Rechargeable batteries play an increasingly important role as energy-storage devices, especially as power sources for electric vehicles and for stationary storage of intermittent renewable energy. However, significant increase in energy density and reduction in cost is needed for widespread penetration of storage in these applications. The two strategies that are commonly used to improve the energy density (thereby deceasing the cost) are to develop new materials and/or to develop better electrode/battery designs. The former approach has led to a big focus on next-generation cathodes and anodes for Li-ion batteries, and on next generation “beyond Li-ion” systems such as Li-S. The latter approach, wherein new electrode designs are used to improve the energy density/decrease cost, is the focus of this paper.

A main focus of the efforts related to electrode design is on increasing the thickness of the electrode. This has the effect of decreasing the fraction of inactive mass and volume in the cell (current collectors and separators) thereby providing a straightforward method to increase the energy density. However, as the electrode thickness increases, electrolyte-phase mass transfer limitations become more important impeding the power delivery, thereby leading to an inability to satisfy the requirement of the chosen application. This interplay between increasing the energy density and reduction in cost, requires tuning the electrolyte phase limitations in the system. The compromise between increasing the energy while decreasing the polarization from the electrolyte phase requires careful tuning of the porosity and thickness of the electrode. Mathematical models, based on continuum equations, have been used in conjunction with optimization protocols to identify the optimal porosity and thickness to maximize the energy density for a given discharge time. Tiedemann and Newman first illustrated an approach to optimize porous electrodes. The porous model was simplified to obtain an analytical solution and used to identify the optimal design. Over the years, Newman and co-workers removed the simplifications and used a generalized model to optimize different battery systems. In addition to approaches where the optimization is performed manually, optimization algorithms have been coupled with cell physics-based models to optimize over multiple parameters, a more effective approach than manually varying individual parameters. However, it is not clear that these approaches have resulted in any changes in design in commercial batteries, mostly due to the lack of manufacturing methods to fabricate thick electrodes that exhibit the lifetimes needed for most applications.

Recently, new electrode fabrication methods have been proposed that attempt to circumvent the manufacturing challenges with using traditional slot die casting to fabricate thick electrodes. These approaches have proposed to go beyond the basic approach of optimizing the porosity and thickness by focusing on varying the porosity. Such a “gradient porosity” approach is thought to ensure greater access to the electrolyte, thereby allowing higher thickness/loading to increase the energy density without sacrificing power capability.

Model-based optimization methods have been used to examine this approach and quantify the improvements. Ramadasigan et al. reported that a 15–30% reduction in electrolyte resistance was possible when using a varying-porosity design compared to a constant porosity design. Furthermore, Golmon et al. investigated the design optimization of batteries using varying-porosity electrodes. Relative to an initial design with a constant-porosity electrode structure, the optimal, varying-porosity design was demonstrated to improve the discharge capacity by approximately 30% for a half-cell configuration and by 60% for a full cell. These researchers attributed most of the improvement in capacity to the varying-porosity distribution, which reduces the liquid-phase resistance.

However, we note that these studies compare optimized, varying-porosity designs to arbitrarily chosen base case designs. In other words, while the optimization does show improvement in energy density compared to the base case, the studies do not show unequivocally that the increase is caused by the varying porosity. Rather, a simple optimization of the porosity and thickness, without a varying porosity, would also provide an increase in energy density compared to the base case. Varying-porosity electrodes, which are more difficult to manufacture than constant-porosity electrodes, must demonstrate significant improvements to motivate a focus on this topic.

The purpose of this paper is to provide, for the first time, a clear and unambiguous quantification of the improvements of a varying porosity design using a mathematical approach. We achieve this by comparing,
Model Development and Optimization Protocol

Three important aspects comprise the model-based optimization of battery design: the physical battery model and design parameters, objective function definition, and optimization algorithm.

Physical battery model and design parameters.—A pseudo-two-dimensional (P2D) model, based on porous electrode and concentrated solution theory, was implemented as the battery model for this work.7,9,21-26 Previous studies have shown that such a model can predict experimental data adequately.7,9,21,25,26 The model considers physical process changing along the electrode thickness direction of a Li-ion battery as illustrated in Figure 1a and diffusion process in the solid active material, which are coupled together through interfacial reaction. A schematic of the cell modeled is presented in Figure 1b.

The mass balance for Li\(^+\) in the liquid phase electrolyte is given by:

\[
\varepsilon_{i,j} \frac{\partial c_{ce}}{\partial t} = -\nabla \cdot \left( -D_{\text{eff},i,j} \nabla c_{ce} \right) + \frac{1}{F} I_j, \quad j = \text{pos, sep, neg}\]

where \(\varepsilon_{i,j}\) is the porosity in cell component \(j\) (\(j = \text{pos}\) for the positive electrode, \(j = \text{sep}\) for the separator, and \(j = \text{neg}\) for the negative electrode); \(c_{ce}\) is the concentration of Li\(^+\) in the liquid phase electrolyte; \(D_{\text{eff},i,j}\) is the effective diffusivity of Li\(^+\) in the liquid phase electrolyte; \(\sigma\) is the transport number of Li\(^+\); \(F\) is Faraday’s constant; and \(I_j\) is the local reaction current density (A m\(^{-2}\)). At the current collector/electrode interface, the flux of Li\(^+\) in the liquid phase electrolyte is zero. Hence, the boundary conditions for Eq. 1 at the current collector/positive electrode (\(x = 0\)) and current collector/negative electrode (\(x = L_p + L_s + L_n\)) are presented as following:

\[
-D_{\text{eff},\text{pos}} \nabla c_{ce} |_{x=0} = 0 \quad [2]
\]

\[
-D_{\text{eff},\text{neg}} \nabla c_{ce} |_{x=L_p + L_s + L_n} = 0 \quad [3]
\]

At the separator/electrode interface, the flux of Li\(^+\) in the liquid phase electrolyte is continuous. The boundary conditions for Eq. 1 at the separator/positive electrode (\(x = L_p\)) and separator/negative electrode (\(x = L_p + L_s\)) interface are presented as following,

\[
-D_{\text{eff},\text{pos}} \nabla c_{ce} |_{x=L_p} = -D_{\text{eff},\text{neg}} \nabla c_{ce} |_{x=L_p + L_s} \quad [4]
\]

\[
-D_{\text{eff},\text{neg}} \nabla c_{ce} |_{x=L_p} = -D_{\text{eff},\text{pos}} \nabla c_{ce} |_{x=L_p + L_s} \quad [5]
\]

where superscripts (+ and −) denote the left and right side of interfaces, respectively.

The potential in the solid phase, \(\phi\), is given by:

\[
\nabla \cdot (-\sigma_{\text{eff},j} \nabla \phi_j) = -I_j, \quad j = \text{pos, neg}\]

where \(\sigma_{\text{eff},j}\) is the effective electronic conductivity in the solid phase. At the current collector/electrode interface, the entire current is carried by the solid phase. The boundary condition for Eq. 6 at the current collector/positive electrode (\(x = 0\)) is presented as following:

\[
-\sigma_{\text{eff},\text{pos}} \nabla \phi |_{x=0} = I_{\text{app}} \quad [7]
\]

where \(I_{\text{app}}\) is the applied current density, which is positive for charge and negative for discharge. \(\phi\) at the current collector/positive electrode (\(x = L_p + L_s + L_n\)) is selected as the reference point of potential, and is set to zero,

\[
\phi |_{x=L_p + L_s + L_n} = 0 \quad [8]
\]

At the separator/electrode interface, the entire current is carried by the liquid phase. Hence, the solid phase current is zero at the separator/positive electrode (\(x = L_p\)) and separator/negative electrode (\(x = L_p + L_s\)) interface. Hence, the corresponding boundary conditions for Eq. 6 are presented as following,

\[
-\sigma_{\text{eff},\text{pos}} \nabla \phi |_{x=L_p} = 0 \quad [9]
\]

\[
-\sigma_{\text{eff},\text{neg}} \nabla \phi |_{x=L_p + L_s} = 0 \quad [10]
\]

Figure 1. (a) Schematic of a Li-ion battery; (b) Schematic of pseudo-two-dimensional (P2D) Model. This model only considers physical process changing along electrode thickness direction of a Li-ion battery and diffusion process in the solid active material, which are coupled together through the interfacial reaction.
The potential in liquid phase, \( \phi_2 \), is given by,

\[
\nabla \left( k_{eff,f} \nabla \phi_2 - 2 \frac{k_{eff,f}RT}{F} \left( 1 - \frac{\theta_j}{\theta_{max}} \right) \nabla \ln \epsilon_j \right) = I_j, \quad \epsilon_j = \text{constant,} \quad \partial \text{the temperature.}
\]

where \( k_{eff,f} \) is the effective conductivity in the liquid phase, \( R \) is the gas constant, \( T \) is the temperature.

The current in the liquid phase is given by,

\[
i_2 = - \left( k_{eff,f} \nabla \phi_2 - 2 \frac{k_{eff,f}RT}{F} \left( 1 - \frac{\theta_j}{\theta_{max}} \right) \nabla \ln \epsilon_j \right) \]

At the current collector/electrode interface, the entire current is carried by the solid phase and the current should be zero in the liquid phase. The boundary conditions for Eq. 11 at the current collector/positive electrode (\( x = 0 \)) and current collector/negative electrode (\( x = L_p + L_a \)) are presented as follows,

\[
i_2|_{x=0} = 0 \quad \text{[13]} \quad \text{and} \quad i_2|_{x=L_p+L_a} = 0 \quad \text{[14]}
\]

At the separator/electrode interface, the current in the liquid phase is continuous. The boundary conditions for Eq. 11 at the separator/positive electrode (\( x = L_p \)) and separator/negative electrode (\( x = L_p + L_s \)) are presented as follows,

\[
i_2|_{x=L_p} = i_2|_{x=L_p+L_s} \quad \text{[15]} \quad \text{and} \quad i_2|_{x=L_p+L_s} = i_2|_{x=L_p+L_a} \quad \text{[16]}
\]

The local current density, \( I_j \), is zero in the separator; in the positive electrode and negative electrode this is described by,

\[
I_j = a_j \gamma_j, \quad j = pos, \ neg \quad \text{[17]}
\]

where \( a_j \) is the specific surface area for the \( Li^+ \) insertion/deinsertion reaction and is defined as,

\[
a_j = \frac{3 \varepsilon_{1,j}}{R_{eff,j}} \quad \text{[18]}
\]

where \( \varepsilon_{1,j} \) is the volume fraction of the particles in region \( j \) and \( R_{eff,j} \) is the radius of the particle. \( i_j \) is the transfer current of the \( Li^+ \) insertion/deinsertion reaction on the surface of a particle and is described by the Butler-Volmer expression as follows:

\[
i_j = i_{0,j} \left[ \exp \left( \frac{a_j \gamma_j F}{RT} \eta_j \right) - \exp \left( - \frac{a_j \gamma_j F}{RT} \eta_j \right) \right] \quad \text{[19]}
\]

where \( i_{0,j} \) is the exchange current density in region \( j \) and is defined as

\[
i_{0,j} = \frac{F k_{Brugg,j} \gamma_j^{0.5} \sigma_{Li,j} \epsilon_{Li,j}^{0.5 \gamma_j} C_{max,j} - C_{surf,j} \epsilon_{Li,j}^{0.5 \gamma_j}}{\epsilon_{Li,j}^{0.5 \gamma_j}} \quad \text{[20]}
\]

where \( k_{Brugg,j} \) is the reaction rate constant, \( \sigma_{Li,j} \) is the surface concentration of \( Li^+ \) on the particles, and \( C_{max,j} \) is the maximum concentration of \( Li^+ \) in the particles. The overpotential in region \( j \) is given by,

\[
\eta_j = \frac{\phi_{j+} - \phi_{j-} - U_j}{\theta_j} \quad \text{[21]}
\]

where \( U_j \) is the open-circuit potential for a particle in region \( j \).

It is assumed that the particles of the active material are spheres. The material balance in the particles is given by:

\[
\frac{\partial \phi_{Li,j}}{\partial t} = - \nabla \cdot J_j, \quad j = pos, \ neg \quad \text{[22]}
\]

with the following two boundary conditions:

\[
J_j|_{t=0} = 0 \quad \text{[23]}
\]

\[
J_j|_{t=R_{pos,j}} = \frac{i_j}{F} \quad \text{[24]}
\]

where

\[
J_j = -D_{eff,j} \nabla c_{Li,j}, \quad j = pos, \ neg \quad \text{[24]}
\]

Here, \( D_{eff,j} \) is the diffusion coefficient in the particles, \( R_{pos,j} \) is the radius of particle and \( c_{Li,j} \) is the \( Li^+ \) concentration in the particles.

In summary, the model is composed of Eqs. 1, 6, 11 and 22 with corresponding boundary conditions.

The cell potential, \( \phi_{cell} \), is defined as,

\[
\phi_{cell} = \phi_{1,neg} - \phi_{1,po} + L_e + L_a \quad \text{[25]}
\]

For the varying porosity design (the graded electrode), we divided the electrodes into several domains, as performed in previous studies. At the interface between two adjacent domains, the flux of \( Li^+ \) and currents in solid and liquid phase are continuous. The corresponding boundary conditions for Eqs. 1, 6 and 11 are presented as following, respectively,

\[
D_{eff,sep,k} \nabla \phi_{Li,j}|_{x=L_k} = -D_{eff,sep,k} \nabla \phi_{Li,j}|_{x=L_{k+1}} \quad \text{[26]}
\]

\[
-\sigma_{eff,k} \nabla \phi_{Li,j}|_{x=L_k} = -\sigma_{eff,k} \nabla \phi_{Li,j}|_{x=L_{k+1}} \quad \text{[27]}
\]

\[
i_2|_{x=L_k} = i_2|_{x=L_{k+1}} \quad \text{[28]}
\]

where \( k \) denotes specific domain of \( k \) in the electrode, \( L_k \) is distance between current collector/electrode interface (\( x = 0 \)) and domain of \( k/k + 1 \) interface.

The effective electronic conductivity in the solid-phase is given by:

\[
\sigma_{eff,j} = \underbrace{Brugg_j}_{\sigma_j} \quad j = pos, \ neg \quad \text{[29]}
\]

where \( Brugg_j \) and \( \sigma_j \) are Bruggeman exponent and bulk electronic conductivity in the solid phase. The effective ionic conductivity and diffusion coefficient in the liquid-phase are given by:

\[
k_{eff,j} = \underbrace{Brugg_j}_{\kappa_j} \quad j = pos, \ neg \quad \text{[30]}
\]

\[
D_{eff,j} = \underbrace{Brugg_j}_{\Gamma_j} \quad j = pos, \ neg \quad \text{[31]}
\]

where \( Brugg_j, \kappa_j \) and \( \Gamma_j \) are Bruggeman exponent, bulk ionic conductivity, bulk diffusion coefficient in the liquid phase electrolyte. The Bruggeman exponent describes the tortuosity of electrode.

The capacity of the negative electrode is always larger than that of the positive electrode for safety and stability in a practical cell design. The capacity ratio between the negative and positive electrode, \( \gamma \), is defined as,

\[
\frac{L_{neg}}{L_{pos}} C_{max,neg} \theta_{max,neg} - \theta_{min,neg} = \frac{L_{pos}}{L_{neg}} C_{max,pos} \theta_{max,pos} - \theta_{min,pos} \quad \text{[32]}
\]

where the dimensionless concentration, \( \theta \), is defined by

\[
\theta = \frac{c_j}{C_{max}} \quad \text{[33]}
\]

\( \theta_{max} \) and \( \theta_{min} \) represent the maximum and minimum dimensionless concentration that \( Li^+ \) can insert into and be extracted from, respectively.

We now discuss the various parameter values used to generate the results shown in the paper. A Li-ion battery with a Li2Mn2O4 cathode, a graphite anode with liquid electrolyte (LiPF6 in a non-aqueous solvent) was used for the optimization study. The model parameters include material (e.g \( C_{max,pos}, C_{max,neg}, R_{pos}, R_{neg} \)), thermodynamic (e.g \( U_{pos}, U_{neg} \)), kinetic (e.g \( k_{li,pos}, k_{li,neg} \)) and transport properties (e.g \( \sigma_{pos}, \sigma_{neg}, brugg_{pos}, brugg_{neg}, \Gamma_j, \kappa_j \)). Some of the parameters used in this paper are from, or close to, those used in the literature for Li2Mn2O4, graphite and liquid electrolyte, which have been validated in the literature by comparing to experimental data.

Of these various parameters, previous studies suggest that the model result is most sensitive to parameters that describe diffusion process in the solid particle and ion transport in the liquid phase.
Moreover, values for those parameters vary as measured in the literature, possibly due to difference in sample and measured method.因此 any design needs to start with this constraint. Thus, the cell energy is defined as

\[ E = \frac{1}{m_{cell}} \int_0^{t_f} V_{cell} I_{app} dt \]  

where \( m_{cell} \) is the cell mass, including that of the active material, electrolyte, separator, additive, and current collector. \( V_{cell} \) is cell potential. \( I_{app} \) is the applied current, which is constant for each discharge time and is varied with the cell design to ensure that the cell reaches the cutoff voltage in the fixed time. The cell output energy density is a monotonically decreasing function of the applied current, assuming that temperature-related effects are unimportant. Thus, \( I_{app} \) can be determined iteratively by monitoring the difference between the simulated discharge time and the required fixed time to reach a specific relative tolerance (e.g., \( \text{tol} = 5\% \)).

**Optimization method.**—In this work, the optimization problem was solved using the direct search method, which is a gradient-free optimization algorithm. Unlike the gradient-based method, the direct search method does not require information about gradients; therefore, the objective function does not need to be continuous, and the algorithm can tolerate computational errors in the simulation. Although the direct search method is computationally expensive for high-order optimization problems, it remains attractive for many applications, especially with the development of parallel and distributed computing. There are two main reasons that a direct search was implemented as the optimization algorithm in this work. First, a unique algorithm was designed to find the optimal current for a fixed discharge time, which resulted in an objective function that was not smooth and continuous as function of design parameters. This function would not be handled properly using the gradient-based method. Second, direct search method does not incur large computational cost for problems with a small number of variables, such as those in this study.

The solution procedure is summarized in Figure 2. The optimization algorithm calls the physical battery model repeatedly to verify whether the objective function has reached the maximum. The optimization was conducted with a battery model solved in Fortran and a pattern search solver in Matlab (Global Optimization Toolbox).

**Results and Discussion**

**Battery chosen for optimization.**—We first demonstrate that the LiMn2O4/graphite cell chosen for study is limited by the liquid phase. Figures 3a and 3b show the rate performance of a cell consisting of 159 μm thick positive electrode with a porosity 0.219, and a 92 μm thick negative electrode with a porosity of 0.208. Figure 3a presents the discharge curves of the cell at different C-rates, with 1C defined as the current necessary to discharge the cell in 1 h before reaching the cutoff voltage. The curves show a decreasing discharge capacity with increasing C-rates. Figure 3b shows the electrolyte-phase Li⁺ concentration across the cell at end of discharge. In the C/10 case, there is enough Li⁺ in the electrolyte at the end of discharge to achieve full

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**Figure 2.** Flow chart of optimization approach.
capacity. In the 3C case, however, the Li\textsuperscript{+} concentration decreases to zero long before the theoretical capacity is reached. This finding suggests that liquid-phase Li\textsuperscript{+} transport is a limiting factor with increasing C-rates, which effectively prevents full utilization of the active material, as illustrated in Figure 3a. This argument is consistent with those discussed in previous work.\textsuperscript{9,11,26} This study strongly proves that the transport process in the liquid phase electrolyte is critical for battery performance, representing an ideal test system to examine the use of optimization protocols and varying the design.

Accuracy of the optimization protocol.— We next illustrate the accuracy of the chosen optimization method by comparing a manual approach, wherein the model is repeatedly executed by varying the design parameters to visually identify the optimal design, to that of the optimization protocol described above. To show the comparison clearly, we present the energy density as function of two design parameters, shown as a contour plot. It should be noted that the primary goal of this section is to demonstrate the accuracy of the optimization protocol; therefore the specific design chosen is not meant to represent a practical design.

Figure 4 shows the specific energy density of the cell as a function of the positive electrode thickness ($L_p$) and porosity ($\varepsilon_{2,\text{pos}}$) for a specific 1-h discharge scenario. The negative electrode porosity ($\varepsilon_{2,\text{neg}}$) is kept constant, while the negative electrode thickness ($L_n$) is varied to maintain a constant $\gamma$. The specific energy density in each contour line was calculated by varying the $L_p$ and $\varepsilon_{2,\text{pos}}$ in the battery model. In the simulation, 91 and 41 points were evenly taken with $L_p$ ranging between 50 $\mu$m and 230 $\mu$m and $\varepsilon_{2,\text{neg}}$ ranging between 0.15 and 0.55.

The plot clearly shows that the cell energy density varies significantly when changing the design parameters. The maximum energy density was visually identified to be ca. 184.2 Wh/kg, with optimum porosity and thickness values of ca. 0.23 and 160 $\mu$m, respectively. It should be noted that the changing the thickness and porosity around the optimal design does not lead to a dramatic decrease in energy density. In other words, the maxima is broad.

Instead of a manual approach, the optimization protocol was used to identify the optimal cell design to maximum the energy density. The positive electrode thickness was constrained between 50 $\mu$m and 250 $\mu$m and the positive porosity between 0.15 and 0.6. Ten different initial conditions were tested; in all cases a maximum energy density of 184.2 Wh/kg was obtained. It is close to the values obtained using the manual approach, showing the accuracy of the optimization protocol. More importantly, this automated optimization approach is needed when considering multiple parameters, wherein the manual approach would be time prohibitive.

Comparison of constant and varying porosity optimized systems.— In this part, we aim to clearly quantify any advantage of a varying porosity design over a constant one, by investigating and comparing the optimal cell design based on two design approaches with the aforementioned optimization algorithm. In a constant-porosity design, $L_p$ and $\varepsilon_{2,\text{pos}}$ as well as $\varepsilon_{2,\text{neg}}$ were used as the design parameters with $L_n$ varying to maintain a constant $\gamma$. In a varying-porosity design, both the positive and negative electrodes are further divided into several domains, each of which may have a different porosity. For simplicity, each electrode was divided into 5 equally thick domains. We also tested 10 domains to ensure that the number of domains did not impact the results. Thus, there are 3 and 11 design parameters for the constant-porosity and varying-porosity designs, respectively. The electrode thickness was constrained between 50 $\mu$m and 250 $\mu$m and the porosity between 0.15 and 0.6.

Figure 5 plots the optimized energy density of these two designs as a function of discharge time, with Figure 5a showing results for specific energy (Wh/kg) and (b) for volumetric energy density (Wh/l). Surprisingly, no obvious difference in energy density is observed between the two designs, both for specific energy and volumetric energy density. For example, the energy density of the varying-porosity design is only 2.8% higher than that of the constant-porosity design even at 10C (6-min discharge) in specific energy and 3.1% better in energy density. This minimal improvement in performance differs from the results of previous studies,\textsuperscript{15,20} which claimed that a varying-porosity design could result in decreased cell ohmic losses and thereby significantly increase the energy density. While such a conclusion is correct...
when comparing the optimized varying porosity system to an arbitrary base-case system, Figure 4 illustrates that this “advantage” becomes negligible when comparing the optimized constant porosity system to that of a varying porosity system. The reason for this minimal improvement lies in the relatively loose dependence of the energy density on the porosity and thickness around the optimal design, as described in Figure 4. In other words, a small variation away from the optimal point does not lead to a dramatic change in energy density. Varying the porosity allows for further fine tuning of the design leading to improvements in energy density, but the bulk of the advantage is already realized with judicious choice of a constant porosity system, therefore, the improvements are negligible.

The conclusion above deviates from studies in the literature. In the work of Ramadesigan et al., the optimal varying-porosity design was reported to decrease the ohmic resistance by 15–30% for a constant active material loading. However, the study kept the thickness a constant, an unwanted constraint of a design parameter that is probably the simplest to vary in a manufacturing setting. Similar thickness invariance was also assumed by work reported in references. Further, Ramadesigan et al. reported liquid-phase potential (φ2) in the optimal case is approximately 0.1 V lower than the base case when used in a constant potential application. Mapping this potential difference onto the energy density, the change in the energy density of a normal 3.7-V battery is only 3%. Golmon et al. also reported an improvement in cell performance using a varying-porosity design relative to a constant-porosity base case. In their optimization, the authors not only allowed the porosity to vary, but the loading of the active material and the average porosity of the electrode was also allowed to change. Hence, not all the improvement in performance was necessarily associated with the varying-porosity. In other words, since the cell performance is highly dependent on the design parameters, as illustrated in Figure 4, if a different constant porosity were selected in the base case, the degree of improvement using the varying-porosity may not have been that large, in accordance with the results reported in this work. In summary, the results in Figure 5 clearly show that the improvement from varying porosity is not significant and that optimal choice of a constant porosity can lead to similar improvements in energy density. Moreover, we note that achieving a constant porosity requires little manufacturing innovation, making it a more straightforward route for high-energy electrodes.

To gain insight into the result shown in Figure 5, more detailed information is now presented. The rest of the discussion is based on specific energy optimization, but the conclusions remain the same for the volumetric energy density maximization. Figures 6a–6c show the optimal values for thickness and loading of active material and porosity profile in the positive electrode for the two design approaches. The negative electrode exhibits a similar trend and is thus not shown here. The thickness and loading profiles are close between the two designs, much like the cell performance, although the porosity profiles are different. As shown in Figures 6a and 6b, the thickness and loading of the active material decreases with decreasing discharging time to ensure maximum energy density is achieved. As illustrated in Figure 3b, this is because Li⁺ cannot be delivered fast enough through the porous electrode at high current, which results in incomplete utilization of active material. Therefore, the maximum energy density of a cell for short-time applications requires a balance between reduced loading of active material and decreased resistance of liquid-phase. Figure 6c shows the detailed porosity profiles for the two designs along the positive electrode for different discharge C-rates. Unlike the constant-porosity design, the porosity is higher near the electrode/separator interface in the varying-porosity design, as reported in previous studies. This becomes more obvious with increasing C-rate. Compared to the constant-porosity design, this design provides more porosity to allow for Li⁺ transport through the front of the electrode. Although the Li⁺ transport distance increases as the active material moves farther from the interface of separator/electrode, improved Li⁺ transport near the interface leads to an overall decrease in resistance, which leads to the improvement associated with the varying-porosity design over the constant-porosity design. However, judicious choice of the constant porosity can provide much of the benefits described above, leading to insignificant improvement in the overall energy density between the two cases.

Next, the internal cell behavior is presented for two different optimal designs for a 1-h discharge. In Figure 7, the normalized volume-averaged Li⁺ concentration in the solid particle (C_{avg}/C_{max}) is plotted along each electrode. The concentration profile as a function of time reveals that the Li⁺ insertion processes of both designs are very similar, consistent with the ability of a judicious choice of constant porosity to offset much of the gains from varying the porosity. Figure 8 shows the deviations of φ2 between the electrode/separator interface and electrode/current collector interface in both the positive and negative electrodes of each design. This deviation is a measure of the liquid phase limitation in the cell. The deviation of φ2 is very similar in the two designs, although the porosity profiles are quite different as presented in Figure 6c. These results show that when optimized correctly, the internal profiles in the battery, which ultimately control the performance, remain the same between a constant porosity design and a varying porosity design. In summary, an optimal constant porosity and a varying porosity allow for an ideal compromise between energy density and polarization losses in a similar fashion. Therefore, no differences are apparent in the liquid phase polarization, in liquidation profiles, and in the energy density of the cell. Considering the difficulty of varying the porosity in present-day manufacturing methods, these results argue that such an approach is not warranted.

It could be argued that while a gradient in porosity does not lead to a significant difference in the volumetric energy density and specific

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Figure 5. Optimization performance for specific energy (Wh/kg) and (b) for volumetric energy density (Wh/l) based on two designs: constant and varying-porosity.
energy, the advantages can become significant during pulse operation. We now briefly examine this scenario. We use a typical testing protocol of EV battery, where the discharge time is 3h, and examine the pulse performance for a 30s pulse at a rate of 2C at 50% SOC (state of charge). First we take the optimized designs of battery for a 3h application from the two cases (constant vs. varying porosity) and discharge each battery at a slow C/10 rate to 50% SOC, then rest the battery for 1h followed by a 2C pulse for 30s operation. Figure 9 shows the results of the simulation for the two designs of battery during the pulse period. Both designs satisfy the requirement for a 30s operation, with the varying porosity design exhibiting a smaller

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**Figure 6.** (a) The thickness and (b) the loading of active material in positive electrode in two different optimal designs (c) Porosity distribution along positive electrode for 1C (black) and 0.2C (red) in the varying-porosity design. Distance = 1 represents the interface of separator/positive electrode.

**Figure 7.** Normalized volume-averaged Li\(^+\) concentration in the solid particle ($C_{s,\text{avg}}/C_{s,\text{max}}$) across the cell: constant-porosity (a) and varying-porosity (b) design. Dimensionless distance of [0 1] is positive electrode region; [1 2] is the separator, and [2 3] is the negative electrode.

**Figure 8.** Deviation of liquid-phase potential (b) at positive (black) and negative (blue) electrodes, that is, their difference between interface of electrode/seperator and electrode/current collector, in constant-porosity (dashed) and varying-porosity (solid) cells.
resistance, consistent with the results reported above. However, the differences are not significant between the two designs, with the varying porosity design resulting in a resistance of $23.9$ $\Omega$-$\text{cm}^2$ vs. $28.1$ $\Omega$-$\text{cm}^2$ for the varying porosity design. In summary, we do not see the varying porosity design being impactful during typical EV pulse operation.

Finally, we show that the conclusions reached above are universal, and not for a specific set of parameters. We illustrate two specific cases in Figures 10a and 10b, where we vary the Bruggeman exponent and the particle size over a wide range to confirm the conclusions of the paper. A larger Bruggeman exponent implies a larger electrolyte transport resistance in porous electrode due to a larger tortuosity. To investigate the diffusion process variation in the solid particle, we vary the characteristic diffusion time, $\tau (\tau = R_s^2/D)$, by changing the radius. A larger particle size implies a larger transport resistance within the active material particles, which is equal to the effect of a smaller diffusion coefficient. Figure 10a summarizes the results for varying Bruggeman exponent and Figure 10b for changing particle size. Here again, the model shows minimal improvement when using a varying porosity electrode compared to a constant porosity electrode, suggesting that a varying porosity design does not provide an improvement over a well-optimized constant porosity design electrode. Moreover, we have checked the generality of the conclusion based on a specific validated set of model parameters in Appendix B. By performing a similar comparison between the two designs, and the lack of a dramatic difference in energy density, we show the generality of the conclusions.

However, Figure 10a shows an extremely important design parameter that can lead to a significant improvement in the performance of the cell, namely the tortuosity, consistent with reports in the literature. The figure shows that decreasing the tortuosity, represented as a decreasing Bruggeman exponent, shows a significant increase in energy density. Decreasing the exponent from 3 to 2 results in a 12% improvement in energy density while going down to an exponent of 1 results in as much as a 25% improvement at a 1C discharge; much more significant than any variation in porosity across the electrode thickness. We suggest that new manufacturing methods focus on this aspect of electrode design.

Conclusions

In this paper we critically examined the advantages of using a porosity gradient within the electrode as a design tool to improve the energy density of batteries. We choose a Li-ion battery with a LiMn$_2$O$_4$ cathode and a graphite anode and develop a mathematical model for the system using the macrohomogeneous approach. We then developed an optimization algorithm that allows identification of the optimal design (porosity and thickness) to maximize the energy density for a given time of discharge. We compared the optimized constant porosity system to that of an optimized varying porosity system, to examine the advantages of the varying porosity approach. Surprisingly, we see little improvement when using a varying porosity design when compared to a constant porosity design. The reason lies in the ability of a well-optimized design to provide the ideal compromise between loading (to increase the energy) and polarization losses (to ensure that the discharge time is achieved). Judicious choice of a constant porosity can compensate for much of the advantages seen when allowing the porosity to vary. This conclusion is true when maximizing specific energy (Wh/kg) and volumetric energy density (Wh/l) and is not dependent on the properties used for the simulations. By comparing the concentration profiles in the electrode, and the potential drop in the electrolyte phase between the two designs, we show that indeed, the two optimized designs show very similar behavior. Considering the manufacturing challenges associated with varying the porosity, we argue for a more careful examination of the impact of this design. We suggest that focusing on decreasing the tortuosity would be a promising approach, wherein significant improvement in energy density of cell level can be realized.

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Appendix A

Parameters.—The concentration-dependent ionic conductivity and the diffusion coefficient in the electrolyte are given by,

\[ \kappa = 10^{-4} \times c_{eq} \left( -10.5 + 0.668 \times 10^{-3}c_{eq} + 0.494 \times 10^{-6}c_{eq}^2 + 0.0747T \right) \] \[ + 2.80 \times 10^{-4}c_{eq}T^2 \] \[ [A1] \]

for \( c_{eq} < C_{eq} \) (\( 4500 \) mol/m\(^3\)).

\[ D_s = 10^{-4} \times 10^{-4.43 - \frac{54}{T - 229.35 \times 10^{-0.365}} - 0.22 \times 10^{-0.365}c_{eq} \] \[ [A2] \]

Because conductivity in Eq. (A1) increases at high concentrations (>4500 mol/m\(^3\)), a different function that remains a constant conductivity after \( c_{eq} \geq 4500 \) mol/m\(^3\) is used. A corresponding change on diffusion coefficient is also made. No salt precipitation at high concentrations is included in this work.

The open-circuit potentials for the LiMn\(_2\)O\(_4\) positive electrode as functions of the SOC are given by:

\[ U_{soc} = 4.19829 + 0.056561 \ln(1 - 14.5546/\theta_{soc} + 8.60492) \]

\[ - 0.0275479 \left( \frac{0.998432 - \theta_{soc}}{1 - 0.99111} \right) \]

\[ - 0.157123 \exp \left( -0.047380/\theta_{soc} \right) + 0.810239 \exp \left( -40 \left( \theta_{soc} - 0.133875 \right) \right) \] \[ [A5] \]

The open-circuit potentials of the graphite negative electrode as functions of the SOC are given by:

\[ U_{soc} = 0.7222 + 0.138688/\theta_{soc} + 0.028952/\theta_{soc}^{1.5} - 0.017189/\theta_{soc} + 0.0019144/\theta_{soc}^{1.5} \]

\[ + 0.28082\exp(15(0.06 - \theta_{soc})) - 0.79844\exp(0.44649(\theta_{soc} - 0.92)) \] \[ [A6] \]

Appendix B

In order to prove the conclusion is general and realistic, we provide an example in Appendix B by applying a specific validated set of model parameters to investigate the battery performance with two designs: constant and varying porosity design. First, we validate the model by comparing the model prediction with experimental rate performance data in Ref. 44. The rate performance data is generally used to validate the model, because it covers different rate-determining steps for battery performance, such as ionic transport in solid particle and in the electrolyte solutions. As shown in Figure B1a, the model prediction agrees well with experimental data in different C-rates. This proves the validity of model parameters. The model parameters used to generate this simulations are the same as those listed in Tables A1 and AII, except for the ones listed in Table B1. Most of the parameters in Table B1 are design specific parameters taken from Ref. 44. Three material specific parameters were changed compared to Tables I and II, namely, the solid concentration and the solid diffusion coefficient in the positive, the solid diffusion coefficient in the negative, and the Bruggeman exponent. This is because the specific materials and electrode designs used in Refs. 27 and 28 are different from the ones used in this study.

In Figure 10 we explore the effect of changes to these properties to show the generality of the conclusion. It should be noted that the parameters used here are close to the investigated range in Figure 10. For example, the Bruggeman exponent of 3 used here is within the investigated range in Figure 10, which is between 1 and 3. The characteristic diffusion time (\( \tau = R_s/\sqrt{D_e} \)) is 117.8s and 500.0s for LiMn\(_2\)O\(_4\) and graphite, respectively. These are around the investigated range of [5.35s to 434s] (and 668s to 7030s) for LiMn\(_2\)O\(_4\) and graphite in Figure 10, respectively.

Figure B1b presents the results with validated parameters. Consistent with results in Figures 5 and 10, the model shows minimal improvement when using a varying porosity electrode compared to a constant porosity electrode. This suggests that the result is general, and not dependent on the choice of specific parameters and hence specific samples.

| Table II. Model Parameters. |
|-----------------------------|
| Parameters                  | LiMn\(_2\)O\(_4\) | Separator | Graphite |
| \( L_e \) (m)               | 7.5 \times 10^{-6} | -         | 5 \times 10^{-6} |
| \( \rho_e \) (g/cm\(^3\))   | 2.7\(^e\)         | -         | 8.9\(^e\) |
| \( \sigma \) (S m\(^{-1}\)) | 10\(^f\)          | -         | 10\(^f\) |
| Brugg\(_1\)                 | 1.0\(^f\)         | -         | 1.0\(^f\) |
| Brugg\(_2\)                 | 2.0\(^i\)         | 1.5\(^i\) | 2.0\(^i\) |
| Thickness (um)              | -                 | 25\(^d\)  | -         |
| porosity                    | 0.724\(^e\)       | -         | 0.032\(^e\) |

| Parameters                  | LiMn\(_2\)O\(_4\) | Separator | Graphite |
|----------------------------|------------------|------------|----------|
| \( F \) (C equiv\(^{-1}\)) | 96487            | -          | -        |
| \( R \) (J mol\(^{-1}\) K\(^{-1}\)) | 8,314          | -          | 298,15   |

\(^a\) Obtained from Ref. 26.  \(^b\) Assumed.  \(^c\) Obtained from Table I.  \(^d\) Obtained from Ref. 8.  \(^e\) Obtained from Ref. 43.

| Table B1. Validated Model Parameters. |
|-------------------------------------|
| Parameters                  | Value |
|----------------------------|------|
| Thickness (um)              | 57.5 \times 10^{-6}a | 55 \times 10^{-6}a |
| \( R_e \) (m)               | 8 \times 10^{-6}a | 10 \times 10^{-6}a |
| porosity                    | 0.35\(^a\)          | 0.46          |
| Volume fraction of active material | 0.62\(^b\) | 0.50\(^b\) |
| \( \theta_{soc} \)          | 0.3\(^b\)          | 0.65\(^b\) |
| Brugg\(_2\)                 | 3.0\(^c\)          | -            |
| \( D_s \) (m\(^2\) s\(^{-1}\)) | 3.6 \times 10^{-13}b | 2.0 \times 10^{-13}b |

\(^a\) Obtained from Ref. 44.  \(^b\) Fitted to data.
specific surface area, \( m^2 \ m^{-1} \)

Brugg 

concentration of Li\(^+\) in the liquid phase, \( \text{mol} \ m^{-3} \)

concentration of lithium ions in the solid phase, \( \text{mol} \ m^{-3} \)

maximum concentration of Li\(^+\) in the particle of active material

volume-averaged concentration of Li\(^+\) in the particle of active material

Li\(^+\) diffusion coefficient in the electrolyte, \( \text{m}^2 \ \text{s}^{-1} \)

li \( \text{diffusion coefficient in the solid phase, } \text{m}^2 \ \text{s}^{-1} \)

Energy density, \( \text{Wh/kg} \)

Faraday’s constant, \( 96487 \ \text{C equiv}^{-1} \)

applied current density, \( \text{A} \ m^{-2} \)

exchange current density, \( \text{A} \ m^{-2} \)

transfer current on the surface of particle, \( \text{A} \ m^{-2} \)

local current density, \( \text{A} \ m^{-3} \)

flux of reaction on the surface of particle, \( \text{mol} \ m^{-2} \)

specific domain of \( k \) in the electrode

Li intercalation/deintercalation reaction rate constant, \( \text{A} ^{2.5} \ \text{mol}^{-1} \text{s}^{-1} \)

thickness of positive electrode, \( \text{m} \)

thickness of separator, \( \text{m} \)

thickness of negative electrode, \( \text{m} \)

distance between current collector/positive electrode interface and domain of \( k/k+1 \) interface, \( \text{m} \)

mass, \( \text{kg} \)

negative electrode

positive electrode

radial coordinate, \( \text{m} \)

universal gas constant, \( \text{J} \ \text{mol}^{-1} \text{K}^{-1} \)

radius of the particle, \( \text{m} \)

separator

time, \( \text{h} \)

Li\(^+\) transference number in the electrolyte

environment temperature, \( \text{K} \)

equilibrium potential of Li interaction/deinteraction reaction, \( \text{V} \)

spatial coordinate, \( \text{m} \)

List of Symbols

\( L_k \) anodic transfer coefficient

\( \alpha_k \) cathodic transfer coefficient

\( \xi_1 \) volume fraction of solid phase active material in the electrode

\( \xi_2 \) porosity in the electrode

\( \theta \) normalized concentration of lithium ions in the particle \( \theta = c_{i,\text{avg}}(c_{i,\text{max}}) \)

\( \theta^0 \) initial normalized concentration of lithium ions in the particle

\( \kappa \) ionic conductivity of the electrolyte, \( \text{S} \ m^{-1} \)

\( \kappa_{\text{eff}} \) effective ionic conductivity of the electrolyte, \( \text{S} \ m^{-1} \)

\( \sigma \) electronic conductivity of the solid phase, \( \text{S} \ m^{-1} \)

\( \sigma_{\text{eff}} \) effective electronic conductivity of the solid phase, \( \text{S} \ m^{-1} \)

\( \phi_i \) solid phase potential, \( \text{V} \)

\( \eta \) overpotential, \( \text{V} \)

\( \gamma \) capacity ratio between the negative and positive electrode

\( \rho \) density, \( \text{g/cm}^3 \)

Subscripts

avg average

max maximum

min minimum

j electrode region (pos, sep, neg)

cc current collector

l solid phase

2 liquid phase

Superscript

+, − left and right side of interfaces

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