

Supporting Information

High-Power Na-Ion and K-ion Hybrid Capacitors Exploiting Cointercalation in Graphite Negative Electrodes

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Experimental section

1. Materials

Natural graphite (SLP-30, IMERYYS), activated carbon (YP-47, KURARAY CO.), sodium carboxymethyl cellulose (CMC, Dow Wolff Cellulosics), carbon black (Super C45, IMERYYS Graphite & Carbon), dendritic copper foil (Schlenk), aluminum foil (Hydro), sodium metal (Acros Organics, 99.8%), glass fiber sheet (Whatman GF/D), sodium hexafluorophosphate (NaPF_6 , FluoroChem, battery grade), potassium metal (Sigma-Aldrich, 99.5%), potassium hexafluorophosphate (KPF_6 , Sigma-Aldrich, 99.5%), dimethyl carbonate (DMC, UBE) were directly used without further purification. Diethylene glycol dimethyl ether (diglyme, Sigma-Aldrich, anhydrous, 99.5%) was dried using molecular sieves (Merck, 3 Å) for 3 days to remove the residual water in the solvent before it was used to prepare the electrolytes.

2. Characterization

Scanning electron microscope (SEM) of the SLP-30 graphite was performed on a Zeiss LEO 1550 microscope. X-ray diffraction was conducted using a Bruker D8 Advance diffractometer (Bruker, Germany) with $\text{Cu-K}\alpha$ radiation. The electrodes for the ex-situ XRD were taken from the cells, which were disassembled in an Ar-filled glove box with H_2O and O_2 levels of <0.1 ppm. The obtained electrodes were thoroughly washed with DMC, which was finally removed under vacuum. During the XRD measurement, the electrodes were kept in a closed sample holder filled with argon.

3. Fabrication of the electrodes

The electrodes were fabricated via doctor-blade casting of the aqueous slurries on metallic current collectors. For graphite electrodes, the dendritic copper foil and aluminium foil were used as the current collector, and the electrodes contain 95 wt % graphite, 3 wt % C45, and 2 wt % CMC binder. Without further notification, the graphite electrodes with dendritic copper foil were used. For activated carbon electrodes, aluminum foil was used as

the current collector, and the electrodes consist of 90 wt % activated carbon, 5 wt % C45, and 5 wt % CMC. After the evaporation of water solvent in an oven at 80 °C, electrodes with a diameter of 12 mm were punched and further dried at 120 °C under vacuum for 12 h. After being weighted in the dry room, the electrodes were further dried at 120 °C under vacuum for 4 h, and then transferred to an Ar-filled glovebox with H₂O and O₂ levels of <0.1 ppm for use. The average mass loadings of graphite and activated carbon are around 1.1 and 3.1 mg cm⁻², respectively.

4. Cell assembly

All the cell assembly was carried out in an Ar-filled glove box with H₂O and O₂ levels of <0.1 ppm.

4.1. Fabrication of half-cells

To evaluate the capacity and electrochemical behavior of as-fabricated graphite electrodes and activated carbon electrodes separately, three electrode Swagelok-type cells were assembled. For sodium-based cells, sodium metal was used as both the counter and reference electrodes. The as-fabricated graphite electrodes or activated carbon electrodes were used as the working electrodes. GF/D disks served as separators. For each cell, 150 μL of 1 M NaPF₆ in diglyme electrolyte solution was added. For potassium-based cells, the configuration is very similar to the sodium-based cells. The sodium counter and reference electrodes were replaced with potassium metal, and the 1 M NaPF₆ in diglyme electrolyte was replaced with 1 M KPF₆ in diglyme.

4.2. Fabrication of SIHCs and PIHCs

For full cell tests, CR2032-type coin cells were assembled using as-fabricated graphite electrodes as anodes, activated carbon electrodes as cathodes, and GF/D disks as separators. In each SIHC, 150 μL of 1 M NaPF₆ in diglyme was added as the electrolyte. For each PIHC, 150 μL of 1 M KPF₆ in diglyme were added as the electrolyte.

4.3. Electrochemical measurements

The rate performance and cycling ability of the assembled cells were evaluated via the MACCOR series 4000 battery cycler. Cyclic voltammetry (CV) measurements were conducted using the galvanostat/potentiostat VMP2 (Bio-Logic, France). In order to enhance the stability of sodium and potassium anodes, the three electrode Swagelok-type cells were held at its open circuit voltage (OCV) for 6 hours before any electrochemical measurements. But for as-assembled SIHCs and PIHCs, such the OCV process was not applied.

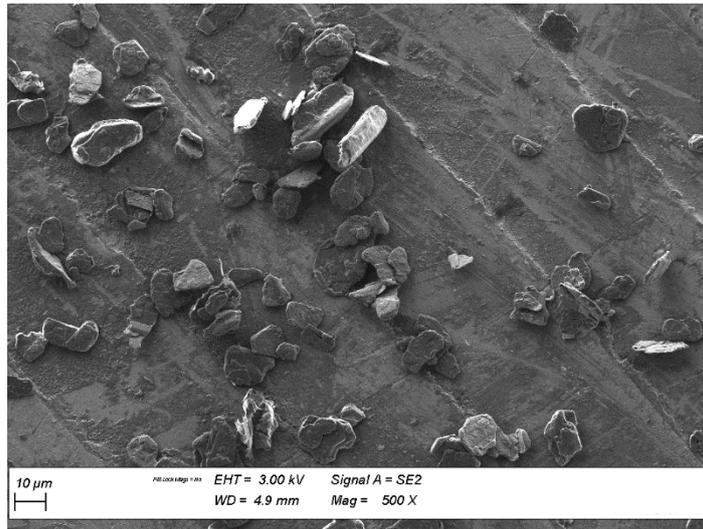


Figure S1. SEM image of the graphite (SLP-30, IMERYS).

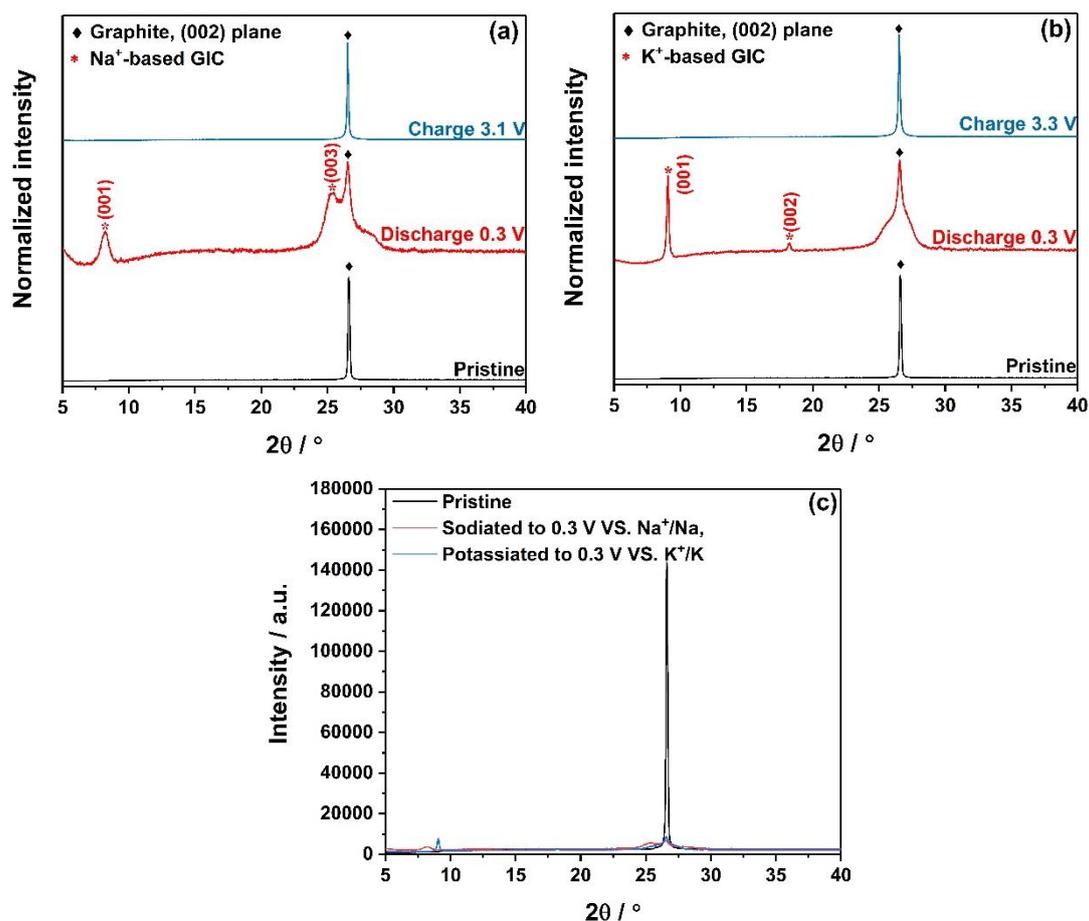


Figure S2. (a) Normalized XRD patterns of pristine, sodiated, and de-sodiated graphite electrodes. (b) Normalized XRD patterns of pristine, potassiated, and de-potassiated graphite electrodes. (c) XRD patterns of pristine, sodiated, and potassiated graphite electrodes.

Fig. S2(a) exhibits the normalized XRD patterns of pristine, sodiated, and de-sodiated electrodes. In 5-40° of pristine electrode, only a sharp peak at 26.6°, corresponding to the (002) plane of graphite, is observed in the pattern. After being discharged to 0.3 V vs. Na⁺/Na, two peaks at 8.2° and 25.2° appear, corresponding to the (001) and (003) plane of one layered compound with an interlayer distance of 10.78 Å which is very close to the reported value, 11.62 Å, of stage 1 Na-diglyme-graphite ternary graphite intercalated compounds (GICs) (*Energy Environ. Sci.* 2015, 8, 2963). Although a strong graphite peak is still observed, its intensity is ten times lower than that of pristine electrode (Fig. S2(c)). After being charged to 3.1 V vs. Na⁺/Na, the peaks from the GICs totally disappear, indicating the high reversibility

and matching well with the high coulombic efficiency. The similar phenomenon can be observed from Fig. S2(b) showing the normalized XRD patterns of potassiated and depotassiated electrodes. For the formed K^+ -based GIC, the interlayer distance is 9.75 Å. The different interlayer distance of the Na^+ -GIC and K^+ -GIC may result from different coordination of the diglyme- Na^+ and diglyme- K^+ or different geometry of the GICs. These results demonstrate that the sodium and potassium storage mechanism of graphite is quite similar and highly reversible.

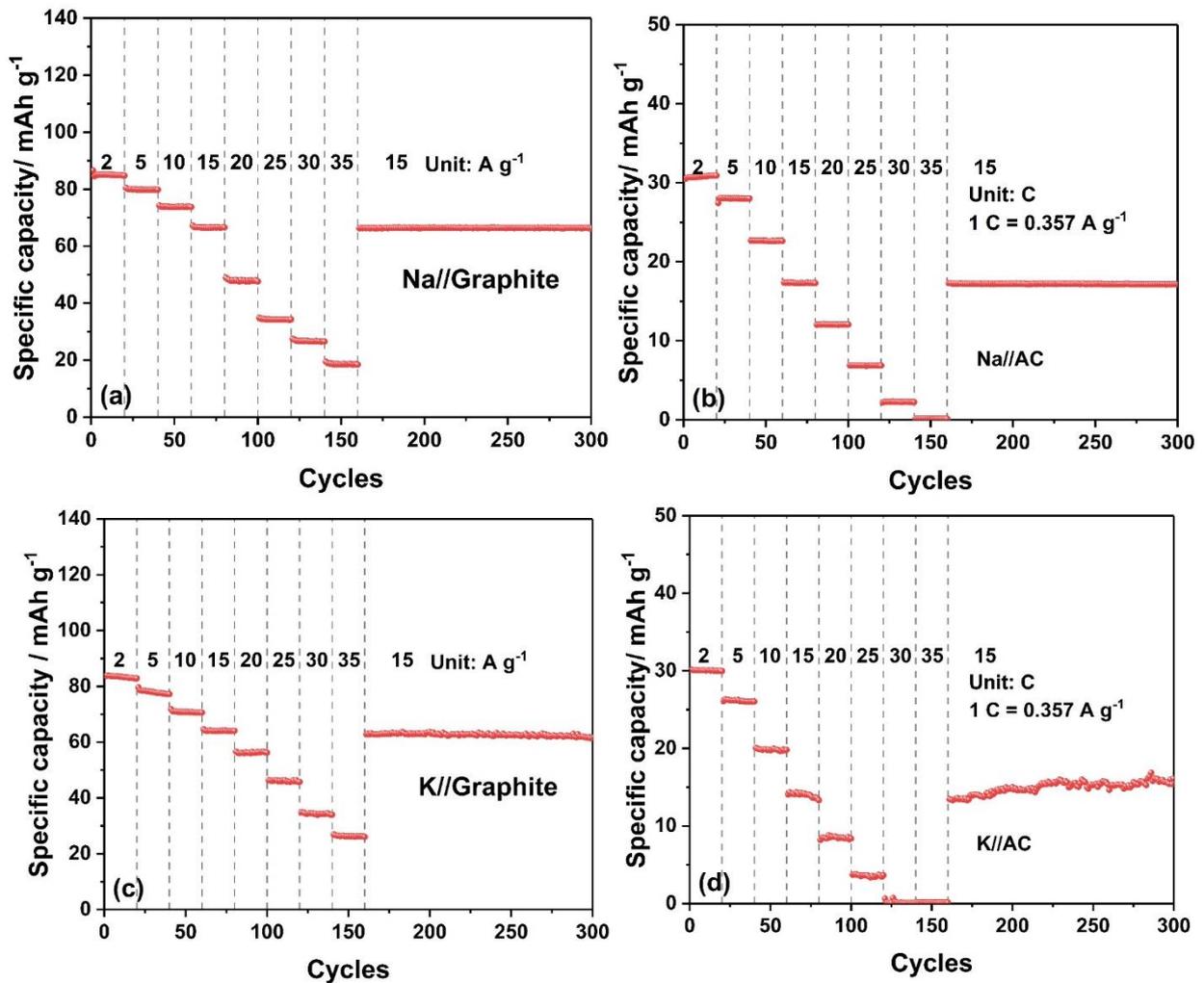


Fig. S3. Specific discharge capacity of graphite in (a) Na//graphite and (c) K//graphite half-cells, and AC in (b) Na//AC and (d) K//AC half-cells at different currents.

Comparing the capacity of the graphite in half-cells with that in SIHC and PIHC (Fig. 3(a)), one can find that at specific currents larger than $10 \text{ A g}_{\text{graphite}}^{-1}$, the capacity in half-cells is much lower. The situation is more severe for AC electrodes. One possible reason is that the kinetics of metallic counter cannot catch up the reaction on working electrode sides. Hence, the obtained capacity cannot reflect the real storage ability of as-fabricated graphite and AC electrodes. Because of the poor kinetics and stability of potassium counter in the electrolyte of 1 M KPF_6 in diglyme, coulombic efficiency is in chaos after tens cycles. Hence, the CE of these cells are not displayed.

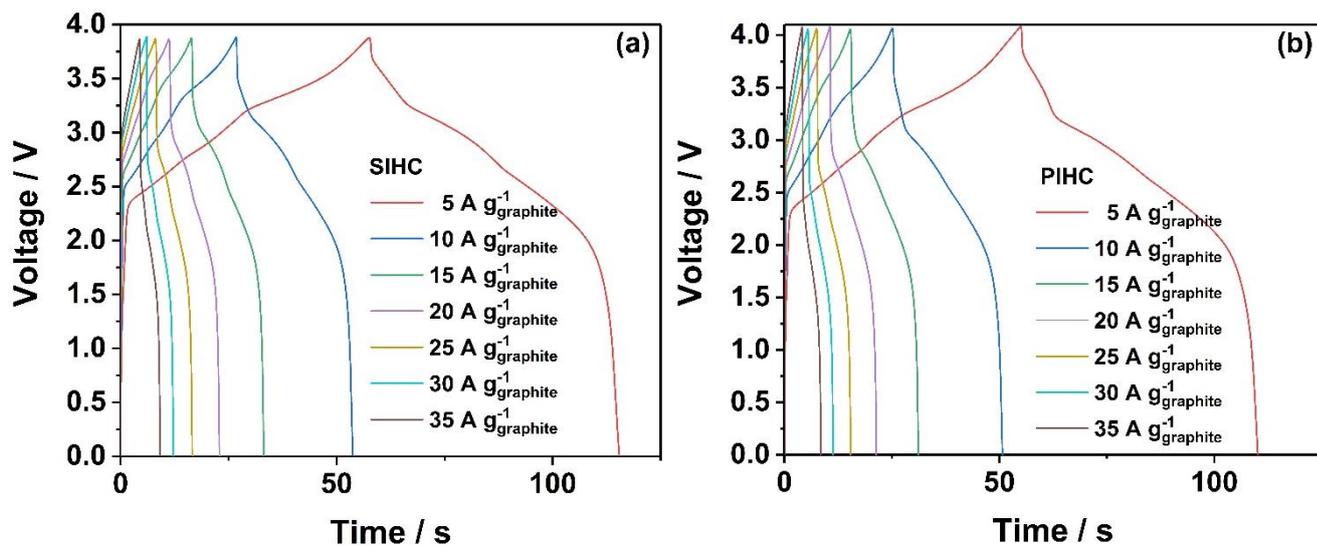


Fig. S4. Charge-discharge curves of (a) SIHC and (b) PIHC at different currents.

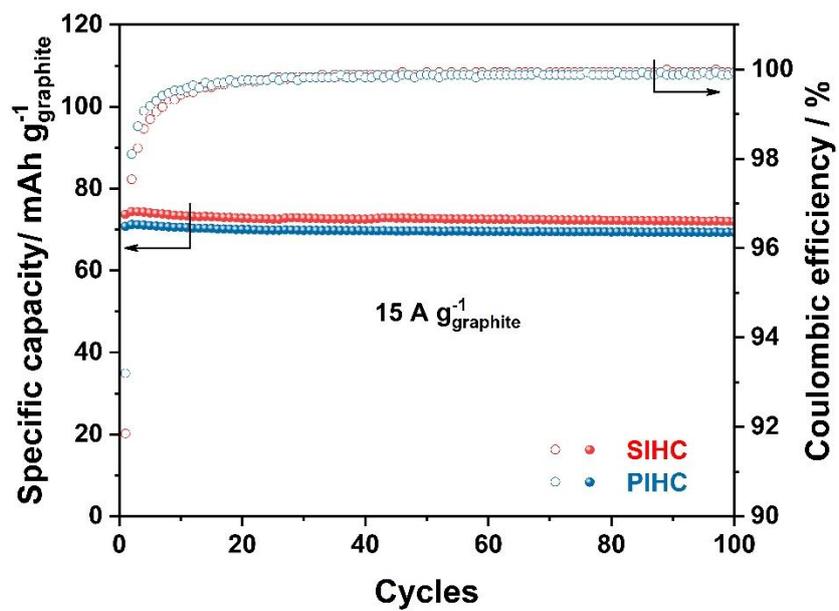


Fig. S5. Capacity and coulombic efficiency of the SIHC and PIHC in the initial 100 cycles at 15 A g⁻¹_{graphite}.

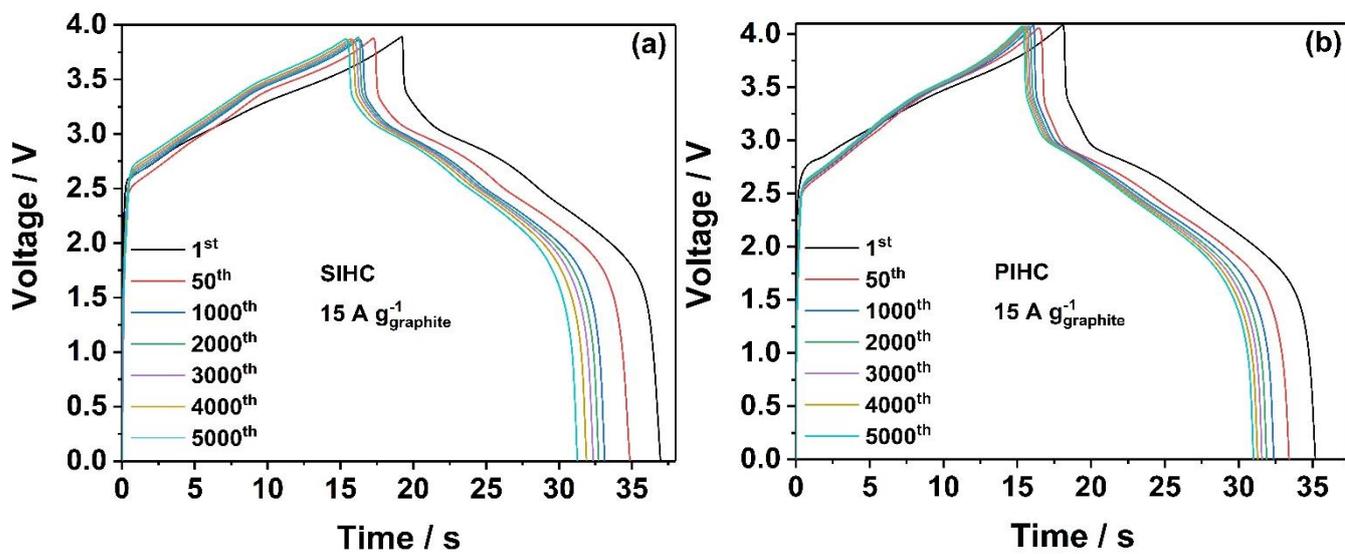


Fig. S6. Charge-discharge curves of (a) SIHC and (b) PIHC at selected cycles of the prolonged cycling tests.

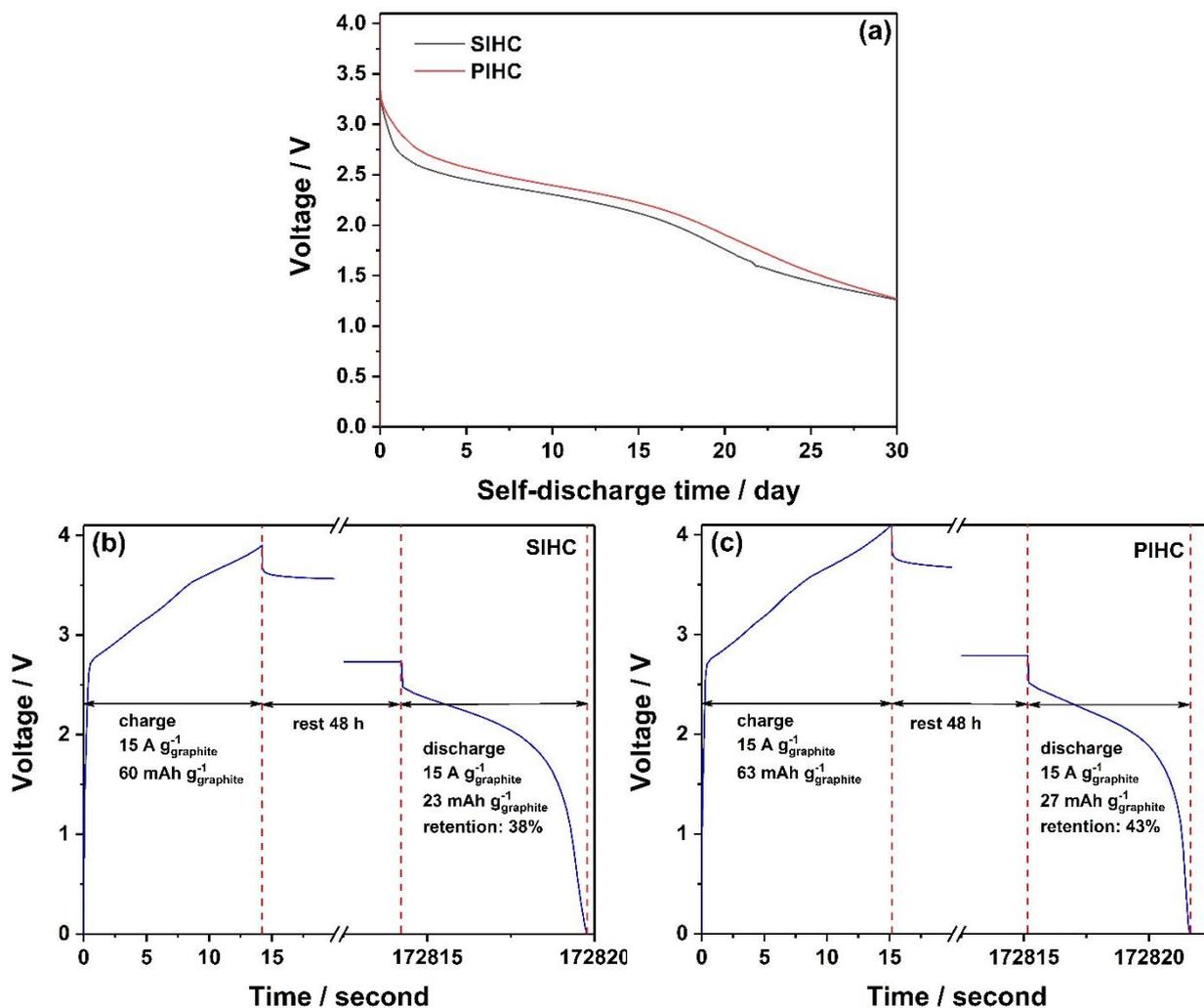


Fig. S7. (a) Voltage evolution of the SIHC and PIHC during the rest process, after being fully charged at $15 \text{ A g}_{\text{graphite}}^{-1}$. Charge-discharge curves of (b) SIHC and (c) PIHC for measurements of self-discharge.

After being fully charged at $15 \text{ A g}_{\text{graphite}}^{-1}$ (the charging time is around 16 s), the capacitors were kept at OCV to monitor the voltage evolution. For the initial 15 days the cell voltage is higher than 2V, reaching the 1.2V after 30 days, for both the SIHC and PIHC. Besides the OCV evolution upon time, the residual capacity after storage has been also evaluated fully charging the cells at $15 \text{ A g}_{\text{graphite}}^{-1}$ and then measuring the discharge capacity after 48 h rest. Fig. S7(b) and (c) show that the SIHC and PIHC still keep the 38% and 43% of the charge capacity, respectively. The reported results reveal an acceptable self-discharge of the system.

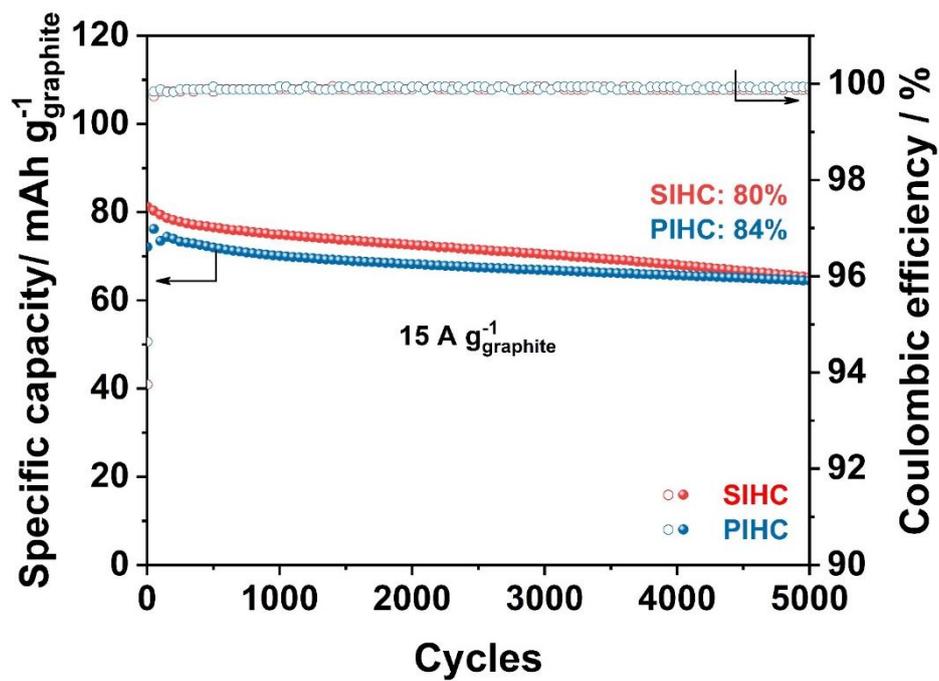


Fig. S8. Capacity and coulombic efficiency of the SIHC and PIHC at $15 \text{ A g}_{\text{graphite}}^{-1}$ using the Al current collector for the graphite and the AC.

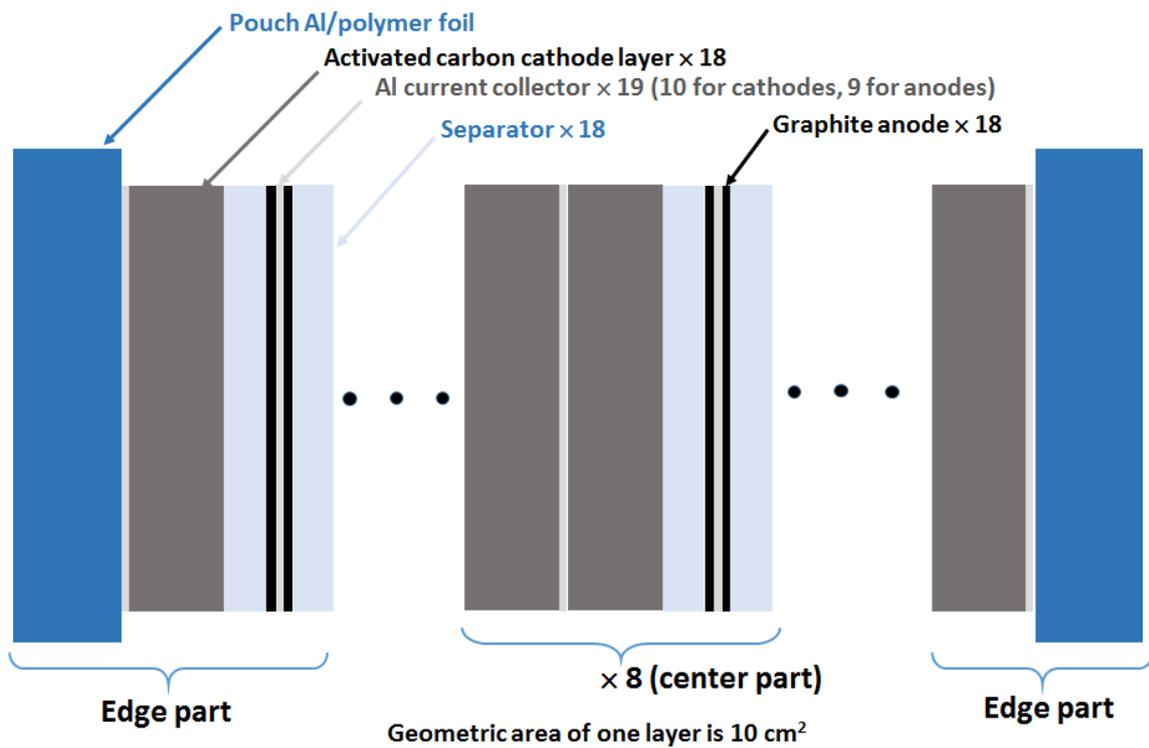


Fig. S9. Configuration of the SIHC pouch cell used to calculate the energy density and power density.

Calculation of the volume of the minimum electrolyte for the SIHC pouch cell

One 19-layer pouch cell

For each layer, the area is 10 cm².

AC mass loading 10 mg cm⁻²; porosity is 30%; the density of AC is 0.65 g cm⁻³.

Graphite mass loading 3.57 mg cm⁻²; porosity is 30%; the density of graphite is 2.2 g cm⁻³.

In total, the mass of graphite is 0.642 g, while that of AC is 1.8 g.

(1) The electrolyte required to wet the electrodes

Graphite electrode:

Volume of electrode – Volume of graphite = $(0.642 / 2.2) * ((1/(1-0.3))-1) = 0.125$ mL

AC electrode:

Volume of electrode – Volume of AC = $(1.8 / 0.65) * ((1/(1-0.3))-1) = 1.187$ mL

In total: 0.125 + 1.187 = 1.312 mL

(2) The electrolyte required to maintain the capacity of graphite electrode

No matter how many glyme molecules are co-intercalated, the amount of Na⁺ intercalated can be calculated. The intercalated Na⁺ comes from the electrolyte, and the PF₆⁻ adsorbed by AC also comes from the electrolyte.

The density of 1 mol L⁻¹ NaPF₆ in diglyme is 1.04 g cm⁻³.

The specific capacity of Na is 1166 mAh g⁻¹; molar weight of Na is 23 g mol⁻¹.

The specific capacity of graphite is 84 mAh g⁻¹.

Capacity of the cell with 0.642 g graphite:

$$\text{Specific capacity} * \text{weight} = 84 \text{ mAh g}^{-1} * 0.642 \text{ g} = 53.92 \text{ mAh}$$

The molar of Na⁺ needed to maintain the 53.92 mAh:

$$(53.92 \text{ mAh} / 1166 \text{ mAh g}^{-1}) / 23 \text{ g mol}^{-1} = 0.00201 \text{ mol}$$

The volume of the electrolyte needed to provide the Na⁺: 0.00201 mol / 1 mol L⁻¹ = 2.01 mL

(3) The solvent required for co-intercalation

If the molar ratio of diglyme to Na is 2:1, the molar of diglyme intercalated is calculated to be 0.00402 mol, **corresponding to 0.57 mL diglyme** (0.00402 mol * 134.17 g mol⁻¹ / 0.944 g cm⁻³).

If the depletion of salts does not affect the volume a lot, for the cell with 2.01 mL electrolytes at fully charged state, the residual diglyme solvents (1.44 mL) are still enough to wet the electrodes. Hence, the electrolyte required to maintain the capacity of graphite electrode is used as the minimum electrolyte. Note that in practical cells, more salts or electrolytes should be added to enhance the ionic conductivity at the fully charged state.

Table S1 Parameter used for the calculation of the practical energy density of the graphite//AC SIHCs.

Parameter	Value
Graphite density / g cm ⁻³	2.2
AC density / g cm ⁻³	0.65
Electrolyte 1M NaPF ₆ in diglyme density / g cm ⁻³	1.04
Separator density (PE polymer) / g cm ⁻³	0.92
Current collector density (Al) / g cm ⁻³	2.7
Pouch Al/polymer pouch density / g cm ⁻³	2
Porosity NG and AC electrode / %	30%
Porosity separator / %	40%
Current collector thickness/ μm	18
Pouch-package thickness/ μm	250