Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supporting Information

Enhanced catalytic performance of pillared δ-MnO_2 with enlarged layer spaces for lithium- and sodium-oxygen batteries: A theoretical investigation

Jia-Hui Li and Yang-Xin Yu*

Laboratory of Chemical Engineering Thermodynamics, Department of Chemical Engineering, Tsinghua University, Beijing 100084, P. R. China

*Corresponding author. E-mail: yangxyu@mail.tsinghua.edu.cn

Phone: +86-10-62782558

Fax: +86-10-62770304

Table S1 and Figure S1 include the information for C-C bond lengths of various molecules. Figure S2 records the density of states of bare-MnO_2. Figure S3 is the information for the d-electron states of three pillared structures. Figure S4 is the AIMD simulation configurations of three pillared structures. The configurations of deep reduction product Li_3O_2 and Li_4O_2 adsorbed H-MnO_2 are shown in Figure S5 (a) and (b). The configurations of deep reduction product Li_3O_2, Li_4O_2, Na_3O_2 and Na_4O_2 adsorbed Cl-MnO_2 are shown in Figure S5 (c) and (f).

The complete battery reaction including the deep reduction of lithium and sodium is

$$\mathrm{X} + \mathrm{Sub} \rightarrow \mathrm{X@Sub} \xrightarrow{+\mathrm{O_2}} \mathrm{XO_2@Sub} \xrightarrow{+\mathrm{X}} \mathrm{X_2O_2@Sub} \xrightarrow{+\mathrm{X}} \mathrm{X_3O_2@Sub} \xrightarrow{+\mathrm{X}} \mathrm{X_4O_2@Sub} \quad (\mathrm{X = Li\ or\ Na}) \tag{S1}$$

The d-band center (E_d) of substrates can be computed by:

$$E_d = \frac{\int \varepsilon \cdot P(\varepsilon)\ d\varepsilon}{\int P(\varepsilon)\ d\varepsilon} \tag{S2}$$

where ε denotes the energy-level of electrons and $P(\varepsilon)$ is the number of electrons occupied in energy level ε. The upper and lower limits of the integral are selected as electrons below the Fermi level.

Table S1 The various C-C bond lengths of bare molecules and molecules in pillared systems.

system	C-C bond length (Å)

	①	②	③	④	⑤	⑥
$C_6H_4O_6S_2$	1.397	1.398	1.395	1.398	1.397	1.395
H-MnO_2	1.397	1.392	1.380	1.397	1.393	1.383
$C_6H_3O_6S_2Cl$	1.406	1.401	1.395	1.397	1.396	1.397
Cl-MnO_2	1.414	1.406	1.391	1.397	1.389	1.402
$C_6H_3O_6S_2F$	1.399	1.398	1.396	1.396	1.397	1.389
F-MnO_2	1.405	1.402	1.391	1.398	1.392	1.391

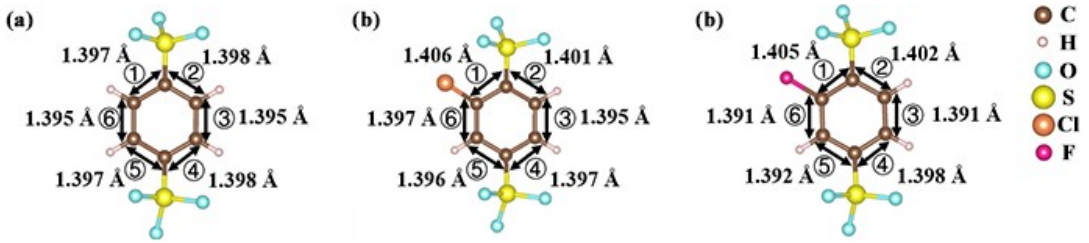

Fig. S1 The C-C bond lengths of bare anions of (a) 1,4-benzenedisulfonic acid, (b) 2-chloro-1,4-benzenedisulfonic acid, and (c) 2-fluoro-1,4-benzenedisulfonic acid.

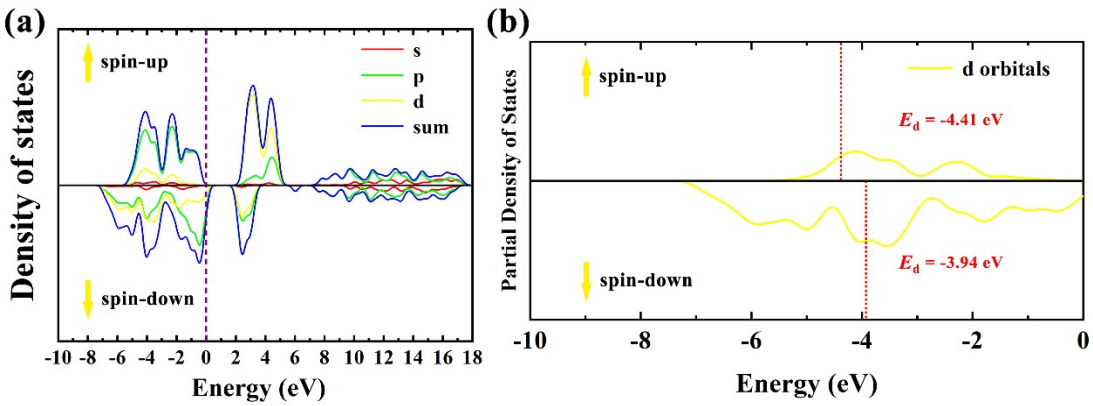

Fig. S2 (a) The partial density of states of bare-MnO_2 and (b) d-orbital density of states. Both spin-up and spin-down electrons are plotted and their d-band centers are calculated.

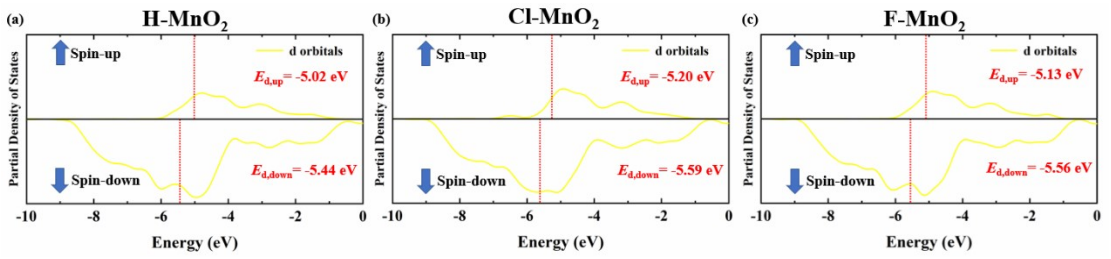

Fig. S3 The d-orbital density of states and corresponding d-band centers of (a) H-MnO_2, (b) Cl-MnO_2, and (c) F-MnO_2 pillared structures. States of both spin-up and spin-down electrons are plotted and their d-band centers are calculated separately.

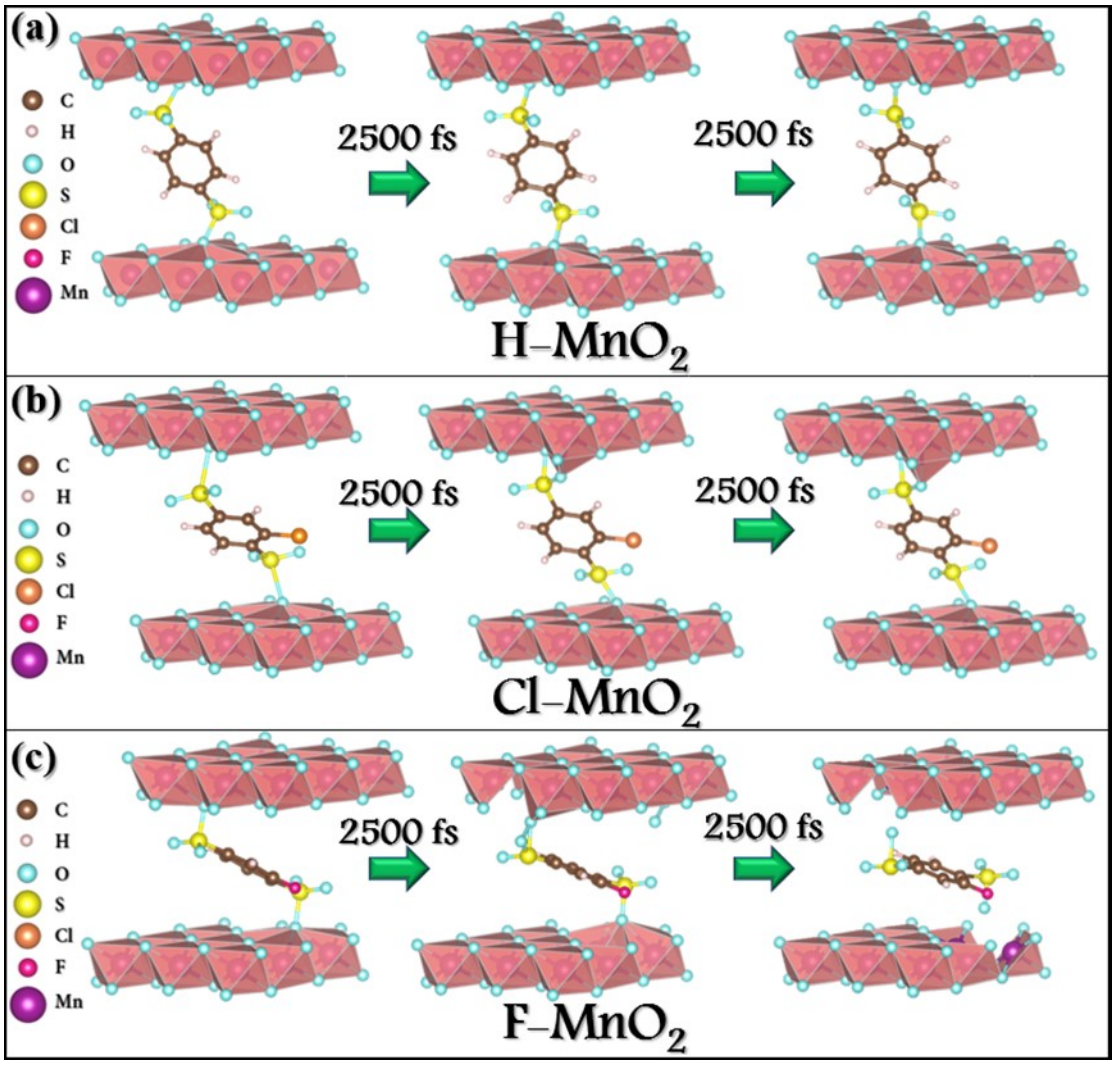

Fig. S4 The configurations of (a) H-MnO_2, (b) Cl-MnO_2, and (c) F-MnO_2, in the AIMD

simulations at initial stage (0 fs), middle stage (2500 fs), and final stage (5000 fs).

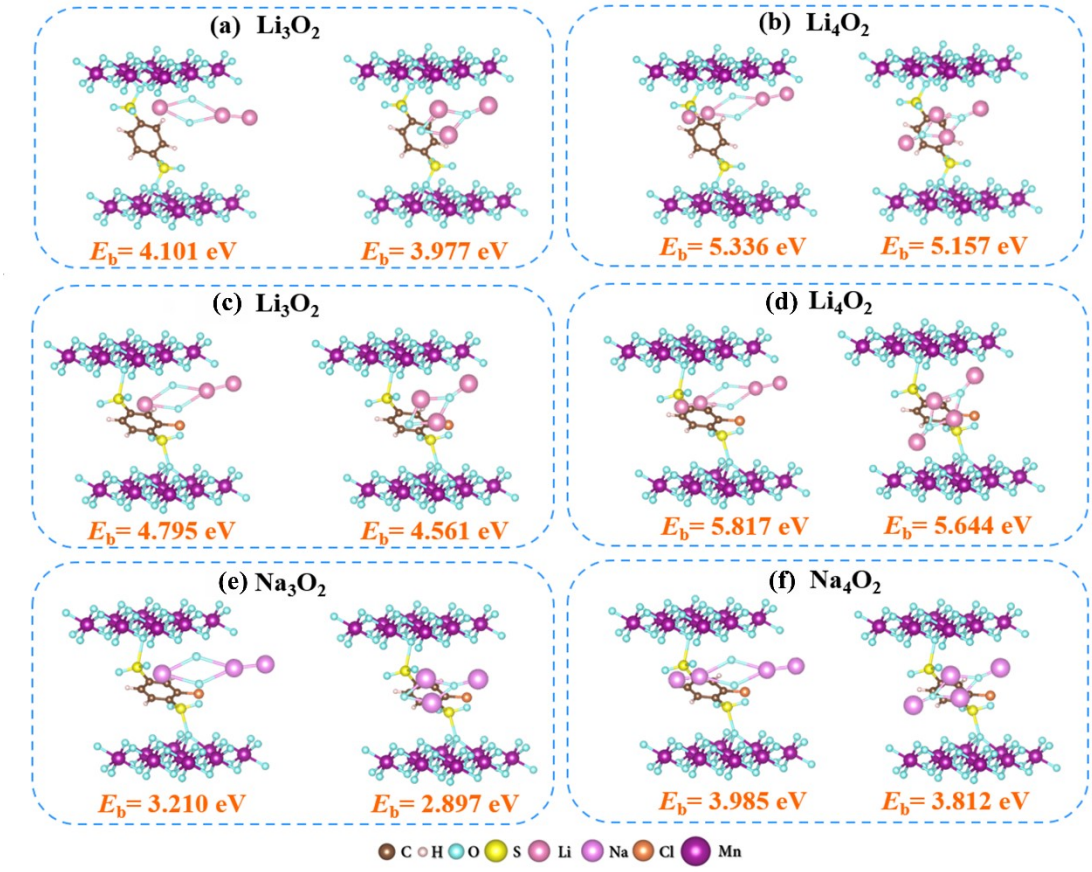

Fig. S5 The configurations of deep reduction product (a) Li_3O_2 and (b) Li_4O_2 adsorbed H-MnO_2. The configurations of deep reduction product (c) Li_3O_2, (d) Li_4O_2, (e) Na_3O_2 and (f) Na_4O_2

adsorbed Cl-MnO_2. In each group, the configuration on the left is more stable than the configuration on the right.