
Supplementary information

**Fundamentals, status and promise of
sodium-based batteries**

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Supplementary Information

Fundamentals, status and promise of sodium-based batteries

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Table S1 | Theoretical maximum efficiencies of several Li and Na battery reactions

Reaction	$\eta_{\max}$ (%)
<i>Na battery reactions</i>	
$\text{Na} + \frac{1}{2}\text{I}_2 \rightleftharpoons \text{NaI}$	99
$2\text{Na} + \text{NiCl}_2 \rightleftharpoons 2\text{NaCl} + \text{Ni}$	98
$2\text{Na} + \frac{1}{8}\text{S}_8 \rightleftharpoons \text{Na}_2\text{S}$	97
$2\text{Na} + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{Na}_2\text{O}$	91
$2\text{Na} + \text{O}_2(\text{g}) \rightleftharpoons \text{Na}_2\text{O}_2$	88
<i>Li battery reactions</i>	
$\text{Li} + \frac{1}{2}\text{I}_2 \rightleftharpoons \text{LiI}$	100
$2\text{Li} + \text{NiCl}_2 \rightleftharpoons 2\text{LiCl} + \text{Ni}$	100
$\text{Li} + \text{FePO}_4 \rightleftharpoons \text{LiFePO}_4$	98
$2\text{Li} + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{Li}_2\text{O}$	94
$2\text{Li} + \text{O}_2(\text{g}) \rightleftharpoons \text{Li}_2\text{O}_2$	90

Theoretical maximum efficiencies ($\eta_{\max}$) of reactions for which thermodynamic data are available, calculated from $\eta_{\max} = \Delta_r G^\circ / \Delta_r H^\circ$ (where $\Delta_r G^\circ$ and $\Delta_r H^\circ$ are the standard Gibbs free energy and enthalpy of reaction, respectively) at 25 °C and 1 bar pressure¹⁻³.

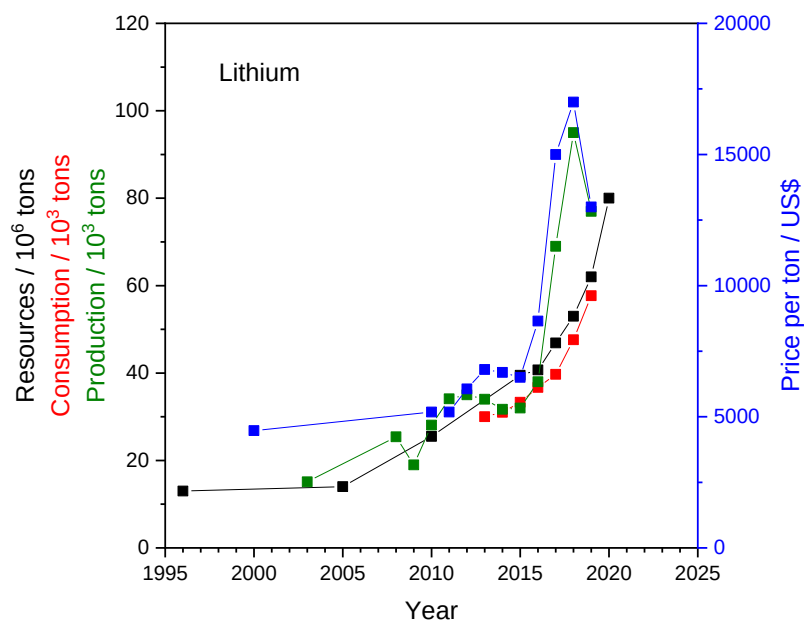


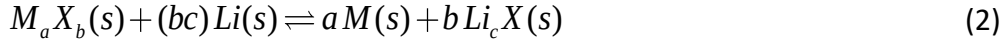
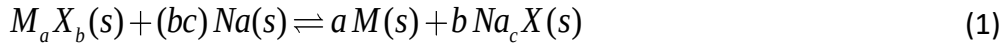
Figure S1. Lithium resources, consumption, production, and price.⁴ Resources refers to the total geologic amount worldwide whose location, quality, and quantity are estimated from specific geologic evidence. Consumption and production are annual global values. Price is the annual U.S. average for one metric ton of battery-grade Li_2CO_3 . For comparison, the price of battery-grade Na_2CO_3 (soda ash) is roughly estimated to be \$500 per metric ton.⁵

Table S2. More basic parameters for sodium and lithium.⁶⁻⁸ Electron affinity refers to free atoms in the gas phase.

Parameter	Na	Li
Standard reduction potential / (V vs SHE)	-2.71	-3.04
Electron affinity	0.55	0.62
Density at standard state / (g cm ⁻³)	0.97	0.53
Atomic radius / Å	1.90	1.67
Electronic polarizability of the atom / Å ³	24.1	24.3
Melting point / °C	98	180
Approximate radii in water / Å	2.8	3.4
Sublimation enthalpy at standard state / kJ mol ⁻¹	159.3	107.5

Analysis S1. Voltage differences of conversion reactions at open circuit.

The complete conversion of a binary line compound by sodiation or lithiation can be written as:



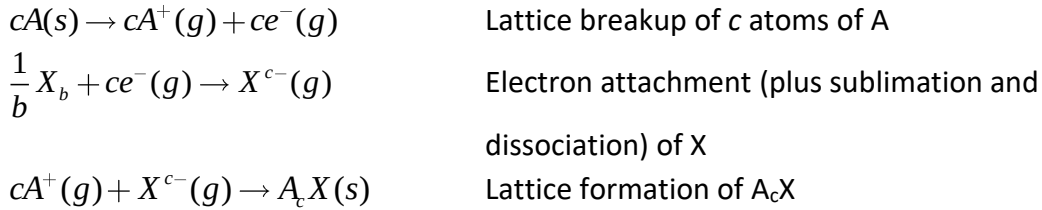
where a , b , and c are constants. When these reactions are subtracted, M and a drop out, so the difference between the open circuit voltages of these reactions is independent of M , as discussed by Klein et al.⁹ Thus the voltage difference for a given X can be calculated from the simplest case where $a = 0$:



The difference in open circuit voltage between these equations equals

$$\delta E \equiv E_{Na_c X}^0 - E_{Li_c X}^0 = -\frac{\delta \Delta_f G^0}{cF} \quad (5)$$

where $\delta \Delta_f G^0 \equiv \Delta_f G^0(Na_c X) - \Delta_f G^0(Li_c X)$ is the difference in standard Gibbs energy of formation between $Na_c X$ and $Li_c X$. Equations (3) and (4) can each be considered as the sum of



The formation enthalpy of $A_c X$, $\Delta_f H$, equals the sum of three enthalpies:

$$\Delta_f H = c\Delta_M H + \Delta_E H + \Delta_L H \quad (6)$$

where $\Delta_M H$ is the lattice enthalpy of the metal A , $\Delta_E H$ corresponds to sublimation, dissociation, and attachment of c electrons to X , and $\Delta_L H$ is the lattice enthalpy of $A_c X$.

Applying equation (6) to the enthalpies and entropies in both $Na_c X$ and $Li_c X$ and inserting into equation (5), the terms involving X drop out, and one finds

$$\delta E = -\frac{1}{cF} \left[c \delta \Delta_M H^0 - T \delta \Delta_M S^0 + \delta \Delta_L H^0 - T \delta \Delta_L S^0 \right] \quad (7)$$

The entropy terms can be calculated directly from tabulated standard entropies (when available) by

$$T \delta \Delta S^0 \equiv T \left(\left[S^0(Na_c X) - cS^0(Na) \right] - \left[S^0(Li_c X) - cS^0(Li) \right] \right) \quad (8)$$

This contribution is plotted in Figure S2 for several elemental anions at 25 °C. It is relatively small, showing a magnitude of 30 mV or less, which can be neglected for the purposes here.

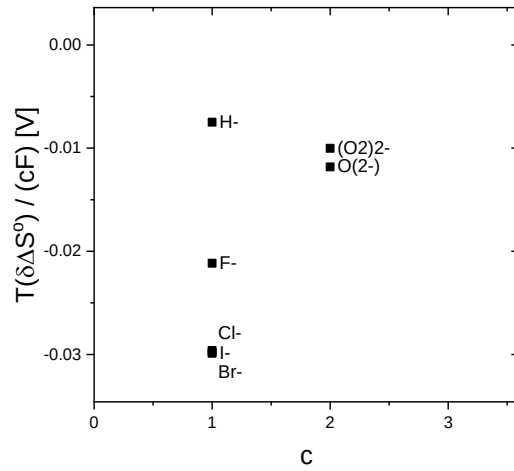


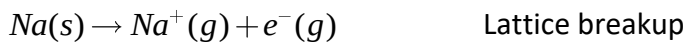
Figure S2. Entropy contribution to the voltage difference at 25 °C. It is less than 30 mV in magnitude.

Equation (7) then simplifies to

$$\delta E = \frac{-1}{F} \left[\delta \Delta_M H^0 + \frac{1}{c} \delta \Delta_L H^0 \right] \quad (9)$$

Thus the voltage difference is driven by a competition between $\delta \Delta_M H^0$ (the lattice enthalpy difference between the metals Na and Li) and $\frac{1}{c}$ times $\delta \Delta_L H^0$ (the lattice enthalpy difference between Na_cX and Li_cX).

The first term in Equation (9) was derived by Klein et al.⁹ The derivation is repeated here with a bit more detail. The lattice breakup



can be divided into two steps:



For sodium, the standard sublimation enthalpy $\Delta_s H^0(\text{Na})$ is reported to be 107.5 ± 0.7 kJ/mol [NIST webbook]. The ionization enthalpy $\Delta_i H^0(\text{Na})$ can be calculated from the ionization energy IE by

$$\begin{aligned} \Delta_i H^0 &= (IE) * F + \frac{5}{2} RT \\ &= 5.139 \text{ eV} \left(96.485 \frac{\text{kJ/mol}}{\text{eV}} \right) + \frac{5}{2} \left(8.314 \frac{\text{J}}{\text{mol} * \text{K}} * \frac{1 \text{ kJ}}{1000 \text{ J}} \right) 298 \text{ K} \\ &= 502.0 \frac{\text{kJ}}{\text{mol}} \end{aligned} \quad (10)$$

where F is Faraday's constant and R is the universal gas constant. [Ionization energy from the CRC Handbook]. For lithium, the sublimation enthalpy is measured as 159.3 ± 1.0 kJ/mol [NIST webbook], the ionization energy is 5.392 eV, and the ionization enthalpy can be calculated using equation (10) to be 526.4 kJ/mol. Thus

$$\begin{aligned}\delta\Delta_M H^0 &= \delta\Delta_S H^0 + \delta\Delta_I H^0 \\ &= 107.5 - 159.3 + 502.0 - 526.4 \frac{\text{kJ}}{\text{mol}} \\ &= -76.2 \frac{\text{kJ}}{\text{mol}}\end{aligned}$$

Consider now the second term of eqn (9). For a binary compound A_cX , the lattice enthalpy $\Delta_L H$ and lattice energy $\Delta_L U$ are related by [CRC Handbook 12-22; Jenkins 2005 J Chem Ed]

$$\Delta_L H = \Delta_L U + \left[c \left(\frac{3}{2} - 2 \right) + \left(\frac{n_X}{2} - 2 \right) \right] RT \quad (11)$$

where n_X equals 3, 5, or 6, depending if the anion is monatomic, polyatomic linear, or polyatomic nonlinear. In all cases, the second term in equation (11) is independent of the cation A, so it subtracts out when calculating the lattice enthalpy difference between Na_cX and Li_cX . Thus eqn 9 reduces to

$$\delta E = \frac{1}{F} \left[76.2 \frac{\text{kJ}}{\text{mol}} - \frac{1}{c} \delta\Delta_L U^0 \right] \quad (12)$$

A Madelung approach can be used to estimate the lattice energy difference. If the structures of Na_cX and Li_cX are both known, the Born-Mayer equation

$$\Delta_L U = - \frac{N_A f_M z_A z_X e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{\rho}{r_0} \right) \quad (13)$$

can be used, where N_A is Avogadro's number, f_M is the Madelung constant, z is valence, e is the charge of an electron, ϵ_0 is the vacuum permittivity, $\rho \approx 0.0345$ nm is a repulsion constant, and r is the nearest spacing between ions. Kapustinskii reformulated this expression to obtain an estimate that has comparable accuracy, but without requiring knowledge of the crystal structure.¹⁰ For a binary compound A_cX , Kapustinskii gives

$$\Delta_L U = B z_A z_X \nu \left(\frac{1}{r_A + r_X} - \frac{\rho}{(r_A + r_X)^2} \right) \quad (14)$$

where $B = 121.4 \text{ kJ mol}^{-1} \text{ nm}$, z_A and z_X are the moduli of the valence of A^+ and X^c , ν is the number of ions per formula unit (here $\nu = c + 1$), and r_A and r_X are the tabulated thermochemical radii of A^+ and X^c [CRC Handbook of Chemistry and Physics, chapter 12]. The second term in the parentheses in Equation (14) arises from repulsion and is much smaller, so for a rough estimate it can be neglected. With this simplification, the difference in lattice energies between Na_cX and Li_cX is

$$\delta\Delta_L U \approx Bc(c+1) \left(\frac{1}{r_{Na} + r_X} - \frac{1}{r_{Li} + r_X} \right) \quad (15)$$

If $r_{Na}, r_{Li} \ll r_X$, then

$$\frac{1}{r_{Na} + r_X} = \frac{1}{r_X} \left(\frac{1}{1 + r_{Na}/r_X} \right) \approx \frac{1}{r_X} \left(1 - \frac{r_{Na}}{r_X} \right) \quad (16)$$

and

$$\frac{1}{r_{Li} + r_X} \approx \frac{1}{r_X} \left(1 - \frac{r_{Li}}{r_X} \right) \quad (17)$$

and Equation (15) simplifies to

$$\delta\Delta_L U \approx Bc(c+1) \left(\frac{r_{Na} - r_{Li}}{r_X^2} \right) \quad (18)$$

Plugging Equation (18) into (12), we find

$$\delta E = E_{Na_cX}^0 - E_{Li_cX}^0 = \frac{1}{F} \left[76.2 \frac{\text{kJ}}{\text{mol}} - Bc(c+1) \left(\frac{r_{Na} - r_{Li}}{r_X^2} \right) \right] \quad (19)$$

Thus, if the assumption $r_{Na}, r_{Li} \ll r_X$ is valid, the voltage difference is expected to scale linearly with $(c+1)/r_X^2$, as shown in Figure 2 in the main text.

This linear scaling is only approximately valid. The reasons are: most anions are not quite large enough to completely neglect the cation radius in Equation (14); the repulsion term in Equation (14) is not entirely negligible; and the simple Madelung approach used here does not account for covalency, non-spherical ions, and so on.

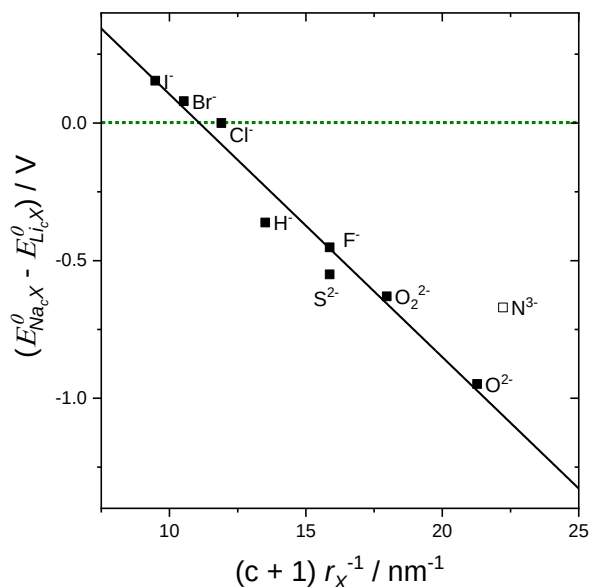


Figure S3. Same as Figure 2 in the main text, except plotted vs $(c+1)/r_X$ instead of $(c+1)/r_X^2$.

Analysis S2. A Madelung estimate for Na and Li metal

The energy difference between Na and Li metal is also driven to a large extent by the difference in atom size. This point can be illustrated using an approach attributed to Haber, in which the bcc lattice is considered to be occupied by metal ions, while electrons are artificially assigned an average position at the edge centers.¹¹ The Born-Landé expression for lattice energy is

$$U = \frac{1}{4\pi\epsilon_0} \frac{N_A f_M e^2}{r} \left(1 - \frac{1}{n_M} \right) \quad (20)$$

where ϵ_0 is the permittivity of free space, N is Avogadro's number, f_M is the Madelung constant (1.763 for body centered cubic), e is the charge of an electron, $n_M \approx 3$ is the repulsion exponent, and r is the shortest distance between oppositely charged species, which can be artificially assigned to be $r = 2r_{A^+}$. The prefactor of $1/(4\pi\epsilon_0)$ was omitted in Ref. ¹¹, but it is necessary when working in SI units.

A straightforward estimate of the quantity $\delta E = E_{Na_cX}^0 - E_{Li_cX}^0$ can then be obtained starting from eqn (9) in the previous analysis. Neglecting entropic contributions,

$$\delta E \approx \frac{-1}{e} \left[U_{Na} - U_{Li} + \frac{1}{c} U_{Na_cX} - U_{Li_cX} \right] \quad (21)$$

Inserting eqn (20) into (21) and using repulsion exponents of 3 and 9 for the metals and ionic compounds, respectively, one finds

$$\delta E \approx \frac{-N_A e}{4\pi\epsilon_0} \left[0.7 f_M \left(\frac{1}{2r_{Na^+}} - \frac{1}{2r_{Li^+}} \right) + \frac{0.9 f_{M_cX}}{c} \left(\frac{1}{r_{Na_cX}} - \frac{1}{r_{Li_cX}} \right) \right] \quad (22)$$

Inserting

$$\frac{1}{r_{Na_cX}} = \frac{1}{r_{Na^+} + r_{X^{c-}}} = \frac{1}{r_{X^{c-}}} \frac{1}{\frac{r_{Na^+}}{r_{X^{c-}}} + 1} \approx \frac{1}{r_{X^{c-}}} \left(1 - \frac{r_{Na^+}}{r_{X^{c-}}} \right) \quad (23)$$

and the analogous expression for Li_cX into eqn (21), and using 0.102 and 0.076 nm for the radii of Na^+ and Li^+ , the following simple result is obtained:

$$\delta E \approx \frac{N_A e}{4\pi\epsilon_0} \left[\frac{0.7 f_M}{2} 0.034 \text{ nm}^{-1} - \frac{0.9 f_{M_cX}}{c} \frac{1}{r_{X^{c-}}^2} 0.26 \text{ nm} \right] \quad (24)$$

This equation offers a rough prediction of the voltage difference between simple sodium and lithium conversion reactions which is based almost entirely on the ionic radii.

This conceptual point must be taken with a major grain of salt. Equation (20) predicts

$$U(Na) - U(Li) = 761 \frac{\text{kJ}}{\text{mol}} - 928 \frac{\text{kJ}}{\text{mol}} = -167 \frac{\text{kJ}}{\text{mol}}, \text{ but the true difference (as calculated from}$$

measured atomization and ionization energies) is $U(\text{Na}) - U(\text{Li}) = -76.2 \frac{\text{kJ}}{\text{mol}}$. The issue here is that although the absolute errors in the lattice energies from the Haber estimate are small, the relative error in the energy *difference* is large, corresponding to a large voltage error of +0.94 V.

In short, the Haber approximation is useful for conceptually illustrating the importance of ion size, but for a more accurate treatment, the measured properties of the metals should be used, as was done in Analysis S1.

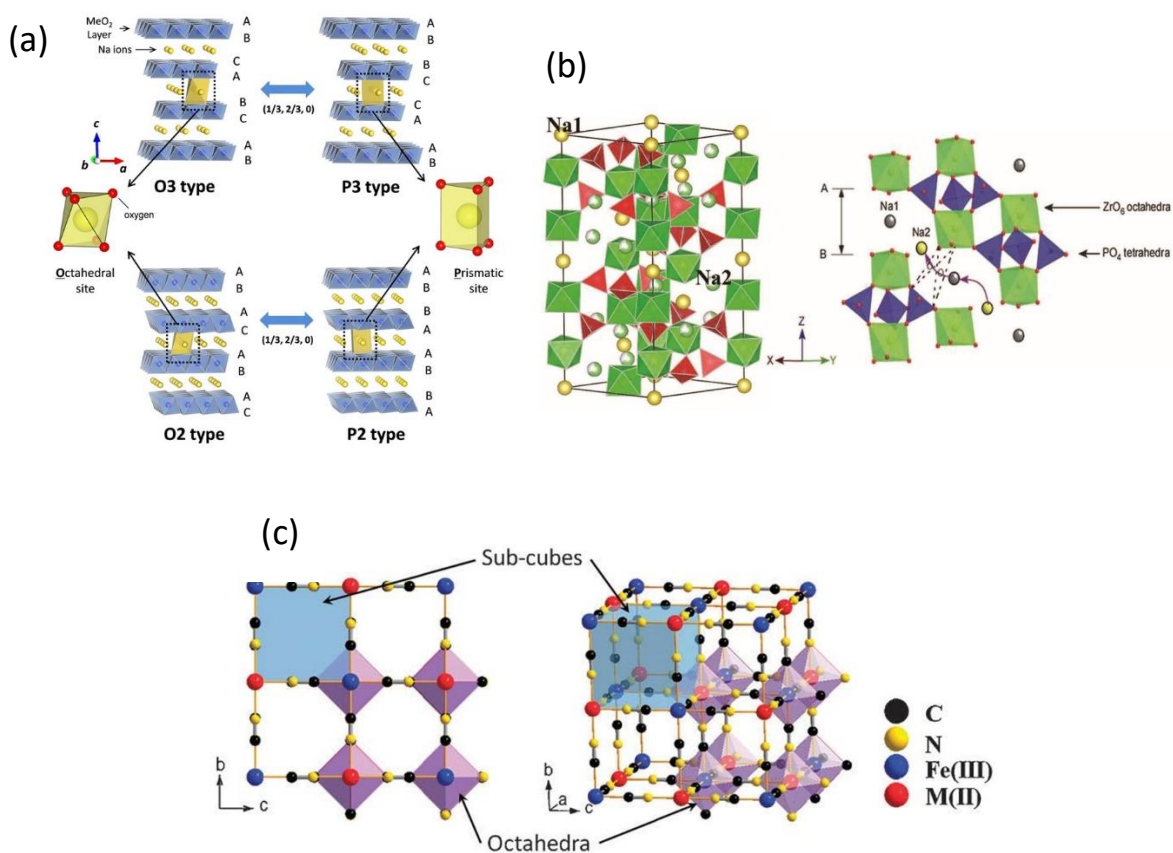


Figure S4: Schematic crystal structures of important cathode materials: (a) NaMO₂ layered oxides of different types,¹² (b) Na₃V₂(PO₄)₃,^{13,14} and (c) a Prussian blue analog NaFeM(CN)₆.¹⁵ Panel S4a reprinted with permission from ref.¹², National Institute for Materials Science. Panel S4b (left) reprinted with permission from ref.¹³, Wiley. Panel S4b (right) reprinted with permission from ref.¹⁴, RSC. Panel S4c reprinted with permission from ref.¹⁵, RSC.

Table S3. Substitutional dopant ions exhibiting an ionic radius within 0.05 Å of Na⁺ or Li⁺, assuming six-fold coordination.⁶

Na ⁺	1.02 Å	Li ⁺	0.76 Å
Bi ³⁺	1.03 Å	Cr ²⁺ (high spin)	0.80 Å
Hg ²⁺	1.02	In ³⁺	0.80
Ca ²⁺	1.00	Pt ²⁺	0.80
Sn ²⁺	~1.0	Fe ²⁺	0.78
		Cu ¹⁺	0.77
		Bi ⁵⁺	0.76
		Pd ³⁺	0.76
		Co ²⁺ (high spin)	0.74
		Sc ³⁺	0.74
		Zn ²⁺	0.74
		Cu ²⁺	0.73
		Mg ²⁺	0.72
		Ta ³⁺	0.72
		Zr ⁴⁺	0.72
		Hf ⁴⁺	0.71

Table S4. Ionic conductivity at 25 °C of bulk samples of the individual compounds typically found in lithium battery SEI layers. All values were measured by impedance spectroscopy. When necessary, extrapolations from measurements starting at 100–300 °C were used, as discussed in the notes.

Compound	$\log_{10}(\sigma_{\text{ion}}(25\text{ °C}) / \text{S cm}^{-1})$	Type	Reference	Notes
Li alkyl carbonates (C1-C8)	<-12	poly	Schafzahl et al., Chem. Mater., 30, 3338 (2018)	Values are from Figure 4 and the text. Abstract incorrectly says -9 for Li methyl carbonate.
Li ethylene monocarbonate (LEMC)	-5.2	poly	Wang et al., Nat. Chem., 11, 789 (2019)	
amorph Li ethylene dicarbonate (LEDC)	<-9	amorph	Wang et al., Nat. Chem., 11, 789 (2019)	
Li methyl carbonate (LMC)	<-9	poly	Wang et al., Nat. Chem., 11, 789 (2019)	
Li ₃ N c-axis	-5 to -5.4	single	Rabenau, Solid State Ionics, 6, 277 (1982)	
Li ₃ N ab-plane, poly	-3 to -3.2	single	Rabenau, Solid State Ionics, 6, 277 (1982)	Originally reported in Alpen et. al., Appl. Phys. Lett., 30, 621 (1977). Agrees with Boukamp & Huggins, Mater. Res. Bull. 13, 23 (1978).
Li ₃ N ab-plane	-5 to -2.2	single	Lapp et al., Solid State Ionics, 11(2), 97 (1983)	doped with Mg, Cu, Al, or H.
Li ₃ N ab-plane	-3.4 to -2.5	single	Hooper et al., Mater. Res. Bull., 14, 1617 (1979)	H-doped
Li ₃ N c-axis	-7.7 to -6.7	single	Hooper et al., Mater. Res. Bull., 14, 1617 (1979)	H-doped
Li ₃ P	-3.3	poly	Nazri, Solid State Ionics, 34, 97 (1989)	
Li ₂ O	-12.1 to -11.3	poly	Lorger, J. Electrochem. Soc., 166, 10, A2215 (2019)	Various dopings

Li ₂ S	-14 to -10	single + poly	Lorger, Adv. Funct. Mater., 1807688 (2018)	Various dopings
LiOH	-13	poly	Johnson, Mater. Res. Bull., 12, 577 (1977)	Extrapolated from 110 °C. Same data as in Biefeld et al., J. Electrochem. Soc., 126, 1 (1979). May be due to Li ⁺ , H ⁺ or both, so Fig. 5 just gives an upper bound.
LiF	-14	single	Lehfeldt, Z. Physik, 717 (1933)	Extrapolated from 250 °C.
LiF	-17 to -15	single	Geschwind, J. Phys. Chem. Solids, 30, 6, 1631 (1969)	Extrapolated from 45 °C. Lower values for “undoped”, higher values for Ca doping. Undoped data were also in Geschwind, J. Am. Ceram. Soc., 51, 9, 539 (1968).
LiF	-16.7 to -14.5	single	Stoebe, J. Phys. Chem. Solids, 28, 1357-1382 (1967)	Higher values were undoped, lower values were doped with LiOH.
LiCl	-12 to -10	single	Sharon, J. Solid State Chem., 40, 20-27 (1981)	Undoped or doped with Sr or Ca. Extrapolated from 275C, roughly accounting for association.
Li ₂ CO ₃	-18 to -14	poly	Mizusaki, Solid State Ionics 53-56, 791 (1992)	Extrapolated from 300 °C, assuming no association. Pure material shows -18 to -14 (anisotropy). Minimal change from NO ₃ or Ca doping. Li ₂ CO ₃ is only 1-2 orders lower than Na ₂ CO ₃ at 300–400 °C, but that extrapolates to 4-5 orders lower at 25 °C.
Li ₂ CO ₃ , PO ₄ -doped	-13 to -10	poly	Mizusaki, Solid State Ionics 53-56, 791 (1992)	Extrapolated from 300 °C, assuming no association. Need ~10 mol% PO ₄ doping to get 10 ⁻¹⁰ S cm ⁻¹ at 25 °C.
Multiphase SEI (liquid electrolytes)	-9 to -7	poly	Peled, J. Electrochem. Soc., 164, 7, A1703 (2017)	Page A1706 gives 10–1000 Ω cm ² for ~10 nm SEI, which corresponds to 10 ⁻⁷ –10 ⁻⁹ S cm ⁻¹ . Apparently agrees with Aurbach, J. Electroanal. Chem., 348 (1994) estimate of 10 ⁻⁷ S cm ⁻¹ .
Multiphase SEI (solid sulfide electrolytes)	-9 to -7	poly	Wenzel et al., Solid State Ionics, 318, 102 (2018); Wenzel et al., Chem. Mater., 28, 2400–2407 (2016); Wenzel et al., Solid State Ionics, 286, 24–33 (2016)	Based on 10–5000 Ω cm ² measured for a roughly 10 nm SEI. Important that pressure was applied to improve solid-solid contact. SEI thickness was not directly measured and may have ~10x uncertainty.

Table S5. Ionic conductivity at 25 °C of bulk samples of the individual compounds typically found in sodium battery SEI layers. All values were measured by impedance spectroscopy. When necessary, extrapolations from higher-temperature measurements were used, as discussed in the notes.

Compound	$\log_{10}(\sigma_{\text{ion}} @ \text{RT} / \text{S cm}^{-1})$	Type	Reference	Notes
Na alkyl carbonates (C1-C8)	<-14	poly	Schafzahl et. al., Chem. Mater., 30, 3338 (2018)	At 100 °C the conductivities are below $10^{-12} \text{ S cm}^{-1}$, so at room temperature we expect below $10^{-14} \text{ S cm}^{-1}$.
NaF	-18.5	single	Lehfelddt, Z. Physik, 717 (1933)	Extrapolated from 250 °C
NaF	-16	single	Bauer, Phys. Stat. Sol., 37, 585 (1970)	Ca-doped. Extrapolated from 450 °C.
Na ₂ S	-10	single	Bertheville et. al., J. Phys. Chem. Solids, 58(10), 1569 (1997)	Extrapolated from 40 °C.
NaOH	-15	poly	Spaeth, Solid State Ionics, 97, 291 (1997)	Extrapolated from 180 °C. Same data as in Spaeth, J Solid State Chem, 148, 169 (1999). Probably due to H ⁺ , but Na ⁺ conduction cannot be ruled out.
NaCl	-18 to -15	single	Dreyfus, Phys. Rev., 126, 4 (1962)	
Na ₂ CO ₃	-10 to -13	poly	Cerisier, J. Solid State Chem., 22, 245 (1977)	Extrapolated from 270 °C. Undoped and Ca doped. Atmosphere matters - air gives higher values, CO2 gives lower values. Guth 1987 Cryst Res Tech predicts lower values but may be unreliable.
Composite SEI (liquid electrolytes)	-8 to -7	poly	Peled, J. Electrochem. Soc., 164, 7, A1703 (2017)	Page A1713 estimates 10 nm SEI, 10–100 $\Omega \text{ cm}^2$.

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