



Multi-layer anodes for high-current applications

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ABSTRACT

In this work, we present a combination of experiments and modeling of a two-layer anode structure designed by EnPower Inc. for high-energy and fast-charge capabilities. The anode consists of lower porosity near the current collector and higher porosity near the separator with comparable active materials in both regions. A pseudo-two-dimensional electrochemical-thermal model was designed to represent the performance of this electrode. Simulations, consistent with experiments, show superior ion transport and lithiation in the multi-layer anode (MLA) compared to a conventional single-layer anode (SLA). Surprisingly, this improved transport in MLA manifests as enhanced cathode performance during high-rate discharge and this, in turn, provides higher energy density for MLA. Similarly, during fast charge, less irreversible lithium is deposited due to this improved transport in MLA, and hence MLA exhibits less capacity fade compared to SLA. Polarization analysis demonstrates marginally lower cumulative overpotential for MLA in different case studies; however, MLA cells maintain a significantly higher capacity in the same conditions and have more than double the cycle life. This means despite the apparently limited polarization benefit provided by MLA; the MLA structure can more reliably be employed in cell designs. Additional design changes are also analyzed by means of the model.

1. Introduction

As electric vehicles share grows in the automotive industry, the range and fast charging of Li-ion batteries attract more attention. Numerous attempts have been made to direct battery technology toward industry requirements including developing novel materials for electrodes and electrolyte and engineering electrode structures. This work focuses on methods of electrode engineering.

Simulation can guide electrode engineering methods. For instance, in an ohmically-limited battery, analytical expressions can be derived to maximize the capacity or specific energy of the cell. A compromise between higher active material loading in the cathode and ohmic limitations determines this capacity improvement [1,2]. However, in real applications, transport limitations and surface reaction overpotential are significant and a high-fidelity model is required to understand all polarization origins. Depending on the discharge time, which plays an important role in electrode engineering [2], variables like cathode thickness, porosity, initial electrolyte concentration, and solid-phase conductivity can be tuned to find the optimum design [3–6]. Additionally, other works considered engineering the electrode design by changing cathode composition [7], particle size [8], and changing electrode geometry to non-conventional shapes such as ring, spiral,

horseshoe, etc. [9]. Nevertheless, as industry and government requirements become more demanding, electrode engineering methods are evolved accordingly to address the trade-off between specific energy and power [5,6].

Novel strategies to minimize ohmic or diffusion loss in the electrolyte are being considered. These methods target efficient utilization of the electrolyte space. Consequently, they can facilitate liquid phase transport for high-current applications while maintaining the electrode thickness. The idea of a secondary-pore network is that some pathways or channels in addition to conventional pore structure are made to enhance Li⁺ diffusion through the residual space between particles. Techniques to implement such a network include a magnetic field to align particles in the out-of-plane direction [10,11], co-extrusion and sintering [12,13], laser patterning [14], or freeze-tape-casting [15,16]. A combination of electrode manufacturing and simulation was used to optimize such techniques. Results illustrated that the improvement due to a secondary-pore network depends on many factors as well as initial porosity, electrode thickness, and loading [17]. As an example, Ye et al. [18] implemented a multi-objective optimization to minimize tortuosity by building “ion highways”. Thick electrodes with

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low porosity (25%) could achieve 2.9 times higher energy density while thin and high porosity electrodes did not show major improvement. In addition to initial conditions of optimization, electrodes with high through-plane tortuosity and low in-plane tortuosity benefit the most from the secondary-pore network [15,17]. A highly-ordered laser-patterned (HOLE) electrode is reported to sustain 600 cycles of 4C and 6C charging [14]. Although these methods proved the benefit of using a secondary-pore network in improving both specific energy and fast-charge applications, they still suffer from high manufacturing complexity and cost.

Bi-layer electrodes have recently attracted researchers as an alternative method. The difference in layers can be in materials [19], composition [20,21], particle size [22], porosity [23] and can be implemented in both anodes and cathodes. During charge, ions flow into the anode from the separator side; therefore, it is crucial to facilitate the transport properties accordingly. Generally, the idea is to construct the layer with poor ion transport at the back of the electrode near the current collector and the layer with better ion transport near the separator. A related approach is to vary the electrochemical activity according to layer, such as by changing particle surface area. For instance, two discrete layers were used by Huang et al. with a porous TiO_2 near the current collector and a non-porous TiO_2 near the separator. This led to higher volumetric capacity and rate capability when compared to using a homogeneous mixture of these two nanoparticles [19]. Additionally, the active material volume fraction and layer thicknesses can be adjusted to achieve lower cell polarization [20] and better rate performance [21].

Implementing a gradient in the porosity of electrodes to effectively redistribute the ionic resistance is one of the most appealing techniques in making multi-layer electrodes. This method enhances the utilization of more active material in the cathode by reducing resistance where the current is larger [24,25]. A gradient with higher porosity near the separator can improve Li^+ transport and inhibit Li deposition inside the anode [23,26]. Simulations of a three-layer design for graphite showed lower inhomogeneous current distribution compared to the blended electrode case [27]. This study illustrated that lower tortuosity is the most effective design variable among all liquid and solid phase variables such as particle size or coating thickness. Graded porosity inside even the cathode is reported to mitigate cell degradation by 8% through enhancing Li^+ diffusion [28]. Recently, Muller et al. [23] manufactured a bi-layer anode with higher porosity near the separator and lower porosity near the current collector. The electrochemical characterization demonstrated higher capacity retention for bi-layer anodes in the first 250 cycles; however, this benefit is lost when Li plating penetrated the lower porosity layer. In fact, the single-layer design maintained its capacity better at the end of cycling [23]. It is worth noticing that the average coating porosity in this study was higher than typical commercial cells, meaning if a commercial-cell-grade porosity was used, this capacity retention benefit would have been lost far earlier.

Most recently, Yang et al. [29] manufactured three-layer graphite with almost the same thicknesses but different porosities with the highest near the separator (35%) and the lowest near the current collector (15%). Another analytical work from the same group [30] implemented a simplified model for a bi-layer and mono-layer graphite half-cell. Both of these works demonstrated superior capacity retention of the multi-layer graphite compared to a monolayer anode at up to 4C charge rate, due to improved transport properties. However, because there is no porous cathode, it is hard to deduce the energy density of cells based on these electrodes operated at high-current discharges. Note that as with some other models, Li plating is predicted using plating overpotential but no actual plating is carried out that would lead to cumulative effects as done here.

On the other hand, some simulations cast doubt on the advantages of manufacturing porosity gradient electrodes. Dai et al. [31] demonstrated little to no benefit in graded porosity cathode compared to an

optimized base case for the single-layer cathode. Their results indicated that the benefit of optimizing a uniform porosity cathode or anode most improves the specific energy and employing a graded porosity cathode only marginally improves cell performance.

To summarize, disagreeing results in the literature reveal a gap in this field about the effectiveness of porosity gradient electrodes on specific energy and capacity retention in fast charge. Furthermore, to use a P2D model for this analysis, accurate parameterization with extensive lab data is required.

This study presents a careful parameterization of a single-layer versus a bi-layer anode model with a porosity gradient. Exemplary graphite electrodes were constructed and tested by EnPower Inc. A modified P2D model including anode aging mechanisms was developed by Brigham Young University. The model was then used to analyze behavior in terms of high-power discharge capacity and extreme fast-charge performance. The model illustrates the subtle effects by which a multi-layer anode can generate advantages over a single-layer anode.

2. Experimental section and methods

The cell manufacturing and the majority of electrochemical tests were done by EnPower. Pouch cell (6.5 Ah) and coin cell were used for full-cell and half-cell electrochemical tests respectively. The anode is based on graphite, the cathode is based on NMC811 and the electrolyte is 1M LiPF_6 in EC/EMC (3/7 v/v). The anodes are either a homogeneous baseline anode that is commercially conventional (called the single-layer anode (SLA) here) or multi-layer anode (MLA). The supporting information summarizes the fabrication steps and compositions of the electrodes.

Fig. 1a illustrates the difference between MLA and SLA morphology through SEM-cross sections taken on preliminary electrodes (i.e. composition differs slightly from cells tested in this work). The MLA consists of two layers in the through-plane direction in which the layer near the separator (layer B) is more porous than the bottom layer near the current collector (layer A). For the MLA tested in this work, the graphites in layers A and B are of essentially the same particle size. The SLA is made from a mixture of graphites A and B, i.e. is made from identical active material and mass fractions as MLA.

The rest of this section discusses the parameterization of the P2D model.

2.1. Porosity profile

The multi-layer anode is expected to have a porosity profile in the through-plane direction which affects the cell performance and therefore is needed to be taken into account in the P2D model. For this purpose, SEM cross-sections of both SLA and MLA were used for image analysis as shown in Fig. 1. In this analysis, color contrast was made between the solid phase and pores, and a Python program was used to detect the darker area which is the pore (Fig. 1b). Two porosity profiles for SLA and MLA in the through-plane axis were made based on this method (Fig. 1c). Each resulting porosity profile is based on an average of 6 SEM images each taken on different electrodes.

As expected the image analysis depends on the threshold settings which must be adjusted to meet material and other constraints. For instance, because SLA and MLA have the same mass loading and coating thickness, the average porosity of the two electrodes (which can be directly computed from these properties) is expected to be the same, namely 24.7%. One distinct difficulty in analyzing porous electrodes is distinguishing between active material, mesoscopic pores, and the nanoporous carbon-binder domain (CBD) [32]. CBD detection is challenging by image analysis, especially in areas with lower porosity. Thus, preliminary porosity profiles from image thresholding were scaled and shifted to attain the same average porosity and to ensure that porosity had a minimum of 10% in the MLA electrode. Note that even the SLA electrode has significant porosity variations in the through-plane direction.

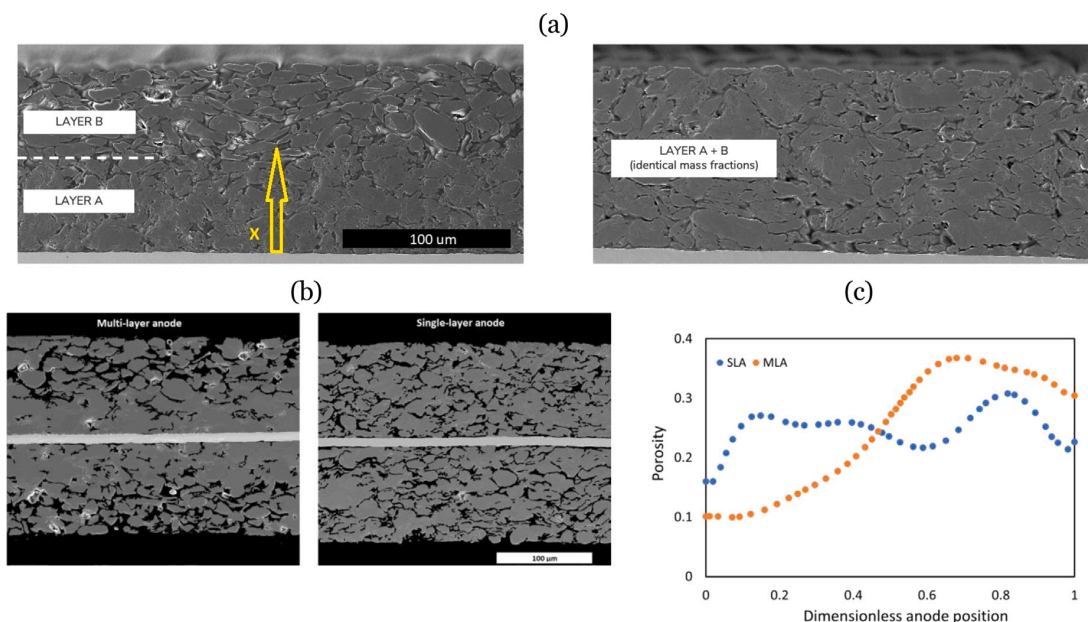


Fig. 1. (a) SEM cross-sections illustrating multi-layer (left side) and single-layer (right side) graphite anodes. The yellow arrow points from the current collector to the separator, (b) An example of SEM cross-section images of two-sided anodes used in image processing to detect porosity, (c) Adjusted porosity profiles for single-layer and multi-layer anodes in the through-plane direction. The current collector is at position 0 and the separator is at 1.

2.2. Ionic conductivity

The blocking electrolyte method [33] was used for anodes and the cathode to measure each electrode's average MacMullin Number (N_m). This technique uses AC current and different frequencies, which change how deep the ionic current penetrates the electrode. There is no Li^+ involved (hence the name 'blocking') and a 50 mM TBAClO_4 salt in a three-electrode stack was used instead. To test how sensitive this method is to ionic conductivity as a function of depth, a model based on [33] was made in COMSOL Multiphysics (finite element solver) to simulate the blocking electrolyte experiment. Simulating this EIS experiment shows, as expected, that the blocking electrolyte method depends mostly on the N_m of the top layer and is much less sensitive to bottom layer ionic conductivity. Ideally, the bottom layer of MLA could be tested separately with the same method to have a better estimation of the average N_m . However, this would require delaminating and inverting the film; several methods were tested to delaminate the aqueous-based MLA film from the current collector without damaging the film and were unfortunately not successful.

Therefore, an alternative method is employed in which an empirical Bruggeman-type equation (Eq. (1)) was used to estimate the N_m profile based on the porosity profiles (ϵ). γ_1 and γ_2 are parameters that depend on a particular solid composition and must be determined experimentally.

$$N_m = (\gamma_1 + \gamma_2 \epsilon) \epsilon^{-1.5} \quad (1)$$

Using the COMSOL blocking electrolyte model, the two parameters (γ_1 and γ_2) were fitted to the EIS spectrum of each experiment. The fitting EIS spectra and the MacMullin number profiles are shown in Fig. 2a–b. Generally, the anodes of this study have large MacMullin numbers partly due to intentionally low porosities of commercial high-energy-density electrodes.

2.3. Electronic conductivity

The electronic conductivity and contact resistance between the film and the current collector were measured by a micro-flexible-surface

probe developed in our laboratory [34]. The measurements were done on 2 cm × 2 cm electrodes at room temperature, and the results are shown in Fig. 2c. For simplicity, SLA and MLA were modeled with the same electronic conductivity and contact resistance.

2.4. Open circuit potential

The P2D model requires knowledge of the open circuit potential (OCP) of each electrode as a function of the state of lithiation (SOL) of that electrode. To determine this relationship, half-cells were run at C/20 at 40 °C in coin cells. The test was conducted between 0.05–1.5 V vs. Li for the anode and 3.0–4.3 V vs. Li for the cathode to make the charge and discharge reversible and minimize any electrode or electrolyte damage. One difficulty is that even at low C-rates an apparent hysteresis is observed for these materials. To address this, averaging charge and discharge curves is required, especially at cut-off voltages [35,36].

Cell OCV was calculated by Eq. (2). When combining two half-cell potentials into a full-cell potential, just as when combining two electrodes into a cell, one must know or determine the states of lithiation of each electrode. In this case, a least-square optimization program is used to fit the calculated OCV to the measured OCV by adjusting the operating window of each electrode in terms of SOL. To summarize, the minimization procedure is

$$U_{\text{calc}} = U_p(\text{SOL}_p) - U_n(\text{SOL}_n) \quad (2)$$

$$f = \text{Min} \sum_{i=1}^N (U_{\text{meas},i} - U_{\text{calc},i})^2 \quad (3)$$

subject to $x_{\min}, x_{\max}, y_{\min}, y_{\max}$

State of lithiation (SOL) is given by the stoichiometry of lithium ions in the chemical formula of each electrode which Li_xC_6 in graphite and $\text{Li}_y\text{N}_{0.8}\text{M}_{0.1}\text{C}_{0.1}\text{O}_2$ for the cathode. The SOL of each electrode can range within the operating window, namely ($x_{\min}, x_{\max}$) for the anode and ($y_{\min}, y_{\max}$) for the cathode. Because this procedure is done after the formation cycles, the x and y values account for any cyclable Li lost during formation. Fig. 3e displays fitting the measured and calculated

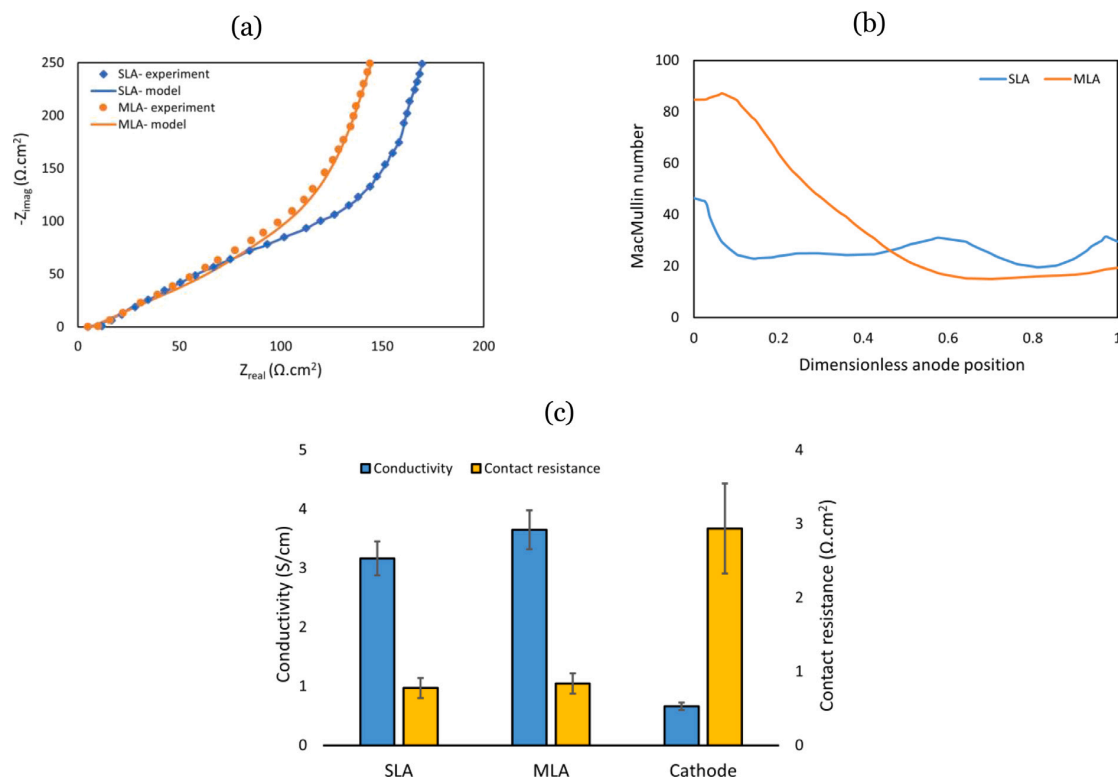


Fig. 2. (a) Nyquist plot of EIS spectra and associated fitting curves from the blocking electrolyte experiments for SLA and MLA. SLA: $\gamma_1 = 2.5, \gamma_2 = 2.8$, MLA: $\gamma_1 = 2.5, \gamma_2 = 2.4$, (b) Estimated MacMullin number profiles of anodes in the through-plane direction. The current collector is at position 0 and the separator is at 1, (c) Electronic conductivity and contact resistance of SLA, MLA, and cathode. 95% confidence intervals are shown as error bars.

full cell OCVs. The calculated operating windows for the anode and cathode are (0.009, 0.81) and (0.13, 0.94) respectively. Equations from Ref. [37] were used to estimate the entropy change which accounts for temperature change in OCP.

2.5. Anode solid diffusion

A delithiation GITT test was carried out on both single-layer and multi-layer anode coin cells. This test was used to calculate the anode solid diffusivity. The test repetitively applies 60-second charge pulses, 1-hour rest, and subsequent charging to adjust the SOC at 10% intervals at 40 °C.

The GITT data are interpreted as follows. According to Ref. [38], the long-time relaxation for any diffusive process in spherical geometry can be described by the time-dependent term

$$\exp\left(-\pi^2 \frac{D^s t}{R^2}\right) \quad (4)$$

where D^s is the solid diffusivity, t is time and R is the particle radius. As a consequence, the concentration overpotential, after skipping the initial portion of the relaxation, can be expressed as

$$\Delta V = m_1 \exp(-m_2 t) \quad (5)$$

This equation was fit to the long-term relaxation potential by adjusting m_1 and m_2 as illustrated in Fig. 3a.

Then, m_2 was used to calculate the solid diffusivity as a function of SOC using $D^s = m_2 R^2 / \pi^2$, as depicted in Fig. 3c. The average of SLA- and MLA-derived diffusivity at each point was then used in the P2D model for both electrodes. For diffusivity variation with temperature, [37] was followed.

Schmalstieg et al. [39] utilized another method to calculate the solid diffusivity from GITT. They modified the GITT analytical theory

equation as in Eq. (6) to be able to linearly fit the short-time relaxation voltage to $\sqrt{t}$:

$$D^s = \frac{4}{\pi} \frac{R^2}{(\Delta t)^2} \left(\frac{\Delta V_\delta}{\frac{dV}{d\sqrt{t}}} \right)^2 \quad \text{for} \quad \Delta t \ll \frac{r^2}{D} \quad (6)$$

where Δt is the pulse duration, ΔV_δ is the OCP difference before and after the pulse, and $\frac{dV}{d\sqrt{t}}$ is the fitting slope of the voltage over the square root of time. The linear fit and the solid diffusion as a function of SOC are shown in Fig. 3b.

Compared to the previous method, the diffusivity as a function of SOC is lower at almost all points. The electrolyte diffusion time constant for this system is around 2 s and it may confound the determination of solid diffusion at short times. Nevertheless, different time segments of initial relaxation up to 140 s were considered for the voltage fitting; the resulting diffusivity profiles did not change remarkably based on the time segment used. It should be noted that due to graphite's phase transitions and flat voltage curve, the solid diffusivity cannot be calculated at all SOC's using the short-time method.

Next, an electrochemical anode half-cell model is built in COMSOL to compare the performance of these two methods. The model simulates the GITT test at 10% SOC using the respective solid diffusivity functions. As Fig. 3d shows, the long-time method can fit the pulse voltage very well, however, it relaxes fairly fast during the initial portion of the relaxation. On the other hand, the short-time method greatly overestimates the voltage during the current pulse but predicts the initial relaxation voltage shape more accurately. The observed underestimation of the solid diffusivity via the short-time GITT analytical theory was observed previously and discussed in Ref. [40]. Although neither of these methods accurately predicts the decay voltage, the long-time method is chosen for the P2D model because of our placing higher importance on voltage match during the application of current.

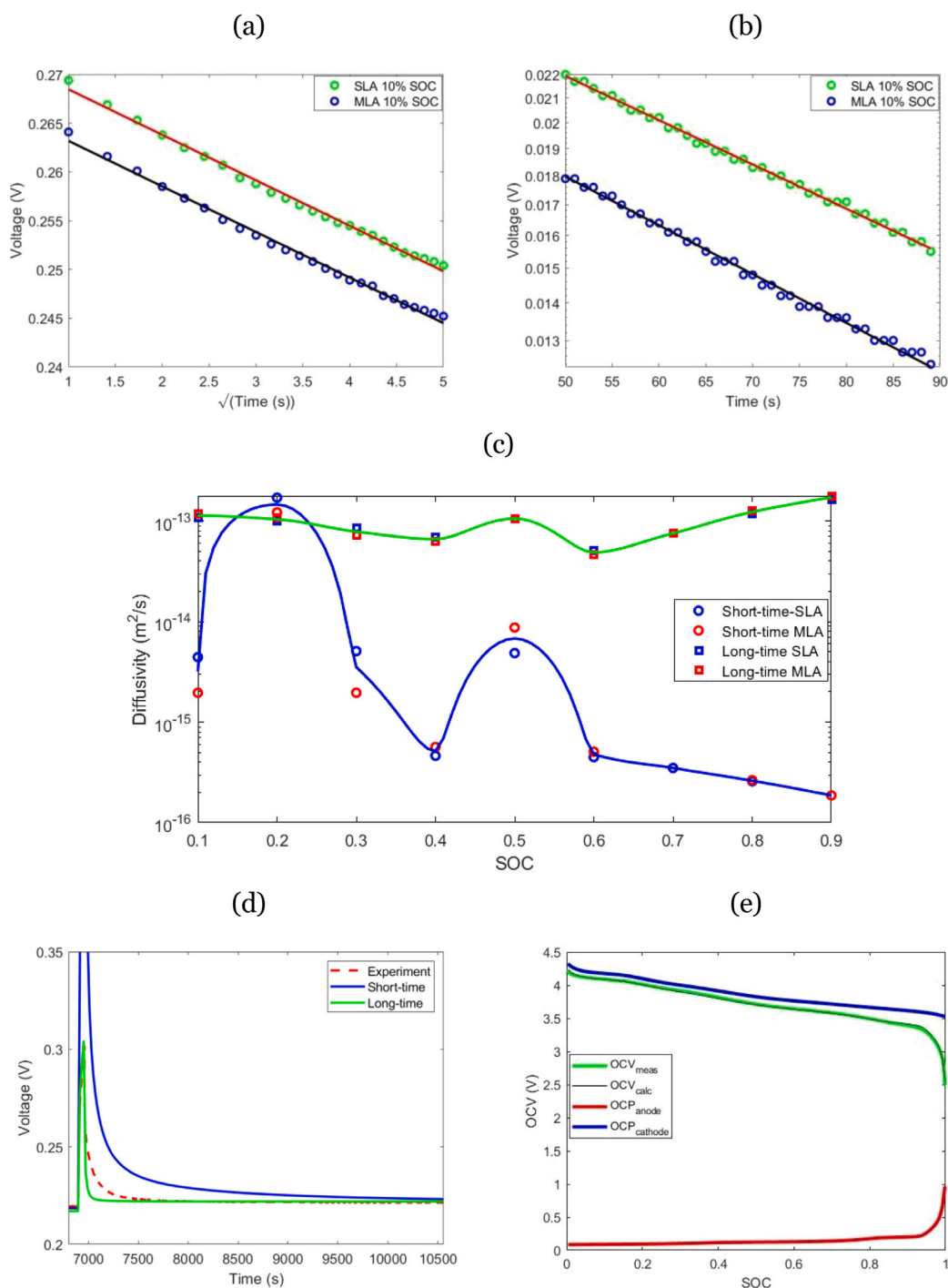


Fig. 3. Overpotential (points) during the relaxation for SLA and MLA fitted with (a) exponential decaying functions by the long-time method, (b) linear function by the short-time method (lines), at 10% SOC. The left edges of the time axes for (a) and (b) are considered to be the respective time origins for relaxation; also, the voltage axis in (b) is logarithmic. (c) Solid diffusivity (log scale) as a function of SOC for SLA and MLA of short-time and long-time methods. The cubic spline of the average values (lines) is used in the P2D model, (d) Solid diffusivity resulting from the short-time and long-term methods are compared via an electrochemical half-cell model simulating GITT at 10% SOC. The peak voltage of the short-time method reaches 1.3 V and is cut in this plot, (e) Fitting measured OCV to simulated OCV of the full cell by changing the operating windows of half-cell OCPs.

2.6. Model description

The baseline model in this work is based on the Doyle–Fuller–Newman P2D model which is relatively established in this field [41] and is founded on the porous electrode and concentrated solution

theories. The main equations and boundary conditions are summarized in Table 1. Furthermore, SEI formation and lithium plating are anode aging mechanisms included in the model. Irreversible Tafel kinetics are used for SEI, and Li plating is modeled using irreversible Butler–Volmer kinetics. In practice, this means the SEI is always growing to

Table 1

Summary of P2D model equations. Boundary conditions are applied at the anode current collector ($x = 0$), separator boundaries ($x = L_N, x = L_N + L_S$), and the cathode current collector ($x = L_N + L_S + L_P$). Variables are defined in Ref. [42].

Governing equation	Boundary conditions
Material balance: $\frac{\partial c_{s,i}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{\text{eff},i}^s r^2 \frac{\partial c_{s,i}}{\partial r} \right)$ $e_i \frac{\partial c_{e,i}}{\partial t} = \frac{\partial}{\partial x} \left(D_{\text{eff},i} \frac{\partial c_{e,i}}{\partial x} \right) + j_i a_i (1 - t^+)$ Charge balance: $\sigma_{\text{eff},i} \frac{\partial^2 \phi_{s,i}}{\partial x^2} = j_i a_i F$ $-\frac{\partial}{\partial x} \left(\kappa_{\text{eff},i} \frac{\partial \phi_{e,i}}{\partial x} \right) + \frac{2RT}{F} (1 - t^+) \left(1 + \frac{\partial \ln f_i}{\partial c_{e,i}} \right) \frac{\partial}{\partial x} \left(\kappa_{\text{eff},i} \frac{\partial \ln c_{e,i}}{\partial x} \right) = j_i a_i F$ Energy balance: $\rho_i C_{p,i} \frac{\partial T}{\partial t} = \lambda_i \frac{\partial^2 T}{\partial x^2} + Q_{\text{rxn},i} + Q_{\text{ohm},i} + Q_{\text{rev},i}$	$-D_{\text{eff},i}^s \frac{\partial c_{s,i}}{\partial r} \Big _{r=0} = 0, \quad -D_{\text{eff},i}^s \frac{\partial c_{s,i}}{\partial r} \Big _{r=R} = j_i$ $-D_{\text{eff},N} \frac{\partial c_{e,N}}{\partial x} \Big _{x=0, L_N+L_S+L_P} = 0$ $-\sigma_{\text{eff},P} \frac{\partial \phi_{s,P}}{\partial x} \Big _{x=L_N+L_S+L_P} = -I_{\text{applied}}$ $\phi_{s,N} \Big _{x=0} = 0, \quad -\sigma_{\text{eff},i} \frac{\partial \phi_{s,i}}{\partial x} \Big _{x=L_N, L_N+L_S} = 0$ $-\kappa_{\text{eff},i} \frac{\partial \phi_{e,i}}{\partial x} \Big _{x=0, L_N+L_S+L_P} = 0$ $-\lambda_N \frac{\partial T_N}{\partial x} \Big _{x=0} = h(T_{\text{amb}} - T_N),$ $-\lambda_P \frac{\partial T_P}{\partial x} \Big _{x=L_N+L_S+L_P} = h(T_P - T_{\text{amb}})$

a greater or lesser degree but the Li plating may start or stop during cycling. A more detailed review of our model equations is in [42]. In a conventional P2D model, porosity and MacMullin number are constant across an electrode. In this model, they are instead functions of anode position and time, with initial profiles given in Sections 2.1 and 2.2. Accordingly, concentrations, potentials, and reaction rates depend on position and time. The addition of porosity and MacMullin number as changeable quantities means they need their own equations of change but otherwise fit into a conventional P2D approach. The reader is again referred to our prior work for more details [42].

3. Results and discussion

3.1. Model validation

The parameters in the model parameterization section were estimated by the separate indicated experiments. In this section, the remaining parameters, e.g. cathode diffusivity and intercalation kinetics, were fitted to full-cell discharge curves. These discharge rate capacity (DRC) tests also served as validation tests on the baseline P2D model. Reasonable agreement between experiment and simulation for a range of discharge rates indicates a satisfactory model. The simulations were done with the identical cathode, separator, electrolyte, and operating conditions except for the differing anodes (single-layer vs. multi-layer). The formation cycle is included in an effective way. The SEI film was given a 5 nm initial thickness. The initial x and y values are selected based on the experimental ranges previously determined.

Using the full-cell capacity of the cathode in the model did not result in an accurate voltage fitting. The reduced amount of electrolyte used in the commercial manufacturing process, compared to that for coin cells, may be leading to a reduced degree of cathode wetting in these experiments; therefore, a lower volume fraction of cathode active material and a higher volume fraction for cathode filler (conductive carbon+ binder) were used to improve the fitting (Table 3). The active material volume fraction can be determined by $1 - \epsilon - \epsilon_f$.

Fig. 4a–b shows measured C-rate performance and the corresponding model fits. These discharge curves are obtained from a sequence of discharges that were part of the DRC test with a constant C/3 charge rate and variable discharge rates ranging from C/5 to 3.5C. It should be noted that there may be a mild difference in starting state of charge due to the previous cycling history between SLA and MLA, however,

we attempted to create consistent starting conditions by tapering the charging current to a low cutoff value (C/50).

Fig. 4a–b demonstrates satisfactory validation of the baseline model with variable discharge C-rates. MLA illustrates higher discharge capacities than SLA, especially for 2C and above. Experimental results showed that the advantage of using MLA starts at a 1.5C discharge rate and increases with higher C-rates. For instance, at 3C, MLA provides about 40% higher energy density than SLA. The maximum temperature simulated by the model during 3C discharge is about 60 °C, a 20 °C increase from the initial temperature.

The model is designed not only to describe fast-charge and discharge behavior, but also degradation reactions. To validate the aging model, we compared the model to accelerated aging experiments. The discharge capacity of the model and the experiments were fitted by adjusting the Li plating exchange current density (i_0^{pl}) and pore-clogging factor (β) during aging. β is the fraction of side-reaction products (SEI+plating) that volumetrically fill the anode pores [42]. SLA and MLA cells were simulated with identical values of the given two parameters.

A combination of fast-charge and cycling performance of these two cells is compared in Fig. 4d and constitutes the set of data used to determine the above aging parameters. The protocol in this test alternates between 5 fast-charge cycles and 1 normal-charge cycle (5F1N) as shown in Fig. 4c. This fast-charge protocol takes the cells from 10%–80% SOC in less than 20 min and uses stepped multi-phase constant current (MPCC) where charge rates progressively decrease from 2.8C to 0.8C (Fig. 4c inset). The MPCC protocol is designed by EnPower to do maximum fast charging while minimizing damage to the cell. When enlarged, Fig. 4c shows a few points that momentarily have zero current which was not intentional and is the artifact of the battery cyclers.

Fig. 4d compares the discharge capacity of SLA and MLA cells during accelerated aging (5F1N) and their respective model results. The MLA cell withstood 22 fast-charge cycles while SLA failed in 9 cycles. The tests ended because of predicted cell failure based on higher-than-expected capacity fade during the discharge of that cycle. The rapid failure is a consequence of the large C rates used here and was intentionally designed to accelerate lithium-plating behavior for model-parameterization purposes. That a single set of parameters can allow an accurate description of both SLA and MLA cells is a significant validation of the model. The maximum temperature simulated by the model for the MPCC charge is around 51 °C which indicates around 11 °C temperature rise.

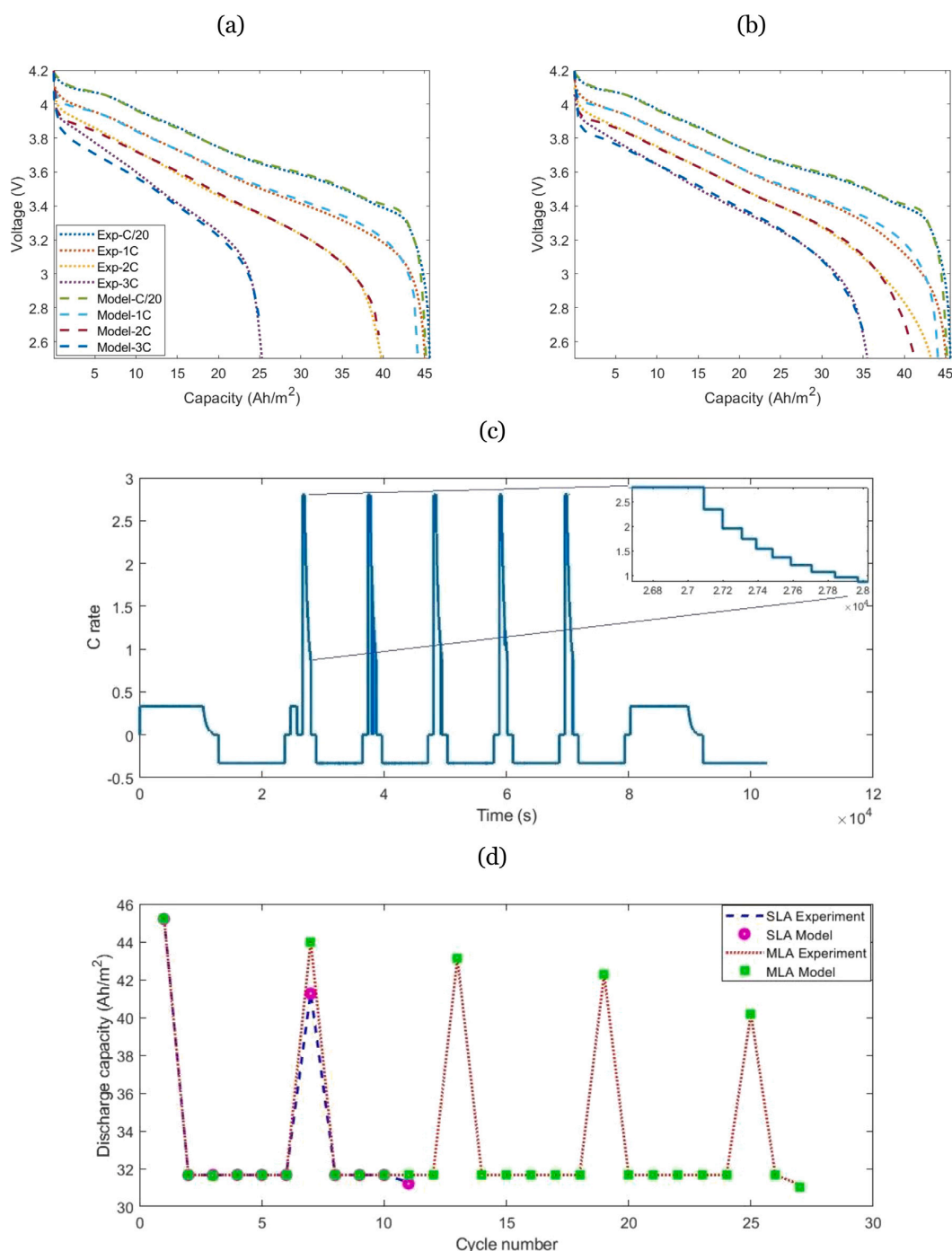


Fig. 4. The baseline P2D validation through discharge capacity for cells with (a) single-layer, (b) multi-layer. Tests were done at 40 °C with C/3 charge rate and variable discharge rates for respective cells that had previous cycling history (see text), (c) Current profile (C rate) of “5 fast 1 normal” (5F1N) charging protocol. The inset shows the multi-phase constant-current (MPCC) part, (d) the Discharge capacity of SLA and MLA cells at 5F1N over multiple cycles for aging kinetics validation. Tests were done at 40 °C with a C/3 discharge rate.

To further check model validity, the aging model was compared to additional fast charging experiments as summarized in Table 2. In this case, the relative error is defined as the absolute value of the difference between simulated and experimental discharge capacities, divided by the experimental value, and then averaged over multiple cycles. The

number of cycles over which averaging was performed varied from one experiment to the next, and was 11–42 cycles beginning with fresh cells. The first row of the table (cell 1) is summarizing the results in Fig. 4d. The next row is for another pair of cells. The final row is for the third pair of cells in which a different fast-charge protocol (3F1N)

Table 2

Comparison of relative error for fast-charge simulation of SLA and MLA cells with different fast-charge protocols and over the course of multiple cycles.

Experiment	Relative error SLA	Relative error MLA
5 fast 1 normal, cell 1	$7.3 \cdot 10^{-4}$	$3.7 \cdot 10^{-4}$
5 fast 1 normal, cell 2	$1.4 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$
3 fast 1 normal, cell 3	$1.1 \cdot 10^{-3}$	$8.1 \cdot 10^{-4}$

was used. All the results confirm that errors are acceptably small and therefore the model predicts the capacity well for a variety of fast-charge experiments over multiple cycles in which cell degradation has noticeably occurred. The capacity losses observed in Fig. 4d are typical for the remaining tests.

The experimental tests with normal cycling protocol showed that both SLA and MLA cells maintain more than 90% of their initial capacities after 500 cycles. On the other hand, under 3 normal, 3 fast-charge protocol (3N3F) SLA fails at 30 cycles (<80% initial capacity) while MLA retains more than 80% of its initial capacity after 500 cycles which is additional proof of superior performance of MLA structure for high-current applications. Furthermore, representative cells were opened for post-mortem study after fast-charge cycling. Top-view surface photographs and cross-sectional SEM images are given in Figure S1 in the supporting information. The cross-sectional images show dendritic lithium deposits consistent with a higher amount of Li plating for SLA cells than MLA cells at the end of life.

Model parameters distinct for the MLA and SLA cells are listed in Table 3. The remaining parameters not listed in 3 are found in our prior publication [42].

3.2. Polarization analysis

After model validation, to investigate and compare the physical phenomena inside the SLA and MLA cells, the work from Nyman et al. [43] was followed to analyze the sources of overpotentials. Six sources of overpotential were calculated for each component (anode, separator, cathode): diffusion loss inside the electrolyte, the ionic ohmic loss inside the electrolyte, diffusion in the solid phase, electronic ohmic loss in the solid phase, intercalation reaction activation at the particle surface, and contact loss at the current collector. Details of the corresponding overpotential equations can be found in Ref. [43].

3.2.1. High-C discharge

In this section, the model is used to simulate overpotentials for 3C discharge currents which followed a C/3 charge.

Fig. 5a–b presents the overpotentials vs. time for the discharge. The ending times correspond to an equal amount of charge being passed in both cells. Fig. 5a reports two overpotentials that are distinct between MLA and SLA and in which MLA shows less overpotential magnitude, namely electrolyte diffusion and ohmic drop. The remaining sources of overpotential are virtually the same between MLA and SLA. Unexpectedly, the differences between the two anodes result in marked differences in overpotentials on the cathode side, Fig. 5b. The enhanced ionic transport in MLA is reflected in its cathode exhibiting lower reaction and solid diffusion overpotential magnitudes. Therefore, MLA presents a lower cumulative overpotential magnitude for the high C-rate discharge current. The fact that anode geometrical differences are reflected in changes to overpotential on the cathode side reveals the complex feedback between anode and cathode and that to optimize the cell, one must optimize the two electrodes simultaneously. However, in this work, only the anode was modified.

To better understand the source of differences in these two cells, simulation variables were determined at the end of the discharge as a function of position. Figs. 5c–d plot the electrolyte concentration and potential across the cell thickness. At this point, the MLA has a slightly larger electrolyte concentration and potential gradients. The reason is

that MLA has a larger MacMullin number near its current collector compared to the SLA (due to lower porosity). The MLA has also discharged a much larger capacity compared to the SLA, which would further exacerbate the concentration gradient. Next, as we observe in Fig. 5e, almost half of the cathode on the current collector side is deprived of Li^+ meaning the cathode works at the limiting current in that region. This deprivation is more severe for SLA because, in spite of the bigger gradient inside the MLA, MLA provides a higher concentration for its cathode compared to the SLA cathode. Finally, surface concentration in Fig. 5f shows MLA more rapidly delithiates the anode and therefore, the surface concentration in the cathode is higher at the end of discharge. Thus, improved transport properties in MLA near the separator make the cathode work more efficiently compared to SLA.

3.2.2. MPCC fast charge

In this section, the model simulates the MPCC fast charge to explore why MLA retains capacity better than SLA. The sources of overpotential during the MPCC fast charge inside the anode are shown in Fig. 6a–b. Fig. 6a demonstrates more facile transport for MLA as it shows lower diffusion overpotential and ohmic drop inside the anode. The rest of the overpotentials inside the anode are almost equal for SLA and MLA. Increased transport in the anode this time noticeably decreases the transport losses in the cathode as shown in Fig. 6b.

The variables at the end of the charge across the anode are shown in Fig. 6c–f. Fig. 6c shows higher electrolyte potential at the anode–separator interface for the SLA. This is particularly important because higher potential increases the likelihood of Li plating at this point. Accordingly, Fig. 6d shows a lower plating overpotential for the SLA at this location; any plating overpotential less than zero means lithium can plate inside the anode. Fig. 6e confirms a higher thickness of plated lithium for SLA, which occurred during this cycle. It is worth mentioning that the electrolyte potential away from the separator does not affect the Li plating directly because the plating overpotential is positive and there is no Li plating in that region. Additionally, Fig. 6f depicts a more uniform surface concentration for MLA compared to SLA. This means the improved transport promotes the particles' lithiation because the cell is electrolyte-transport limited in this fast-charge protocol.

The model suggests that MLA actually delays the onset of Li plating. For instance, during the first cycle of MPCC, the onset of Li plating for SLA and MLA is at 16% and 20% SOC respectively. This trend is true for all simulated fast-charge protocols in this work. Furthermore, Fig. 6c–e shows only a snapshot of the variables at the end of the first cycle charge and does not represent these variables at every time step during the fast charge. The difference between the two electrodes is small at the end of the first charge. However, with repeated cycling, the difference is amplified as shown by Fig. 4d. Due to the delayed onset of Li plating and less intense Li plating during the whole fast charge, MLA maintains capacity better than SLA. This observed delay of Li plating onset is consistent with the conclusions of prior modeling and experimental efforts [29,30].

3.2.3. Drive cycle

The objective of this section is to examine SLA and MLA cell performance in realistic use cases. Two drive cycles are considered: EUcar protocol, which is normally used for HEVs, and US06 for EVs. Note that the C-rates in these two protocols are adjusted to be more suitable for our simulations. Specifically, the more-demanding EUcar C rates were decreased and the US06 rates were matched to our cell capacity. Input current and the simulated output voltage of drive cycles at room temperature are shown in Fig. 7a–b.

The cumulative overpotentials from different sources are shown for the EUcar drive cycle in Fig. 7c–d. The averaging procedure takes into account the current flow [43], which acts to make all cumulative overpotentials positive. SLA and MLA cells show similar overpotential

Table 3
Parameters used to validate the P2D and degradation model.

Symbol	Description	Negative electrode	Separator	Positive electrode	Unit
L	Thickness	98	16	70	μm
R_p	Particle radius	11	—	5.8	μm
ϵ	Average porosity	0.247	0.47	0.231	—
ϵ_f	Filler fraction	0.058	—	0.158	—
τ	Average tortuosity	7.8	3.2	4	—
σ	Electronic conductivity	341	—	66	S m^{-1}
R_{cont}	Contact resistance	$8.1 \cdot 10^{-5}$	—	$2.94 \cdot 10^{-4}$	$\Omega \text{ m}^2$
D^s	Solid-phase diffusivity	[Fig. 3c]	—	$5 \cdot 10^{-14}$	$\text{m}^2 \text{ s}^{-1}$
i_0^{int}	Exch curr dens intercalation	1.91	—	9.15	A m^{-2}
i_0^{SEI}	Exch curr dens SEI	$2 \cdot 10^{-16}$	—	—	m s^{-1}
i_0^{pl}	Exch curr dens Li plating	0.096	—	—	A m^{-2}
β	Pore-clogging factor	0.15	—	—	—
h	Heat transfer coefficient	5	—	5	$\text{W m}^{-2}\text{K}$
T_{amb}	Ambient temperature	40	40	40	$^{\circ}\text{C}$

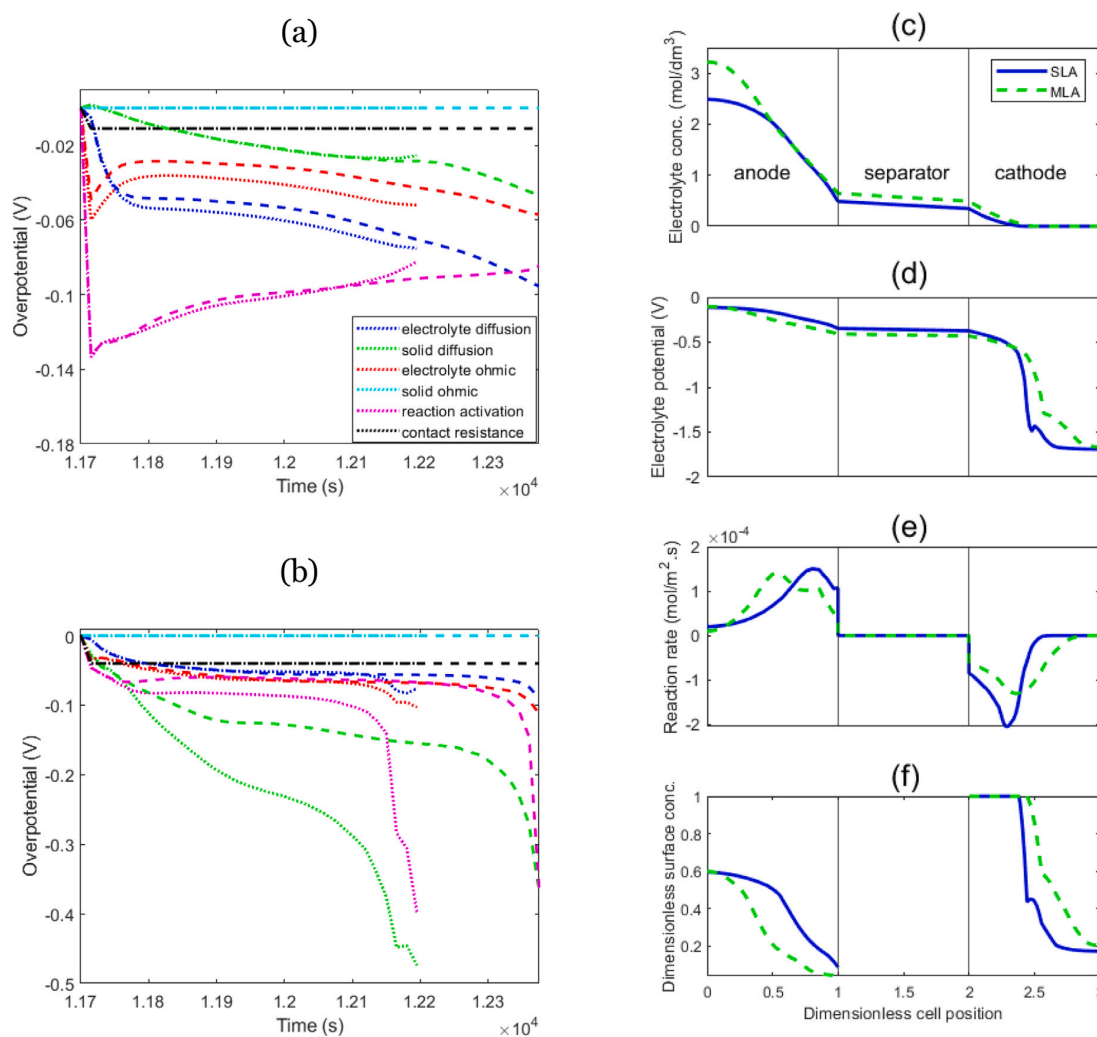


Fig. 5. Six sources of overpotential during 3C discharge at 25 °C for SLA (dotted lines) and MLA cells (dashed lines): (a) anode, (b) cathode. The time origin is the beginning of the C/3 charge step. Variables at the end of discharge: (c) electrolyte concentration, (d) electrolyte potential, (e) surface reaction rate, (f) dimensionless solid surface concentration.

behaviors. For instance, in the anode, the reaction activation overpotential is the greatest source of inefficiency, followed by electrolyte ohmic drop. The total overpotential for SLA is about 3% higher than

MLA. The breakdown analysis also shows that for the cathode, the reaction activation likewise plays the largest role, followed by the contact resistance.

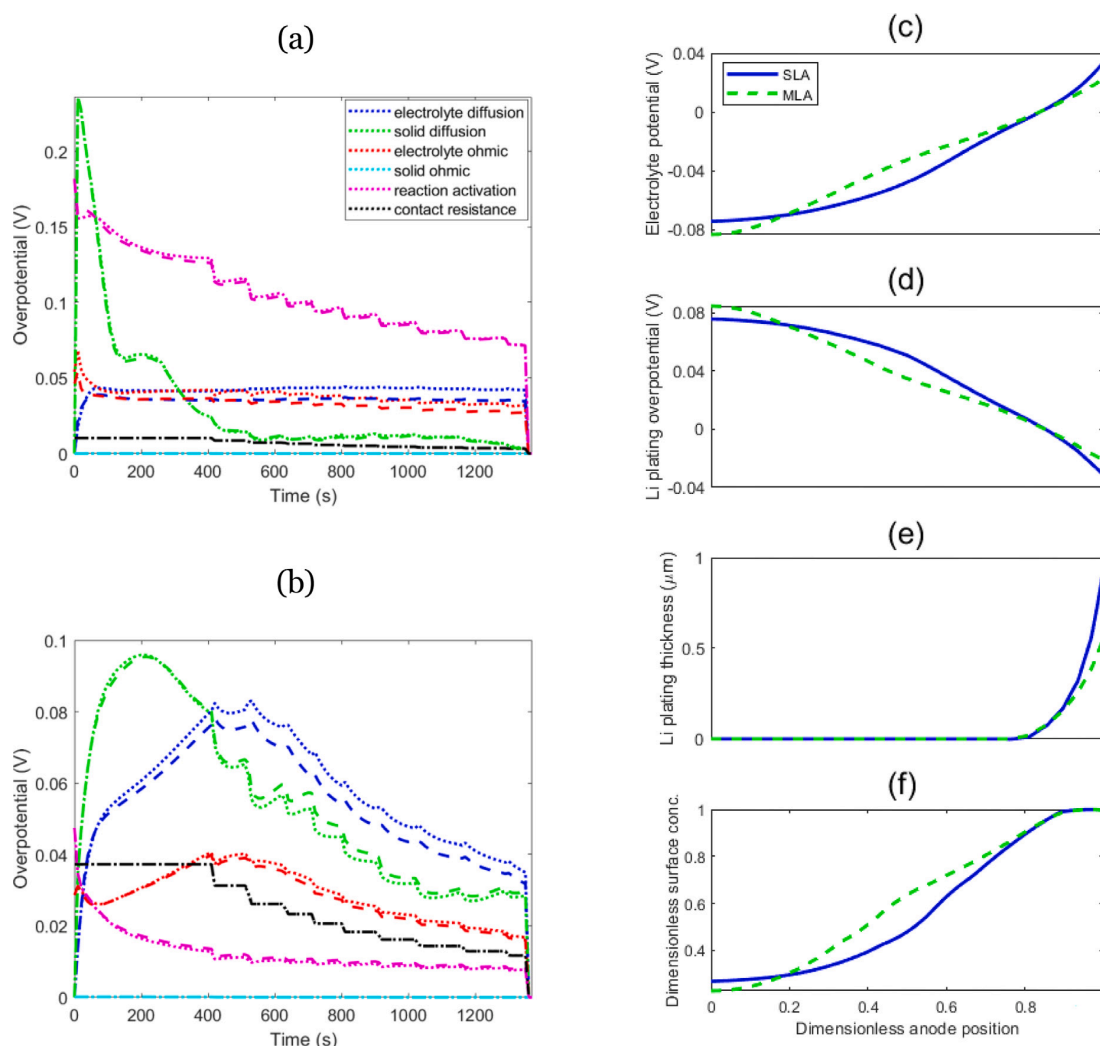


Fig. 6. Six sources of overpotential during MPCC fast-charge protocol at 25 °C for SLA (dotted lines) and MLA cells (dashed lines): (a) anode, (b) cathode. Variables at the end of fast charge (c) electrolyte potential, (d) lithium plating overpotential, (e) lithium plating thickness, (f) dimensionless solid surface concentration. Position 0 is the current collector and 1 is the separator.

The polarization analysis for different tests including the US06 drive cycle, 3C discharge, and MPCC fast charge is summarized in Table 4. The results show that SLA always has a higher total overpotential than MLA. However, this difference seems most noticeable when the cell is pushed to its voltage or capacity limits, as for the 3C discharge. This means although the EUcar drive cycle applies higher currents to the cell, the difference between SLA and MLA cells is not evident because of the limited duration of the high rate. Therefore, modeling comparisons between competing designs such as SLA and MLA can lead to different conclusions, depending on what metrics are used to determine performance. This may explain how in prior work, different conclusions have been made as to the efficacy of gradient electrodes. For instance, Dai et al. [31] reported little to no benefit for a porosity gradient electrode. Another consideration is that polarization analysis, no matter how it is formulated, cannot cleanly discriminate between different confounding effects and nonlinear interactions of different overpotential sources in the cell. Consequently, care should be taken in analyzing the overpotential sources because it may not reflect the true benefit of MLA over SLA cells in all situations.

3.3. Sensitivity analysis

Having elucidated the MLA advantage over SLA, the model can be used to suggest further improvements in the MLA cell performance. According to the polarization analysis breakdown, during high-rate discharges, the biggest overpotential in the anode occurs in reaction activation. On the other hand, for fast-charge applications, electrolyte transport causes the biggest overpotential. Hence, two parameters are selected for sensitivity analysis: the particle surface area for the reaction and the porosity gradient for the electrolyte transport.

Three case studies are considered for the anode particle size. First, a smaller particle size of 7 μm radius on average, and two profiles for the particle size as a function of anode thickness. As shown in Fig. 8a, radius profile 1 assumes larger particles near the separator and smaller particles near the current collector, and radius profile 2 represents the opposite. Likewise, two porosity profiles including a larger (porosity profile 2), and smaller (porosity profile 3) gradient than the baseline MLA profile were also considered (8b). It should be noted that both particle-size and porosity gradients cases considered here have an equal average to the baseline MLA. Additionally, a higher initial concentration of electrolyte (1.2 M instead of 1 M) was considered for the SLA

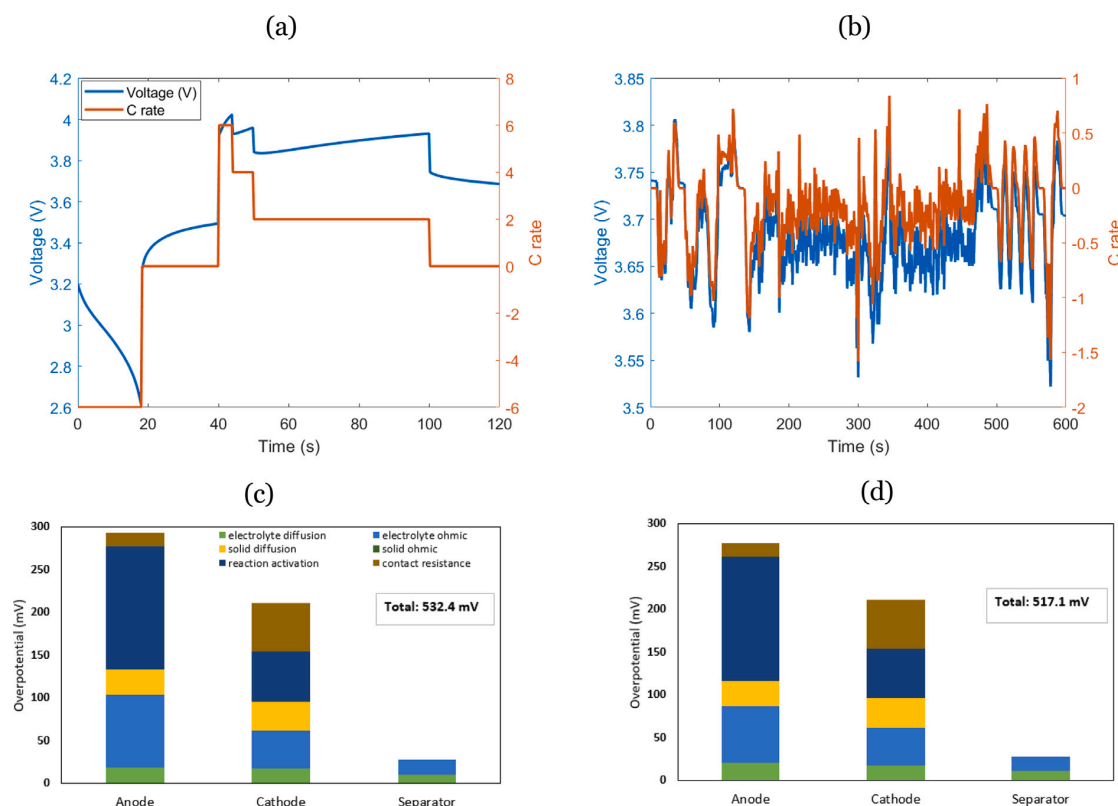


Fig. 7. C-rate and voltage at room temperature for SLA cell for (a) modified EUcar drive cycle, (b) US06 drive cycle. Cumulative polarization for EUcar drive cycle for (c) SLA, (d) MLA.

Table 4
Summary of cumulative overpotentials for four use cases at 25 °C.

Test	Cell type	Anode (mV)	Cathode (mV)	Separator (mV)	Total (mV)
EUcar drive cycle	SLA	293	211	28	532
	MLA	278	211	28	517
US06 drive cycle	SLA	53	30	3	86
	MLA	50	30	3	83
3C discharge	SLA	234	472	27	733
	MLA	232	363	25	620
MPCC fast charge	SLA	248	197	19	464
	MLA	234	194	19	447

cell to judge if this change can replace the MLA. Each of these cases was run separately and all other parameters except for the target parameters were held constant.

To assess the performance of the cell with each of these changes, two case studies were considered. First, a 3C discharge at three different temperatures (10, 25, 40 °C), and second, the 5F1N fast-charge protocol at 25 °C. Fig. 8c–e portrays that a smaller-particle electrode (7 μm) improves the energy density for high-rate discharge, i.e. has a greater area under the discharge curve up to the cut-off voltage. Nevertheless, even greater energy density is observed with particle size profile 2 (smaller particles near the separator) and porosity profile 2 (increased porosity gradient). The advantage for these three cases is more obvious at lower temperatures. This is due to improved intrinsic kinetic and transport rates at higher temperatures.

As for the fast-charge performance shown in Fig. 8f, the greatest effect is seen by using a smaller homogeneous particle size (7 μm). This benefit can be attributed to the general principle that decreasing particle size will decrease solid diffusion distance and increase surface

area for the intercalation reaction. Placing smaller particles near the separator while placing larger particles next to the current collector, i.e. radius profile 2, also improves the capacity retention, due to the small-particle benefits accrued in the region of the electrode where it is most needed. Such will hinder Li deposition in that region. As expected, larger particles near the separator, i.e. radius profile 1, has the opposite effect and deteriorates fast charge performance. Next, increasing the porosity gradient, i.e. porosity profile 2, results in essentially the same performance as of the baseline MLA. Decreasing the porosity gradient, i.e. porosity profile 3, instead deteriorates the fast charge performance. We expect all of these differences in behavior to diminish under conditions where transport and kinetic behaviors are less controlling, such as at higher temperatures. In spite of the apparent benefits of using 7 μm particles, it is worth mentioning that high-surface-area (i.e. smaller) graphite particles are avoided due to manufacturing difficulties and higher capacity loss of formation cycles which were not taken into account in this study.

Finally, increasing the electrolyte concentration to 1.2 M could markedly improve the energy density and fast-charge performance of

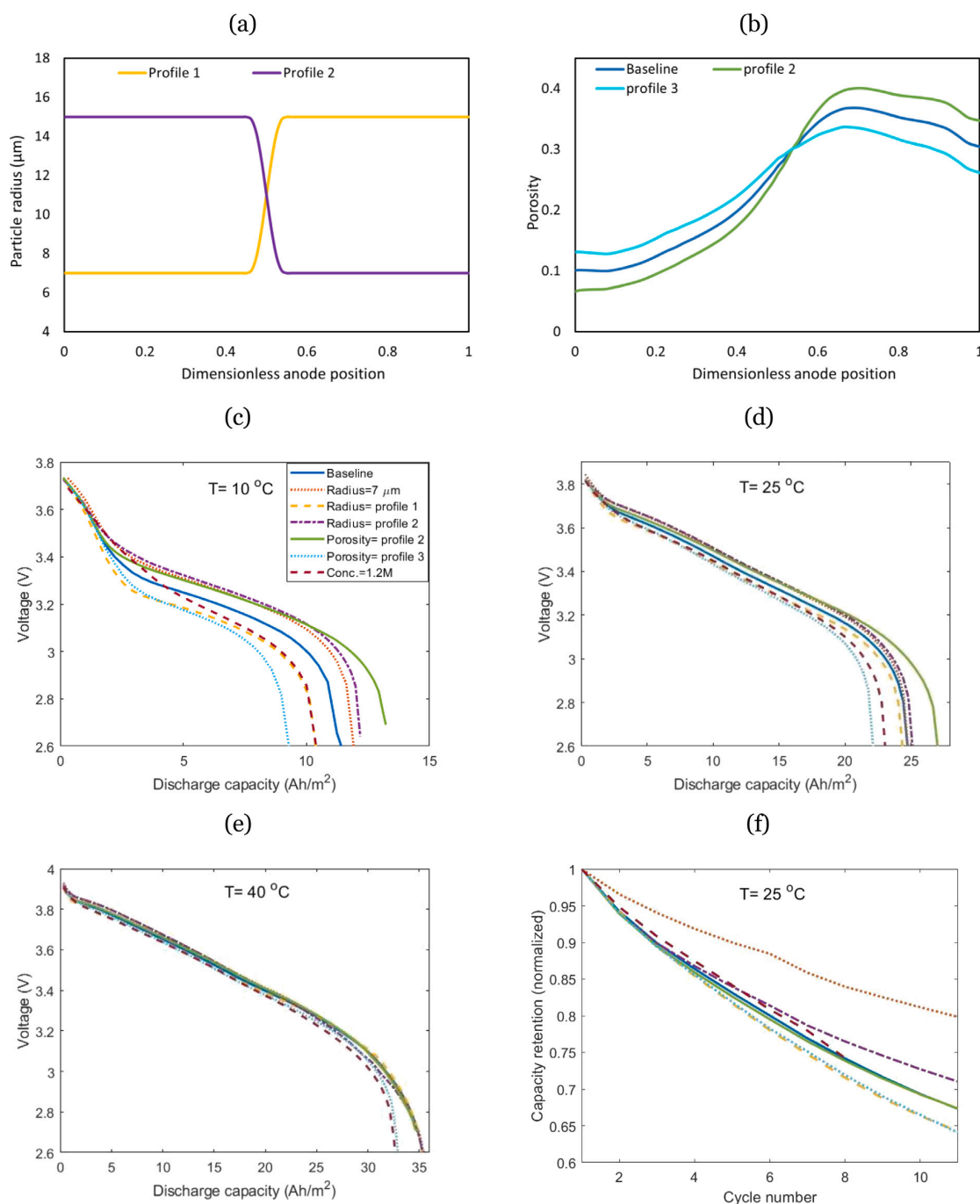


Fig. 8. (a) Anode particle radius as a function of anode position, (b) porosity as a function of anode position. position 0 is the current collector and 1 is the separator. Sensitivity analysis of different anode particle sizes, porosity profiles, and initial electrolyte concentration for 3C discharge at (c) 10 °C, (d) 25 °C, (e) 40 °C, (f) capacity retention with 5F1N protocol at 25 °C.

the SLA cell, yet, these properties are still not as high as for the baseline MLA. In 5F1N cycling, the SLA cell ceases operation at cycle 8 as the porosity reaches zero next to the separator, caused by the initially smaller porosity. Even higher concentrations of electrolyte would improve SLA performance even more, according to the model, but care must be taken because in practice the concentration gradient inside the cell could reach the precipitation limit of the salt at high C-rates. For instance, in the case of 3C discharge at 10°, the maximum

concentration is 3.2 M for the high-concentration-electrolyte (1.2 M average) SLA. This can be compared to the 2.8 M maximum concentration for the baseline (1 M average) MLA case.

4. Conclusions

An experimental comparison of a multi-layer anode against a homogeneous baseline anode demonstrated higher energy density for

high-rate discharge and better capacity retention during fast-charge cycles. To investigate this advantage, a P2D model with anode aging mechanisms was carefully parameterized by experiments. The model demonstrated enhanced performance of the cathode during high-rate discharge that stemmed from better transport in the MLA. Furthermore, during fast charge, this enhanced transport in MLA creates a more uniform particle surface concentration, more positive Li plating overpotential, and consequently less capacity loss. Polarization or overpotential analysis showed 3%–17% lower cumulative overpotential for MLA during different case studies such as high-rate discharge, 5F1N fast charge, and two drive cycles.

As suggested by the polarization and sensitivity analysis, two changes in MLA electrode morphology were predicted to enhance the energy density and capacity retention during fast charge: further increasing the porosity gradient and using smaller anode particles (either uniformly or by implementing a gradient in the particle size with smaller particles near the separator). Other considered cases did not improve the cell performance.

MLA demonstrates only a small difference in the total overpotential relative to SLA. Thus, it is quite unexpected to observe the significantly higher energy density at high rates and the cycle life being more than twice that for SLA under the 5F1N fast-charge protocol. One way to interpret such model results is to observe that because the cells are operated near their performance limits, even small improvements in the total overpotential can have significant beneficial outcomes. Thus, a multi-layer anode can perform much better than might be suggested by some earlier modeling-based analyses.

CRedit authorship contribution statement

Amir-Sina Hamedí: Methodology, Software, Validation, Formal analysis, Writing (original and revision), Visualization. **Adrian Yao:** Conceptualization, Methodology, Validation, Resources, Project administration. **Roxana Martin:** Investigation, Resources. **Raymundo Roig:** Validation, Formal analysis. **Michael Rivas Valadez:** Software, Validation, Formal analysis. **Donald Pile:** Investigation, Data curation. **Annadanesh Shellikeri:** Investigation, Resources. **Baichuan Liu:** Methodology. **Dean R. Wheeler:** Conceptualization, Methodology, Review and editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.electacta.2022.141649>.

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