Supporting Information

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π-conjugation Induced Anchoring of Ferrocene on Graphdiyne Enable Shuttle-Free Redox Mediation in Lithium-Oxygen Batteries

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Figure S1  a) Structures geometry of GDY. b) Side view of GDY. c) 2D nanosheet with interlayer spacing of 0.483 nm for prepared GDY. d) Full atomistic model of GDY depicting the atomistic sexangular pores, with van der Waals openings on the order of 1.63 nm.
Figure S2 Digital photos of a) GDY and b) GDY/Fc.
Figure S3 a) TEM images, b) Elemental mapping. c,d) HRTEM image and e) profile of the interlayer distance of the pristine GDY.

The pristine GDY exhibits the nature of well-defined 2D layered structure (Figure S3a), where C and O evenly distribute (Figure S3b-c). The interlayer spacing of GDY was measured to be 0.462 nm (Figure S3d-e), which is smaller than that of GDY/Fc.
**Figure S4** a) N$_2$ adsorption/desorption isotherms and b) corresponding pore size distribution of GDY and GDY/Fc.

N$_2$ adsorption-desorption analysis (**Figure S4**) was used to determine the surface area and pore size distribution of the materials. It is calculated that the Brunauer-Emmett-Teller (BET) surface areas of GDY and GDY/Fc are 60.51 m$^2$/g and 53.98 m$^2$/g, respectively. The surface areas become smaller with the introduction of Fc, revealing the incorporation of Fc into GDY. In pore-size distribution curves, many mesoporous around 4-7 nm can be observed for GDY/Fc, which is consistent with the porous structure of GDY.
Figure S5 Digital photos of a) TEGDME with GDY/Fc after 1-day, 3-days and 7-days, b) TEGDME with soluble Fc.
Figure S6 Chronopotentiometry curves of GDY with different soluble 1 mM Fc (orange), 5 mM Fc (violet) and 10 mM Fc (green).
Figure S7 OER polarization curves of GDY w with different concentration soluble 1 mM Fc (orange), 5 mM Fc (violet) and 10 mM Fc (green).
Figure S8 Chronopotentiometry curves of GDY (red), GDY/Fc (blue) and GDY with 10 mM Fc (green).
Figure S9 Galvanostatic discharge/charge curves of Li-O₂ cells with KB.
Figure S10 a) The Fe loading on the layered GDY prepared by changing the amounts of Fc addition (Fc: GDY=1:1, 5:1, 10:1) in the synthesis process. b) The corresponding galvanostatic discharge curves of LOB with different immobilized amount of Fc at a current density of 200 mA g\textsuperscript{-1}.
Figure S11 a) Galvanostatic discharge/charge curves of Li-O₂ cells with GDY (red line), GDY/Fc (blue line), GDY with 10 mM Fc at a current density of a) 400 mA g⁻¹ and b) 800 mA g⁻¹.
Figure S12 Galvanostatic discharge/charge curves of cells with a) GDY, b) GDY/Fc, c) GDY with 10 mM Fc at a current density of 500 mA g\(^{-1}\) under an upper-limit capacity of 1000 mA h g\(^{-1}\), and d) with GDY/Fc at a current density of 200 mA g\(^{-1}\) under an upper-limit capacity of 500 mA h g\(^{-1}\).
Figure S13 Cyclic performance of LOB with GDY/Fc at a current density of 2000 mA g\(^{-1}\) with a fixed capacity of 2000 mA g\(^{-1}\).
### Table S1 Performance comparison for other representative published efforts.

| Materials               | Current Density (mA g\(^{-1}\)) | Specific Capacity (mA h g\(^{-1}\)) | Upper-limit Capacity (mA h g\(^{-1}\)) | Stability (cycles) | Reference |
|-------------------------|----------------------------------|--------------------------------------|----------------------------------------|--------------------|-----------|
| Ru\(_{0.3}\) SAs-NC     | 0.02 mA cm\(^{2}\)             | 13424                                | 1000                                   | 60 cycles at 0.02 mA cm\(^{2}\) | [22]      |
| TiO\(_{2}\)             | 100                              | 6568                                 | 500                                    | 40 cycles at 100 mAg\(^{-1}\) | [23]      |
| TiC/MWNTs               | 250                              | 3841                                 | 1000                                   | 90 cycles at 250 mAg\(^{-1}\) | [24]      |
| Co\(_{9}\)S\(_{8}\)@G/NS-PCNF | 100                     | 8269                                 | 1000                                   | 60 cycles at 200 mAg\(^{-1}\) | [25]      |
| Co-MOF-74               | 100                              | 11350                                | 1000                                   | 8 cycles at 250 mAg\(^{-1}\) | [26]      |
| Pt-CNHS                 | 200                              | 13843                                | 600                                    | 100 cycles at 100 mAg\(^{-1}\) | [27]      |
| Co[Co, Fe]O\(_{4}\)/NG  | 100                              | 13312                                | 1000                                   | 110 cycles at 100 mAg\(^{-1}\) | [28]      |
| GDY/Fe                  | 200                              | 14231                                | 1000                                   | 183 cycles at 200 mAg\(^{-1}\) | This work |
|                         |                                  |                                      | 80 cycles at 500 mAg\(^{-1}\)         |                    |           |
Figure S14 SEM images with different magnification of pristine GDY/Fc electrodes before discharging.
Figure S15 SEM images of the cathodes after discharged to 1000 mA h g$^{-1}$ with a-c) GDY, b-d) GDY in the presence of 10 mM Fc, and g-i) GDY/Fc
Figure S16  a) The fitting equivalent circuit and b) EIS spectra of Li-O$_2$ cells with b) GDY, c) GDY in the presence of 10 mM Fc, and d) GDY/Fc at different discharge/charge stages under a current density of 500 mA g$^{-1}$. 
Table S2: The corresponding fitted resistance value at different discharge/charge stages.

| State     | Before | Discharge | Recharge | ΔRecharge-Before |
|-----------|--------|-----------|----------|------------------|
| Candidates | Resistance value / ohm |          |          |                  |
| GDY       | 85.1   | 336       | 298      | 213              |
| GDY/Fc    | 167    | 328       | 287      | 120              |
| 10 mM Fc  | 149    | 309       | 287      | 138              |
Figure S17 a) Optimized structures of the pristine GDY/Fc and GDY/Fc after adsorbing Li$_2$O$_2$. b) Fe 2p XPS of the GDY/Fc cathode with different states. (Bottom: pristine, Top: after discharge).
Figure S18 Raman spectra of Li-O₂ cells with a) GDY, c) GDY in the presence of 10 mM Fc, and d) GDY/Fc at different cycle numbers.
Figure S19 Fe 2p XPS spectra of GDY/Fc cathode at different cycle numbers with a) 1st, b) 20th, c) 50th and d) 84th.
Figure S20 DEMS analysis of LOB with GDY/Fc during charging process for a) 1st cycling, b) 10th cycling and c) 100th cycling.
Equation S1

\[ Q = I \cdot t \]  \hspace{1cm} (1.1)

\[ v (e^-) = Q \cdot e^{-1} \]  \hspace{1cm} (1.2)

\[ v (O_2) = \text{GasEvol.Rate}/60 \cdot \text{NA} \]  \hspace{1cm} (1.3)
Equation S2

\[ \text{Li}^+ + \text{GDY/Fc} \rightarrow \text{GDY/Fc: Li}^+ \quad (2.1) \]

\[ \text{GDY/Fc: Li}^+ + \text{O}_2 + e^- \rightarrow \text{GDY/Fc: LiO}_2 \quad (2.2) \]

\[ \text{GDY/Fc: LiO}_2 + \text{Li}^+ + e^- \rightarrow \text{GDY/Fc: Li}_2\text{O}_2 \quad (2.3) \]

\[ \text{GDY/Fc: Li}_2\text{O}_2 + \text{O}_2 + 2\text{Li}^+ + 2e^- \rightarrow \text{GDY/Fc: (Li}_2\text{O}_2)_2 \quad (2.4) \]
**Figure S21** a, b) Calculated free energy diagrams for the discharge reactions on the active surface of GDY (redline) and GDY/Fc (blue line).
Table S3 the Δ\(G\) for the most endothermic step through different reaction pathways.

| Pathway | Δ\(U\) / eV |
|---------|-------------|
|         | GDY | GDY/Fc |
| **Pathway I** | | |
| *+ 2O\(_2\) + 4Li\(^+\) + 4e\(^-\) → *O\(_2\) + 4Li\(^+\) + O\(_2\) + 4e\(^-\)* | 0.58 | 0.5 |
| *O\(_2\) + 4Li\(^+\) + O\(_2\) + 4e\(^-\) → *LiO\(_2\) + 3Li\(^+\) + O\(_2\) + 3e\(^-\)* | | |
| *LiO\(_2\) + 3Li\(^+\) + O\(_2\) + 4e\(^-\) → *Li\(_2\)O\(_2\) + 2Li\(^+\) + O\(_2\) + 2e\(^-\)* | | |
| *Li\(_2\)O\(_2\) + 2Li\(^+\) + O\(_2\) + 2e\(^-\) → *(Li\(_2\)O\(_2\))\(_2\)* | | |
| **Pathway II** | | |
| *+ 4Li\(^+\) + 2O\(_2\) + 4e\(^-\) → *Li\(^+\) + 3Li\(^+\) + 2O\(_2\) + 4e\(^-\)* | 1.86 | 0.93 |
| * Li\(^+\) + 3Li\(^+\) + 2O\(_2\) + 4e\(^-\) → *LiO\(_2\) + 3Li\(^+\) + O\(_2\) + 3e\(^-\)* | | |
| *LiO\(_2\) + 3Li\(^+\) + O\(_2\) + 4e\(^-\) → *Li\(_2\)O\(_2\) + 2Li\(^+\) + O\(_2\) + 2e\(^-\)* | | |
| *Li\(_2\)O\(_2\) + 2Li\(^+\) + O\(_2\) + 2e\(^-\) → *(Li\(_2\)O\(_2\))\(_2\)* | | |
Figure S22 Optimized structures of GDY: O$_2^-$, GDY: LiO$_2$, GDY/Fc: O$_2^-$ and GDY/Fc: LiO$_2$ and corresponding adsorption energy.

| Structure       | Adsorption Energy |
|-----------------|-------------------|
| GDY: O$_2^-$    | $G_{ads} = -0.06$ eV |
| GDY: LiO$_2$    | $G_{ads} = -0.24$ eV |
| GDY/Fc: O$_2^-$ | $G_{ads} = -0.14$ eV |
| GDY/Fc: LiO$_2$ | $G_{ads} = -0.57$ eV |
Figure S23 Digital images of a) the assembled Li-O₂ pouch cell with GDY/Fc and b) the light-emitting diode lit by the Li-O₂ battery.