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How to Design Lithium Ion Capacitors: Modelling, Mass Ratio of Electrodes and Pre-lithiation

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Lithium ion capacitors (LICs) store energy using double layer capacitance at the positive electrode and intercalation at the negative electrode. LICs offer the optimum power and energy density with longer cycle life for applications requiring short pulses of high power. However, the lack of intercalation based charge transfer resistance at the positive electrode. LICs can also offer higher cycle life than LIBs due to the lack of degradation mechanisms associated with the faradaic reactions and the stresses and strains associated with intercalation at the positive electrode. The negative electrode undergoes faradaic reactions and intercalation, but if a material, such as lithium titanate oxide (LTO), is used with a potential within the electrolyte stability window then degradation at this electrode can also be minimized.

There are many combinations of materials for LICs. One family of LICs are made using a combination of activated carbon (AC), polymer binders and conductive additives as the positive electrode and LTO (Li4Ti5O12) with the same binder and additives, as the negative electrode, with lithium hexafluorophosphate (LiPF6) in a mixture of organic solvents (typically 1 M, EC:DMC) as the electrolyte. As shown in Figure 1a. The LTO electrode, which is considered as a zero-strain material, operates at ca. 1.55 V vs Li/Li+ which is well above the electrolyte reduction potential (0.7 V) unlike graphite electrodes, and therefore offers longer cycle life and higher columbic efficiency. The higher potential also means that lithium-plating is less of a problem. For the same reason, lighter and cheaper aluminum current collectors can be used for the negative electrode instead of copper current collectors.

However, the energy density of a LTO-based LIC is less than a graphite-based LIC due to the lower operating voltage window (1.5-2.8 V) as well as the theoretical capacity of LTO (175 mAh/g) being lower than that of graphite (372 mAh/g). In this study, we focus on a LTO based LIC due to its higher rate capabilities and associated challenges with mass transport optimization.

Equation 1 describes how charge is stored at the positive electrode via charging of the electrochemical double layer with PF6− ions, and Equation 2 describes how charge is stored at the negative electrode via a faradaic charge transfer reaction with Li+ ions.

At positive electrode

\[ \text{AC} + \text{PF}_6^− \xrightarrow{\text{dich}} \text{AC}^+ \cdot \text{PF}_6^− \text{ (double layer)} + e^- \]  

At negative electrode

\[ \text{Li}_4\text{Ti}_5\text{O}_{12} + 3\text{Li}^+ + 3\text{e}^- \xrightarrow{\text{dich}} 3\text{Li}^+ \text{Li}_7\text{Ti}_5\text{O}_{12}. \]

During the intercalation process, Li4Ti5O12 (spinel) changes its phase to Li7Ti5O12 (rock salt). Figure 1b shows the changes of the potentials of the AC and LTO electrodes during charging of a cell from 0 to 2.8 V. The potential of the AC electrode increases from 3.05 to 4.3 V vs Li/Li+ whereas the intercalation/de-intercalation reaction at LTO electrode occurs at ca. 1.55 V (vs Li/Li+) for a wide state-of-charge (SOC) range (7–97.5%). The flat SOC range (7–97.5%) corresponds to the co-existence of the two phases of LTO. However, the LTO electrode undergoes large potential changes when operated close to 0 or 100% SOC, therefore it is considered sensible to avoid these regions. Side reactions due to the electrolyte degradation (1 M LiPF6 in 1:1 EC:DMC) at the AC electrode are negligible below 4.3 V vs Li/Li+. LICs have an important difference compared to LIBs, that the average concentration of charge carriers in the electrolyte of a LIC changes due to the both-in/both-out mechanism during charging/discharging, rather than the one-in-one-out mechanism for LIBs. This means changes in salt concentration must be considered under all operating conditions for LICs, whereas this can often be ignored for LIBs operating at low rates.

An operating condition for a LIC (LTO/AC) with LIBs (Li-ion, LTO/LiCoO2, LTO/LiMn2O4) and supercapacitors (AC/AC) using experimental studies was carried out by Du Pasquier et al. This showed that the cycle life of a LIC is at least one order of magnitude higher than the LIBs, and the LIC delivers 3 to 4 times higher cumulative energy throughput over its lifetime.

The mass ratio of the electrodes due to the unequal specific capacities of the materials is a critical parameter to optimize the cell design. Yang et al. varied the mass ratio of AC and LTO electrode materials and measured the specific capacity of the resulting LICs. The measurements show a maximum in cell specific capacity vs. mass ratio.

Disoke et al. experimentally investigated LICs with three different mass ratios of ACL/TLO and showed that the power and cycle life performance of the LIC are better at a lower mass ratios. The reasons for the poor performance and capacity fade of the LICs at higher mass ratios.
ratio were not clear. They compared the energy and power densities of LICs with EDLCs and the measurements show that the LIC’s energy and power densities are better than the EDLCs.

A similar study on the effect of electrode mass ratio on cycle life and power performance for the graphite (mesocarbon microbeads) based LICs was carried out by Shi et al.16 Though the negative electrode is chemically different, the conclusions were in qualitative agreement with Dsoke et al.’s.6

Pre-lithiation can also affect the cell level energy density of LICs, with Xu et al.17 discussing the role of this in LTO electrodes to avoid larger potential drop/increase during charging/discharging near 0% SOC. Here they presented limits for minimum and maximum pre-lithiation levels with respect to mass ratio of AC/LTO electrodes and AC electrode initial potential.

Due to the combination of charge storage mechanisms, the understanding of the dynamic behavior of a LIC is not straightforward. Optimization of the LIC design for the required power and energy specifications using experiments is time consuming, costly and tiresome. So, a physics-based model is helpful in reducing the development costs and time in providing the best design. Towards this goal, Stewart et al.13 carried out a study using a 1D physics-based model and compared the simulations with the discharge data of a LIC at different currents.

The authors highlighted the scope for the use of a LTO based LIC against LiFePO4/LTO based LIB using the model; they showed that the LICs outperform the high-power LIBs at high currents. Their study also includes how the cell performance can be improved by improving the electrode and electrolyte conductivities.

However, a comprehensive set of guidelines for design of LICs based on the insights from experiments and models on the mass ratio, high currents and pre-lithiation is not yet available. In this paper a physics based model is developed and used to study the effect of different designs on the dynamic behavior of LICs. First, the basic design calculations for the optimum mass ratio of the electrodes and the advantages of pre-lithiation in a LIC are presented. Next, the effect of different mass ratios of the electrodes at different charge/discharge currents is studied using the model and validated against the experimental data reported in the literature.6 The challenges of parameterisation of the model at high currents to predict the data are discussed. Later, the mass ratio of electrodes and the gradients of electrolyte concentration during operation are linked to IR and capacity losses. Finally, the model is used to predict the pre-lithiated LIC profiles. The model predicts the increase in cell capacity by utilizing the pre-lithiated Li and demonstrates electrolyte depletion/precipitation effects are higher in LICs with higher mass ratio.

**Design Aspects**

In this section, design factors such as mass ratio of electrodes, electrolyte volume and role of pre-lithiation are discussed based on theoretical limits of a LIC for optimum design.

**Optimum mass ratio**—The theoretical capacity of LTO is 175 mAh/g; however the experimentally realizable specific capacity (LTO/T2, Clariant, Germany) is approximately 160 mAh/g at 1 C.6 The measured specific capacity for AC (HDLC-20BST-UW, Haycarb, Sri Lanka) in a LIC system is 38.36 mAh/g (110 F/g) between 3.05–4.3 V.6 The capacity balance thus requires 4.17 g of AC per gram of LTO for the current set of materials.

Figure 2 shows the schematics of LICs at four different mass ratios ($r_{m}$)–0.72, 1.54, 4.17 and 6 of the electrodes (AC/LTO). We refer to these LICs as "LIC072", "LIC154", "LIC417" and "LIC600" respectively. The figure shows the schematics of uncharged LICs on the left and charged LICs in the middle with the corresponding potential profiles of the electrodes (vs. Li/Li$^+$) and the cell at very low currents on the right. The voltage profiles are plotted against the specific capacity (mAh/g) of LTO electrode. The mass ratios are chosen in accordance with Dsoke et al.’s.6 The uncharged and charged electrodes of AC and LTO are represented using different colors as per the legends in the figure. The voltage profiles are plotted against the specific capacity (mAh/g) of LTO electrode. The mass ratios are chosen in accordance with Dsoke et al.’s.6 The uncharged and charged electrodes of AC and LTO are represented using different colors as per the legends in the figure. The relative difference between the dark and lighter blue blocks represent the magnitude of depletion of ions at the end of charge (EOC) and the change in average concentration of electrolyte which is initially considered as 1 M in the uncharged LIC using the darker blue block. The area of the electrode blocks in each schematic are proportional to the mass of respective electrodes. SOC of the electrodes at

![Figure 1.](image-url)
Figure 2. The schematics of uncharged and charged LICs at different mass ratios—0.72, 1.54, 4.17 and 6. The uncharged LICs are shown on the left, the charged ones in the middle and corresponding voltage vs. capacity profiles are shown on the right. The cross-patterned area in the voltage vs. capacity figures indicates the available energy for each mass ratio. The change in SOC of LTO and AC and the average concentration of electrolyte at EOC are also indicated at respective LICs. EOC for each mass ratio is indicated using the relative difference in height of the charged and uncharged electrode blocks. The area of the electrolyte block represents the electrolyte volume.

The schematics show that the capacity of a LIC is limited by the AC electrode below mass-ratio ($r_m$) of 4.17 and by the LTO electrode above it. For LIC417, the charging is limited to 97.5% of LTO to avoid the larger potential change near 100% SOC and the cell capacity is limited equally by both the electrodes. For LIC600, the AC electrode is under-utilized (UU) at the higher values of potential, shown as dashed line indicating mass-ratio above 4.17 do not lead to increase in cell capacity. The drop in average concentration of electrolyte at EOC is proportional to the utilization of the limiting electrode. It is assumed that enough volume of electrolyte is present in the cells such that the average electrolyte concentration drops to 0.6 M on 100% charge of LTO electrode.

The cross patterned gray area in the voltage vs. capacity profiles represent the net energy ($\int IVdt$) available for each mass ratio. The upper cutoff potential for cell is 2.8 V, and AC electrode operates between 3.05–4.3 V. The dashed LTO and AC profiles indicate the excess capacity available in the cell for utilization.
Figure 3. Specific capacity of the cell vs. mass ratio between AC and LTO. Based on a) the mass in grams of LTO and on b) the combined mass in grams of LTO and AC. The values are calculated based on the specific capacities of LTO (160 mAh/g) and AC (38.36 mAh/g) and valid at low currents. The capacity is maximum at $r_{m}=4.17$ where the electrode capacities are balanced.

The cell capacity ($Q_{cell}$, mAh) is therefore given by

$$Q_{cell} = \min(C_{LTO} \times m_{LTO}, C_{AC} \times m_{AC})$$

Equation 3 is valid for the case of excess electrolyte in the cell.

Figure 3a shows the specific capacity of the cell based on the mass of LTO at different AC/LTO mass ratios, and Figure 3b shows the specific capacity of the cell based on the combined mass of LTO and AC electrodes at low C-rate assuming that the transport resistances and IR losses are negligible. At $r_{m}=4.17$, the Figures 3a and 3b show that the capacity reaches a plateau w.r.t to LTO mass and a maximum w.r.t to combined mass of LTO and AC active materials. The trends are in qualitative agreement with the experimental observations reported in the literature. However, at high currents, the data shows that LIC with lower mass ratio below 4.17 gives higher capacity and better cycle life.

A trade-off between power and energy density is necessary, which depends on the materials used, to decide the optimum mass ratio of the electrodes for a given application. A model-based study would be helpful in this regard. In addition, how thin and thick the electrodes could be limited by the electrode ink coating machinery for bulk production of the cells. These limitations of the machinery to get the required thickness/mass ratio for mass production of cells also need to be considered during the design of the cell.

Figure 4. a) LIC417 with thicker and thinner separators. The LIC with thicker separator holds sufficient volume of electrolyte to keep the concentration above 0.6 M to minimize the IR losses. b) The ionic conductivity of 1 M LiPF$_6$ in EC:DEC (1:1) as a function of concentration at 298.15 K.
Figure 5. Effect of prelithiation on cell capacity at different mass ratios when operated at low currents. a) LIC417, b) LIC154, and c) LIC072. LIC417 is prelithiated to 7%, and LIC154 and LIC072 are prelithiated to 50%.

Need for excess volume of electrolyte and salt.—The salt depletion effects are significant in LICs. Figure 4 shows the effect of how the average concentration drops to lower values at EOC, with salt depletion possible if enough volume of electrolyte and salt is not available. In these situations a thicker separator would be needed to act as a salt reservoir. The ionic conductivity is a strong function of the concentration for Li based electrolytes. The conductivity vs. concentration of LiPF₆ in EC:DEC (1:1) electrolyte at 298.15 K is shown in Figure 4b. 1 M is often the preferred concentration as the conductivity is highest. Beyond 1 M, the conductivity decreases due to electrostatic, viscous and precipitation effects; less than 1 M, the conductivity decreases due to lower concentration of charge carriers. Again, a model-based study would be helpful in understanding the dynamic evolution of local concentration during charging/discharging and electrolyte depletion/precipitation effects in the porous electrodes at different operating conditions for different cell designs.

Is pre-lithiation necessary?—While several reports indicate that pre-lithiation in LTO is not needed, other reports suggest that it is necessary to avoid the large potential change when SOCₜₒ is near to 0%, increase the cell capacity, and extend the cycle life. In the SOCₜₒ range where potential changes significantly (Figure 1b), the LTO is dominated by a single phase–Li₄Ti₅O₁₂ near 0% SOC and Li₇Ti₅O₁₂ near 100% SOC. The contribution to charge storage is very little in these regions. The flat potential region corresponds to coexistence of the two crystalline phases of LTO and is preferable for charging/discharging.

The experimental measurements of Xu et al. with different pre-lithiation levels in LTO show the effect of SOC range on electrode potential profiles. The authors have shown that the LIC capacity can be improved by pre-lithiating the LTO electrode to an optimum level which is dependent on the mass ratio. The improvement in the capacity is the result of utilizing the AC electrode below 3.05 V (vs. Li/Li⁺) without any abrupt change in potential of LTO electrode. Below 3.05 V, AC electrode becomes negatively polarized and forms double layer with Li⁺ ions used for pre-lithiation which are extracted from the pre-lithiated LTO. However, it is not clear whether they considered pre-lithiated lithium mass in the specific capacity calculations to compare with non-prelithiated LIC capacity values.

Rauhala et al. compared the performance of the pre-lithiated LIC with the non-prelithiated LIC and indicated that the most efficient use of positive carbon electrode occurs in pre-lithiated LIC due to stable voltage profile of the LTO electrode, thereby increasing in coulombic efficiency and cycle life. However, Rauhala et al. did not utilize the negative polarization (NP) of the positive AC electrode to improve the capacity citing that the energy gain is low at lower potentials. If there is no excess electrochemically active Li in LTO, any loss in Li due to side reactions affect the LIC performance. Pre-lithiation would help balance the losses and improve the cycle life.
The potential profiles of LIC417 in Figure 5a shows that pre-lithiation for LIC417 would reduce the utilization of the AC electrode as indicated by ‘UU’. As a result, the energy available for charge/discharge, indicated by the cross-patterned area, is lower. On the other hand, the pre-lithiation becomes useful for lower mass ratios. The representative profiles in Figures 5b and 5c show the effect of pre-lithiation on charge/discharge of LIC154 and LIC072 respectively. The profiles are for LICs pre-lithiated to 50% SOC and then charged to 2.8 V. The corresponding changes in the potentials of AC and LTO electrodes, and the available energy are shown in the figure. These profiles do not account for IR losses which are dominant at high currents.

Figure 6 represents the use of the NP region for LIC154 and LIC072 when the cell is discharged to 1.0 V at a low current. The red line indicates the change in potential of AC electrode when the electrode is negatively polarized to use the pre-lithiated Li to form the double layer. The capacitance data for the AC electrode in 1 M LiPF6 electrolyte from cyclic voltammetry experiments reported by Rauhala et al.7 shows that the capacitance in the NP zone is lower than the positive polarization zone. The difference in slope of voltage vs. time profile of AC electrode above and below 3.05 V vs. Li/Li+ during charge/discharge is also evident in the data presented in the literature.2,7 So, we adapted this difference in capacitance and showed the negatively polarized AC profiles with higher slope, which in turn indicates the lower capacitance.

The red colored cross-patterned shaded area in the figures indicates the energy/capacity gain due to the NP and pre-lithiation. Pre-lithiation becomes particularly advantageous when LIC undergoes degradation with cycling. Figure 6 also points to the need of optimization of pre-lithiation level in LTO electrode w.r.t the mass ratio as pre-lithiation affects the energy density due to added mass by inserted Li.7

Though, the pre-lithiation is advantageous in many ways, the process is time consuming and costly. Also, handling of metallic lithium at mass scale imposes many safety challenges, and the energy gained by NP in a pre-lithiated cell at low voltages may not be significant when compared to a non-prelithiated cell.7 In this context, Rauhala et al.7 demonstrated a way to operate a LIC in a stable voltage range without the need of pre-lithiation by maintaining the discharge cutoff of the cell at a higher value where LTO potential is above 1.5 V. This can be achieved at the cost of energy density from the second cycle. However, if the mass ratio of the electrodes is less than 4.17, the discharge cutoff potential moves higher to maintain SOC_{LTO} > 7% and the energy stored will be less.

Table I shows the maximum change in SOC_{LTO} at EOC and the discharge cutoff for the three mass ratios. The compulsion to maintain SOC_{LTO} > 0.07 during discharge reduces the available charge of LTO with decrease in mass ratio. For example, the available charge for LIC072 is equal to 60% of the stored charge(0.1727-0.07)/0.1727 and the new discharge cutoff cell potential will be 2.0 V. So, the net energy density will decrease accordingly and is reported in the table. Figure 7 shows the schematics of the energy available if a LIC had to operate within the flat SOC range for the three mass ratios. The red dots on the cell profiles indicate the voltage range of operation once the cell is fully charged to 2.8 V. Another way to identify the stable potential range for charge/discharge cycle for a given LIC irrespective of the mass ratio is to look at the cyclic voltammery.7

Next, we develop a 1D electrochemical model and use it to study the effect of varying mass ratio and pre-lithiation on LIC performance under dynamic conditions.

**Model Development**

The 1D electrochemical model for a LIC was developed by combining the governing equations of a LIB anode and an EDLC cathode from earlier works.13,20–24 The model is based on the porous electrode theory developed by Newman and co-workers for electrochemical systems.23 Figure 1a also shows the 1D representation of a LIC with the positive and negative electrodes, the separator and the current collectors. The model solves for four variables: potentials of the electrodes (φ), the concentration of electrolyte (c), and the concentration of Li in LTO particle (c_Li). The electrolyte in the pores connects the positive and negative electrodes through the porous separator.

The assumptions considered in the model are:

i. The electrolyte is binary.
ii. The current collectors are made up of aluminum sheets.

![Figure 6](image-url) Use of negative polarization(NP) in a) LIC154 and b) LIC072 when operated at low currents. Both the LICs are prelithiated to 50% SOC. The red colored cross-patterned area indicates the capacity gain by using AC electrode below 3.05 V in a prelithiated cell.
Figure 7. Voltage profiles and available energy with the discharge cutoff to avoid the need of prelithiation when operated at low currents. a) LIC417, b) LIC154, and c) LIC072.

iii. LTO particles are spherical and all the same size.
iv. The model is based on the concentrated electrolyte solution theory.23
v. The charge stored in the AC electrode is due to double layer alone and in the LTO electrode is due to Li-intercalation alone.
vii. The Li-intercalation in LTO particle is assumed to follow Fick’s law with constant diffusion coefficient.
viii. The double layer formation at the interface of the AC electrode is considered to be instantaneous and included in the model through the source term.24
ix. Structural changes in the electrodes are not accounted in the model.
xi. The convection effects in the electrolyte are considered to be negligible.
xii. The model is isothermal.

**Governing equations.**—Porosity electrodes (±).—Charge balance:
The current density (A/m²) (per unit projected area) of the electrode phase in the porous electrode domain is given by Ohm’s law as (Equation 4):

\[
i = -\sigma_{\text{eff}} \frac{\partial \phi}{\partial x}
\]  

where \(\sigma_{\text{eff}}\) (S/m) is the effective conductivity of the electrode. Then, the charge conservation equation (per unit volume of porous electrode matrix) for the electrode phase is

\[
\frac{\partial i_s}{\partial x} = -a_i j_s
\]

where \(a_i\) (m²/m³) is the inter-facial area of the electrode and \(j_s\) is the source term for double layer in AC electrode (+) and lithium intercalation in LTO electrode (−).

**Charge balance for electrolyte in pores**
The current density (A/m²) (per unit projected area) of the electrolyte phase in the porous electrode is given by:

\[
i_l = -k_{\text{eff}} \frac{\partial \phi_l}{\partial x} + \frac{2k_{\text{eff}}(1-t_s)RT}{F} \left(1 + \frac{\partial \ln f}{\partial \ln c_l}\right) \frac{\partial c_l}{\partial x}
\]

Here, the first term on R.H.S represents the contribution from migration due to the electric field and the second term represents the contribution from the concentration over-potential. \(k_{\text{eff}}\) (S/m) is the effective ionic conductivity of the electrolyte in the pores, \(t_s\) is the transference number of Li-ion in the electrolyte, \(F\) is Faraday constant, \(R\) is the gas constant and \(T\) is the temperature (K). \(f\) is the activity coefficient of the electrolyte and the term represents the correction due to concentrated electrolyte effects.
Then, the charge balance (per unit volume of porous electrode matrix) for the electrolyte phase in the porous electrode is given by
\[
\frac{\partial i_t}{\partial x} = a_i j_t, \quad [7]
\]
The overall charge balance in the porous electrode thus leads to
\[
\frac{\partial N_i}{\partial x} + \frac{\partial i_t}{\partial x} = 0 \quad [8]
\]
and
\[
i_t + i_i = I_{cell}. \quad [9]
\]

Here, \(I_{cell}\) is the current density (per unit projected area) of the cell.

**Mass balance for the electrolyte in pores:**
The ionic flux of electrolyte (per unit projected area) is given as
\[
N_i = -D_{eff} \frac{\partial c_l}{\partial x} + i_t \frac{F}{F_c} \quad [10]
\]
Here, \(D_{eff}\) (m²/s) is the effective diffusivity of electrolyte in the electrodes. The first term on R.H.S represents the flux due to the concentration gradient and the second term represents the flux due to the electric field.

The governing equation for the concentration of electrolyte (per unit pore volume) in the pores of the electrode is given by
\[
\frac{\partial c_l}{\partial t} = \frac{\partial}{\partial x} \left( D_{eff} \frac{\partial c_l}{\partial x} \right) + \frac{i_t}{F} \quad [11]
\]
Here, \(\varepsilon\) is the porosity of the electrode.

**Li ion diffusion in LTO particle:**
The governing equation for the concentration of Li-ions in the spherical LTO particles is given by
\[
\frac{\partial c_{l,t}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_{s} \frac{\partial c_{l,t}}{\partial r} \right) \quad [12]
\]
where
\[
r = \text{radius of LTO particle and } D_s = \text{diffusivity of Li in the particles.}
\]

**Source term in LTO electrode:**
The source term for charge conservation (per unit interfacial area) due to Li intercalation in LTO particles during charging/discharging, as per the Butler-Volmer equation, is given by
\[
j_{s,L} = i_t \left\{ \exp \left( \frac{\alpha_l F \eta}{RT} \right) - \exp \left( -\alpha_l F \eta \right) \right\} \quad [13]
\]
where \(\alpha_l\) is the exchange current density, \(\alpha_s\) and \(\alpha_c\) are apparent transfer coefficients for anodic and cathodic reactions respectively and \(\eta\) (V) is the overpotential.

The exchange current density for the Li-intercalation is given by
\[
i_t = F (k_s)^{\alpha_s} (k_c)^{\alpha_c} (c_{l,max} - c_l)^{\alpha_c} (c_l)^{\alpha_s} \quad [14]
\]
where
\[
k_{s} \text{ and } k_{c} \text{ are the reaction rate constants, } c_{l,max} \text{ is the maximum Li-ion concentration in LTO particle which corresponds to the state of charge (SOC = } c_l/c_{l,max} \text{) as unity, } c_{l,ref} \text{ is the reference concentration of the electrolyte which is, in general, equal to the initial concentration of the electrolyte in the uncharged LIC.}
\]

The overpotential for the Li intercalation is given by
\[
\eta = \phi_l - \phi_i - E_{eq}(SOC) \quad [15]
\]
where \(E_{eq}(SOC)\) is the equilibrium potential for Li intercalation reaction as a function of SOC of LTO electrode.

**Source term in AC electrode:**
The source term for charge conservation (per unit interfacial area) due to the double layer formation in AC electrode is given by
\[
j_{s,A} = C_{dl} \frac{\partial (\phi_l - \phi_i)}{\partial t} \quad [16]
\]
where \(C_{dl}\) (F/cm²) is the double layer capacitance per unit interfacial area of AC electrode.

**Separator:**—The source terms for charge/mass conservation in the separator are zero. The resulting equations are given below.

**Mass balance:**
The governing equation for electrolyte phase (per unit volume) in the separator domain is given by
\[
\frac{\partial c_{l,s}}{\partial t} = \frac{\partial}{\partial x} \left( D_{eff,s} \frac{\partial c_{l,s}}{\partial x} \right) \quad [17]
\]

**Charge balance:**
The current density (per unit projected area) in electrolyte phase is given by
\[
i_i = -k_{eff,i} \frac{\partial \phi_l}{\partial x} + \frac{2k_{eff,i}(1 - t_s)RT}{F} \left( 1 + \frac{\partial \ln f}{\partial \ln c_l} \right) \frac{\partial \ln c_l}{\partial x} \quad [18]
\]
Then, the charge balance for electrolyte in the separator domain is given as
\[
\frac{\partial i_l}{\partial x} = 0 \quad [19]
\]

There is no electrode phase current in the separator, so the potential and current density of solid phase are
\[
\phi_s = 0 \quad \text{and} \quad i_s = 0. \quad [20]
\]

**Current collector—Charge balance:**
There are no electrolyte phase and charge storage mechanisms in this domain, and the governing equations for the electrode current and charge conservation are given as
\[
i_i = -\sigma c_i \frac{\partial \phi_i}{\partial x} \quad [21]
\]

Although, the electrical conductivity is higher for the current collector, a separate domain is useful for accounting the additional resistance in the cell if required.

**Effective transport properties:**—The effective transport properties for the current in the electrode and electrolyte phase of porous electrodes are given by (Bruggeman’s correction)
\[
s_{eff} = s_s^{1.5} \quad [23]
\]
\[
\kappa_{eff} = \kappa_i^{1.5} \quad [24]
\]
\[
D_{eff} = D_i^{1.5} \quad [25]
\]
Here, \(\sigma\) is the conductivity of the electrode material and \(\kappa\) and \(D\) are the transport properties of the bulk electrolyte. Similarly, the effective properties for the electrolyte in the separator are corrected for the tortuosity using Bruggeman’s correction.

**Boundary conditions:**—Table II shows the boundary conditions used in the simulations w.r.t the spatial dimension, \(x = 0\) represents the contact point for the current at the current collector of AC electrode and \(x = L\) represents the contact point for the current at the current collector of the LTO electrode.

At \(x = 0\), \(I_{cell}\) depends on the type of simulation such as charge, discharge, C-rate, and cycling. At \(x = L\), \(\phi_i\) is grounded as the simulations need a reference potential. The individual electrode potentials are measured w.r.t a reference potential probe (\(\phi_{ref}\)) in the separator at the chosen location (Table VI). The boundary conditions for the intercalation into the LTO particle w.r.t r-dimension are also shown in the table. \(r = 0\) represents the center of the particle and \(r = r_p\) represents the surface of the particle.

**Model parameters:**—Table III shows the parameters used in the simulations. The physical parameters were obtained based on the data presented by Dsoke et al. for the LIC417. The calculations are presented in Appendix.
operation at 298.15 K with 1 M LiPF6 in EC:DEC (1:1) is assumed for the simulations. The transference number as a function of the electrolyte concentration is given by

\[ \tau_i = \frac{2.316 c_l^{0.1} + 0.3517 c_l - 0.4893 c_l + 0.4287}{1.03 c_l^{0.1} - 0.3517 c_l + 0.4893 c_l + 0.5713} \]

The diffusivity as a function of the electrolyte concentration is given by

\[ D_i = 7.588 \times 10^{-11} c_l^2 - 3.036 \times 10^{-10} c_l + 3.654 \times 10^{-10} \]

In the above relationships, \( \kappa \) is in \( s/m \), \( c_l \) is in \( M \), \( D_i \) is in \( m^2/s \); the relations were fitted for the measured data between 0.5 and 1.5 M by Lundgren et al. The authors reported that beyond 1.5 M, the electrolyte starts precipitating and the transport properties decrease in value significantly. However, we use these relations with the extrapolation of the properties beyond the concentration range as shown in Fig. 4b and Fig. 8 for the simulations in accordance with the observations.

**Equilibrium potential.**—The equilibrium potential for LTO electrode, \( E_{\text{eq,LTO}} \), as a function of capacity \( \phi \) is shown in Fig. 9.

**Initial conditions.**—The initial values of the variables are adaptive to SOC, pre-lithiation and mass ratio of a LIC as per the relations given in Table IV. The potentials of the electrodes are defined w.r.t Li/Li\(^+\). The influence of pre-lithiation level of LTO and excess LTO is taken into account for a given mass ratio on the initial values are introduced through the parameters “Prelith” and “ExsLTO” respectively. SOC\(_{\text{AC}}\), SOC\(_{\text{TTO}}\) and Prelith values should be between 0 and 1 and self-consistent for a given ExsLTO as per the relations given in the table. These relations also dictate the limits for pre-lithiation for a given mass ratio.

**Simulation details.**—The model simulations were carried out in a finite element analysis based COMSOL Multiphysics (v. 5.3a) software with Lithium-ion battery module on a HP platform with Xeon(R) processors, 64 GB RAM, and Windows 10 operating system. The 1D simulation geometry in x-direction was as per the schematic in

| Parameter | Value | Description |
|-----------|-------|-------------|
| \( a_{\text{AC}} \) | 9.65 \times 10^6 cm\(^2\)/cm\(^3\) | Interfacial area of AC electrode |
| \( a_{\text{TTO}} \) | 11.2 \times 10^4 cm\(^2\)/cm\(^3\) | Interfacial area of LTO electrode |
| \( \alpha_{\text{AC}} \) | 0.5 | Transfer coefficient for reaction at LTO |
| \( A_{\text{cell}} \) | 113 mm\(^2\) | Projected area of the cell |
| \( C_{\text{Li}} \) | 6.45 \times 10^{-6} F/cm\(^2\) | Reference concentration of electrolyte |
| \( c_{i,\text{max}} \) | 22,852 mol/m\(^3\) | Maximum concentration of Li in LTO particle |
| \( D_i \) | 6.8 \times 10^{-15} m\(^2\)/s | Diffusivity of Li in LTO particle |
| \( \delta \) | 1.25 V | Permissible change in potential of AC electrode |
| \( \psi_{\text{AC}} \) | 0.582 | Porosity of liquid phase in LTO electrode |
| \( \psi_{\text{TTO}} \) | 0.717 | Porosity of liquid phase in AC electrode |
| \( \psi_{\text{AC}} \) | 0.283 | Porosity of solid phase in AC electrode |
| \( \psi_{\text{TTO}} \) | 0.418 | Porosity of solid phase in LTO electrode |
| \( \psi_{\text{ex}} \) | 0.9 | Porosity of the separator |
| \( E_{\text{eq,AC,0}} \) | 3.14 V | Potential of AC vs. Li/Li\(^+\) uncharged |
| \( l_{\text{IC}} \) | 0.56 mA/cm\(^2\) | 1 C rate |
| \( k_{\text{AC}}, k_{\text{TTO}} \) | 2 \times 10^{-12} m^4 | Reaction rate constants |
| \( \sigma_{\text{AC}} \) | 560 S/m | Conductivity of AC electrode |
| \( \sigma_{\text{TTO}} \) | 1.21 S/m | Conductivity of LTO electrode |
| \( \sigma_{\text{IC}} \) | 3.55 \times 10^4 S/m | Conductivity of Al current collector |
| \( L_{\text{IC}} \) | 10 \mu m | Thickness of Al current collector |
| \( \rho_{\text{neg}} \) | 367 \Omega \cdot \text{cm} | Radius of LTO particle |
| \( T \) | 298 K | Temperature |
Figure 8. The influence of electrolyte concentration on the transport properties of 1 M LiPF$_6$ in EC:DEC (1:1) liquid electrolyte. a) diffusivity, b) activity dependence factor and c) transference number of Li ion. The parameters are extrapolated for the concentration below 0.5 M and above 1.5 M.

Figure 1a. ‘Direct(PARDISO)’ solver with a relative tolerance of $10^{-5}$ was used in the software. The maximum element size is $1 \times 10^{-7}$ m with refinement in AC and LTO domains. Full Fick’s law for Li-insertion in LTO particle in $r$-direction (radius) was handled by COMSOL. The model solves for solid Li concentration along the radius of the particle at each $x$-position across the LTO electrode. The linear distribution for discretization in the particle $r$-direction with 30 elements was set.

The convergence was tested by varying the mesh size and comparing the voltage vs. time profiles. The simulation results did not change with further mesh refining. The time steps taken were controlled by

| Variable | Value | Description |
|----------|-------|-------------|
| $Q_{LTO}$ | $C_{\text{cell}} \times L_{\text{LTO}}$ | Capacity of LTO electrode, C |
| $Q_{AC}$ | $C_{\text{cell}} \times V_{\text{LAC}}$ | Capacity of AC electrode, C |
| $Q_{\text{cell}}$ | min($Q_{\text{LTO}}$, $Q_{\text{AC}}$) | Capacity of a cell, C |
| $C_{\text{rate}}$ | Input | Current in C-rate |
| $\text{ExsLTO}$ | $Q_{\text{LTO}} / Q_{\text{AC}}$ | A factor which indicates the excess LTO in terms of the ratio of capacities w.r.t AC |
| Prelith | Input | Pre-lithiation level (0,1), 0- unprelithiated cell |
| $\text{SOC}_{\text{AC,0}}$ | Input | SOC of AC electrode, 0-uncharged |
| $\text{SOC}_{\text{LTO,0}}$ | Prelith + $\frac{\text{SOC}_{\text{AC,0}}}{\text{SOC}_{\text{LTO,0}}}$ | SOC of LTO electrode |
| $c_{i,0}$ | $c_{i,\text{ref}} - \frac{F \text{cell}(\text{SOC}_{\text{AC,0}}) \times \text{SOC}_{\text{LTO,0}}}{Q_{\text{cell}} \times \text{SOC}_{\text{LTO,0}}}$ | Concentration of electrolyte |
| $c_{i,LTO}$ | ($c_{i,\text{max}} \times \text{SOC}_{\text{LTO}}$) | Concentration of Li in LTO particles as a function of SOC, mol/m$^3$ |
| $\Phi_{\text{LTO,0}}$ | 0 | Potential of LTO electrode, V |
| $\Phi_{\text{el,0}}$ | $-E_{\text{eq,0}}(\text{SOC}_{\text{LTO}})$ | Potential of the electrolyte, V |
| $\Phi_{\text{el,AC,0}}$ | $E_{\text{eq,AC,0}} + (\beta \times \text{SOC}_{\text{AC}}) + \Phi_{\text{el,0,el}}$ | Potential of AC electrode, V |
| $I_{\text{cell}}$ | $\pm I_{\text{cell}} \times C_{\text{rate}}$ | Cell current, A/m$^2$ |
the software. The charge/discharge times for each simulation are reported in Table V. A SOC of ~0.07% is used to initialize the charge simulations of non-prelithiated LIC. The LIC model file (.mph) built in COMSOL is available under an open-source license agreement at this source.

Results and Discussion

**Effect of mass ratio.**—Figure 11 shows the comparison of the model predictions with the experimental data for LIC072, LIC154 and LIC417 at 10 C, 25 C, 100 C and 200 C. The cells were charged and discharged between 0.0 to 2.8 V. The predictions are obtained for the best fit of AC and LTO profiles during charging. For LIC072, the model predicts the electrode potentials vs. Li/Li$^+$ of LTO and AC well at both low and high currents. For LIC154, the model predicts the electrode potentials vs. Li/Li$^+$ of LTO and AC well at both low and high currents, except the discharge profile of the AC electrode at 200 C. While the model works well at 10 C for LIC417, at high currents (25, 100 and 200 C), the predictions for the LTO electrode deviate significantly from the experimental data. The deviation indicates that the total transport resistance in the LTO electrode is under-predicted. The slower Li insertion kinetics or complete utilization of LTO electrode locally or higher electronic and ion transport resistances in the pores of LTO electrode could be the reasons for the deviation. The deviations in AC electrode during discharge at 200 C for LIC417 and LIC154 and at 100 C for LIC417 indicate that the model over-predicted the IR losses in the electrode at the beginning of discharge. The deviations with similar slopes of voltage vs. time profiles of model and data, as in the AC electrode of LIC417 at 100 C, can be minimized by adjusting separator thickness and reference electrode position in the simulations.

Figure 12 shows the time evolution of the surface concentration of intercalated Li in LTO particles along the thickness of LTO electrode for charge and discharge at 10 C and 200 C for LIC072 and LIC417. The solid lines indicate the charging/discharging process as the increase in concentration with time, and the dashed lines indicate the discharge/de-lithiation process as the decrease in concentration with time. The simulations at the low and high currents for the low and high mass ratios show that the local surface concentration did not

### Table VI. Thickness of electrodes and reference electrode position for different loadings. $L_{\text{ref}}$ is positioned from AC electrode. The cell-to-cell variations in the experimental data in the form of IR losses are captured by adjusting the separator thickness and reference electrode position in each cell. $a$-model fit.

| Cell  | $L_{\text{LTO}}$, $\mu$m | $L_{\text{AC}}$, $\mu$m | $L_{\text{Sep}}$, $\mu$m | $L_{\text{ref}}$, $\mu$m | Resulting mass ratio |
|-------|--------------------------|--------------------------|--------------------------|--------------------------|----------------------|
| LIC072| 20                       | 45                       | 140                      | 135                      | 0.8                  |
| LIC154| 20                       | 90                       | 229                      | 203                      | 1.59                 |
| LIC417| 20                       | 245                      | 260                      | 112                      | 4.33                 |

### Table V. Simulation times for different currents and mass loadings.

| Cell   | 10 C | 25 C | 100 C | 200 C |
|--------|------|------|-------|-------|
| LIC072 | 59   | 23.2 | 4.8   | 1.7   |
| LIC154 | 119  | 45   | 7     | 2     |
| LIC417 | 257.2| 65.2 | 5.7   | 1.4   |

The agreement between the model and the data confirms the validity of the parameters.
Figure 11. Comparison of the simulations with the data at different mass ratios for a given C-rate. a) 10 C, b) 25 C, c) 100 C and d) 200 C. The data (represented with symbols) was taken from Dsoke et al.6 for three cells with different mass ratio of AC/LTO: 0.72, 1.54 and 4.17. The solid black and brown lines indicate the corresponding simulations for each mass ratio.

As C-rate based on the mass of LTO indicates the same inter-facial current density for the same LTO electrode thickness (20 \(\mu\)m) in all the cells, the larger deviation specific to LIC417 cannot be explained using slow Li-insertion kinetics in LTO, especially in the case of lower achievable capacity (Figures 13a and 11c and 11d) of LTO in LIC417 at 100 C and 200 C than the LIC154.

Electrolyte depletion in a electrode is proportional to utilization of the limiting electrode and charge/discharge current. The basic calculations (\(d_{\text{cell}} \varepsilon_{\text{LTO}} = 16.4\)) indicate that there aren’t enough moles of electrolyte ions available in the pores of LTO for complete utilization of LIC417 and ions have to come from the separator reservoir during charging at all current. For AC, the value is 1.08 (\(d_{\text{cell}} \varepsilon_{\text{AC}} = 1.08\)). Figure 14 shows the simulations of electrolyte concentration profiles for the charge and discharge at 10 C and 200 C currents for LIC072 and LIC417. The figure shows the time evolution of electrolyte concentration in the pores of AC electrode, separator and LTO electrode; the solid lines indicate the charging/lithiation process as the decrease in concentration with time, and the dashed lines indicate the discharge/delithiation process as the increase in concentration with time.

The simulations indicate that the gradients are steep in the cells at higher currents and the concentration in the LTO electrode domain drops significantly during charging. Though excess electrolyte is available in the separator, the ions from the separator could not diffuse faster enough to replenish the ions in pores at a rate equivalent to the charging in LTO electrode at high charging currents. The process is limited by the mass transfer of less mobile Li ions to the LTO electrode.
Figure 12. Evolution of surface lithium concentration in the LTO particles with time along the thickness of LTO electrode at low (10 C) and high (200 C) currents for low (0.72) and high (4.17) mass ratios: a) 10 C, 0.72 mass ratio, b) 200 C, 0.72 mass ratio, c) 10 C, 4.17 mass ratio, and d) 200 C, 4.17 mass ratio. The solid lines indicate the charging/lithiation process as the increase in concentration with time, and the dashed lines indicate the discharge/de-lithiation process as the decrease in concentration with time. The LTO domain values in simulations are different for the two cells due to different separator thickness (Table VI).

Figure 13. Achieved capacity (a) and cell utilization (b) of LICs during charging at different currents and three mass loadings. The values are calculated from the charging times given in Dsoke et al.6 The initial capacities of the cells are estimated using the thickness of the electrodes. 1 C = 175 mA/g of LTO.
Figure 14. The time evolution of electrolyte concentration during charging and discharging at 10 C and 200 C rate for 0.72 and 4.17 mass ratios: a) 10 C and 0.72 mass ratio, b) 200 C and 0.72 mass ratio, c) 10 C and 4.17 mass ratio, and d) 200 C and 4.17 mass ratio. The solid lines indicate the charging process as depletion in the concentration with time, and the dashed lines indicate the discharge process as increase in the concentration with time.

The difference in mobility of Li$^+$ and PF$_{6}^-$ ions and the condition of electroneutrality cause the unequal drop in concentration of a binary electrolyte in the positive and negative electrodes.23,24 Even at 10 C, the depletion is higher in LTO of LIC417 due to higher utilization. The profiles for 25 C and 100 C of LIC417 also show higher depletion in LTO electrode due to higher utilization and higher current (not shown here). The figure indicates that more the utilization of LTO and/or higher the charge current, more the depletion effects. As the electrolyte conductivity is a strong function of the concentration, in this operating domain, the electrolyte resistance increases and reduces the utilization by reaching the cutoff potential much earlier.

It is reported20,31 that a simplified Bruggeman correction for tortuosity in ion-conductivity is insufficient and further reduction of ionic conductivity in pores of battery electrodes is required to account the additional IR losses. The under-accounted tortuosity in ion-conductivity further increases the depletion effects and IR losses, and thereby reduction in capacity utilization.24 In the present cells, the under-accounted tortuosity of both the AC and LTO electrodes for the transport properties (Equations 23, 24 and 25) through the simplified Bruggeman relationship could be one of the reasons for the difference between the model and the data for the deviation. The role of thicker AC electrodes for under-utilization of LIC417 and LIC154 cannot be avoided.

The deviations in LTO at the beginning of charge in all the three cells, even at 10 C, cannot be explained by depletion effects as they are absent. Variation in $D_e$ and $\sigma_{LTO}$ when LTO changes$^{14-16}$ from single phase to two phase at the beginning of charging can be the reasons. It is also possible that the experimental data$^6$ is taken from cycling experiment after few cycles instead of a single charge/discharge experiment where the initial conditions are different from the simulations. This can lead to over prediction of IR drop in thicker AC electrodes at high currents when LIC changes from charging to discharge.

Figure 14b also shows the buildup of concentration of LiPF$_6$ during the discharge at 10 C (indicated by dashed lines) in the LTO electrode of LIC417. The local concentration profiles in the electrolyte phase of the LTO electrode beyond 1.5 M indicate the regions where salt precipitation is possible. These precipitation effects are minimal for the lower mass ratio as observed from the simulations for LIC072, in terms of the lower peak concentration in the LTO electrode. During cycling of a LIC in the given potential range, the cumulative precipitation effects could be one of the reasons for capacity fade at 10 C in higher mass ratio cells as observed in Dsoko et al.

Further analysis on capacity fade in LICs is reported in a separate communication.32 It is to be noted that the precipitation effects are dependent on the discharge current and utilization of the cell together.

Therefore, the excess LTO electrode for lower mass ratios, in the form of larger thickness, alleviates the precipitation effects by providing more pore volume for the same number of moles.13 The depletion effects can also be minimized by excess LTO at lower mass ratio.

Unambiguous conclusion about the reasons for deviation between the model and the data of LTO and AC at high currents requires accurate parameterisation of tortuosity effects for electrolyte depletion in both the porous electrodes and additional in-detailed 3-electrode LIC measurements for different designs, which are unavailable for the current study. Li diffusion/kinetics in LTO as a function of SOC would also help establish the reasons. The model file (.mph) available under
Pre-lithiation studies.—In this section, the model’s ability to predict the different cases of pre-lithiation at 1 C was demonstrated. Figure 15a shows the charge-discharge simulations of LIC417 at 1 C operated between 7-97.5% SOC. For the current LTO material, the optimum SOC range corresponds to 11 mAh/g\textsubscript{LTO} (7% SOC) to 156 mAh/g\textsubscript{LTO} (97.5% SOC). The LTO is pre-lithiated to 7% SOC using \textit{Prelith} parameter to avoid the large changes in potential during charge-discharge. The model predicts the relatively flat charge-discharge profiles of LTO.

The other use of pre-lithiation is to increase the capacity of the cell by utilizing the NP region of the AC electrode. Figure 15b shows the galvanostatic charge/discharge simulation of LIC154 with pre-lithiation to 50% SOC. The cycling of LIC154 is carried out between 1.0-2.8 V cell potential by utilizing pre-lithiated LTO to get higher capacity. In these simulations, the AC electrode is discharged to below 3.05 V vs Li/Li\textsuperscript{+} to use the NP region albeit with reduced value of double layer capacitance (0.7 C\textsubscript{dl} for V\textsubscript{AC} < 3.05 V and C\textsubscript{dl} for V\textsubscript{AC} ≥ 3.05 V). As discussed before, the double layer capacitance of the AC electrode with Li\textsuperscript{+} ions is lower than that of with PF\textsubscript{6} ions.\textsuperscript{7,17} This phenomena can be observed as increase in slope of AC potential below 3.05 V and cell potential below 1.5 V in charge/discharge profiles.

These simulations are in qualitative agreement with the experimental data reported in Xu et al.\textsuperscript{17} and generated for the first time using a physics based model.

Figure 15c shows the simulations in which LIC417 is cycled at 1 C in the stable SOC range without the need for pre-lithiation. For the first cycle, the LIC is charged to 2.8 V and then discharged only to higher discharge cutoff potential of 1.6 V which corresponds to SOC\textsubscript{LTO} > 7%. Later on, the cell is cycled between 1.6-2.8 V. The simulations show that the LIC is operated in the stable potential limits of LTO and the AC electrode is efficiently utilized through out the cycling. However, in this operating protocol, the available energy is lower for the lower mass ratio. These simulations confirm that the model can be used for predicting the optimum pre-lithiation level for given mass ratio.

Conclusions

In this work, we proposed the set of guidelines for optimization of mass ratio of electrodes, electrolyte volume and pre-lithiation level in negative electrode based on theoretical principles for LTO-based LICs at low currents. We used a 1D physics-based model for a LIC based on Newman’s porous electrode theory to assist the cell designers for high current performance. We parameterised the model based on the data reported in the literature for a capacity balanced mass ratio cell i.e. LIC417 at 1 C and studied the effect of charge/discharge current and electrolyte depletion/precipitation effects at three mass-ratios. The model works well for the lower mass ratios, LIC072 and LIC154, at both low and high currents but parameterisation of the model to predict the data at high currents for LIC417 was a challenge. The deviations could be due to electrolyte depletion in the pores of both the electrodes. Accurate parameters and quantification of ion tortuosity effects on ionic conductivity in pores using additional in-detailed experimental data are required for the predictions at higher currents. However, the qualitative conclusions do not change. The model shows the electrolyte precipitation/depletion effects are higher at higher mass ratio and lead to poorer power performance at high currents.

Furthermore, the model predicts the limitations for pre-lithiation w.r.t mass ratio and the use of negative polarization of the AC electrode to improve the capacity of the cell. The model also demonstrates the protocol for cycling the cell without pre-lithiation to avoid the costs associated with it. The model framework developed here can be used for optimizing the power and energy performance of different designs of LICs. The model file (.mph) built in COMSOL is available under an open-source license agreement\textsuperscript{26} for further development of LICs.

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Appendix: Estimation of Physical Parameters

The values with their sources for calculation of physical parameters are given in Table A1.
Table A1. Values used for calculation of physical parameters.

| Parameter            | LIC417 | LTO | AC  |
|----------------------|--------|-----|-----|
| Specific capacity, mAh/g | 160    | 38.36 |     |
| DL Capacitance, F/g  | –      | 4.10 |     |
| Thickness, µm        | 20     | 245  |     |
| Mass loading, mg/cm² | 3.2    | 13.87 |     |
| Projected area, cm²  | (A_{cell})^2 | 1.13 | 1.13 |
| 1 C rate, mA/cm²     | –      | 0.56  | –   |
| Specific surface area, m²/g | 7²       | 1705 |
| Voltage change in AC, V | –      | 1.25 (3.05–4.3 V) | – |
| \(v_{\text{s,act}}\), mol/m³ | 22982 | –   | –   |

**LTO electrode:** 1 C rate per unit projected area (\(\phi_{\text{LTO}}\)) = 175 mA/cm² × 3.2 mg/cm²

Inter-facial area (\(A_{\text{inter}}\)) = \(\frac{1.22 \times 3.2 \times 10^{-10}}{20 \times 10^{-10}} \text{ m}^2 = 1.12 \times 10^{-7} \text{ m}^2\)

Capacity (\(Q_{\text{LTO}}\)) = 160 mA/cm² × 3.2 cm × 1.3 cm = 1.035 C

Density of porous LTO electrode = \(1.6 \text{ g/cm}^3\)

Porosity of solid phase = \(1 - \frac{\rho_{\text{LTO}}}{\rho_{\text{LTO} \text{p}}\sqrt{\alpha}}\)

Porosity of electrolyte phase (\(\phi_{\text{LTO}}\)) = 1 - \(\phi_{\text{LTO}}\)

Density of LTO particles = \(1.8 \text{ g/cm}^3\)

Radius of LTO particle = \(3.83 \text{ g/cm}^3\)

**AC electrode:** Inter-facial area (\(A_{\text{inter}}\)) = \(\frac{1.22 \times 3.2 \times 10^{-10}}{20 \times 10^{-10}} \text{ m}^2 = 6.45 \times 10^{-7} \text{ m}^2/\text{cm}^2\)

Density of porous AC electrode = \(0.566 \text{ g/cm}^3\)

Density of AC = \(2 \text{ g/cm}^3\)

Inter-facial DL capacitance (\(C_{\text{f}}\)) = \(1.8 \text{ F/cm}^2\)

Diffusivity of Li ion in LTO electrode, m²/s

Diffusivity of electrolyte in porous electrode, m²/s

Equilibrium potential of LTO electrode as a function of SOC

Activity coefficient of electrolyte

Current density at 1 C rate, A/m²

Cell current density, A/m²

Cathodic and anodic rate constants, m/s

Thicknes of AC electrode, m

Thickness of LTO electrode, m

Thickness of separator, m

Thickness of current collector, m

Cell capacity, C

Radius of LTO particle, m

Time, s

Transference number of cation

Temperature, K

Cell voltage, V

Position, m

**Greek**

\(\alpha_{\text{AC}}, \alpha_{\text{LTO}}\) Transfer coefficients of anodic and cathodic Li intercalation at LTO electrode

\(\varepsilon\) Porosity, subscripts: \(l\)–liquid phase, \(s\)–solid phase, \(sep\)–separator

\(\eta\) Over-potential for reaction at LTO, V

\(\kappa\) Electrolyte conductivity, S/m

\(\sigma\) Conductivity of material, i, S/m

\(\phi_{\text{LTO}}\) Electrode potential, V

\(\phi_{\text{AC}}\) Electrolyte potential, V

**Constants**

\(F\) Faraday constant, 96.485 C/mol

\(R\) Gas constant, 8.314 J/mol·K

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