Supplementary information

Mass transfer analysis of Boron-doped Carbon Nanotubes

Cathode for Dual-electrolyte Lithium-air Batteries

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1. **Modeling part**
2. **Analysis**

1. Modeling part

1.1 molecular dynamics
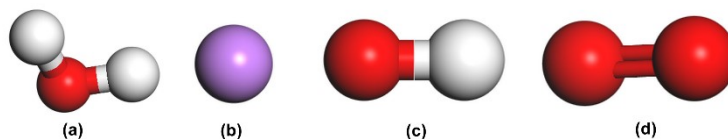
Fig. S1 Microscopic particles: (a)H_2O, (b)Li^+, (c)OH^-, (d)O_2.

The Universal force field was adopted in the model, the biggest advantage of which is full element coverage. The H_2O molecular model is an SPC/E model where the intermolecular forces were approximated by the Leonard-Jones potential and electrostatic interactions.

$$U_{ij} = 4\varepsilon_{ij}\left[(\frac{\sigma_{ij}}{r_{ij}})^{12} - (\frac{\sigma_{ij}}{r_{ij}})^6\right] + \sum_i\sum_j\frac{q_iq_j}{r_{ij}} \tag{1}$$

Where q_i and q_j are the charge of the i_{th} and j_{th} particle respectively, r_{ij} is the distance between particle i and particle j, ε_{ij} is the potential well depth of particle, σ_{ij} is the effective distance of particle. Parameters of each particle are shown in **Table S1**. m is the relative atomic mass of atom.

Table S1 Particle parameters.

| Name		ε/(KJ·mol^{-1})	σ/nm	m	q/e
H_2O	Ow	0.65	0.3166	16	-0.84
	Hw	0	0	1	+0.42
LiOH	OH	0.251	0.275		-1.1029
	Li	0.5	0.30	6.9	+0.6791
O_2	O	0.65	0.3166	16	0

1   The calculated water molecular bond length and bond angle are shown in Fig. 1(a).

2 The bond length of O-H is 0.990 Å, the bond angle of H-O-H is 104.510 °. They are

3 consistent with the conclusion of Zhou[1] et al and the experimental results. For BC_3, the

4 calculated bond length of B-C is 1.509 Å, the calculated bond angle of C-B-C is 119.2

5 °. As Fig. 1(b), they are consistent with the conclusion of Seifollah[2] et al. Therefore,

6 Universal force field is reliable for our system.

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(a)   (b)
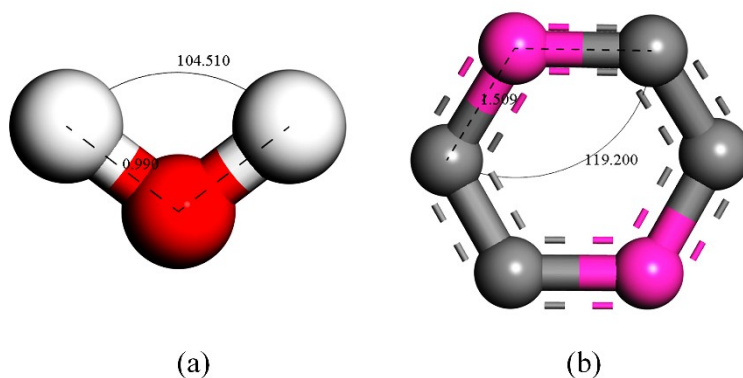
8   Fig.1 (a) Model of H_2O, (b) Structure of the ring.

9   The model was geometrically optimized, relaxed, and annealed to obtain a

10 relatively stable structure after it was established. The energy of the system was the

11 lowest, and the structure was relatively stable. This article used molecular dynamics to

12 simulate the particle motion process and uses isothermal molecular dynamics

13 simulation based on the Nosé-Hoover temperature-controlled NVT ensemble method.

14 The relaxing time step was 0.1 fs, and the total simulation time was 10 ps. The

15 molecular dynamics time step was 1 fs, and the total simulation time was 800 ps. The

16 Edward method was used for electrostatic interactions. For the intermolecular force

17 were needed to calculate, that was, the van der Waals interaction force, the cutoff

18 method used Atom-based cutoffs. Fig. 2 showed the energy changes during geometric

19 optimization, relaxation and molecular dynamics. In the process of geometric

1 optimization, the energy was gradually reduced to make the body shape more stable. It

2 could be seen from the energy change of the relaxation process and the dynamic process

3 that they both reached convergence.
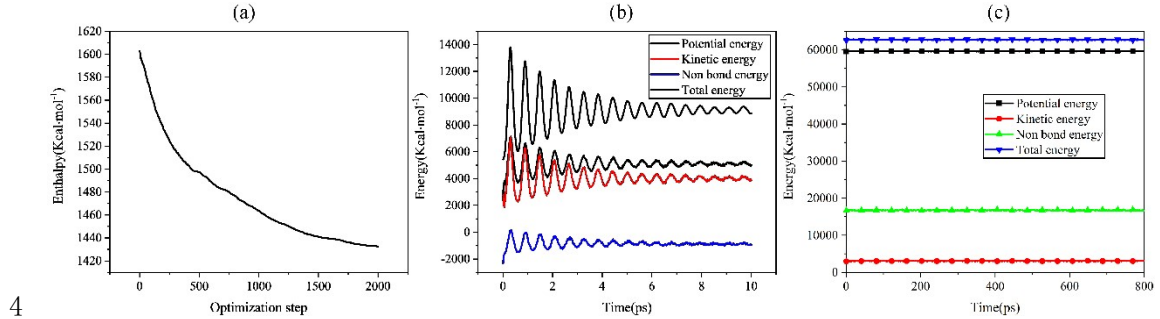
5 Fig. 2 Energy change process: (a) geometric optimization, (b) relaxation, (c) molecular dynamics.

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7 In this paper, according to Einstein's equation, the diffusion coefficient was

8 calculated by means of the mean square displacement (MSD) analysis method:

$$MSD(\Delta t) = \frac{1}{\tau - \Delta t} \int_{0}^{\tau - \Delta t} [r(t - \Delta t) - r(t)]^2 dt = \langle [r(t - \Delta t) - r(t)]^2 \rangle \qquad (2)$$

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$$D = \frac{1}{6} \lim_{\Delta t \to \infty} \frac{dMSD}{d\Delta t} \qquad (3)$$

10 Among them, $r(t)$ represents the coordinates of the molecule at time t, $r(t+\Delta t)$ represents

11 the coordinates of the molecule at time $t+\Delta t$, $[r(t-\Delta t)-r(t)]^2$ is the mean square

12 displacement, and τ is Total simulation time, N represents the total number of

13 molecules.

14 Radial distribution function calculation formula：

$$\rho g(r) 4\pi r^3 = dN \qquad (4)$$

15 ρ is the density of the system, when the number of molecules in the system is N:

$$\int_0^\infty \rho g(r) 4\pi r^3 = \int_0^N dN = N \tag{5}$$

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2 **1.2 DFT calculation**

3   The calculation method of the diffusion energy barrier of particles (such as

4 sidewall) is: First, placing the particles outside the nanotube, directly above the defect

5 ring, and perform geometric optimization to obtain the optimized structure of the

6 particles outside the nanotube. Then place the particles inside the nanotube, right above

7 the defect ring, and perform geometric optimization to obtain an optimized structure of

8 the particles inside the nanotube. Find the optimal path for particles to pass through the

9 defect ring from the outside to the inside, and search for the transition state on this path

10 to obtain the particle diffusion energy barrier. The transition state search includes LST

11 and QST methods
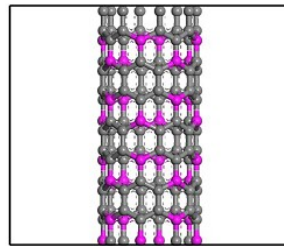
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13   Fig. 3 Model of nanotube
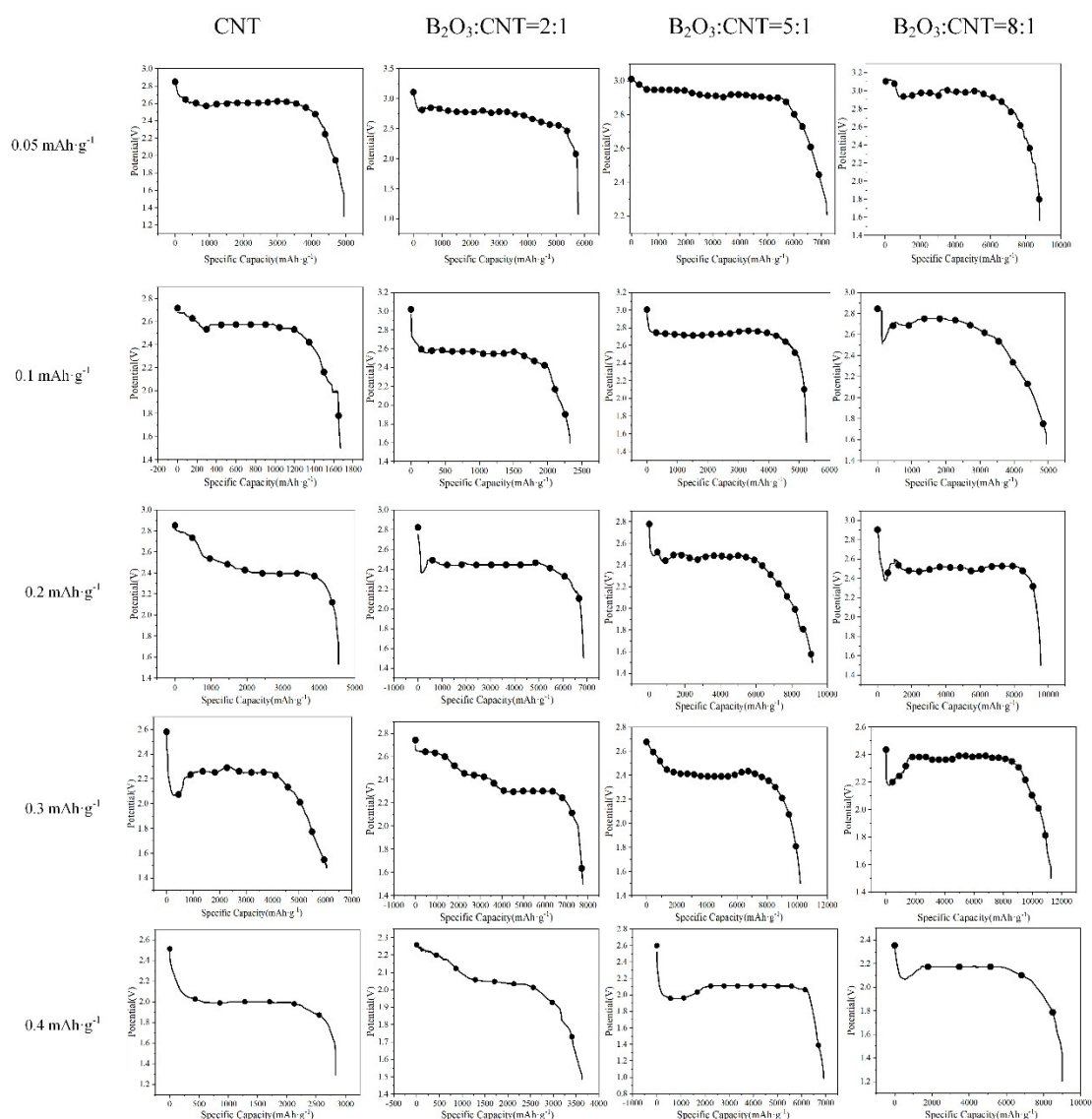14
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9 **2. Analysis**
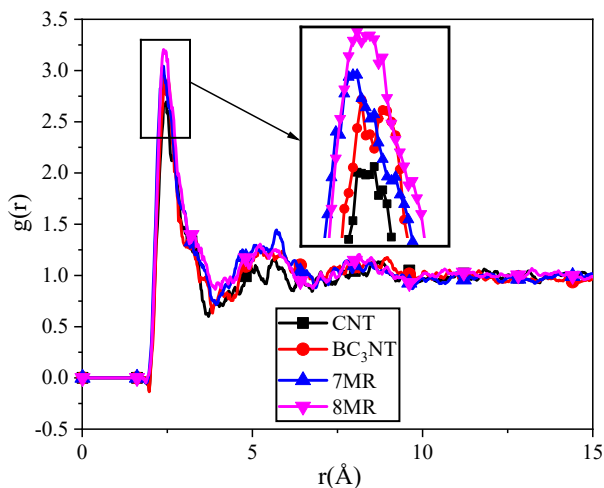

Fig. S2 The deep discharge diagram of the battery.

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Table S2 Impedence of interfacial transfer.

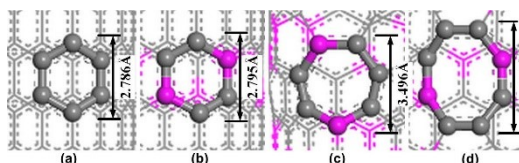|	CNT	B_2O_3:CNT=2:1	B_2O_3:CNT=2:1	B_2O_3:CNT=2:1
Impedence/Ω	309	283	146	134

Fig. S3 Radial distribution of Li^+-O_2.
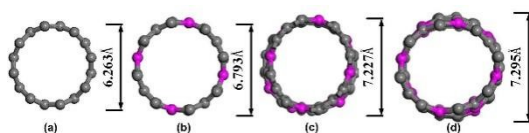

Fig. S4 Diameter of nanotube ring: (a)CNT, (b)BC_3NT, (c)7MR, (d)8MR.

Fig. S5 Diameter of nanotubes (a)CNT, (b)BC_3NT, (c)7MR, (d)8MR.

1 J. Zhou, X. Lu, Y. Wang and J. Shi, *Fluid Phase Equilibria*, 2002, **194–197**, 257–270.

2 S. Jalili, E. Hosseinzadeh and J. Schofield, *Chemical Physics*, 2014, **438**, 16–22.