High-performance Li-ion capacitor via anion-intercalation process

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Abstract
Supercapacitors are characterized by their fast charge/discharge capability, high-power capability, and long cycle life, but low-energy-density impedes their practical application. The requirement of achieving a highly efficient energy storage system demands the hybridization of supercapacitors and batteries. The anion-intercalation chemistry of graphite with high insertion potential creates a possibility of using graphite as a cathode, which works as an acceptor-type graphite intercalation compound. Herein, we report the reversible PF$_6^-$ anion storage on the graphite cathode, which occurs by the combination of pseudocapacitive and diffusion-limited redox reaction at a higher working potential. Furthermore, a dual carbon lithium-ion capacitor (LIC) using commercial graphite as anion-intercalation type, battery type cathode, and commercial-activated carbon (AC) as supercapacitor type anode is designed. The assembled preanion intercalated Graphite/AC-based LIC assembly displayed a high-energy density of 90.73 Wh kg$^{-1}$. Moreover, the device with low-temperature stability is advantageous over traditional electrical double-layer capacitors, mainly in terms of its energy and low cost with much more safety features than commercial lithium-ion batteries.

KEYWORDS
anion intercalation, dual carbon Li-ion capacitor, energy density, graphite cathode

1 | INTRODUCTION

Of late, the increase in the global energy crises, together with the plummeting fossil fuel reserves, necessitates the importance of electrochemical energy storage devices like rechargeable batteries, capacitors, and fuel cells, which can reduce the reliance on nonrenewable resources and promote the harnessing of sustainable energy from renewable energy sources. The conventional electrical double-layer capacitors (EDLCs), having the symmetric configuration of activated carbon (AC) electrodes, possess a high-power density and longer cycle life than most secondary batteries. Despite possessing such alluring features, their practical application is still hindered by the low energy density generated by their low working potentials due to the anodic electrolyte decomposition. In general, a practical energy density of $<10$ Wh kg$^{-1}$ is only deliverable by this device. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

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Constructing supercapacitors in an asymmetric fashion, that is, replacing one of the AC electrodes with a battery-type electrode that can undergo a Faradaic reaction, is found to enhance the working potential of the device and thereby improve the energy density. The lithium-ion capacitor (LIC) configuration comprises the battery-type negative electrodes like graphite in its prelithiated state (LiC₆) paired against the capacitive type AC electrode. Here, the graphite anode is involved in the reversible insertion and extraction of Li ions. Even though this system could successfully moderate the differences between Li-ion batteries and supercapacitors, an internal metal source requirement for prelithiation impedes its application.⁶,⁷ The graphitic carbon (KS series) as the cathode in place of AC is introduced by Yoshio et al.,⁸ and such configuration is called a “megalo-capacitance capacitor.” Interestingly, the new kind of capacitor offers high-energy storage capability (20 Wh kg⁻¹) than the EDLC capacitor, which leads to a drastic reduction in the device cost. The charge storage mechanism proceeds via the Faradaic (insertion/extraction) charge-transfer reactions of anions (A⁻) at the cathode and the adsorption of cations (C⁺) at the anode in anion-intercalation-based metal-ion capacitors, which is represented in Equations (1) and (2).¹⁸

\[
\text{Cathode: } C + xA^- \rightleftharpoons A_xC + xe^- . \quad (1)
\]

\[
\text{Anode: } AC + xC^+ + xe^- \rightleftharpoons AC/xC. \quad (2)
\]

Various aspects influencing the performance of such “megalo-capacitance capacitors” were also thoroughly examined, such as the mass ratio of the negative to the positive electrode and the type of electrolyte. The small-sized cations (Na⁺ and K⁺) except Li⁺ could yield better performance and improved cyclability due to a relatively low degree of solvation and associated decomposition. The effect of size, structure, and oxidative stability of the anion, ion-pair formation, and self-aggregation effects of electrolytes are all variables that impact the reversible capacity for anion intercalation. The electrolytic solvent’s affinity for the ions is also critical in influencing the performance of Graphite/AC capacitors. For example, the solvent ethylene carbonate (EC), which is firmly bound to anions in contrast to other solvents like propyl carbonate, is known to cause intercalant retardation of anions into the interlayer gallery of graphite. In addition to these parameters, properties of graphite such as its crystallinity, size, and morphology of particles are also reported to significantly have a role in the functioning of megalo-capacitance capacitors.⁹

Recently, Yu et al.¹⁹ reported the boron-doped graphite cathode for the reversible PF₆⁻ anion insertion/extraction for Na-ion capacitor (NIC) applications. The constructed NIC could deliver an energy density of 108 Wh kg⁻¹ with 97% retention after 5000 cycles, in which the author’s calculated the specific capacitance of the Faradaic reaction. This calculation subsequently leads to a higher energy density, but the cell rendered an excellent cycling profile.

Herein, we attempted to explore the possibility of fabricating a high-energy LIC based on an anion-intercalation process, using commercial graphite as cathode and AC anode to target a low-cost, high-energy charge storage device in a more systematic way. We studied the reversible PF₆⁻ anion storage on the cathode that occurs both by pseudocapacitive and diffusion-limited redox reaction at a high operating voltage of 0–4.4 V. Besides, the electrochemical activity and calendar life of fabricated LICs were also subjected to various (low and high temperature) atmospheric conditions.

2 | EXPERIMENTAL SECTION

2.1 | Reagents and instruments

Commercial graphite powder from Sigma-Aldrich was employed as the active material of the cathode and commercial AC (YP-80F; Kuraray) as the active anode material. The electrolyte utilized is 1 M LiPF₆ in dimethyl carbonate (DMC; Sigma-Aldrich). The surface morphology of bulk graphite powder was explored via a field-emission scanning electron microscope (FE-SEM S-4700; Hitachi). X-ray diffraction (XRD, Rigaku; Smartlab 9 kW) was also studied using Cu Kα radiation (λ = 0.15406 nm). The chemical state of the graphite surface was investigated by X-ray photoelectron spectroscopy (XPS; Multilab 2000). Commercial graphite powder, conductive acetylene black (AB), HSV900 polyvinylidene fluoride (PVdF) binder were employed as the active material, conductive additive, and binder, respectively, for the cathode electrode preparation. The composition of these three components was varied to identify the combination that guaranteed decent discharge capacities along with substantial cycle life. Here the active material concentration ranged from 65 to 95 percentage with the other components alternating accordingly. The graphite powder was mixed with AB and PVdF using N-methyl pyrrolidone to attain a homogeneous slurry with constant stirring for 4 h. Later, this viscous slurry was cast onto Al foil using Automatic Thick Film Coater (MTI Corporation). The slurry-coated Al-foils were dried for another 6 h and then pressed under a hot roll press (Tester Sangyo) to enable better adhesion with the
current collector. The electrodes with a diameter of 12 mm were punched out, and the active material loading in each disc was estimated to be in the range of 2.5–4 mg. In the same fashion, the counter electrode, AC, was formulated by mixing AC, AB, and teflonized AB, TAB-2 (binder), in a mortar and pestle at the ratio of 80:10:10 using ethanol. The homogeneous mixture was then pressed over a stainless-steel mesh current collector with a diameter of 16 mm (Goodfellow) and subsequently dried at 75°C in a vacuum oven for 4 h. Both the half-cells and the Graphite/AC full-cells were then fabricated in coin-cell configuration (CR 2016) using 1 M LiPF₆ in DMC (Sigma-Aldrich) electrolyte. The reason for avoiding standard electrolyte (1 M LiPF₆ in EC:DMC, 1:1) is by considering the fact that the solvent EC employs an “intercalant retardant” effect in AC/graphite capacitors as it binds strongly with the PF₆⁻, and hence, the EC-solvated anions have larger sizes, which either outcomes in hardly any intercalation (EC-solvated PF₆⁻) or the significant expansion of the graphitic crystal. This is in agreement with the slightly lower binding energy between EC and PF₆⁻ (−16.7 kcal mol⁻¹) in comparison with that of DMC and PF₆⁻ (−7.1 kcal mol⁻¹) ions. In both half-cells and full-cell assemblies, Whatman paper (1825-047, GF/F) was used as a separator. The half-cells were assembled with graphite and AC electrodes with Li metal-foil as the counter and reference electrode.

2.2 | Electrochemical measurements of cells

The electrochemical measurements of both the half-cells and the full-cells were carried out using BCS 805 (Biologic) battery cycler. The ac impedance (EIS) studies were executed for half-cells (Li/Graphite), (Li/AC), and the LICs based on anion-intercalation with applied ac amplitude of 10 mV between 10 kHz and 1 Hz. Galvanostatic studies were carried out in the potential window of 3–5.2 V versus Li for graphite and 1.5–4.5 V versus Li for AC-based half-cells, respectively. In the case of Graphite/AC full-cells, we attempted to optimize the voltage range by varying the potential window from 0–3.5 to 0–5 V. The electrochemical performance of the LIC at various temperatures were also analyzed using the environmental chamber (Espec), where the potential window was 0–4.4 V.

3 | RESULTS AND DISCUSSION

The structural feature of the graphite powder was studied via powder XRD measurements. Figure 1A shows the XRD profile of graphite powder, which exhibits a strong and sharp reflection centered at 26.54° that can be assigned to the crystallographic (002) plane of graphite. Raman spectrum of the graphite sample unveiling three obvious peaks positioned at approximately 1355, 1573, and 2726 cm⁻¹, which can be ascribed to D, G, and 2D bands, respectively (Figure 1B). The D-band corresponds to the disordered structure of graphene layers, which can be related to the chaotic nature of graphite flakes. The G band rises in graphitic materials is due to the stretching of the C–C bond, which is present in all sp² carbon materials. Moreover, the ratio of the D band to the G band can be used to predict the degree of graphitization (IB/IG = 0.098). The lower value of the ratio suggests the perfect ordering of the graphite with fewer defects. The XPS analysis on graphite powder revealed two high-intensity peaks (Figure S1). The deconvoluted C1s spectrum shows a high-intensity peak at 284.6 eV and other less intense peaks positioned at 285.9 and 287.6 eV, attributing to sp²-carbon, sp³-carbon, and C=O species, respectively. Similarly, the O 1s spectrum of graphite XPS exhibits three peaks at 532.3, 533.7, and 530.7 eV assigned to C=O, O=C=O, and C=O, respectively. The above-mentioned results suggest a stable crystalline structure of graphite possessing minimum defects. The surface morphology of the material was analyzed by FE-SEM technology that exhibited the flaky nature of graphitic particles, as shown in Figure 1E,F.

3.1 | Half-cell studies

The cathodic half-cell was optimized by varying the weight ratio of active material, conductive carbon, and binder, generating 22 different combinations of electrodes. These 22 combinations of electrodes were further classified into six sets based on the active material concentration, Table S1. This study equipped us with the idea of how various factors like discharge capacities, cycle life would change in response to the change in electrode compositions and thus enabling us to identify the best combination that would yield maximum discharge capacities with decent cycle stability and eliminate those which does not comply to above results. The electrochemical performance of graphite powder was evaluated as the cathode using CR 2016-coin-cell in which Li metal serves as a counter/reference electrode in the presence of 1 M LiPF₆ in DMC.
electrolyte. It is well-known that the presence of EC in electrolyte solution leads to the formation of a passivation layer which eventually hinders the anion intercalation in the graphite. Therefore, we have used DMC-based electrolyte in which optimization in electrode compositions is essential to attain a high-performance ratio. Even though the first discharge capacities of all the aforesaid combinations are in the range of 50–65 mAh g\(^{-1}\) (at a current density of 100 mA g\(^{-1}\)), and varied significantly with cycling stability (Figure S2). Apparently, with the very high concentration of active material and low binder concentration, the cells generally open up after a couple of cycles owing to the reduced mechanical integrity of the electrode associated with the poor adherence of active material-graphite to the Al foil. When the weight ratios of conductive carbon and binder were increased, electronic connection and mechanical stability of the cell is improved and hence resulting in better cyclability of the cells. However, when the binder concentration increases further, it is evident that both the discharge capacities and the cycle life deteriorates in response to the increasing impedance to the movement of PF\(_6^-\) by the free PVdF molecules.\(^{23}\) In general, the optimum binder-PVdF concentration is found to be 10% (wt/wt) of the electrode. Thus the combination of the electrode that met our requirements is the one with the weight ratios of 65:25:10 of graphite:AB:PVdF binder,
respectively. The initial discharge capacity of the combination is $\sim 62$ mAh g$^{-1}$ and possesses fair stability. The coulombic efficiency of the half-cell is over 80% at the end of 100 cycles.

The mass/charge balance between the electrodes is essential, which is very important to attain high-energy density. Therefore, the capacitive type AC has to be studied for the wide range of potential windows, which offers physisorption of both anion and cations in a reversible manner. The initial discharge capacity that could be delivered by this half-cell is $\sim 108$ mAh g$^{-1}$ and has decent cyclic stability. The coulombic efficiency of the device is around 100% at the end of 80 cycles, owing to the charge storage mechanism through the non-Faradaic reaction of adsorption. During the galvanic charge–discharge cycle, the insertion and extraction of solvated anion PF$_6^-$ takes place in the graphite electrode. Figure 2A,B displays the typical galvanostatic charge–discharge profiles of the AC and graphite half-cells. The cyclic stability of both the half cells is shown in Figure 2C. The ex situ powder XRD study suggests that in the anion-intercalated graphite is charged at 5.2 V versus Li, the (002) peak has completely disappeared, and two new peaks appeared at lower values of 26.35° and 25.44° with reduced intensity due to the increase in the interlayer distance ($d_{002}$) with anion-intercalation process (Figure S3).

### 3.2 Full-cell studies

The Graphite/AC full-cell fabrication could be achieved by combining graphite cathode with AC anode of balanced mass by employing three different approaches:

a) Direct linking of the two electrodes.
b) Usage of “preamion intercalated cathode” with AC anode.
c) Full-cell fabrication with “pretreated cathode.”

In the first case, the anode and cathode electrodes were fabricated according to the mass balance principle and directly used as electrodes in the full-cell assembly. For the second case, the preanion intercalation of the graphite electrode was performed in coin-cell assembly (CR 2016) in a half-cell configuration with Li metal as reference/counter electrode. The intercalation and deintercalation of solvated anion PF$_6^-$ takes place in the graphite electrode upon the charge–discharge process. Under the charged state (at 5.2 V vs. Li), the test cell was decrimped, and the anion-intercalated graphite electrode was recovered and assembled with the AC counter electrode under the balanced charge/mass loading conditions (standard equations are given in Supporting Information). In the third case, the cathode undergoes three complete galvanostatic cycles in half-cell...
configuration, and then the cell is discharged to 3 V versus Li. The cell was dismantled, and the graphite electrode in discharged condition was clubbed with the mass-balanced AC electrode to device the full-cell, LIC. Even though all the above-mentioned steps were attempted, they gave varying results. The cells fabricated via the direct linking of the two electrodes did not work and exhibited a very negligible open circuit potential when measured by a multimeter. While the cells utilizing “pretreated cathodes” could work only a few cycles (<5 cycles), probably due to the limited availability of the solvated anion, PF$_6^−$. Only the LICs containing “pre-anion intercalated cathodes” could persist for a longer number of cycles with greater stability. These “pretreatment” and “preintercalation” processes certainly help to validate the half-cell results, besides mitigating the irreversible loss in the first charge. Thus, a LIC was thus assembled by using preanion intercalated graphite electrode as the cathode, AC electrode as the anode, and Whatman paper as the separator in the presence of 1 M LiPF$_6$ in DMC as the electrolyte. Keeping the obtained specific capacities of both electrodes in half-cell assemblies, the graphite at 3–5.2 V versus Li (≈55 mAh g$^{-1}$ at 100 mA g$^{-1}$) and AC at 1.5–4.5 V versus Li (108 mAh g$^{-1}$ at 100 mA g$^{-1}$), the Graphite/AC LIC was fabricated with cathode and anode in the mass loading ratio of 2:1, respectively. The active mass loading of the cathode was fixed to ∼1.7 mg cm$^{-2}$. We also experimented with the operating potential window by varying it from the 0–3.5 to 0–5 V range. The galvanostatic studies were conducted at different current densities from 0.1 to 1.5 A g$^{-1}$ for each of the voltage ranges. For LICs, the potential windows of 0–4.8 and 0–5 V, the cell lost mechanical stability at higher current rates and opened up (Figure S4).

**FIGURE 3**  Electrochemical performance of Graphite/AC-based LIC assembly with 1 M LiPF$_6$ in DMC. (A–F) Galvanostatic charge–discharge profiles at various current densities (0.1–1.5 A g$^{-1}$). (G) Ragone plot of fabricated LIC at various operating voltages. (H) Long-term cyclability of assembled LIC at 1 A g$^{-1}$ between the potential window of 0–4.4 V. AC, activated carbon; DMC, dimethyl carbonate; LIC, lithium-ion capacitor.
Although we have attempted to optimize the potential window, we are emphasizing maximum energy density rather than other parameters like power capability, cyclability, and so forth. Unlike energy density, other mentioned parameters can be improved by further studies. In general, the galvanostatic charge–discharge curves exhibited nonlinearity in the profile, which is a characteristic of the two different charge-storage mechanisms involved in the typical hybrid capacitors (Figure 3A–F). The energy and power densities of all the LICs were deliberated based on the total mass loading of active material in both graphite and AC electrodes (–3–5 mg) (given in the Supporting Information). The LIC delivered a maximum energy density of 90.73 Wh kg⁻¹ (power density: 0.22 kW kg⁻¹) in the potential range of 0–4.4 V at a low current density of 0.1 A g⁻¹ at ambient conditions. The lowest energy density dispensed by this device was 34.56 Wh kg⁻¹ with a power density of 3.495 kW kg⁻¹ (current density: 1.5 A g⁻¹) (Figure 3G). The assembled LIC in DMC solvent with a preanion intercalated graphite electrode as the cathode and AC anode establishes the combination of two different charge-storage mechanisms. Both the pseudocapacitive insertion/extraction and diffusion-controlled intercalation/deintercalation process of PF₆⁻ ions take place at the cathode, graphite. Simultaneously, the physisorption (adsorption/desorption) of the Li⁺ ions takes place from the electrolyte into the AC anode. Furthermore, the cyclability of the aforementioned LIC was conducted at 1 A g⁻¹ reveals that the fabricated LIC renders ~17% of the initial value even after 6000 cycles with a coulombic efficiency of >99 (Figure 3H).

We observed the poor performance of the fabricated LIC in the ambient temperature conditions. Therefore, we have studied the feasibility of using the fabricated LIC in various temperature conditions. Accordingly, the Graphite/AC-based LIC was studied at various temperature conditions (0°C, 10°C, 25°C [room temperature], and 50°C). However, at 50°C, the cell lost its mechanical stability and opened up, and hence unable to record any electrochemical performance. It was observed at low temperatures, the charge–discharge time was relatively shorter than those at higher temperatures (Figure 4A). The gravimetric energy and power densities of the LICs functioning at various temperatures were calculated and plotted in a Ragone plot (Figure 4B). It revealed that at 10°C, the highest energy density deliverable by the system was 72.41 Wh kg⁻¹ (power density: 0.27 kW kg⁻¹), at the current density is 0.1 A g⁻¹. The least energy density that could be obtained from the device at
this temperature is $11.64 \text{ Wh kg}^{-1}$ (power density: $3.3 \text{ kW kg}^{-1}$). The cell tested at 0°C delivered a maximum and minimum energy of 51.76 and 4.03 Wh kg$^{-1}$ with maximum and minimum power ranging from 3.15 to 0.242 kW kg$^{-1}$, respectively. It is also observed that with decreasing temperatures, the stability of the resulting LIC increases (Figure 4C). At the current density of 1 A g$^{-1}$, the cell at 0°C could retain about $-64.2\%$ of its initial value at the end of 1500 cycles, and that at 10°C exhibited capacity retention of 49.24%. The LIC at 25°C had retained its initial capacity by 35.45% by the end of 1500 cycles. Thus it can be confirmed that the higher the temperature, the lower will be the lifetime of the assembled dual carbon anion-intercalation-based LIC, owing to the acceleration of deteriorating side reactions. Further studies are desperately required for this kind of safer charge storage system to match the commercial reality. At present, we are working on several parameters to improve the room temperature performance (including cycling stability) without compromising the energy density.

Moreover, major encounters in the developments of Graphite/AC-based LICs are electrolyte decomposition at the cathode-electrolyte interface, exfoliation of graphite, and corrosion of Al current collectors. The unusually high working voltage required for anion-intercalation results in the oxidation of electrolyte, and thus there is the formation of an solid electrolyte interphase (SEI) layer of few nanometers thick on the surface of graphite cathode. Whereas the structure, composition, and formation mechanism of the SEI layer on the surface of positively charged graphite electrode still remains unclear.

4 | CONCLUSION

We have thereby developed a dual-carbon electrode LIC with high-energy, high-power capability, and long cycle life based on the anion-intercalation mechanism by pairing commercial graphite as cathode and AC as the anode in the presence of DMC electrolyte. The concentrations of active material, conductive additive, and binder of the Faradaic type electrode have been optimized in the cathodic half-cell assembly to attain the best performance. The best performance was warranted by the electrode composition of 65:25:10 of graphite:AB:PVdF binder, which yielded a discharge capacity of $-65 \text{ mAh g}^{-1}$ with decent stability. The LICs were then devised using three different techniques: direct linking of the electrodes, “pretreated cathode,” and “preanion intercalated cathode.” Nevertheless, only the “preanion intercalated cathode” cells delivered meaningful results and supplied maximum energy of 90.73 Wh kg$^{-1}$. The LICs were also exposed to a variety of temperatures to investigate their temperature dependences, and it was discovered that as the temperature drops, the maximum energy and power densities supplied by the device fall, but cycle stability rises. In a nutshell, in comparison to EDLC capacitors, the constructed (anion intercalated) Graphite/AC-based hybrid capacitor offers greater energy densities at lower costs.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data will be made available with a reasonable request to the corresponding author.

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Additional supporting information may be found in the online version of the article at the publisher’s website.

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