Supporting Information

Lithium-Air Capacitor-Battery based on Hybrid Electrolyte

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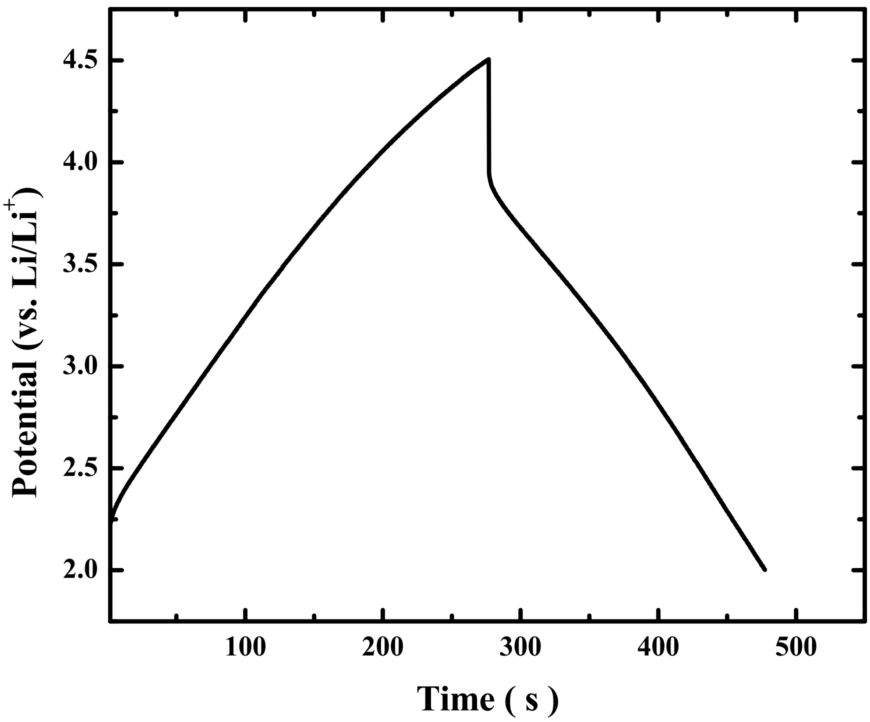

Figure S1 Charge-discharge curve of the capacitor electrode with a current of 20mA in organic electrolyte solution. A composite electrode was used for charge-discharge test. This electrode was prepared as follows. A mixture containing 85 wt.% of activated carbon (AC), 5 wt.% of acetylene black, and 10 wt.% of polytetrafluoroethylene (PTFE) was well mixed and then pressed onto a titanium mesh (100 mesh) which served as a current collector. The mass loading of the AC within the prepared composite electrode was 10mA/cm^2. The area of electrode is 2 cm^2. Lithium metal was used as both counter electrode and reference electrode. The electrolyte was 1m $LiClO_4$ in ethylene carbonate/dimethyl carbonate (1/1 by volume).

The special capacitance of the activated carbon can be calculated as:

$$C_m = \frac{C}{m} = \frac{I \times t}{\triangle V \times m} \qquad (1)$$

Where, I is charge-discharge current (20mA), t is the discharge time, ΔV is 2.5 V, m is 20 mg. According to equation 1, the calculated capacitance of AC is 80 F/g. The total capacitance of the AC is 1.6 F (= 80F/g × 0.02 g).

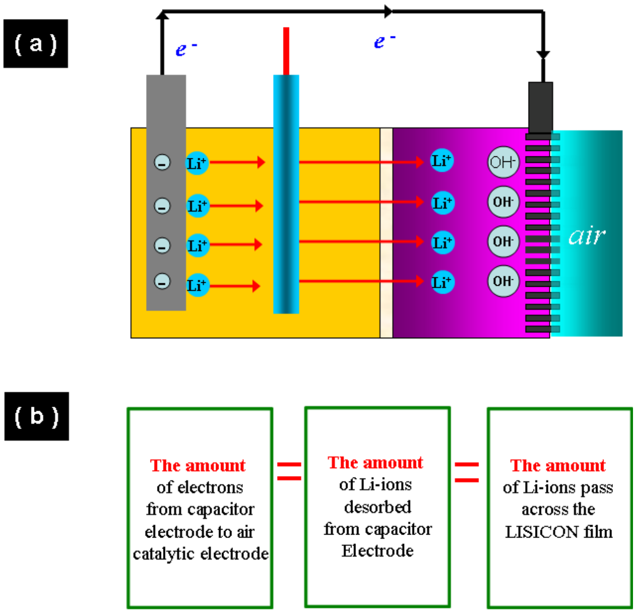

Figure S2 (a) Schematic showing the operating principle of self-charge process **(It is sample version of Fig. 2 c);** (b) charge transfer on the self-charge process within a definite time

As mentioned in discussion of Fig.6, there should be a potential difference between the air catalyst electrode and capacitor electrode in a very short time just after high current discharge process. At this situation, the lithium-carbon capacitor should be charged by the lithium-air battery. On self-charge process, the electrons flow from capacitor electrode to the air catalytic electrode (See Figure S2a; It is sample version of Fig. 2 c). Within the air catalyst electrode, O_2 from air is reduced into OH^- after coupling electrons from the capacitor electrode with desorbing lithium-ions from the surface of the capacitor electrode. Then, these desorbed lithium-ions diffuse from organic electrolyte to aqueous electrolyte. The charge transfer on the self-charge process within a definite time can be summarized as Figure S2 b.

The self-charge rate should depend on the charge current (= the amount of charge transfer within a definite time). However, as shown in Figure S2b, the self-charge current is limited by the poor conductivity of ceramic LISICON film. Thereby, device can not be self-charged back to ~ 3V after 5 minutes post-rest step, although capacity of the Li-air battery is much higher than that of supercapacitor. Certainly, if the longer post-rest step is applied, the device would be self-charged to initial cell voltage (3.3 V) of Li-air battery. It is also very important to optimize the mass or area ratio of the capacitor electrode to the air electrode to improve this self-charge process. This is because that the capacitance (F) of capacitor electrode is potential dependence. The recovered potential ($\triangle V$) of the electrode can be calculated as following equations:

$$C = \frac{Q}{\Delta V} = \frac{I \times t}{\Delta V} \qquad (1)$$

$$\Delta V = \frac{Q}{C} = \frac{I \times t}{C} \qquad (2)$$

Where ΔV is the voltage difference between the beginning and end of self-charge process (V), I is self-charge current (A), t is self-charge time (= the time of rest step = 300 seconds), and C is the capacitance (F) of capacitor electrode. According to equation (2), the growth of ΔV is proportional to I, $1/C$ and t. For present device, the self-charge current (I) is still limited by the poor conductivity of ceramic LISICON film. Accordingly, it can not be self-charge to its initial voltage (3.3 V) within 5 minutes. On the other hand, it can also improve the self-charge rate to reduce the capacitance value (*C*) by varying the mass and/or area of the capacitor electrode. Thereby, in the future study, it is necessary to further the conductivity of LISICON film and optimize the mass or area ratio of the capacitor electrode to the air electrode. Certainly, if the longer rest step is applied, the device would be self-charged to initial cell voltage (3.3 V).

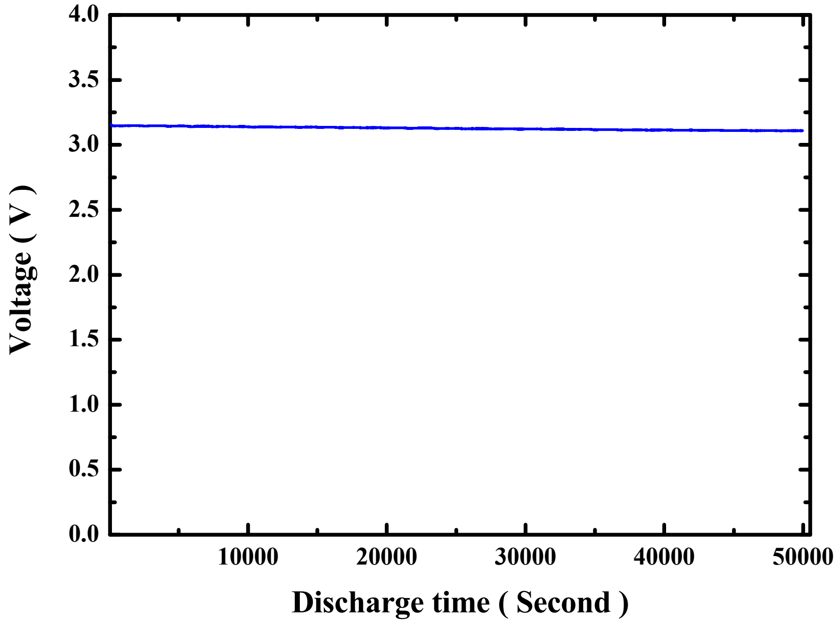

Figure S3 long-time discharge curve of lithium-air capacitor-battery with a low discharge current of 0.5 mA. After the power tests (shown in Fig. 3a), the voltage of the prepared lithium-air capacitor-battery recovered to its initial state with a long-time rest step. Then, we took a long-time discharge with low discharge current of 0.5 mA. The result is given in Figure S2.