Supporting information for:

Compactness of the Lithium Peroxide Thin Film Formed in Li-O_2 Batteries and Its Link to Charge Transport Mechanism: Insights from Stochastic Simulations

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Deduction of Jumping Frequency

All the mobile species can move to the neighbor grid units which are occupied by solvent molecules. The rate of the translation is described by the jump frequency (v_j), which can be obtained from the Einstein equation of random walk

$$v_j = \frac{2D}{z^2} \qquad [S1]$$

where z is the size of the grid unit and D is the diffusion coefficient given by the Stokes-Einstein equation

$$D = \frac{kT}{6\pi\mu r} \qquad [S2]$$

where k is the Boltzmann constant, T is temperature, μ is the viscosity of the electrolyte and r is the hydrodynamic radius of the concerned species. Combining equations S1 and S2, we have

$$v_j = \frac{kT}{3\pi\mu r z^2} \qquad [S3]$$

Collective Motion of Li^+

To improve the simulation efficiency, in the present work, the motion of Li^+ in the electrolyte is described in a collective way. Instead of the displacement of individual Li^+, the collective motion of Li^+ is achieved by shuffling the Li^+ distribution after a certain duration of simulation time, during which the Li^+ is considered to be immobile. The demonstration of collective motion approach here refers to cylindrical pores and the wall of the pore is carbon. Same approach is applied to the CNF system as presented in the paper.

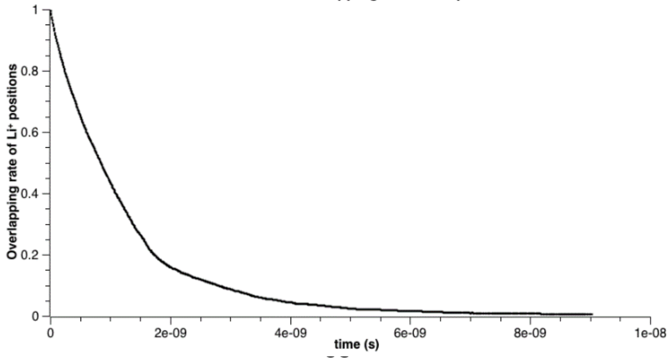
There are two important criteria to apply the Li^+ collective motions procedure. Firstly, the Li^+ displacement should be overwhelming comparing to any other events in the model. Secondly, the spatial distribution of Li^+ should be homogeneous. To apply the collective motion procedure, the overlapping rate of Li^+ in the system between two random fillings is defined (**Table S1**). At the same time, simulations considering the displacement of individual Li^+ are conducted to track the evolution of the Li^+ overlapping ratio comparing to its initial configuration. A typical example for a cylindrical pore with a diameter of 20 nm and length of 40 nm is shown in **Figure S1**. Then, the shuffling time step for a certain system is obtained by finding the time corresponding to the overlapping rate of Li^+ between two random fillings.

Table S2 The overlapping rates of Li^+ positions between two random fillings in cylinders with different diameters but the same length of 40 nm; the overlapping rates are mean values after 500

Diameter / nm	10	20	30	40	50	60
Overlapping ratio	7.73%	7.17%	7.81%	8.51%	8.30%	8.47%
Standard deviation	0.60%	0.30%	0.21%	0.15%	0.14%	0.13%

iterations.

Figure S1 The evolution of the Li^+ overlapping rate; cylinder diameter is 20 nm, length is 40 nm,



Li^+ concentration is 1 M, Li^+ jump frequency is 1×10^{10} s^{-1}

Table S3 The time steps of Li^+ collective motion in cylinders with several diameters and same length of 40 nm; Li^+ concentration is 1 M, Li^+ jump frequency is 1×10^{10} s^{-1}.

Diameter (nm)	10	20	30	40	50	60
Time step (ns)	6.049	6.427	6.549	6.611	6.434	6.587
Standard deviation (ns)	0.268	0.131	0.091	0.053	0.052	0.045

Flow-Chart of the Model

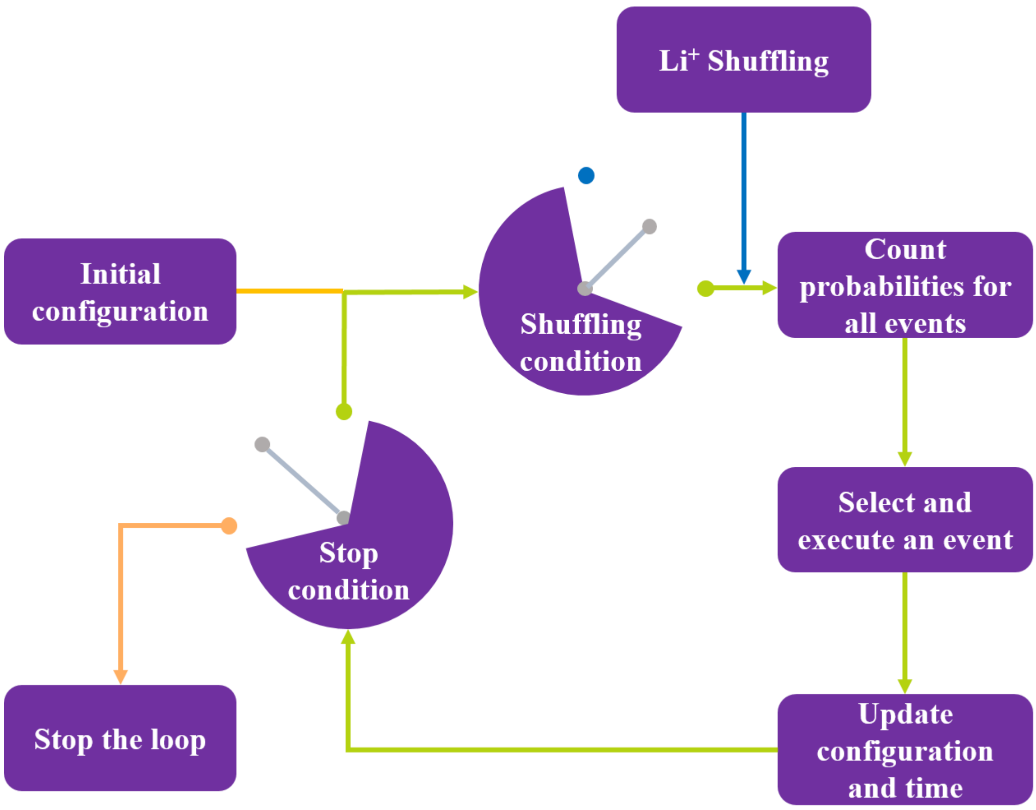


Figure S2 Flow-chart of the model.

Li_2O_2 Formation on CNF with High Diffusion Rate of $LiO_{2(ip)}$

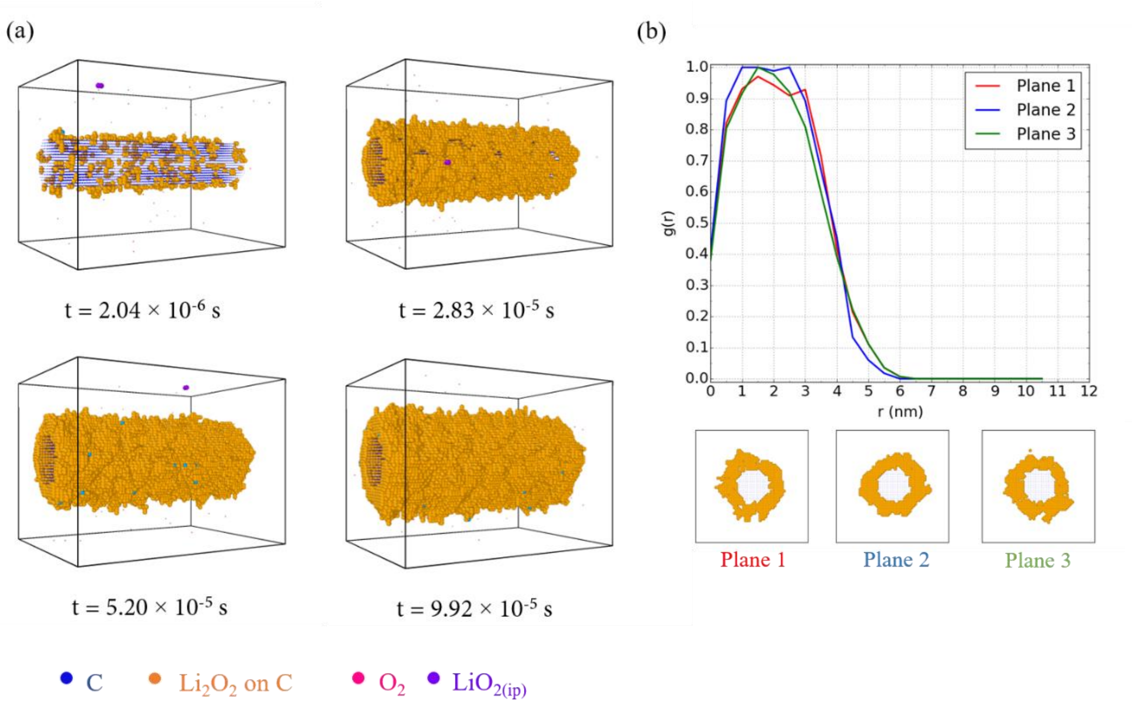


Figure S3 The evolution of the Li_2O_2 thin film formation and RDF analysis at fully-discharged state on cat-CNF with high diffusion rate of $LiO_{2(ip)}$ The diameter and the length of the fiber are 8 nm and 40 nm, the dimensions of the cell are 30×30×40 nm in height, depth and length and the diffusion coefficient of $LiO_{2(ip)}$ is 1×10^{-10} m^2 s^{-1}. The Planes 1, 2 and 3 correspond to the intersection of the nanofiber at 5, 20 and 35 nm, respectively. The compactness of the Li_2O_2 is high regardless the higher of $LiO_{2(ip)}$ diffusion rate.