SUPPORT INFORMATION

Theoretical investigation of Vanadium Carbides as electrocatalysts for HER and OER

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Theoretical calculations

1. The hydrogen evolution reaction (HER) in the acidic condition

The HER reaction in the acid media could be expressed by:

$$H^+ + e^- \rightarrow \frac{1}{2}H_2 \uparrow$$

There are three possible reaction steps for the HER process in the acid media, the first step is called as Volmer:

$$H^+ + e^- \rightarrow H^*$$

Where * and H^* were the surface of catalysts and the hydrogen atom adsorbed on the surface of electrodes, respectively. The second reaction step was the generation of hydrogen, it was called Tafel step or Heyrovsky step:

Tafel step: $H_{ad} + H_{ad} \rightarrow H_2 \uparrow$

Heyrovsky step: $H_{ad} + H^+ + e^- \rightarrow H_2 \uparrow$

For the HER, the Gibbs free energy $\Delta G(H^*)$ was generally considered as an descriptor, and the $\Delta G(H^*)$ was calculated by the following steps:

(1) $\Delta G(H^*) = \Delta E(H^*) + \Delta ZPE(H^*) - T\Delta S(H^*)$

(2) $\Delta E(H^*) = E(H^*) - E(slab) - 1/2\, E(H_2)$

(3) $\Delta ZPE(H^*) = ZPE(H^*) - 1/2\, ZPE(H)$

(4) $\Delta S(H^*) = S(H^*) - 1/2\, S(H_2) - S(slab)$

2. The hydrogen evolution reaction (HER) in the alkaline condition

The HER reaction in the alkaline media was conducted by:

$$2H_2O + 2e^- + * = H_2 + 2OH^-$$

Like HER in the acid media, and the total reaction can be divided into three possible reactions, called Volmer, Tafel and Heyrovsky steps.

(1) H_2O + e- + cat → H*-cat + OH^- (Volmer step)

(2) 2H*-cat → $H_2\uparrow$ (Tafel step)

(3) H*-cat +H_2O + e- → cat + OH^- + $H_2\uparrow$ (Heyrovsky step)

The Volmer step is a key step in splitting water, thus the energy barrier of splitting water is an important descriptor for HER in the alkaline solutions. In this work, in order to calculate the energy barrier of splitting water, the nudged elastic band method (NEB) was carried.

3. The oxygen evolution reaction (OER) in acidic condition

the total reaction for oxidation of water to produce oxygen is

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Four steps were built to describe OER:

(1) $2H_2O + * \rightarrow H_2O + OH^* + e^- + H^+$

(2) $OH^* + H_2O \rightarrow O^* + H_2O + e^- + H^+$

(3) $O^* + H_2O \rightarrow OOH^* + e^- + H^+$

(4) $OOH^* \rightarrow O_2 + e^- + H^+$

Gibbs free energy of these reaction can follow Nørskov et al $\Delta G(i^*) = \Delta E(i^*) + \Delta ZPE(i^*) - T\Delta S(i^*)$, and total energy of O, OH and OOH can be calculated relative to H_2O and H_2.

(5) $E(OH^*) = E(H_2O) - 1/2\,E(H_2)$

(6) $E(O^*) = E(H_2O) - E(H_2)$

(7) $E(OOH^*) = 2E(H_2O) - 3/2\,E(H_2)$

The Gibbs free energy change for steps (1-4) can be calculated by:

(8) $\Delta G1 = \Delta G(OH^*) - eU$

(9) $\Delta G2 = \Delta G(O^*) - \Delta G(OH^*) - eU$

(10) $\Delta G3 = \Delta G(OOH^*) - \Delta G(O^*) - eU$

(11) $\Delta G4 = 4.92 - \Delta G(OOH^*) - eU$

Where U is the potential measured against normal hydrogen electrode (NHE) at standard conditions (T = 298.15 K, P =1 bar, pH = 0). Then reaction overpotential is defined as $\eta = \max(\Delta G1, \Delta G2, \Delta G3, \Delta G4)/e - 1.23$. For the calculation of $\Delta G(i^*)$, $\Delta E(i^*)$ is the binding energy; $\Delta ZPE(i^*)$ is the changes in zero point energy, calculated through frozen phonon approach, which can be approximated by the formula: $ZPE = 1/2\,[\sum h\nu_i]$, where h and ν_i are Planck constant and zone center vibrational frequencies of system; $T\Delta S(i^*)$ is entropic contribution at standard condition (T=298 K and P=1 bar), as listed in CRC Hanbook.

Table S1 lattice and sites information of Vanadium Carbides

Lattice information			
	Lattice constants (Å)	Space group	Sites information
V_4C_3	8.219	Fm-3m	
V_8C_7	8.315	$P4_332$	V1 (0.125, 0.375, 0.125) V2 (0.375, 0.375, 0.375) C1 (0.125, 0.125, 0.125) C2 (0.125, 0.625, 0.625) C3 (0.125, 0.375, 0.875)
VC	8.305	Fm-3m	V (0, 0, 0) C (0.5, 0.5, 0.5)

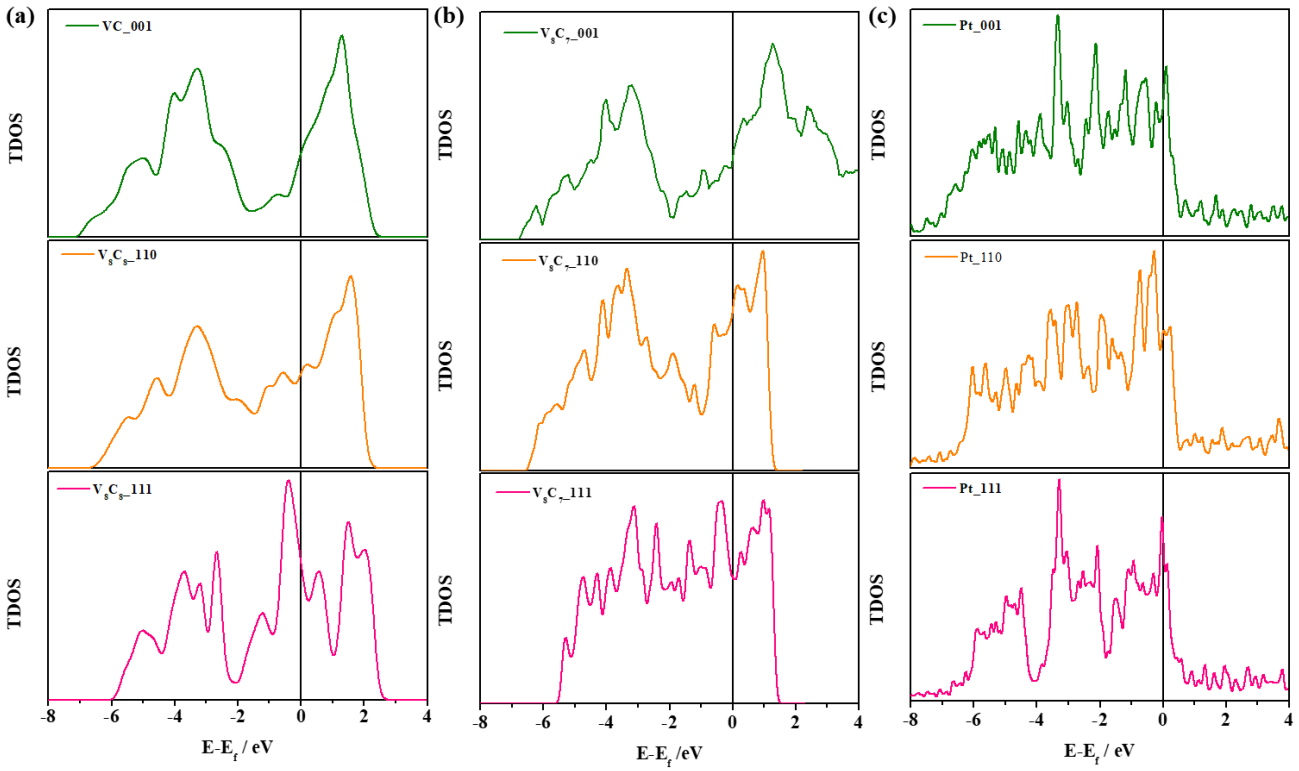

Figure S1 density of state (DOS) of Vanadium Carbides and Pt, (a), (b) and (c) are VC, V_8C_7 and Pt.

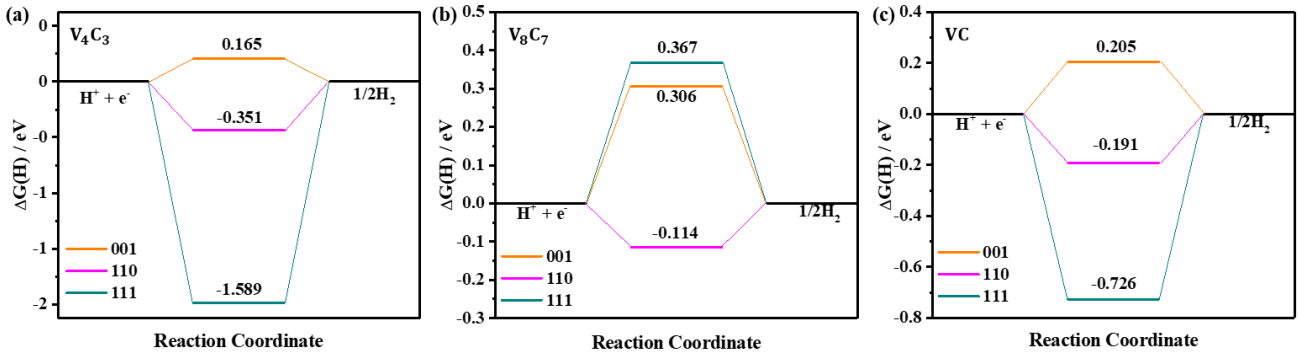

Figure S2 (a), (b) and (c) are the free energy curve of V_4C_3, V_8C_7 and VC, respectively.

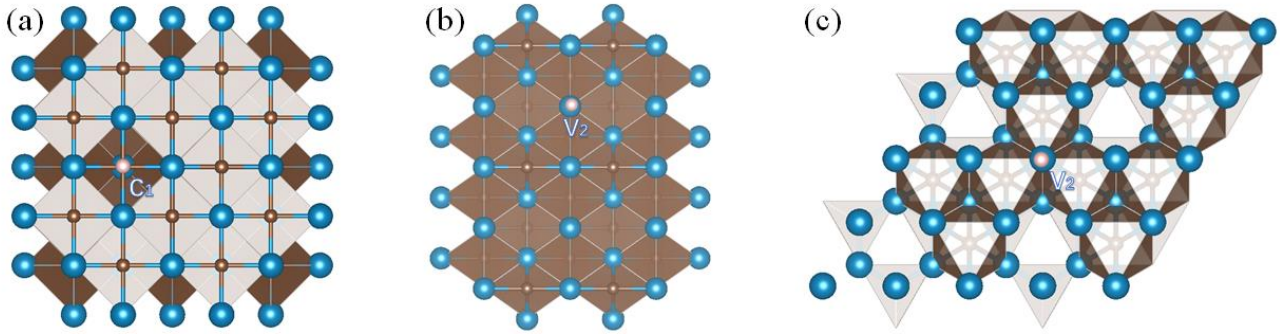

Figure S3. The H* sites with the lowest adsorption energy in V_4C_3. (a) Adsorption site C_1 for (100) surface, (b) adsorption site V_2 for (110), (c) adsorption site V_2 for (111).

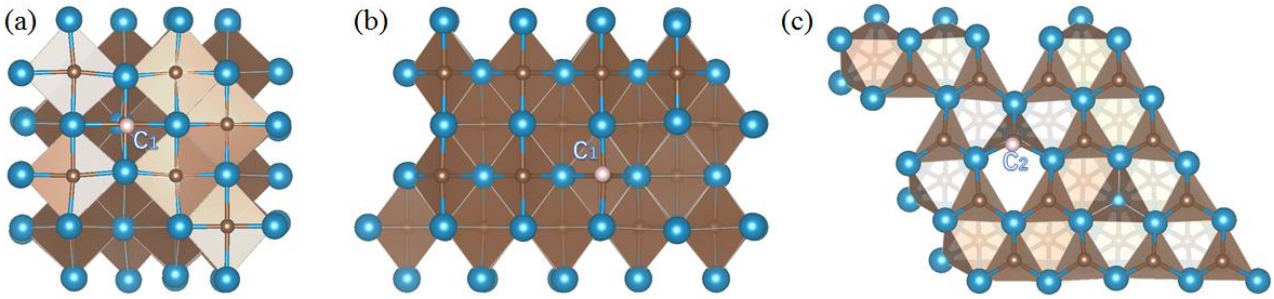

Figure S4. The H* sites with the lowest adsorption energy in V_8C_7. (a) Adsorption site C_1 for (100) surface, (b) adsorption site C_1 for (110), (c) adsorption site C_2 for (111).

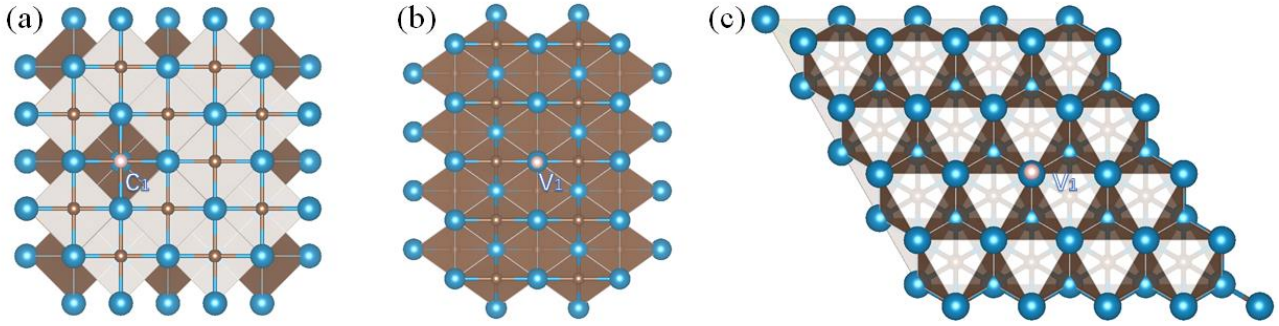

Figure S5. The H* sites with the lowest adsorption energy VC. (a) Adsorption site C_1 for (100) surface, (b) adsorption site V_1 for (110), (c) adsorption site V_1 for (111).

Table S2 The values of $\Delta E(H^*)$,$ZPE(H^*)$, $\Delta ZPE(H^*)$ and $\Delta G(H^*)$ of hydrogen atoms at the different adsorption sites on the surface of V_4C_3 (100), (110), and (111).

Surface	**Absorption site**	$\Delta E(H^*)$ **eV**	$ZPE(H^*)$ **eV**	$\Delta ZPE(H^*)$ **eV**	$\Delta G(H^*)$ **eV**
001	C1	-0.06	0.154	0.015	0.165
	C2	-1.445	0.159	0.02	-1.215
	V1	0.663	0.124	-0.014	0.859
	V2	-2.1638	0.124	-0.014	-1.967
110	C1	-0.621	0.194	0.055	-0.356
	V1	-2.003	0.126	-0.012	-1.805
	V2	-0.555	0.126	-0.012	-0.351
111	V1	-2.049	0.122	0.012	-1.827
	V2	-1.785	0.124	-0.014	-1.589
	V3	-2.05	0.123	-0.016	-1.856

Table S3 The values of $\Delta E(H^*)$,$ZPE(H^*)$, $\Delta ZPE(H^*)$ and $\Delta G(H^*)$ of hydrogen atoms at the different adsorption sites on the surface of V_8C_7 (100), (110), and (111)

Surface	**Absorption site**	$\Delta E(H^*)$ **eV**	$ZPE(H^*)$ **eV**	$\Delta ZPE(H^*)$ **eV**	$\Delta G(H^*)$ **eV**
001	C1	0.089	0.155	0.016	0.306
	V1	-0.635	0.149	0.009	-0.425
110	C1	-0.374	0.200	0.060	-0.114
	C2	-0.575	0.226	0.086	-0.289
	V1	-0.363	0.123	0.015	-0.178
	V2	-0.374	0.122	-0.016	-0.191
111	C1	-0.707	0.245	0.106	0.401
	C2	-0.575	0.237	0.098	0.367
	V1	-0.753	0.123	-0.015	-0.569
	V2	-0.780	0.123	-0.015	-0.595

Table S4 The values of $\Delta E(H^*)$,$ZPE(H^*)$, $\Delta ZPE(H^*)$ and $\Delta G(H^*)$ of hydrogen atoms at the different adsorption sites on the surface of VC (100), (110), and (111).

Surface	**Absorption site**	$\Delta E(H^*)$ **eV**	$ZPE(H^*)$ **eV**	$\Delta ZPE(H^*)$ **eV**	$\Delta G(H^*)$ **eV**
100	C1	-0.009	0.154	0.015	0.205
	V1	-0.01	0.154	0.015	0.205
110	C1	-0.989	0.211	0.073	-0.715
	V1	-0.375	0.123	-0.015	-0.191
111	C1	-1.464	0.225	0.085	-1.178
	V1	-0.912	0.124	-0.014	-0.726

Table S5 free energies of OH*, O*, OOH*

Samples	Adsorption	ΔG (eV)	Overpotential (V)
V_4C_3_001	OH*	0.768	
	O*	1.109	1.55
	OOH*	3.89	
V_4C_3_110	OH*	-1.498	
	O*	-0.068	6.505
	OOH*	-2.815	
V_4C_3_111	OH*	-0.424	
	O*	-1.376	6.677
	OOH*	-2.987	
VC_001	OH*	0.644	
	O*	0.759	1.7
	OOH*	3.898	
VC_110	OH*	-0.969	
	O*	0.020	5.155
	OOH*	-1.465	
VC_111	OH*	-1.752	
	O*	-1.087	7.657
	OOH*	-3.967	
V_8C_7_001	OH*	0.317	
	O*	0.657	1.803
	OOH*	3.443	
V_8C_7_110	OH*	-0.217	
	O*	-1.383	5.68
	OOH*	-1.99	
V_8C_7_111	OH*	-0.703	
	O*	-1.641	4.101
	OOH*	2.143	

Table S6. The surface energies of V_8C_6, V_8C_7, V_8C_8, with the lowest adsorption energy in V_8C_6. (a) Adsorption site C_1 for (100) surface, (b) adsorption site V_2 for (110), (c) adsorption site V_2 for (111).

Sample	Planes	Surface energy (J.m^{-2})
V_4C_3	001	1.845
	110	3.249
	111	4.261
V_8C_7	001	1.737
	110	4.405
	111	5.056
VC	001	1.408
	110	3.261
	111	4.776

Table S7 calculated formation of V_4C_3, V_8C_7, VC

Sample	$\mathbf{\Delta E_f/eV}$
V_4C_3	-0.429
V_8C_7	-0.617
VC	-0.502

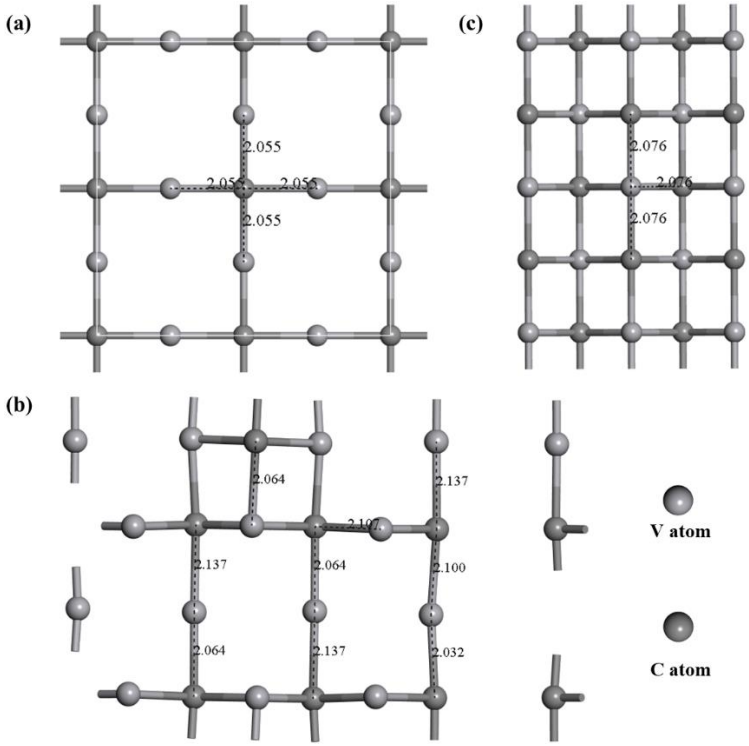

Figure S6. (a)V-C bonds length of V_4C_3_001, (b) V-C bonds length of V_8C_7_110, (c) V-C bonds length of VC_110.