Supporting Information for

"Dynamic stability of Pt-based alloys for fuel-cell catalysts calculated from atomistics"

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1 RPBE optimized lattice constants

Table S1: RPBE optimized lattice constants of the Pt-based alloys considered in this study

System	a (Å)	b (Å)	c (Å)
$L1_0$-PtFe	3.903	3.903	3.795
$L1_0$-PtCo	3.822	3.822	3.797
$L1_0$-PtNi	3.867	3.867	3.689
$L1_2$-Pt_3Fe	3.887	3.887	3.887
$L1_2$-Pt_3Co	3.889	3.889	3.889
$L1_2$-Pt_3Ni	3.900	3.900	3.900
$L1_2$-Pt_3Sc	4.031	4.031	4.031

2 Standard reduction potentials

Table S2: Standard reduction potentials (pH 0) for pure metals considered in this study obatained from Reference [1]

Metal	Number of electrons transferred	Standard dissolution potential (V_{SHE})
Pt	2	1.18
Co	2	-0.28
Ni	2	-0.26
Fe	2	-0.45
Sc	3	-2.08

3 Schematics showing diffusion pathway in cubic alloys

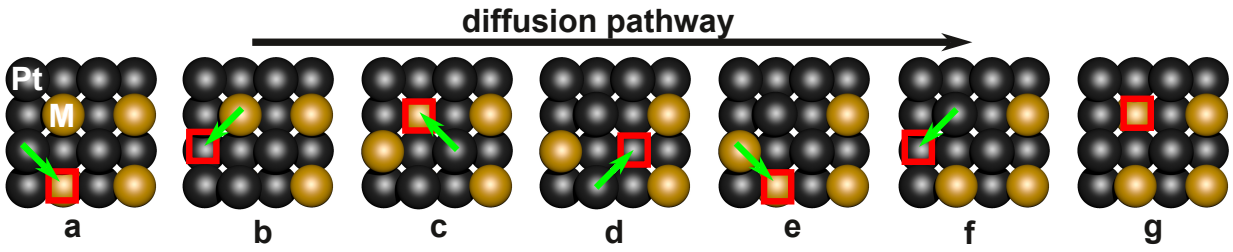

Figure S1: Schematic showing vacancy mediated bulk diffusion pathway for $L1_2$-Pt_3M systems.

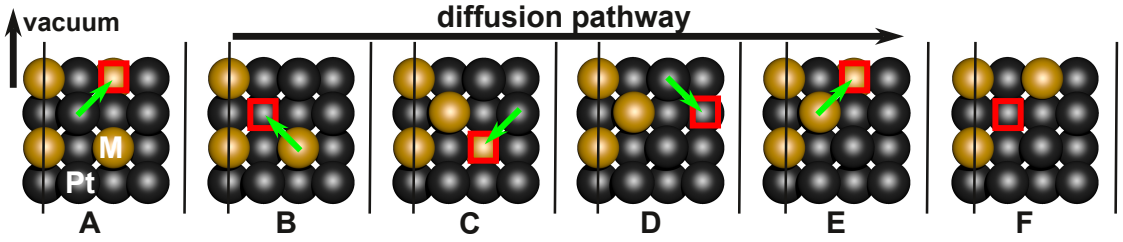

Figure S2: Schematic showing vacancy mediated "near-surface" diffusion pathway for $L1_2$-Pt_3M systems.

4 DFT calculated dissolution potentials for elements in FCT and FCC Pt-based alloys

Table S3: Dissolution potential (ϕ) of Pt (in V_{SHE}) on 111 facet of $L1_0$-PtM and $L1_2$-Pt_3M surfaces as a function of Pt overlayers. Here, Pt_n denotes "n" overlayers of Pt on an alloy system, created by replacing solute metal (M) with Pt.

System	Dissolution Potential (V_{SHE})	System	Dissolution Potential (V_{SHE})
$L1_0$-PtFe	1.90	$L1_2$-Pt_3Fe	2.07
$L1_0$-PtFe/Pt_1	1.96	$L1_2$-Pt_3Fe/Pt_1	1.76
$L1_0$-PtFe/Pt_2	1.76	$L1_2$-Pt_3Fe/Pt_2	1.69
$L1_0$-PtCo	1.86	$L1_2$-Pt_3Co	2.04
$L1_0$-PtCo/Pt_1	1.91	$L1_2$-Pt_3Co/Pt_1	1.74
$L1_0$-PtCo/Pt_2	1.73	$L1_2$-Pt_3Co/Pt_2	1.69
$L1_0$-PtNi	1.82	$L1_2$-Pt_3Ni	1.91
$L1_0$-PtNi/Pt_1	1.74	$L1_2$-Pt_3Ni/Pt_1	1.73
$L1_0$-PtNi/Pt_2	1.62	$L1_2$-Pt_3Ni/Pt_2	1.68
-	-	$L1_2$-Pt_3Sc	1.91
-	-	$L1_2$-Pt_3Sc/Pt_1	1.78
-	-	$L1_2$-Pt_3Sc/Pt_2	1.52

Table S4: Dissolution potential (ϕ) of M (in V_{SHE}) on 111 facet of $L1_0$-PtM and $L1_2$-Pt_3M surfaces

System	Dissolution Potential (V_{SHE})	System	Dissolution Potential (V_{SHE})
$L1_0$-PtFe	0.13	$L1_2$-Pt_3Fe	0.27
$L1_0$-PtCo	0.15	$L1_2$-Pt_3Co	-0.01
$L1_0$-PtNi	0.17	$L1_2$-Pt_3Ni	0.12
-	-	$L1_2$-Pt_3Sc	-0.76

Table S5: Change in free energy, ΔG associated with substitution of solute metal (M) with a Pt atom in $L1_0$-PtM and $L1_2$-Pt_3M surfaces. Here, ϕ represents the potential in SHE scale.

System	ΔG (eV)	System	ΔG (eV)
$L1_0$-PtFe	-3.39	$L1_2$-Pt_3Fe	-2.75
$L1_0$-PtCo	-3.30	$L1_2$-Pt_3Co	-3.20
$L1_0$-PtNi	-3.08	$L1_2$-Pt_3Ni	-3.01
-	-	$L1_2$-Pt_3Sc	-8.9 - $e\phi$

5 Climbing-Image Nudged Elastic Band (CI-NEB) pathways for bulk diffusion

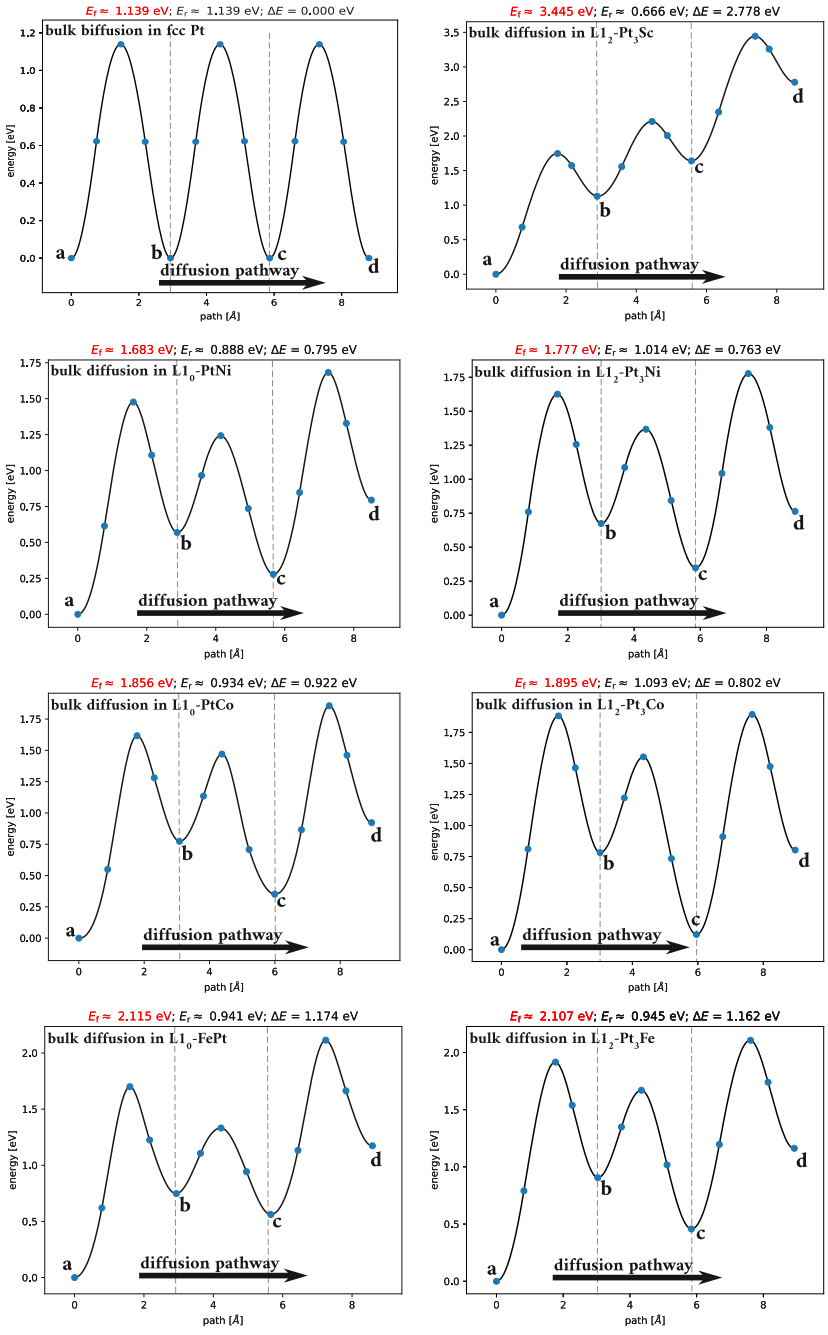

Figure S3: DFT calculated CI-NEB pathways for bulk diffusion in fcc Pt, $L1_0$-PtM and $L1_2$-Pt_3M structures. The overall barrier (in eV) from configuration "a" to "d" (*i.e.*, the forward barrier, E_f) is highlighted in red. E_r and ΔE represents the reverse barrier (in eV) and the potential energy difference (in eV) between configuration "d" and "a", respectively.

6 Climbing-Image Nudged Elastic Band (CI-NEB) pathways for "near surface" diffusion

6.1 Diffusion in FCC systems

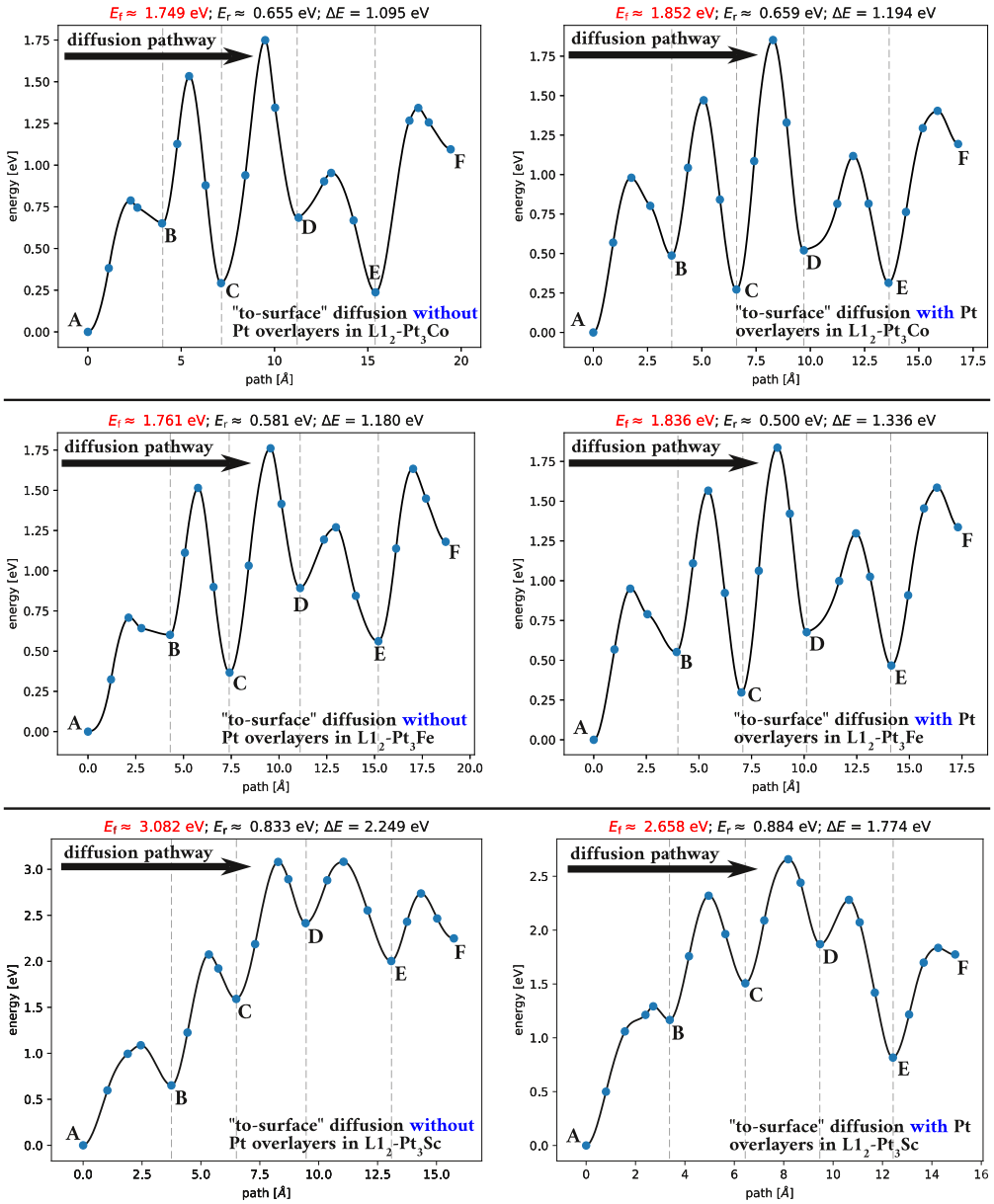

Figure S4: DFT calculated CI-NEB pathways for "near surface" diffusion in $L1_2$-Pt_3M structures. The overall barrier (in eV) from configuration "A" to "F" (*i.e.*, the forward barrier, E_f) is highlighted in red. E_r and ΔE represents the reverse barrier (in eV) and the potential energy difference (in eV) between configuration "F" and "A", respectively.

6.2 Diffusion in FCT systems

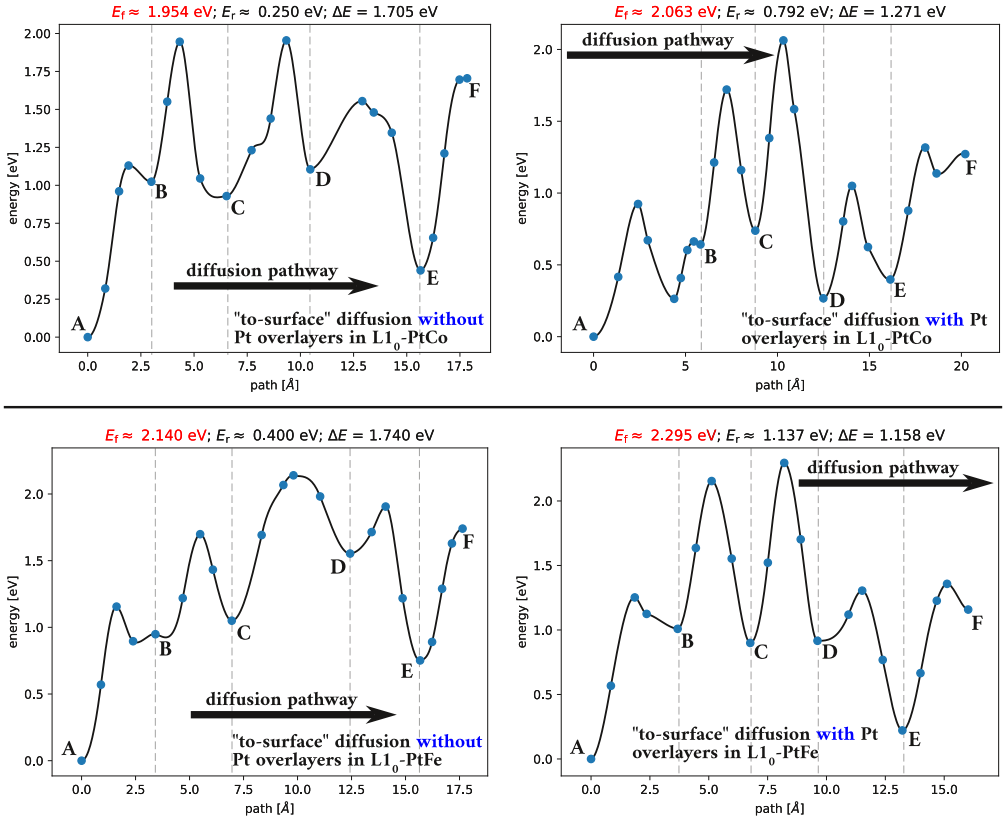

Figure S5: DFT calculated CI-NEB pathways for "near surface" diffusion in L1$_0$-PtM structures. The overall barrier (in eV) from configuration "A" to "F" (*i.e.*, the forward barrier, E_f) is highlighted in red. E_r and ΔE represents the reverse barrier (in eV) and the potential energy difference (in eV) between configuration "F" and "A", respectively.

7 Rate (or time constant) comparisons

The diffusion barrier can be correlated to the rate of diffusion by

$$k = Ae^{-\frac{\Delta E}{k_B T}}$$

Here, ΔE is the overall diffusion barrier of a system for a given pathway (in eV), k_B is the Boltzmann constant (in eV/K), k is the rate of overall diffusion, A is the pre-expoenential factor, and T is the temperature (in K). We compared two systems in terms of their rates of diffusion by

$$\frac{k_1}{k_2} = e^{\frac{\Delta E_2 - \Delta E_1}{k_B T}}$$

$$\ln \frac{k_1}{k_2} = \frac{\Delta E_2 - \Delta E_1}{k_B T}$$

Here, k_1 and k_2 are the rate of overall diffusion for the reference and target systems, respectively. A more positive value of $\ln \frac{k_1}{k_2}$ suggests rate of diffusion in target system to be slower than the reference system by a factor of $e^{\frac{\Delta E_2 - \Delta E_1}{k_B T}}$ and vice-versa.

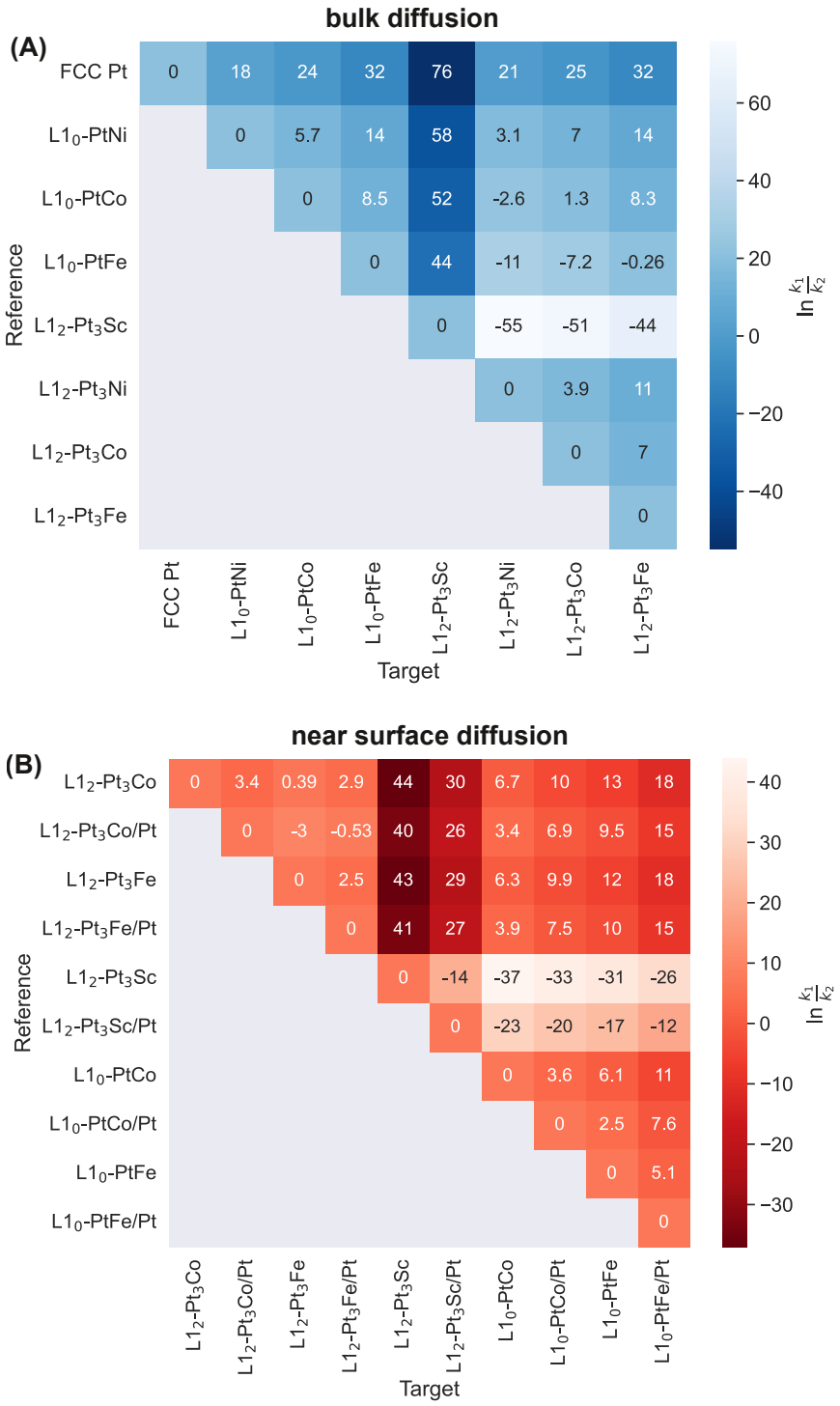

Figure S6: Comparison heatmap for rate of overall diffusion at T=80 °C for (A) bulk diffusion pathway and (B) near surface diffusion pathway.

References

[1] CRC Handbook, *CRC Handbook of Chemistry and Physics, 88th Edition*. CRC Press, 88 ed., 2007.