

Supplementary Information for: Comparison of computational methods for the electrochemical stability window of solid-state electrolyte materials

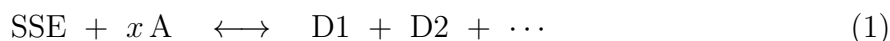
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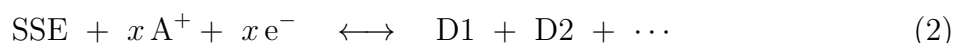
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Derivation of Nernst equation

We derive the Nernst equation for the cell reaction



The corresponding half-cell reactions are the SSE reaction at the working electrode (WE) interface



and the A-metal counter electrode (CE) reaction



For electrochemical equilibrium of reactions (2) and (3), the conditions must be fulfilled that the stoichiometric sums of the chemical potentials of reactants and of products are equal,

$$\mu_{\text{SSE}} + x \mu_{\text{A}^+} + x \mu_{\text{e}^-}^{\text{WE}} = \mu_{\text{D1}} + \mu_{\text{D2}} + \dots \quad (4)$$

$$x \mu_{\text{A}} = x \mu_{\text{A}^+} + x \mu_{\text{e}^-}^{\text{CE}} \quad (5)$$

In equilibrium, the chemical potential μ_{A^+} of A^+ is constant throughout the electrolyte and therefore identical at CE and WE. The equilibrium potential of reaction (2) vs. the reference potential defined by reaction (3) is given by the difference of the electron chemical potentials of WE and CE divided by the electron charge,

$$\begin{aligned}\Phi_{\text{eq}} &= \frac{1}{-e} (\mu_{e^-}^{\text{WE}} - \mu_{e^-}^{\text{CE}}) \\ &= \frac{1}{-e x} (\mu_{\text{D1}} + \mu_{\text{D2}} + \dots - \mu_{\text{SSE}} - x \mu_{\text{A}}) \\ &= -\frac{\Delta G}{e x}\end{aligned}\tag{6}$$

In the first step, we resolved and inserted equations (4) and (5) for the electron chemical potentials of WE and CE, respectively. In the second step, we used the fact that the chemical potential of a compound is equal to its Gibbs free energy per unit.

Equation (6) is not the Nernst equation in its typical form, which expresses the equilibrium potential as a function of the activities a_i of reactants and products. The typical form of the Nernst equation is simply obtained from equation (6) by inserting the definitions of the reactant and product activities $\mu_i = \mu_i^0 + k_B T \log(a_i/a^0)$, with Boltzmann constant k_B , temperature T , standard activity a^0 , and standard chemical potential μ_i^0 .

Stoichiometry stability window: Simplest model

We develop a simple model for the dependence of the SSE stoichiometry $A_{n+z}M$ (where $A = \text{Li, Na, } \dots$) as a function of the electrode potential Φ that the SSE is in contact with. Very similar models were derived for the Li-insertion into electro-active materials [1]. We first derive a simplified expression of the Gibbs free energy $G(z) := G_{A_{n+z}M}$ for $|z| \ll n$, i.e. for small deviations from the stable composition. For this purpose, the Gibbs free energy (per unit cell) $G = U + pV - TS$ is first approximated by $G = E_0 - TS_{\text{conf}}$, in which only the energy E_0 at $T = 0\text{ K}$ and the configurational entropy S_{conf} of A-site occupation are taken into account. The configurational entropy carries the dominant part of the dependence of the Gibbs free energy on the A-stoichiometry. It therefore cannot be neglected for deriving z as a function of Φ . Other contributions like the pV term, the vibrational zero-point energy, the vibrational internal energy, and the vibrational entropy are neglected, which is well justified if an error of $\pm 0.1\text{ V}$ is acceptable on the calculated stability potential window.

For $|z| \ll n$, the energy of adding one A to the general composition $A_{n+z}M$ is approximately constant, i.e. $E_0 \approx E_0^0 + \Delta E_0^{+/-} z$, for $z \gtrless 0$, respectively. Here, as explained in

detail in the main article, it is taken into account that the energy $\Delta E_0^{+/-}$ of adding A is discontinuous at $z = 0$, resulting in two different constant values $\Delta E_0^+ > \Delta E_0^-$ for $z \gtrless 0$, respectively.

Within this simplified 1-type A-site model, it is assumed that all A-sites are energetically equivalent. In the next section, a more general 2-type A-site model is derived. Assuming a total number $n + m$ of A-sites, either occupied or unoccupied, per unit cell of the material $A_{n+z}M$, the configurational entropy S_{conf} results from the combinatorics of filling $n + z$ out of a total of $n + m$ sites:

$$S_{\text{conf}} = \frac{1}{N_c} k_B \log \left(\frac{N_c (n + m)}{N_c (n + z)} \right) \quad (7)$$

$$\approx k_B ((n + m) \log(n + m) - (n + z) \log(n + z) - (m - z) \log(m - z)) \quad (8)$$

where k_B is the Boltzmann constant and where Stirling's approximation was applied, because the total number N_c of unit cells in the entire crystal is very large.

According to the equations derived in the main article, we obtain for the A-chemical potential in the SSE

$$\mu_{\text{SSE}}^A(z) = \frac{dG}{dz} = \Delta E_0^{+/-} - k_B T \log \left(\frac{n + m}{n + z} - 1 \right) \quad (9)$$

where the $+/-$ refer to $z > 0$ and $z < 0$, respectively, and for the corresponding equilibrium potential

$$\Phi_{\text{eq}} = -\frac{1}{e} (\mu_{\text{SSE}}^A(z) - \mu_A^A) \quad (10)$$

$$= \Phi_{\text{I/II}} + \frac{k_B T}{e} \log \left(\frac{n + m}{n + z} - 1 \right) \quad (11)$$

where

$$\Phi_{\text{I/II}} := -(\Delta E_0^{+/-} - \mu_A^A)/e \quad (12)$$

again for $z > 0$ and $z < 0$, respectively, and with $\Phi_{\text{I}} < \Phi_{\text{II}}$ because $\Delta E_0^+ > \Delta E_0^-$.

Vice versa, for a given electrode potential Φ , the equilibrium stoichiometry deviation z of the SSE in contact with the respective electrode is obtained by resolving Equation (11) with $\Phi_{\text{eq}} = \Phi$:

$$z = \begin{cases} \frac{(n+m)}{1+\exp((\Phi-\Phi_{\text{I}})/\gamma)} - n & , \Phi < \Phi_{\text{I}} + \delta \\ 0 & , \Phi_{\text{I}} + \delta \leq \Phi \leq \Phi_{\text{II}} + \delta \\ \frac{(n+m)}{1+\exp((\Phi-\Phi_{\text{II}})/\gamma)} - n & , \Phi_{\text{II}} + \delta < \Phi \end{cases} \quad (13)$$

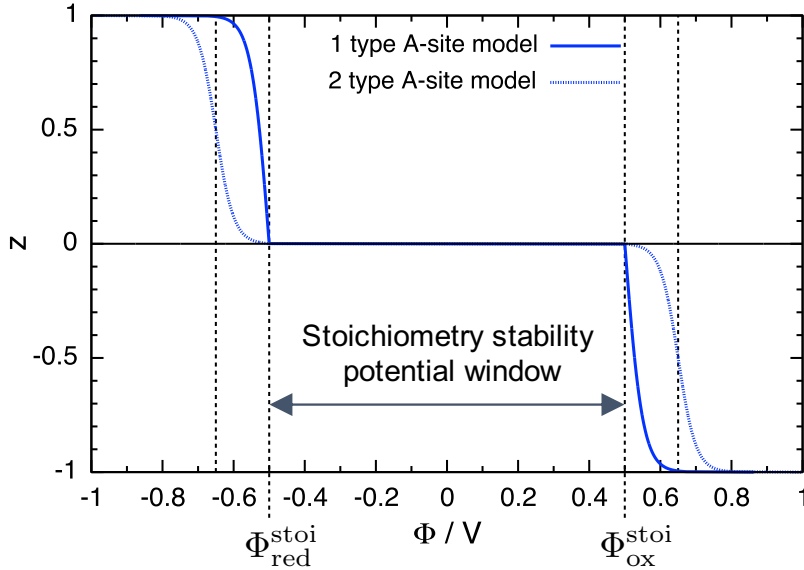


Figure S1: The stoichiometry deviation z in the general SSE material $A_{n+z}M$ as a function of the potential Φ as derived from the two models in the limit $|z| \ll n$: The ‘1 type A-site model’ considers all A-sites energetically equivalent, whereas the ‘2 type A-site model’ takes into account two energetically different types of A-sites. The values of the model parameters used for the plotted curves are given in the text.

where $\gamma = \frac{k_B T}{e}$ and $\delta = \gamma \log(m/n)$. Thus, the limits of the stoichiometry stability window are given by $\Phi_{\text{red}}^{\text{stoi}} = \Phi_{\text{I}} + \delta$ and $\Phi_{\text{ox}}^{\text{stoi}} = \Phi_{\text{II}} + \delta$. For an acceptable error of ± 0.1 V on the stability limits, the shift δ can be neglected: For a practical SSE material, the number of occupied and unoccupied A-sites will be of the same order of magnitude. Even for $m/n = 10^{\pm 1}$, it follows $|\delta| \approx 2\gamma$ with $\gamma = 0.025$ V for $T \approx 300$ K.

Figure S1 plots the deviation z as a function of the electrode potential Φ as described by Equation (13) for an arbitrary choice of $n = 1$, $m = 1$, $\Phi_{\text{red}}^{\text{stoi}} = -0.5$ V, $\Phi_{\text{ox}}^{\text{stoi}} = +0.5$ V, and for $\gamma = 0.025$ V corresponding to $T \approx 300$ K. The stoichiometry dramatically changes in two step steps below and above $\Phi_{\text{red}}^{\text{stoi}}$ and $\Phi_{\text{ox}}^{\text{stoi}}$, respectively, the width of each step being defined by the scale γ . The step below $\Phi_{\text{red}}^{\text{stoi}}$ corresponds to SSE reduction, whereas the step above $\Phi_{\text{ox}}^{\text{stoi}}$ corresponds to SSE oxidation. Within the stoichiometry stability window, i.e. for potentials $\Phi_{\text{red}}^{\text{stoi}} \leq \Phi \leq \Phi_{\text{ox}}^{\text{stoi}}$, the stoichiometry deviation is equal to zero, $z = 0$, and the SSE is stable in the composition $A_n M$.

Within the present model we assume that all $n + m$ A-sites within the SSE material $A_n M$ are energetically equivalent, i.e. every distribution of the n A over the $n + m$ sites has the same energy. However, in general, there will be energetic variations between different

distributions. In the following section, we present an extended model which takes into account two different classes of A-sites in the material A_nM : one class of n occupied ground-state sites, and another class of m vacant excited-state sites.

Stoichiometry stability window: Model with two classes of A-sites

We consider a general solid-state electrolyte (SSE) material with n occupied and m unoccupied A-sites per unit cell, the latter unoccupied sites referred to as vacancies V , in its stable stoichiometry. Further, it is assumed that the occupied and unoccupied A-sites are separated by a non-zero energy gap, which is plausible if the vacancies correspond to interstitial sites or if they are generated by a dopant. In order to distinguish these two classes of A-sites, the m unoccupied ‘excited’ state sites are denoted on the left-hand side, whereas the n occupied ‘ground’ state sites are denoted on the right-hand side of the composition formula V_mMA_n .

If more A is added to the stable configuration V_mMA_n , it has to occupy vacant sites of the class of ‘excited’ state sites. Consequently, the additional A is added on the left-hand side to yield $A_\delta V_{m-\delta}MA_n$. Vice versa, if A is extracted from the stable configuration V_mMA_n , vacancies are generated among the previously occupied ‘ground’ state sites denoted on the right-hand side to yield $V_mMA_{n-\epsilon}V_\epsilon$. Of course, also combinations of both processes are possible, such that the general state of the SSE material can be described by the formula $A_xV_{m-x}MA_{n+y}V_{-y}$, where $0 \leq x \leq m$ and $-n \leq y \leq 0$. Furthermore, as discussed for the simpler model in the main article, the total stoichiometry $n + x + y$ of A must be compared against the stable stoichiometry n , since the latter separates two distinct energetic manifolds for compositions with A-excess, i.e. $x + y > 0$, and A-deficiency, i.e. $x + y < 0$, respectively.

According to the equations derived in the main article, the equilibrium potential of the A-exchange reactions with a general electrode material is given by

$$\Phi_{\text{eq}} = -\frac{1}{e} (\mu_{\text{SSE}}^{\text{A}}(z) - \mu_{\text{A}}^{\text{A}}) \quad (14)$$

where $\mu_{\text{A}}^{\text{A}}$ is the chemical potential of A-metal defining the reference potential $\Phi_{\text{ref}} = -\mu_{\text{A}}^{\text{A}}/e$. The chemical potential $\mu_{\text{SSE}}^{\text{A}}$ of species A for the general SSE composition $A_xV_{m-x}MA_{n+y}V_{-y}$ is given by the derivative of the Gibbs free energy $G(x, y) := G_{A_xV_{m-x}MA_{n+y}V_{-y}}$ w.r.t. the

total A-stoichiometry deviation $z = x + y$,

$$\mu_{\text{SSE}}^{\text{A}}(z) = \frac{dG}{dz} \quad (15)$$

$$= p_x(z) \left. \frac{\partial G}{\partial x} \right|_{(x(z), y(z))} + p_y(z) \left. \frac{\partial G}{\partial y} \right|_{(x(z), y(z))} \quad (16)$$

where $p_x = dx/dz$ and $p_y = dy/dz = 1 - p_x$ are the thermodynamic weights of the excited state sites and ground state sites, respectively. For given $z = x + y$, the values of $x(z)$, $y(z)$, $p_x(z)$, and $p_y(z)$ are fixed by the thermodynamic equilibrium requirement of minimum $G(x, y)$, as calculated below.

In the following, an expression for the Gibbs free energy $G(x, y)$ is derived for $|x|, |y| \ll n$, i.e. for small deviations from the stable composition. As for the simpler model presented in the previous section, the total Gibbs free energy $G = U + pV - TS$ is first approximated by $G = E_0 - TS_{\text{conf}}$, i.e. only the energy E_0 at $T = 0$ K and the configuration entropy S_{conf} of the combinatorics of A-site occupation are taken into account. For $|x|, |y| \ll n$, the energies ΔE_0^e and ΔE_0^g of adding one A either to the excited state or to the ground state class of A-sites in $\text{A}_x \text{V}_{m-x} \text{MA}_{n+y} \text{V}_{-y}$, respectively, are approximately constant. Furthermore, in the same way as for the simpler model, the energy discontinuity between $x + y < 0$ and $x + y > 0$ must be taken into account by a term $\Delta E_0^{+/-}(x + y)$, resulting in an expression for the total energy in the limit $|x|, |y| \ll n$,

$$E_0 \approx E_0^0 + \Delta E_0^e x + \Delta E_0^g y + \Delta E_0^{+/-}(x + y) \quad (17)$$

for $x + y \gtrless 0$, respectively.

The configuration entropy has two contributions, $S_{\text{conf}} = S_e + S_g$, resulting from the combinatorics of filling excited state or ground state A-sites, respectively:

$$S_e = \frac{1}{N_c} k_B \log \left(\frac{N_c m}{N_c x} \right) \quad (18)$$

$$\approx k_B (m \log(m) - x \log(x) - (m - x) \log(m - x)) \quad (19)$$

where Stirling's approximation has been applied, $0 \leq x \leq m$, and k_B is the Boltzmann constant. Likewise,

$$S_g \approx k_B (n \log(n) - (n + y) \log(n + y) - (-y) \log(-y)) \quad (20)$$

where $-n \leq y \leq 0$.

In order to find the thermodynamic weights $p_{x/y}$, first the thermodynamic equilibrium value of x for a fixed value of the total stoichiometry deviation $z = x + y$ must be derived that is defined by the minimum of the function $G(x, y = z - x)$, i.e. by the condition $dG(x, y = z - x)/dx = 0$, which is equivalent to the condition $\partial G/\partial x = \partial G/\partial y$ or

$$y = \frac{-n(m - x)}{x \exp(\Delta E/k_B T) + (m - x)} \quad (21)$$

where $\Delta E = \Delta E_0^e - \Delta E_0^g$ is the energy difference between excited and ground state sites. Inserting $y = z - x$ and resolving for x , we obtain

$$x = \frac{z(e^{\Delta E/k_B T} - 1) - n - m}{2(e^{\Delta E/k_B T} - 1)} + \frac{\sqrt{(z(e^{\Delta E/k_B T} - 1) - n - m)^2 + 4m(n + z)(e^{\Delta E/k_B T} - 1)}}{2(e^{\Delta E/k_B T} - 1)} \quad (22)$$

where the positive solution of the quadratic equation has been used according to the requirement $0 \leq x$. Thus, the following expression is obtained for $p_x = dx/dz$,

$$p_x = \frac{1}{2} + \frac{1}{2} \frac{m - n + z(e^{\Delta E/k_B T} - 1)}{\sqrt{(z(e^{\Delta E/k_B T} - 1) - n - m)^2 + 4m(n + z)(e^{\Delta E/k_B T} - 1)}} \quad (23)$$

The chemical potential as a function of z follows from Equation (16),

$$\begin{aligned} \mu_{\text{SSE},+/-}^{\Lambda} = & \Delta E_0^{+/-} + p_x \Delta E_0^e + p_y \Delta E_0^g - p_x k_B T \log\left(\frac{m}{x} - 1\right) \\ & - p_y k_B T \log\left(\frac{n}{n + y} - 1\right) \end{aligned} \quad (24)$$

for $z > 0$ and $z < 0$, respectively, where x as a function of z is given by Equation (22), $y = z - x$, p_x is given by Equation (23), and $p_y = 1 - p_x$. The corresponding equilibrium potential Φ_{eq} as a function of z is obtained from Equation (14),

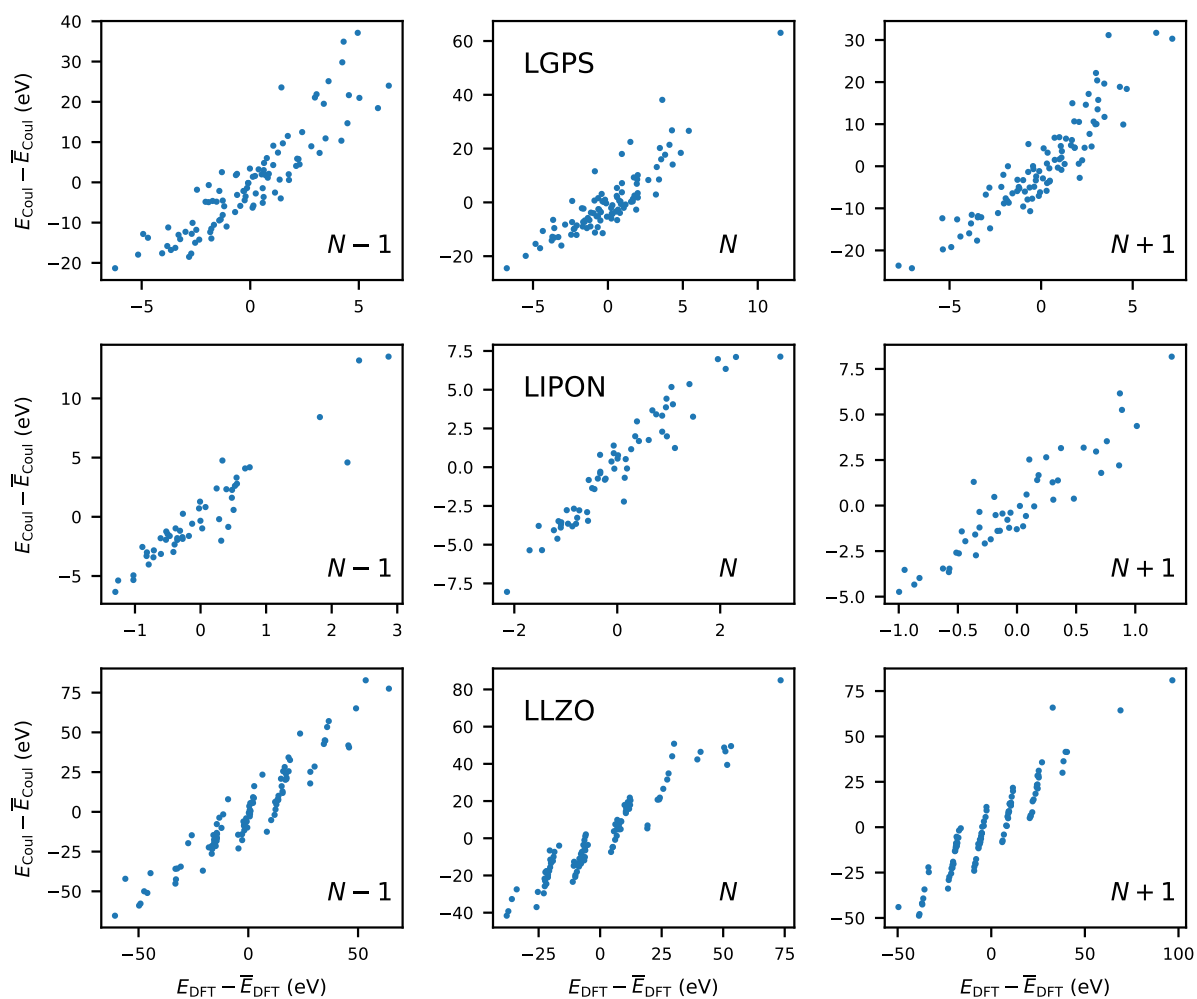
$$\begin{aligned} \Phi_{\text{eq}} = & \Phi_{\text{I/II}} + p_x \Delta \Phi_e + p_y \Delta \Phi_g + p_x \frac{k_B T}{e} \log\left(\frac{m}{x} - 1\right) \\ & + p_y \frac{k_B T}{e} \log\left(\frac{n}{n + y} - 1\right) \end{aligned} \quad (25)$$

where $\Phi_{\text{I/II}} = -(\Delta E_0^{+/-} - \mu_{\text{A}}^{\Lambda})/e$ for $z > 0$ and $z < 0$, respectively, and $\Delta \Phi_{e/g} = -\Delta E_0^{e/g}/e$.

Unlike for the simpler model presented in the main article, expression (25) cannot be analytically resolved to obtain the equilibrium stoichiometry deviation z as a function of an applied potential Φ . Nevertheless, the latter can be plotted as shown in Figure S1 for an

arbitrary choice of $m = n = 1$, $\Phi_{I/II} = \mp 0.5$ V, $\Delta\Phi_{e/g} = \mp 0.15$ V, and for $k_B T = 0.025$ eV. The main qualitative features of the simpler model are preserved, i.e. the stoichiometry changes in two step steps starting at approximately $\Phi_{I/II}$, the width of each step being defined by the scale $k_B T/e$. However, the energetic splitting between excited and ground state sites results in a smoother shape of the steps around $\Phi_{I/II}$ and the turning points of the steps are shifted to approximately $\Phi_{I/II} + \Delta\Phi_{e/g}$.

Ewald vs. DFT energies



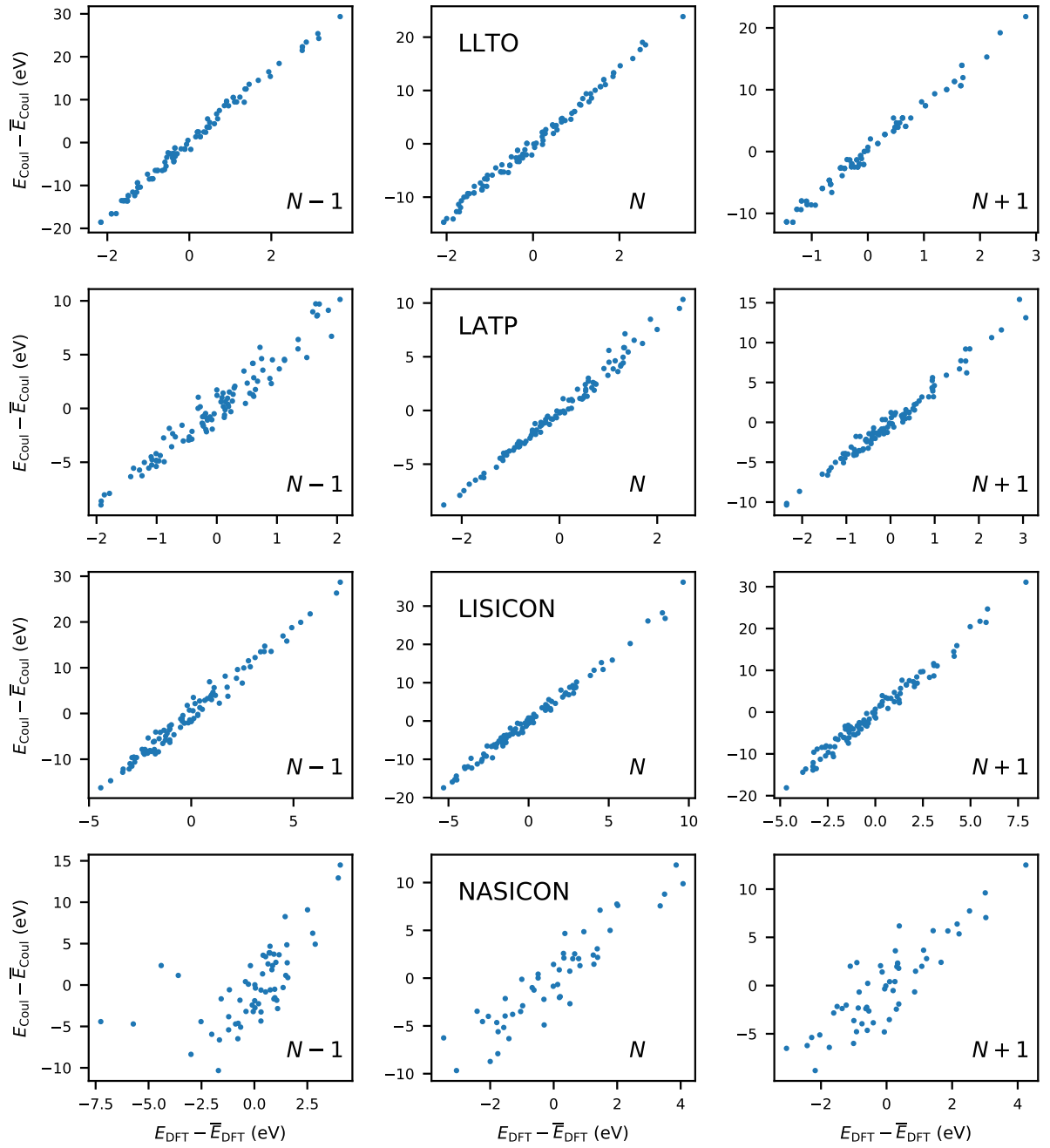


Figure S2: Ewald (Coulomb) energies vs. DFT energies for selected SSE materials. Plotted are the total energies of the supercells given in Table 1 of the main article for a number of random configurations across partially occupied sites, with plotted energies centered at the mean energy for each respective supercell.

References

- [1] I. D. Raistrick, A. J. Mark, and R. A. Huggins. Thermodynamics and kinetics of the electrochemical insertion of lithium into tungsten bronzes. *Solid State Ionics*, 5:351 – 354, 1981.