ROLE OF SURFACE VACANCIES IN CHLORIDE-INDUCED CORROSION OF FE(100)

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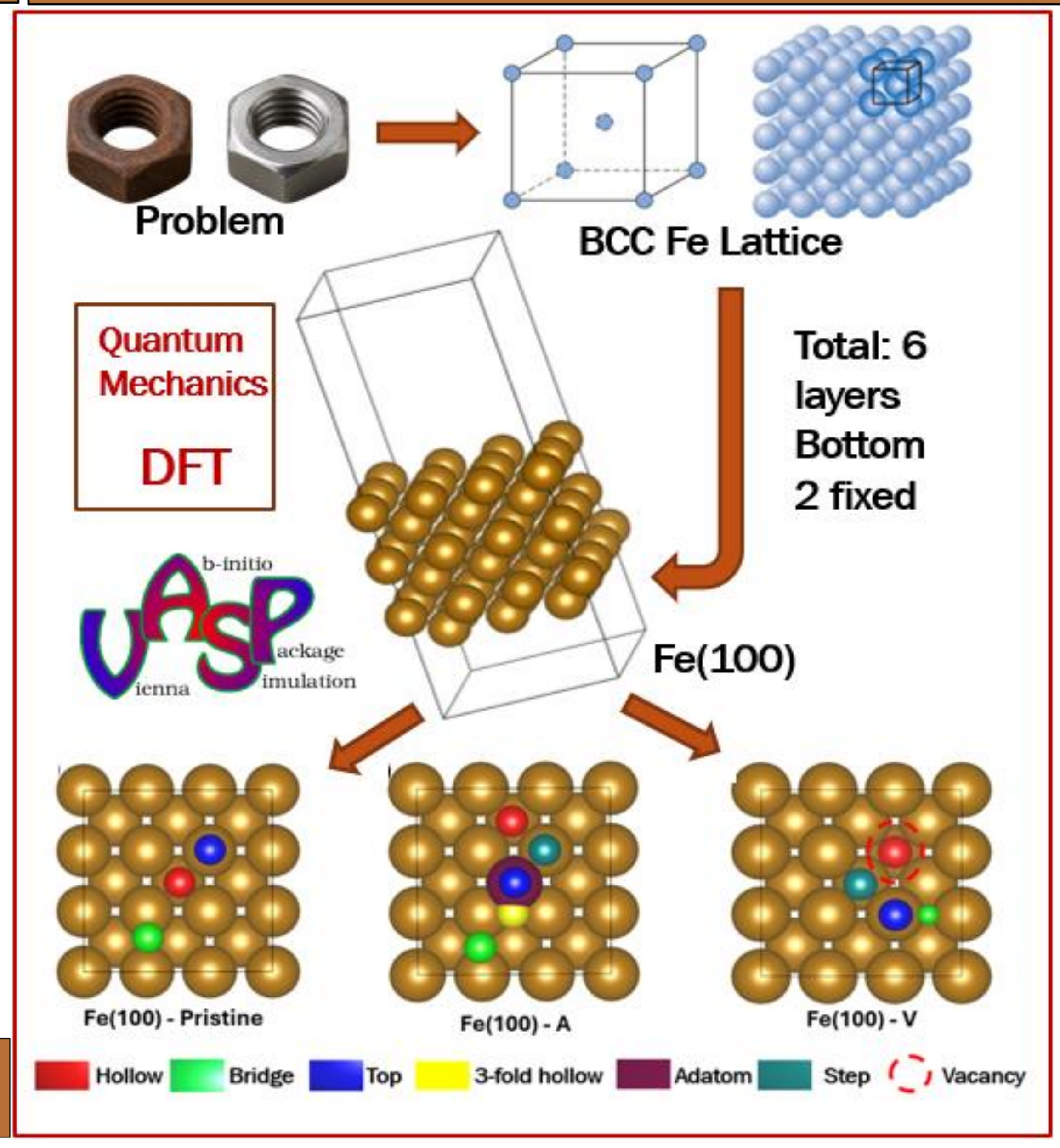
INTRODUCTION & AIM

- ❑ Steel corrosion in chloride environments drives major economic and safety losses across infrastructure, transport, and marine sectors.
- ❑ Corrosion onset is set by competition between oxygen adsorption (passivation) and chloride adsorption (depassivation), which can destabilise protective oxides and trigger localised attack.
- ❑ Real Fe surfaces (Fe(100)-P are not perfectly crystalline — defects like adatoms (Fe(100)-A) and vacancies (Fe(100)-V) alter local electronic structure and reactivity.
- ❑ Knowing how these defects shape O and Cl adsorption is key to predicting corrosion susceptibility at the atomic scale.

Aim: To use spin-polarised DFT to determine how point defects (adatoms and vacancies) on Fe(100) influence oxygen and chloride adsorption and thereby govern surface passivation and chloride-induced depassivation at the atomic scale.

METHOD



RESULTS & DISCUSSION

O Adsorption

Energetics & Geometry

Description	Fe(100)-P	Fe(100)-A	Fe(100)-V
Most Stable Adsorption Site	Hollow	Hollow	Bridge
Adsorption Energy	-3.53, -3.41[1], -3.47[2]	-3.20	-2.97
d (Fe-O)/Å (Vertical)	0.03	0.03	0.10
d (Fe1-Fe2)/Å	1.52	1.58	1.52
O charge	-1.312	-1.304	-1.065
Fe charge (First Layer)	0.340	0.324	0.456
Fe charge (Second Layer)	-0.065	-0.042	-0.149

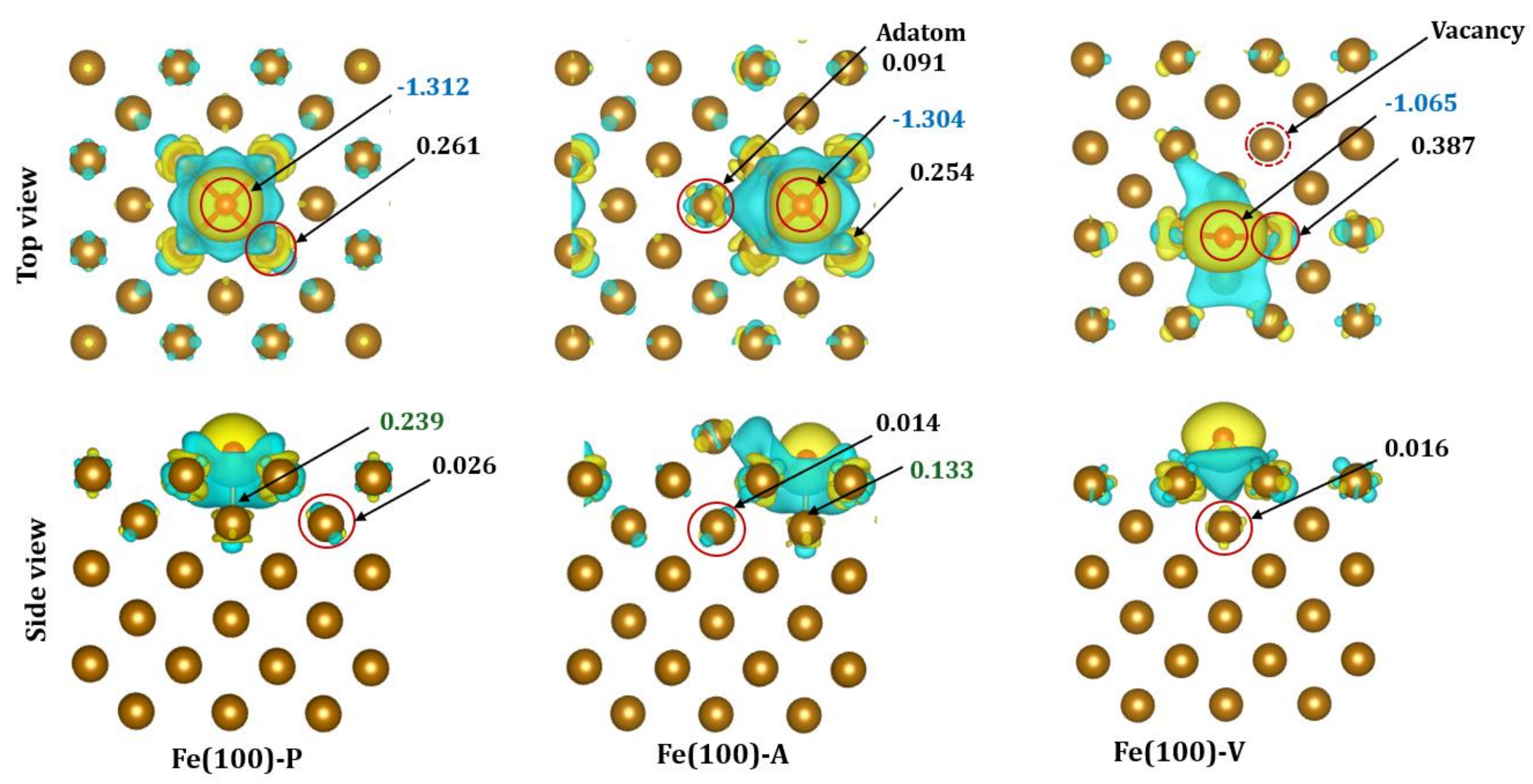
Most Stable
Fe (100)-P
Fe(100)-A
Fe(100)-V
Least Stable

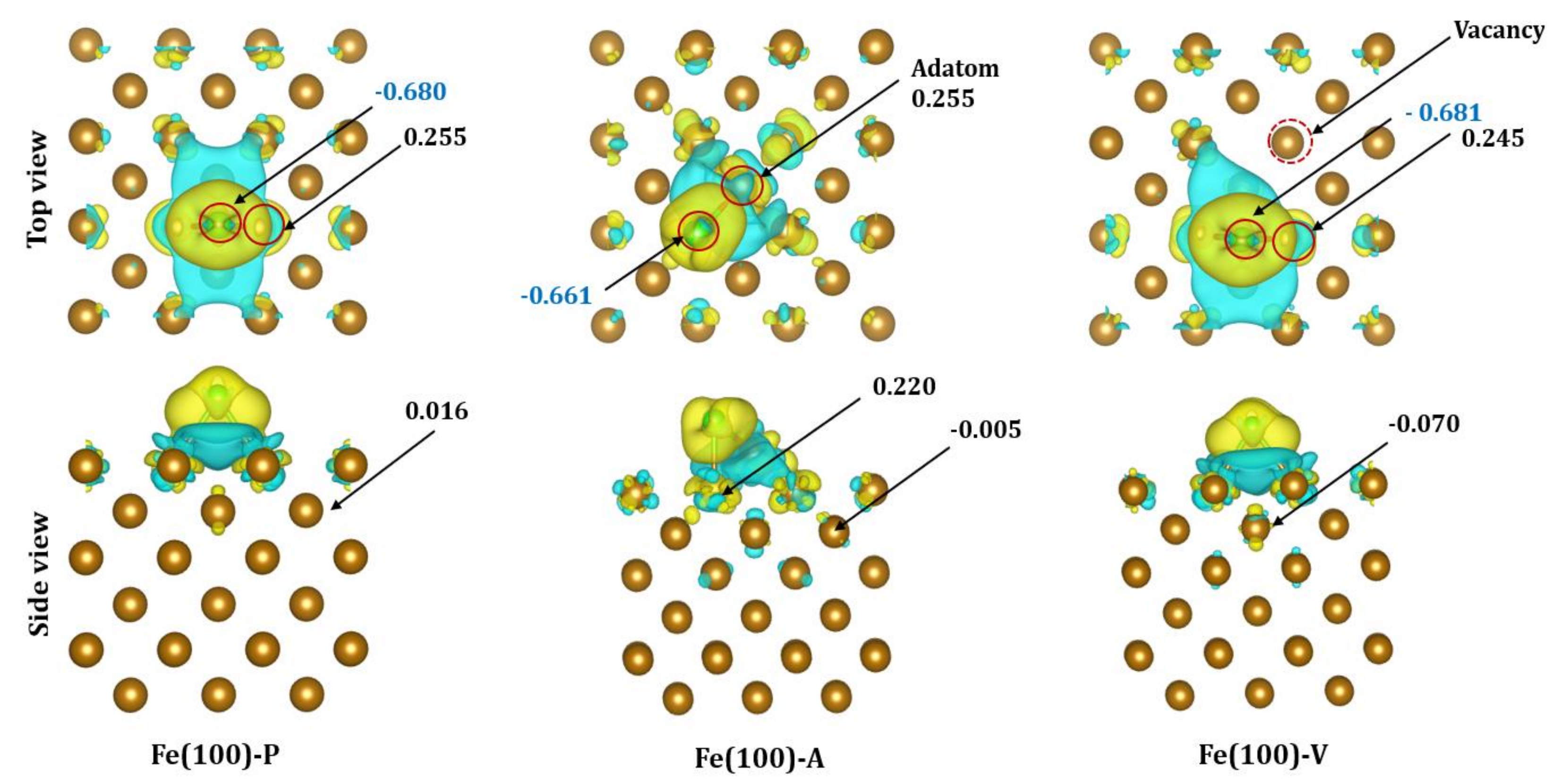
Cl Adsorption

Description	Fe(100)-P	Fe(100)-A	Fe(100)-V
Most Stable Adsorption Site	Bridge	Step	Bridge
Adsorption Energy	-2.67,-2.52[1]	-2.63	-2.78
d (Fe-Cl)/Å (Vertical)	0.18	0.19	0.15
d (Fe1-Fe2)/Å	1.53	1.54	1.42
Cl charge	-0.680	-0.661	-0.681
Fe charge (First Layer)	0.255	0.234	0.244
Fe charge (Second Layer)	0.016	-0.005	-0.070

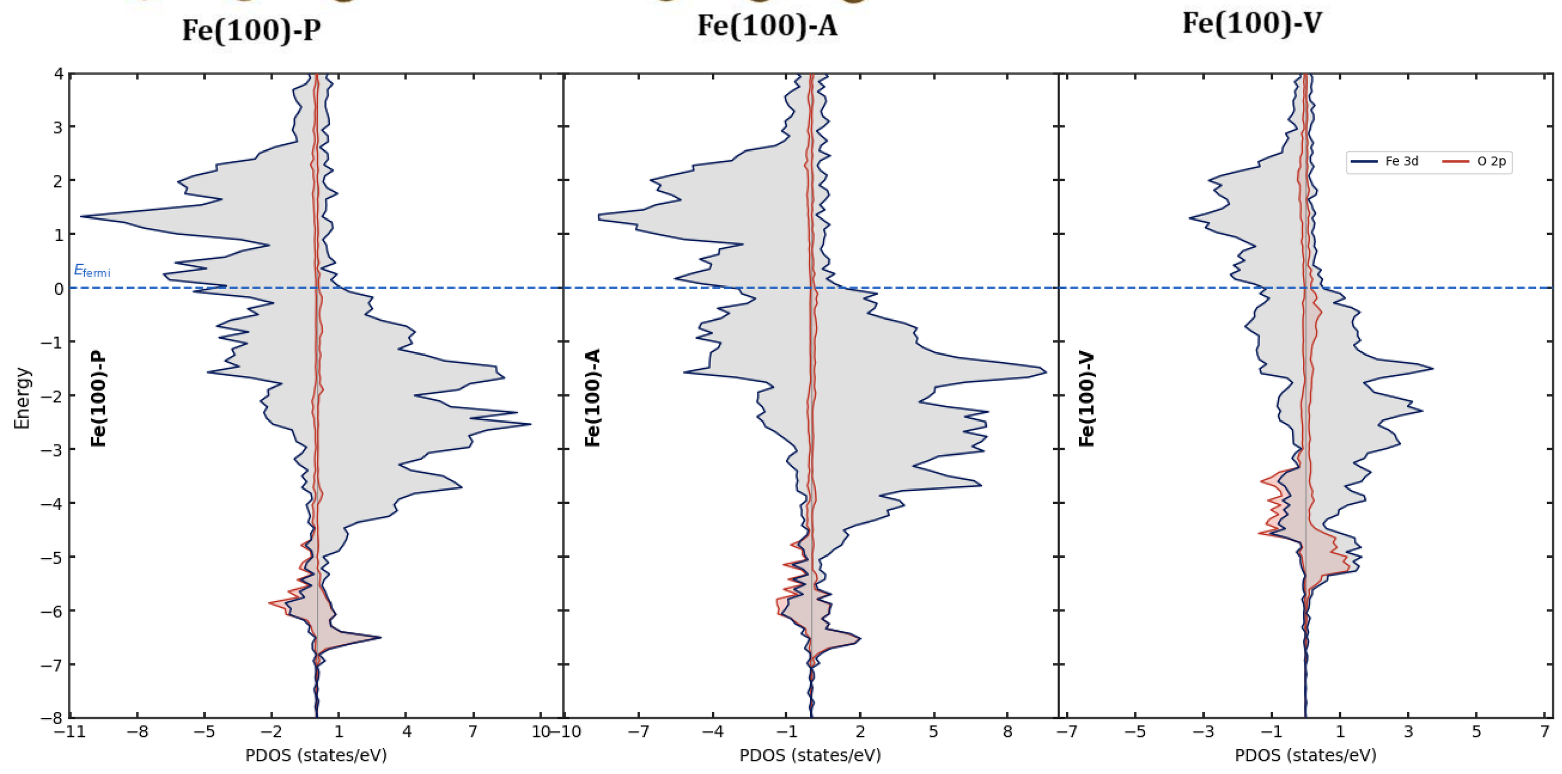
Most Stable
Fe (100)-V
Fe(100)-P
Fe(100)-A
Least Stable

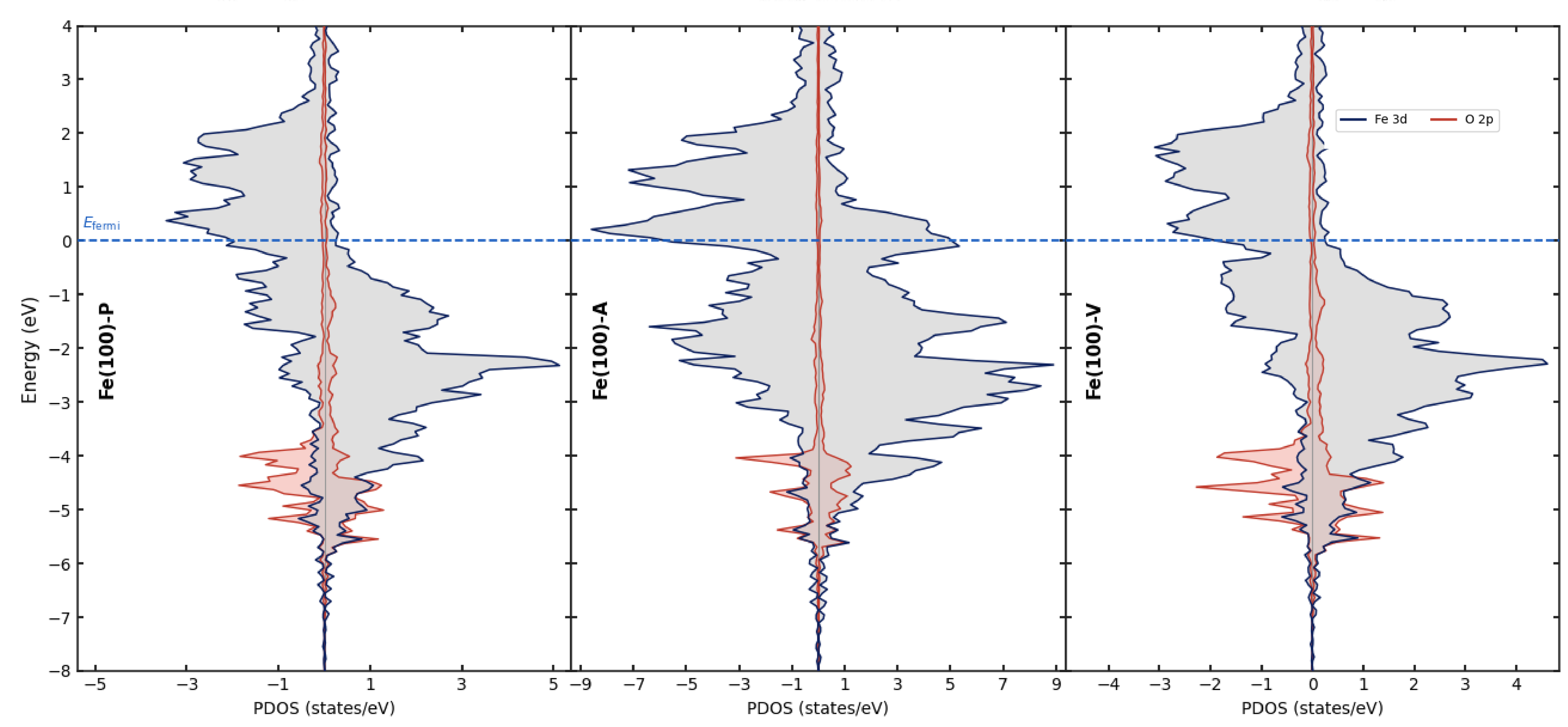
VCDD





PDOS





CONCLUSIONS

Vacancy defects act as dual corrosion promoters on Fe(100), suppressing O passivation while enhancing Cl depassivation.

Passivation impaired: O binding weakens (P→A→V, −3.53 → −2.97 eV) as vacancy coordination drops to two-fold, cutting charge transfer (−1.31 → −1.07 e).
Depassivation enhanced: Cl binds strongest at the vacancy (−2.78 eV), embedding in the pocket with its d-band centre shifting toward the Fermi level.

REFERENCES/ACKNOWLEDGMENT

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