SUPPORTING INFORMATION

Towards the Realization of Larger-Capacity and Higher-Stability Lithium Storages via Constructing Quinone-2D MnO_2 Pillared Structrures

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List of Tables and Figures

Supporting information includes two graphs and four tables. Figures S1 present the total density of states and band structures of two-dimensional MnO_2. The blue and red lines represent different spin of electrons. The Binding energies for different numbers of lithium atoms are listed in Table S1 and S2. Table S3-S4 recorded the open circuit voltages of systems at different lithium concentrations. Figure S2 is the temperature profiles of $C_6H_4O_2$-2D MnO_2, $C_6F_4O_2$-2D MnO_2 and $C_6Cl_4O_2$-2D MnO_2 in molecular dynamic simulations. The thermodynamic properties (Figure S6) and corresponding zero-point-energy (Table S5) are utilized for the lithium diffusivity calculation. Figure S4 are the lithium diffusion energy profiles of the bulk MnO_2 and 2D-MnO_2. The enthalpy and entropy at 300 K of Li adsorbed H-MnO_2 local minima and transition state, and bulk bcc Li crystal, are listed in the Table S5. The corrected Gibbs free energy change could be calculated by:

$$\Delta G_{\text{barrier}} = \Delta H - T\Delta S + \Delta E_{\text{ZPE}} \quad (1)$$

where T is the temperature, ΔH, ΔS and ΔE_{ZPE} are the total energy changes between local minima and transition states, respectively.

Table S1. Binding energies for different numbers of lithium atoms in eV per lithium atom

System	1 Li	2 Li	3 Li	4 Li	5 Li	6 Li	7 Li	8 Li	9Li
H-MnO_2	2.80	2.76	2.69	2.65	2.62	2.58	2.54	2.51	2.48
F-MnO_2	3.32	3.07	2.98	2.92	2.88	2.84	2.81	2.78	2.74
Cl-MnO_2	3.09	2.95	2.90	2.87	2.84	2.81	2.78	2.72	2.66

Table S2. Binding energies for different numbers of lithium atoms in eV per lithium atom

System	10Li	11Li	12 Li	13 Li	14 Li	15 Li	16 Li	17 Li	18 Li
H-MnO_2	2.45	2.42	2.39	2.36	2.33	2.3	2.27	2.24	2.21
F-MnO_2	2.69	2.64	2.59	2.54	2.49	2.43	2.37	2.31	2.25
Cl-MnO_2	2.61	2.55	2.50	2.45	2.40	2.35	2.31	2.27	2.23

Table S3. Open circuit voltages of systems at lithium concentration x_{Li} in unit of V

System	x_{Li}								
	0.056	0.111	0.167	0.222	0.278	0.333	0.389	0.444	0.500
H-MnO_2	2.80	2.72	2.55	2.53	2.50	2.38	2.30	2.30	2.24
F-MnO_2	3.32	2.82	2.80	2.74	2.72	2.64	2.63	2.57	2.42
Cl-MnO_2	3.09	2.81	2.80	2.78	2.72	2.66	2.60	2.30	2.18

Table S4. Open circuit voltages of systems at lithium concentration x_{Li} in unit of V

System	x_{Li}								
	0.556	0.611	0.667	0.722	0.778	0.833	0.889	0.944	1.000
H-MnO_2	2.18	2.12	2.06	2.00	1.94	1.88	1.82	1.76	1.70
F-MnO_2	2.24	2.14	2.04	1.94	1.84	1.59	1.47	1.35	1.23
Cl-MnO_2	2.16	1.95	1.95	1.85	1.75	1.65	1.65	1.63	1.62

Table S5. The enthalpy, entropy at 300 K, and zero-point-energy of Li adsorbed H-MnO_2 local minima, transition state, and bulk bcc Li crystal

Substance	Enthalpy (eV)	Entropy (meV K^{-1})	Zero-point-energy (eV)
local minima	7.675	9.106	6.085
transition state	7.849	9.627	6.215
bcc Li	0.078	1.288	0.009

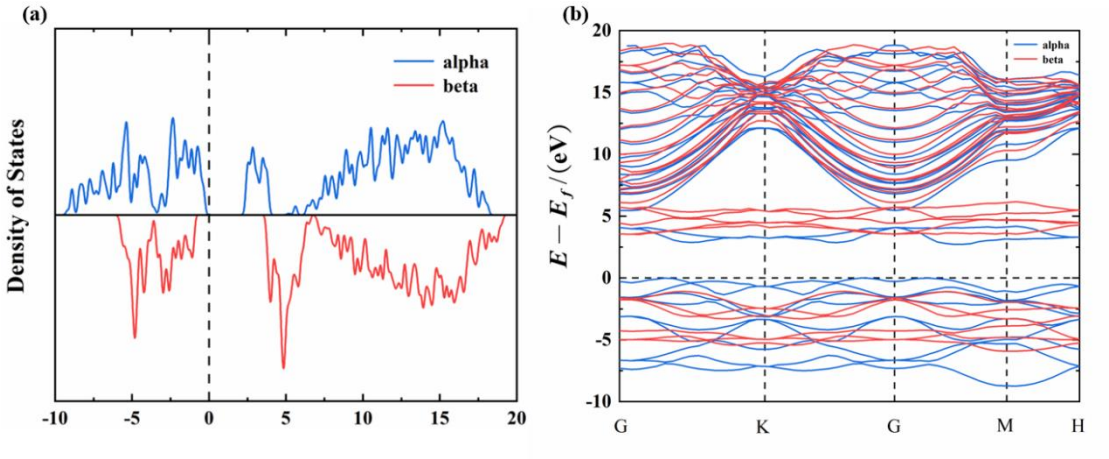

Figure S1. (a) The Density of states and (b) band structure for 2D-MnO_2 calculated by HSE06 hybrid functional.

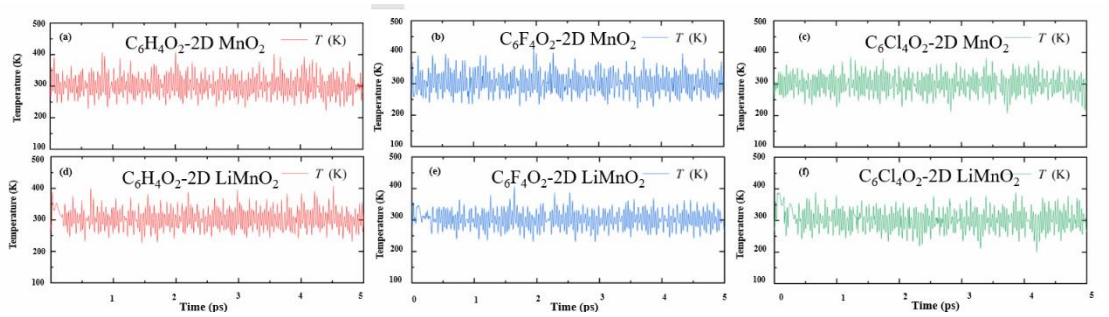

Figure S2. Temperature profiles in AIMD simulations for (a)-(c) pristine pillared structures and (d)-(f) lithium fulfilled pillared structures at 300 K.

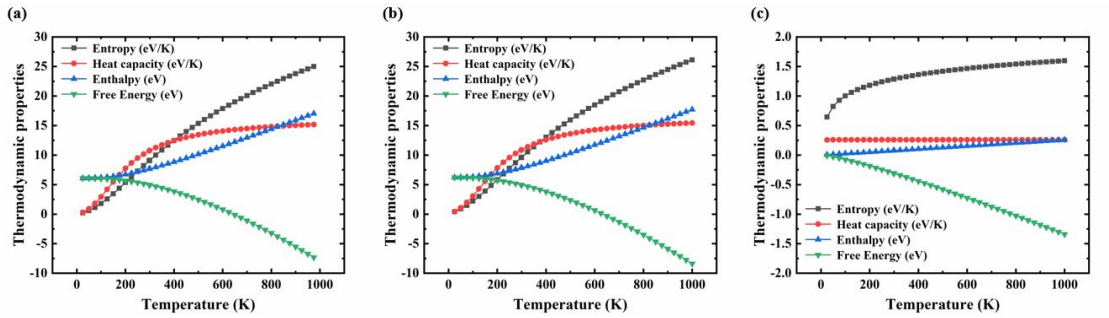

Figure S3. The entropy (grey line), heat capacity (red line), enthalpy (blue line), and free energy (green line) at 0-1000 K of (a) H-MnO_2, (b) Li adsorbed H-MnO_2 and (c) bcc Li bulk.

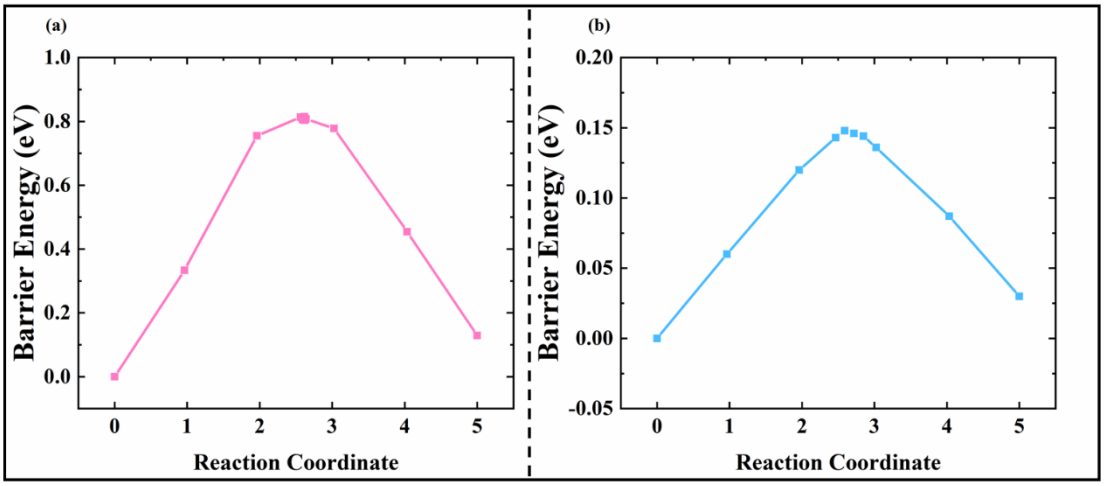

Figure S4. Lithium diffusion energy profiles of the (a) bulk MnO_2 and (b) 2D-MnO_2. The corresponding energy barriers are 0.81 and 0.15 eV, respectively.