Supporting Information

Enhanced Electrochemical Performance by Facile Oxygen Vacancies from Lower Valence-State Doping for Ramsdellite-MnO_2

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Table S1 Formation energies of substituional doping on the surfaces for R-MnO_2. (Units: eV)

	110			010		
Doping sites	**SS**	**SF**	**NS**	**SS**	**SF**	**NS**
Zn-doped	6.70	5.27	6.70	6.29	5.52	6.80

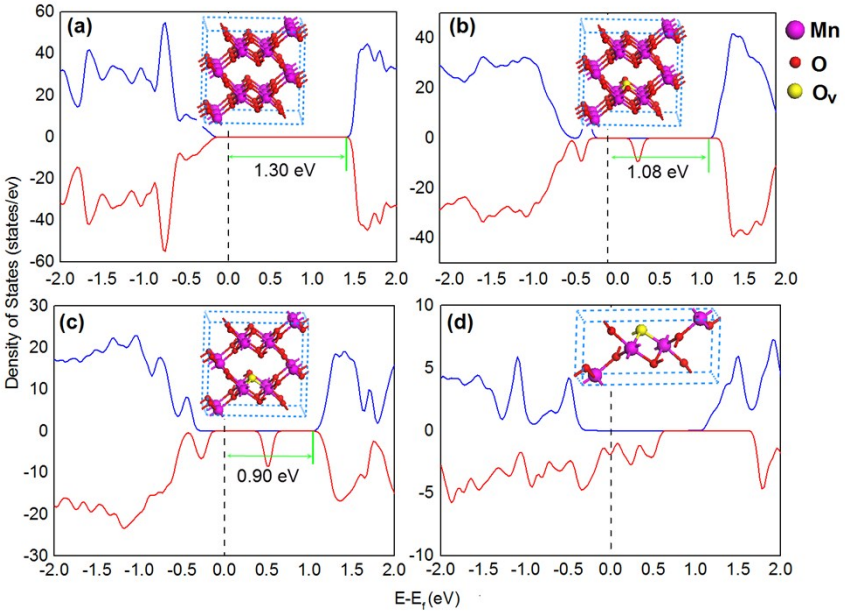
Table S2 Formation energies for the dilute oxygen vacancy at surfaces of NS Zn-doped R-MnO_2. (Units: eV)

	Vacancy Sites	Zn-doping NS
110	**I**	0.08
	II	1.48
010	**I**	0.58
	II	1.39

Table S3 Predicted magnetic moments of surface Mn/Zn atoms on low energy surfaces for pristine and Zn-doped R-MnO_2.

	Mn/Zn sites	**Pristine**	**Zn-doping**		**Zn-doping with vacancy I**	
Doping sites			**SS**	**SF**	**SS**	**SF**
bulk		3.02				
110	**SS**	3.13	− 0.08	3.13	− 0.03	3.19
	SF	3.36	3.78	0.00	3.85	0.03
010	**SS**	3.15	− 0.03	3.14	− 0.14	3.26
	SF	3.38	3.25	− 0.01	3.28	-0.16

Figure S1 The total density of states for 1×2×3 supercell without vacancy, 1×2×3, 1×2×2 and 1×1×1 supercell with one vacancy of R-MnO_2.



As shown in Figure S1, four models are chosen as 1×2×3 supercell without vacancy, 1×2×3, 1×2×2 and 1×1×1 supercell with one vacancy, to represent four oxygen concentrations 0.00%, 2.08%, 3.12% and 12.50%, respectively. The total density of states for these modes are also shown in Figure S1. After introducing oxygen oxides, it could be seen that the conduction-band minimum will shift down gradually because of the broken of Mn-O bonds, and some impurity peaks are introduced within the band gap. It could be calculated out that the band gaps of these structures are 1.30 eV, 1.08 eV, 0.90 eV and 0.00 eV, respectively. In other words, the band gap will be narrowed down gradually with the increasing of oxygen vacancies concentration and the MnO_2 will be metallic finally. Therefore, the band gap reduction of bulk MnO_2 after introducing oxygen vacancy is crucial to enhancing the electric conductivity.

Figure S2 Partial density of states of NS Zn-doped R-MnO_2.

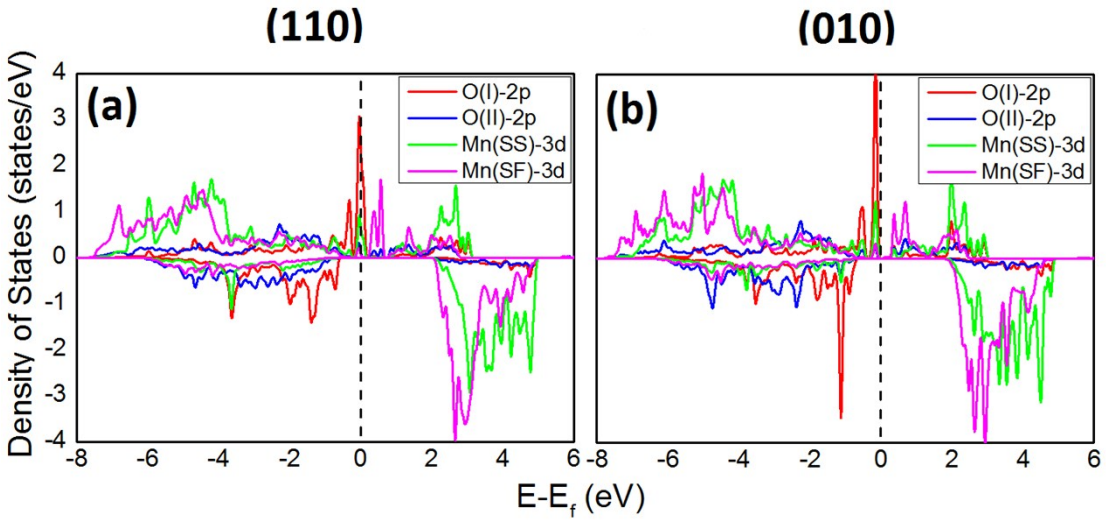


Figure S3 Charge density difference of NS Zn-doped R-MnO_2.