Experimental and Simulation Investigations of Porosity Graded Cathodes in Mitigating Battery Degradation of High Voltage Lithium-Ion Batteries

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LiNi0.5Mn1.5O4 (LNMO) is one of the high potential cathodes for lithium-ion batteries due to high operating voltage (4.7 V vs. Li) and high specific energy (650 Wh·kg−1). However, severe accelerated performance degradation occurring especially at the interface between electrode and electrolyte, hinder the implementation of the LNMO. In this work, porosity-graded cathodes are designed to mitigate LNMO degradation. The LNMO is synthesized using the solid-state reaction. We confirm the crystalline phase and electrochemical performance of the synthesized LNMO via X-ray powder diffraction (XRD), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). Scanning electron microscope (SEM), transmission electron microscope (TEM), and energy dispersive spectroscopy (EDS) are utilized. The porosities are measured by both 2-D imaging method (i.e., through ImageJ) and 3-D pore size analyzer in this study. Cycling tests show that porosity-graded cells reduce the capacity fade about 8.285% in full cell and 5.29% in half-cell, respectively. The porosity increase can improve the conductivity and diffusivity of lithium-ions through the electrode. Also, solid electrolyte interphase (SEI) formation can be variated and controlled when the porosity is different inside the electrode. Furthermore, we adopted Elitist Non-Dominated Sorting Genetic Algorithm (NSGA-II) to demonstrate the porosity grading as a strategy for mitigating battery degradation.

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As one promising candidate for high-voltage lithium-ion batteries (LIBs), LiNi0.5Mn1.5O4 (LNMO) cathode possesses a high theoretical capacity of 146.7 mAh·g−1, high operating voltage of 4.7 V vs. Li, and high specific energy of 650 Wh·kg−1.8,9 Compared to other cathode materials such as LiMn2O4 (400 Wh·kg−1), LiFePO4 (145 Wh·kg−1), and LiNi0.5Co0.2Mn0.3O2 (576 Wh·kg−1),8,9 However, severe performance degradation, especially at the electrode/electrolyte interface, hinders the implementation of the LNMO.7,10,11 Besides developing new electrolytes,8,10 more attention needs to be focused on understanding as well as mitigating the LNMO cathode degradation within most common battery systems (e.g., graphite/LNMO),7,12,13 which is the focus of this paper.

The LNMO battery cell suffers from capacity fading issues similar to those encountered in other manganese-based spinel cathode materials when paired with graphite anodes.7,13,14 Pieczonka et al. systematically examined the Mn and Ni dissolution in different LNMO crystal structures under various conditions such as state of charge, temperature, and storage time.13 Also, the LNMO suffers severe capacity fade due to a high operating voltage greater than the stability window of conventional electrolytes (e.g., LiPF6 in an organic solution), which leads to electrolyte oxidation.15,16 LNMO battery cells are usually exposed to high temperatures due to the high power operation in many applications such as hybrid electric vehicles (HEVs),15 which can accelerate the side reactions at the electrode/electrolyte interface, and reduce the stability of LNMO lattice structure. Kim et al. indicated that fluorine-containing additives could form a protective layer on the electrode to promote a longer cycle life.8 The high operating voltage is beyond the stability window of conventional electrolytes, which results in low coulombic efficiency due to the decomposition of the electrolyte.15,16 The decomposition products are believed to react with electrodes, particularly at the electrode/electrolyte interface, which leads to severe capacity fade.7,10 Leitner et al. developed a Li4+xTi5O12 based separator to scavenge and neutralize the decomposition products.12 Also, room temperature ionic liquids (IL), reported by Wilkes and Zaworotko,13 are used as electrolyte materials due to its electrochemical stability (4.0–5.7 V).18 Furthermore, the degradation of the LNMO battery is closely related to the composition and structure of the electrode.8,19,20 Most of the LIB degradation mechanisms, such as active materials dissolution,13,19,21 solid-electrolyte interphase (SEI) layer formation,22–25 and mechanical failure,26–28 are also directly connected to the microstructure of the electrodes. One of the approaches that can improve the battery performance is to optimize the microstructure of the electrode (e.g., particle size, porosity, and thickness). Numerical models have been developed to study the optimization of the electrodes. For instance, Newman et al. established pseudo two-dimensional (P2D) models (e.g., reaction-zone model) to design optimal porosity and thickness of electrodes for LIBs.29,30 Jiang et al. carried out a P2D lattice Boltzmann simulation of ion and electron transport within LIB porou electrode.31 Their work demonstrated the lithium concentration in smaller particles is higher than that in large particles. To achieve better performance, cathodes with smaller particles size and larger porosity should be produced. Just et al. developed an active thermography method to quantify the effects of coating thickness and porosity of electrodes on battery performance.32 Suthar et al. developed a numerical model to investigate the effects of porosity, thickness, and tortuosity on capacity fade.33 Inoue et al. built a correlation between a porous electrode structure and the effective conductivity to design an optimal structure for a thick electrode layer of a high-capacity battery.34 The numerically optimal design by Ramadesigan et al. reduced the ohmic resistance by 15%–33% without increasing the amount of active material.35 Kashkooli et al. established an imaged-based multiscale model to study the real microstructure of electrodes.36 De et al. carried out an optimization of electrode design parameters using a physics-based porous electrode theory to improve battery performance.37 Chung et al. developed a microstructure model to demonstrate that the battery performance could be improved by controlling the transport paths, maximizing the surface area for intercalating lithium ions, and controlling the spatial distribution and particle sizes of active material.40

White et al. investigated the effect of porosity on the capacity fade of LIBs.34 Dai and Srinivasan investigated the feasibility of grading electrode porosity as a design tool for improving battery energy density.41 Furthermore, Liu et al. developed a multi-objective optimization framework to improve battery performance by optimizing its design variables.42,43 However, no experimental investigation has been done to confirm the performance improvement through grading the porosity of electrodes. Also, understanding of interfacial phenomena like the SEI-layer concept occurring on the cathode side of the
cell is still tenuous. We herein focus on cathode-related SEI phenomena for LNMO degradation mitigation. Our previous work shows SEI growth is location dependent due to its growth related to the electron current flow and Li\(^+\) diffusion, which vary at different locations in the electrode.\(^{2,23,44,46-49}\) Therefore, the SEI formation varies when the porosity is different inside the electrode. Also, porous electrodes with larger active surface areas allow utilization of high electrochemical reaction rates per unit volume.\(^{90,93}\) The increase in porosity can improve the conductivity and diffusivity of lithium-ions through the electrode.\(^{55,51,52}\) Very recently, Yang’s study reveals LIBs nonlinear degradation phenomena as well.\(^{53}\) Thus, in this paper, the double layered porosity-graded LNMO cathodes are investigated both experimentally and numerically to mitigate cell degradation. Furthermore, we adopt Elitist Non-Dominated Sorting Genetic Algorithm (NSGA-II) to demonstrate the porosity-grading as a strategy for mitigating the degradation of batteries.

### Methodologies

**Material synthesis and cell fabrication.—** CR2032 coin cells were fabricated to investigate the LNMO cathode degradation mitigation by adopting porosity-graded structures. Spinel LNMO powders were synthesized by the solid state reaction method.\(^{54-57}\) The chemicals, NiO, MnO\(_2\) and Li\(_2\)CO\(_3\) used in the experiment were from SIGMA-ALDRICH Co., Ltd. Li\(_2\)CO\(_3\), NiO and MnO\(_2\) were mixed with a molar ratio of Li\(_2\)CO\(_3\):NiO:MnO\(_2\) = 1 : 1 : 3. Referring to Figure 1, precursors were initially ground for 30 minutes in a ceramic mortar inside the glove box filled with Argon gas. Then the SFM-3 High-Speed Vibrating Ball Miller (MTI) was used to mix the chemicals for six hours. The mixture was then placed in a crucible and put in a heating oven. In order to shorten the heating process of the mixture, the oven was pre-heated to a temperature of 290 °C before the crucible was placed inside. Subsequently, the mixed precursors were heated up to 900 °C with a heating rate of 15 °C/min. Then the cathode slurry was casted onto Cu foils via the doctor-blade method. The viscous slurries were acquired after the mixture. The cathode slurry was cast using a doctor blade, as the bottom layer with a thickness of 150 μm, on the surface of an Aluminum current collector. This laminate was then dried at 60 °C for 24 hours in the vacuum oven filled with Argon. A hot roller was used to press the bottom layer to 96 μm at 100 °C. Then the cathode slurry was casted on the surface of the bottom layer with a thickness of 80 μm. Then the laminate was dried at 70 °C for 24 hours in the vacuum oven again. Hot roller was used to press the top layer to 64 μm at 100 °C. The laminates were stored in the glove box and pouches with the diameter of 1/2 inch for cathode. The weights of the electrodes were recorded for the compute of theoretical capacity. Both conventional reference and graded cathodes have a same amount of loading of 2.47 × 10\(^{-3}\) Kg LNMO. The conventional reference LNMO cathode has a uniform porosity of 25.6%, while the graded cathodes has its top-layer porosity around 34% and bottom-layer porosity around 23%. Due to the porosity difference in conventional and graded-LNMO cathodes, the thickness is different. The graded-LNMO cathode is 10 μm thicker compared to that of conventional LNMO cathodes of around 156 μm. The cells were assembled in our glove box (VTI) filled with argon. Due to lacking of electrolytes working in a high operating voltage window, like other LNMO batteries research,\(^{58-60}\) we also adopted a conventional electrolyte solution. The electrolyte used in the LIB was 1 mol/L LiPF\(_6\) (EC : DMC : DEC = 4 : 3 : 3). Although the adopted conventional electrolyte will breakdown at high voltages, research shows that either first a few of tens’ cycles or low C-rate cycling has less degradation or better rate capacity.\(^{61,62}\) Thus, we limit all tests to 50 cycles with a small C-rate to mitigate the degradation from electrolyte oxidation and decomposition at high voltages. Graphite was used as the anode in both conventional- and porosity-graded full cell tests. The graphite anodes consists of 87 : 5 : 8 wt% of conductive graphite, acetylene back, and PVDF. Each electrode material was mixed with NMP to form anode slurry. Then, the slurry was coated onto Cu foils via the doctor-blade method. The doctor blade was set for a height of 280 μm. The laminate was dried at 60 °C for 24 hours in the vacuum oven filled with Argon gas. Then the laminate was pressed to 180 μm at 100 °C. The porosity of the graphite is estimated in the range of 20−40%. All anodes used in the tests follow the same fabrication procedure mentioned above. Thus, any changes in cell performance may solely come from the cathodes.

**Experimental analysis and testing.—** The X-ray powder diffraction (XRD) measurement using Cu Ka radiation was performed to confirm the crystalline phase of the synthesized LNMO. The analysis
was carried out by a Bruker SMART APEX diffractometer. The scan range is $0 < 2\theta < 80^\circ$, and a step of 0.05°/min was used. Then the particle size and morphology of the electrode were observed by scanning electron microscope (SEM) with an accelerating voltage of 10 kV. SEM images were also used to estimate the porosity of the electrode using image processing tools in ImageJ (i.e., an open source image processing code). Also, the porosity of the cathode was measured using a porosity analyzer from Quantachrome Instruments. The as-fabricated cathode was taken off from the current collector and put in a glass cell. The cell was placed in the porosity analyzer. The test results would be the pore volume of the material, and the porosity was calculated by dividing the pore volume by the sample volume. Furthermore, energy dispersive spectroscopy (EDS) was employed to identify the chemical composition of the electrode. Both full- and half-cells were fabricated and tested. Graphite was adopted as the anode for constructing full-cells. Also, lithium metal was used instead of graphite in all half-cell tests. Electrochemical cycling was performed using CR2032 coin cell at room temperature. The LNMO half cells were charged and discharged between 3.7 V to 4.7 V using a Xinwei cycler. The LNMO full cells were cycled with a voltage window between 4.2 V to 5.2 V. The C-rate used initially in the test was C/20 for both half-cell and full-cell. C/10 was used as the charging and discharging C-rate after the first five cycles. Also, cyclic voltammetry (CV) tests were performed in the voltage window of 3.3 – 5.0 V at a scanning rate of 5 mV/s. Furthermore, electrochemical impedance spectroscopy (EIS) was carried out using a LNMO cathode deployed in the CR2032 coin cell with three-electrode structure. The EIS measurements were recorded by an electrochemical workstation (CHI760E, CH Instruments, Austin, TX) over the frequency range of 0.1 Hz–100 kHz at full discharge state. The measurement voltage amplitude was fixed at 10 mV. Furthermore, transmission electron microscopy (TEM) was utilized to visualize and measure SEI layer. The detail of TEM sample preparation can be found in our previous paper.25

Results and Discussion

SEM image of as-fabricated LNMO cathode is shown in Figure 2a, where fine secondary particles with agglomerate structure are observed. The crystal structure of the synthesized LNMO is investigated by XRD, as shown in Figure 2b, where the red bar is the standard reference for LiNi0.5Mn1.5O4. Based on the XRD spectrum, we can conclude that the synthesized material has a single phase of LiNi0.5Mn1.5O4. All peaks appeared in the XRD spectrum are sharp, which indicates a high crystallinity of the synthesized powder. The Miller index for each peak is determined based on a spinel structure having Fd-3m space group. There is a small peak shift around 68°, which may be due to the occurrence of strain or suggest a solid-solution behavior.63 CR2032 coin cells are assembled with Li metal as counter electrodes to evaluate the electrochemical performance (e.g., testing specific capacity). As shown in Figure 2c, the as-fabricated LNMO cathode shows a specific capacity of 143 mAh/g. The CV test confirms (see Figure 2d) that two voltage plateaus are shown at around 4 V and in the region of 4.7–4.9 V, which are attributed to the redox processes of Ni3+/Ni2+ and Mn3+/Mn4+ couples of Mn3+ impurities. Also, the CV test confirms that the synthesized LNMO is dominant by Fd-3m space group due to the oxidation peak splitting into two separated peaks around 4.7 V. The two separated peaks are originated from the voltage difference between Ni3+/Ni2+ and Ni3+/Ni4+ couples, which are enhanced in the nonstoichiometric spinel.64

The morphological and structural features of synthesized LNMO cathode are characterized by SEM and pore size analyzer, which are presented in Figure 3. Figure 3a shows a top view, and Figure 3b shows a cross-section view of the as-fabricated porosity-graded cathode. Figure 3b shows the SEM results and porosity measurement of the top- and bottom layers, respectively. The open-source code ImageJ is used to measure the porosities. The porosity of the top layer is around 34%, and the porosity of the bottom layer is around layer is around 23%. These numbers may vary due to the inherent limitation of 2D

Figure 2. Material characterization, electrochemical testing, and imaging of synthesized LNMO cathode powder, (a) SEM image of as-fabricated LNMO cathode powder, where fine particle were observed, (b) The XRD result with a scan range $0 < 2\theta < 80^\circ$ was used to confirm the LNMO, (c) Charge-discharge curves of synthesized LNMO at a current of C/7 shows a specific capacity of 143 mAh/g, and (d) CV curves of synthesized LNMO scanned at 5 mV/s.
Figure 3. LNMO porosity-graded cathode SEM images of (a) top view, (b) cross-section view, and (c) Porosity was also directly measured by using pore size analyzer and SEM image for pore measurement. Also, plot (a) show the SEM results and porosity analysis of the top layer and bottom layer, respectively. ImageJ was used to measure the porosities. (d) EDS mapping showing elements distribution.
for 50 cycles to minimize the capacity fade due to a high operating voltage which confirms that the porosity-graded full cell improves the performance difference between the top- and bottom layers is in a range of less than 10%. Energy dispersive spectrometry (EDS) mapping analysis confirms that the porosity of the top layer is larger than that of the bottom layer. In order to quantify the sensitivity of porosity measurement, a 3D porous structure. However, the results can confirm that the porosity of the top layer is larger than that of the bottom layer. In order to quantify the sensitivity of porosity measurement, we further utilize a pore size analyzer from Quantachrome Instruments to measure the porosities in 3D, as shown in Figure 3c. In addition to SEM imaging of manual pore size measurement and 2D ImageJ measurements, the pore size analyzer confirms that the porosity difference between the top- and bottom layers is in a range of less than 10%. Energy dispersive spectrometry (EDS) mapping analysis (Figure 3d) indicates that Ni and Mn are homogeneously distributed in the cathode.

Figure 4 shows the capacity drop during cycling for both half- and full cells. The LNMO half cells are charged and discharged between 3.7 V to 4.7 V using a Xinwei cycler. The LNMO full cells are cycled within a voltage window between 4.2 V to 5.2 V. The results shown herein are the averaged tests of three cells made in the same batch. Error bars for the minimum and maximum values are included in all plots in both figures. All three tests of porosity-graded half cells are very consistent, which makes the error bar less visible.

Figure 4. LNMO porosity-graded cathodes capacity losses are reduced in both (a) half-cells (LNMO/Li-metal) and (b) full cells (LNMO/Graphite) after adopting graded porosities. The data are the averaged tests of three cells made in the same batch. Error bars for the minimum and maximum values are included in all plots in both figures. All three tests of porosity-graded half cells are very consistent, which makes the error bar less visible.

The side reaction product protons comes from the SEI layer growth. The capacity of the conventional cell drops faster than double-layered cell at the beginning of the test in Figure 4. Since the SEI layer formation is during the first several charging and discharging cycles. The battery performance improvement can be related to the SEI formation. Comparing with single layer electrode, the results show that the porosity-graded LNMO cathode reduced the capacity fade about 8.285% in full cells and 5.29% in half-cells, respectively.

Electrochemical Impedance Spectroscopy (EIS) tests are done using conventional- and porosity-graded LNMO cathodes deployed in the CR2032 coin cell with three-electrode structure, which is shown in Figure 5. The electroplating is found when placing the graphite anode in the coin cell negative case. After cell assembled in the common procedure, there is a distance between graphite electrode and the coin cell negative case due to the spacer and wave spring. During charging, the potential of the coin cell negative case is slightly lower than the potential of the graphite anode. Therefore, it’s likely for lithium ions to get electrons from the coin cell negative case instead of the graphite anode. As we predicted, lithium plating is found on both the wave spring and coin cell negative case in experiments. By switching the positions of the electrodes, the lithium deposition on the negative case can be avoided. In order to avoid the electroplating effect, the anode is placed in the coin cell positive case, and the cathode is placed into the coin cell negative case. The schematic of the three-electrode cell is shown in Figure 5a. The assembling process of the three-electrode coin cell is carried out in the glove box filled with argon. A piece of lithium metal is pressed on the Cu strip. The Cu strip is wrapped by the separator to prevent the strip from touching the coin cell case. The Nyquist impedance plots show that porosity-grades structure changes the ratio of the electron-transfer rate constant and diffusion coefficient, which agrees with previous EIS electrode/electrolyte interface studies. Furthermore, we investigate the effects of porosity grading on battery degradation mitigation occurring at the electrolyte/electrode interface. The impedance spectra were evaluated by fitting the impedance data with the equivalent circuit shown in Figure 5d. The equivalent circuit consists of an electrolyte resistance (Rₑ) in series with an electrode element consisting of an interfacial resistance (Rᵢ), a charge transfer resistance (Rₓ) and a constant phase element (CPE). The CPE has an impedance $Z_{CPE} = 1/(çjω)^α$, where $α = 1$ reflects a perfect capacitance, while lower values can be the result of roughness or non-ideality in the electrode geometry. Fitted curves for tested cells are provided in Figures 5b and 5c, which capture the depressed semi-circles and diffusion tails. In addition to the obvious reduction in both $Rᵢ$ and $Rₓ$, utilizing EIS analytical equations proposed in the study, the ratio between electron-transfer rate constant and diffusion coefficient (i.e., $k/D^{0.5}$) is increased up to 10$^3$ after adopting the porosity-graded design.

Furthermore, we carried out numerical simulation for battery degradation analysis and optimization. Our comprehensive battery degradation model is adopted herein. The detail of this model can be found in our previous papers. The modeling equations, simulation parameters are provided in the appendix (i.e., Tables A1–A4). The comprehensive degradations are considered by taking account of several major side reactions. These reactions occur in both electrodes. In anode, SEI growth, manganese deposition, and reduction of $H^+$ are generated as a result of solvent oxidation and salt decomposition) are the main side reactions. As SEI grows thicker, the side reaction rate is slowing down because the electrolyte needs diffuse through the thicker SEI to reach the graphite surface. A decay function $exp(-λδ)$ is applied to approximate the decaying growth rate with respect to the thickness of the SEI. In cathode, SEI layer formation, dissolution of manganese, solvent oxidation, and salt decomposition are the main side reactions. The side reaction product protons $H^+$ coming from electrolyte oxidation and $LiPF₆$ decomposition on the cathode surface, which cause manganese dissolution. $Mn^{2+}$ and $H₂O$ are generated as a result of these reactions. The dissolution of manganese plays a key role in cathode capacity fading because of the active material loss, resistance increase, particle structure distortion, and isolation. Figure 6 show calibration and validation of our battery model. Figure 6a and 6b show...
Figure 5. (a) Three-electrode coin cell assembly for EIS measurement, where Li metal serves as a reference electrode, EIS tests of LNMO (b) conventional full cell, (c) porosity-graded full cell, where black dots present experimental data and blue lines are fitting curves, and (d) equivalent circuit for data fitting blue curves in plots (b) and (c), where $R_{e}$ represents electrolyte resistance, $R_{i}$ represents interfacial resistance, $R_{ct}$ represents charge transfer resistance, $CPE_{i}$ is interfacial constant phase element (CPE), $CPE_{ct}$ is interfacial CPE, and $CPE_{g}$ is cell CPE.

Figure 6. Experimental validation and model calibration (a) capacity loss for conventional single-layer cells vs. numerical simulation, where the experimental data are averaged over three sets of tests including error bars, (b) capacity loss for double-layered porosity-graded cells vs. numerical simulation, where the experimental data are averaged over three sets of tests including error bars, The averaged experimental results are plotted with the error bars. Compared with single-layer cells’ tests, the double layer design shows higher capacity at the end of 50 cycles test. (c) cathode SEI layer thickness simulation calibrated by TEM imaging measurement, where the TEM image included showing the SEI layer thickness near the area between current collector and cathode, and (d) Mn deposition layer numerical and experimental investigations, where the SEM images showing the imaged top- and cross-section areas and EDS confirming Mn deposition and thickness above the anode.

That the discharge capacity of the porosity-graded and conventional battery cells are measured during the 0.1 C-rate 50 cycles test. The averaged discharge capacity is presented in solid lines, and error bars are also plotted. We can see from the plots that the capacity decreases over cycles are nonlinear in both cells. The capacity loss at 50 cycles is 35% and 29% for single-layer and double-layer cells, respectively. The porosity-graded cells are 8% higher capacity retention after 50 cycles than the conventional battery cells. The simulation result in
red lines agrees with the experimental results overall. Figures 6c and 6d show the simulation and experimental results of SEI layer growth in LNMO cathode. The TEM image shows the SEI layer formation around cathode/current collector see Figure 6c. Utilized the calibrated SEI kinetic reaction rate, our simulation shows that the SEI thickness is around 20 nm near the current collector and 120 nm around the SEI kinetic reaction rate, our simulation shows that the SEI thickness around cathode/current collector see Figure 6c. Utilized the calibrated in LNMO cathode. The TEM image shows the SEI layer formation near the anode/separator interface due to higher electron current density faster near the anode/separat

Figure 7. Schematic diagrams of LNMO cathodes used in the study. Plots (a) and (b) show the conventional cathode and porosity graded cathode, respectively. SEI layer grows uniformly along the anode thickness direction. It grows

Maximize specific energy

$$\text{Max} \left\{ E_{\text{cell}} = \frac{1}{M_e} \int_{t=0}^{\text{Discharge time}} \int U(t) \, dt \right\}$$

Design variable $x$ subject to $x_{\text{lower}} < x < x_{\text{upper}}$

where $C_a$ and $C_i$ are the capacity in the $n^{th}$ cycle and initial, and $M_e$ is the mass of the active material of cathode. The NSGA-II further helps us to explore performance improvement by changing the porosity/loading of LNMO cells. Figure 8 shows multi-objective optimization stops and gives Pareto-optimal solutions.

Utilizing validated battery model, Elitist Non-Dominated Sorting Genetic Algorithm (NSGA-II) is adopted to optimize design of porosity-graded battery cells. The details of this algorithm can be found in our previous study. In summary, the optimization algorithm is listed in five steps.

Step 1, NSGA-II starts by randomly generating the parent population $P_i$ with size $N$ among all the possible decision variables $x$. Then, the offspring population $Q_i$ is generated from the $P_i$ with the same size $N$.

Step 2, combining $P_i$ and $Q_i$ together to form a population $R_i$ with size $2N$. $R_i$ is evaluated by a non-dominated sorting, which is an algorithm that sorts a population into an ascending level of non-dominance.

Step 3, the solution of the non-dominated sorting forms the new parent population $P_{i+1}$ with the size of $N$.

Step 4, an offspring population $Q_{i+1}$ is created from $P_{i+1}$ by using the elite-preserving operators like, crowded tournament selection, crossover and mutation to keep the diversity.

Step 5, repeating Step 2 to Step 4 until the stopping criterions of maximum generations and function tolerance are satisfied. Then, the optimization stops and gives Pareto-optimal solutions.

The NSGA-II adjusts design variables based on these feedbacks and optimization objectives. The objectives are defined as below in Equations 1 and 2. The design variable $x$ in Equation 3 includes both porosity and thickness for in top and bottom layers of porosity-graded cathodes. Porosity is chosen from the range of 15% to 45%; thickness is the range of 10 μm to 100 μm.

Minimize capacity loss

$$\text{Min} \{ C_{\text{Loss}} = (C_n - C_i)/C_i \} \quad [1]$$

Maximize specific energy

$$\text{Max} \left\{ E_{\text{cell}} = \frac{1}{M_e} \int_{t=0}^{\text{Discharge time}} \int U(t) \, dt \right\} \quad [2]$$

Design variable $x$ subject to $x_{\text{lower}} < x < x_{\text{upper}} \quad [3]$

In this work, porosity-graded electrodes are designed to mitigate the LNMO degradation. The LNMO was synthesized by solid-state reaction. X-ray powder diffraction (XRD) experiment was applied to confirm the crystal structure of the LNMO. Scanning electron microscope (SEM) experiment was used to observe and measure the

Conclusions

In this work, porosity-graded electrodes are designed to mitigate the LNMO degradation. The LNMO was synthesized by solid-state reaction. X-ray powder diffraction (XRD) experiment was applied to confirm the crystal structure of the LNMO. Scanning electron microscope (SEM) experiment was used to observe and measure the
porosities in the electrode. A double-layered porosity-graded electrode with different porosities was fabricated and compared with conventional single-layer electrode during tests. The increase in porosity can improve the conductivity and diffusivity of lithium-ions through the electrode. Also, SEI growth is location dependent due to its growth related to the electron current flow and lithium-ion diffusion. The test results showed, compared with conventional cells, the double-layer porosity-graded LNMO cells reduced the capacity fade about 8.285% in full cells and 5.29% in half-cells. Also, EIS tests show that the ratio between electron-transfer rate constant and diffusion coefficient is increased up to 10^3 after adopting the porosity-graded design. Moreover, Elitist Non-Dominated Sorting Genetic Algorithm (NSGA-II) is applied to optimize the design of porosity-graded battery cells. Multi-objective (i.e., large specific energy and less capacity loss) optimization solutions are obtained battery porosity-grading optimization. However, as shown in Figure A1 in the Appendix, there is certain mechanism leading to the variation between both conventional and graded LNMO cathodes during battery charging and discharging, particularly at above 2 C, which is unclear. We are currently carrying out more experiments. Also, we are further testing of changing the porosity of conventional cell to explore if there is a point at which a constant porosity in a conventional case beats a graded cathode or reduces the improvement seen with graded cathodes. More experimental tests on furthering validating the optimization results are ongoing in our group to further investigate this matter.

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Appendix

**Table A1. A summary of equations of battery model.**

| Governor equation | Boundary conditions |
|-------------------|---------------------|
| **Mass balance**  |                                 |
| \( \frac{\partial c}{\partial t} = \frac{D_i}{\partial x} \left( \frac{\partial c}{\partial x} \right) \) |                                 |
| \( \frac{\partial c_{Li}}{\partial t} = \frac{D_{Li}}{\partial x} \left( \frac{\partial c_{Li}}{\partial x} \right) + \frac{1}{\rho} j_{loc} \) (Anode) |                                 |
| \( \frac{\partial c_{Mn}}{\partial t} = \frac{D_{Mn}}{\partial x} \left( \frac{\partial c_{Mn}}{\partial x} \right) + \frac{1}{\rho} j_{loc} + \frac{2c_{Li}j_{loc}}{F} \) (Cathode) |                                 |
| **Charge balance** |                                 |
| \( \frac{\partial j}{\partial t} = \frac{\partial j^{eff}}{\partial x} \left( \frac{\partial c_{Li}}{\partial x} \right) + j_{loc} = 0 \) |                                 |
| \( \frac{\partial j^{eff}}{\partial x} = \frac{2}{\rho} \left( k_1 \frac{\partial c_{Li}}{\partial x} \right) - \frac{2}{\rho} \left( k_2 \frac{\partial c_{Mn}}{\partial x} \right) \) |                                 |
| **Electrochemical kinetics** |                                 |
| \( j_{loc} = a_{Li} \left[ \exp \left( \frac{\nu_{Li}}{RT} \phi_1 - \phi_2 - U_a - \frac{R_T}{\rho} j_{loc} \right) \right] \exp \left( - \frac{\nu_{Li}}{RT} \left( \phi_1 - \phi_2 - U_a - \frac{R_T}{\rho} j_{loc} \right) \right) \) |                                 |
| \( i_0 = F k_{cat} \frac{\alpha_i}{\rho} (c_{1,max} - c_{1,i}) \) |                                 |
| **SOC calculation** |                                 |
| Cathode: \( SOC = \frac{c_{Li}}{c_{Li,max}} \) |                                 |
| Anode: \( SOC = \frac{c_{Li}}{c_{Li,max}} \) |                                 |

**Figure 8.** Eighteen sets are obtained from NSGA-II optimization with the population size of 50 and generation size of 50. The result of optimization is plotted in bar chart (specific energy) and line chart (capacity loss). The design parameters of porosity and thickness are listed under each optimization solution, where \( L_{top} \) and \( t_{top} \) represent the thickness and porosity of the top layer, \( L_{bot} \) and \( t_{bot} \) represent the bottom layer thickness and porosity, respectively.
Table AII. A summary of equations of side reactions.

\[ \frac{dh}{dt} = \frac{\dot{\rho}}{\rho} \left( D_{H^2}^{\text{eff}} \frac{\partial^2 \rho}{\partial x^2} \right) - \frac{1}{\rho} \frac{\partial j_{\text{salt}}}{\partial x} \]

**Side reactions in anode**

SEI side reaction rate

\[ i_{\text{SEI}} = -\exp(-\lambda_{\text{SEI}} b) F k_{\text{SEI}} e^{-\frac{\phi - \phi_0}{2}} \exp \left[ \frac{q \cdot \varepsilon_{\text{SEI}} F}{R T} \left( \phi_1 - \phi_2 - \frac{R T}{q} j_{\text{loc}} \right) \right] \]

SEI layer growth rate

\[ \frac{dh}{dt} = -\frac{\varepsilon_{\text{SEI}} F k_{\text{SEI}}}{\varepsilon_{\text{SEI}}} \frac{\dot{\rho}}{\rho} \]

SEI layer resistance

\[ R_{\text{SEI}} = k_{\text{SEI}} \]

Manganese deposition

\[ i_{\text{Mn, dep}} = -e^{-\lambda_{\text{Mn, dep}} k_{\text{Mn, dep}}} F k_{\text{Mn, dep}} c_{\text{Mn, dep}} e^{-\frac{\phi - \phi_0}{2}} \exp \left[ -\frac{2 n_{\text{Mn, dep}} F}{R T} (\phi_1 - \phi_2) \right] \]

\[ i_{\text{H_2}} = -e^{-\lambda_{\text{H_2}}} F k_{\text{H_2}} c_{\text{H_2}} e^{-\frac{\phi - \phi_0}{2}} \exp \left[ -\frac{2 n_{\text{H_2}} F}{R T} (\phi_1 - \phi_2) \right] \]

**Side reactions in cathode**

Solvent oxidation

\[ j_{\text{oxid}} = \alpha_{\text{o}} d_{\text{o}} \exp \left[ \frac{q \cdot \varepsilon_{\text{OX}} F}{R T} (\phi_1 - \phi_2 - U_{\text{eq}}) \right] \]

Proton generation

\[ j_{\text{H_2}} = \alpha_{\text{f}} d_{\text{f}} \exp \left[ \frac{q \cdot \varepsilon_{\text{F}} F}{R T} (\phi_1 - \phi_2 - U_{\text{eq}}) \right] \]

Manganese dissolution

\[ i_{\text{Mn, diss}} = i_{\text{Mn, diss}} \cdot F k_{\text{Mn, diss}} c_{\text{Mn, diss}} e^{-\frac{\phi - \phi_0}{2}} \exp \left[ -\frac{2 n_{\text{Mn, diss}} F}{R T} (\phi_1 - \phi_2) \right] \]

**Cathode interface layer formation**

Interface layer growth rate

\[ \frac{dh}{dt} = -\frac{\varepsilon_{\text{cath}} F k_{\text{cath}} e^{-\frac{\phi - \phi_0}{2}}}{\varepsilon_{\text{cath}}} \exp \left[ -\frac{q \cdot \varepsilon_{\text{cath}} F}{R T} (\phi_1 - \phi_2 - U_{\text{eq}}) \right] \]

\[ \frac{dL_{\text{interface}}}{dt} = -k_{\text{interface}} d_{\text{interface}} \]

\[ L_{\text{interface}} = L_{\text{interface}} \cdot e^{-\frac{\phi - \phi_0}{2}} \exp \left[ -\frac{q \cdot \varepsilon_{\text{interface}} F}{R T} (\phi_1 - \phi_2 - U_{\text{eq}}) \right] \]

\[ \frac{dc_{\text{Li}}}{dt} = \frac{k_{\text{Li, cap}}}{d_{\text{Li}}} \]

\[ c_{\text{Li, max}} = c_{\text{Li}} \exp \left( \frac{q \cdot \varepsilon_{\text{Li}} F}{R T} (\phi_1 - \phi_2 - U_{\text{eq}}) \right) \]

Change of volume fraction

Max. concentration of Li per unit electrode volume

Concentration of lithium ion per unit electrode volume

Table AIII. Battery simulation parameters.

| Solid phase Li diffusion coefficient \( D_1 (m^2 s^{-1}) \) | 3.9 \times 10^{-14} | 1 \times 10^{-11} |
| Initial electrode SOC | 0.01 | 0.99 |
| Anode electrode equilibrium potential \( U_{\text{a}} (SOC) \) | 0.036 \cdot SOC^{0.725} |
| Cathode electrode equilibrium potential \( U_{\text{c}} (V) \) | |
| \( U_{\text{a}} (SOC) = 4.8 + 0.1 \cdot \text{tanh}(-4 \cdot \text{SOC} + 8.61) \) | |
| \(-0.03 \cdot (1 - \text{SOC})^{0.835} - 1.5 \) | |
| +0.16 \cdot \exp(0.05 \cdot \text{SOC}^8) +0.81 \cdot (\exp(-40 \cdot (\text{SOC} - 0.13))) | |

\*Calibrated values.
\*From Reference 55.
\*Fitted.

Figure A1. Cell voltage at 1st cycle under 2C charge and discharge.

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### Table AIV. Side reaction parameters.

| Parameter | Value |
|-----------|-------|
| $k_{SEI}$ | $1 \times 10^{-10}$ m$^{-1}$ s$^{-1}$ |
| $a_{SEI}$ | 0.5 |
| $c_{SEI}$ | 5 x $10^{-10}$ mol$^{-1}$ |
| $a_{SEI}^{\text{SEI}}$ | 0.5 |
| $M_{SEI}$ | 0.162 kg mol$^{-1}$ |
| $\rho_{SEI}$ | 1690 kg m$^{-3}$ |
| $k_{\text{SEI, dep}}$ | 1 x $10^{-5}$ m s$^{-1}$ |
| $a_{\text{SEI, dep}}^{\text{SEI}}$ | 0.5 |
| $\lambda_{SEI}$ | 1.0 x $10^{5}$ m$^{-1}$ |
| $k_{i, \text{SEI}}$ | 2.07 x $10^{-8}$ m s$^{-1}$ |
| $\lambda_{\text{SEI, d}}$ | 2 x $10^{-8}$ m s$^{-1}$ |

Calibrated values.

From Reference 55.

### List of Symbols

- $a_{\text{SEI}}^a$: Active surface area per anode electrode unit volume (m$^{-1}$)
- $a_{\text{SEI}}^b$: Active surface area per cathode electrode unit volume (m$^{-1}$)
- $A_{\text{e}}$: Electrode plate area (cm$^2$)
- $c_i$: Concentration in solid phase (mol m$^{-3}$)
- $c_{\text{SEI,max}}$: Maximum concentration of lithium ion per unit cathode electrode volume (mol m$^{-3}$)
- $c_{\text{SEI}}^\text{SEI,max}$: Maximum concentration of lithium ion per unit anode electrode volume (mol m$^{-3}$)
- $c_2$: Concentration in liquid phase (mol m$^{-3}$)
- $c_{\text{SEI, dep}}$: Counter concentration of proton in liquid phase (mol m$^{-3}$)
- $c_{\text{SEI, C}}$: Solvent concentration (mol m$^{-3}$)
- $c_{\text{SEI, O}}$: H$_2$O concentration (mol m$^{-3}$)
- $c_{\text{SEI, Mn$^{2+}$}}$: Manganese$^{2+}$ concentration (mol m$^{-3}$)
- $c_{\text{SEI, Li$^{+}$Pf6}}$: Lithium$^{+}$PF$_6$ concentration (mol m$^{-3}$)
- $C_{\text{cell}}$: Battery capacity loss (Ah)
- $C_{\text{b}, \text{SEI}}$: Current battery capacity (Ah)
- $C_{\text{b}}$: Initial battery capacity (Ah)
- $C_{\text{H}{\text{eff}}}$: Coefficient
- $D_{\text{Li}}$: Diffusion coefficient of lithium species in liquid phase (m$^2$ s$^{-1}$)
- $D_{\text{Li, eff}}$: Diffusion coefficient of lithium species in solid phase (m$^2$ s$^{-1}$)
- $D_{\text{eff, Li}}$: Effective electrolyte phase Li diffusion coefficient (m$^2$ s$^{-1}$)
- $D_{\text{eff, Li, dep}}$: Effective solid phase Li diffusion coefficient (m$^2$ s$^{-1}$)
- $D_{\text{Li, eff}}^{\text{H$^+$}}$: Effective diffusion coefficient of H$^+$ (m$^2$ s$^{-1}$)
- $D_{\text{Li, eff}}^{\text{Mn$^{2+}$}}$: Effective diffusion coefficient of Mn$^{2+}$ (m$^2$ s$^{-1}$)
- $D_{\text{Li, eff}}^{\text{Mn$^{2+}$, dep}}$: Effective diffusion coefficient of Mn$^{2+}$ (m$^2$ s$^{-1}$)
- $D_{\text{Li, eff}}^{\text{H$_2$O}}$: Effective diffusion coefficient of H$_2$O (m$^2$ s$^{-1}$)
- $E_{\text{cell}}$: Specific energy/kWh kg$^{-1}$
- $F$: Faraday’s constant, 96,487 (C mol$^{-1}$)
- $I$: Applied current (A)
- $j_{\text{SEI, eff}}$: Exchange current density of the solvent oxidation reaction (A m$^{-2}$)
- $j_{\text{SEI, dep}}$: Current density of Mn reaction (A m$^{-2}$)
- $j_{\text{SEI, dep}}$: Current density of SEI reaction (A m$^{-2}$)
- $j_{\text{H$_2$}}$: Current density of Mn deposition (A m$^{-2}$)
- $j_{\text{Li$_2$}}$: Current density of H$_2$ generation (A m$^{-2}$)
- $j_{\text{Li$_2$}}$: Current density of solid phase deposition (A m$^{-2}$)
- $j_{\text{Li$_2$}}$: Reaction flux of Mn deposition (mol m$^{-3}$)
- $j_{\text{Li$_2$}}$: Reaction flux of Mn deposition (mol m$^{-3}$)
- $k_{\text{Li$_2$}}$: Reaction flux of salt deposition (mol$^6$ m$^{-3}$ s$^{-1}$)
- $k_{\text{SEI, dep}}$: Reaction coefficient of acid attack on the active material (m s$^{-1}$)
- $K_{\text{eff}}$: Effective solid phase conductivity (S m$^{-1}$)
- $K_{\text{eff}}$: Effective liquid phase conductivity (S m$^{-1}$)
- $k_{\text{H$_2$}}$: Reaction coefficient of H$_2$ generation (m s$^{-1}$)
- $k_{\text{H$_2$}}$: Reaction coefficient of particle isolation coefficient
- $k_{\text{exo}}$: Resistivity of the SEI film (Ω m$^{-1}$)
- $k_{\text{Mn$_2$ dep}}$: Reaction coefficient of Mn deposition (m s$^{-1}$)
- $k_{\text{SEI, C}}$: Reaction coefficient of SEI (m s$^{-1}$)
- $k_{\text{SEI, dep}}$: Reaction rate coefficient of cathode SEI (m s$^{-1}$)
- $k_{\text{SEI, dep}}$: Reaction rate coefficient of interfacial SEI (m s$^{-1}$)
- $k_{\text{SEI, dep}}$: Reaction rate coefficient of cathode SEI (m s$^{-1}$)
- $k_{\text{SEI, dep}}$: Reaction rate coefficient of interfacial SEI (m s$^{-1}$)
- $k_{\text{SEI, dep}}$: Reaction rate coefficient of cathode SEI (m s$^{-1}$)
- $k_{\text{SEI, dep}}$: Reaction rate coefficient of interfacial SEI (m s$^{-1}$)
- $L_{\text{top}}$: Top layer thickness [μm]
- $L_{\text{bot}}$: Bottom layer thickness [μm]
- $L_{\text{C}}$: Cathode thickness [μm]
- $L_{\text{S}}$: Separator thickness [μm]
- $L_{\text{A}}$: Anode thickness [μm]
- $M_{\text{SEI}}$: Mass of cathode (kg)
- $M_{\text{SEI}}$: SEI molar mass (kg mol$^{-1}$)
- $R$: Gas constant (J mol$^{-1}$ K$^{-1}$)
- $\beta_{\text{SEI}}$: SEI resistance (Ω m$^{-2}$)
- $r_{\text{c}}$: Radius of particles
- $\text{SOC}$: State of charge
- $T$: Temperature (K)
- $\nu$: Li transference number
- $\nu$: Time (s)
- $U_{\text{cell}}$: Anode electrode equilibrium potential
- $U_{\text{cell}}$: Cathode electrode equilibrium potential
- $\eta_{\text{eq}}$: Equilibrium potential of solvent oxidation
- $U$: Cell voltage
- $x$: Special variable
- $X$: Battery design variables
- $N_{\text{lower}}$: Lower constraints of the battery design variables
- $N_{\text{upper}}$: Upper constraints of the battery design variables
- $\gamma$: Molar volume of LNMO (m$^3$ mol$^{-1}$)

### Greek Symbols

- $\alpha_{\text{SEI}}$: Cathodic charge transfer coefficient for H$_2$ generation
- $\alpha_{\text{H$_2$}}$: Cathodic charge transfer coefficient for H$_2$ generation
- $\alpha_{\text{Mn$_2$ dep}}$: Cathodic charge transfer coefficient for Mn deposition
- $\alpha_{\text{SEI}}$: Cathodic charge transfer coefficient for SEI formation
- $\alpha_{\text{SEI}}$: Anodic charge transfer coefficient for solvent oxidation
- $\alpha_{\text{SEI}}$: Anodic charge transfer coefficient for lithium intercalation or deintercalation
- $\alpha_{\text{SEI}}$: Cathodic charge transfer coefficient for lithium intercalation or deintercalation
- $\lambda_{\text{eff}}$: Effective solid phase conductivity (S m$^{-1}$)
- $\lambda_{\text{eff}}$: Effective liquid phase conductivity (S m$^{-1}$)
- $\rho_{\text{H$_2$}}$: Solid phase potential (V)
- $\rho_{\text{H$_2$}}$: Liquid phase potential (V)
- $\eta$: Overpotential (V)
- $\delta$: SEI layer thickness (mm)
- $\theta$: Usable active material volume fraction
- $\theta$: Cathode active material volume fraction
- $\theta$: Cathode electrolyte phase volume fraction
- $\theta$: Separator porosity
- $\theta$: Anode active material volume fraction
- $\theta$: Anode electrolyte phase volume fraction
- $\theta$: SEI layer porosity
- $\theta$: Top layer porosity
- $\theta$: Bottom layer porosity
- $\gamma_{\text{Mn$_2$ dep}}$: Limiting coefficient of Mn deposition (m$^{-1}$)
- $\gamma_{\text{SEI}}$: Limiting coefficient of SEI reaction (m$^{-1}$)
- $\gamma_{\text{SEI, C}}$: Limiting coefficient of cathode SEI reaction (m$^{-1}$)
- $\gamma_{\text{H$_2$}}$: Limiting coefficient of H$_2$ generation (m$^{-1}$)
- $\gamma_{\text{SEI}}$: SEI density (kg m$^{-3}$)

### Subscripts

- s: Solid phase
- L: Liquid phase

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