# Supporting Information

#### Highly Stable Two-dimensional Iron Monocarbide with Planar

#### Hypercoordinate Moiety and Superior Li-ion Storage Performance

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### **Computational details**

We also carried out crystal orbital Hamilton population (COHP) analysis to investigate the bonding mechanism of the monolayers.<sup>[1]</sup> The COHP presents an atom-specific analysis of the bonding information in a specified energy region. Normally, the positive COHP indicates antibonding while the negative value indicates bonding state. Figure S14 contains the orbital Hamilton population and their integrated COHP data, showing their corresponding values after integration up to Fermi level. Most of the states below the Fermi level are Fe-C and Fe-Fe bonding for t-FeC and o-FeC monolayer. Interestingly, for o-FeC monolayer, compared with the Fe-C bonding contribution, C-C bonding is also important for the stability of the such perfect planar structure.

Considering the charging/discharging processes of t-FeC monolayer anode can be assumed as:

$$t - FeC + xLi^+ + xe^- \leftrightarrow t - FeCLi_x$$

thus, the average open circuit voltage (OCV) for Li intercalation on the t-FeC monolayer was estimated by (volume and entropy effects are neglected):<sup>[2,3]</sup>

$$\text{OCV} \approx \frac{E_{t-FeCx_1} - E_{t-FeCx_2} + (x_2 - x_1)E_{Li}}{(x_2 - x_1)e}$$

where  $E_{t-FeCx_1}$ ,  $E_{t-FeCx_2}$  and  $E_{Li}$  represent the total energy of t-FeCLi<sub>x1</sub>, t-FeCLi<sub>x2</sub> and metallic Li, respectively.

The formation energies of t-FeCLi<sub>x</sub> with respect to the bulk Li and t-FeC monolayer were defined as:

$$E_f = \frac{E_{t-FeCLi_x} - E_{t-FeC} - xE_{Li}}{x+1}$$

We then. plot the convex hull according to the calculated formation energies.<sup>[4]</sup> Generally, the phases lying on the convex hull are stable against decomposition, while phases above the convex hull are not stable (or metastable), and will decompose into the structures lying on the hull.<sup>[4,5]</sup>

A crucial parameter in evaluating the performance of LIBs, theoretical capacity, can be assessed from by following equation:

$$C = \frac{n_{Li} Z_{Li} F}{M_{t-FeC} + n M_{Li}}$$

where  $n_{Li}$  is the number of adsorbed Li adatoms,  $Z_{Li}$  is the valence state of the Li atoms, F is the Faraday constant (26,801 mAh mol<sup>-1</sup>),  $M_{FeC}$  is the molecular weight of the t-FeC sheet, and  $M_{Li}$  is the molecular weight of the Li adatoms (The weight of the adsorbed Li atom is neglected approximately).

**Table S1 |** The relative energies ( $\delta$ F) per formula (eV/f.u.) under 0 K and zero strain of o-FeC, square-FeC, and honeycomb-FeC with respect to t-FeC monolayer *via* different functionals.

Method	t-FeC	o-FeC	square-FeC	honeycomb-FeC
PBE	0	0.336	0.843	1.175
LDA	0	0.326	0.864	1.375

Phase	Lattice Parameters(Å)	C <sub>11</sub> / GPa	C₂₂/ GPa	C <sub>12</sub> / GPa	C <sub>66</sub> / GPa	In-plane stiffness /N m <sup>-1</sup>	Poisson's ratio
Graphene	<b>α</b> = <b>b</b> = 2.47 α =β=90° γ = 120°	358	358	65	147	346.73	0.18
Borophone <sup>*[6]</sup>	<b>a</b> = 5.004 <b>b</b> = 2.889	398	170	-7	94	398( <b>a</b> )	-0.04( <b>a</b> )
	$\alpha = \beta = \gamma = 90^{\circ}$					170( <b>b</b> )	-0.02( <b>b</b> )
B <sub>2</sub> C	<b>a</b> = 2.558 <b>b</b> = 3.453	642.9	533.	79.0	230.	524.0	0.12
Graphene <sup>*[7]</sup>	$\alpha = \beta = \gamma = 90^{\circ}$	042.8	7		6		
t-EoC	<b>a</b> = <b>b</b> = 3.49	130	130	03	88	77	0.67
l'iec	$\alpha = \beta = \gamma = 90^{\circ}$	139	123	33	00	//	0.07
o-FeC	<b>a</b> = 5.96, <b>b</b> = 4.49	226	242	74	65	203( <b>a</b> )	0.31( <b>a</b> )
0-160	$\alpha = \beta = \gamma = 90^{\circ}$	220	242	74	05	218( <b>b</b> )	0.33( <b>b</b> )

**Table S2** | Calculated lattice parameters, elastic constants, in-plane Young's modulus andPoisson's ratio of the different 2D materials at GGA-PBE level.

\*The in-plane Young's modulus and Poisson's ratio can be derived the elastic constants by:

$$E_{a} = \frac{C_{11}C_{22}-C_{12}C_{21}}{C_{22}} \quad E_{b} = \frac{C_{11}C_{22}-C_{12}C_{21}}{C_{11}}$$
$$\nu_{a} = \frac{C_{21}}{C_{22}} \quad \nu_{b} = \frac{C_{12}}{C_{11}}$$

**Table S3** | Calculated relative energies (in eV per formula unit) of the monolayered systems with different magnetic configurations: nonmagnetic (NM), ferromagnetic (FM), and anti-ferromagnetic (AFM). AFM orderings for o-FeC phases are shown in Figure S5.

	NM	FM	AFM-1	AFM-2	AFM-3	
t-FeC	0	0.011	-	-	-	
o-FeC	1.059	0	1.060	0.708	0.163	



**Figure S1 |** Top and side views of the (a) t-FeC, (b) o-FeC, (c) honeycomb-FeC, and (d) square-FeC monolayers. The cyan and magenta spheres refer to Fe and C atoms, respectively. The black lines indicate the unit cell.



**Figure S2** | Fluctuations of total energy of (a) t-FeC and (b) o-FeC supercell (3 × 3 for t-FeC and 2 × 3 for o-FeC) as a function of the *ab initio* molecular dynamics (AIMD) step at 500 K, 1500 K, and 2000 K, respectively. The trajectories of the structures are stable over the entire simulation time at different temperatures.



**Figure S3** | Snapshots of the (a, b, c) t-FeC and (d, e, f) o-FeC equilibrium structures at (a, d) 500 K, (b, e) 1500 K, (c, f) and 2000 K at the end of 5 ps AIMD simulations



**Figure S4** | Fluctuations of the (a) total energy and (b) root mean-square deviation (RMSD) of t-FeC 5  $\times$  5 supercell (containing 100 atoms pre cell) as a function of the AIMD step at 2000 K. The trajectories of the structures are stable over the entire simulation time at such high temperatures. (c) Radial distribution functions for t-FeC monolayer obtained in AIMD simulation. (d) Snapshots of the t-FeC supercell at the end of 10 ps AIMD simulations at 2000 K.



**Figure S5** | Distributions of spin charge density of o-FeC monolayer with different magnetic ordering (a) FM, (b) AFM-1, (c) AFM-2, and (d) AFM-3, respectively. The red and green color label the spin-up and spin-down charges, respectively.



**Figure S6** | The calculated local density of states projected on orbitals of Fe and C atoms for t-FeC (upper panel) and o-FeC (bottom panel) monolayer, respectively. The Fermi level is at 0 eV.



**Figure S7** | Band structure for t-FeC (Left) and o-FeC (Right) calculated by using the GGA-PBE and GGA+U scheme, respectively. The Fermi level is assigned at 0 eV.



**Figure S8** | HSE06 band structure of (a) t-FeC and (b) o-FeC, respectively. The Fermi level is assigned at 0 eV.



**Figure S9 |** (a) Side and (b) top views of deformation charge density for single Li-adsorbed t-FeC supercell. The isosufaces value is 0.01 *a.u.* Red color and green color cloud represent electron increasing and reducing zone, respectively.



**Figure S10** | Optimized structure of (a) t-FeCLi<sub>2</sub>, (b) t-FeCLi<sub>3</sub>, and (c) t-FeCLi<sub>4</sub> monolayers with the supercell. For clarity, the Li atoms of the different adsorbed layers are marked (Layer 1  $\sim$  Layer 4).



**Figure S11** | (a) Top and side views of the t-FeCLi<sub>1</sub> supercell system. (b) Calculated projected density of states (PDOS) of the t-FeCLi<sub>1</sub> adsorption configuration at the PBE level. Fermi levels are set to zero and marked with dashed lines.



**Figure S12** | Calculated projected densities of states (PDOS) of t-FeCLi<sub>x</sub> ( $x = 2 \sim 4$ ) adsorption configurations using the PBE functional. The Fermi level is set to zero.



**Figure S13** | Calculated ELF map of t-FeC monolayer with (a) one-layer and (b) three-layer Li atoms, t-FeCLi<sub>1</sub> and t-FeCLi<sub>3</sub>, respectively.



**Figure S14** | The crystal orbital Hamilton population (COHP) analysis of (a) t-FeC and (b)o-FeC bonding interactions based on the *ab initio* calculations. The ICOHP values are also listed here to show the corresponding interactions.

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