SUPPORTING INFORMATION

Chinese Journal of Structural Chemistry

The Structural and Chemical Reactivity of Lattice Oxygens on β-PbO_2 EOP Electrocatalysts

Wenwen Li[1], Ge Feng[1], Jia Liu[1], Xing Zhong[1], Zihao Yao[1], Shengwei Deng[1], Shibin Wang[1]* and Jianguo Wang[1]

[1]*Institute of Industrial Catalysis, State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, P.R. China*

**Corresponding author. S. B. Wang. Email: wangshibin@zjut.edu.cn*

n LIST OF FIGURES AND TABLES

Table S1. Calculated Gibbs Adsorption Energies (ΔG_a), Gibbs Reaction Energies (ΔG_r) and Energy Barriers (ΔG_b) for LOM-1/LOM-2/ LOM-3/AEM and H_2O Dissociation on the PbO_2 (110) Surface

	H_2O Splitting	**ΔG_a (eV)**	**ΔG_r (eV)**	**ΔG_b (eV)**
DF-O_{latt-2}	$H_2O + Pb \rightarrow Pb\text{-}OH + H\text{-}O_{latt-1}$	-0.10	-0.41	0.15
DF-O_{latt-2}	$H_2O + Pb \rightarrow Pb\text{-}OH + H\text{-}O_{latt-2}$	-0.10	0.41	0.46
O_{vac-1}	$H_2O + Pb + O_{vac-1} \rightarrow Pb\text{-}OH + H\text{-}O_{latt-1} + O_{vac-1}$	-0.29	-0.20	0.19
O_{vac-2}	$H_2O + Pb + O_{vac-2} \rightarrow Pb\text{-}OH + H\text{-}O_{latt-1} + O_{vac-2}$	-0.04	-0.57	0.19
AEM-step-1	$OH^- \rightarrow OH^* + e^-$	–	2.15	–
AEM-step-2	$OH^* + OH^- \rightarrow O^* + H_2O(l) + e^-$	–	2.08	–
AEM-step-3	$O^* + OH^- \rightarrow OOH^* + e^-$	–	-1.93	–
AEM-step-4	$OOH^* + OH^- \rightarrow O_2^* + H_2O(l) + e^-$	–	2.24	–
AEM-step-5	$O_2^* + OH^- \rightarrow O_2^* + OH^* + e^-$	–	2.24	–
AEM-step-6	$O_2^* + OH^* + OH^- \rightarrow O_2^* + O^* + H_2O(l) + e^-$	–	2.03	–
AEM-step-7	$O_2^* + O^* \rightarrow O_3^* + *$	–	-0.67	–
LOM-1/step-1	$OH^- \rightarrow OH^* + e^-$	–	0.96	–
LOM-1/step-2	$OH^* + OH^- + O_{latt} \rightarrow OO_{latt}^* + H_2O(l) + e^-$	–	-0.05	–
LOM-1/step-3	$OO_{latt}^* + OH^- \rightarrow OO_{latt}^* + OH^* + e^-$	–	1.90	–
LOM-1/step-4	$OO_{latt}^* + OH^* + OH^- \rightarrow OO_{latt}^* + O^* + H_2O(l) + e^-$	–	2.63	–
LOM-1/step-5	$OO_{latt}^* + O^* \rightarrow O_3^* + *$	–	-1.16	–
LOM-2/step-1	$OH^- \rightarrow OH^* + e^-$	–	0.96	–
LOM-2/step-2	$OH^* + OH^- + O_{latt} \rightarrow OO_{latt}^* + H_2O(l) + e^-$	–	-0.05	–
LOM-2/step-3	$OO_{latt}^* + O_{latt} \rightarrow O_3^*$	–	-0.55	–
LOM-3/step-1	$O_{latt} + O_{latt} \rightarrow O_2^*$	–	0.49	–
LOM-3/step-2	$O_2^* + OH^- \rightarrow O_2^* + OH^* + e^-$	–	1.28	–
LOM-3/step-3	$O_2^* + OH^* + OH^- \rightarrow O_2^* + O^* + H_2O(l) + e^-$	–	0.94	–
LOM-3/step-4	$O_2^* + O^* \rightarrow O_3^* + *$	–	0.48	–

Table S2. Calculated Electronic Energy (E_{elect}, eV), Zero-Point Energy (ZPE, eV), Entropy (S, eV/K) and ΔG (eV) at 298 K for Reaction Intermediates in AEM Pathway

	E_{elect}	ZPE	-TS	G	S (eV/K)	ΔG
H_2 (g)	-6.80	0.27	-0.40	-6.93	0.001354 (ref.1)	
O_2 (g)	-9.86	0.10	-0.63	-10.39	0.002126 (ref.1)	
H_2O (g)	-14.22	0.57	-0.58	-14.23	0.001957 (ref.1)	
110-DF	-753.26	0	0	-753.26	0	
OH*	-762.10	0.34	-0.12	-761.88	0.000386	2.15
O*	-765.31	0.05	-0.07	-756.34	0.000241	2.08
OOH*	-769.24	0.39	-0.20	-769.04	0.000659	-1.93
O_2*	-763.16	0.11	-0.29	-763.33	0.000959	2.24
O_2* + OH*	-772.04	0.44	-0.26	-771.86	0.000888	2.24
O_2* + O*	-766.23	0.16	-0.29	-766.37	0.000988	2.03
O_3*	-767.00	0.21	-0.24	-767.03	0.000802	-0.67

Ref. 1. NIST Chemistry WebBook, NIST Standard Reference Database Number 69 (Eds: P.J. Linstrom, W.G. Mallard), National Institute of Standards and Technology, Gaithersburg MD, p. 20899 (retrieved 2019).

Table S3. Calculated Electronic Energy (E_{elect}, eV), Zero-Point Energy (ZPE, eV), Entropy (S, eV/K) and ΔG (eV) at 298 K for Reaction Intermediates in LOM-1 Pathway

	E_{elect}	ZPE	-TS	G	S (eV/K)	ΔG
H_2-mol	-6.80	0.27	-0.40	-6.93	0.001354 (ref.1)	
O_2-mol	-9.86	0.10	-0.63	-10.39	0.002126 (ref.1)	
H_2O	-14.22	0.57	-0.58	-14.23	0.001957 (ref.1)	
110-DF	-753.26	0	0	-753.26	0	
OH*	-763.37	0.43	-0.12	-763.06	0.000414	0.96
OO_{latt} *	-759.47	0.11	-0.29	-759.65	0.00098	-0.05
OO_{latt} *+ OH*	-768.58	0.45	-0.39	-768.52	0.001333	1.90
OO_{latt} *+ O*	-762.24	0.15	-0.33	-762.43	0.001109	2.63
O_3*	-763.52	0.19	-0.26	-763.59	0.000879	-1.16

Ref. 1. NIST Chemistry WebBook, NIST Standard Reference Database Number 69 (Eds: P.J. Linstrom, W.G. Mallard), National Institute of Standards and Technology, Gaithersburg MD, p. 20899 (retrieved 2019).

Table S4. Calculated Electronic Energy (E_{elect}, eV), Zero-Point Energy (ZPE, eV), Entropy (S, eV/K) and ΔG (eV) at 298 K for Reaction Intermediates in LOM-2 Pathway

	E_{elect}	ZPE	-TS	G	S (eV/K)	ΔG
H_2-mol	-6.80	0.27	-0.40	-6.93	0.001354 (ref.1)	
O_2-mol	-9.86	0.10	-0.63	-10.39	0.002126 (ref.1)	
H_2O	-14.22	0.57	-0.58	-14.23	0.001957 (ref.1)	
110-DF	-753.26	0	0	-753.26	0	
OH*	-763.37	0.42	-0.12	-763.07	0.000414	0.96
O_2*	-759.47	0.11	-0.29	-759.65	0.00098	-0.05
O_3 + 2O_v*	-759.03	0.19	-0.28	-759.10	0.000924	-0.55

Ref. 1. NIST Chemistry WebBook, NIST Standard Reference Database Number 69 (Eds: P.J. Linstrom, W.G. Mallard), National Institute of Standards and Technology, Gaithersburg MD, p. 20899 (retrieved 2019).

Table S5. Calculated Electronic Energy (E_{elect}, eV), Zero-Point Energy (ZPE, eV), Entropy (S, eV/K) and ΔG (eV) at 298 K for Reaction Intermediates in LOM-3 Pathway

	E_{elect}	ZPE	-TS	G	S (eV/K)	ΔG
H_2-mol	-6.80	0.27	-0.40	-6.93	0.001354 (ref.1)	
O_2-mol	-9.86	0.10	-0.63	-10.39	0.002126 (ref.1)	
H_2O	-14.22	0.57	-0.58	-14.23	0.001957 (ref.1)	
110-DF	-753.26	0	0	-753.26	0	
OO_{latt} *	-754.47	0.13	-0.15	-754.49	0.000519	0.49
OO_{latt} *+ OH*	-764.16	0.47	-0.29	-763.98	0.000974	1.28
OO_{latt} *+ O*	-759.46	0.17	-0.29	-759.58	0.000981	0.94
O_3*	-759.03	0.20	-0.28	-759.10	0.000924	0.48

Ref. 1. NIST Chemistry WebBook, NIST Standard Reference Database Number 69 (Eds: P.J. Linstrom, W.G. Mallard), National Institute of Standards and Technology, Gaithersburg MD, p. 20899 (retrieved 2019).