# Electronic Supporting Information (ESI)

**A quasi-solid-state Li-ion capacitor of high energy density based on $Li_3VO_4$/carbon nanofibers and electrochemically-exfoliated graphene sheets**

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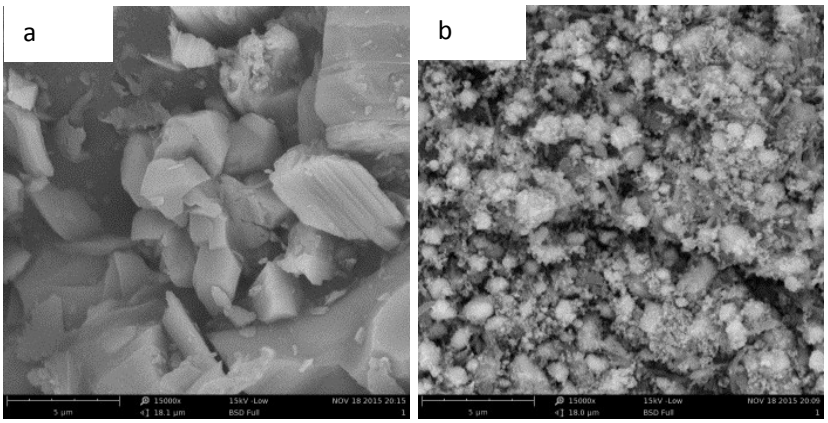


Figure S1. SEM micrographs of the (a) $Li_3VO_4$ and (b) $Li_3VO_4$/CNFs.

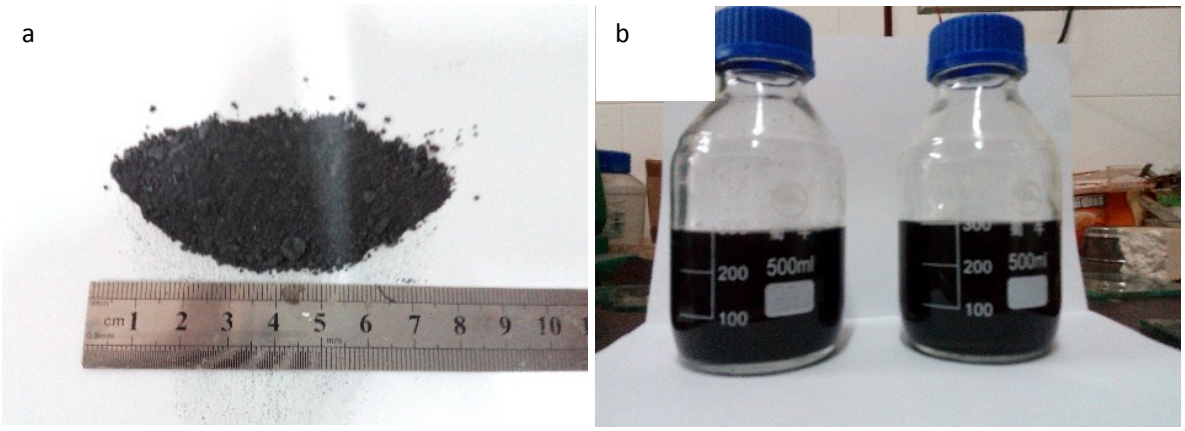


Figure S2. Optical photographs showing a high production of the (a) $Li_3VO_4$/CNFs and (b) graphene prepared by electrochemical exfoliation.

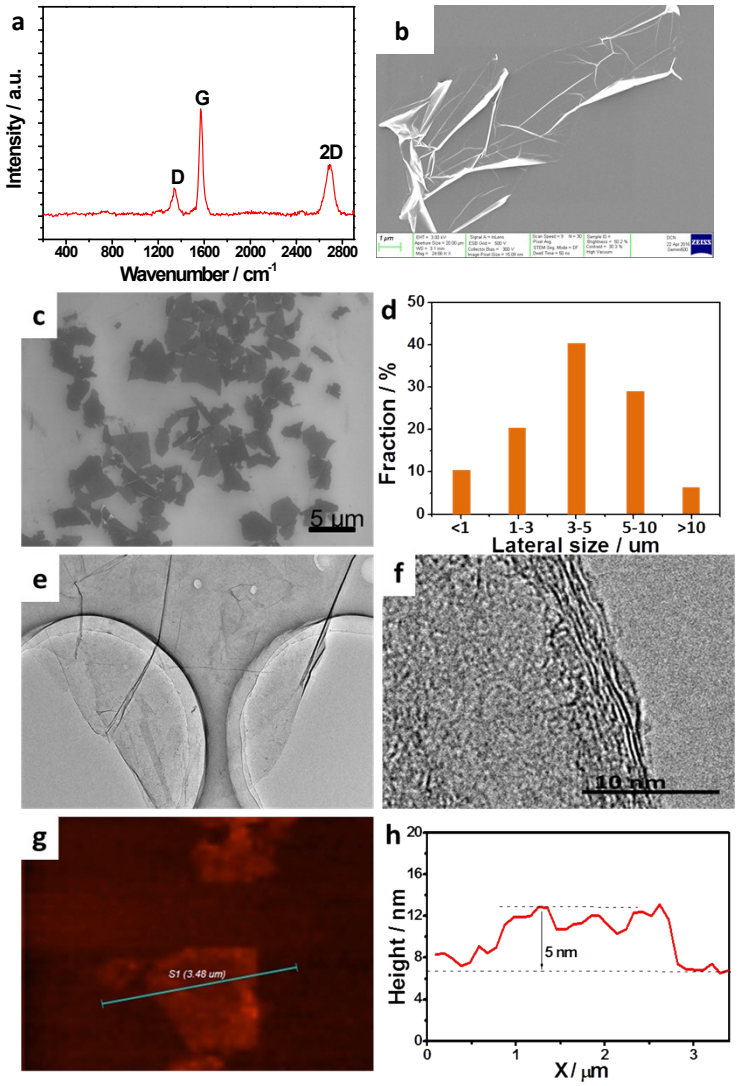


Figure S3. Physical characterization of electrochemically-exfoliated graphene sheets. (a) Raman spectrum. SEM micrographs on (b) conductive plastic and (c) $Si/SiO_2$ wafer. (d) Statistical calculation of flake sizes from SEM micrograph from $Si/SiO_2$ wafer. (e) TEM and (f) HRTEM micrographs. (g) AFM image and (h) the corresponding height profile.

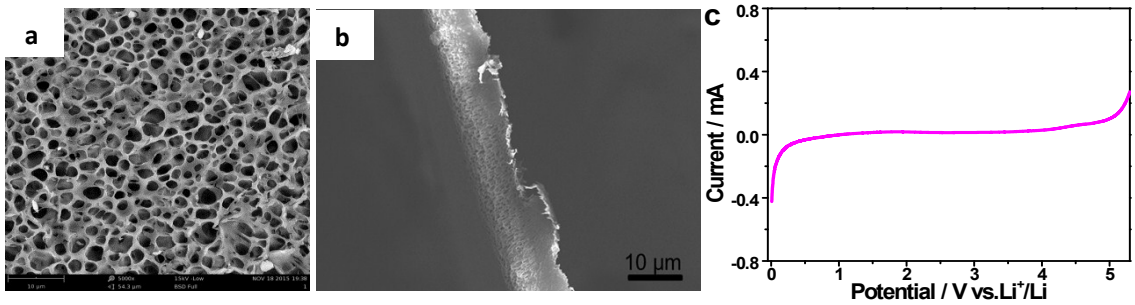


Figure S4. (a) and (b) SEM micrographs of the polymer matrix for Li-ion conducting gel polymer electrolyte and (c) linear sweep voltammogram at a scan rate of 2 m $V^{-1}$ for the gel polymer electrolyte.

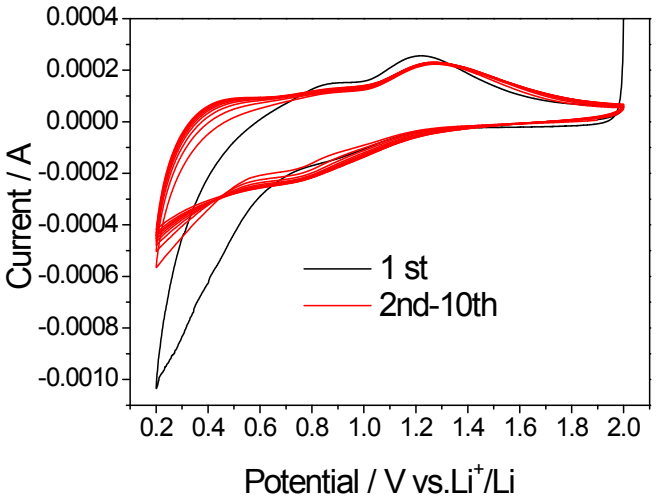


Figure S5. CV curves of the initial ten cycles for the $Li_3VO_4$/CNFs composites anode.

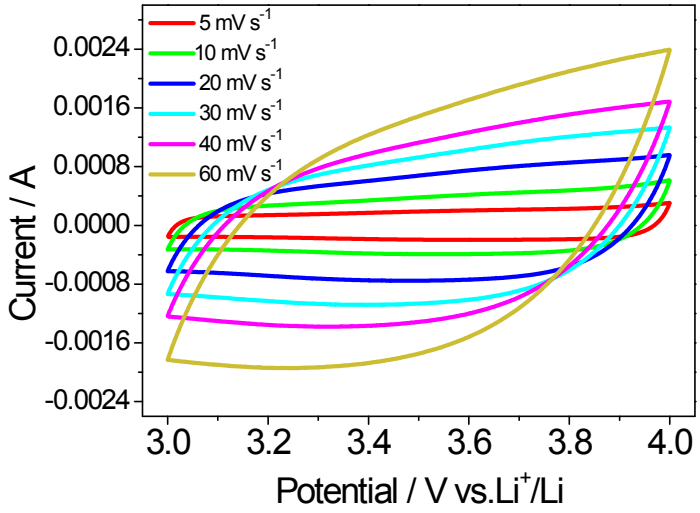


Figure S6. CV curves of electrochemically-exfoliated graphene sheets at different scan rates.

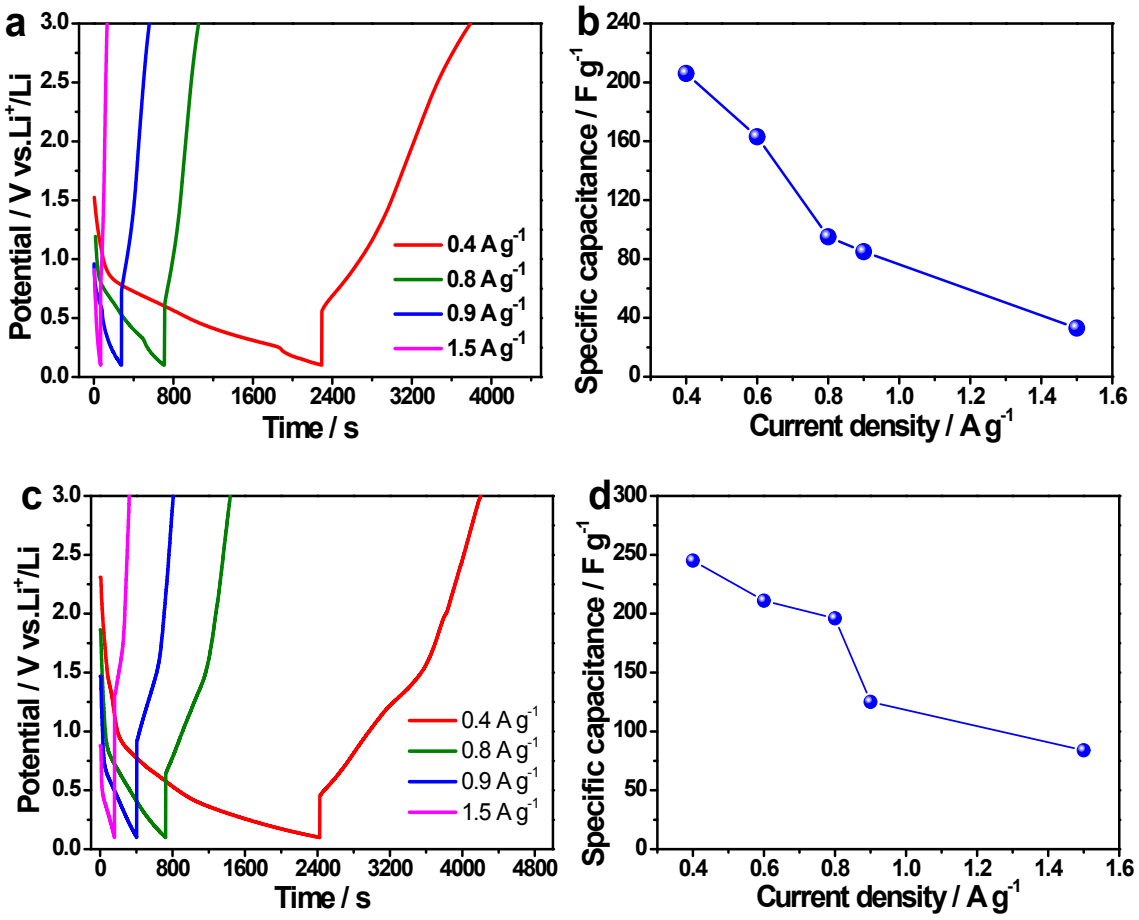


Figure S7. Galvanostatic charge/discharge curves and specific capacitance of the pure $Li_3VO_4$ (a,b) before and (c,d) after ball-milling without CNFs at different current densities.

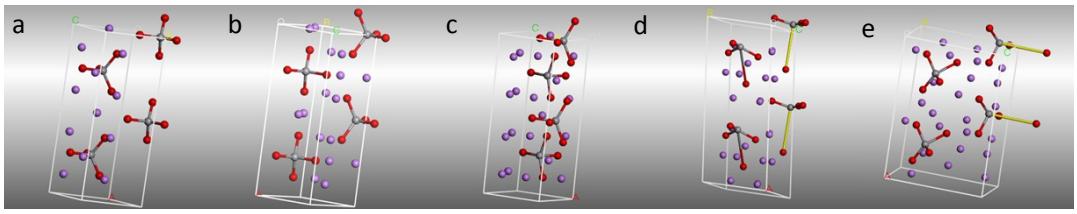


Figure S8. (a–e) Optimized structures with 0, 1, 2, 2.5, 3 $Li^+$ ions in [4($Li_3VO_4$)]. The purple, red, and gray balls correspond to Li, O, and V atoms, respectively. The selected bond of V-O (in yellow) is also illustrated.

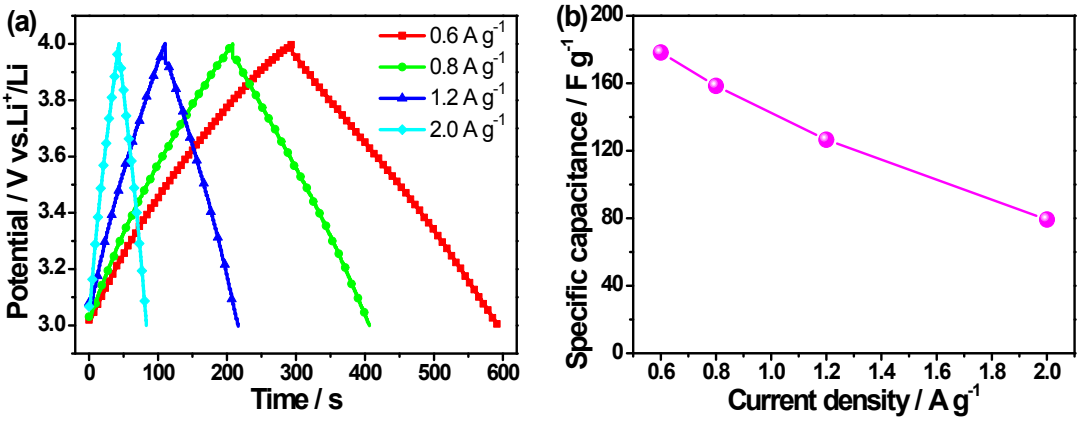


Figure S9. (a) Galvanostatic charge/discharge curves of electrochemically-exfoliated graphene sheets, and (b) specific capacitance of the electrochemically-exfoliated graphene sheets at different current densities.

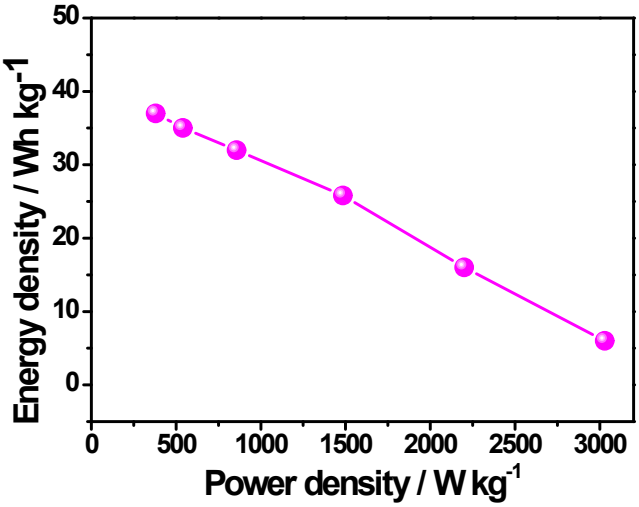


Figure S10. Ragone plots of the graphene//graphene symmetric supercapacitor in gel polymer electrolyte.

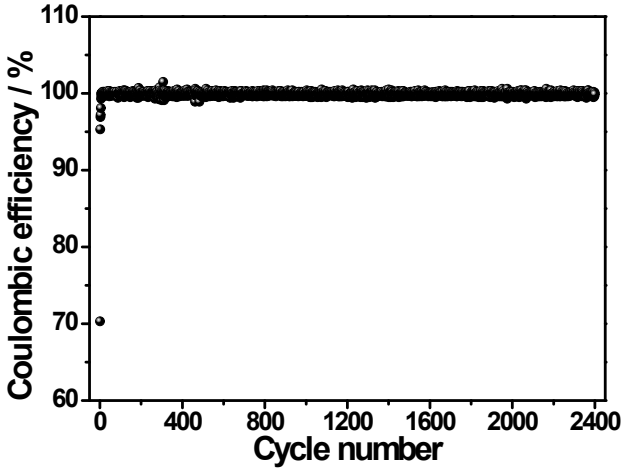


Figure S11. The Coulombic efficiency of the quasi-solid-state Li ion capacitor at 0.4 A $g^{-1}$.

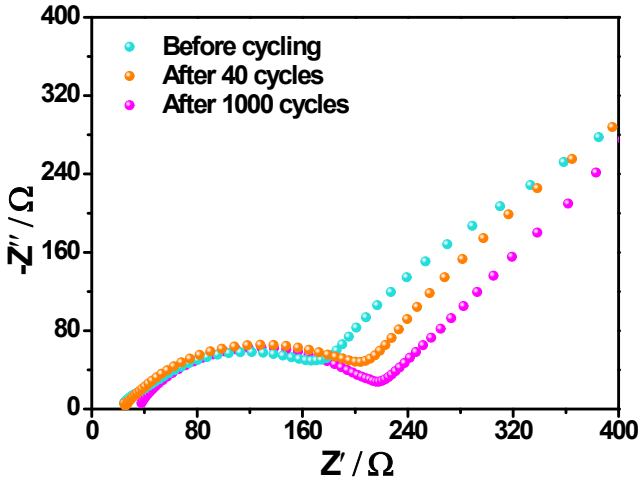


Figure S12. Nyquist plots of the fabricated quasi-solid-state LICs.

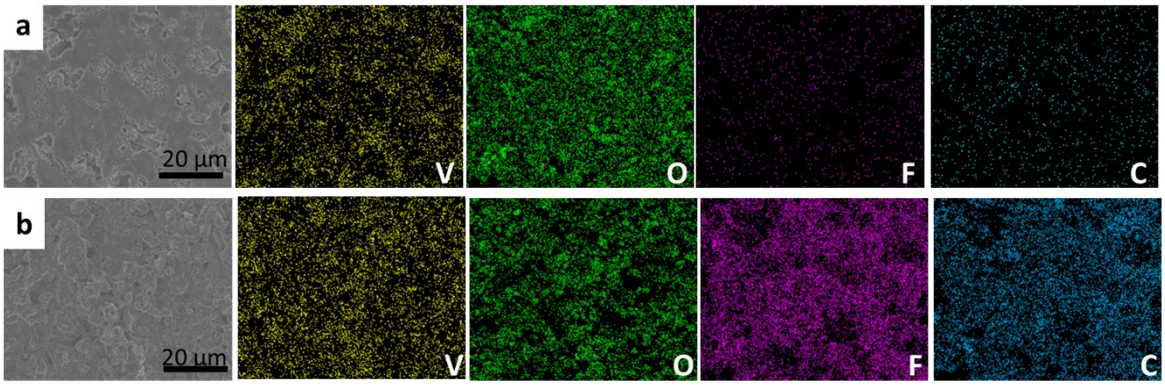


Figure S13. SEM images and elemental mapping images of the $Li_3VO_4$/CNFs electrodes (a) before and (b) after 1000 cycles.

Figure S14. Two optical photographs showing a lighted white LEDs (3V), which was powered by the quasi-solid-state Li ion capacitor.

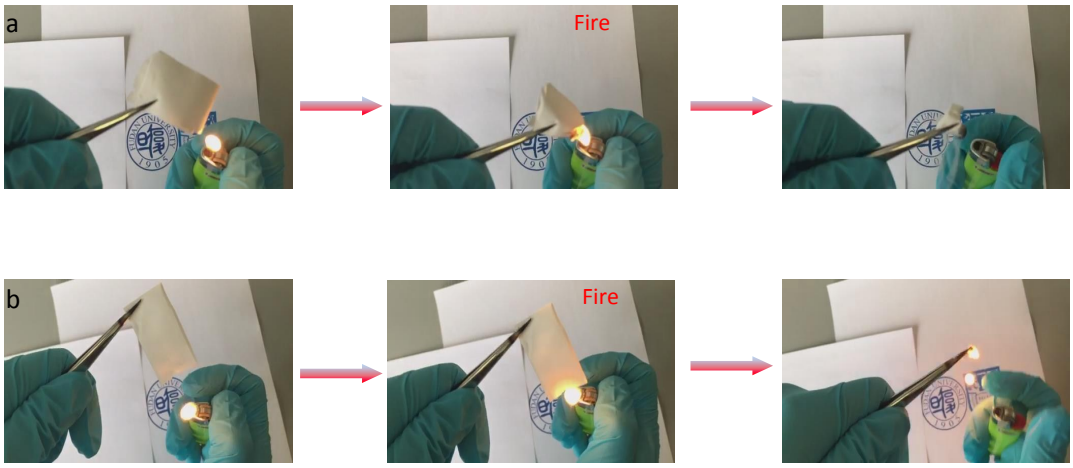


Figure S15. The combustion tests of the matrix for (a) our gel polymer electrolyte and (b) liquid electrolyte.

| | a, Å | b, Å | c, Å | α | β | γ | Space group | V-O,Å |
|---|---|---|---|---|---|---|---|---|
| $Li_3VO_4$ | 12.81 | 5.52 | 5.06 | 90.00 | 90.00 | 90.00 | Pmn21 | 1.73 |
| $Li_{3+1}VO_4$ | 12.70 | 5.41 | 5.82 | 90.49 | 90.42 | 89.13 | P1 | 1.83 |
| $Li_{3+2}VO_4$ | 12.72 | 5.40 | 6.20 | 90.00 | 90.00 | 90.00 | Pmn21 | 2.04 |
| $Li_{3+2.5}VO_4$ | 15.03 | 5.39 | 6.19 | 90.00 | 70.80 | 90.00 | PM | 4.00 |
| $Li_{3+3}VO_4$ | 12.07 | 5.34 | 8.11 | 84.59 | 89.36 | 91.70 | P1 | 3.87 |

Table S1. Calculated lattice parameters, cell volumes and suggested space groups for the lithium inserted phases.

| LIC | Electrolyte | Energy density / Wh $kg^{-1}$ | Power density /W $kg^{-1}$ | Cycle | Ref. |
|---|---|---|---|---|---|
| $TiO_2$-CNT//AC | $LiPF_6$ | 60 | 120 000 | 87% after 1000 | *Adv. Mater.* **2014**, *26*, 339. |
| $TiNb_2O_7$-carbon//CF | $LiPF_6$ | 110 | 5464 | 77% after 1500 | *Nano Energy* **2015**, *15*, 104. |
| Graphite//N-doped C-graphene | $LiPF_6$ | 80 | 352 000 | 93% after 4000 | *Nano Energy* **2015**, *15*, 43. |
| $Nb_2O_5$-C//AC | $LiPF_6$ | 48 | 14164 | 93% after 1000 | *ACS Nano* **2014**, *8*, 8968. |
| $TiO_2$//AC | $LiPF_6$ | 42 | 8000 | 80% after 100 | *Adv. Energy Mater.* **2013**, *3*, 1500. |
| $Fe_3O_4$-graphene//graphene | $LiPF_6$ | 204 | 4600 | 70% after 1000 | *Energy Environ. Sci.* **2013,** *6*, 1623. |
| AC//$LiNi_{0.5}Mn_{1.5}O_4$ | $LiPF_6$ | 30 | 19000 | 81% after 3000 | *Nano Energy* **2015**, *12*, 69. |
| **$Li_3VO_4$-CNF//graphene** | **GPE** | **110** | **3870** | **86% after 2400** | **This work** |

Table S2. The summary of electrochemical performances comparison between our designed quasi-solid-state LIC and other LICs in liquid electrolytes. Note: CNT=carbon nanotubes, AC= activated carbon, CNF= carbon nanofiber, GPE=Gel polymer electrolyte. The values of energy densities are based on the total mass of the cathode and the anode, not including the electrolytes. Energy density and power density mean the maximum value reported in these references.