

Screening Effective Single-atom ORR and OER Electrocatalysts from Pt Decorated MXenes by First-principles Calculations

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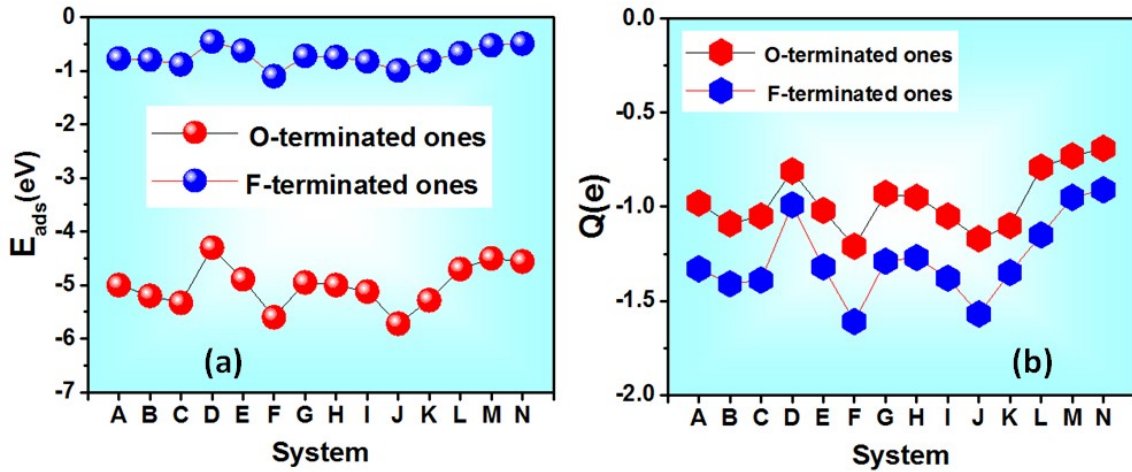


Figure S1 a) The adsorption energies (E_{ads}) of O/F groups on bare MXenes; **b)** The charges that O/F terminators gained from the bare MXenes, where A-N represented $Ti_2CT_2-V_T-Pt$, $V_2CT_2-V_T-Pt$, $Nb_2CT_2-V_T-Pt$, $Mo_2CT_2-V_T-Pt$, $Ti_3C_2T_2-V_T-Pt$, $Zr_3C_2T_2-V_T-Pt$, $Ti_3(C,N)_2-CT_2-V_T-Pt$, $Ti_3(C,N)_2-NT_2-V_T-Pt$, $Nb_4C_3T_2-V_T-Pt$, $Ta_4C_3T_2-V_T-Pt$, $Ti_4N_3T_2-V_T-Pt$, $Cr_2TiC_2F_2-V_F-Pt$, $Mo_2TiC_2T_2-V_T-Pt$, $Mo_2Ti_2C_3T_2-V_T-Pt$ ($T = O; F$), respectively.

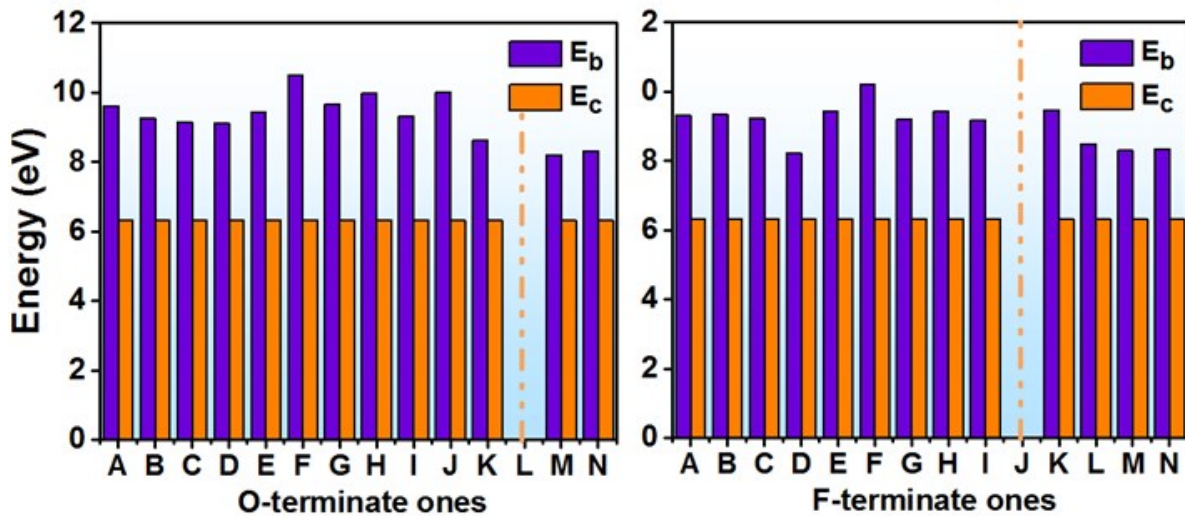


Figure S2 The binding energies (E_b) of Pt SA on the defected MXenes and the cohesive energies (E_c) of Pt, where A-N represented $Ti_2CT_2-V_T-Pt$, $V_2CT_2-V_T-Pt$, $Nb_2CT_2-V_T-Pt$, $Mo_2CT_2-V_T-Pt$, $Ti_3C_2T_2-V_T-Pt$, $Zr_3C_2T_2-V_T-Pt$, $Ti_3(C,N)_2-CT_2-V_T-Pt$, $Ti_3(C,N)_2-NT_2-V_T-Pt$, $Nb_4C_3T_2-V_T-Pt$, $Ta_4C_3T_2-V_T-Pt$, $Ti_4N_3T_2-V_T-Pt$, $Cr_2TiC_2F_2-V_F-Pt$, $Mo_2TiC_2T_2-V_T-Pt$, and $Mo_2Ti_2C_3T_2-V_T-Pt$ ($T = O; F$), respectively.

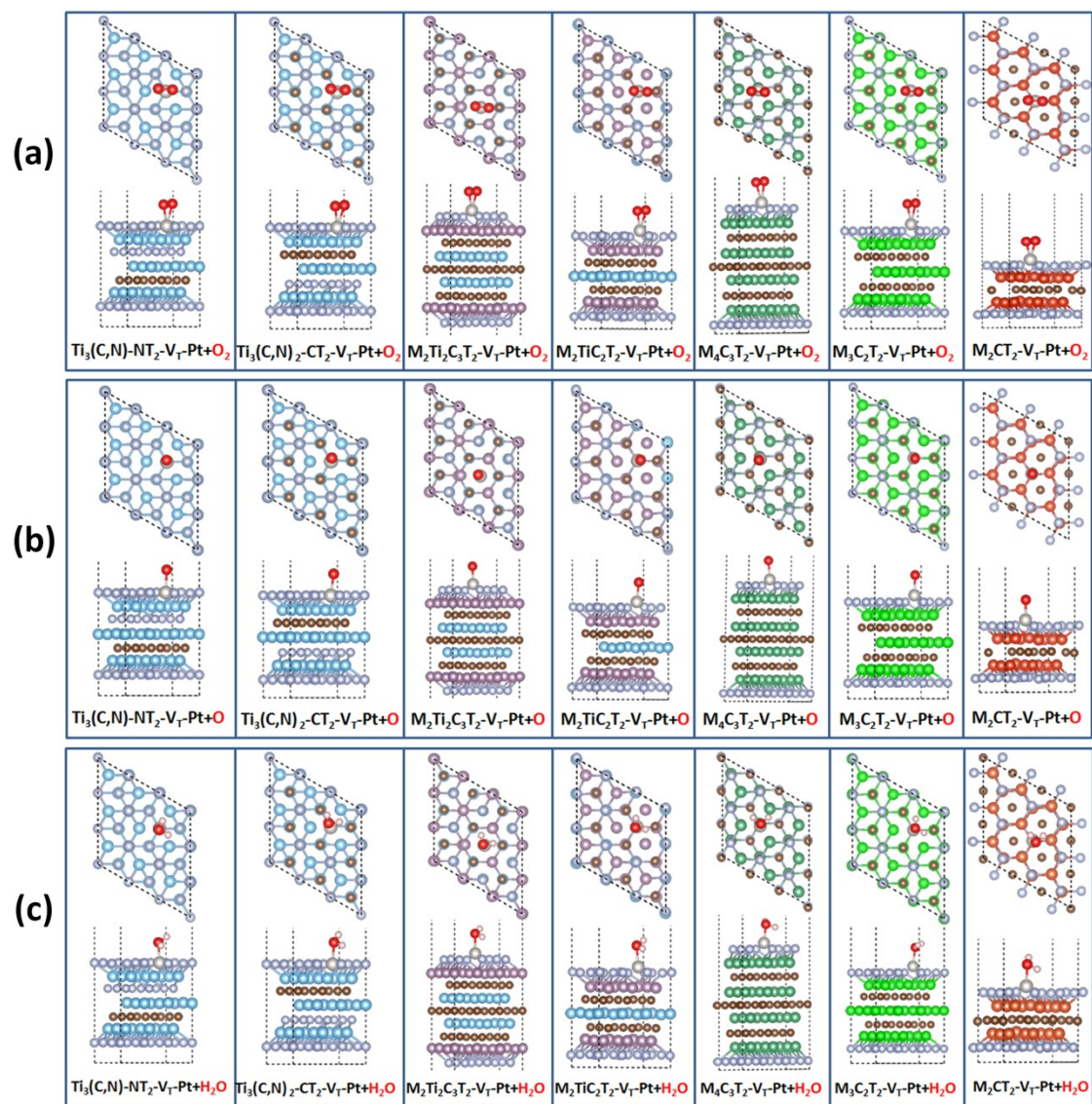


Figure S3. The geometric structures of O-atom, O₂, and H₂O adsorbed on the surface of Pt decorated SACs **a)-c)**, respectively).

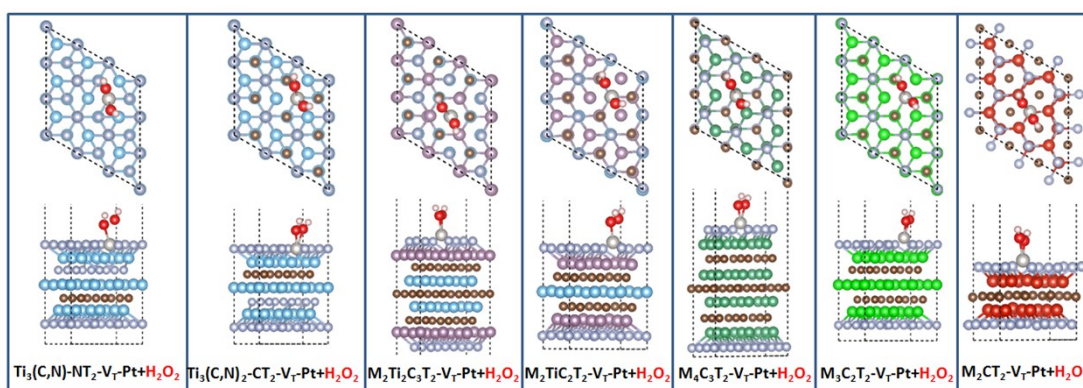


Figure S4. The geometric structures of H_2O_2 adsorbed on the surface of Pt decorated SACs.

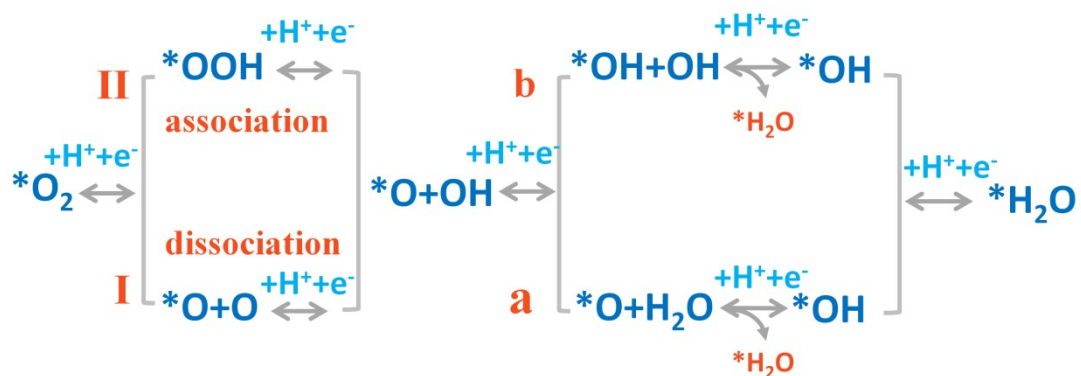


Figure S5. The $4 e^-$ reaction processes of ORR, where the I-II paths represent the dissociation and association mechanisms, respectively.

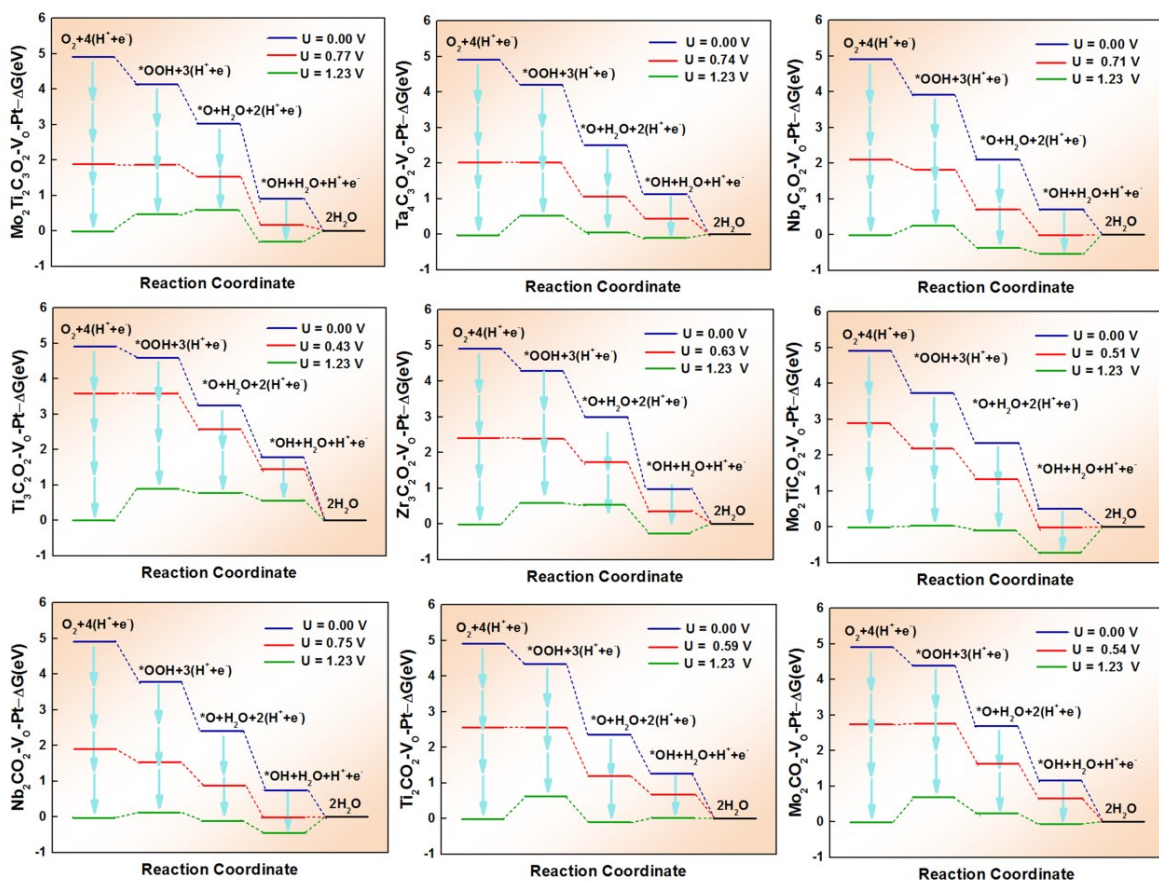


Figure S6. The free energy diagrams and theoretical voltages of ORR on the O-terminated SACs.

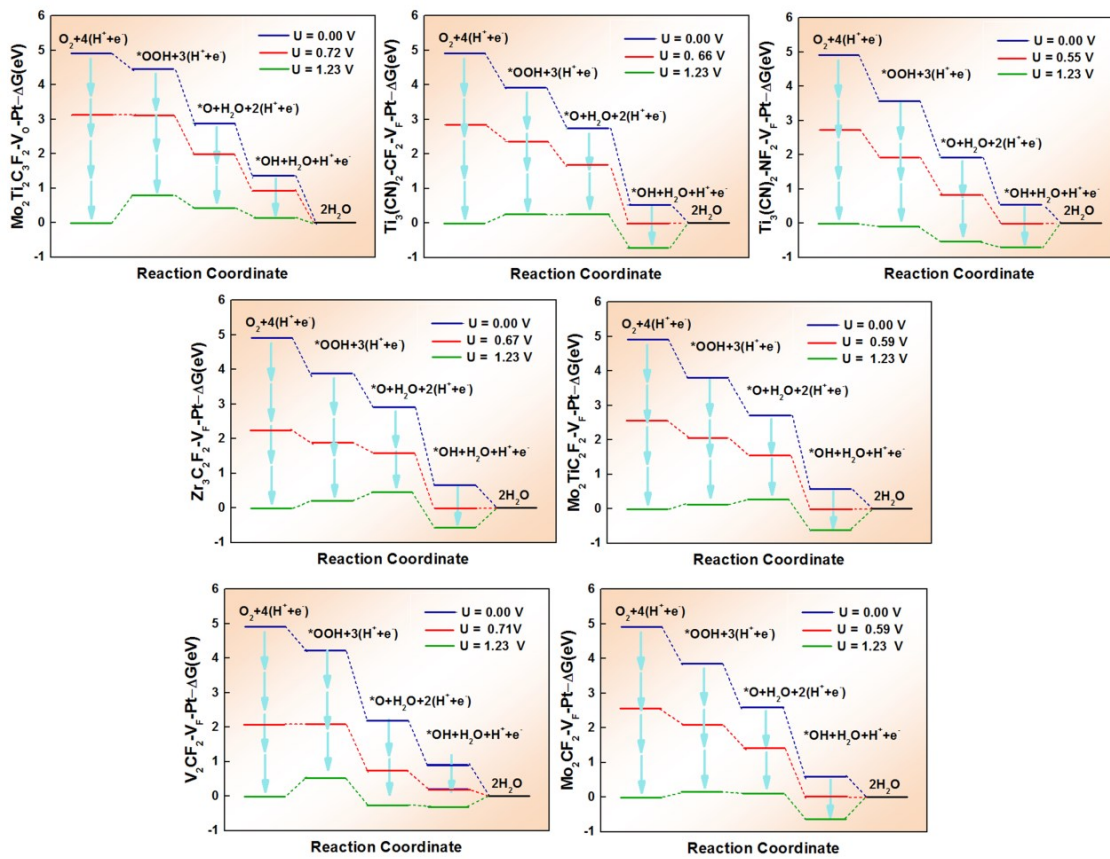


Figure S7. The free energy diagrams and theoretical voltages of ORR on the F-terminated SACs.

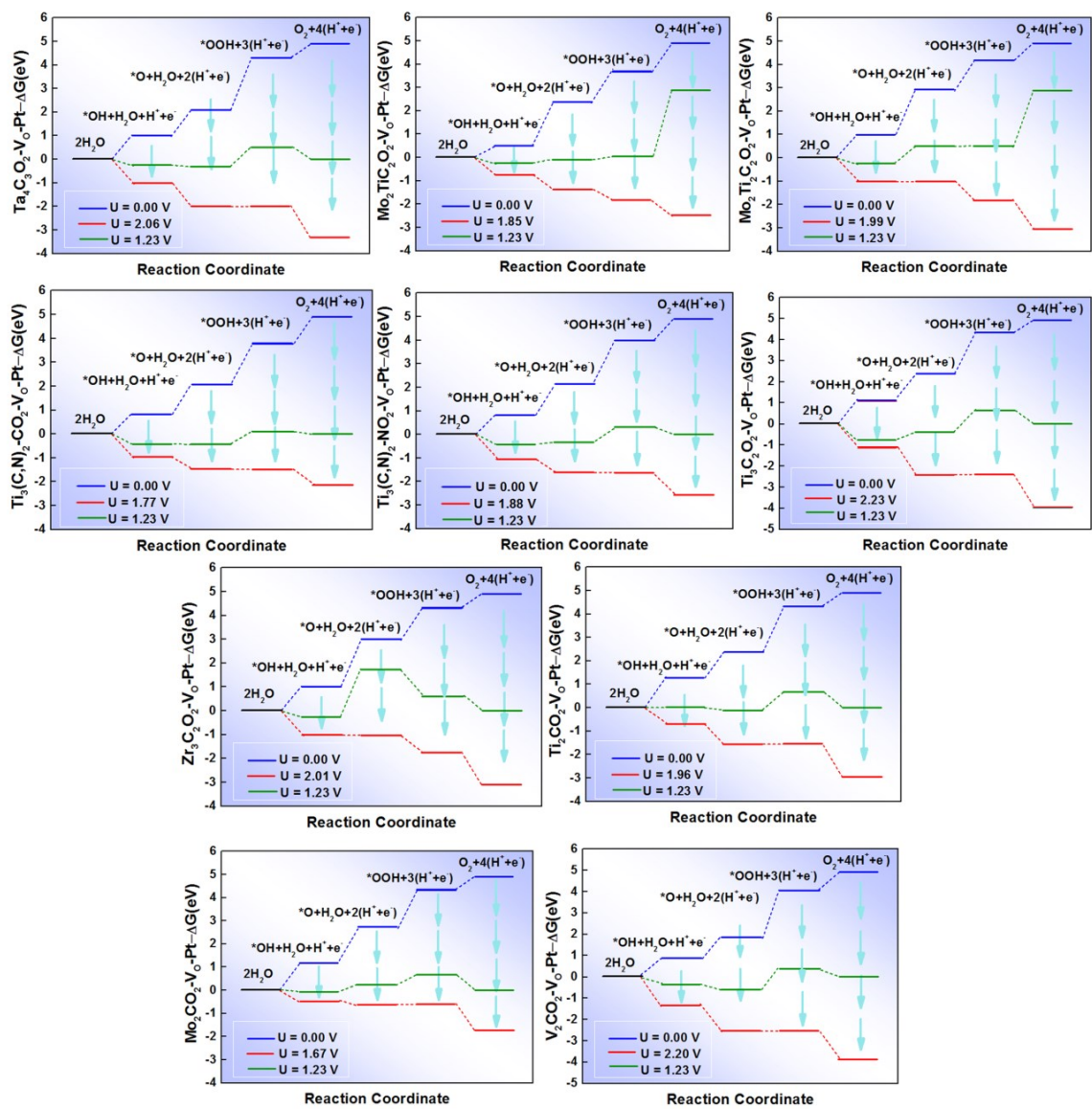


Figure S8. The free energy diagrams and theoretical voltages of OER on the O-terminated SACs.

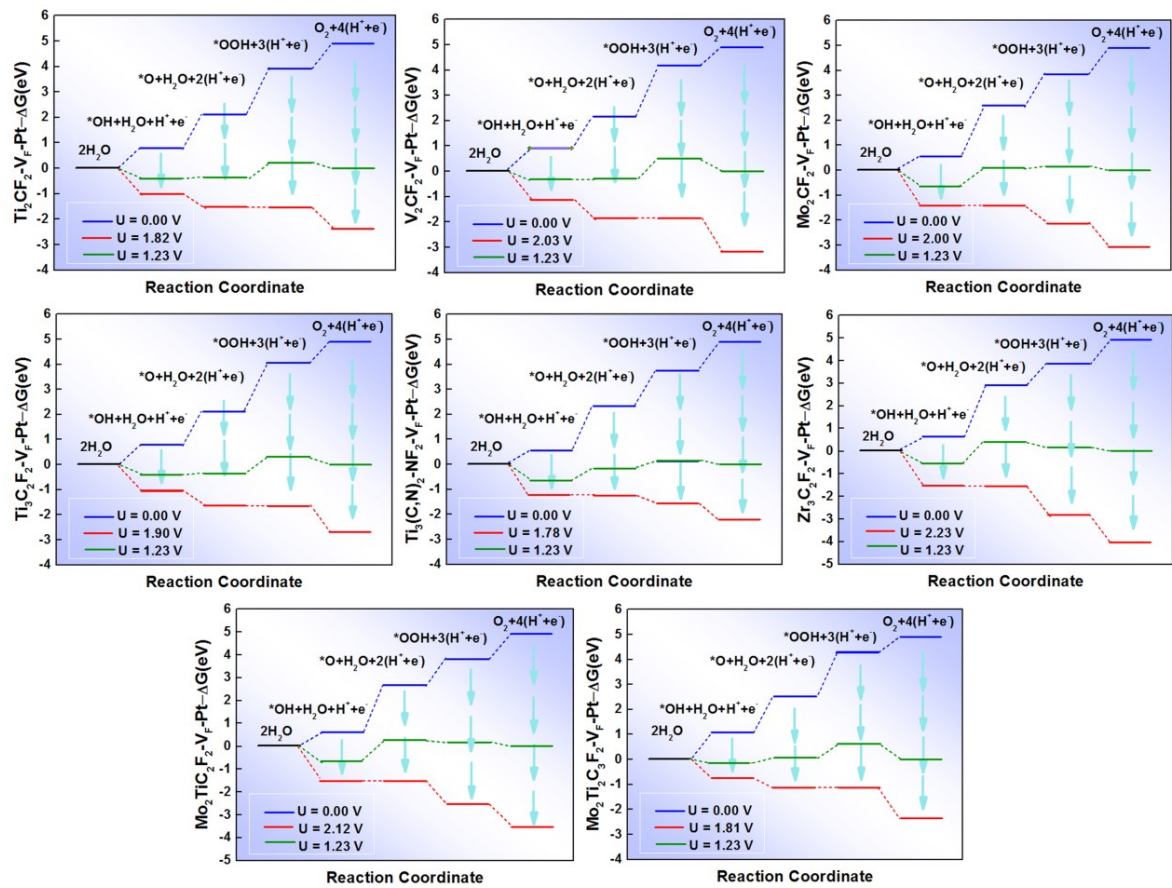


Figure S9 The free energy diagrams and theoretical voltages of OER on the F-terminated SACs.

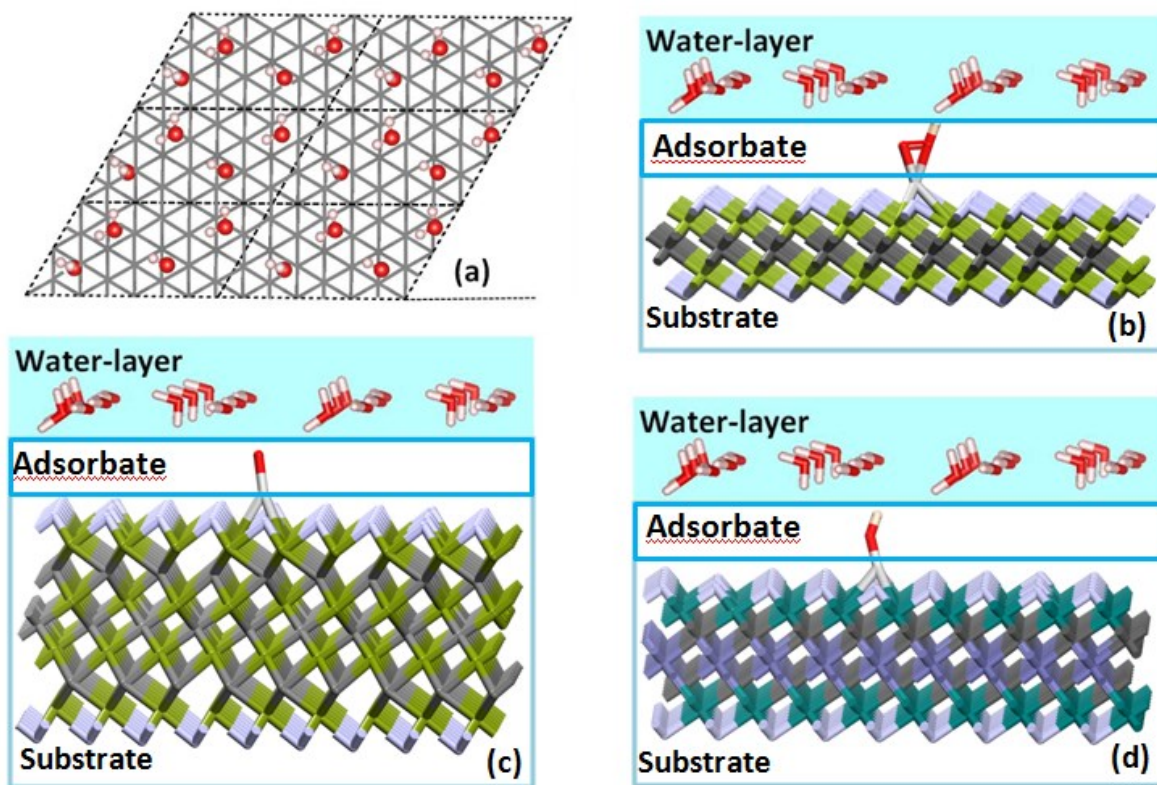


Figure S10 Top view of the solvation system (a) and the solvation model of Nb₂C₂F₂-V_F-Pt, Nb₄C₃F₂-V_F-Pt, and Cr₂TiC₂F₂-V_F-Pt with adsorbed intermediates (b-d, respectively).

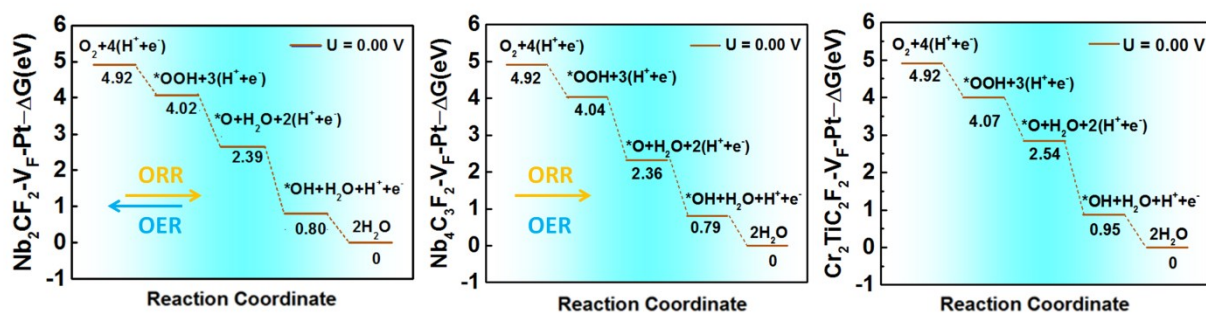


Figure S11 The free energy diagrams and theoretical voltages of ORR/OER on Nb₂C₂F₂-V_F-Pt, Nb₄C₃F₂-V_F-Pt, and Cr₂TiC₂F₂-V_F-Pt with the considering of the solvation effect.

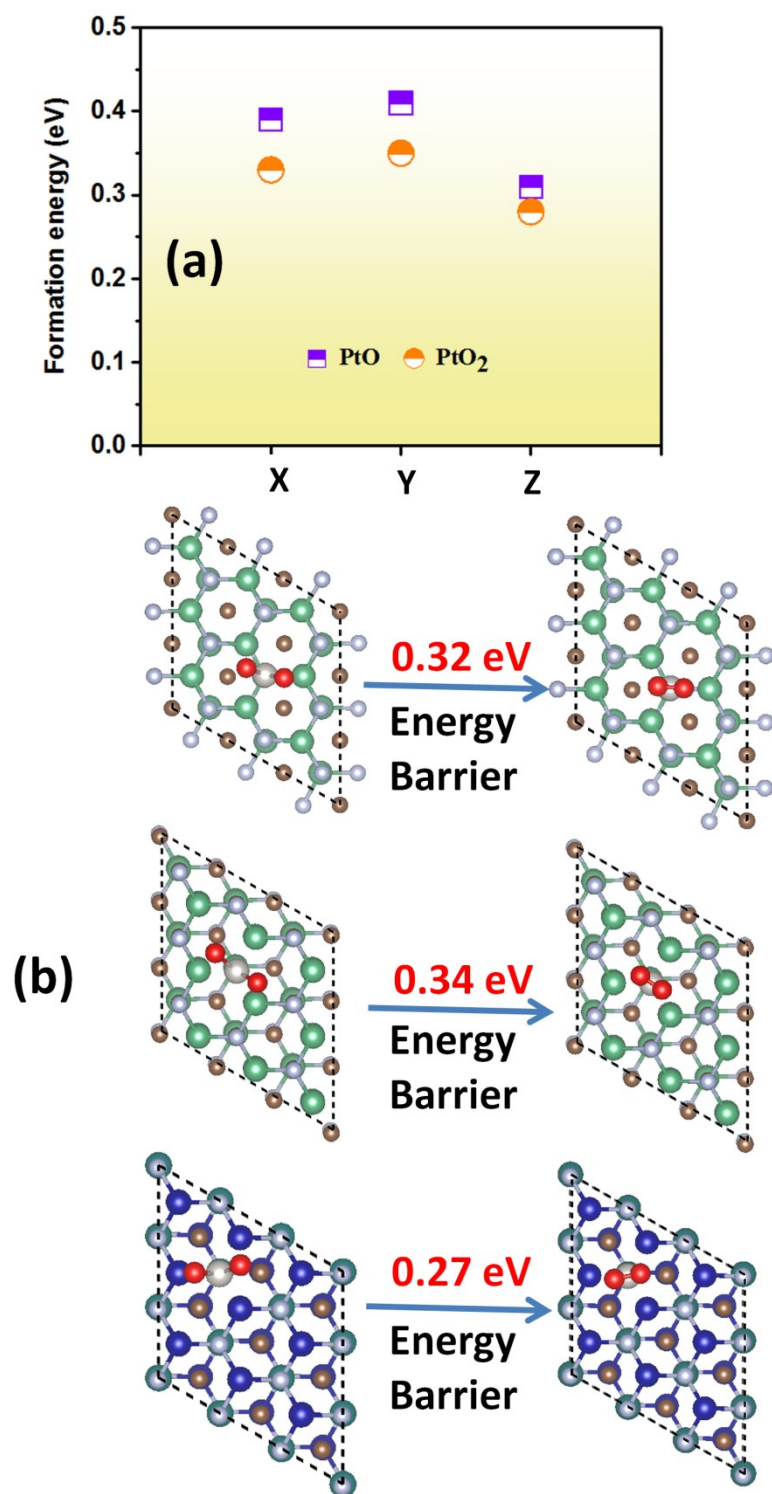


Figure S12 (a) The formation energy of PtO and PtO₂ on SACs, where X, Y, Z represent Nb₂C₂F₂-V_F-Pt, Nb₄C₃F₂-V_F-Pt, and Cr₂TiC₂F₂-V_F-Pt, respectively; (b) the energy barriers of *2O → O₂ on Nb₂C₂F₂-V_F-Pt, Nb₄C₃F₂-V_F-Pt, and Cr₂TiC₂F₂-V_F-Pt.

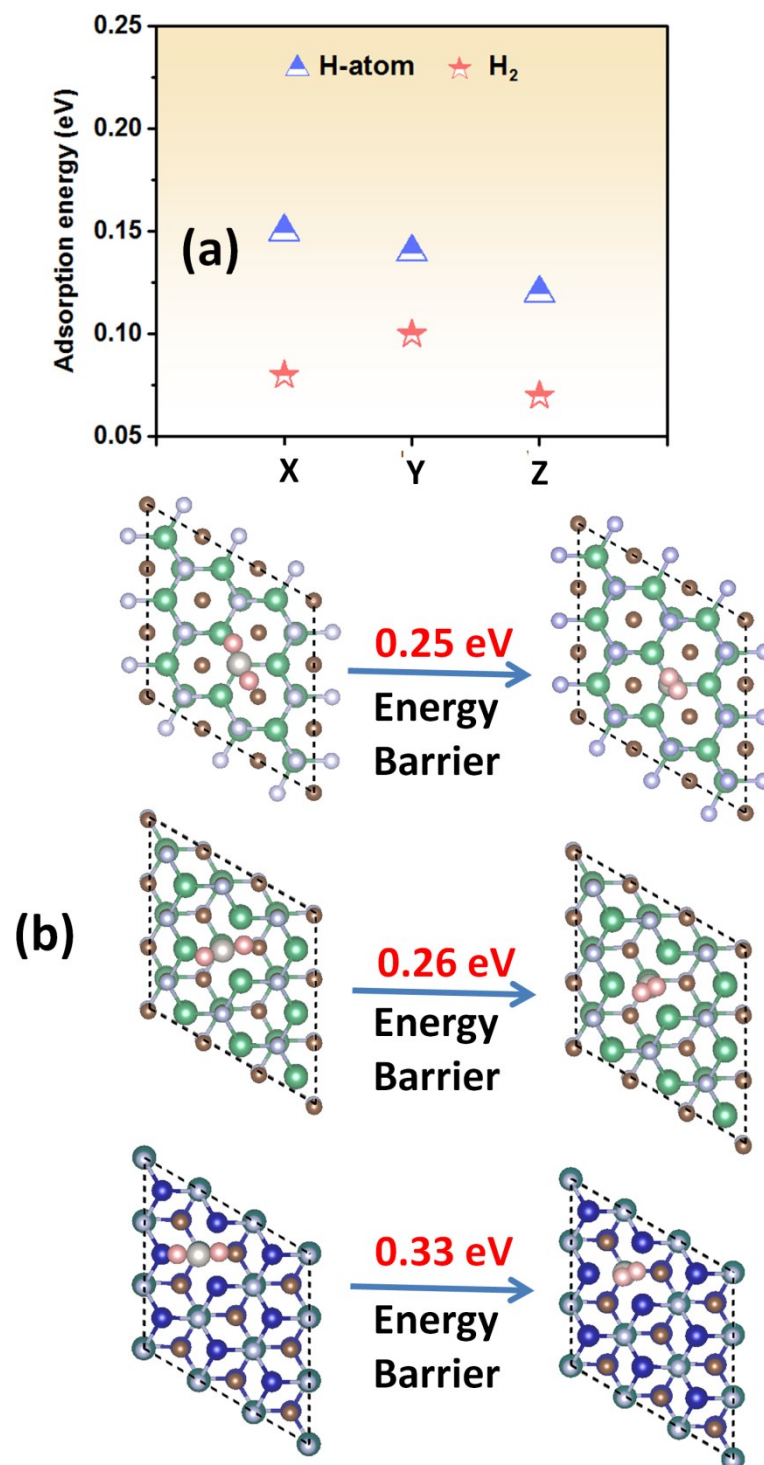


Figure S13 (a) The adsorption energy of H-atom and H₂ on SACs, where X, Y, Z represent Nb₂C₂F₂-V_F-Pt, Nb₄C₃F₂-V_F-Pt, and Cr₂TiC₂F₂-V_F-Pt, respectively; (b) the energy barriers of 2*H→H₂ on Nb₂C₂F₂-V_F-Pt, Nb₄C₃F₂-V_F-Pt, and Cr₂TiC₂F₂-V_F-Pt.

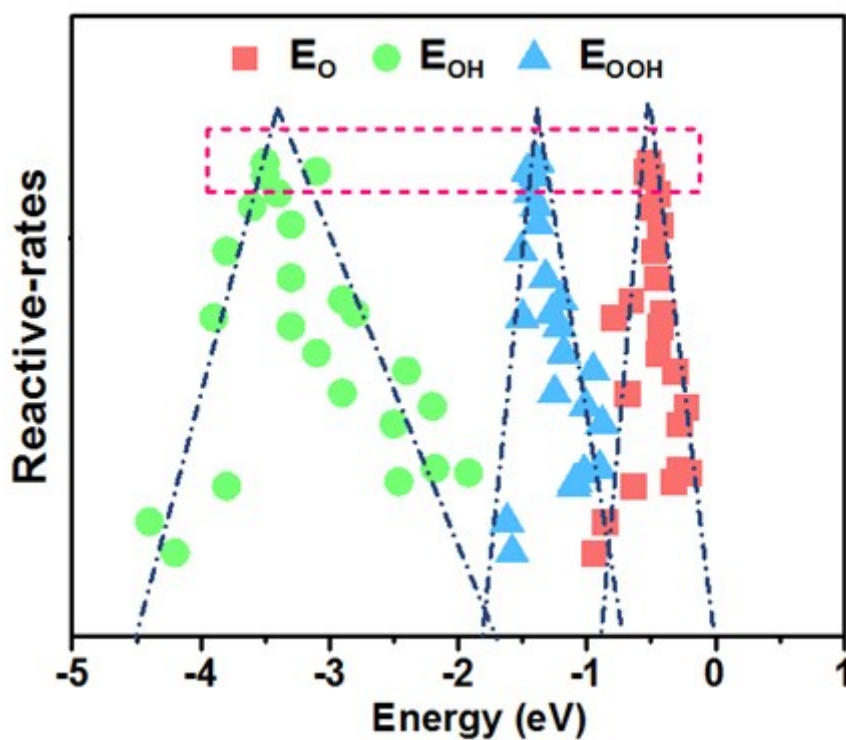


Figure S14 The volcano plots of the SACs, which describe the relationship between activities and adsorption energies for intermediates.

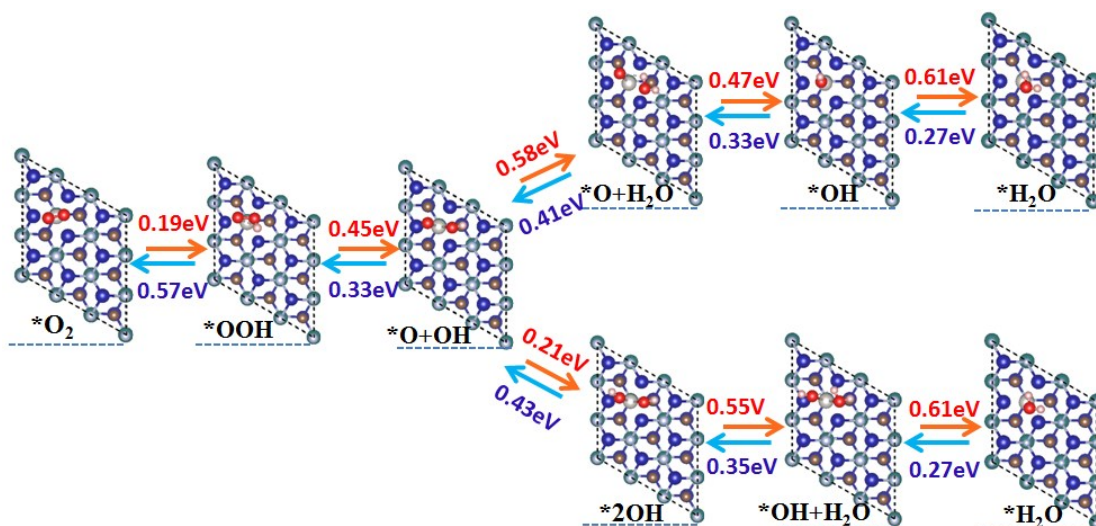


Figure S15 The possible reaction pathways and energy barrier for the ORR/OER process on $\text{Cr}_2\text{TiC}_2\text{F}_2\text{-VF-Pt}$.

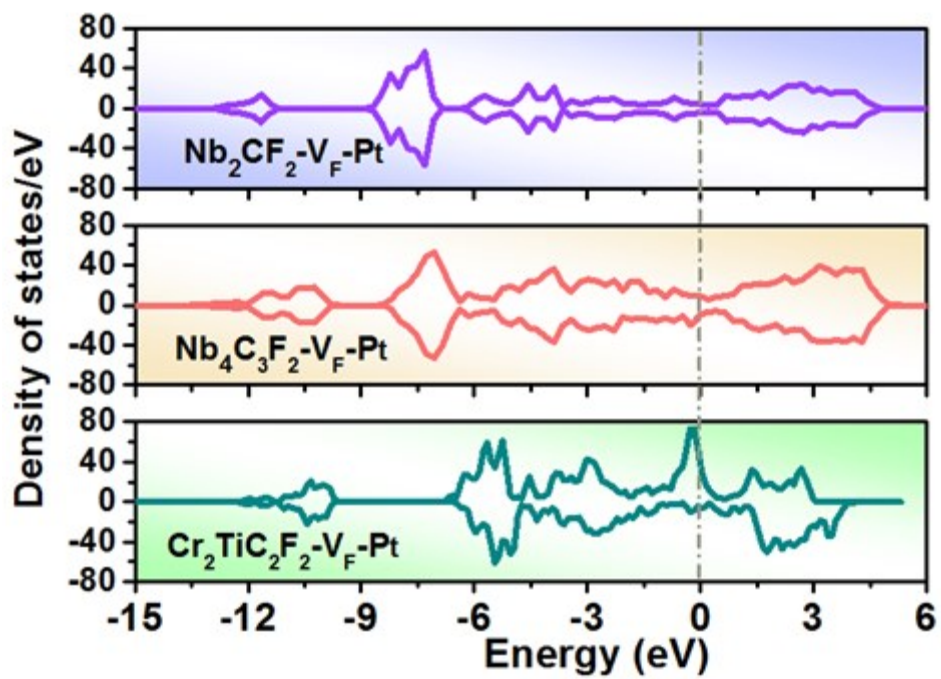


Figure S16 The density of states (DOS) of $\text{Nb}_2\text{C}_2\text{F}_2\text{-V}_\text{F}\text{-Pt}$, $\text{Nb}_4\text{C}_3\text{F}_2\text{-V}_\text{F}\text{-Pt}$, and $\text{Cr}_2\text{TiC}_2\text{F}_2\text{-V}_\text{F}\text{-Pt}$.

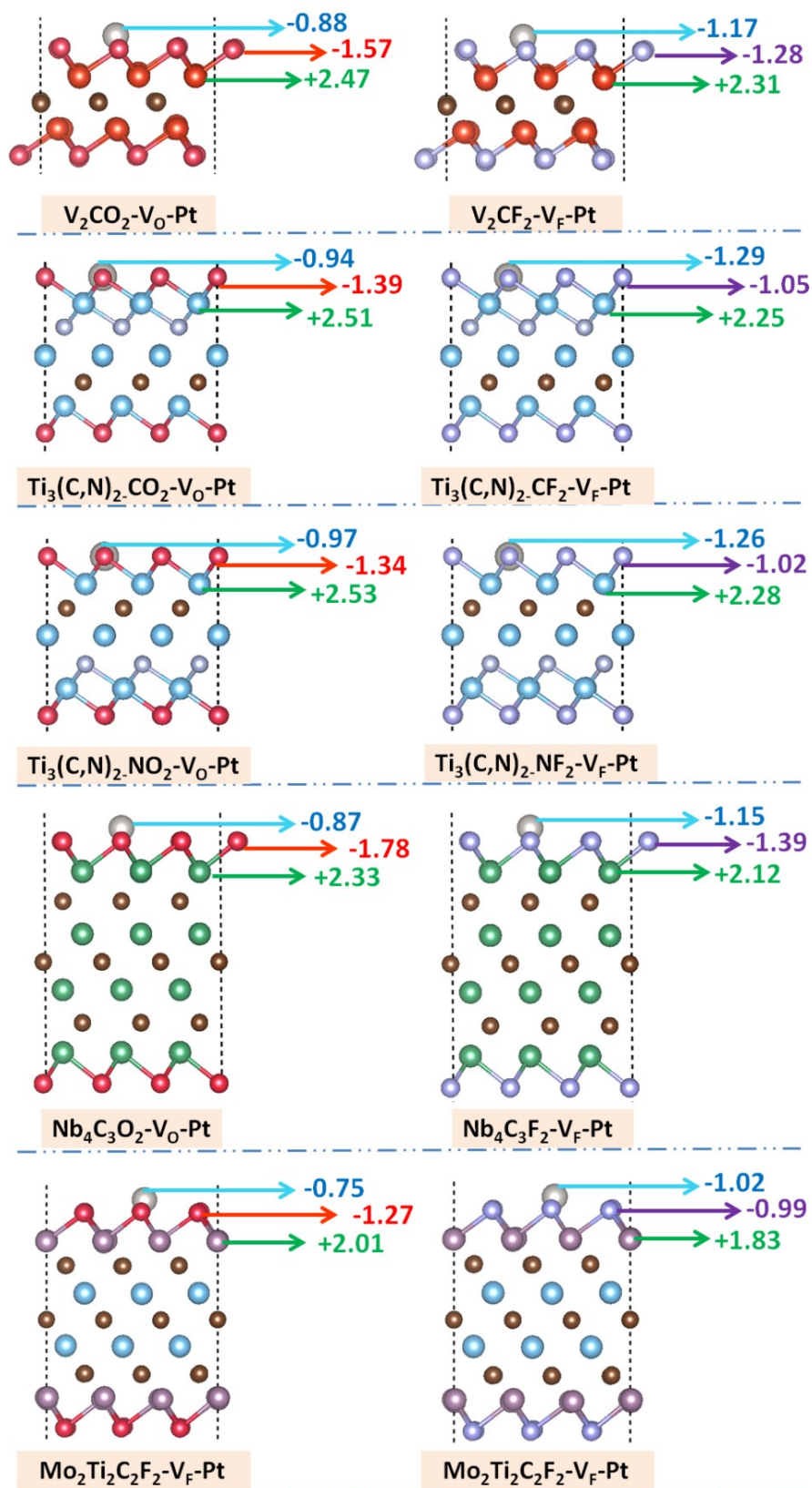


Figure S17. Bader charge populations of the Pt doped recombinant SACs.

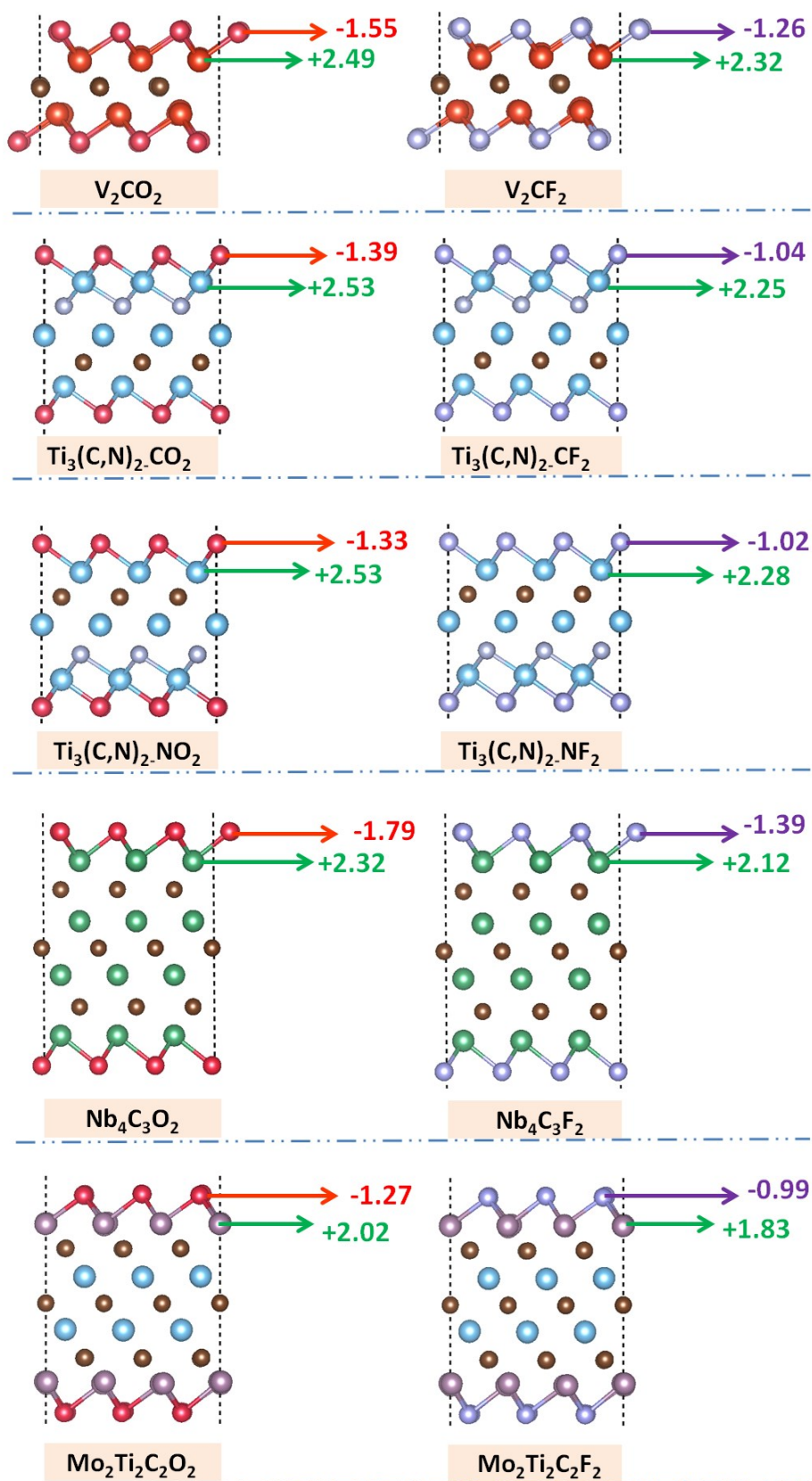


Figure S18. Bader charge populations of the O/F terminated MXenes.

Table S1. The Gibbs free energy of each step on the recombinant SACs toward ORR and OER

System	G_{OOH^*} (V)	G_{O^*} (V)	G_{OH^*} (V)
$\text{Ti}_2\text{CO}_2\text{-V}_\text{O}\text{-Pt}$	4.33	2.81	0.77
$\text{Ti}_2\text{CF}_2\text{-V}_\text{F}\text{-Pt}$	3.91	2.09	0.80
$\text{V}_2\text{CO}_2\text{-V}_\text{O}\text{-Pt}$	4.06	2.57	0.88
$\text{V}_2\text{CF}_2\text{-V}_\text{F}\text{-Pt}$	4.21	2.69	0.93
$\text{Nb}_2\text{CO}_2\text{-V}_\text{O}\text{-Pt}$	3.81	2.37	0.75
$\text{Nb}_2\text{CF}_2\text{-V}_\text{F}\text{-Pt}$	3.85	2.25	0.83
$\text{Mo}_2\text{CO}_2\text{-V}_\text{O}\text{-Pt}$	3.88	2.17	0.64
$\text{Mo}_2\text{CF}_2\text{-V}_\text{F}\text{-Pt}$	3.86	2.15	0.69
$\text{Ti}_3\text{C}_2\text{O}_2\text{-V}_\text{O}\text{-Pt}$	4.29	2.73	0.79
$\text{Ti}_3\text{C}_2\text{F}_2\text{-V}_\text{F}\text{-Pt}$	4.03	2.15	0.81
$\text{Ti}_3(\text{C,N})_2\text{-CO}_2\text{-V}_\text{O}\text{-Pt}$	3.82	2.05	0.82
$\text{Ti}_3(\text{C,N})_2\text{-CF}_2\text{-V}_\text{F}\text{-Pt}$	3.57	1.92	0.75
$\text{Ti}_3(\text{C,N})_2\text{-NO}_2\text{-V}_\text{O}\text{-Pt}$	4.01	2.13	0.83
$\text{Ti}_3(\text{C,N})_2\text{-NF}_2\text{-V}_\text{F}\text{-Pt}$	3.82	2.12	0.77
$\text{Zr}_3\text{C}_2\text{O}_2\text{-V}_\text{O}\text{-Pt}$	4.29	2.79	1.05
$\text{Zr}_3\text{C}_2\text{F}_2\text{-V}_\text{F}\text{-Pt}$	4.25	2.81	1.09
$\text{Nb}_4\text{C}_3\text{O}_2\text{-V}_\text{O}\text{-Pt}$	4.21	2.68	0.81
$\text{Nb}_4\text{C}_3\text{F}_2\text{-V}_\text{F}\text{-Pt}$	3.85	2.24	0.84
$\text{Ta}_4\text{C}_3\text{O}_2\text{-V}_\text{O}\text{-Pt}$	4.18	2.70	1.02
$\text{Cr}_2\text{TiC}_2\text{F}_2\text{-V}_\text{F}\text{-Pt}$	3.94	2.42	0.85
$\text{Mo}_2\text{TiC}_2\text{O}_2\text{-V}_\text{O}\text{-Pt}$	3.91	2.14	0.67
$\text{Mo}_2\text{TiC}_2\text{F}_2\text{-V}_\text{F}\text{-Pt}$	3.82	2.11	0.69
$\text{Mo}_2\text{Ti}_2\text{C}_3\text{O}_2\text{-V}_\text{O}\text{-Pt}$	4.18	2.67	0.69
$\text{Mo}_2\text{Ti}_2\text{C}_3\text{F}_2\text{-V}_\text{F}\text{-Pt}$	3.99	2.23	0.71

Table S2 The solvation energy corrections (ΔSol) and the free energies after considering the solvation effect (ΔG_{sol}) on $\text{Nb}_2\text{CF}_2\text{-V}_\text{F}\text{-Pt}$, $\text{Nb}_4\text{C}_3\text{F}_2\text{-V}_\text{F}\text{-Pt}$ and $\text{Cr}_2\text{TiC}_2\text{F}_2\text{-V}_\text{F}\text{-Pt}$.

	ΔSol (eV)			ΔG_{sol} (V)		
	*OOH	*O	*OH	*OOH	*O	*OH
$\text{Nb}_2\text{CF}_2\text{-V}_\text{F}\text{-Pt}$	-0.45	-0.50	-0.56	4.02	2.39	0.80
$\text{Nb}_4\text{C}_3\text{F}_2\text{-V}_\text{F}\text{-Pt}$	-0.44	-0.51	-0.54	4.04	2.36	0.79
$\text{Cr}_2\text{TiC}_2\text{F}_2\text{-V}_\text{F}\text{-Pt}$	-0.37	-0.42	-0.53	4.07	2.54	0.95

Table S3 The energy corrections and the adsorption free energies in ORR and OER on all the catalysts.

	ΔZPE	TS	ΔZPE	TS
	$\text{Ti}_2\text{CO}_2\text{-V}_\text{O}\text{-Pt}$		$\text{Ti}_2\text{CF}_2\text{-V}_\text{F}\text{-Pt}$	
*OOH	0.49	0.29	0.50	0.30
*O	0.08	0.13	0.12	0.11
*OH	0.42	0.11	0.41	0.10
	$\text{V}_2\text{CO}_2\text{-V}_\text{O}\text{ Pt}$		$\text{V}_2\text{CF}_2\text{-V}_\text{F}\text{-Pt}$	
*OOH	0.51	0.27	0.52	0.25
*O	0.11	0.13	0.12	0.14
*OH	0.41	0.12	0.38	0.11
	$\text{Nb}_2\text{CO}_2\text{-V}_\text{O}\text{-Pt}$		$\text{Nb}_2\text{CF}_2\text{-V}_\text{F}\text{-Pt}$	
*OOH	0.52	0.26	0.52	0.27
*O	0.10	0.13	0.10	0.12
*OH	0.40	0.13	0.39	0.13
	$\text{Mo}_2\text{CO}_2\text{-V}_\text{O}\text{-Pt}$		$\text{Mo}_2\text{CF}_2\text{-V}_\text{F}\text{-Pt}$	
*OOH	0.50	0.28	0.50	0.28
*O	0.11	0.12	0.12	0.12

*OH	0.39	0.14	0.41	0.12
	Ti₃C₂O₂-V_O-Pt		Ti₃C₂F₂-V_F-Pt	
*OOH	0.53	0.28	0.51	0.26
*O	0.12	0.13	0.12	0.10
*OH	0.40	0.11	0.40	0.12
	Ti₃(C,N)₂-CO₂-V_O-Pt		Ti₃(C,N)₂-CF₂-V_F-Pt	
*OOH	0.52	0.28	0.52	0.29
*O	0.11	0.12	0.11	0.13
*OH	0.41	0.13	0.41	0.11
	Ti₃(C,N)₂-NO₂-V_O-Pt		Ti₃(C,N)₂-NF₂-V_F-Pt	
*OOH	0.50	0.26	0.53	0.28
*O	0.12	0.12	0.12	0.11
*OH	0.41	0.12	0.42	0.13
	Zr₃C₂O₂-V_O-Pt		Zr₃C₂F₂-V_F-Pt	
*OOH	0.52	0.25	0.49	0.27
*O	0.11	0.14	0.10	0.12
*OH	0.41	0.10	0.40	0.09
	Nb₄C₃O₂-V_O-Pt		Nb₄C₃F₂-V_F-Pt	
*OOH	0.53	0.29	0.52	0.36
*O	0.10	0.13	0.10	0.10
*OH	0.39	0.11	0.38	0.12
	Ta₄C₃O₂-V_O-Pt		Cr₂TiC₂F₂-V_F-Pt	
*OOH	0.49	0.27	0.51	0.26
*O	0.10	0.13	0.11	0.12
*OH	0.43	0.13	0.41	0.13
	Mo₂TiC₂O₂-V_O-Pt		Mo₂TiC₂F₂-V_F-Pt	
*OOH	0.48	0.30	0.50	0.29
*O	0.11	0.11	0.12	0.11
*OH	0.39	0.12	0.38	0.14
	Mo₂Ti₂C₃O₂-V_O-Pt		Mo₂Ti₂C₃F₂-V_F-Pt	
*OOH	0.51	0.28	0.52	0.27

*O	0.0.8	0.12	0.13	0.12
*OH	0.41	0.12	0.38	0.11

The reaction energies barriers of ORR/OER on Cr₂TiC₂F₂-V_F-Pt

The possible reaction pathways and the reaction barrier of ORR/OER on Cr₂TiC₂F₂-V_F-Pt were summarized in Figure S15. For the ORR processes, the adsorbed O₂ molecule went through a sequential coupled proton-electron transfer process to form H₂O firstly. Then, *OOH was formed which dissociated to *O and *OH with an activation barrier of 0.45 eV. This was followed by two possible reaction paths. One was the OH* hydrogenation to release a H₂O molecule firstly and then the remained *O was reduced to *OH and H₂O with activation barriers of 0.58, 0.47, and 0.61 eV, respectively. The other was the *O reduced to form *OH and H₂O with activation barriers of 0.55 and 0.61 eV. In addition, the OER on Cr₂TiC₂F₂-V_F-Pt was followed by a reversed process of ORR, where the rate-limiting reaction barrier was the H₂O dissociation, with an energy barrier of 0.61 eV.

More calculation details

The adsorption energies of oxygen-containing intermediates on catalysts were calculated by Eq. (1)-(3):

$$\Delta E_{O^*} = E_{O^*} - E_* - [E_{H_2O} - E_{H_2}] \quad (1)$$

$$\Delta E_{OH^*} = E_{OH^*} - E_* - [E_{H_2O} - 1/2E_{H_2}] \quad (2)$$

$$\Delta E_{OOH^*} = E_{OOH^*} - E_* - [2E_{H_2O} - 3/2E_{H_2}] \quad (3)$$

where E*, E_{OOH*}, E_{OH*}, and E_{O*} were the total energies of the catalyst substrate without and with the adsorption of OOH, OH, and O. E_{H₂O} and E_{H₂} were the total energies of free H₂O and H₂ molecules in gas phases, respectively. The Gibbs free energies (ΔG) of the ORR intermediates can be obtained from the computational hydrogen electrode (CHE) model proposed by Nørskov et al (J. Phys. Chem. B 2004, 108, 46, 17886-17892). The free energy change is defined as

$$\Delta G = \Delta E + \Delta ZPE - T \Delta S + \Delta G_U + \Delta G_{pH} \quad (4)$$

where ΔE was the reaction energy obtained from the DFT calculations, ΔZPE was the zero-point energy change, T was the temperature (298.15 K in this work), and ΔS was the entropy

change. $\Delta G_U = -neU$, where n was the number of electrons transferred and U was the electrode potential. G_{pH} was refer to the corrected free energy of the H^+ ion concentration; the pH was assumed to be zero for the acid media Besides, the ZPE and S for the adsorbed ORR intermediates were obtained from the calculation of the vibrational frequencies, while the ZPE and S values of the free gas molecules were obtained from the NIST database (ACS Catal. 2014, 4, 2, 674-680). The ZPE values of the adsorbed ORR species are similar among different substrates, including pure metals, metal alloys, oxides, two-dimensional materials and so on. The free energy of $1/2 H_2$ is used instead of $(H^+ + e^-)$. The free energy of O_2 was calculated according to the following equation:

$$G_{O_2}(g) = 2G_{H_2O}(l) + 2G_{H_2} - 4 \times 1.23 \text{ (eV)} \quad (5)$$

The energy correction of the solvation energy (ΔSol) was defined by the following equations (equation 6-7):

$$\Delta Sol = E_{tot} - E_{(sur + adsorbate)} - E_{water} + E_{(sur + water)} \quad (6)$$

$$\Delta G = \Delta E + \Delta ZPE - T \Delta S + \Delta Sol + xeU - 4eU \quad (7)$$

where E_{tot} , $E_{(sur + adsorbate)}$, E_{water} , and $E_{(sur + water)}$ represent the computed electronic energies of the surface with the adsorbates as well as the single water layer, the surface with the adsorbates only, the single water layer, and the surface with single water layer only, respectively. The number of transferred electrons x was 1-3 for the OOH^* , O^* , and OH^* intermediates, respectively.