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An *in-situ* fabricated graphene/bi-polar polymer hybrid material delivers ultra-long cycle life over 15,000 cycles as a high-performance electrode material

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Keywords: lithium-ion batteries, organic electrode material, 3D graphene hybrid material, ultra-long cycle life

Abstract

Organic electrode materials are promising for the future energy storage systems owing to their tunable structures, abundant resources and environmental friendliness *etc*. Many advanced lithium-ion batteries (LIBs) with organic electrodes are developed and show excellent performance. However, developing organic materials with overall superior performance still face great challenges such as low capacity, poor stability, inferior conductivity and low utilization of active sites. To address these issues, a bi-polar polymer (Fc-DAB) is designed and further polymerized *in-situ* with three-dimensional graphene (3DG), offering a hybrid material (Fc-DAB@3DG) with a variety of merits. Fc-DAB possesses stable polymer backbone and multiple redox-active sites that could improve stability and capacity simultaneously. The imbedded highly conductive 3DG network endows Fc-DAB@3DG with stable conductive framework, large surface area and porous morphology

all together, so the fast ions/electrons diffusion could be achieved, leading to high utilization of active sites and enhanced electrochemical performance. As a result, Fc-DAB@3DG cathode delivers capacity of ~260 mA h g⁻¹ at 25 mA g⁻¹, ultra-long cycle life over 15,000 cycles at 2,000 mA g⁻¹ with retention of 99.999 % per cycle and remarkable rate performance. The quasi-solid Li metal battery and full cell fabricated using this material also exhibit superior electrochemical performance.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely used in various areas for decades and would play an even bigger role in the future energy storage systems.^[1] Most conventional and commercial LIBs are fabricated by inorganic electrode materials such as LiCoO₂ and LiMn₂O₄, which face challenges of limited resources, environmental pollutions, low capacity and toxicity etc.^[2] In contrast to these lithium transition metal oxides based inorganic electrode materials, organic materials are endowed with a variety of merits. Organic materials mainly consist of light and naturally abundant elements (C, H, O and N etc), showing features of plenty resources, environmental friendliness, high gravimetric capacity, nontoxicity and flexibility.^[3] Together with their tunable structure, it's possible to design organic electrode materials with excellent performance and reusability, being promising for the next generation of LIBs.^[4] Various advanced organic electrode materials have been designed and synthesized for LIBs with high electrochemical performance, which can be classified into three types based on the redox reactions.^[5] N-type materials are likely to be reduced from their neutral state and combine cations from electrolyte, while p-type materials intend to be oxidized and interact with anions of electrolyte. Bi-polar materials possess both n-type and p-type moieties that could be reduced or oxidized from the neutral state, containing multiple redox states.^[5]

Many LIBs based on organic electrodes exhibit good electrochemical performance. However, the development of organic battery materials has been limited by several factors.^[2] Organic small molecules containing multiple redox groups could deliver high capacity, but they generally exhibit a fast capacity decay due to their high solubility in electrolyte.^[6] Polymers with stable backbones show less dissolution and thus improved stability, but their capacity would be sacrificed when introducing excess redox-inactive moieties into the structure.^[7] So, high capacity and stability are difficult to be balanced in one organic material. More importantly, the intrinsic shortcoming of most organic materials is their insufficient electronic conductivity, leading to inferior rate performance/capacity.^[8] To address this intrinsic issue of organic electrode materials, various approaches have been carried out, such as using carbon-based materials as conductive additives^[6, 9] or loading these materials on carbon-based conductive skeletons.^[10] While the conductivity between grains of active materials could be greatly improved using these approaches,^[11] organic batteries based on the composite materials still exhibit limited capacity and rate performance. This is most likely caused by the stacked morphology and buried active sites of materials, that is, inhomogeneous dispersion state of conducting and active materials exists widely in these materials.^[12] As a result, organic electrode materials with simultaneously high theoretical capacity, superb stability, ideal conductivity and desired morphology for LIBs with comprehensively high performance is still largely envisioned.

To achieve such a goal, both the chemical structures of molecules and the morphologies of materials should be carefully considered and elaborately designed. N-type and p-type organic electrodes use cations and anions as charge carriers, respectively.^[8] N-type organic electrodes feature with high capacity but low redox potential, while p-type organic electrodes show high working voltage but limited capacity. Bi-polar organic electrode materials could simultaneously have cation and anion units, which could combine the advantages of both n-type and p-type organic electrodes, exhibiting more characteristics than that with only

anionic or cationic units.^[13] Besides, bi-polar organic electrode materials could exhibit wide working potential and improved capacity. Bi-polar polymers possess stable polymer skeleton and multiple redox states, which could maximize the number of transferred electrons per unit and promote theoretical capacity, giving balanced high stability and capacity.^[13a, 13b] Highly conductive carbon-based materials with large surface area and stable framework could facilitate electrons transportation and suppresses the dissolution of active materials, becoming important components of electrode materials to improve poor conductivity and stability.^[14] Various carbon-based materials in the form of 0D dots, 1D fiber, 2D sheets and 3D network are used as conducive additives or matrixes for advanced organic electrode materials, such as carbon nanotube, carbon fiber, graphene and so on.^[11, 15] Among these highly conductive carbon-based materials, three-dimensional crosslinked graphene (3DG) possesses advantages of stable continuous/interconnected conductive network and ideal compatibility with organic compounds, which makes it one of the best candidates to prepare high-performance electrode materials.^[16] Besides, 3DG/polymer composite and hybrid materials with porous morphology could be in-situ constructed by using organic molecules and graphene oxide (GO) units through simple one-step solvothermal synthesis, which is effective to restrain the accumulation of polymer particles and expose adequate active sites of materials.^[17] So, it is believed that by *in-situ* integrating 3DG network and bi-polar polymer into one hybrid material, a high-performance organic electrode material could be generated with simultaneously high capacity, superb stability, superior conductivity, fast ions/electrons diffusion and high utilization of active sites.

Herein, we first designed and synthesized a new bi-polar polymer (Fc-DAB) with maximized redox-active sites per unit by condensation between ferrocene-1,1'-dicarbaldehyde (Fc) and 1,4-diaminobenzene (DAB) monomers.^[12a] Upon the electrochemical reaction, p-type Fe^{2+} moiety can be oxidized by removing electrons and combining anions (PF₆⁻) from electrolyte,^[18] and n-type C=N group could be reduced through

accepting electrons and binding cations (Li⁺) of electrolyte, bringing theoretical capacity of 256 mA h g⁻¹.^[19] Furthermore, 3DG is *in-situ* introduced in the Fc-DAB preparation process by the efficient solvothermal method, generating a quite stable and porous highly conductive hybrid material (Fc-DAB@3DG). Therefore, Fc-DAB@3DG has much favorable characters of ultra-stable crosslinked scaffold, highly conductive interconnected network, porous morphology and improved ions/electrons accessibility to multiple redox-active sites. All these together synergistically lead to an overall remarkable electrochemical performance. As results, the half-cell made of Fc-DAB@3DG cathode delivers capacity of ~ 260 mA h g⁻¹ at 25 mA g⁻¹, much higher than that of Fc-DAB without 3DG (210 mA h g⁻¹). Fc-DAB@3DG cathode also shows superior rate performance, which is contributed from its higher conductivity and utilization of the redox-active sites. For example, under current of 2,000 mA g^{-1} , the hybrid material exhibits ultra-high cycling stability over 15,000 cycles with excellent retention of 99.999 % per cycle. Furthermore, quasi-solid Li metal battery and full cell fabricated by Fc-DAB@3DG cathode also display high overall performance, suggesting that Fc-DAB@3DG has feasible compatibility with different electrolytes and anode materials, being promising for practical high-performance LIBs. These results reveal that the strategy of *in-situ* combining graphene network with bi-polar polymer could greatly enhance overall performance of organic electrode materials.

2. Results and discussion

2.1 Material synthesis and characterization

Fc-DAB was synthesized by condensation between Fc and DAB monomers in n-butyl alcohol (*n*-BuOH) solvent with acetic acid as the catalyst under 120 °C for 72 h (Figure 1a), and the experimental details are given in supporting information (Section S3).^[12a] C=N bond with redox activeness is produced during the reaction, helping construct stable polymer

skeleton without sacrificing too much of its capacity. During the polymerization process, the polymer is generated and may pack into irregular particles (Scheme 1a). The *in-situ* fabricated 3DG/polymer hybrid material (Fc-DAB@3DG) was obtained by mixing GO unit with the two monomers directly during the polycondensation. With a series of optimization, 10 wt% of GO was found to offer the best results. Thus, the hybrid material Fc-DAB@3DG with multiple active sites and stable highly conductive porous framework could be gained directly by the simple and effective one-step solvothermal method without extra complicated post treatment (Scheme 1b).



Scheme 1. Schematic diagram of preparation, morphology and ions/electrons diffusion for a) Fc-DAB and b) Fc-DAB@3DG.

From the results of thermogravimetric analysis (TGA), both polymer Fc-DAB and hybrid material Fc-DAB@3DG show high thermal stability, and over 96 % of the weight could be maintained under 300 °C (Figure 1b). Clear G and D bands appear in the Raman spectrum of Fc-DAB@3DG compared to Fc-DAB, which indicates the successfully integration of 3DG network into the hybrid material as expected (Figure 1c).^[17b] By *in-situ* forming porous

interconnected 3DG scaffold, larger surface area of 151.03 m² g⁻¹ can be achieved for Fc-DAB@3DG, while the pure polymer only shows surface area of 19.95 m² g⁻¹ (Figure 1d). The larger surface area of Fc-DAB@3DG would facilitate to expose more redox-active sites and accessibility of ions/electrons to these sites, promoting utilization of active sites (Scheme 1b).^[20] FT-IR spectra for Fc-DAB and Fc-DAB@3DG show peaks of C=N group at 1575 cm⁻¹, indicating the formation of redox-active bond during polymerization (Figure S1).^[21] Besides, the disappeared peaks of -NH₂ (3100-3400 cm⁻¹) from DAB and -CHO (1660 cm⁻¹) from Fc suggest the consumption of the end groups of monomers.^[12a] Figure S2 gives XPS survey spectra of Fc-DAB and Fc-DAB@3DG, from which peaks of C 1s, N 1s, O 1s and Fe 2p could be observed. Moreover, Fc-DAB@3DG has much higher electronic conductivity of 1.70×10^{-5} S cm⁻¹ than that of Fc-DAB (5.81×10⁻⁸ S cm⁻¹), which benefits from the highly conductive 3DG network.



Figure 1. Structure and characterization of Fc-DAB and Fc-DAB@3DG. a) Structure of Fc-DAB. b) Thermogravimetric analysis (TGA) of 3DG, Fc-DAB and Fc-DAB@3DG in the range of 40-1000 °C under N₂. c) Raman shifts of Fc-DAB and Fc-DAB@3DG. d) Brunauer-Emmett-Teller (BET) isotherms of Fc-DAB and Fc-DAB@3DG at 77K. Scanning electron microscopy (SEM) images of e) Fc-DAB and f) Fc-DAB@3DG.

Note the morphology of these two materials, Fc-DAB and Fc-DAB@3DG show significant difference. For example, packed particles with irregular shapes and sizes are observed in Fc-DAB (Figure 1e). Such aggregation may restrain the completely penetration of electrolyte and the accessibility of ions/electrons into the redox-active sites inside the granules, leading to low utilization of active sites and thus poor electrochemical performance (Scheme 1a). As a contrast, a porous 3D crosslinked graphene network with conformal polymer coating is observed in Fc-DAB@3DG, indicating successful suppression of polymer aggregation. (Figure 1f and S4b).^[22] Besides, energy dispersive spectroscopy (EDS) analysis shows that C, N and Fe elements distribute evenly in the porous hybrid material (Figure S4c), further revealing the uniform dispersion of polymer on the 3DG scaffold. This porous structure enables efficient bulk ions/electrons diffusion pathways and accessibility of ions/electrons to the redox-active sites, conductive to promoted electrochemical performance (Scheme 1b).^[23]

2.2 Electrochemical performance of half-cells

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The theoretical capacity of organic electrode material can be calculated by the equation: C = n*F/(3.6*M), where n is the number of the transferred electrons of molecule, F is the Faraday constant (96485 C mol⁻¹) and M is the molecular mass (g mol⁻¹).^[8] In one repeating unit of Fc-DAB, n is 3 and M equals to 314 g mol⁻¹, so the theoretical capacity of Fc-DAB is 256 mA h g⁻¹.

All the electrochemical experiments of the half-cells are conducted in the potential range of 1.2-4.0 V (*vs* Li/Li⁺). The redox reaction of Fc-DAB is first evaluated using cyclic

voltammetry (CV) as shown in Figure S5, and two pair of redox peaks located at 3.2-3.6 V and 1.8-2.4 V (*vs* Li/Li⁺) are observed. The first one can be ascribed to transformation between Fe²⁺ and Fe³⁺, which is p-type redox-active moiety,^[18] and the latter are related to n-type redox-active moiety (C=N group).^[6, 12a] The bi-polar feature endows it with wide working potential window and maximized number of transferred electrons per unit of polymer, improving its theoretical capacity. From Capacity-voltage profiles (Figure S6a), Fc-DAB gives reversible capacity of ~210 mA h g⁻¹ at 25 mA g⁻¹, much lower than its theoretical value. This relatively low utilization of redox-active sites is probably caused by the aggregation of polymer particles and thus poor accessibility of ions/electrons to the active sites.



Figure 2. Electrochemical performance of half-cells based on Fc-DAB and Fc-DAB@3DG cathode and Li metal anode in the potential range of 1.2-4.0 V (*vs* Li/Li⁺). a) Cyclic voltammetry (CV) curves at 0.3 mV s⁻¹ in the initial three cycles for Fc-DAB@3DG. b) Capacity-voltage profiles of Fc-DAB@3DG at 25 mA g⁻¹ in the initial 3 cycles. c) Cycle performance of Fc-DAB and Fc-DAB@3DG cathode at 50 mA g⁻¹. d) Rate performance of Fc-DAB@3DG cathode. e) Long-cycle performance for Fc-DAB and Fc-DAB@3DG cathode at 2,000 mA g⁻¹.

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After *in-situ* hybridizing with 3DG, Fc-DAB@3DG shows similar shapes of CV curves and capacity-voltage profiles (Figure 2a and 2b), indicating reversible redox process dominated by Fc-DAB active material as expected. Since C=N bonds exist in a large polymer system and 3DG has capacity contribution/influence on Fc-DAB@3DG (Figure S20), the redox peaks at 1.8-2.4 V (*vs* Li/Li⁺) become broad and difficult to identify.^[14b] This phenomenon is also common in other organic/carbon composite materials.^[14c] Regarding to capacity, as expected, Fc-DAB@3DG delivers much higher reversible capacity of ~260 mA h g⁻¹ at 25 mA g⁻¹, suggesting ideal utilization of redox-active sites for the *in-situ* prepared hybrid material. The practical capacity is higher than its theoretical value, which is caused by the capacity contribution from the conductive additive (Ketjen Black KB) (Figure S21). If subtracting the capacity contribution from KB in our electrode material, the practical capacity of Fc-DAB@3DG is ~220 mA h g⁻¹ at 25 mA g⁻¹.

Even at a higher current density of 50 mA g⁻¹, Fc-DAB@3DG still exhibits reversible capacity of 246.8 mA h g⁻¹ and a small capacity decay (<1.3%) can be observed after 100 cycles (Figure 2c). As comparison, Fc-DAB only displays initial capacity of ~200 mA h g⁻¹ at 50 mA g⁻¹, and only 74.8 % of its capacity can be retained after 100 cycles. Furthermore, Fc-DAB@3DG also gives capacity of 162.5 mA h g⁻¹ with retention of 98.0 % after 500 cycles under current of 1,000 mA g⁻¹ (Figure S7). Gradually activation process could be observed with elevated capacity of 140 mA h g⁻¹ at 2,000 mA g⁻¹ during long-cycle experiments, which is a common phenomenon in carbon-based organic electrode materials (Figure 2e). The capacity self-activation process happens slowly in the carbon-based hybrid material, so the capacity increase slowly during the initial hundreds of cycles, which has also been observed in many related studies.^[10c, 13a] Remarkably, Fc-DAB@3DG delivers reversible capacity of 120 mA h g⁻¹ even after 15,000 cycles (over 200 days) at 2,000 mA g⁻¹, achieving excellent retention of 99.999 % per cycle. These results indicate that Fc-DAB@3DG demonstrates both relatively higher capacity and longer cycle life

simultaneously when compared to other organic cathode materials from previous studies (Figure S8 and Table S1). The ultra-long cycle life and superb cycling stability of Fc-DAB@3DG should benefit from its highly stable conductive scaffold provided by 3DG network. Meanwhile, larger surface area and porous morphology endow Fc-DAB@3DG with higher accessibility of ions/electrons to its redox-active sites and thus higher capacities when compared to Fc-DAB. It achieves reversible capacity of 222, 201, 173, 155, 130 and 114 mA h g⁻¹ at currents of 100, 200, 500, 1000, 2500 and 5000 mA g⁻¹, respectively (Figure 2d and S6c). As a result, both the unique molecular structure of polymer and the elaborate network of hybrid material contribute to the overall excellent electrochemical performance of Fc-DAB@3DG.

2.3 Redox mechanism

The proposed redox process of Fc-DAB is given in Figure 3a. After charging (Fc-DAB-PF₆), Fe²⁺ moiety of the polymer could be oxidized to Fe³⁺ and interact with PF₆⁻ from electrolyte.^[19] When discharging, Fe³⁺ would be reduced to Fe²⁺ firstly, then C=N bonds could be reduced and combine Li⁺, forming Fc-DAB-Li.^[12a] These two-step three-electrons redox process maximizes the capacity by integrating multiple redox-active sites into one unit of polymer. The geometry optimization for the two repeating units of Fc-DAB (2Fc-DAB) at three redox states is conducted by DFT calculation (Figure 3b).^[24] Fe²⁺ is oxidized and PF₆⁻ locates adjacent to Fe³⁺ after charging in 2Fc-DAB-2PF₆, and Li⁺ interacts with nitrogen atom after discharging in 2Fc-DAB-4Li, which is consistent with the proposed redox mechanism.^[25]

Ex-situ XPS and ATR-IR spectra for Fc-DAB@3DG cathode are studied at different states during one charge/discharge cycle (Figure 3c). "a" and "d" represent the initial state (Fc-DAB@3DG), which is a neutral state. "b" and "e" are charged state (Fc-DAB@3DG-PF₆) with positively charged polymer and PF₆⁻. "c" is discharged state

(Fc-DAB@3DG-Li) containing negatively charged polymer and Li⁺. High-resolution XPS spectra for P 2p at different states exhibit peaks corresponding to PF_6^- , showing reversible appearance and disappearance, indicating the reversible insertion/de-insertion of PF_6^- into/from the cathode during charge/discharge process, respectively (Figure 3d).^[26] High-resolution XPS spectra for Li 1s at different states display the adverse trend as compared to P 2p spectra (Figure 3e). Peak of Li⁺ reversibly decreases and increases, revealing reversible de-intercalation/intercalation of Li⁺ from/into the cathode after charging/discharging, respectively.^[27] *Ex-situ* XPS characterizations for high-resolution spectra of N 1s and Fe 2p at different states also show reversible changes of this bi-polar cathode material during redox process (Figure S9), which is also consistent with the proposed redox process.



Figure 3. Redox mechanism. a) Redox process of Fc-DAB. b) The geometry optimization of different states for 2Fc-DAB through DFT calculations. c) Capacity-voltage profiles and different redox states of Fc-DAB@3DG for *ex-situ* XPS and ATR-IR measurement. *Ex-situ* XPS spectra of Fc-DAB@3DG cathode for d) P 2p and e) Li 1s. f) *Ex-situ* ATR-IR spectra of Fc-DAB@3DG cathode.

To further confirm the redox mechanism, *ex-situ* ATR-IR spectra of Fc-DAB@3DG cathode at different states during charge/discharge process are evaluated (Figure 3f). In the spectrum of Fc-DAB@3DG-PF₆ cathode (state "b" and "e"), peaks of PF₆⁻ at 552 and 838 cm⁻¹ strengthen after charging, suggesting the combination with PF₆⁻.^[28] Peaks of PF₆⁻ and C=N for Fc-DAB@3DG-Li cathode (state "c") become weaker when discharging, along with

the appearance of peak for N-Li located at 1389 cm⁻¹, corresponding to the de-insertion of PF₆⁻ and the reduction of C=N bond.^[27] Peak of C=N group could reversibly recover during the charge process, with the disappearance of peak from N-Li, suggesting ideal reversibility of redox reaction related to n-type moiety.^[29] All the results from DFT calculations, *ex-situ* XPS and ATR-IR analysis are consistent and support the proposed redox process for Fc-DAB and Fc-DAB@3DG.

2.4 Kinetic analysis

The half-cells made of Fc-DAB@3DG cathode show higher capacity, better rate performance and longer cycle life than that of Fc-DAB, which could be attributed to the well introduced stable conductive network of 3DG. Electrochemical impedance spectroscopy (EIS) measurements are conducted on half-cells fabricated by Fc-DAB@3DG and Fc-DAB cathode before and after 100 cycles under 2,000 mA g⁻¹, respectively (Figure 4a). As expected, Fc-DAB@3DG shows a smaller charge transfer resistance (R_{CT}) of 125.0 Ω before cycling, while Fc-DAB exhibits a much larger R_{CT} of 230.8 Ω . Furthermore, after 100 cycles, the R_{CT} of Fc-DAB@3DG cathode decreases to 14.21 Ω , while R_{CT} of Fc-DAB cathode only decreases to 41.8 Ω , still much larger than that of Fc-DAB@3DG cathode. The lower R_{CT} for Fc-DAB@3DG is in accordance with its higher electric conductivity, improving the transportation of electrons in the electrode and thus superior rate performance.^[30]

Galvanostatic intermittent titration technique (GITT) was used to obtain the Li⁺ diffusion coefficients of (D_{Li+}) for these two materials (Figure 4b). The D_{Li+} of Fc-DAB@3DG could reach 2.71×10⁻⁹ cm² s⁻¹ at 3.4 V (*vs* Li/Li⁺) when discharging with a relaxation time of 60 min, of which the magnitude is almost similar with those organic electrode materials in the reported studies (Figure 4d).^[30] Fc-DAB exhibits D_{Li+} of 1.06×10⁻⁹ cm² s⁻¹ at 3.4 V (*vs* Li/Li⁺) when discharging, lower than that of Fc-DAB@3DG. The GITT studies with different

tic Accebt relaxation time also give similar results as detailed in Figure S24. It reveals that Fc-DAB@3DG shows lower overvoltage and larger D_{Li+} than that of Fc-DAB in the GITT study, suggesting faster Li⁺ diffusion and better kinetics in Fc-DAB@3DG cathode.^[13a, 30] To further study the electrochemical reaction kinetics of Fc-DAB and Fc-DAB@3DG, CV curves at different scan rates were collected and analyzed (Figure S22). The results suggest that the kinetics of Fc-DAB and Fc-DAB@3DG cathode in half-cells are dominated by a combination of diffusion-controlled and surface capacitive-controlled process.^[31]

To sum up, the porous interconnected skeleton of 3DG in Fc-DAB@3DG provides highly conductive network and larger surface area, synergistically contributing to faster electrons/ions diffusion and effective utilization of redox-active sites. As a result, half-cells by using Fc-DAB@3DG cathode show comprehensively high electrochemical performance, such as higher capacity, ultra-long cycling stability and remarkable rate performance.



Figure 4. Kinetic analysis of Fc-DAB and Fc-DAB@3DG. a) Electrochemical impedance spectroscopy (EIS) in the frequency of 0.01-100,000 Hz for Fc-DAB and Fc-DAB@3DG in their initial states and after 100 cycles, respectively. b) Galvanostatic intermittent titration technique (GITT) analysis of Fc-DAB and Fc-DAB@3DG. The Li⁺ diffusion coefficients (D_{Li+}) of the Fc-DAB and Fc-DAB@3DG cathode in the corresponding potential range during c) charge process and d) discharge process.

2.5 Electrochemical performance of quasi-solid Li metal battery and full cell

As half-cells based on Fc-DAB@3DG cathode exhibit excellent electrochemical behaviors, then the quasi-solid Li metal battery and full cell are fabricated and studied. The quasi-solid Li metal battery are made of Fc-DAB@3DG cathode, in-situ gel electrolyte and Li metal anode (Figure 5a). The gel is *in-situ* polymerized by using triethylene glycol dimethacrylate (TEGDMA) monomer and 2,2'-azobisisoheptonitrile (ABVN) initiator.^[32] Commercial electrolyte is directly added before polymerization to provide Li salt and plasticizer, and the details are given in Section S4. Linear sweep voltammetry (LSV) reveals that the prepared *in-situ* gel electrolyte is stable at 4.5 V (vs Li/Li⁺), which is suitable for electrolyte of our organic cathode (Figure S10). The quasi-solid electrolyte gives moderate ion conductivity of 4.40 mS cm⁻¹ by EIS experiment (Figure S11). The quasi-solid Li metal battery exhibits similar CV curves and capacity voltage profiles with that of half-cell (Figure S12 and S13). Capacity of ~250 mA h g^{-1} could be remained after 100 cycles at 50 mA g^{-1} , showing neglectable capacity loss, which is comparable to that of half-cell (Figure S14). At higher rate, the quasi-solid Li metal battery gives capacity 146.7 mA h g⁻¹ at 2,000 mA g⁻¹ with retention of 99.998 % per cycle over 8,000 cycles, suggesting its ultra-high stability (Figure 5b). Reversible capacity of 201, 185, 167, 153 and 129 mA h g⁻¹ could be achieved under currents densities of 100, 200, 500, 1000 and 2500 mA g⁻¹, respectively, suggesting excellent rate performance of the quasi-solid Li metal battery (Figure 5c).

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More importantly, full battery fabricated by Fc-DAB@3DG cathode, prelithiated graphite anode and commercial electrolyte also exhibits comprehensively high electrochemical performance (Figure 5d). The observed redox peaks of CV curves shown in Figure S15 demonstrate the reversible redox reaction in the full cell, similar as that of half-cell. Reversible capacity of 236 mA h g⁻¹ at 50 mA g⁻¹ could be remained after 100 cycles, exhibiting high capacity and stability simultaneously (Figure S17). The full cell gives capacity of 163 mA h g⁻¹ at 500 mA g⁻¹ in the voltage range of 1.2-4.0 V after 600 cycles, indicating good cycling stability (Figure 5e). The full cell also exhibits superior rate performance as that of quasi-solid Li metal battery (Figure 5f). Capacity of 211, 190, 166, 147 and 120 mA h g⁻¹ could be obtained at 100, 200, 500, 1000 and 2500 mA g⁻¹, respectively. At higher current density of 1,000 mA g⁻¹, reversible capacity over 150 mA h g⁻¹ could be achieved after gradual activation, and 97.0 % of its capacity could be retained after 1,200 cycles, showing superior stability (Figure S18).



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Figure 5. Electrochemical performance of quasi-solid Li metal battery and full cell based on Fc-DAB@3DG cathode. a) Diagram b) Cycle performance at 2,000 mA g⁻¹ and c) Rate performance in the potential range of 1.2-4.0 V (*vs* Li/Li⁺) for quasi-solid Li metal battery by using Fc-DAB@3DG cathode and *in-situ* gel electrolyte. d) Diagram e) Cycle performance at 500 mA g⁻¹ and f) Rate performance in the voltage range of 1.2-4.0 V for full cell by using Fc-DAB@3DG cathode and graphite anode. g) Picture h) Capacity-voltage profiles and i) Cycle performance at 25 mA g⁻¹ from 1.2 to 4.0 V of pouch cell by using Fc-DAB@3DG cathode.

Pouch cell is also made by using Fc-DAB@3DG cathode and prelithiated graphite anode, and a red light emitting diode (LED) can be successfully powered by the pouch cell (Figure 5g). The pouch cell delivers capacity over 200 mA h g⁻¹ under current of 25 mA g⁻¹ with an average output voltage of ~2.3 V, which is difficult to achieve in pouch cells made of bi-polar organic cathode materials (Figure 5h). The pouch cell also possesses tolerable cycling stability (Figure 5i), promising for practical use. The excellent performance of quasi-solid Li metal battery and full cell indicates feasible compatibility of Fc-DAB@3DG with different electrolytes and anode materials, being potential for the future LIBs.

3. Conclusions

In this work, a 3DG/bi-polar polymer hybrid electrode material has been designed and synthesized through efficient one-step *in-situ* solvothermal method. The obtained Fc-DAB@3DG hybrid material possess multiple redox-active sites, stable highly conductive network, favorable ions/electrons diffusion pathways and high utilization of active sites. As expected, the LIBs fabricated by Fc-DAB@3DG cathode deliver high capacity, ultra-long cycle life and remarkable rate performance all together. The quasi-solid Li metal battery and the full cell made of Fc-DAB@3DG cathode also exhibit superior electrochemical performance. The overall ideal electrochemical performance suggests that our strategy of

in-situ fabrication 3DG/bi-polar polymer hybrid material is effective to design remarkable organic electrode materials for future LIBs.

4. Experimental Section

Experimental details are described in the Supporting Information.

Statistical Analysis

The measurements of weight (active materials, conductive additive, binder and electrode discs) are conducted three times by analytical balance with accuracy of 0.01 mg, then the average values are taken. The mass error for each cathode disc is less than 0.03 mg. The diameter of each electrode disc is 10.0 ± 0.1 mm. The temperature for solvothermal synthesis is 120.0 ± 2.0 °C. The temperature for material characterizations and electrochemical measurements is 25.0 ± 0.5 °C. The electrochemical measurements were conducted at least three times (five batteries each time) and the repetitive results were given in the manuscript. The data for material and electrochemical characterizations were directly used without smoothing. No software was used for statistical analysis.

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Conflict of interest

The authors declare no conflict of interest.

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Table of Contents



A graphene/bi-polar polymer hybrid material (Fc-DAB@3DG) is *in-situ* fabricated through a simple one-step solvothermal method. The Fc-DAB component provides high capacity and stability, while the three-dimensional interconnected conductive graphene network (3DG) endows Fc-DAB@3DG with fast ions/electrons diffusion and thus improved rate performance. Therefore, combined together, the material exhibits simultaneously high capacity, ultra-long cycle life and superior rate performance.