This is the pre-peer reviewed version of the following article:

Beyond Activated Carbon: Graphite-Cathode-Derived Li-Ion Pseudocapacitors with High Energy and High Power Densities

Gang Wang, Steffen Oswald, Markus Löffler, Klaus Müllen, Xinliang Feng

Advanced Materials, **2019**, Volume 31, Issue 14, 1807712

which has been published in final form at <https://doi.org/10.1002/adma.201807712>.

This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.

DOI: 10.1002/((please add manuscript number))

Article type: Communication

Beyond activated carbon: graphite cathode-derived Li-ion pseudocapacitors with high energy and high power densities

*Gang Wang, Steffen Oswald, Markus Löffler, Klaus Müllen and Xinliang Feng**

Dr. G. Wang, Prof. X. Feng

Center for Advancing Electronics Dresden (cfaed) & Department of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany.

E-mail: xinliang.feng@tu-dresden.de

Dr. G. Wang, Prof. K. Müllen

Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Dr. S. Oswald

Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden (IFW) e.V.,
Helmholtzstraße 20, 01069 Dresden, Germany

Dr. M. Löffler

Dresden Center for Nanoanalysis (DCN), Center for Advancing Electronics Dresden (cfaed),
Technische Universität Dresden, 01062 Dresden, Germany.

Keywords: graphite cathode, anion intercalation, Li-ion capacitors, pseudocapacitors

Abstract:

Supercapacitors have aroused considerable attention due to their high power capability, which enables charge storage/output in minutes or even seconds. However, to achieve high energy density of supercapacitors has been a long-standing challenge. Here we report graphite as a high-energy alternative to the frequently used activated carbon (AC) cathode for supercapacitor application due to its unique Faradaic pseudocapacitive anion intercalation behavior. The graphite cathode manifests both higher gravimetric and volumetric energy density (498 Wh/kg and 431.2 Wh/l) than AC cathode (234 Wh/kg and 83.5 Wh/l) with peak power densities of 43.6 kW/kg and 37.75 kW/l. New-type Li-ion pseudocapacitors (LIpCs) are thus proposed and demonstrated with graphite as cathode and prelithiated graphite or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as anode. The resultant graphite-graphite LIpCs deliver high energy densities of 167-233 Wh/kg at power densities of 0.22-21.0 kW/kg (based on active mass in

both electrodes), much higher than 20-146 Wh/kg of AC-derived Li-ion capacitors and 23-67 Wh/kg of state-of-the-art metal oxide pseudocapacitors. Excellent rate capability and cycling stability are further demonstrated for LTO-graphite LIpCs.

Supercapacitors (electrochemical capacitors), as an attractive alternative to rechargeable batteries, are highly promising to meet the fast energy storage demands in portable electronic devices, electric automotive and regenerative energy harvesting due to their high power, short charging time and long cycle life.^[1] The main challenge associated with supercapacitors lies in their low energy densities (5-10 Wh/kg^[1d, 2] vs 387 Wh/kg^[3] for Li-ion batteries), making them only functioning as a complement rather than an independent power source for compact energy applications. As a consequence, considerable efforts including development of high-capacitance electrode materials and building high-voltage devices have been made to enhance the energy density.^[4]

Compared to conventional electrical double layer capacitors (EDLCs, Figure S1), Li-ion capacitors (LICs) comprising a battery-type anode (graphite or $\text{Li}_4\text{Ti}_5\text{O}_{12}$) and a capacitor-type cathode exhibit improved energy density (20-146 Wh/kg) (**Figure 1a, c**), which profits from efficient utilization of cathode and an enlarged operating voltage.^[5] The cathodes applied in LICs are mainly carbonaceous materials, such as activated carbon (AC), graphene, carbon nanotubes and porous carbon.^[5g, 6] Among them, AC is still the most frequently used cathode material benefiting from its low manufacturing cost and high surface area. However, the energy density of LICs based on the AC cathode is approaching its limit due to the following reasons: Firstly, AC stores energy via reversible electrostatic ion adsorption on the carbon surface^[4f] instead of bulk and the charges increase nonlinearly with surface area,^[6a] leading to relatively low capacitance. Secondly, the high surface area of AC raises the risk of electrolyte decomposition^[5h] and limits the working potential of AC below 4.5-4.6V (vs

Li/Li⁺). Thirdly, the porous AC is often accompanied with a low tap density of electrodes (<0.5 g/cm³), resulting in an inferior volumetric energy density. Fourthly, the low graphitization of AC brings about a low electrical conductivity of AC cathode. Therefore, it is highly desirable to develop new-type high-energy and high-power LICs based on cost-efficient and sustainable materials beyond AC.

Graphite, an abundant layer-structured crystalline allotrope of carbon, consists of numerous graphene layers stacked via van der Waals force, which allows reversible intercalation of both cations and anions. Graphite is generally regarded as a battery-type electrode material to construct Li-ion batteries, dual-ion batteries^[7] and hybrid energy storage devices^[8], while intercalation kinetics has been rarely investigated. Herein we disclose that graphite stores anion charges via a pseudocapacitive intercalation process; graphite is thus re-categorized as a pseudocapacitive rather than a battery-type cathode material. Considering the bulk energy storage, high working potential (3-5.3V vs Li/Li⁺) and high tap density, graphite cathode exhibits both higher gravimetric and volumetric energy density (498 Wh/kg and 431.2 Wh/l) than AC cathodes (234 Wh/kg and 83.5 Wh/l) with peak power densities of 43.6 kW/kg and 37.75 kW/l. Consequently, new Li-ion pseudocapacitors (LIpCs) based on graphite cathode are proposed (Figure 1b, d). A high energy density of 233 Wh/kg, a peak power density of 21 kW/kg and excellent cycling stability (96.1% capacity retention after 1400 cycles at 1A/g) can be achieved in graphite-graphite LIpCs (G-G LIpCs), surpassing state-of-the-art AC-based LICs and other pseudocapacitors. Replacing graphite anode with zero-strain and durable Li₄Ti₅O₁₂ (LTO), similar rate capability and long-term cycle life (10000 cycles) are assessed in LTO-G LIpCs.

To show the advantages of graphite cathode over AC cathode for capacitor applications, AC with a high surface area of 2201 m²/g (Figure S2) was selected for comparison with commercial graphite powders. The AC possesses abundant micropores (<2 nm) and irregular particles ranging from 1 to 10 μm (Figure S3), while graphite sizing in the range of 10-80 μm

shows no specific porous structure and a limited surface area of 7 m²/g. AC cathode and graphite cathode were then prepared by a conventional slurry casting method on stainless steel foils, where alginate sodium was used as the binder (see SI for fabrication details). Due to limited porous structure and high graphitization degree, graphite cathode exhibits a high tap density of 0.866 g/cm³ (Figure S4) and a high electrical conductivity of 158 S/cm (Figure S5), which are ~2.4 and 24.7 times larger than 0.357 g/cm³ and 6.4 S/cm of AC cathode, respectively.

The electrochemical performance of two cathodes was evaluated in half cells with Li foil as the counter and reference electrode. The electrolyte was 2M LiPF₆ in ethyl methyl carbonate (EMC). Ethylene carbonate (EC), the commercial electrolyte additive, was avoided due to its hindrance on anion intercalation.^[9] The maximum upper potential of AC cathode was determined to be 4.6 V (vs Li/Li⁺, Figure S6). Above this value, severe electrolyte decomposition occurs, leading to a rather low Coulombic efficiency (CE, <23%). In contrast, graphite cathode can efficiently perform at high potentials up to 5.3 V. Therefore, operating potential windows of 3.0-4.6 V and 3.0-5.3 V were adopted for AC and graphite cathodes in cyclic voltammetry (CV) and galvanostatic charge-discharge measurements.

The pseudocapacitive response of graphite cathode was characterized by the CV measurement. Figures 2a and b show CV curves of a graphite cathode with a mass loading of ~2 mg/cm², rather than a thin-film electrode (<0.1 mg/cm²)^[10]. Several pairs of redox peaks are observed on the CV curve, indicating reversible Faradaic reaction involved (**Figure 2a**). The anion intercalation into graphite can be expressed as $x\text{A}^- + \text{C}_6 \leftrightarrow \text{C}_6(\text{A})_x + xe^-$, where A^- and C_6 represent anions and graphite. Generally, the reaction kinetics can be evaluated by the power law $i = av^b$ to analyze the dependency of current response on the sweep rate in a CV measurement. A b value of 1 is an indicator of a capacitor-like charge storage process; whereas a b value of 0.5 suggests that the electrochemical reaction is controlled by semi-infinite linear diffusion.^[4e] As shown in Figure 2b and S7, the redox peaks of graphite cathode

display b values of 0.91, 0.92, 0.91, 0.74, 0.94, 1 and 0.97, much higher than 0.5. It indicates that the dominant charge storage in graphite cathode is pseudocapacitive. Regarding the AC cathode, the perfect rectangular-shape CV in Figure 2a represents a pure electrical double layer capacitance mechanism.^[1d]

During the galvanostatic charge-discharge measurements, three evident stages appear on the charge-discharge curves of graphite cathode (Figure 2c), which imply a staging intercalation/deintercalation behavior. Increasing the current densities from 0.1 to 10 A/g, the capacity of graphite cathode slightly decreases from 106.4 to 80.5 mAh/g, highlighting the pseudocapacitive behavior of graphite cathode. Under the same current densities, the AC cathode only delivers capacities of 61.1 and 31 mAh/g (Figure S8). Figure 2d further confirms the high reversibility of anion intercalation/deintercalation into/from graphite cathode. After 2000 cycles at 1 A/g, a capacity up to 96.7% is still maintained.

Besides capacity, the graphite cathode also demonstrates higher discharge voltage than AC cathode. The midpoint discharge voltage (V_m) of graphite cathode decreases from 4.68 V at 0.1 A/g to 4.36 V at 10 A/g, which is >0.8 V higher than 3.83/3.54 V of AC cathode at the same current densities (Figure 2e). Based on the capacity and V_m , the calculated gravimetric energy density of graphite cathode varies from 351.1 to 498 Wh/kg at the gravimetric power density of 0.468-43.6 kW/kg, superior to 111.3-234 Wh/kg of AC cathode at 0.383-35.5 kW/kg (Figure 2f). Taking into account the differences in tap density, graphite cathode possesses a more significant advantage than AC cathode. The volumetric energy densities of graphite cathode reach 304.1-431.2 Wh/l at volumetric power densities of 0.405-37.75 kW/l, which are over 5 times of 39.7-83.5 Wh/l of AC cathode at 0.137-12.7 kW/l (Figure S9). The above results highlight that graphite cathode outperforms AC cathode for high-energy and high-power capacitor applications.

To elucidate the structural evolution of graphite cathode during galvanostatic charge-discharge cycles, multiscale characterizations including *ex-situ* X-ray diffraction (XRD),

Raman, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) have been carried out. The XRD patterns of graphite cathode at specific charge states (**Figure 3a**) are shown in Figure 3b. The pristine graphite cathode shows a characteristic graphite (002) peak at $2\theta=26.5^\circ$, corresponding to a layer spacing of 0.336 nm. Once charge potential is above 4.4 V (Li/Li⁺), the original graphite (002) peak splits into two new peaks located at $22-25^\circ$ and $29-35^\circ$, which can be assigned to (00n) and (00n+1) peaks of graphite intercalation compounds.^[7a] The appearance of (00n+1) peak is a clear indication of PF₆⁻ intercalation between graphene layers. Charging graphite to higher potentials (up to 5.3V), it is found that the (00n) peak gradually shifts to lower angle and (00n+1) to higher angle, representing a staging process of PF₆⁻ intercalation from stage 4 to stage 1 (Figure S10). Upon discharging, the (00n) and (00n+1) peaks shift in a reverse way until disappearance of (00n+1) peak and recovery of graphite (002) peak. Two-stage structure (stage 1&2) of graphite cathode is also noticed at 4.78V, which is associated with stage transition.^[11] Compared with pristine graphite, the graphite cathode after one charge-discharge cycle presents a broadened and declined graphite (002) peak, implying decreased crystallinity.^[7a]

The *ex-situ* Raman spectroscopy was also conducted on graphite cathode to probe anion intercalation/deintercalation (Figure S11). The pristine graphite cathode shows a strong G band at 1579 cm⁻¹, which is credited to the E_{2g} vibration mode and is due to the bond stretching of sp² carbon atoms. In the charging process, the graphite G band splits into a doublet (~1584 cm⁻¹ for E_{2g2}(i) mode and ~1606 cm⁻¹ for E_{2g2}(b) mode) owing to symmetry variation of the boundary graphene layer and electronic effects of the intercalant species.^[12] Meanwhile, the intensity of E_{2g2}(b) mode is enhanced along with charge potentials, suggesting that more PF₆⁻ anions are intercalated into graphite cathode. During discharging, the spectral changes are reversed and graphite G band can be recovered at 3.0V, demonstrating reversible anion deintercalation from graphite cathode.

The chemical composition of graphite cathode at pristine, intercalated (5.3V) and deintercalated (3.0V) states was analyzed by XPS. The C1s peak of intercalated graphite cathode exhibits a broad shoulder at higher energy (Figure S12), confirming electrochemical oxidation of graphite by PF_6^- intercalation. In the meantime, a 0.4 eV shift of C1s peak to lower energy was detected, which differs from AlCl_4^- intercalated graphite^[13] and needs more investigation. The PF_6^- intercalation was verified by the appearance of strong F1s and P2p peaks (Figure 3c). The atomic ratio of F to P in graphite electrodes is around 5.6 (Table S4), approaching the theoretical value of 6. Discharging to 3.0 V, the C1s peak of graphite cathode well overlaps that of the pristine graphite cathode due to PF_6^- deintercalation (Figure S12), which is accompanied by substantial reduction of F1s and P2p signals (Figure 3c). The residue F1s and P2p signals can be attributed to trapped/adsorbed species in graphite samples. Further, energy-dispersive X-ray (EDX, Figure S13a) spectrum and SEM elemental mapping images (C, F and P, Figure 3d) of intercalated graphite cathode demonstrate intense yet uniform C, F and P elements over the electrode; whereas deintercalated graphite cathode shows much weak F and P signals (Figure S13b and 3e). These results signify the PF_6^- intercalation/deintercalation involved in graphite cathode.

In order to demonstrate the “LIpCs” concept, G-G LIpC full devices were first constructed using graphite as the cathode and prelithiated graphite as the anode (Figure 1b, d). The prelithiated graphite was selected since it can work under an operating potential below 0.2 V (vs Li/Li^+) and function as additional Li source to compensate Li loss during solid-electrolyte interphase (SEI) formation and long-term operation, thus endowing full devices with a high working voltage, enhanced energy density and long cycle life.^[6a] In this work, the graphite anode was activated and prelithiated in a vinylene carbonate (VC)-containing electrolyte (2M LiPF_6 +3 wt% VC/EMC) via a “polarity switch” method^[14] in half cells, where graphite electrode was initially cycled in the cathode range and subsequently shifted to anode range (Figure S14a-c). The polarity switch process induced dense particle-like SEI on graphite

anode (Figure S14d) and activated graphite anode with a high reversible capacity of ~ 360 mAh/g (Figure S14a), which is close to the theoretical value (372 mAh/g) of graphite anode. Then the graphite anode was prelithiated to a capacity of 200 mAh/g (Figure S15) followed by disassembly and pairing with graphite cathode for full devices. And 2M LiPF₆ in EMC was used as the electrolyte. Equal masses of graphite cathode and graphite anode were used to balance the energy and power of G-G LIpCs.^[5f, 5h]

The electrochemical performance of G-G LIpCs was investigated by CV and the galvanostatic charge-discharge test. The G-G LIpCs show similar redox peaks to graphite cathode (Figure 2a) with a downward voltage shift of 0.14 V (**Figure 4a**). As shown in Figure 4b, three typical intercalation/deintercalation stages are well identified on the charge-discharge profile of G-G LIpCs, which are quite similar to but ~ 0.15 V lower than those in Li-graphite half cells (Figure 2c). The V_m of G-G LIpCs is determined to be 4.5 V, much higher than 1.5-3.25 V of conventional EDLCs^[5a] or LICs^[15]. At the current density of 0.1 A/g, the G-G LIpCs deliver initial charge and discharge capacities of 108.4 and 95.1 mAh/g (calculated on graphite mass in cathode), corresponding to an initial CE of 87.7%. After a few cycles, the discharge capacity quickly increases to 99.2 mAh/g and stabilizes afterwards with an average CE of 96% (Figure 4c). Under accelerated current rates, the G-G LIpCs show very slight capacity decay and polarization on the charge-discharge curves (Figure S16). High reversible capacities of 99.7, 98.7, 97, 96.6 and 94.4 mAh/g are retained at 0.2, 0.4, 0.8, 1 and 2 A/g, respectively (Figure 4d). In particular, when the current density switched back to the initial 0.2 A/g, the capacity of G-G LIpCs totally recovered. The cycling stability of G-G LIpCs was further evaluated through repeated galvanostatic cycling under 1 A/g (Figure 4e). After 1400 cycles, the capacity retention was as high as 96.1% accompanied with an average CE of 98.3%; and the charge-discharge curves at different cycles well overlapped with each other (Figure S17). The electrochemical impedance spectra (EIS) revealed that no charge

transfer resistance increase was observed during the cycling test (Figure 4f), suggesting excellent electrochemical stability of electrodes, electrolyte and SEI in the G-G LIpCs.

Applying a wider voltage window of 3-5.2 V, the performance of G-G LIpCs could be further pushed forward. As shown in Figure 4g, the charge-discharge curves of G-G LIpCs maintained the similar shape even at a high current density of 10 A/g, implying ultrafast electrochemical kinetics of G-G LIpCs. High capacities of 104.3, 102.2 and 80 mAh/g were achieved at 0.1, 1, and 10 A/g, respectively, with the corresponding V_m in the range of 4.30-4.56 V. In addition, the G-G LIpCs allowed rapid charge (at 2 A/g, in 3min) and gradual discharge (down to 0.1 A/g) over 1h (Figure 4h) while keeping the capacity nearly constant (~100 mAh/g, and S18). Such a quick charge capability is highly appealing for practical energy storage applications. The Ragone plots of G-G LIpCs are shown in Figure 4i, where the energy density and power density are calculated on the masses of graphite in both electrodes and pre-doped lithium. A maximum energy density of 233 Wh/kg is obtained at a power density of 445 W/kg. Even at a high power density of 21 kW/kg, the G-G LIpCs still deliver a high energy density of 168 Wh/kg. Note that neither nanomaterials nor porous materials are involved; the energy density and power density of the G-G LIpCs based on micrometer-scale graphite powders surpass those of state-of-the-art LICs and metal oxide pseudocapacitors, such as graphite-AC,^[5f, 5h] LTO-AC,^[5a] NC-NC,^[5g] NC-TiC,^[16] TiO₂/rGO-AC,^[17] CNT/V₂O₅-AC,^[18] Nb₂O₅-PANI/CNT^[19] and BNC-BNC^[20] LICs, and symmetric LaMnO₃^[10] and Zn_xCo_{1-x}O^[21] pseudocapacitors.

Furthermore, the electrochemical performance of G-G LIpCs was found to be sensitive to the prelithiation strategy of graphite anode. The activation of graphite anode in 1M LiPF₆ EC/EMC at C/10 for 4 cycles and prelithiation of 200 mAh/g led to a limited power capability (~70 mAh/g at 2 A/g) and inferior cycling stability (89% capacity retention after only 230 cycles at 1 A/g) of the resultant G-G LIpCs (Figure S19-S20). It can be mainly attributed to

slower kinetics of graphite anode rather than that prepared by the polarity switch method (Figure S21).

Our LIpCs concept can be conveniently expanded to other anode materials. For example, LTO-G LIpCs were constructed by replacing graphite anode with the well-known zero-strain and durable LTO anode (Figure S22). Due to the high working potential of LTO anode (1.5 V vs Li/Li⁺, Figure S23a), the resultant LTO-G LIpCs performed in a voltage window of 1.5-3.7 V and showed a moderate V_m of 3.04 V (Figure S23c), which is also higher than 2.25 V of reported LTO-AC LICs.^[5a] Similar to G-G LIpCs, the LTO-G LIpCs exhibited a notable rate capability with 89% capacity retention when the current density increased from 0.2 to 2 A/g (Figure S23d). During the long term test (2-3 months), the LTO-G LIpCs kept 88% of its initial capacity at 1 A/g after 10000 cycles (Figure S23e, f).

In summary, we have demonstrated graphite as a low-cost, high-capacity, high-voltage and high-rate pseudocapacitive cathode material for supercapacitor application, which outperforms the currently used AC cathode on tap density, conductivity and energy density. The graphite cathode stores anion charge via pseudocapacitive intercalation rather than surface adsorption of AC cathode. As confirmed by multiscale characterizations, the anion intercalation into graphite cathode is a staging and highly reversible process. New-type graphite cathode-derived LIpCs have also been proposed and demonstrated. The resultant G-G LIpCs showed both high energy densities and power densities, superior to those of reported LICs and pseudocapacitors. Considering the recent significant progress in nano-engineering, new compounds and hybridization on electrochemical energy storage, the electrochemical performance of graphite cathode-derived LIpCs can be further promoted by pairing graphite cathode with various powerful anode materials. This work will inspire the development of novel metal-ion pseudocapacitors based on different graphitic carbon materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was financially supported by the ERC grant for HIPER-G (Project ID 768930), the Federal State of Saxony (ESF-Project “GRAPHD”, TU Dresden), the EC under the Graphene Flagship (grant number CNECT-ICT-604391) and MAXNET Energy Project. The authors acknowledge the CFAED and the Dresden Center for Nanoanalysis (DCN) at TU Dresden. The authors thank Dr. Minghao Yu for providing activated carbon sample. The authors would like to thank Dr. Tao Zhang, Dr. Tao Zhang and Mingchao Wang for their help with XRD, Raman and conductivity measurements.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] a) V. Augustyn, P. Simon, B. Dunn, *Energy Environ. Sci.* **2014**, 7, 1597-1614; b) P. Simon, Y. Gogotsi, B. Dunn, *Science* **2014**, 343, 1210-1211; c) J. R. Miller, P. Simon, *Science* **2008**, 321, 651-652; d) P. Simon, Y. Gogotsi, *Nat. Mater.* **2008**, 7, 845.
- [2] P. Simon, Y. Gogotsi, *Acc. Chem. Res.* **2013**, 46, 1094-1103.
- [3] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J.-M. Tarascon, *Nat. Mater.* **2012**, 11, 19-29.
- [4] a) T. Brezesinski, J. Wang, S. H. Tolbert, B. Dunn, *Nat. Mater.* **2010**, 9, 146; b) H. Sun, L. Mei, J. Liang, Z. Zhao, C. Lee, H. Fei, M. Ding, J. Lau, M. Li, C. Wang, X. Xu, G. Hao, B. Papandrea, I. Shakir, B. Dunn, Y. Huang, X. Duan, *Science* **2017**, 356, 599-604; c) M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall'Agnese, P. Rozier, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum, Y. Gogotsi, *Science* **2013**, 341, 1502-1505; d) H. S. Kim, J. B. Cook, H. Lin, J. S. Ko, S. H. Tolbert, V. Ozolins, B. Dunn, *Nat. Mater.* **2017**, 16, 454-460; e) V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P.-L. Taberna, S. H. Tolbert, H. D. Abruña, P. Simon, B. Dunn, *Nat. Mater.* **2013**, 12, 518-522; f) C. Largeot, C. Portet, J. Chmiola, P.-L. Taberna, Y. Gogotsi, P. Simon, *J. Am.*

- Chem. Soc.* **2008**, *130*, 2730-2731; g) Y. Wang, Y. Song, Y. Xia, *Chem. Soc. Rev.* **2016**, *45*, 5925-5950.
- [5] a) G. G. Amatucci, F. Badway, A. Du Pasquier, T. Zheng, *J. Electrochem. Soc.* **2001**, *148*, A930-A939; b) T. Aida, K. Yamada, M. Morita, *Electrochem. Solid-State Lett.* **2006**, *9*, A534-A536; c) M. S. Park, Y. G. Lim, J. H. Kim, Y. J. Kim, J. Cho, J. S. Kim, *Adv. Energy Mater.* **2011**, *1*, 1002-1006; d) K. Naoi, W. Naoi, S. Aoyagi, J.-i. Miyamoto, T. Kamino, *Acc. Chem. Res.* **2013**, *46*, 1075-1083; e) V. Aravindan, J. Gnanaraj, Y.-S. Lee, S. Madhavi, *Chem. Rev.* **2014**, *114*, 11619-11635; f) P. Jeżowski, O. Crosnier, E. Deunf, P. Poizot, F. Béguin, T. Brousse, *Nat. Mater.* **2017**, *17*, 167; g) F. Sun, X. Liu, H. B. Wu, L. Wang, J. Gao, H. Li, Y. Lu, *Nano Lett.* **2018**, *18*, 3368-3376; h) V. Khomenko, E. Raymundo-Piñero, F. Béguin, *J. Power Sources* **2008**, *177*, 643-651.
- [6] a) B. Li, J. Zheng, H. Zhang, L. Jin, D. Yang, H. Lv, C. Shen, A. Shellikeri, Y. Zheng, R. Gong, J. P. Zheng, C. Zhang, *Adv. Mater.* **2018**, *30*, 1705670; b) X. Wang, G. Shi, *Energy Environ. Sci.* **2015**, *8*, 790-823.
- [7] a) J. A. Seel, J. R. Dahn, *J. Electrochem. Soc.* **2000**, *147*, 892-898; b) T. Ishihara, M. Koga, H. Matsumoto, M. Yoshio, *Electrochem. Solid-State Lett.* **2007**, *10*, A74-A76; c) W. Märkle, N. Tran, D. Goers, M. E. Spahr, P. Novák, *Carbon* **2009**, *47*, 2727-2732; d) T. Placke, O. Fromm, S. F. Lux, P. Bieker, S. Rothermel, H.-W. Meyer, S. Passerini, M. Winter, *J. Electrochem. Soc.* **2012**, *159*, A1755-A1765; e) J. A. Read, A. V. Cresce, M. H. Ervin, K. Xu, *Energy Environ. Sci.* **2014**, *7*, 617-620; f) S. Rothermel, P. Meister, O. Fromm, J. Huesker, H. W. Meyer, M. Winter, T. Placke, *ECS Trans.* **2014**, *58*, 15-25; g) S. Rothermel, P. Meister, G. Schmuelling, O. Fromm, H.-W. Meyer, S. Nowak, M. Winter, T. Placke, *Energy Environ. Sci.* **2014**, *7*, 3412-3423; h) M. Sheng, F. Zhang, B. Ji, X. Tong, Y. Tang, *Adv. Energy Mater.* **2016**, 1601963-n/a; i) K. Beltrop, S. Beuker, A. Heckmann, M. Winter, T. Placke, *Energy Environ. Sci.* **2017**, *10*, 2090-2094; j) L.

- Fan, Q. Liu, S. Chen, Z. Xu, B. Lu, *Adv. Energy Mater.* **2017**, 7, 1602778; k) B. Ji, F. Zhang, N. Wu, Y. Tang, *Adv. Energy Mater.* **2017**, 7, 1700920.
- [8] a) H. Wang, M. Yoshio, *Electrochem. Commun.* **2006**, 8, 1481-1486; b) M. Yoshio, H. Nakamura, H. Wang, *Electrochem. Solid-State Lett.* **2006**, 9, A561-A563; c) H. Wang, M. Yoshio, *J. Power Sources* **2010**, 195, 1263-1265; d) N. Gunawardhana, G.-J. Park, N. Dimov, A. K. Thapa, H. Nakamura, H. Wang, T. Ishihara, M. Yoshio, *J. Power Sources* **2011**, 196, 7886-7890; e) A. K. Thapa, G. Park, H. Nakamura, T. Ishihara, N. Moriyama, T. Kawamura, H. Wang, M. Yoshio, *Electrochim. Acta* **2010**, 55, 7305-7309; f) L. Zhao, L. Qi, H. Wang, *J. Power Sources* **2013**, 242, 597-603; g) G. Park, N. Gunawardhana, C. Lee, S.-M. Lee, Y.-S. Lee, M. Yoshio, *J. Power Sources* **2013**, 236, 145-150.
- [9] a) H. Wang, M. Yoshio, *Chem. Commun.* **2010**, 46, 1544-1546; b) G. Wang, F. Wang, P. Zhang, J. Zhang, T. Zhang, K. Mullen, X. Feng, *Adv. Mater.* **2018**.
- [10] J. T. Mefford, W. G. Hardin, S. Dai, K. P. Johnston, K. J. Stevenson, *Nat. Mater.* **2014**, 13, 726.
- [11] J. A. Read, *J. Phys. Chem. C* **2015**, 119, 8438-8446.
- [12] L. J. Hardwick, M. Hahn, P. Ruch, M. Holzapfel, W. Scheifele, H. Buqa, F. Krumeich, P. Novák, R. Kötz, *Electrochim. Acta* **2006**, 52, 675-680.
- [13] M.-C. Lin, M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B.-J. Hwang, H. Dai, *Nature* **2015**, 520, 324-328.
- [14] G. Wang, F. Wang, P. Zhang, J. Zhang, T. Zhang, K. Mullen, X. Feng, *Adv. Mater.* **2018**, 30, e1802949.
- [15] B. Li, F. Dai, Q. Xiao, L. Yang, J. Shen, C. Zhang, M. Cai, *Adv. Energy Mater.* **2016**, 6, 1600802.
- [16] H. Wang, Y. Zhang, H. Ang, Y. Zhang, H. T. Tan, Y. Zhang, Y. Guo, J. B. Franklin, X. L. Wu, M. Srinivasan, H. J. Fan, Q. Yan, *Adv. Funct. Mater.* **2016**, 26, 3082-3093.

- [17] H. Kim, M.-Y. Cho, M.-H. Kim, K.-Y. Park, H. Gwon, Y. Lee, K. C. Roh, K. Kang, *Adv. Energy Mater.* **2013**, 3, 1500-1506.
- [18] Z. Chen, V. Augustyn, J. Wen, Y. Zhang, M. Shen, B. Dunn, Y. Lu, *Adv. Mater.* **2011**, 23, 791-795.
- [19] X. Wang, P. S. Lee, *J. Mater. Chem. A* **2015**, 3, 21706-21712.
- [20] Q. Xia, H. Yang, M. Wang, M. Yang, Q. Guo, L. Wan, H. Xia, Y. Yu, *Adv. Energy Mater.* **2017**, 7, 1701336-n/a.
- [21] T. Ling, P. Da, X. Zheng, B. Ge, Z. Hu, M. Wu, X.-W. Du, W.-B. Hu, M. Jaroniec, S.-Z. Qiao, *Science Advances* **2018**, 4.

Figure 1. Comparison of conventional LICs and the proposed LpCs. Configuration and typical charge-discharge curves of (a, c) LICs and (b, d) LpCs.

Figure 2. Electrochemical performance of AC and graphite cathodes. (a) Typical CV curves of AC and graphite cathodes at 1 mV/s; (b) CV curves at different scan rates, (c) charge-discharge curves at various current rates (d) cycling performance at 1 A/g of graphite cathode; (e) capacity and V_m comparison of AC and graphite cathodes; (f) Ragone plots of AC and graphite cathodes based on cathode mass.

Figure 3. Structure evolution of graphite cathode. (a) The galvanostatic charge-discharge profile of graphite cathode at 0.1A/g; (b) *Ex-situ* XRD patterns of graphite cathode at different charge states, as marked on the corresponding electrochemical profiles. (c) High resolution F1s and P2p XP spectra of pristine, intercalated and deintercalated graphite cathode. SEM elemental mapping images of (d) intercalated and (e) deintercalated graphite cathode.

Figure 4. Electrochemical performance of G-G LIPCs. (a) CV curve at 1 mV/s; (b) charge-discharge curve and (c) cycling performance at 0.1 A/g; (d) rate performance; (e) long-term cycling stability at 1 A/g; (f) EIS of G-G LIPCs; (g) rate performance in an expanded voltage window of 3-5.2V; (h) quick charge ability; (i) Ragone plots of G-G LIPCs.

Graphite cathode stores charge via a Faradaic pseudocapacitive intercalation process, which is distinct from the surface electrostatic adsorption of activated carbon (AC). Higher energy density can be achieved on graphite cathode than AC cathode, while maintaining excellent power capability. Li-ion pseudocapacitors based on graphite cathode are proposed and demonstrated for the first time.

Li-ion pseudocapacitors

Gang Wang, Steffen Oswald, Markus Löffler, Klaus Müllen and Xinliang Feng*

Beyond activated carbon: graphite cathode-derived Li-ion pseudocapacitors with high energy and high power densities