Titles

SV1. FIB-SEM cross-sectional images for baseline cathode.

SV2. FIB-SEM cross-sectional images for cathode from single layer pouch cell with ISP at 120 MPa, RT conditions.

SV3. FIB-SEM cross-sectional images for cathode from single layer pouch cell with ISP at 120 MPa, 90 °C conditions.

SV4. FIB-SEM cross-sectional images for cathode from single layer pouch cell with ISP at 414 MPa, RT conditions.

SV5. Adhesion testing video of baseline cathode.

SV6. Adhesion testing video for cathode from single layer pouch cell with ISP at 120 MPa, RT conditions.