A hydrogen storage nanotank: lithium-organic pillared graphite

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Supporting Material

S.1 Force fields used in grand canonical Monte-Carlo simulations

In performing the grand canonical Monte-Carlo (GCMC) simulation, force fields (FFs) developed by Deng et al.[1] and Han et al.[2,3] were used for the van der Waals (vdW) interactions between H_2 and Li-organic-GIC sorbent. The FFs (Table 1) were Morse potential types (equation 1) with the parameters determined by fitting to accurate *ab initio* calculations. For the H_A---H_A (H_A indicates hydrogen atom in a H_2 molecule) vdW term, the potential curves were fitted between two H_2 molecules using CCSD(T) with the aug-cc-pVQZ basis set.[1] For the C_3---H_A (C_3 indicates *sp³* carbon) vdW term, the interaction between H_2 and C_2 molecules were calculated using the MP4 method with aug-cc-pVTZ basis set plus midpoint bond functions.[1] For the C_R---H_A (C_R indicates aromatic *sp²* carbon) and H_---H_A (H_ indicates hydrogen atom bonded to carbon atoms) vdW terms, the potential curves were fitted between a benzene (C_6H_6) and a H_2 molecule by a combination of the MP2 method and triple zeta valence basis supplemented with polarization functions from the cc-pVTZ basis, which is denoted as TZVPP.[2] For the O---H_A vdW term, the interaction between boroxine (B_3O_3) and H_2 molecules were calculated using the MP2 method with the QZVPP basis set.[3] And to determine the interactions between doped Li ions and hydrogen molecules, considered was a planar C_{32} cluster (ten aromatic rings) doped with one Li atom on each side to which one H_2 was bonded.[1] With this methodology, the first author (SSH) s work successfully showed a good agreement between theoretical and experimental results on hydrogen storage in various metal-organic frameworks and covalent-organic frameworks.[2-7]

$$U_{ij}(r_{ij}) = D\left\{ \exp[\alpha(1 - \frac{r_{ij}}{r_o})] - 2 \cdot \exp[\frac{\alpha}{2}(1 - \frac{r_{ij}}{r_o})] \right\}$$

(1)

Table S1. vdW force field parameters obtained from QM data. Here, C_R and C_3 mean sp^2 and sp^3 carbon atoms, respectively. And H_ indicates hydrogen bonded to carbon atoms in tetrahydrofuran or 2,5-dihydrofuran and H_A indicates hydrogen in a H_2 molecule.

Term	D (kcal/mol)	r_0 (Å)	α
C_R---H_A	0.10082	3.12022	12.00625
C_3---H_A	0.03594	3.74425	12.16757
H_---H_A	0.00087	3.24722	12.00625
H_A---H_A	0.01815	3.56980	10.70940
O---H_A	0.02515	3.32249	12.00187
Li---H_A	2.15752	2.01844	7.12510

S.2 Fitting of Force Fields for Li^+-Tetrahydrofuran

In this work, we investigated an optimized structure of a ternary Li-THF(tetrahydrofuran)-GIC(graphite intercalation compound) by molecular dynamics simulation with DREIDING FF. To more accurately describe interaction between Li and THF, we developed a FF for lithium-oxygen bond stretch with the Morse potential where the parameters were determined by fitting to density functional theory (X3LYP level) with 6-311G** basis set, which is shown in Fig. S1.
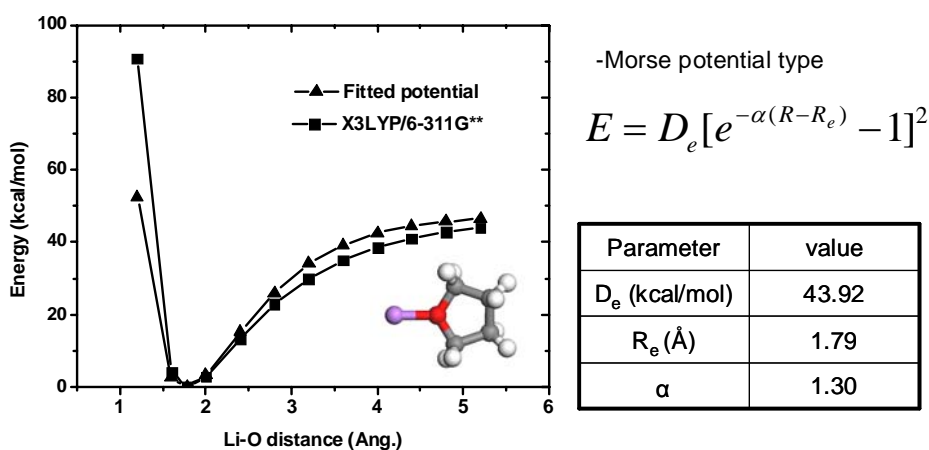

-Morse potential type

$$E = D_e[e^{-\alpha(R-R_e)} - 1]^2$$

Parameter	value
D_e (kcal/mol)	43.92
R_e (Å)	1.79
α	1.30

Figure S1. Fitted Li^+-O bond stretch function from DFT calculations. Here color code is pink=Li, red=O, gray=C, and white=H.

S.3 Simulated hydrogen storage capacity for compound **1** at 77 and 300 K.

Compound **1** (77 K)				
Pressure (bar)	Gravimetric uptake (wt%)		Volumetric uptake (kg/m3)	
	excess	total	excess	total
1	1.52	1.53	11.78	11.83
5	2.31	2.32	18.01	18.14
10	2.85	2.87	22.37	22.59
20	3.11	3.16	24.51	24.93
30	3.29	3.36	25.97	26.57
40	3.33	3.43	26.32	27.11
50	3.39	3.51	26.77	27.75
100	3.55	3.76	28.06	29.83

Compound **1** (300 K)				
Pressure (bar)	Gravimetric uptake (wt%)		Volumetric uptake (kg/m3)	
	excess	total	excess	total
1	0.01	0.01	0.06	0.09
5	0.03	0.04	0.22	0.30
10	0.06	0.07	0.44	0.57
20	0.12	0.14	0.89	1.10
30	0.17	0.21	1.30	1.60
40	0.22	0.27	1.70	2.08
50	0.27	0.33	2.06	2.54
100	0.47	0.59	3.62	4.52

S.4 Simulated hydrogen storage capacity for compound **2** at 77 and 300 K.

Compound **2** (77 K)				
Pressure (bar)	Gravimetric uptake (wt%)		Volumetric uptake (kg/m3)	
	excess	total	excess	total
1	1.69	1.70	15.17	15.22
5	2.55	2.56	23.04	23.19
10	2.78	2.81	25.24	25.49
20	2.98	3.03	27.07	27.53
30	3.08	3.15	27.97	28.66
40	3.15	3.25	28.69	29.58
50	3.16	3.27	28.69	29.80
100	3.22	3.43	29.31	31.33

Compound **2** (300 K)				
Pressure (bar)	Gravimetric uptake (wt%)		Volumetric uptake (kg/m3)	
	excess	total	excess	total
1	0.01	0.01	0.07	0.10
5	0.03	0.04	0.26	0.35
10	0.06	0.07	0.54	0.67
20	0.12	0.15	1.04	1.30
30	0.18	0.21	1.58	1.90
40	0.23	0.27	2.01	2.43
50	0.27	0.33	2.42	2.93
100	0.47	0.58	4.16	5.13

S.5 Simulated hydrogen storage capacity for compound **Li-1** with a LiC_6 concentration at 77 and 300 K.

Compound **Li-1** (77 K, LiC_6)				
Pressure (bar)	Gravimetric uptake (wt%)		Volumetric uptake (kg/m3)	
	excess	total	excess	total
1	4.07	4.08	34.71	34.75
5	4.48	4.49	38.32	38.46
10	4.65	4.68	39.90	40.12
20	4.77	4.81	40.99	41.35
30	4.90	4.95	42.11	42.60
40	4.96	5.03	42.72	43.34
50	4.96	5.04	42.66	43.44
100	5.05	5.20	43.47	44.89

Compound **Li-1** (300 K, LiC_6)				
Pressure (bar)	Gravimetric uptake (wt%)		Volumetric uptake (kg/m3)	
	excess	total	excess	total
1	0.64	0.64	5.27	5.29
5	1.23	1.24	10.16	10.25
10	1.50	1.52	12.48	12.62
20	1.79	1.82	14.92	15.14
30	1.99	2.03	16.62	16.91
40	2.10	2.14	17.55	17.91
50	2.21	2.26	18.47	18.89
100	2.54	2.63	21.28	22.06

S.5 Simulated hydrogen storage capacity for compound **Li-2** with a LiC_6 concentration at 77 and 300 K.

Compound **Li-2** (77 K, LiC_6)				
Pressure (bar)	Gravimetric uptake (wt%)		Volumetric uptake (kg/m3)	
	excess	total	excess	total
1	4.11	4.11	40.50	40.55
5	4.28	4.29	42.28	42.42
10	4.36	4.39	43.13	43.36
20	4.44	4.48	43.98	44.35
30	4.53	4.58	44.84	45.35
40	4.53	4.59	44.84	45.48
50	4.53	4.61	44.87	45.65
100	4.56	4.70	45.19	46.62

Compound **Li-2** (300 K, LiC_6)				
Pressure (bar)	Gravimetric uptake (wt%)		Volumetric uptake (kg/m3)	
	excess	total	excess	total
1	0.76	0.76	7.24	7.27
5	1.35	1.36	12.95	13.04
10	1.64	1.65	15.76	15.91
20	1.92	1.95	18.55	18.78
30	2.11	2.14	20.39	20.70
40	2.25	2.29	21.76	22.13
50	2.32	2.37	22.49	22.93
100	2.60	2.68	25.22	26.00

S.6 Simulated hydrogen storage capacity for compound **Li-1** with a LiC_3 concentration at 77 and 300 K.

Compound **Li-1** (77 K, LiC_3)				
Pressure (bar)	Gravimetric uptake (wt%)		Volumetric uptake (kg/m3)	
	excess	total	excess	total
1	4.54	4.54	41.49	41.50
5	4.70	4.71	43.09	43.12
10	4.73	4.74	43.38	43.44
20	4.75	4.77	43.57	43.67
30	4.77	4.78	43.69	43.83
40	4.78	4.79	43.76	43.94
50	4.78	4.81	43.85	44.05
100	4.79	4.82	43.86	44.22

Compound **Li-1** (300 K, LiC_3)				
Pressure (bar)	Gravimetric uptake (wt%)		Volumetric uptake (kg/m3)	
	excess	total	excess	total
1	2.63	2.63	23.56	23.57
5	3.11	3.11	28.01	28.05
10	3.32	3.33	29.99	30.04
20	3.47	3.48	31.35	31.43
30	3.56	3.58	32.25	32.36
40	3.62	3.64	32.80	32.94
50	3.65	3.67	33.05	33.22
100	3.77	3.80	34.15	34.45

S.7 Simulated hydrogen storage capacity for compound **Li-2** with a LiC_3 concentration at 77 and 300 K.

Compound **Li-2** (77 K, LiC_3)				
Pressure (bar)	Gravimetric uptake (wt%)		Volumetric uptake (kg/m3)	
	excess	total	excess	total
1	4.79	4.79	50.80	50.82
5	4.85	4.86	51.45	51.53
10	4.90	4.91	52.00	52.12
20	4.96	4.98	52.67	52.87
30	4.98	5.01	52.92	53.22
40	4.99	5.02	52.97	53.35
50	4.98	5.03	52.95	53.42
100	4.97	5.04	52.73	53.61

Compound **Li-2** (300 K, LiC_3)				
Pressure (bar)	Gravimetric uptake (wt%)		Volumetric uptake (kg/m3)	
	excess	total	excess	total
1	2.60	2.60	26.94	26.95
5	3.20	3.21	33.37	33.43
10	3.39	3.40	35.38	35.48
20	3.56	3.57	37.26	37.41
30	3.70	3.72	38.77	38.97
40	3.75	3.77	39.27	39.51
50	3.82	3.85	40.13	40.43
100	3.94	3.94	41.37	41.94

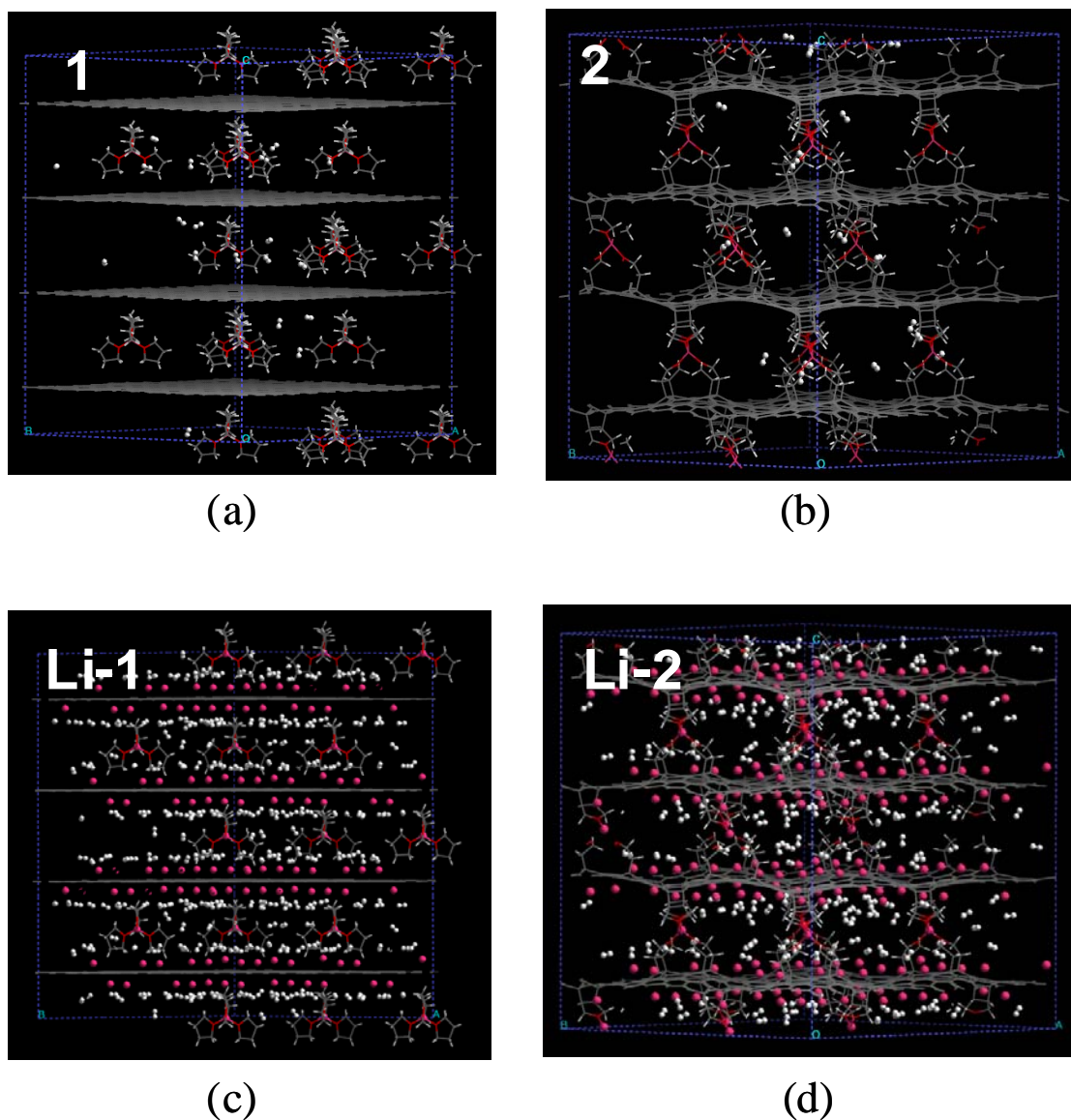S.8 H$_2$ adsorption sites in lithium-organic pillared graphite

Figure S2. GCMC snapshots of the structures of compounds **1** (a), **2** (b), **Li-1** (c), and **Li-2** (d) with adsorbed H$_2$ at 20 bar and 300 K. Here, the atoms are colored as follows: gray = C, red = O, pink = Li, and white = H. Note that H$_2$ molecules are adsorbed with a two-layer form in an interlayer space between two graphene layers, and most H$_2$ is positioned in a parallel orientation rather than in a vertical orientation.

S.9 References

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