

Supporting Information

Iron-Arsenide monolayers as an anode material for lithium-ion batteries: A first-principles study

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Spin-polarisation term

To determine the exchange-correlation potential for transition metal atoms. Specifically, for the exchange component, the functional is expressed as:

$$E_x^{SDFT}[n_\uparrow, n_\downarrow] = \frac{1}{2}(E_x^{DFT}[n_\uparrow] + E_x^{DFT}[n_\downarrow])$$

Additionally, the correlation energy of the spin-polarized homogeneous electron gas is assessed within the random-phase approximation, where E_c also accounts for the fractional spin polarization factor (ξ):

$$\xi = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow}$$

The spin-dependent exchange-correlation energy E_c^{SDFT} is determined by integrating over-space d^3r and is a function of the local electron density $n(\vec{r})$ and the local spin polarization factor $\xi(\vec{r})$

$$E_c^{SDFT} = \int d^3r \varepsilon_c(n(\vec{r}), \xi(\vec{r}))$$

In DFT, the exchange-correlation energy typically exhibits minimal dependence on the orbitals. However, in systems characterized by narrow 3d- or 5f-bands with localized orbitals, DFT inadequately considers the strong Coulomb repulsion between electrons occupying these bands. Consequently, DFT fails to accurately predict the enhanced exchange splitting between occupied and empty eigenstates in such systems for simple GGA exchange-correlation potential.

Calculation of Hubbard potential for Fe by linear response method

The Hubbard potential (U) value has been chosen from the literature where FeAs phases have been reported *{Nanoscale, 2019, 11, 16508-16514}*. To verify the U value for 1H-FeAs and 1T-FeAs, the linear response approach has been used to calculating the density response function to determine the on-site Coulomb interaction in a self-consistent manner. This approach is particularly relevant for systems with strong electron correlation effects, such as transition metal oxides and other correlated electron materials *{Phys. Rev. B, 2005, 71, 035105}*.

The basic idea is that we are applying a potential to the correlated orbitals (generally d - and f -orbitals of transition metals) of a single site and observing how this changes the d occupancies on all the sites. This tells us about the screened on-site Coulomb interaction. For this, we have done three types of calculations:

1. Normal GGA-PBE calculation, where the correlation potential ($\alpha=0$) is zero.
2. Self-consistent (SC) calculations for a series by varying the value of α ("interacting" response).
3. Non-Self-consistent (NSC) calculations for a series by varying the value of α ("bare" response).

The calculation 1, gives us the number of d -electrons and the charge density for the unperturbed system. The 2 and 3 calculations use the unperturbed charge density for a series of calculations with α . In the second type, we allow the charge density to converge to screen this perturbation, while for the third type, we do not.

$$\chi_{IJ}^0 = \frac{\partial n_I^{NSCF}}{\partial V_J} ; \chi_{IJ} = \frac{\partial n_I^{SCF}}{\partial V_J}$$

$$U = \frac{1}{\chi_{IJ}} - \frac{1}{\chi_{IJ}^0} = \left(\frac{\partial n_I^{SCF}}{\partial V_J} \right)^{-1} - \left(\frac{\partial n_I^{NSCF}}{\partial V_J} \right)^{-1}$$

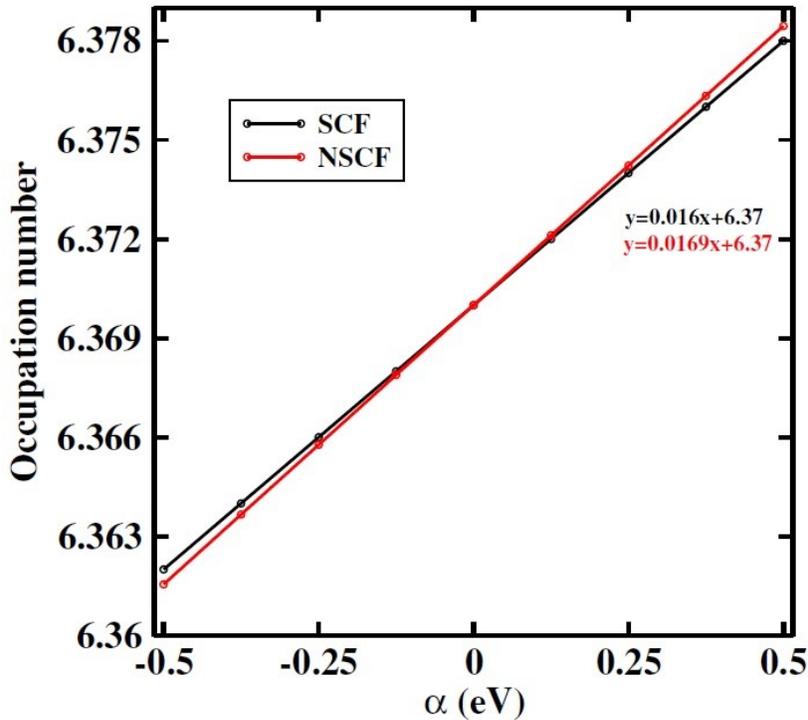


Fig. S1: Occupation number vs alpha potential plot to estimate the Hubbard potential for Fe using linear response method.

$$U = \frac{1}{0.016} - \frac{1}{0.0169} = 62.5 - 59.17 = 3.33 \text{ eV}$$

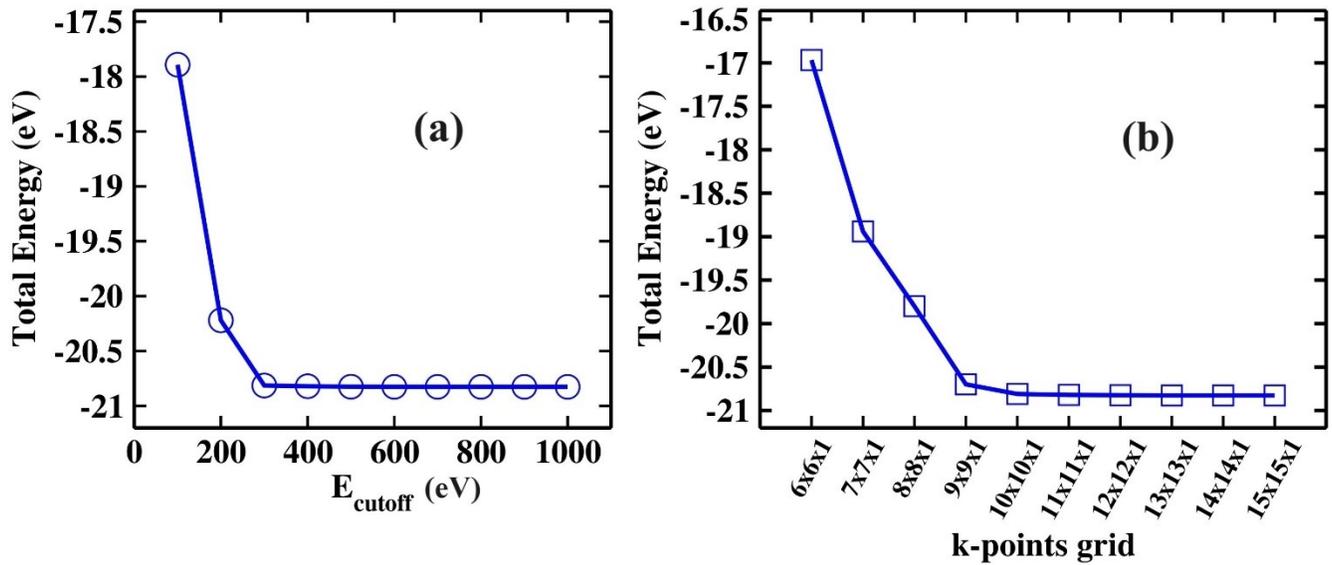


Fig. S2 The convergence test for (a) plane wave energy cutoff and (b) k-points grid for the 1T-FeAs phase.

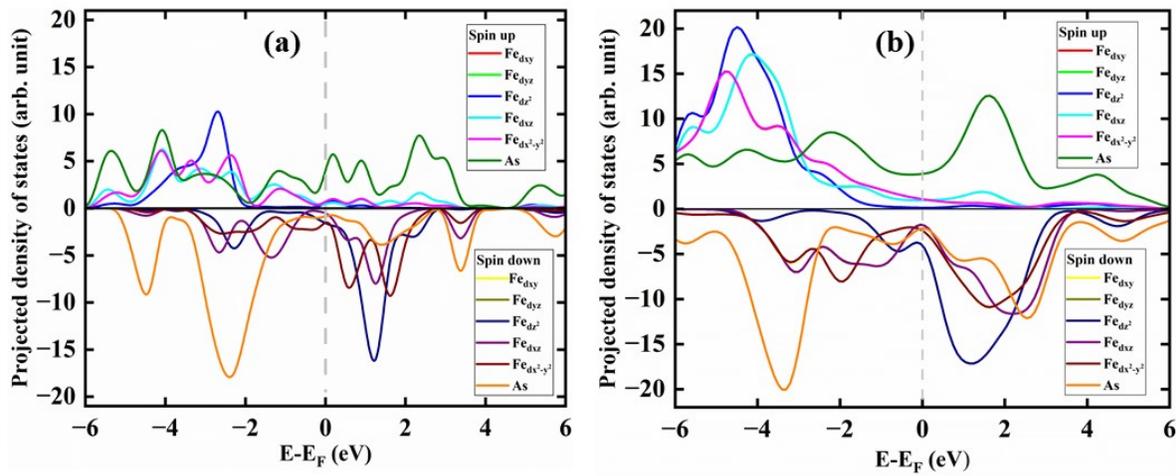


Fig. S3: Spin-polarized projected density of states (a) 1H-FeAs and (b) 1T-FeAs monolayers. The positive of the y-axis is spin up, and the negative is spin down density of states.

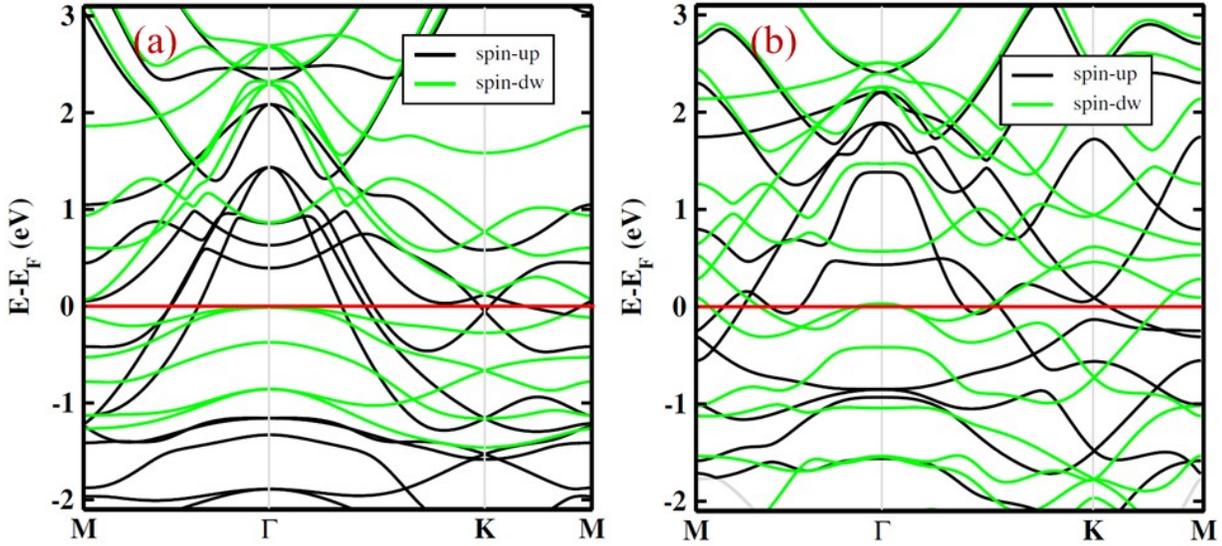


Fig. S4. Spin-polarized electronic band spectra of Li adsorbed on the (a) H-site of 1H-FeAs and (b) Fe2'-site of 1T-FeAs phases. The plots illustrate the electronic band structures, providing insights into the behaviour of Li adsorption at favourable sites of FeAs monolayers.

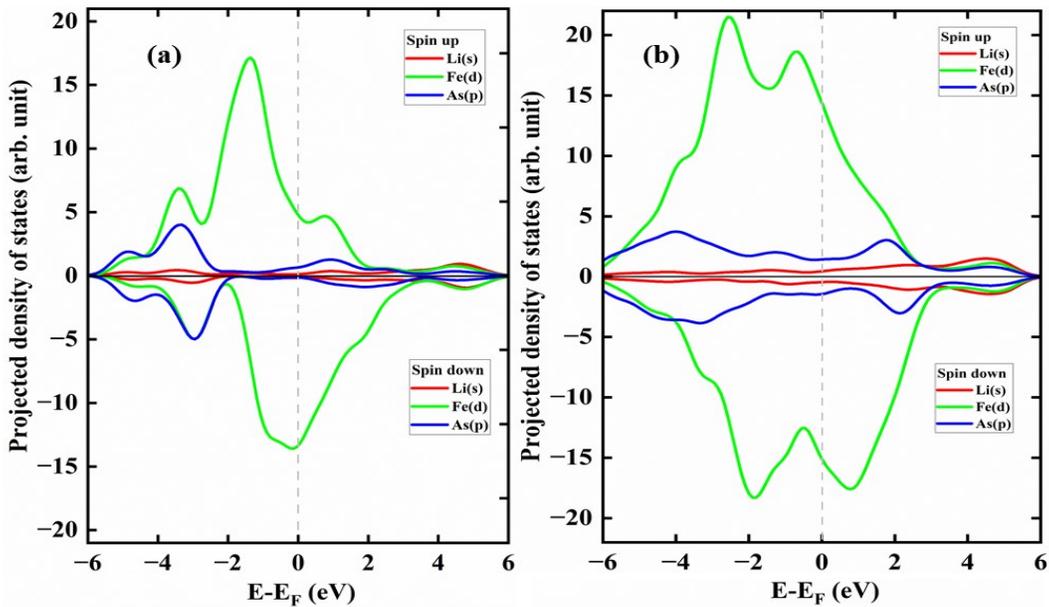


Fig. S5: Spin-polarized projected density of states Li-adsorbed at the most favourable site; (a) H-site for 1H-FeAs and (b) Fe2'-site for 1T-FeAs monolayers. The positive of the y-axis is spin up and the negative is spin down density of states.

Phases	$E_{\text{ave/single}}$ (eV)	$E_{\text{ave/layer-2}}$ (eV)	$E_{\text{ave/layer-4}}$ (eV)
1H-FeAs	-2.08	-1.265	-0.091
1T-FeAs	-1.79	-0.98	-0.072

Table S1: - The calculated layer-by-layer average adsorption energy $E_{\text{layer-}n}$ for Li adsorbed FeAs monolayers.

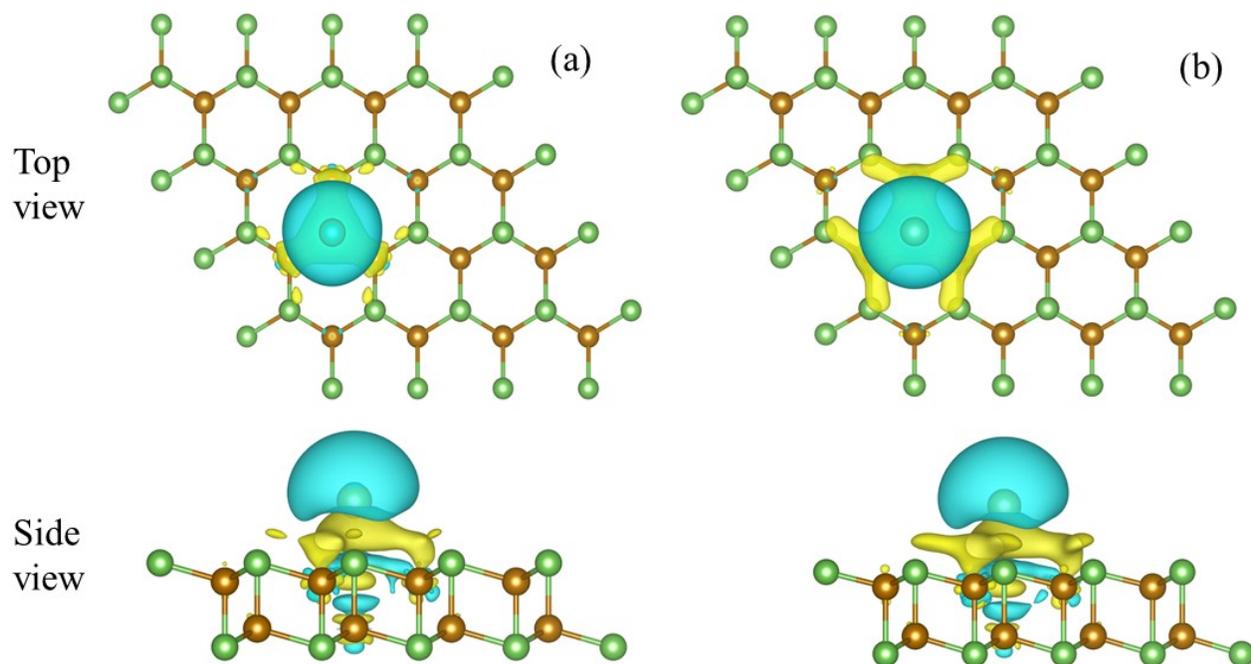


Fig. S6. The electron density difference plots of Li adsorbed at (a) Fe-site and (b) A'-site in 1H-FeAs with an iso-surface of $0.002 \text{ e}/\text{\AA}^3$

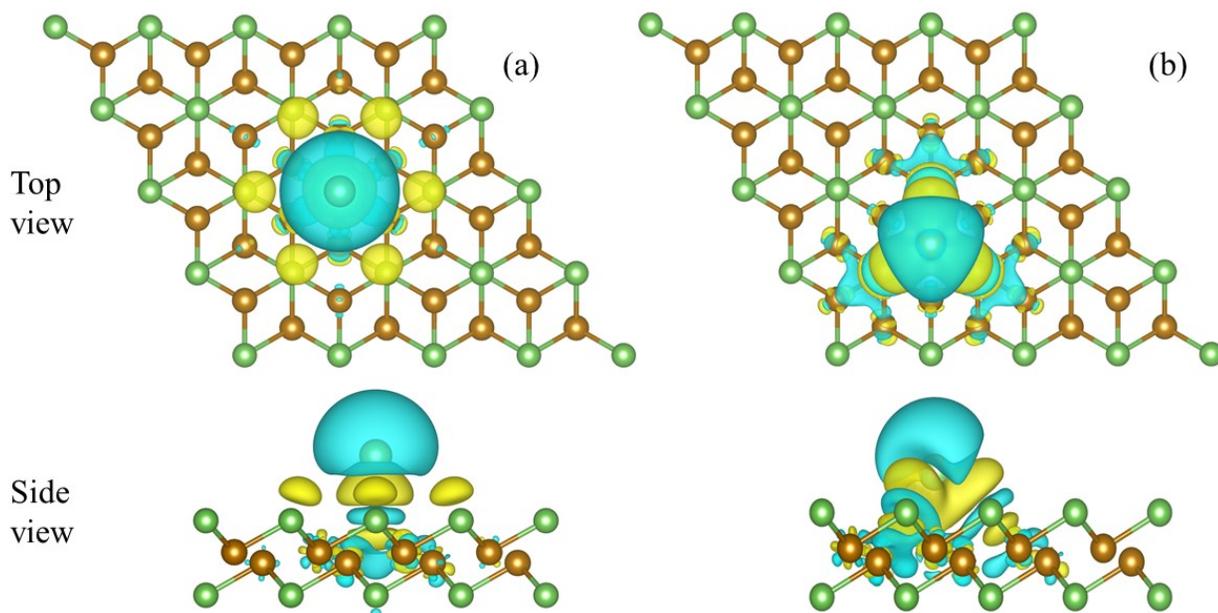


Fig. S7. The electron density difference plots of Li adsorbed at (a) Fe'-site and (b) As'-site in 1T-FeAs with an iso-surface of $0.002 \text{ e}/\text{\AA}^3$

A rough estimation for $P\Delta V$ terms in equation 5 of the manuscript:

To assess the $P\Delta V$ terms during lithiation, we evaluated the pressure exerted by the maximum number of Li atoms adsorbed on the FeAs monolayer while constraining the volume. For the 1H-FeAs configuration, the pressure value has been found to be 0.36 KBar, and for 1T-FeAs is 0.19 KBar. The reported change in area for these configurations is 5.57% (0.71 \AA^2) and 4.85% (0.72 \AA^2), respectively. Consequently, the calculated $P\Delta V$ values for 1H-FeAs and 1T-FeAs amount to 0.000225 and 0.000118 eV, respectively. These values, on the order of 10^{-4} eV, are notably smaller when compared to the change in internal energy, which falls within the range of 1-2 eV. As a result, we have ignored the $P\Delta V$ term because of its minimal contribution.

Note: $1 \text{ eV/\AA}^3 = 160.2 \text{ GPa} = 1602 \text{ kbar} \Rightarrow 1 \text{ kbar} = 0.000625 \text{ eV/\AA}^3$

The width of monolayers remains unchanged during lithiation, and the units are reduced to a 2D scale.

Spin polarisation configurations for both FeAs phase

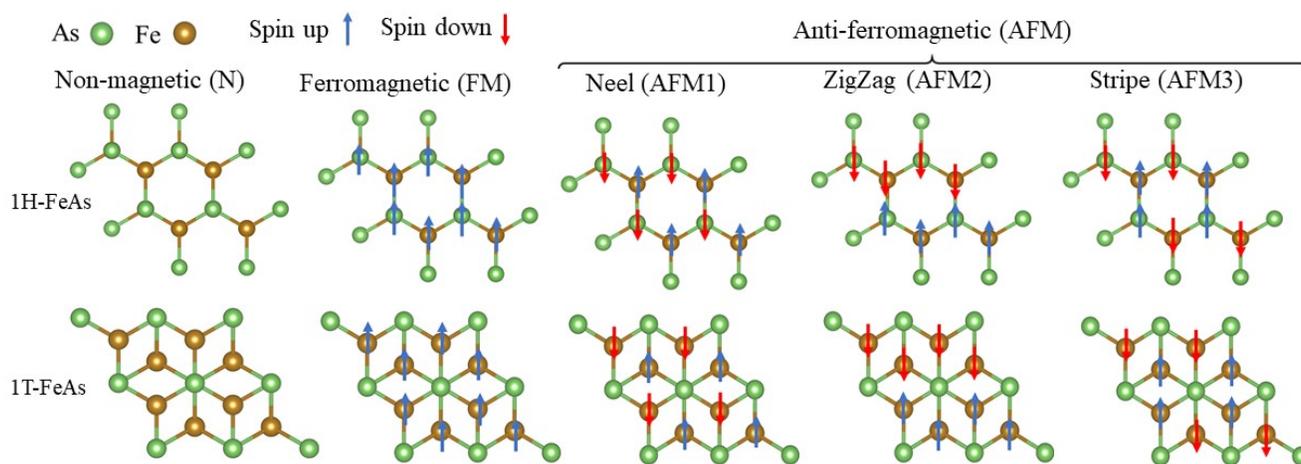


Fig. S8. Spin-polarisation configuration of 1H-FeAs and 1T-FeAs monolayers.

Note: In 1H-FeAs, the spin symbol at the top of As represents Fe, which is overshadowed by As.