

Supplementary information S1

S1.1: Table of P2D input parameters

Parameter symbol	Parameter unit	Parameter description	Value for LIB	Source/Comment	Value for NIB	Source/Comment
$l_{cc,a}/2$	[m]	0.5*thickness of current collector anode (Cu sheet for LIB, Al sheet for NIB)	4×10^{-6}	Value from ref. ¹	4×10^{-6}	Same values were assumed as for LIB
$l_{cc,c}/2$	[m]	0.5*thickness of current collector cathode (Al sheet for both LIB and NIB)	10×10^{-6}	Value from ref. ¹	10×10^{-6}	Value from ref. ¹
l_a	[m]	Thickness of anode	Variable	Optimized for discharge requirement	Variable	Optimized for discharge requirement
l_c	[m]	Thickness of cathode	Variable (see chapter 1.2.4 below for more details)	Optimized for discharge requirement	Variable (see chapter 1.2.4 below for more details)	Optimized for discharge requirement
l_s	[m]	Thickness of separator	25×10^{-6}	Celgard specification sheet	25×10^{-6}	Celgard specification sheet
ϵ_a	[-]	Porosity anode	Variable	Optimized for discharge requirement	Variable	Optimized for discharge requirement
ϵ_c	[-]	Porosity cathode	Variable	Optimized for discharge requirement	Variable	Optimized for discharge requirement
ϵ_s	[-]	Porosity separator	0.39	Celgard specification sheet	0.39	Celgard specification sheet
$\epsilon_{f,a}$	[-]	Filler fraction anode (total volume fraction of binder + conductive additive in anode)	$\frac{0.07\rho_a - 0.07\epsilon_a\rho_a}{0.93\rho_f + 0.07\rho_a}$	Electrode composition: 93 wt.% active material and 7 wt.% filler (3 wt.% binder + 4 wt.% conductive additive)	$\frac{0.07\rho_a - 0.07\epsilon_a\rho_a}{0.93\rho_f + 0.07\rho_a}$	Electrode composition: 93 wt.% active material and 7 wt.% filler (3 wt.% binder + 4 wt.% conductive additive)
$\epsilon_{f,c}$	[-]	Filler fraction cathode (total volume fraction of binder + conductive additive in cathode)	$\frac{0.07\rho_c - 0.07\epsilon_c\rho_c}{0.93\rho_f + 0.07\rho_c}$	Electrode composition: 93 wt.% active material and 7 wt.% filler (3 wt.% binder + 4 wt.% conductive additive)	$\frac{0.07\rho_c - 0.07\epsilon_c\rho_c}{0.93\rho_f + 0.07\rho_c}$	Electrode composition: 93 wt.% active material and 7 wt.% filler (3 wt.% binder + 4 wt.% conductive additive)
c_e^{init}	[mol/m ³]	Initial Li ⁺ or Na ⁺ concentration in electrolyte	1,000	Assumed	1,000	Assumed
$c_{s,a}^{max}$	[mol/m ³]	Maximum solid phase Li ⁺ or Na ⁺ concentration in anode active material	30,500	Calculated	Present scenarios: 20,900 Future scenarios: 30,500	Present scenarios: calculated based on ref. ²
$c_{s,a}^{init}$	[mol/m ³]	Initial solid phase Li ⁺ or Na ⁺ concentration in anode active material	$0.90c_{s,a}^{max} = 27,450$	Calculated	Present scenarios: $0.90c_{s,a}^{max} = 18,810$ Future scenarios: $0.90c_{s,a}^{max} = 27,450$	Calculated
$c_{s,a}^{min,avg}$	[mol/m ³]	Minimum average solid phase Li ⁺ or Na ⁺ concentration in anode active material (equivalent to cut-off state-of-charge)	$0.01c_{s,a}^{max} = 305$ (cut-off SoC = 1%)	Calculated	Present scenarios: $0.10c_{s,a}^{max} = 2,090$ (cut-off SoC = 10%) Future scenarios: $0.01c_{s,a}^{max} = 305$ (cut-off SoC = 1%)	Calculated

$c_{s,c}^{max}$	[mol/m ³]	Maximum solid phase Li ⁺ or Na ⁺ concentration in cathode active material	49,200	Calculated	Present scenarios: 42,200 Future scenarios: 49,200	Calculated
$c_{s,c}^{init}$	[mol/m ³]	Initial solid phase Li ⁺ or Na ⁺ concentration in cathode active material	$0.44c_{s,c}^{max} = 21,648$	Calculated based on ref. ³	Present scenarios: $0.50c_{s,c}^{max} = 21,100$ Future scenarios: $0.44c_{s,c}^{max} = 21,648$	Present scenarios: calculated based on ref. ⁴
D_e $D_{e,eff,a}$ $D_{e,eff,s}$ $D_{e,eff,c}$	[m ² /s]	Electrolyte diffusion coefficient of Li ⁺ or Na ⁺ Effective diffusion coefficient in anode Effective diffusion coefficient in separator Effective diffusion coefficient in cathode	3×10^{-10} $D_e \varepsilon_a^{brugga}$ $D_e \varepsilon_s^{bruggs}$ $D_e \varepsilon_c^{bruggc}$	Assumed based on ref. ⁵	Pessimistic scenarios: 3×10^{-10} Base scenarios: 3.84×10^{-10} Optimistic scenarios: 6×10^{-10}	In the base scenarios, we assume that electrolyte diffusion coefficients (Li ⁺ vs. Na ⁺) are proportional to self-diffusion coefficients of Li ⁺ /Na ⁺ in diluted aqueous solution. ⁶
$D_{s,a}$	[m ² /s]	Solid phase diffusion coefficient of Li ⁺ or Na ⁺ in anode	4.02×10^{-14}	Similar to ref. ⁷	4.02×10^{-14}	Same value as for LIB assumed
$D_{s,c}$	[m ² /s]	Solid phase diffusion coefficient of Li ⁺ or Na ⁺ in cathode	4×10^{-15}	Similar to ref. ⁸	4×10^{-15}	Same value as for LIB assumed
k_a	[m ^{2.5} /(mol ^{0.5} s)]	Heterogeneous reaction rate constant anode	2×10^{-11}	Value from ref. ³	Pessimistic scenarios: 2×10^{-11} Base scenarios: 2×10^{-9} Optimistic scenarios: 2×10^{-8}	Scenarios defined based on refs. ⁹⁻¹¹ . Note that if desolvation is the rate-limiting step in the charge transfer reaction, the heterogeneous rate constant may be several orders of magnitude higher in NIBs than LIBs.
k_c	[m ^{2.5} /(mol ^{0.5} s)]	Heterogeneous reaction rate constant cathode	2×10^{-11}	Value from ref. ³	Pessimistic scenarios: 2×10^{-11} Base scenarios: 2×10^{-9} Optimistic scenarios: 2×10^{-8}	Scenarios defined based on refs. ⁹⁻¹¹ . Note that if desolvation is the rate-limiting step in the charge transfer reaction, the heterogeneous rate constant may be several orders of magnitude higher in NIBs than LIBs.
$R_{p,a}$	[m]	Particle radius of anode active material	2×10^{-6}	Assumed	2×10^{-6}	Same values were assumed as for LIB
$R_{p,c}$	[m]	Particle radius of cathode active material	2×10^{-6}	Assumed	2×10^{-6}	Same values were assumed as for LIB
$\rho_{cc,a}$	[kg/m ³]	Density anode current collector	8,960	Value from ref. ¹	2,700	Value from ref. ¹
$\rho_{cc,c}$	[kg/m ³]	Density cathode current collector	2,700	Value from ref. ¹	2,700	Value from ref. ¹
ρ_a	[kg/m ³]	Density anode active material (fully delithiated/desodiated state)	2,200	Value from ref. ¹	Present scenarios: 1,700 Future scenarios: 2,200	Assumed

ρ_c	[kg/m ³]	Density cathode active material (fully lithiated/sodiated state)	4,750	Value from ref. ¹	4,750	Same value as for LIB was assumed
ρ_b	[kg/m ³]	Density binder	1,800	Value from ref. ¹	1,800	
ρ_{cond}	[kg/m ³]	Density conductive additive	2,260	Value from ref. ¹	2,260	Same value as for LIB assumed
ρ_f	[kg/m ³]	Density filler (mixture of binder + conductive additive in 3:4 wt. ratio)	2,063	Calculated	2,063	Calculated
ρ_e	[kg/m ³]	Density electrolyte	1,200	Value from ref. ¹	1,200	Same value as for LIB assumed
ρ_s	[kg/m ³]	Density separator polymer	946	Value from ref. ¹	946	Same value as for LIB assumed
$\sigma_{cc,a}$	[S/m]	Electronic conductivity anode current collector	5.96×10^7	Value from ref. ⁷	3.55×10^7	Value from ref. ⁷
$\sigma_{cc,c}$	[S/m]	Electronic conductivity cathode current collector	3.55×10^7	Value from ref. ⁷	3.55×10^7	Value from ref. ⁷
σ_a $\sigma_{a,eff}$	[S/m]	Electronic conductivity of composite anode Effective electronic conductivity of composite anode	10 $\sigma_a(1 - \varepsilon_a)$	Value assumed	10 $\sigma_a(1 - \varepsilon_a)$	Same value as for LIB assumed
σ_c $\sigma_{c,eff}$	[S/m]	Electronic conductivity of composite cathode Effective electronic conductivity of composite cathode	1 $\sigma_c(1 - \varepsilon_c)$	Value assumed	1 $\sigma_c(1 - \varepsilon_c)$	Same value as for LIB assumed
a_a	[m ² /m ³]	Anode active material area to surface ratio	$\frac{3(1 - \varepsilon_a - \varepsilon_{f,a})}{R_{p,a}}$	Calculated	$\frac{3(1 - \varepsilon_a - \varepsilon_{f,a})}{R_{p,a}}$	Calculated
a_c	[m ² /m ³]	Cathode active material area to surface ratio	$\frac{3(1 - \varepsilon_c - \varepsilon_{f,c})}{R_{p,c}}$	Calculated	$\frac{3(1 - \varepsilon_c - \varepsilon_{f,c})}{R_{p,c}}$	Calculated
$brugg_a$	[-]	Bruggeman coefficient anode	2.5	Value assumed based on ref. ¹²	2.5	Same value as for LIB assumed
$brugg_c$	[-]	Bruggeman coefficient cathode	2.5	Value assumed based on ref. ¹²	2.5	Same value as for LIB assumed
$brugg_s$	[-]	Bruggeman coefficient separator	2.5	Value assumed based on ref. ¹²	2.5	Same value as for LIB assumed
t^+	[-]	Transference number of Li ⁺ or Na ⁺	0.4	Assumed based on ref. ¹³	Pessimistic scenarios: 0.4 Base scenarios: 0.5 Optimistic scenarios: 0.5	Assumed
F	[C/mol]	Faraday constant	96,485		96,485	
R	[mol/(J K)]	Universal gas constant	8.3145		8.3145	

S1.2 Additional P2D input parameters and discussion

S1.2.1 Parameters LIB

Electrolyte ionic conductivity $\kappa(c)$: fit to experimental conductivity of LiPF₆ in EC:DMC (3:7 wt.)¹⁴, T = 30 °C was assumed. Note that $\kappa_{eff}(c) = \varepsilon^{brugg}\kappa(c)$.

$$\kappa(c) = 3.01 * 10^{-3} * c - 2.4845 * 10^{-6} * c^2 + 8.9583 * 10^{-10} * c^3 - 1.241 * 10^{-13} * c^4$$
$$\kappa(c) \quad \text{in units of} \quad \left[\frac{S}{m} \right] \quad \quad c \quad \text{in units of} \quad \left[\frac{mol}{m^3} \right]$$

The open circuit potentials were taken from the below references:

- Graphite: ref.⁷
- LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂: ref.³

Cut-off voltage LIB: 2.80 V.

S1.2.2 Parameters NIB

Remark regarding heterogeneous rate constant: Browning et al.¹⁰ compared desolvation activation energies of Na⁺ and Li⁺ and found values of ca. 20 kJ/mol and 50 kJ/mol, respectively. Assuming that desolvation is the rate determining step in the intercalation process one finds that the heterogeneous rate constant is a factor $\exp(-30,000/RT) \approx 1.8 \times 10^5$ higher for Na⁺ than for Li⁺. Nikitina et al.⁹, in contrast, found a 10-100 times higher charge transfer resistance for Li⁺ than for Na⁺, implying that the heterogeneous rate constant is ca. 10-100 times higher for Na⁺ than Li⁺. These considerations provide the basis for the scenarios in this study.

Electrolyte ionic conductivity pessimistic scenarios: $1.0 * \kappa_{Li}(c) = \kappa_{Na}(c)$

Electrolyte ionic conductivity base scenarios: $1.2 * \kappa_{Li}(c) = \kappa_{Na}(c)$

Electrolyte ionic conductivity optimistic scenarios: $1.5 * \kappa_{Li}(c) = \kappa_{Na}(c)$

Open circuit potential of hard carbon was obtained by fitting to discharge curve in ref.²:

$$U = 0.06319 + 14.18 * \exp(-16.84 * \theta) - 1.402 * \exp(-14.17 * \theta) - 21.5 * \exp(-23.19 * \theta) + 10.8 * \exp(-32.34 * \theta)$$

$\theta = \frac{c_s^*}{c_s^{max}}$ where c_s^* denotes the solid phase Na⁺ surface concentration and c_s^{max} the maximum solid phase Na⁺ concentration.

Open circuit potential of $\text{NaNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ was obtained by fitting to discharge curve in ref.⁴:

$$U = -0.022893 * \left(\frac{\theta - 0.72957}{0.14747}\right)^5 - 0.051731 * \left(\frac{\theta - 0.72957}{0.14747}\right)^4 + 0.087786 \\ * \left(\frac{\theta - 0.72957}{0.14747}\right)^3 + 0.23729 * \left(\frac{\theta - 0.72957}{0.14747}\right)^2 - 0.5341 * ((\theta \\ - 0.72957)/0.14747) + 2.717$$

$\theta = \frac{c_s^*}{c_s^{max}}$ where c_s^* denotes the solid phase Na^+ surface concentration and c_s^{max} the maximum solid phase Na^+ concentration.

Cut-off voltage NIB present scenarios: 1.80 V.

Cut-off voltage NIB future scenarios: 2.47 V.

S1.2.3 General comments

- In this study, diffusion in the active material particles was modeled using the higher-order polynomial approximation provided in the LIONSIMBA P2D model implementation.
- Balanced anode and cathode capacities were assumed and the loss of lithium/sodium due to SEI formation was assumed to be 10% (therefore, $c_{s,a}^{init} = 0.90c_{s,a}^{max}$).
- Volume expansion of graphite/hard carbon upon lithiation/sodiation is neglected.
- Following ref.¹², Bruggeman coefficients of 2.5 (non-ideal case for spherical particles) were assumed in this study. However, it should be noted that there are somewhat conflicting experimental findings. For instance, Wood and co-workers found Bruggeman coefficients in porous electrodes close to 1.5, corresponding to the Bruggeman ideal behavior.^{15,16}

S1.2.4 Cathode thickness

With reference to what is described in the main part of the manuscript, the cathode thickness t_c is not an independent design variable when optimizing battery cell design as it is fully specified by the choice of anode thickness t_a , anode porosity ε_a , and cathode porosity ε_c . Given a set of cell design parameters $\{t_a, \varepsilon_a, \varepsilon_c\}$, t_c is computed according to the below equation. $c_{s,a}^{max}$ and $c_{s,c}^{max}$ denote the maximum solid phase Li^+ or Na^+ concentration in the anode and cathode active material, $c_{s,c}^{init}$ the initial solid phase Li^+ or Na^+ concentration in

cathode active material, and $\varepsilon_{f,a}$ and $\varepsilon_{f,c}$ the filler fraction in anode and cathode, respectively (see table S1.1).

$$t_c = t_a \cdot \frac{c_{s,a}^{max}}{(c_{s,c}^{max} - c_{s,c}^{init})} \cdot \frac{(1 - \varepsilon_a - \varepsilon_{f,a})}{(1 - \varepsilon_c - \varepsilon_{f,c})}$$

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