Supporting Information (SI)

Oxygen Defect Regulation, Catalytic Mechanism, and Modification of HfO_2 as a Novel Catalyst for Lithium-oxygen Batteries

Liwei Su,*[a] Lei Zhang,[a] Xingyi Zhan,[a] Yifan Zhang,[a] Lianbang Wang*[a], Yuanhao Wang,[b]*

[a] *State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China*

[b] *Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, Shenzhen 518055, P. R. China*

*Corresponding author.

E-mail: suliwei@zjut.edu.cn (L. Su); wanglb99@zjut.edu.cn (L. Wang); wangyuanhao@szpt.edu.cn (Y. Wang)

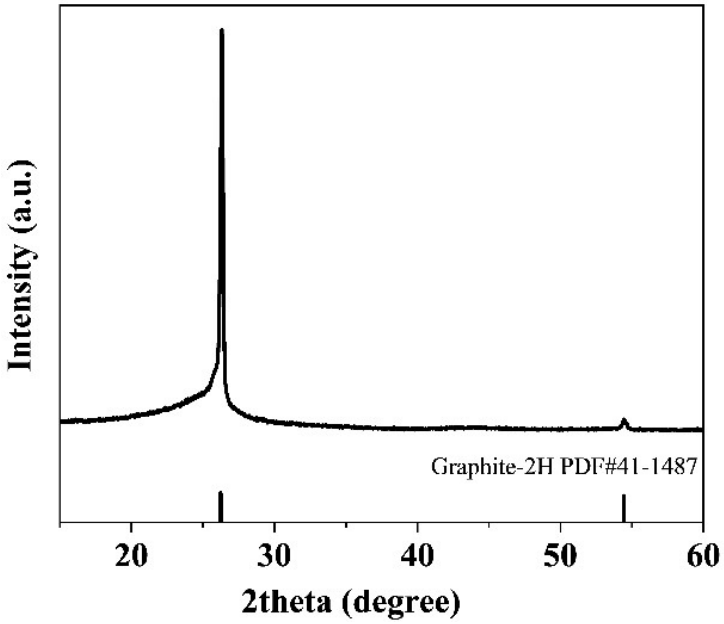

Figure S1. XRD pattern of carbon paper.

Table S1. Surface energy of HfO_2 crystal planes.

Planes	A (Å^2)	E_{slab} (eV)	E_{bulk} (eV)	n	γ (eV/Å^2)
(111)	50.12	-361.53	-124.12	3	0.11
(-111)	44.76	-353.22	-124.12	3	0.21
(020)	27.28	-236.74	-124.12	2	0.21
(200)	27.98	-240.51	-124.12	2	0.14
(110)	39.08	-362.67	-124.12	3	0.12

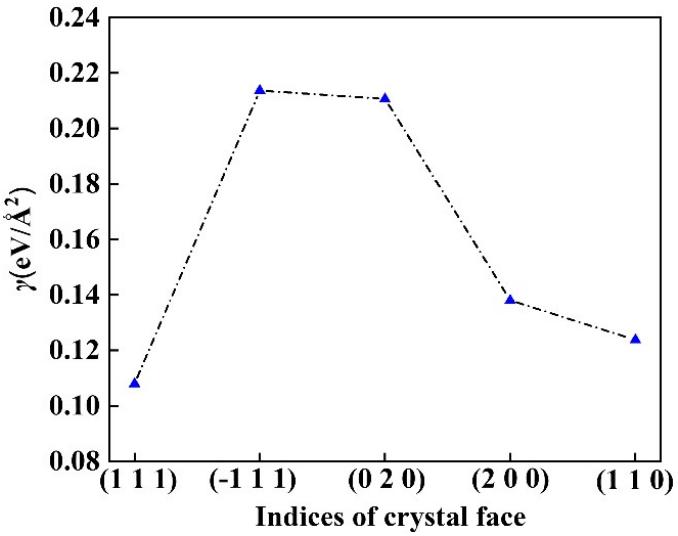

Figure S2. Surface energy curve of HfO_2 crystal planes.

Computational details of the formation energy:

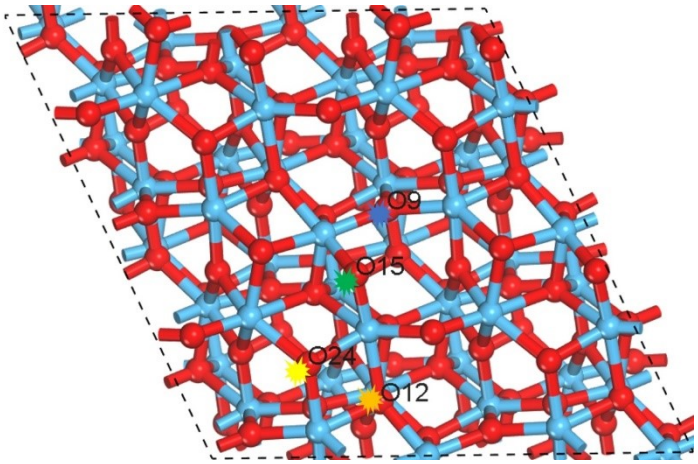

Figure S3. Schematic diagram of the vacancy types (O24, O15, O12, and O9) in 12 HfO_2 units.

The formation energy of oxygen vacancies ($E_{form\text{-}ovac}$) was calculated using the following formula: ($E_{form\text{-}ovac}$) = (E_{ovaC}+1/2μ(O_2))- E_{slab}, where E_{ovac} is the structural energy (eV) after oxygen vacancy formation, μ(O_2) is the chemical potential (eV) of O_2, and E_{slab} is the energy (eV) of the complete (111) crystal plane. Considering the large error in the energy calculation of O_2 in the triplet state using DFT, the calculation process combines the ORR experimental values to calculate μ(O_2). That is:

$2H_2$ (g, 298.15K,1 atom) + O_2 (g, 298.15K, 1atom) = $2H_2O$ (l, 298.15K, 1atom) = $2H_2O$ (g, 298.15K, 0.035atom) $\quad \Delta G_{exp}^{298.15}$ = -4.92 eV

μ(O_2) can be derived from the above equation:

μ(O_2 (g, 298.15K, 1atom)) = 2μ(H_2O(g, 298.15K, 0.035atom))-2μ(H_2(g, 298.15K, 1atom)) - $\Delta G_{exp}^{298.15}$

Table S2. Statistics data to calculate μ(O_2).

	E_{DFT} (eV)	dG (eV)	G (eV)
H_2O (g, 298.15K, 0.035bar)	-14.22	0.00	-14.22

H_2 (g, 298.15K, 1bar)	-6.77	-0.04	-6.81
O_2 (g, 298.15K, 1bar)			-9.90

Table S3. Formation energy for four types of oxygen vacancies.

	E_{ovac_x} (eV)	E_{2slab} (eV)	μ (O_2) (eV)	$E_{form\text{-}ovac}$ (eV)
O_{vca24}	-1434.61	-1446.11	-9.90	6.55
O_{vca15}	-1434.44	-1446.11	-9.90	6.72
O_{vca12}	-1434.94	-1446.11	-9.90	6.22
O_{vca9}	-1434.47	-1446.11	-9.90	6.69

Table S4. Calculated free energies of each component involved in reactions

	E_{DFT} (eV)	dG (eV)	G_{tot} (eV)
Li_2O_2*HfO_x	-369.1329	0.1743	-368.9586
LiO_2*HfO_2	-375.2276	0.0949	-375.1327
LiO_2*HfO_x	-369.8218	0.1279	-369.6940
Li_{bulk}	-3.9738		-3.9738
HfO_2(111)	-361.5251		-361.5251
O_2			-9.90338
HfO_2	-361.5251		
HfO_x	-349.9398		

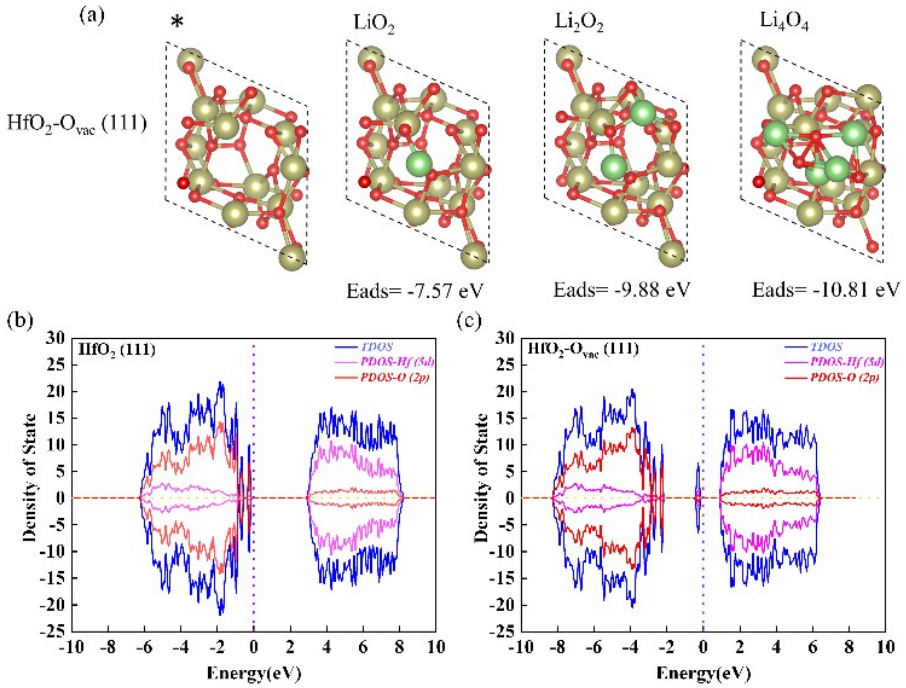

Figure S4. (a) The structure and corresponding adsorption energies of LiO_x on oxygen-defect HfO_2(111) plane; calculated total DOS of (b) HfO_2(111) and (c) oxygen-defect HfO_x(111) plane.

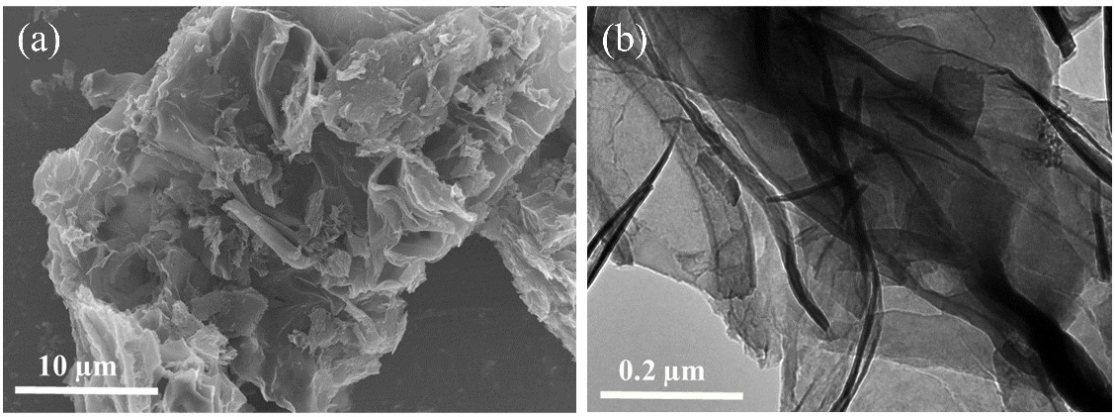

Figure S5. (a) SEM and (b) TEM images of pure NC nanosheets.

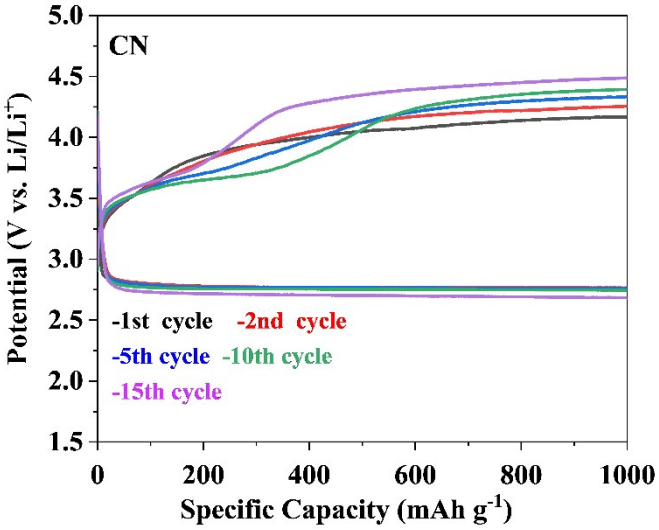

Figure S6. Charge/discharge curves of pure NC nanosheets under the limited-capacity mode.