Interpretable Tree-Based Approaches for Novel Solid State Electrolyte Discovery and Design

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Li batteries

Typical Li-ion batteries

- **cathode**: $LiCoO_2$, $LiFePO_4$, $LiNiMnCoO_2$ etc.
- **anode**: graphite
- **electrolyte**: $LiPF_6$/$LiBF_4$/$LiClO_4$ in dimethyl carbonate/diethyl carbonate (liquid)

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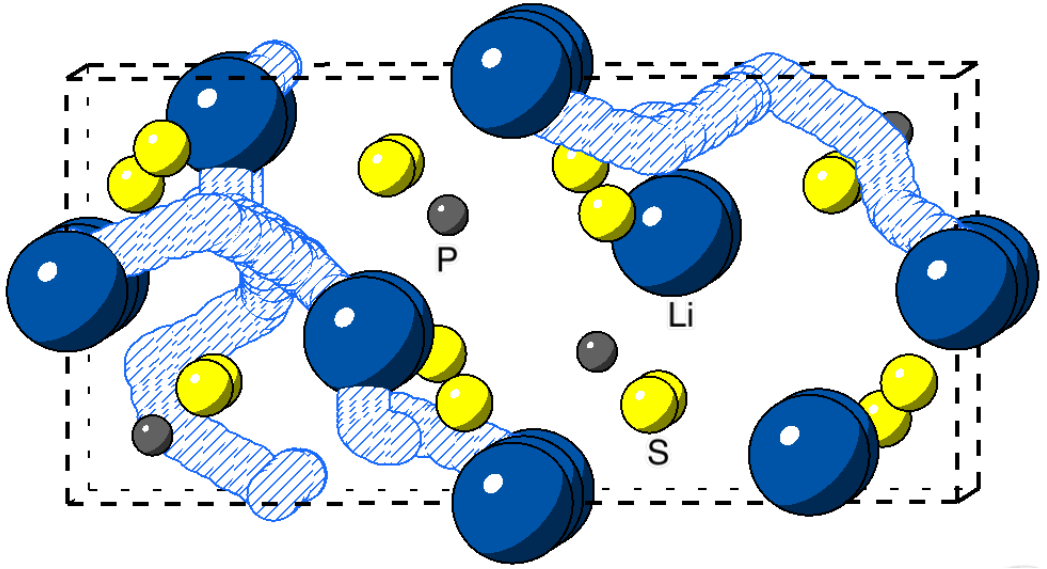
ASSB w/ Li anode – require *solid electrolytes* and *anode coatings*

- high ionic conductivity
- low electronic conductivity
- wide electrochemical window
- good stability against Li metal
- inertness to environmental elements like water and air

Methods

Current approaches to study ionic migration:

- experimental measurements
- ab-initio MD, NEB
- space topology analysis
- bond valence (BV) estimation



Percolation (3D) barriers

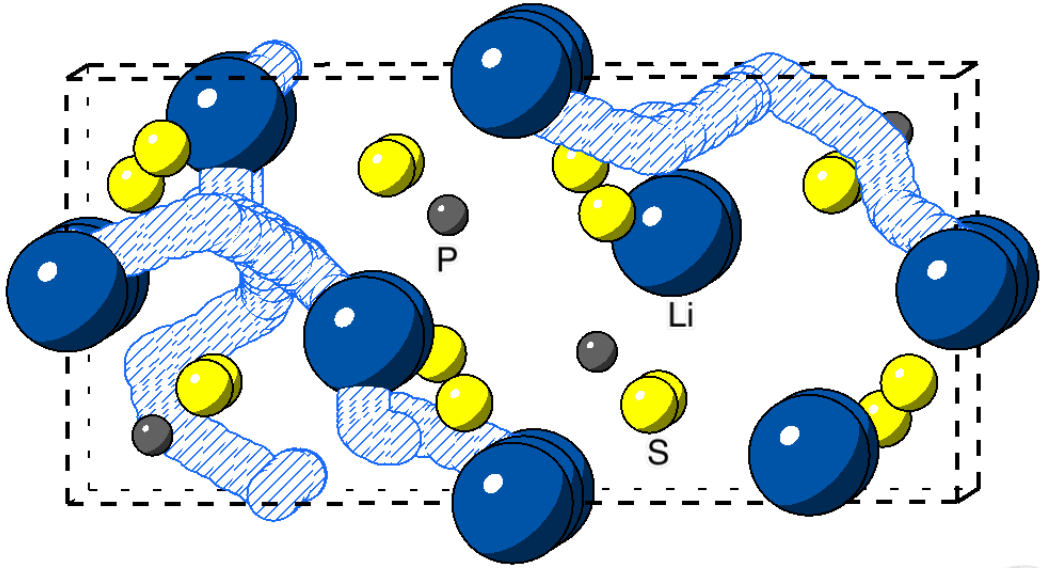
Methods

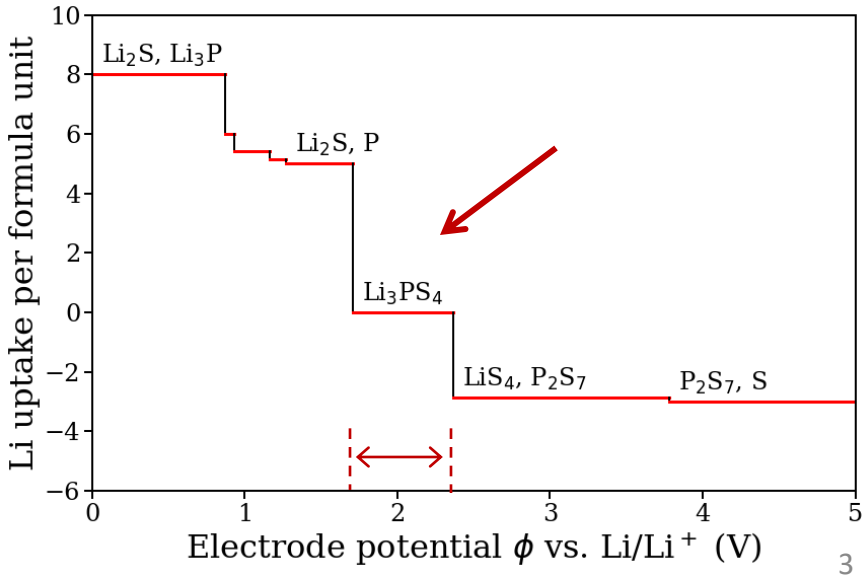
Current approaches to study ionic migration:

- experimental measurements
- ab-initio MD, NEB
- space topology analysis
- bond valence (BV) estimation

To compute electrochemical stability windows:

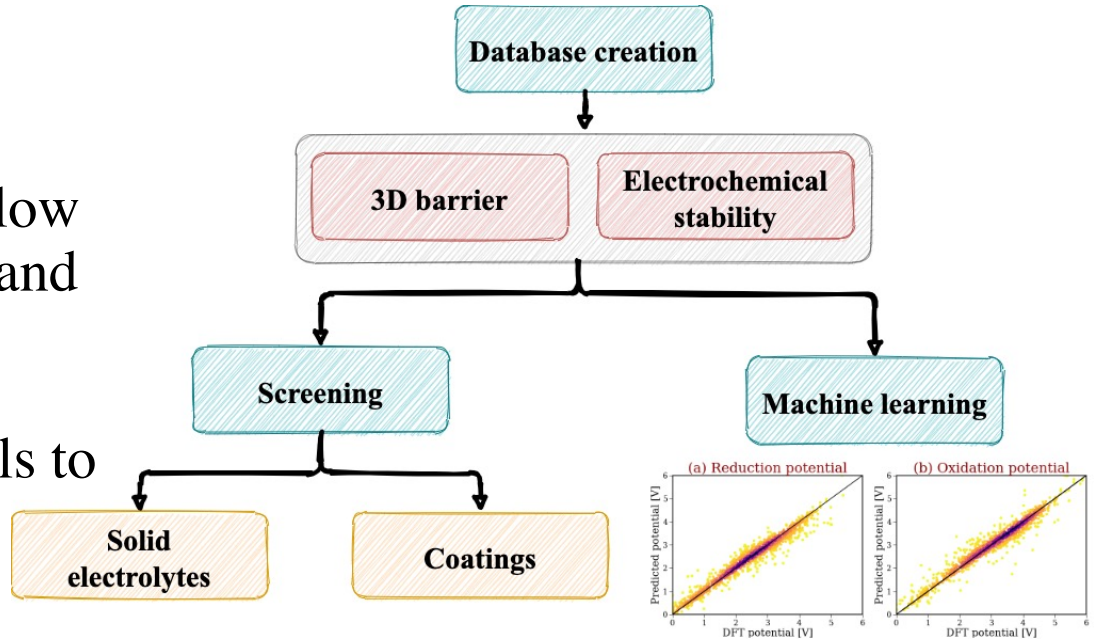
- Grand potential phase diagram analysis





Our approach

- Generate a database of battery-related material properties
- Screen through the database for candidates with low Li^+ migration barriers and good thermodynamic and electrochemical stabilities
- Train interpretable machine learning (ML) models to predict migration barriers and oxidation and reduction potentials
- Explain individual predictions and provide model-level interpretation of feature importance



Screening results

Electrolytes

3D barrier < 0.5 eV

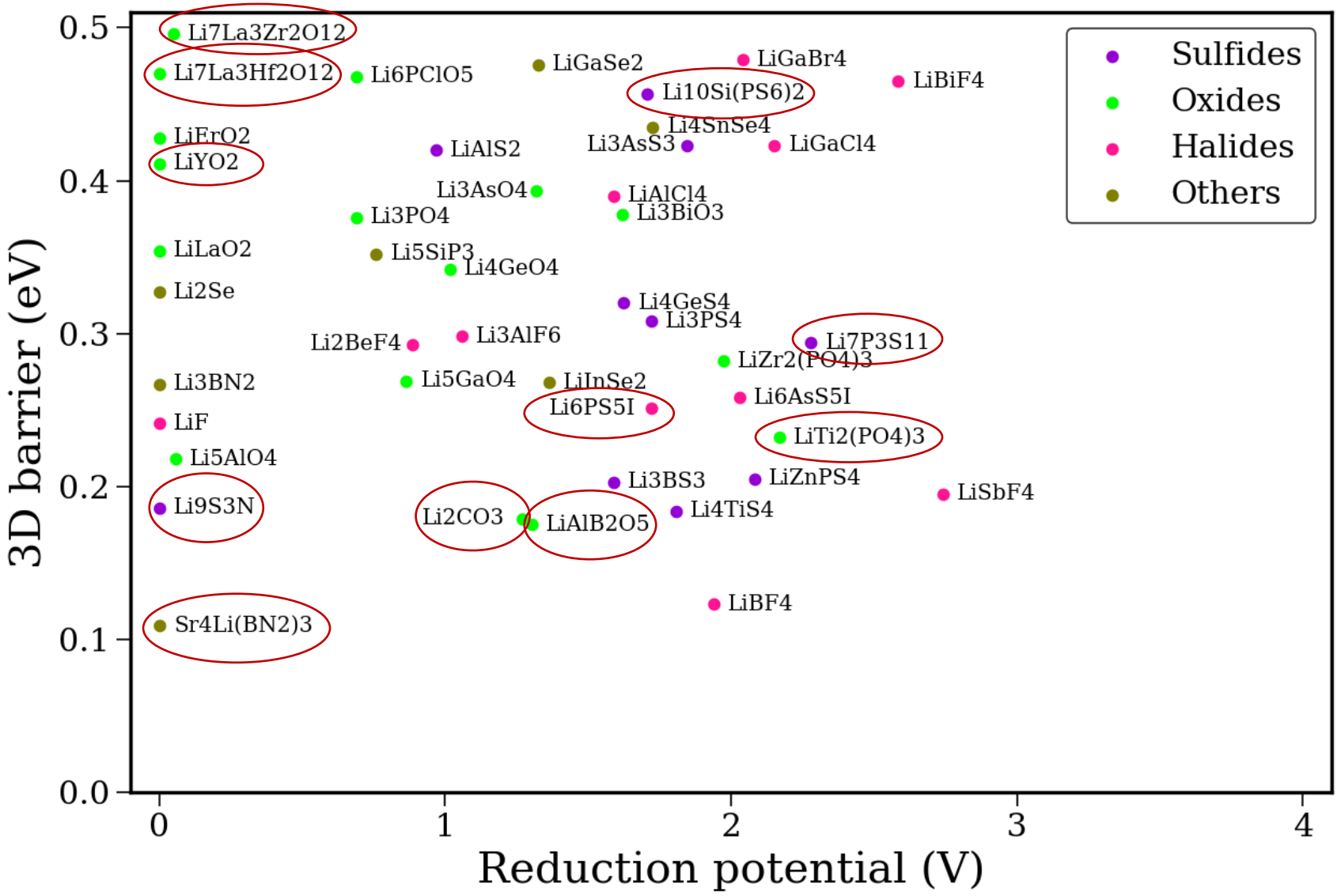
Anode coatings

3D barrier < 1 eV

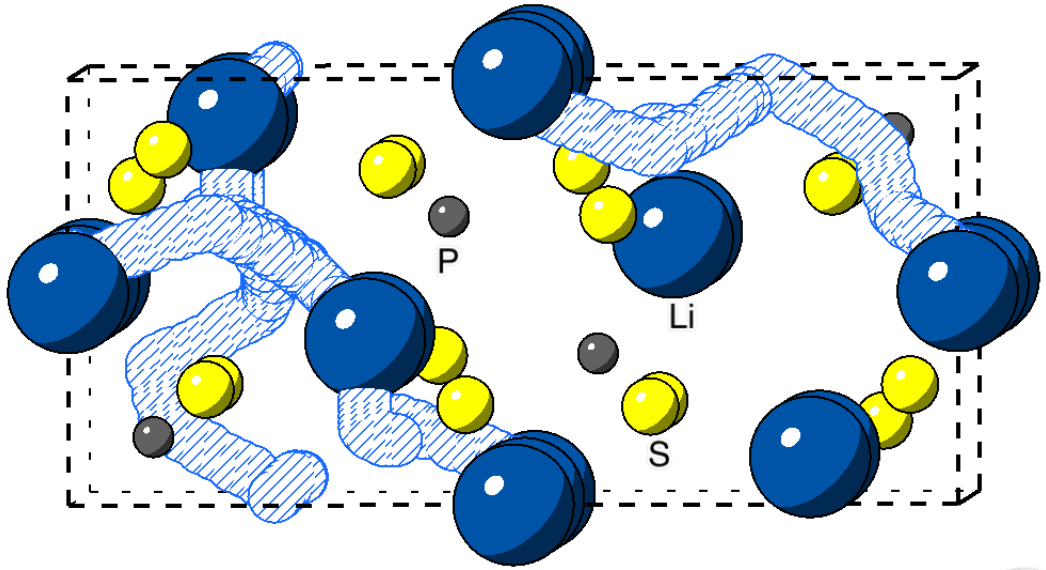
Reduction potential = 0 V

Stability window > 1 V

* E_{hull} < 30 meV
* E_g > 1 eV



ML Features: 3D barriers



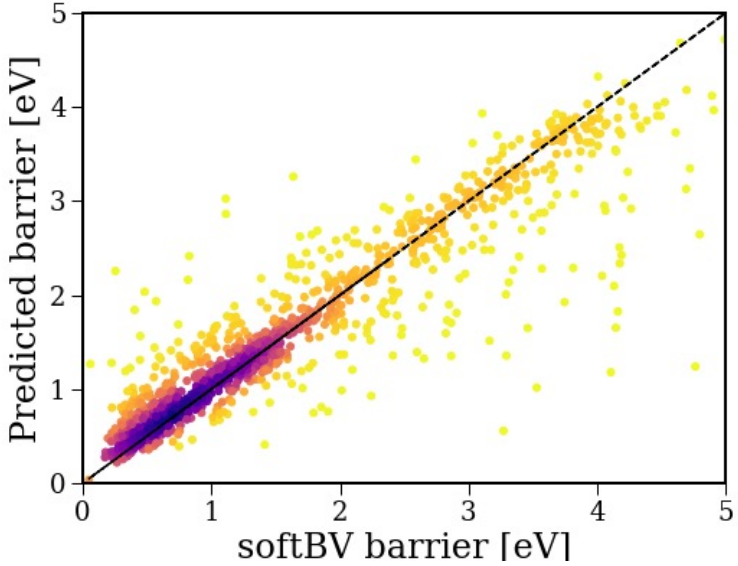
No.	Feature	Acronym
1.	*Li atomic fraction*	Li
2.	*Mean Li neighbor count*	LNC
3.	*Mean Li-Li bonds per Li*	LLB
4.	*Mean Sublattice neighbor count*	SNC
5.	*Mean Sublattice bond ionicity*	SBI
6.	*Mean Electronegativity of sublattice*	ENS
7.	*Mean Li-Li separation distance*	LLSD
8.	*Mean Li-anion separation distance*	LASD
9.	*Mean Anion-anion separation distance*	AASD
10.	*Mean neighbor distance variation*	NDV
11.	*Mean ordering parameter shell 1*	OP_1
12.	*Mean ordering parameter shell 2*	OP_2
13.	*Mean ordering parameter shell 3*	OP_3
14.	*Diameter of largest free sphere*	DLFS
15.	*Mean Straight Line Path Width*	SLPW
16.	*Sublattice packing fraction*	SPF
17.	*Max packing efficiency*	MPE
18.	*XRD principal component 1*	XRD_1
19.	*XRD principal component 2*	XRD_2
20.	*XRD principal component 3*	XRD_3
21.	*XRD principal component 4*	XRD_4
22.	*XRD principal component 5*	XRD_5

Sendek, Yang, Cubuk, et al., *Energy Environ. Sci.* **10**, 306-320 (2017)
Ward, Agrawal, Choudhary, et al., *npj Comput. Mater.* **2,** 16028 (2016)

ML Results: 3D barriers

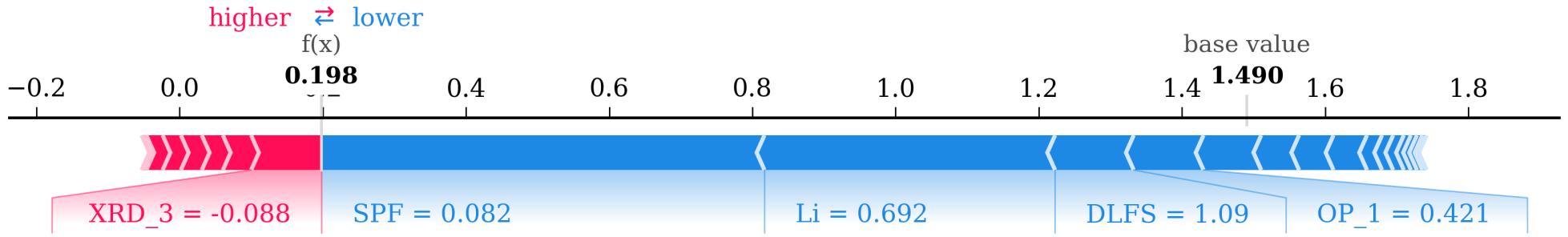
Features + Model	R^2	**vector length**
Current work + RF	0.84	22
Current work + GB	0.86	22
Sendek model features + GB	0.76	20
Coulomb matrix + GB	0.72	200
Powder X-ray diffraction pattern + GB	0.70	128

GB model predictions



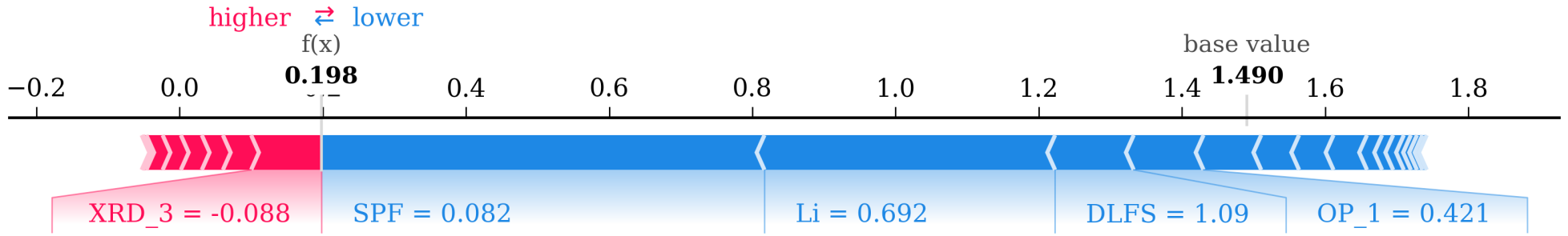
Shapley Additive Explanations (SHAP)

Li_9S_3N

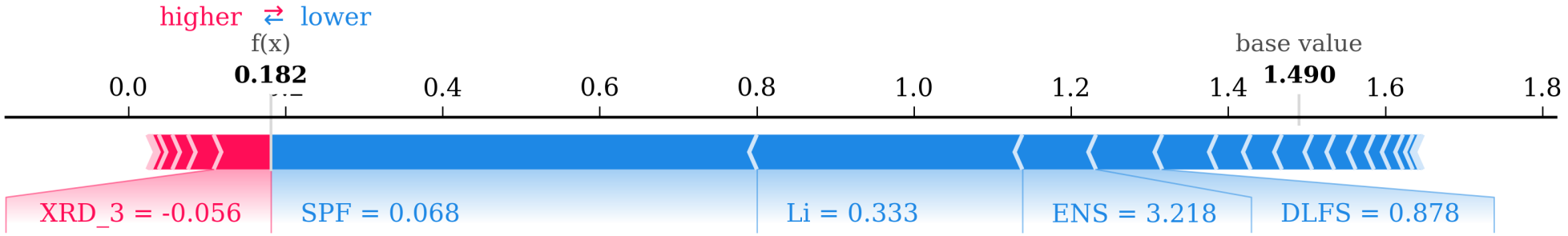


Shapley Additive Explanations (SHAP)

Li_9S_3N

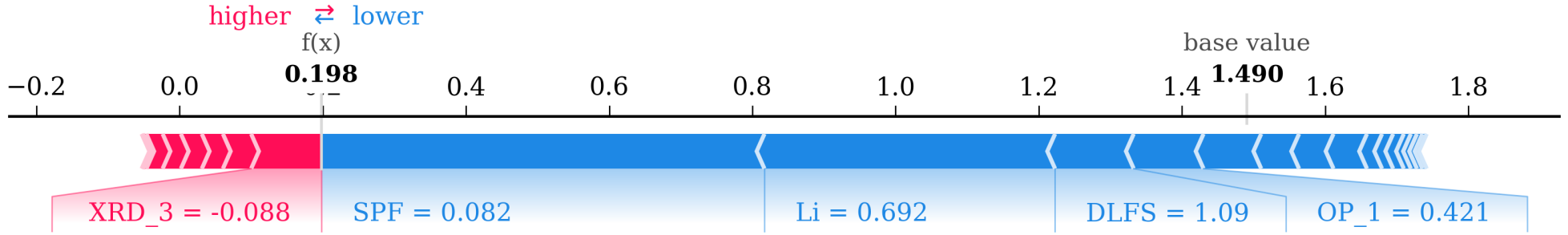


Li_2CO_3

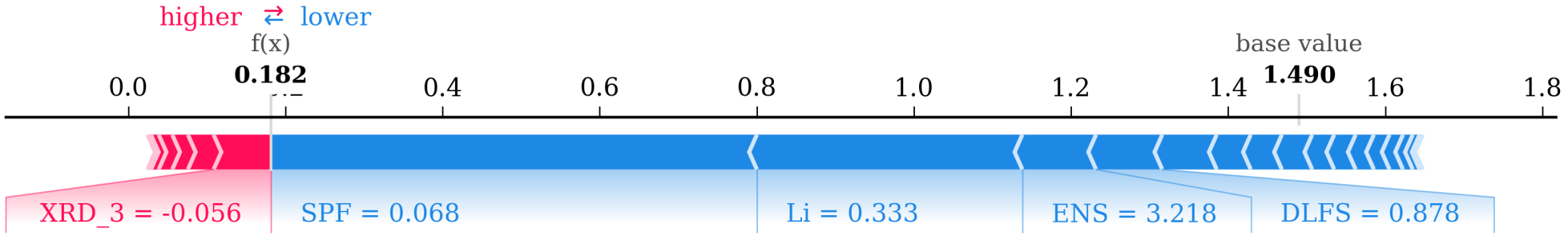


Shapley Additive Explanations (SHAP)

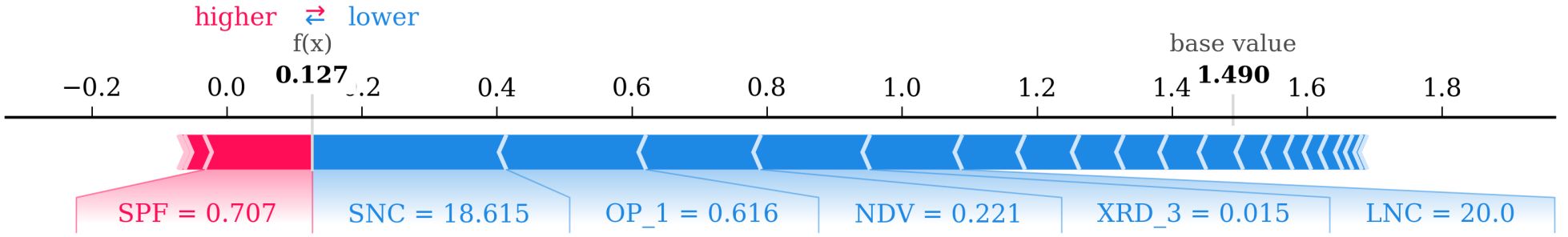
Li_9S_3N



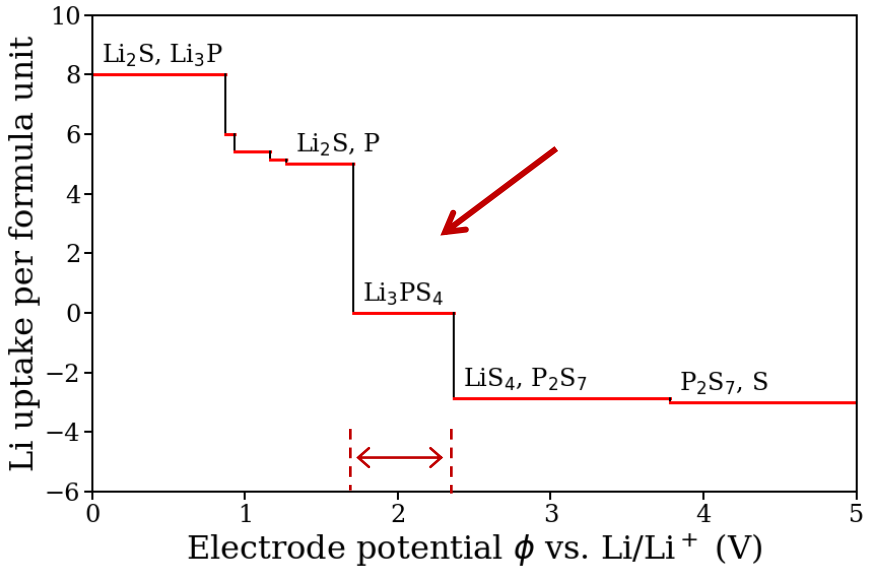
Li_2CO_3



$Sr_4Li(BN_2)_3$



ML Features: electrochemical stability



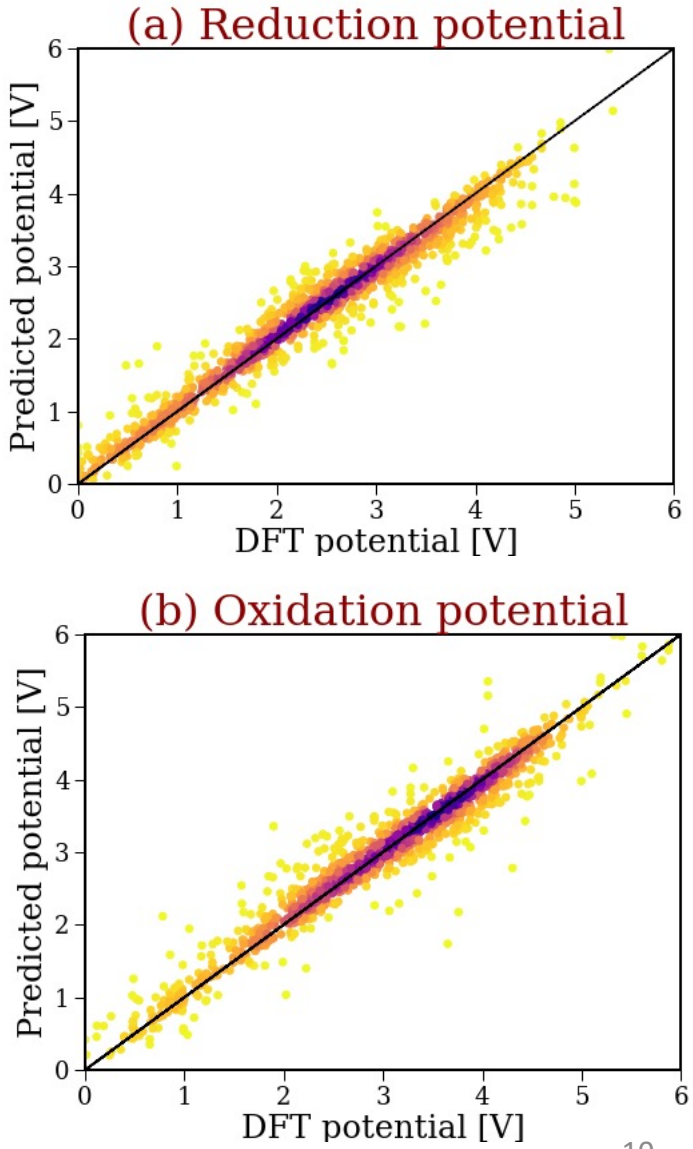
Composition-weighted element properties	Statistics
— standard features —	
Atomic number	Mean
Electronegativity	Maximum
Valence d-electrons	Range
Unfilled d-electrons	
Unfilled p-electrons	
Band gap	
Magnetic moment	
Melting Temperature	
— new oxidation state features —	
oxidation state − min. oxidation state	
max. oxidation state − oxidation state	
*(oxidation state − min. oxidation state) * E_neg*	
*(max. oxidation state − oxidation state) * E_neg*	

Ward, Liu, Krishna, et al., *Phys. Rev. B* **96**, 024104 (2017)

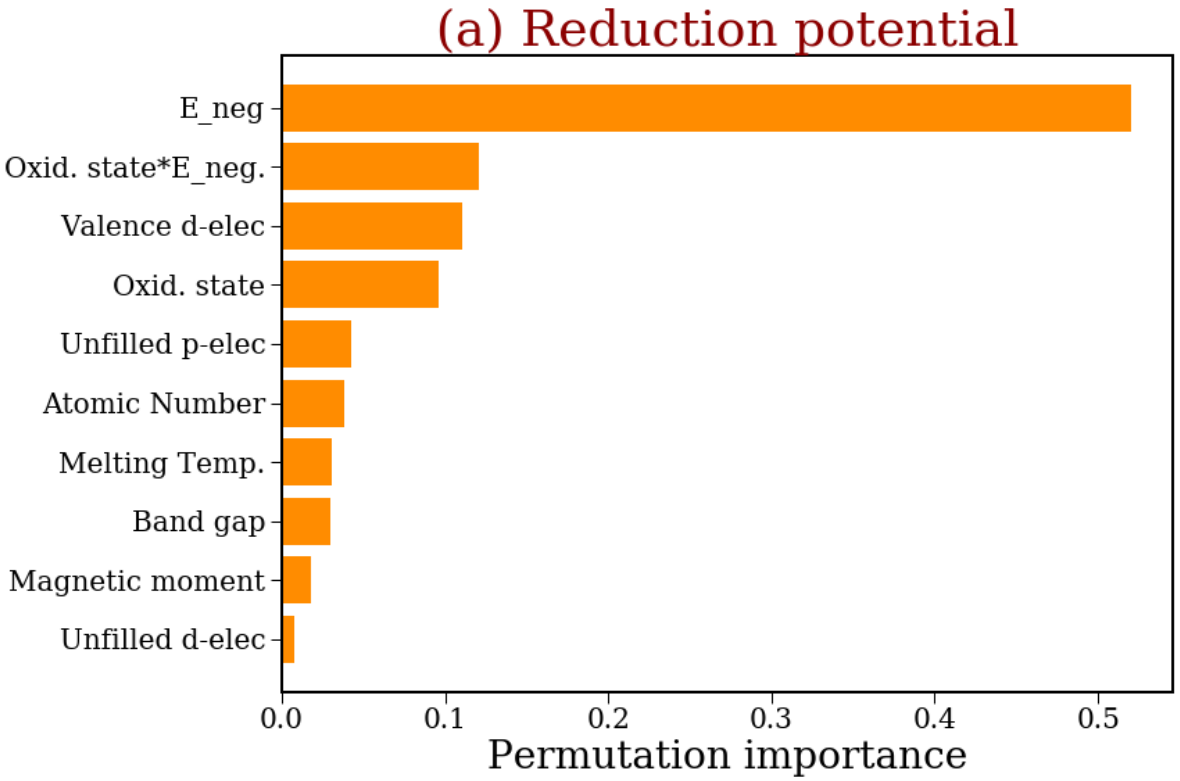
ML results: electrochemical stability

Features + Model	reduction potential	oxidation potential	vector length
Current work + RF	0.93	0.91	28
Current work + GB	0.95	0.92	28
Roost + neural network	0.92	0.92	64
Magpie element features + GB	0.89	0.84	132
Element fractions + GB	0.87	0.87	103

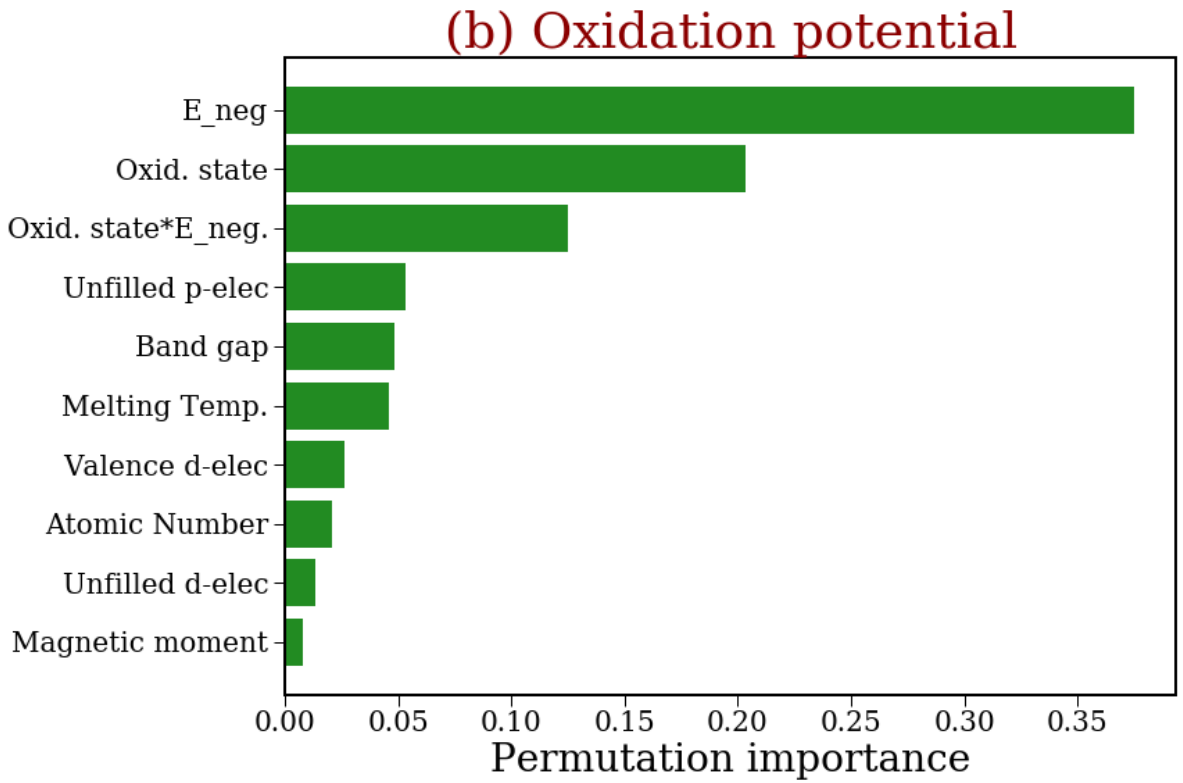
GB model predictions



Permutation Feature Importance (PFI): electrochemical stability



GB model



GB model

Summary

- We developed a materials informatics approach to explore and identify candidates for solid electrolytes and anode coatings in all solid-state Li metal batteries
- Generated a database of battery-related material properties
- Screened through the database to identify over 200 candidates with low Li^+ migration barriers and good thermodynamic and electrochemical stabilities (Li_9S_3N, $LiAlB_2O_5$, $Sr_4Li(BN_2)_3$, $LiYO_2$, $Li_7La_3Hf_2O_{12}$, etc.)
- Trained machine learning (ML) models to predict migration barriers and oxidation and reduction potentials
- Explained individual predictions from screening and ML model, provided model-level interpretation of feature importance

Thank you

Interpretable Tree-Based Approaches for Novel Solid State Electrolyte Discovery and Design

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SSI-23

Back-up slides

Bond valence method

- Valence sum rule: the sum of bond valences (S_{ij}) around any atom, i, with neighboring atoms j, should be equal to the atomic valence, (V_i) i.e., the oxidation state.

$$V_i = \sum_j S_{ij}$$

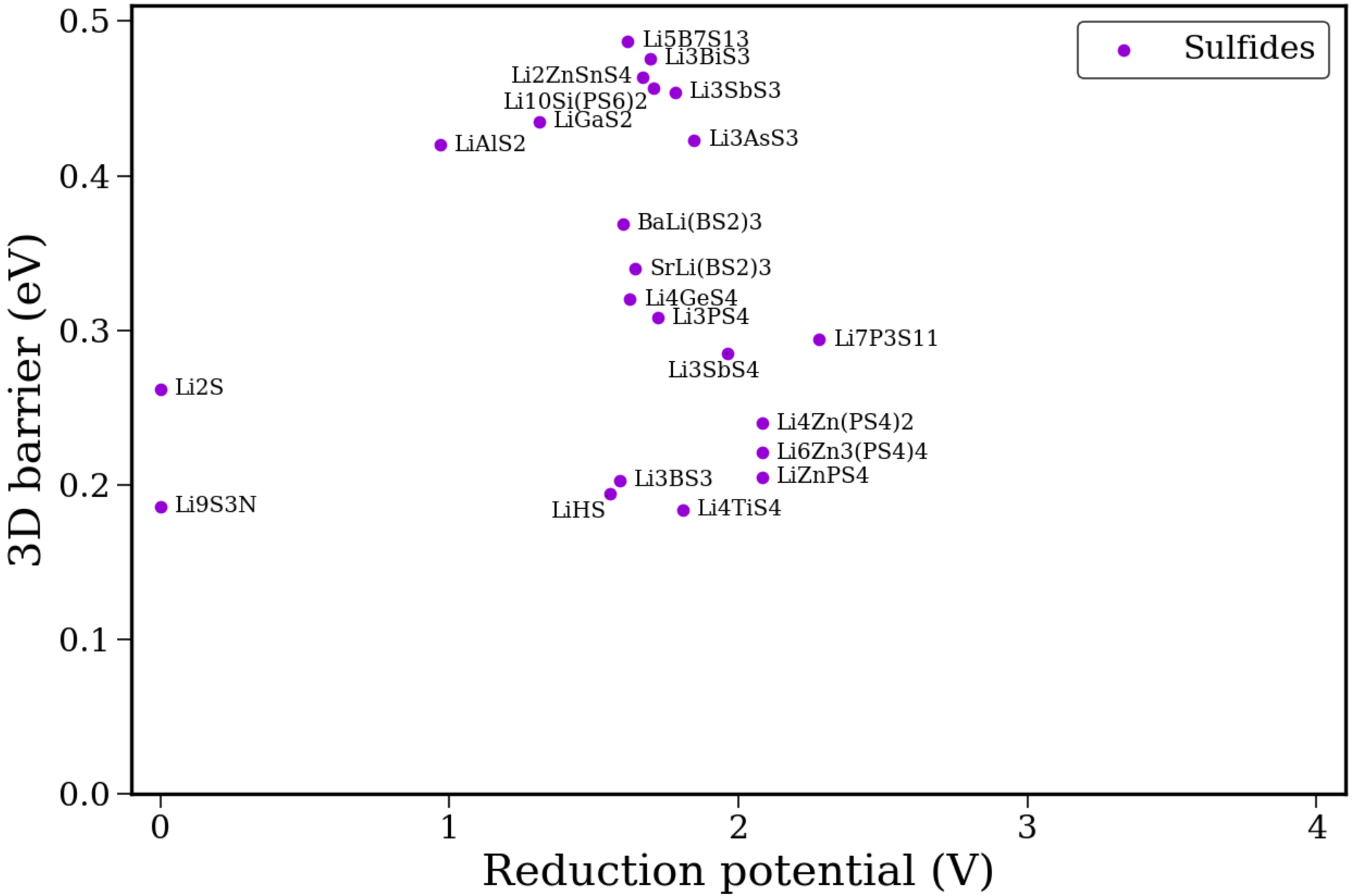
- S_{ij} is considered a measure of the electrostatic strength of a bond.

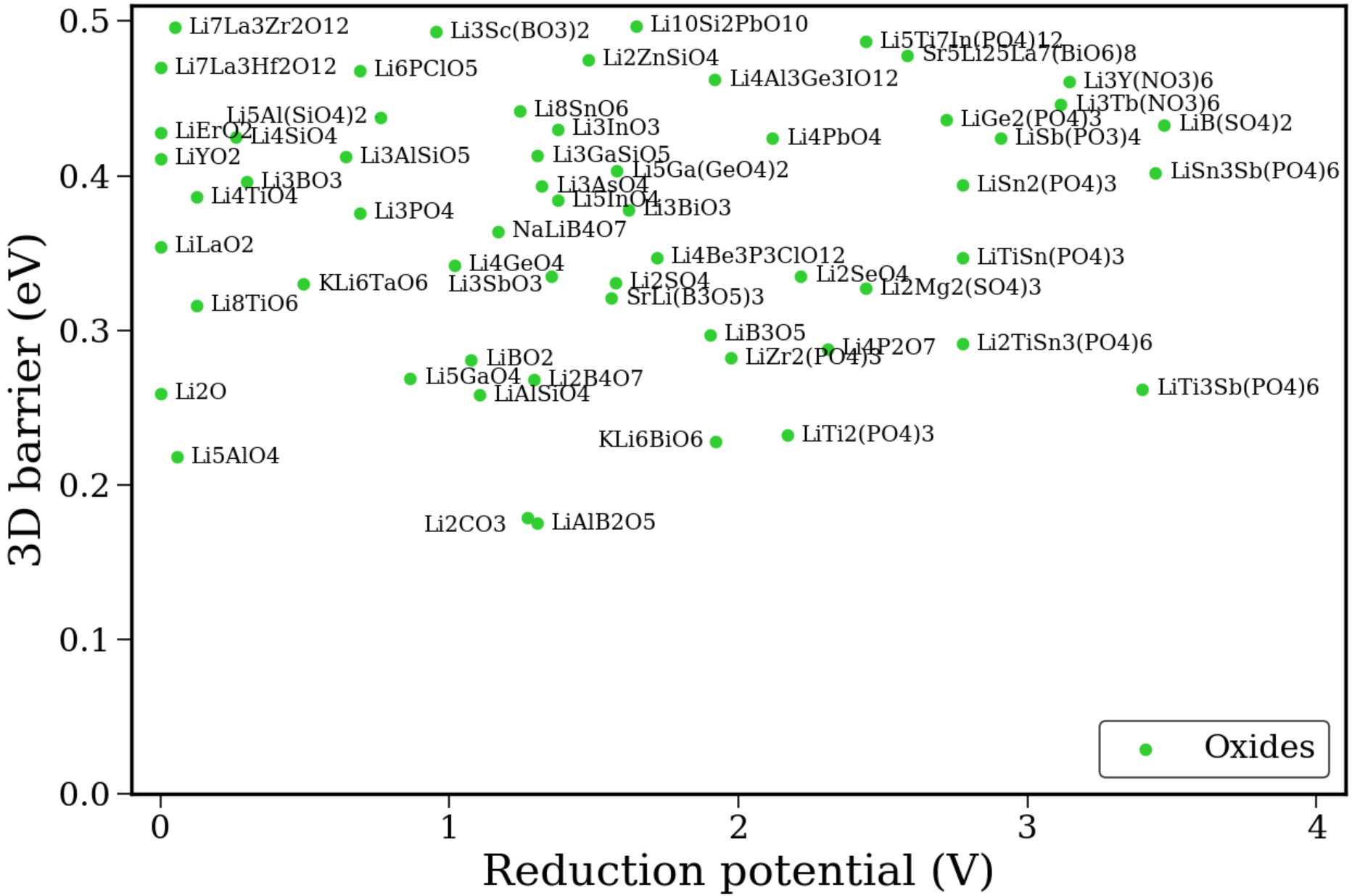
$$S_{ij} = \left(\frac{R_0 - R_{ij}}{b} \right)$$

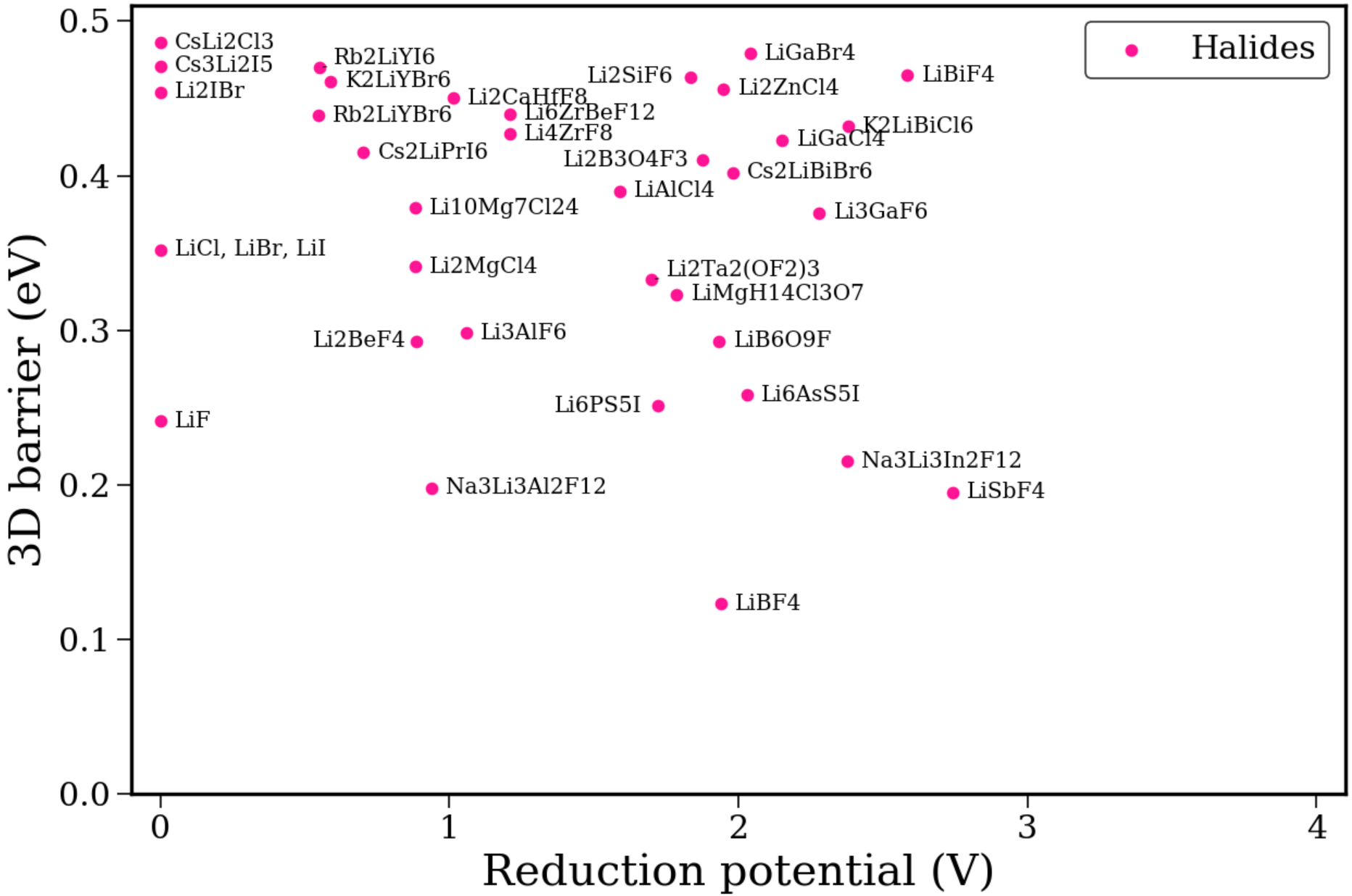
- Every pair of elements can be fitted with unique R_0 and b values associated with their interaction.

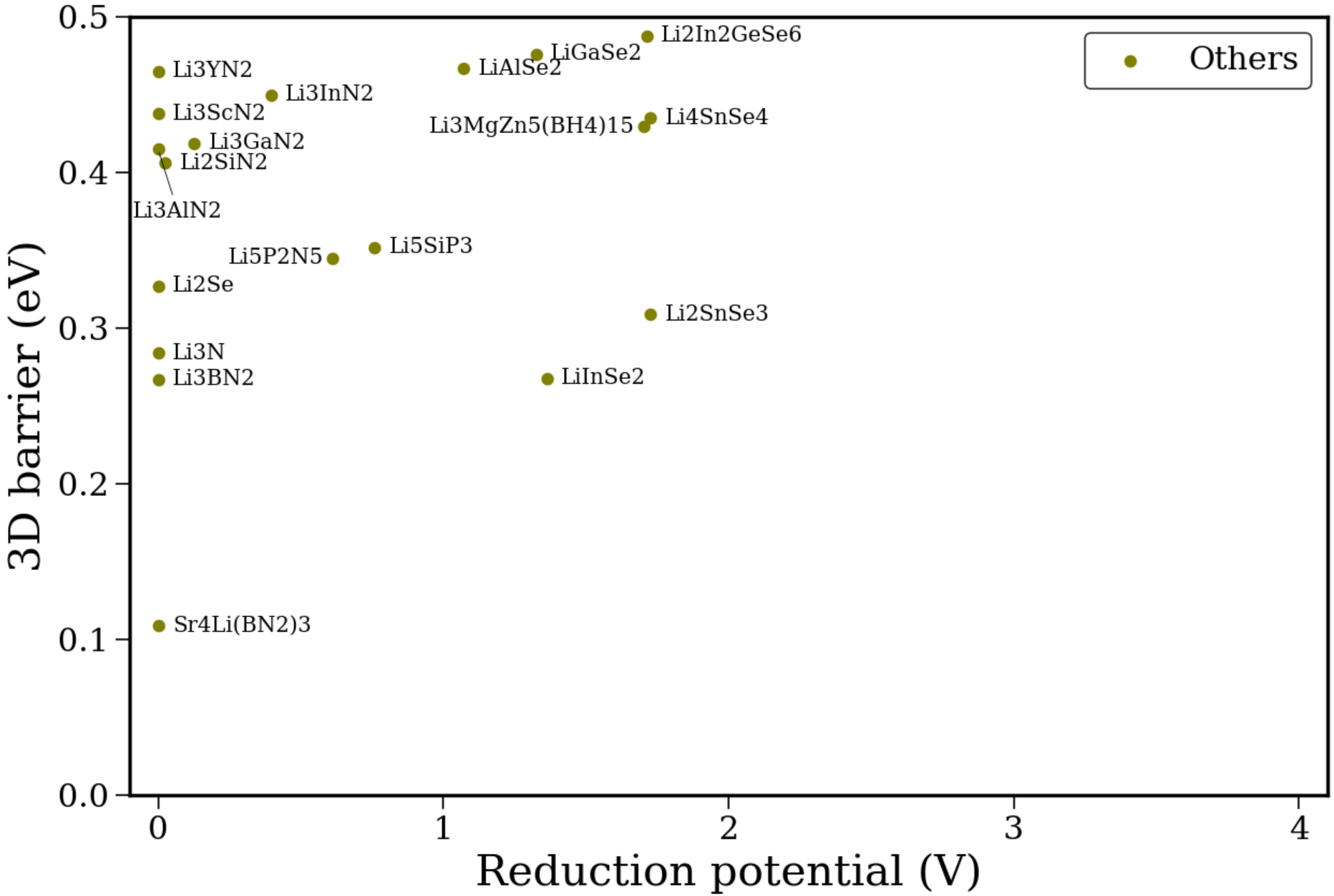
$$|\Delta V_i| = V_i - V_i^{id},$$

- Sites in a crystal structure where mismatch $|\Delta V_{ij}| \approx 0$ are considered accessible sites for atom i.
- Paths between accessible sites along which $|V_{ij}|$ remains low represent probable ion transport pathways.


Sulfides
Li5B7S13
Li3BiS3
Li2ZnSnS4
Li3SbS3
Li10Si(PS6)2
LiGaS2
LiAlS2
Li3AsS3
BaLi(BS2)3
SrLi(BS2)3
Li4GeS4
Li3PS4
Li7P3S11
Li3SbS4
Li2S
Li4Zn(PS4)2
Li6Zn3(PS4)4
Li3BS3
LiZnPS4
Li9S3N
LiHS
Li4TiS4
3D barrier (eV)
Reduction potential (V)
0.0
0.1
0.2
0.3
0.4
0.5
0
1
2
3
4


Li7La3Zr2O12
Li3Sc(BO3)2
Li10Si2PbO10
Li5Ti7In(PO4)12
Sr5Li25La7(BiO6)8
Li7La3Hf2O12
Li6PClO5
Li2ZnSiO4
Li4Al3Ge3IO12
Li3Y(NO3)6
Li3Tb(NO3)6
Li5Al(SiO4)2
Li8SnO6
LiGe2(PO4)3
LiB(SO4)2
LiErO2
Li4SiO4
Li3InO3
Li4PbO4
LiSb(PO3)4
LiYO2
Li3AlSiO5
Li3GaSiO5
Li5Ga(GeO4)2
LiSn3Sb(PO4)6
Li3BO3
Li3AsO4
LiSn2(PO4)3
Li4TiO4
Li5InO4
Li3BiO3
Li3PO4
NaLiB4O7
LiLaO2
Li4Be3P3ClO12
LiTiSn(PO4)3
Li4GeO4
KLi6TaO6
Li3SbO3
Li2SO4
Li2SeO4
Li2Mg2(SO4)3
SrLi(B3O5)3
Li8TiO6
LiB3O5
Li4P2O7
Li2TiSn3(PO4)6
LiBO2
LiZr2(PO4)3
Li5GaO4
Li2B4O7
LiTi3Sb(PO4)6
Li2O
LiAlSiO4
KLi6BiO6
LiTi2(PO4)3
Li5AlO4
Li2CO3
LiAlB2O5
Oxides
3D barrier (eV)
Reduction potential (V)
0.0
0.1
0.2
0.3
0.4
0.5
0
1
2
3
4


Halides
CsLi2Cl3
Cs3Li2I5
Li2IBr
Rb2LiYI6
K2LiYBr6
Rb2LiYBr6
Li2CaHfF8
Li6ZrBeF12
Li4ZrF8
Cs2LiPrI6
LiGaBr4
Li2SiF6
Li2ZnCl4
LiBiF4
K2LiBiCl6
LiGaCl4
Li2B3O4F3
Cs2LiBiBr6
LiAlCl4
Li10Mg7Cl24
Li3GaF6
LiCl, LiBr, LiI
Li2MgCl4
Li2Ta2(OF2)3
LiMgH14Cl3O7
Li2BeF4
Li3AlF6
LiB6O9F
Li6PS5I
Li6AsS5I
LiF
Na3Li3In2F12
Na3Li3Al2F12
LiSbF4
LiBF4
3D barrier (eV)
Reduction potential (V)
0.0
0.1
0.2
0.3
0.4
0.5
0
1
2
3
4


0.5
0.4
0.3
0.2
0.1
0.0
3D barrier (eV)
0
1
2
3
4
Reduction potential (V)
Others
Li2In2GeSe6
LiGaSe2
LiAlSe2
Li3YN2
Li3InN2
Li3ScN2
Li3MgZn5(BH4)15
Li4SnSe4
Li3GaN2
Li2SiN2
Li3AlN2
Li5SiP3
Li5P2N5
Li2Se
Li2SnSe3
Li3N
Li3BN2
LiInSe2
Sr4Li(BN2)3

Screening results: Li anode coatings

TABLE S1: Compounds identified as promising candidates for coatings on Li metal anode. [Reduction potential (*vs.* Li) = 0 V, stability window > 1 V, 3D barrier < 1 eV, E_{hull} < 30 meV, E_g > 1 eV]

No.	mp_id	Formula	3D barrier (eV)	electochemical window (V)
1.	mp-9723	$Sr4Li(BN_2)_3$	0.109	1.39
2.	mp-1960	Li_2O	0.259	2.90
3.	mp-1153	Li_2S	0.262	2.13
4.	mp-2286	Li_2Se	0.327	1.89
5.	mp-1185319	LiCl	0.349	4.25
6.	mp-976280	LiBr	0.350	3.14
7.	mp-570935	LiI	0.352	2.47
8.	mp-756544	$LiLaO_2$	0.354	2.90
9.	mp-7020	$LiYO_2$	0.411	2.92
10.	mp-752922	Li_8HfO_6	0.419	2.90
11.	mp-10970	$LiErO_2$	0.428	3.00
12.	mp-1222669	Li_2IBr	0.454	2.47
13.	mp-1198622	$Li_7La_3Hf_2O_{12}$	0.470	3.02
14.	mp-1181918	$Cs_3Li_2I_5$	0.471	2.35
15.	mp-1190687	$CsLi_2Cl_3$	0.486	4.25
16.	mp-1185301	LiF	0.536	6.36
17.	mp-1080534	$Cs_2Li_3I_5$	0.544	2.35
18.	mp-28237	$RbLiBr_2$	0.590	3.14
19.	mp-1190087	$CsLiI_2$	0.601	2.35
20.	mp-1184020	$CsLi_3I_4$	0.668	2.35
21.	mp-28243	$RbLiCl_2$	0.703	4.25
22.	mp-606680	$CsLi_2Br_3$	0.774	2.96
23.	mp-569055	$CsLi_2I_3$	0.817	2.35
24.	mp-770805	$Li_6Hf_2O_7$	0.845	3.22
25.	mp-23057	$CsLiBr_2$	0.882	2.96
26.	mp-9610	Li_2CN_2	0.982	2.12

S1.1. Li atomic fraction, Li

Ratio of number of lithium atoms (N_{Li}) to the total number of atoms (N_{atoms}) in the unit cell.

$$\text{Li} = \frac{N_{Li}}{N_{atoms}}$$

S1.2. Mean Li neighbor count, LNC [1]

Average number of neighbors within a radius of 4 Å for lithium atoms in the unit cell.

$$\text{LNC} = \frac{1}{N_{Li}} \sum_{j \neq i}^{N_{atoms}} \sum_{i \in \{Li\}}^{N_{Li}} 1\{r_{ij} < 4\text{Å}\}$$

S1.3. Mean Li-Li bonds per Li, LLB [1]

Average number of lithium neighbors within a radius of 4 Å for lithium atoms in the unit cell.

$$\mathrm{LLB} = \frac{1}{N_{Li}} \sum_{j \in \{Li\}, j \neq i}^{N_{Li}} \sum_{i \in \{Li\}}^{N_{Li}} 1\{r_{ij} < 4\text{Å}\}$$

S1.4. Mean sublattice neighbor count, SNC [1]

Average number of neighbors within a radius of 4 Å for non-lithium atoms in the unit cell.

$$\mathrm{SNC} = \frac{1}{N_{atoms} - N_{Li}} \sum_{j \neq i}^{N_{atoms}} \sum_{i \notin \{Li\}}^{N_{atoms} - N_{Li}} 1\{r_{ij} < 4\text{Å}\}$$

S1.5. Mean sublattice bond ionicity, SBI [1]

Average difference in the Pauling electronegativity of bonds (EN) between a sublattice atom and another atom within 4 Å of each other.

$$\mathrm{SBI} = \frac{1}{N_{ij}} \sum_{j \neq i}^{N_{atoms}} \sum_{i \notin \{Li\}}^{N_{atoms}-N_{Li}} |\mathrm{EN}_i - \mathrm{EN}_j| \; 1\{r_{ij} < 4\text{Å}\}$$

S1.6. Mean Electronegativity of sublattice, ENS [1]

Average Pauling electronegativity (EN) of all sublattice atoms in the unit cell.

$$\mathrm{ENS} = \frac{1}{N_{atoms} - N_{Li}} \sum_{i \notin \{Li\}}^{N_{atoms}-N_{Li}} \mathrm{EN}_i$$

S1.7. Mean Li-Li separation distance, LLSD [1]

Average min. Li-Li distance for all lithium atoms in the unit cell.

$$\mathrm{LLSD} = \frac{1}{N_{Li}} \sum_{i \in \{Li\}}^{N_{Li}} min_{j \in \{Li\}, j \neq i} \{r_{ij}\}$$

S1.8. Mean Li-anion separation distance, LASD [1]

Average min. Li-anion distance for all lithium atoms in the unit cell, where anion (A) refers to the atom with the highest electronegativity in the unit cell.

$$\mathrm{LASD} = \frac{1}{N_{Li}} \sum_{i \in \{Li\}}^{N_{Li}} min_{j \in \{A\}} \{r_{ij}\}$$

S1.9. Mean anion-anion separation distance, AASD [1]

Average min. anion-anion distance for all anions in the unit cell, where anion (A) refers to the atom with the highest electronegativity in the unit cell.

$$\mathrm{AASD} = \frac{1}{N_{A}} \sum_{i \in \{A\}}^{N_{A}} min_{j \in \{A\}, j \neq i} \{r_{ij}\}$$

S1.10. Mean neighbor distance variation, NDV [2]

Average standard deviation in bond lengths for all neighbors of a particular atom, weighted by the corresponding face area of the Voronoi cell. *Refer to the SI accompanying ref. [2] for details.*

S1.11. Mean ordering parameter shell 1, OP_1 [2]

Warren-Cowley-like ordering parameters [3] of the first neighbor shell, weighted by the corresponding face areas of the Voronoi cell for each neighboring atom in that shell. *Refer to the SI accompanying ref. [2] for details.*

S1.12. Mean ordering parameter shell 2, OP_2 [2]

Warren-Cowley-like ordering parameters [3] of the second neighbor shell, weighted by the corresponding face areas of the Voronoi cell for each neighboring atom in that shell. *Refer to the SI accompanying ref. [2] for details.*

S1.13. Mean ordering parameter shell 3, OP_3 [2]

Warren-Cowley-like ordering parameters [3] of the third neighbor shell, weighted by the corresponding face areas of the Voronoi cell for each neighboring atom in that shell. *Refer to the SI accompanying ref. [2] for details.*

S1.14. Diameter of largest free sphere, DLFS

The max. diameter of a sphere that can percolate across any one direction of the unit cell without intersecting any atoms. We calculate DLFS using the Zeo++ tool [4].

S1.15. Mean Straight Line Path Width, SLPW [1]

Average max. radius of the cylinder that connects each lithium atom with its nearest lithium neighbor without intersecting any other atoms.

S1.16. Sublattice packing fraction, SPF [1]

Ratio of total volume occupied by all sublattice atoms (V_i) to the total volume of the unit cell (V_{cell}).

$$\mathrm{SPF} = \frac{1}{V_{cell}} \sum_{i \notin \{Li\}}^{N_{atoms}-N_{Li}} V_i$$

S1.17. Max packing efficiency, MPE [2]

The ratio of sum of volumes of largest spheres that fit inside the Voronoi cell around each atom (VS_i) to the total volume of the unit cell (V_{cell}).

$$\mathrm{MPE} = \frac{1}{V_{cell}} \sum_{i \in \{atoms\}}^{N_{atoms}} \mathrm{VS}_i$$

S1.18. XRD principal component 1, XRD_1

First principal component of the powder X-ray diffraction (XRD) pattern computed using pymatgen [5].

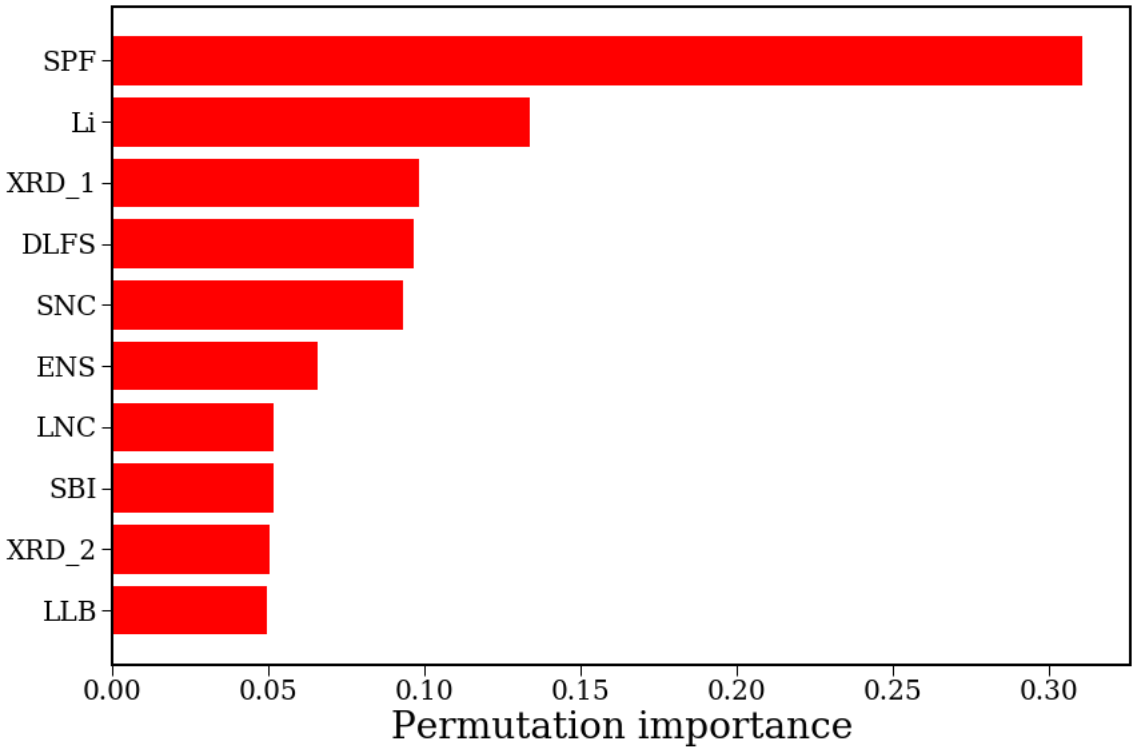
S1.19. XRD principal component 2, XRD_2

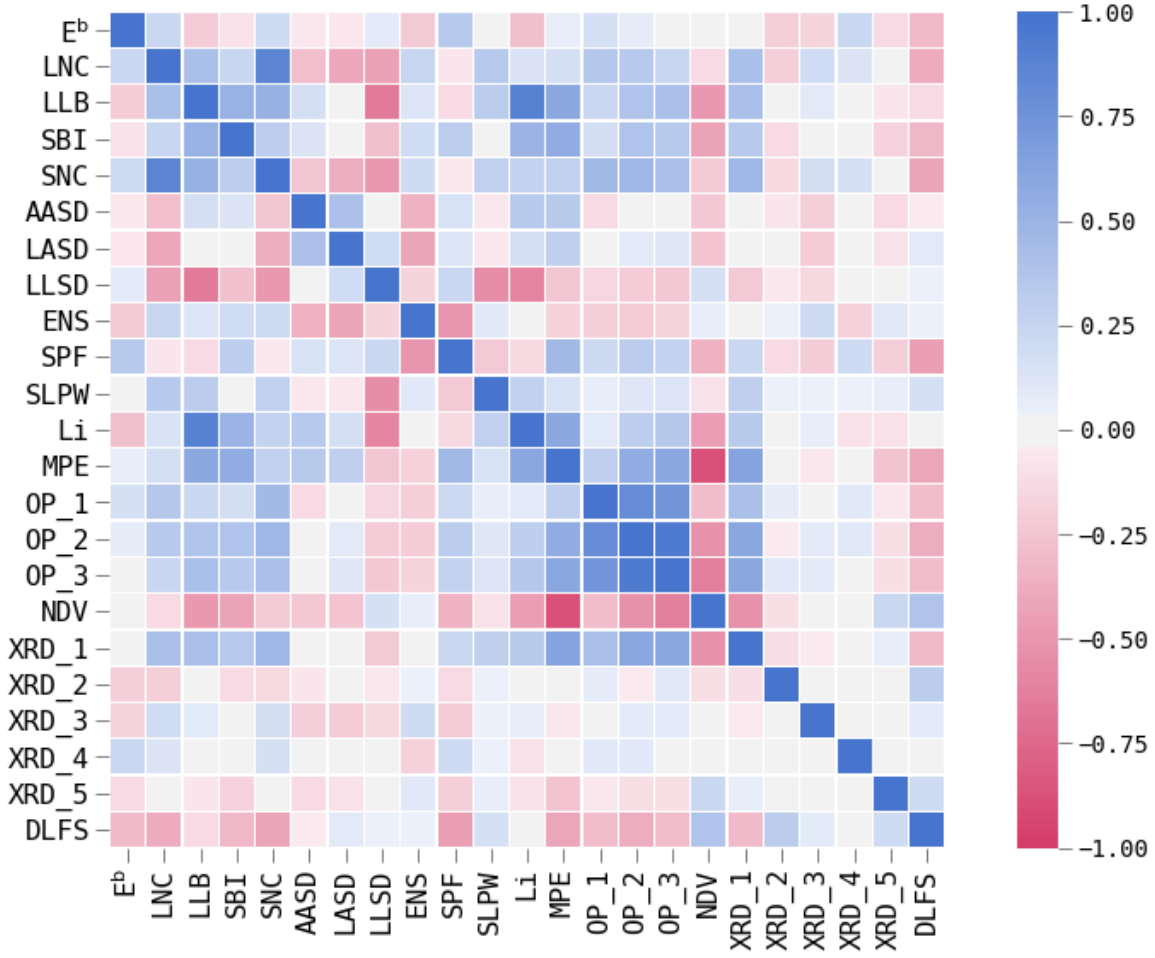
Second principal component of the powder X-ray diffraction (XRD) pattern computed using pymatgen [5].

S1.20. XRD principal component 3, XRD_3

Third principal component of the powder X-ray diffraction (XRD) pattern computed using pymatgen [5].

Permutation Feature Importance: 3D barriers



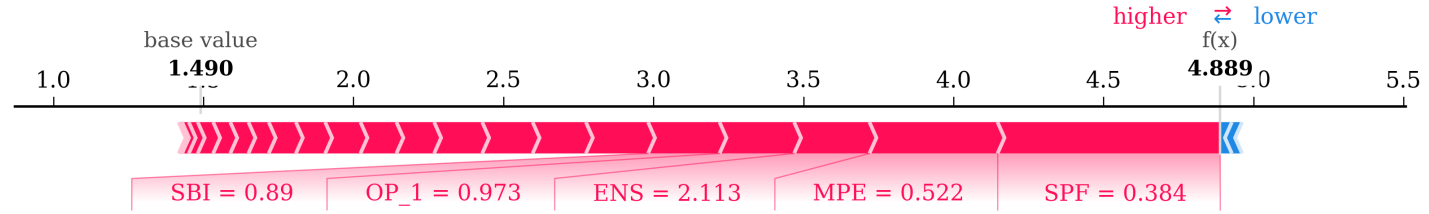


Sendek model

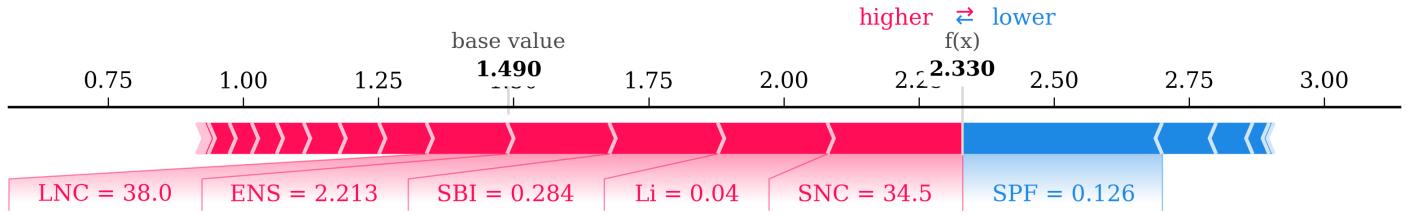
TABLE IV: Li compounds identified as possible superionic conductors by the Sendek model [59] are arranged in increasing order of their softBV 3D barriers. Where calculated barriers are missing, ML predictions are used instead. The rightmost column indicates whether the compound was predicted to have an ionic conductivity $> 10^{-4}$ S/cm based on high temperature DFT-MD simulations by Sendek *et al.* [60].

No.	mp_id	Formula	3D barrier (eV)	DFT-MD predicted ionic conductivity $> 10^{-4}$ S/cm
1.	mp-558219	$SrLi(BS_2)_3$	0.340	x
2.	mp-532413	$Li_5B_7S_{13}$	0.487	yes
3.	mp-643069	Li_2HIO	0.519	yes
4.	mp-7744	$LiSO_3F$	0.529	yes
5.	mp-569782	$Sr_2LiCBr_3N_2$	0.548	marginal
6.	mp-676109	Li_3InCl_6	0.595	yes
7.	mp-676361	$LiErCl_6$	0.664	yes
8.	mp-22905	LiCl	0.735	x
9.	mp-559238	$CsLi_2BS_3$	0.780	yes
10.	mp-29410	$Li_2B_2S_5$	0.972[d]	yes
11.	mp-34477	$LiSmS_2$	0.977	x
12.	mp-8430	KLiS	1.720[d]	x
13.	mp-8751	RbLiS	1.727[d]	x
14.	mp-554076	$BaLiBS_3$	2.035	x
15.	mp-866665	$LiMgB_3(H_9N)_2$	2.330[d]	yes
16.	mp-19896	Li_2GePbS_4	2.835	x
17.	mp-561095	$LiHo_3Ge_2(O_4F)_2$	3.259	x
18.	mp-15791	$LiErS_2$	4.698[d]	x
19.	mp-15790	$LiHoS_2$	4.749[d]	x
20.	mp-15789	$LiDyS_2$	4.872	x
21.	mp-15797	$LiErSe_2$	4.884	marginal

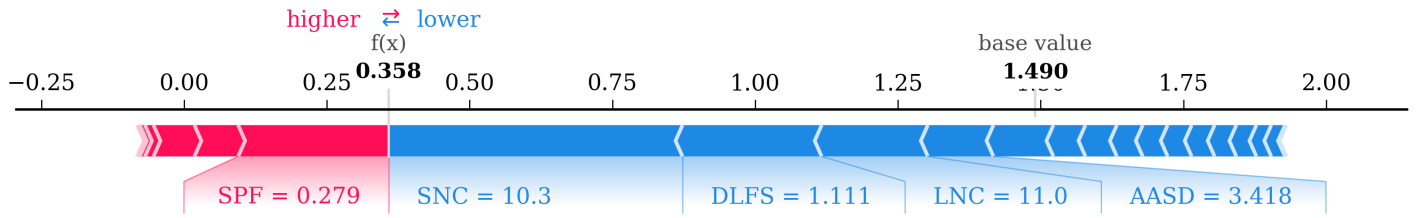
[d] ML prediction



$LiErSe_2$



$LiMgB_3(H_9N)_2$



$SrLi(BS_2)S_3$

Sendek, Cubuk, Reed, *et al*. *Energy Environ*. *Sci*. **10**, 306 (2017)