

Boosting a practical lithium carbon dioxide battery through a decoupled electrolyte

Corresponding Author: Professor Zaiping Guo

This manuscript has been previously reviewed at another journal. This document only contains information relating to versions considered at Nature Communications.

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This manuscript addresses a critical issue in Li–CO₂ battery systems: the dual requirement of maintaining high ionic conductivity while achieving long-term interfacial stability. The authors propose a novel “decoupled electrolyte” system, incorporating a TEGDME co-solvent into a highly conductive DMF-based electrolyte.

The work is novel, well-structured, and data-rich, with clear implications for energy storage research. However, there are some questions that should be addressed to strengthen the scientific rigor and clarity of the manuscript.

1. The term “decoupled” should be better contextualized. Is this concept applicable to other co-solvent systems beyond TEGDME/DMF?
2. Could the authors clarify if the decoupling is purely spatial (interface vs. bulk) or also temporal (e.g., during discharge vs. charge)?
3. Authors’ claim that TEGDME enables formation of more stable SEI (with high LiF and C-N content) is intriguing. Could the authors elaborate on how TEGDME decomposition contributes to inorganic SEI (LiF) when only LiFSI salt is the fluorine source?
4. The interpretation of ESP (Electrostatic potential) values and their preferential adsorption relies heavily on MD simulations. Did authors validate the force field used for this simulations with DFT or with any experimental parameters?
5. Have these ESP trends been validated with DFT calculations? Including this comparison would add robustness.
6. Supplementary figures (especially RDFs, ESP maps) should be referenced more clearly in the main text.
7. The frequent use of abbreviations (e.g., ESP, IHL, OHL) without initial definition in figures could confuse non-specialist readers.
8. “Decoupled” and “localized environment” are used frequently and interchangeably—clarify distinctions.
9. How do you distinguish between ESP-driven preferential adsorption and other effects such as viscosity or wettability on cathode surfaces?

Recommendation: Accept with minor revisions (subject to satisfactory response to the above comments and incorporation of suggestions).

Reviewer #2

(Remarks to the Author)

In this manuscript, the authors report a decoupled electrolyte design that stabilizes the electrolyte/cathode interface in Li–CO₂ batteries while preserving high ionic conductivity. Combining theoretical calculations with in-situ and ex-situ characterizations, they demonstrate that the TEGDME-rich interfacial environment suppresses DMF-related side reactions and enhances Li₂CO₃ reversibility. The findings are well supported and offer valuable insights into electrolyte and interface engineering for metal-gas batteries. Overall, I recommend minor revisions before publication in Nat. Commun.

1. Please add more description of the abbreviations IHL and OHL in the Figure 1 caption for clarity to readers unfamiliar with EDL structure.
2. The asterisk * used to mark side reaction products should be explained in the Figure 2g caption.

3. The radar plot in Fig. 3a compares co-solvent candidates. A brief explanation of how the $|ESP_{min}| - ESP_{max}$ value reflects the solvent's coordination strength with Li^+ ions should be presented in the main text.
4. In the theoretical calculation section, the manuscript mentions ESP values obtained via Gaussian. Please specify the level of theory and whether geometry optimizations were performed prior to ESP mapping, to ensure reproducibility.
5. In Supplementary Fig. 19 and 21, the MD snapshots show solvent distributions under different charge states. A brief discussion of the applied surface charge density ($\pm 1.8 \mu C cm^{-2}$) would help readers better understand the simulation conditions.
6. In Fig. 6a-b, the authors correlate the intensity of C-N peaks in the C 1s and N 1s spectra with improved catalytic property toward Li_2CO_3 decomposition. A brief explanation of how C-N species in the SEIs function catalytically during charge/discharge processes should be added for better understanding.
7. Please carefully check the reference list to ensure all citations are presented in correct numerical order and with accurate formatting. Reference 2 cites the year 2024 but Chem. Rev. 104 was published in 2004.

Reviewer #3

(Remarks to the Author)

This manuscript presents the design of a decoupled electrolyte for $Li-CO_2$ batteries, focusing on enhancing interfacial stability and maintaining high ionic conductivity simultaneously. By incorporating TEGDME into a DMF-based electrolyte, the authors effectively suppress DMF-related side reactions, thereby promoting Li_2CO_3 reversibility and extending battery cycle life. The combination of theoretical calculations and characterizations provides a comprehensive understanding of electrolyte composition and interfacial structure during cycling. The work is well-structured and demonstrates significant potential for advancing electrolyte design strategies for metal-gas batteries. Minor revisions are recommended before acceptance in Nat. Commun.

1. In Fig. 2f, the rate performance data are presented, but the specific values for each current density are not clearly stated. Please add these values in the figure caption or main manuscript to facilitate a more quantitative comparison.
2. The ESP values are critical to the proposed mechanism. Please specify the Gaussian basis set and functional used to ensure reproducibility in the computational method.
3. The Raman spectra in Supplementary Fig. 14 indicate distinct shifts with increasing TEGDME content. An explanation of how these shifts correlate with changes in Li^+ solvation structures should be included to enhance the understanding of the observed differences.
4. The decoupled electrolyte is presented as a mixture of DMF and TEGDME, but the rationale for selecting the optimal volume ratio of 3:7 is not fully discussed. Please address how other ratios (e.g., 1:9, 5:5) impact electrochemical performance to provide a more comprehensive perspective on electrolyte composition design.
5. Several key findings, such as LUMO energy values for TEGDME and DMF, are discussed but not directly presented in the main manuscript. Please add a brief reference to the Supplementary Figure or Table in the relevant sections.
6. In Fig. 6, the XPS analysis highlights C-N species as key catalytic components in the SEI. However, Fig. 6 only compares the XPS results of cycled cathodes in the DMSO and decoupled electrolytes. To provide a more comprehensive understanding of SEI formation across different electrolyte systems, the XPS analysis for C-N species in the DMF-only electrolyte should be compared with these electrolytes.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

I believe the authors have addressed all of my questions and concerns. In my opinion, the manuscript is now ready for publication.

Reviewer #2

(Remarks to the Author)

The revision is satisfied and should be published as soon as possible.

Reviewer #3

(Remarks to the Author)

The authors have addressed the concerned issues clearly. The revised manuscript can be accepted.

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Point-by-Point Response to the Reviewers' Comments

Reply to Reviewer 1

Overall comment: *This manuscript addresses a critical issue in Li-CO₂ battery systems: the dual requirement of maintaining high ionic conductivity while achieving long-term interfacial stability. The authors propose a novel “decoupled electrolyte” system, incorporating a TEGDME co-solvent into a highly conductive DMF-based electrolyte.*

The work is novel, well-structured, and data-rich, with clear implications for energy storage research. However, there are some questions that should be addressed to strengthen the scientific rigor and clarity of the manuscript.

Recommendation: Accept with minor revisions (subject to satisfactory response to the above comments and incorporation of suggestions).

Reply: We value your comments and suggestions, which have been very helpful for improving the quality of our manuscript. We have carefully revised the paper according to these suggestions and have done our best to answer your questions. We sincerely hope that the manuscript will meet with your approval after revision.

Comment 1: *The term “decoupled” should be better contextualized. Is this concept applicable to other co-solvent systems beyond TEGDME/DMF?*

Reply: Thank you for your valuable suggestion. In this work, the term “decoupled electrolyte” refers to a dual-solvent system in which the roles of ionic conduction and interfacial stabilization are separated during dynamic discharge/charge processes. Specifically, during discharge, DMF contributes high ionic conductivity in the bulk electrolyte, while TEGDME forms a localized, inert interfacial environment near the cathode surface that suppresses DMF-related side reactions.

This “decoupled” concept is not limited to the TEGDME/DMF system. Such a design of decoupled electrolytes - modulating the solvation structure through ESP distribution to guide selective interfacial adsorption of a stable co-solvent - can be extended to other battery systems that face similar interfacial issues, such as metal-air or high-voltage lithium-ion batteries. In these electrolyte systems, one solvent offering high ion transport efficiency and another possessing low reactivity or good compatibility at the electrode interface. We have revised the Introduction sections (Page 5, lines 14-17) to better clarify the “decoupled” definition.

Comment 2: *Could the authors clarify if the decoupling is purely spatial (interface vs. bulk) or also temporal (e.g., during discharge vs. charge)?*

Reply: Thank you for this important question. While the concept of “decoupled” in our work primarily refers to spatial separation of two solvents with DMF dominating the bulk electrolyte and TEGDME enriching the cathode/electrolyte interface, this distribution is not static, but is dynamically governed by the charge/discharge processes.

This spatial decoupled electrolyte is achieved through differences in electrostatic potential (ESP) distributions of Li⁺ ions and preferential adsorption behavior, as supported by MD simulations and theoretical calculations. Specifically, during discharge, Li⁺ ions solvated with TEGDME to exhibit higher

positive ESP values than those solvated with DMF, thus creating an inert, TEGDME-rich localized environment near the cathode. This environment effectively suppresses DMF-related side reactions, as illustrated in Fig. 1. Meanwhile, highly conductive DMF remains in the bulk electrolyte, ensuring excellent rate capability for the batteries. The relevant discussions have been added in the Introduction sections (Page 5, lines 7-11) in the revised manuscript.

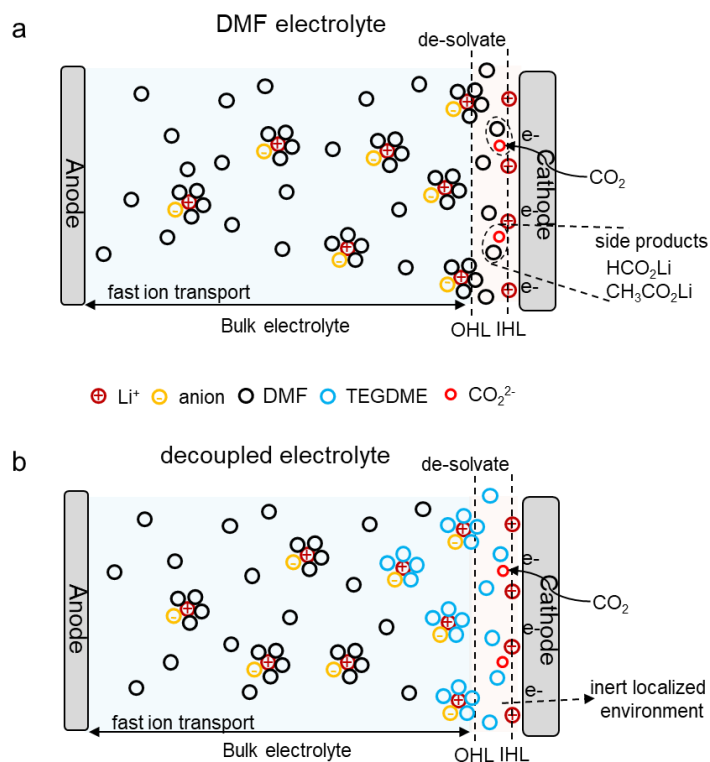


Figure 1. Schematic illustrations of the bulk electrolyte and the electric double layer (EDL) structure, including the inner Helmholtz layer (IHL) and the outer Helmholtz layer (OHL), during discharge. EDL is an interfacial region between the electrode and the bulk electrolyte, where electrical charges are spatially distributed. It consists of two sublayers: IHL and OHL. The IHP is the inner layer of the EDL on the electrode surface, which determines the competitive adsorption of cations, anions, and solvent molecules near the electrode surface, thus being strongly associated with the electrolyte/electrode interfacial stability and the formation of SEI layers. The OHL is positioned farther from the electrode surface than the IHL and primarily comprises solvated cations.^[20-22] (a) In the bare DMF electrolyte, side reactions between DMF and CO_2^{2-} on the cathode surface result in the formation of irreversible side reaction products ($\text{HCO}_2\text{Li}/\text{CH}_3\text{CO}_2\text{Li}$). (b) The inert, TEGDME-rich localized environment near the cathode surface in the decoupled electrolyte inhibits side reactions, enhancing interfacial stability and maintaining high conductivity in the bulk electrolyte.

Comment 3: Authors' claim that TEGDME enables formation of more stable SEI (with high LiF and C-N content) is intriguing. Could the authors elaborate on how TEGDME decomposition contributes to inorganic SEI (LiF) when only LiFSI salt is the fluorine source?

Reply: Thank you for your insightful suggestions. To clarify the role of TEGDME and the formation mechanism of LiF, we have now included additional XPS data of the cycled cathode in the bare DMF electrolyte (Fig. 6 and Supplementary Fig. 29), which provides a more comprehensive comparison with

the 3G7F and DMSO systems.

As correctly noted, TEGDME itself does not contribute fluorine atoms and therefore does not directly generate LiF. Instead, LiF formation originates from LiFSI decomposition, which is enhanced in DMF-based systems due to their interfacial chemical environment. Specifically, the 3G7F and bare DMF electrolytes show significantly stronger LiF signals at 56.2 eV in the Li 1s and 685.5 eV in the F 1s spectra (**Fig. 6d-e**), compared to the DMSO cell. This indicates that LiFSI-derived SEI components dominate in DMF-based systems, consistent with the higher inorganic content (e.g., Li_2SO_4 , Li_2SO_3) seen in **Supplementary Fig. 29**.

TEGDME contributes indirectly by forming a TEGDME-rich interfacial environment, which suppresses parasitic reactions from DMF decomposition, thereby allowing more selective and efficient LiFSI decomposition. As a result, a more robust inorganic SEI layer enriched with LiF is formed.

Additionally, the comparison of C-N species content in different electrolytes highlights their role in enhancing the decomposition of Li_2CO_3 . As shown in **Fig. 6a-b**, both 3G7F cell exhibits higher C-N peaks and significantly reduced Li_2CO_3 residue compared to the DMSO system, correlating with lower polarization (~1.0 V vs. 1.62 V).

These findings have been discussed in the revised manuscript (Page 15, line 16 – Page 16, line 20), and the newly added **Fig.6** and **Supplementary Figs. 29** further support the proposed mechanism.

To evaluate the effect of C-N species content on enhancing the reversibility of Li_2CO_3 and reducing overpotential, the cathodes cycled in the DMSO and DMF cells were used for comparison. In the N 1s XPS spectra (**Fig. 6a**), the peak corresponding to C-N species at 399.9 eV exhibited significantly higher intensity in both the bare DMF and 3G7F cells,^[34,59,60] due to the catalytic effect of C-N species in facilitating CRR and CER reactions, thus contributing to the reduced overpotential (~1 V). In contrast, only a small peak associated with C-N species can be observed for the DMSO cell, correspondingly, the DMSO cell delivered a relatively larger polarization (1.62 V). Meanwhile, the C 1s XPS spectra (**Fig. 6b**) reveal that the 3G7F cell, with a higher content of C-N species, enabled the complete decomposition of Li_2CO_3 , unlike the DMSO cell, which remained a large amount of Li_2CO_3 residuals.^[35]

In addition to C-N species, the most distinguishing difference between the DMSO cell and DMF-based cells (bare DMF and 3G7F) lies in the content of FSI-derived SEI components. The peaks at 56.2 eV in the Li 1s spectra (**Fig. 6d**) and 685.5 eV in the F 1s spectra (**Fig. 6e**), assigned to LiF, present significantly stronger intensities in the DMF-based cells compared to the DMSO cell.^[63] This suggests that the SEI layers formed in the DMF-based cells contain more LiF. Additionally, other inorganic species, such as Li_2SO_4 and Li_2SO_3 , also show higher contents in the DMF-based cells (**Supplementary Fig. 29**).^[5] This indicates that the SEI layers in the DMF-based electrolytes are primarily formed through anion-induced decomposition, as FSI⁻ is the only fluorine source.

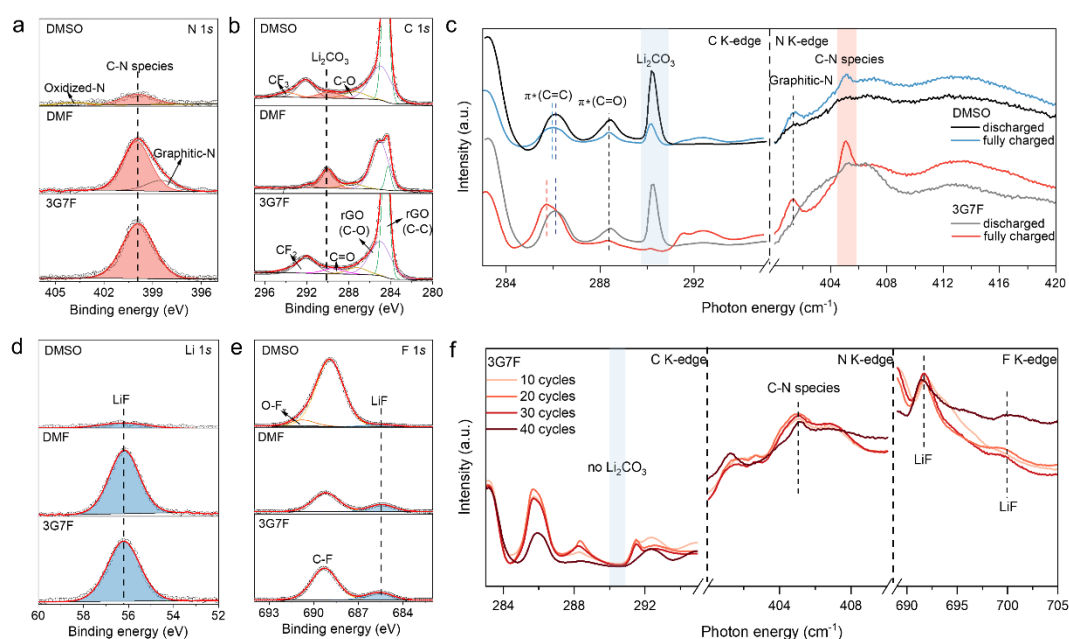
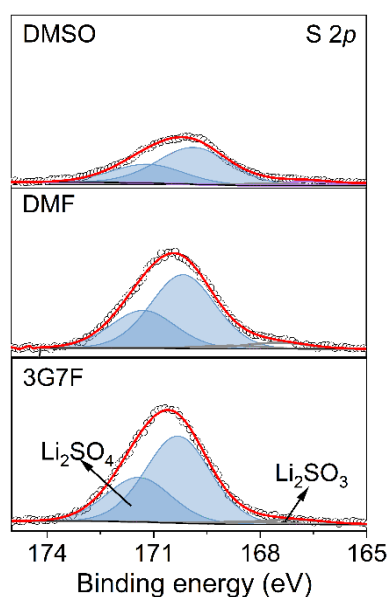


Figure 6. Characterization of the SEI composition on cathodes cycled in Li-CO₂ batteries. (a) N 1s, (b) C 1s, (d) Li 1s, and (e) F 1s XPS spectra for the cathodes after 5 cycles (fully charged state) in the cells using the bare DMSO, bare DMF, and 3G7F electrolytes. Notably, Li₂CO₃ residuals in the bare DMF electrolyte (Fig. 6b) was caused by side reaction products that decompose at lower charging voltage, as discussed in previous sections. (c) C K-edge and N K-edge XANES spectra for the cathodes discharged and after 5 cycles (fully charged state) in the DMSO and 3G7F cells, respectively. (with the peaks at 285.4, 288.6, and 291.7 eV corresponding to $\pi^*(C=C)$, $\pi^*(C=O)$, and $\sigma^*(C=C)$, respectively). (f) C K-edge, N K-edge, and F K-edge XANES spectra for the cathodes after prolonged cycling (10, 20, 30, and 40 cycles, fully charged state) in the 3G7F cell. (The intense peak at 692 eV and a small post peak at 700 eV are assigned to LiF.)



Supplementary Fig. 29. S 2p XPS spectra for the cathodes after 5 cycles (fully charged state) in the bare DMSO, bare DMF, and 3G7F cells.

Comment 4: *The interpretation of ESP (Electrostatic potential) values and their preferential adsorption relies heavily on MD simulations. Did authors validate the force field used for this simulations with DFT or with any experimental parameters?*

Reply: Thank you for your valuable comments. Yes, we have validated our force field selection based on the system's physical properties. Specifically, the simulated density of the 3G7F electrolyte was found to be 1.11 g/mL, which agrees well with the experimentally measured value of 1.15 g/mL, indicating the reliability of the force field in reproducing bulk structural properties. This consistency supports the accuracy of the MD simulations in describing solvent-ion interactions and ESP-related distributions.

Comment 5: *Have these ESP trends been validated with DFT calculations? Including this comparison would add robustness.*

Reply: Thank you for your valuable comments. For better clarification, we have added the relevant description to the Theoretical calculations section in the Supplementary Information.

The analysis of MD trajectories (i.e., mean square displacement and diffusion coefficient) was performed using standard tools within GROMACS. Density functional theory (DFT) was used to investigate several Li solvation structures observed from the MD simulations. DFT calculations were implemented using the Vienna ab-initio simulation package (VASP) with the core and valence electronic interactions being modelled using the projector augmented wave (PAW) method. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation function was employed. Molecular orbital energy levels (i.e., lowest unoccupied molecule orbital (LUMO) and highest occupied molecular orbital (HOMO)) and different species interactions in solution were calculated using VASP with a kinetic energy cut-off of 500 eV and a single Gamma k-point. Gaussian was used to obtain the electrostatic potential (ESP) of Li solvation structures. In this work, the solvation structures were taken from the MD simulations and underwent further DFT geometry optimization before the ESP calculations were performed. DFT calculations were conducted using Gaussian with B3LYP (Becke, 3-parameter, Lee–Yang–Parr) functional with 6-31G(d,p) basis set. And the geometry optimization was performed prior to the ESP mapping.

Comment 6: *Supplementary figures (especially RDFs, ESP maps) should be referenced more clearly in the main text.*

Reply: Thank you for your kind comment. We have revised the main text to reference the relevant Supplementary Figures - particularly the RDFs (**Supplementary Fig. 17**) and ESP maps (**Supplementary Fig. 11, 12, 20**) - more clearly in the manuscript.

Supplementary Fig. 11, Page 9, lines 14-17:

Second, TEGDME exhibits strong coordination ability with Li^+ ions, as indicated by the largest disparity between the absolute values of the lowest ESP ($|\text{ESP}_{\text{min}}|$) and the highest ESP ($|\text{ESP}_{\text{max}}|$) (**Fig. 3b**) and further supported by comparative data in **Supplementary Fig. 11**.

Supplementary Fig. 12, Page 9, lines 21-23:

Furthermore, Li^+ ions solvated with TEGDME display more positive ESP values compared to those

solvated with DMF, as shown in the calculated ESP maps in **Supplementary Fig. 12**, promoting the preferential adsorption of TEGDME on the cathode during discharge.

Supplementary Fig. 17, Page 10, lines 16-19:

Furthermore, radial distribution function (RDF) calculations show that in the 3G7F electrolyte, the peak of Li-O (TEGDME) bond presents a higher intensity and a shorter distance (2.02 Å) compared to that (2.06 Å) of Li-O (DMF) bond, as shown in **Supplementary Fig. 17**.

Supplementary Fig. 20, Page 12, lines 7-10:

These solvation structures exhibit more positive ESP values compared to those solvated with DMF (Fig. 4d and **Supplementary Fig. 20**), resulting in a larger electric potential difference between the negatively charged cathode (during discharge) and these solvated Li⁺ ions.

Comment 7: *The frequent use of abbreviations (e.g., ESP, IHL, OHL) without initial definition in figures could confuse non-specialist readers.*

Reply: Thank you for your valuable suggestion. We have added some descriptions of the abbreviations ESP, IHL and OHL in the revised manuscript:

ESP, Page 4, line23 - Page 5, line5:

An electrostatic potential (ESP) of a solvated cation reflects the spatial distribution of charge around the cation and its coordinating solvent molecules.^[23-25] Through theoretical calculations, we reveal that during discharge, solvated cations with relatively high positive ESP values preferentially adsorb onto the cathode surface. This finding guides us to introduce a low concentration of the co-solvent TEGDME into DMF-based electrolytes to regulate solvation structures and their ESP values, finally tailoring the preferential adsorption of TEGDME onto the cathode surface.

23. Murray, J.S., Politzer, P., Molecular electrostatic potentials and noncovalent interactions. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **7**, e1326 (2017).

24. Wang, Z., Wang, Y., Li, B., Bouwer, J.C., Davey, K., Lu, J., Guo, Z., Non-flammable ester electrolyte with boosted stability against Li for high-performance Li metal batteries. *Angew. Chem. Int. Ed.* **134**, e202206682 (2022).

25. Wu, Y., Hu, Q., Liang, H., Wang, A., Xu, H., Wang, L., He, X., Electrostatic potential as solvent descriptor to enable rational electrolyte design for lithium batteries. *Adv. Energy Mater.* **13**, 2300259 (2023).

IHL and OHL, Page 4, lines 4-15:

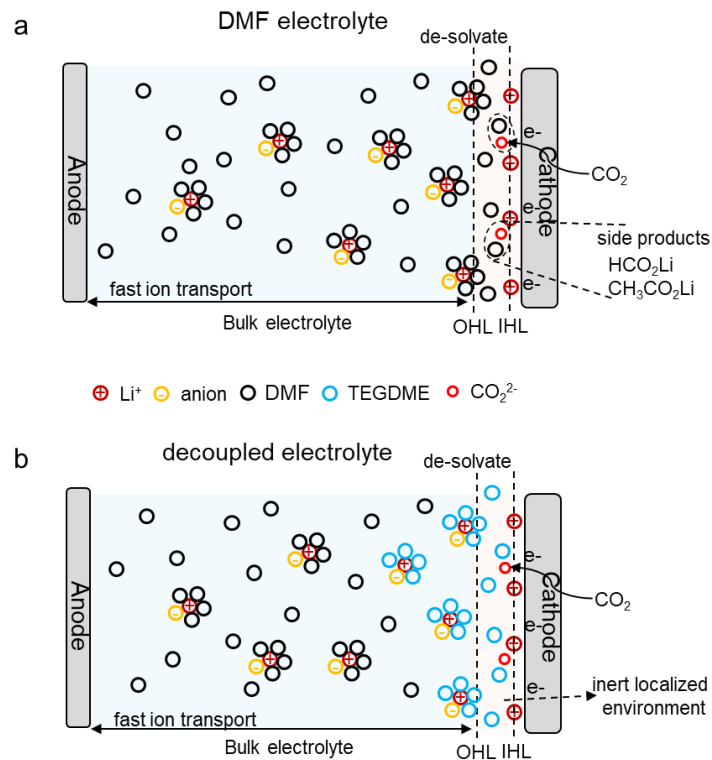


Figure 1. Schematic illustrations of the bulk electrolyte and the electric double layer (EDL) structure, including the inner Helmholtz layer (IHL) and the outer Helmholtz layer (OHL), during discharge. EDL is an interfacial region between the electrode and the bulk electrolyte, where electrical charges are spatially distributed. It consists of two sublayers: IHL and OHL. The IHP is the inner layer of the EDL on the electrode surface, which determines the competitive adsorption of cations, anions, and solvent molecules near the electrode surface, thus being strongly associated with the electrolyte/electrode interfacial stability and the formation of SEI layers. The OHL is positioned farther from the electrode surface than the IHL and primarily comprises solvated cations.^[20-22] (a) In the bare DMF electrolyte, side reactions between DMF and CO_2^{2-} on the cathode surface result in the formation of irreversible side reaction products ($\text{HCO}_2\text{Li}/\text{CH}_3\text{CO}_2\text{Li}$). (b) The inert, TEGDME-rich localized environment near the cathode surface in the decoupled electrolyte inhibits side reactions, enhancing interfacial stability and maintaining high conductivity in the bulk electrolyte.

20. Yan, C., Li, H.R., Chen, X., Zhang, X.Q., Cheng, X.B., Xu, R., Huang, J.Q., Zhang, Q., Regulating the inner Helmholtz plane for stable solid electrolyte interphase on lithium metal anodes. *J. Am. Chem. Soc.* **141**, 9422-9429 (2019).

21. Luo, J., Xu, L., Yang, Y., Huang, S., Zhou, Y., Shao, Y., Wang, T., Tian, J., Guo, S., Zhao, J., Zhao, X., Stable zinc anode solid electrolyte interphase via inner Helmholtz plane engineering. *Nat. Commun.* **15**, p.6471 (2024).

22. Ma, S., Zhao, J., Xiao, H., Gao, Q., Li, F., Song, C., Li, G., Modulating the Inner Helmholtz Plane towards Stable Solid Electrolyte Interphase by Anion- π Interactions for High-Performance Anode-Free Lithium Metal Batteries. *Angew. Chem.* **137**, p.e202412955 (2025).

Comment 8: “Decoupled” and “localized environment” are used frequently and interchangeably—clarify distinctions.

Reply: Thank you for your insightful comment. We have clarified the distinction between the terms "decoupled electrolyte" and "localized environment" to avoid ambiguity.

Specifically, "decoupled electrolyte" refers to the overall design strategy in which the functional solvents of high ionic conductivity and interfacial stability are separated between two different solvents - DMF serving as the high-conductivity bulk component, and TEGDME as the interfacial stabilizing component. In contrast, "localized environment" specifically describes the spatial enrichment of TEGDME molecules near the cathode surface during discharge, as driven by preferential adsorption. This TEGDME-rich localized environment near cathode can protect the DMF from decomposition.

We have revised the manuscript to ensure that these two terms are used with consistent and precise meaning throughout the manuscript.

Comment 9: *How do you distinguish between ESP-driven preferential adsorption and other effects such as viscosity or wettability on cathode surfaces?*

Reply: Thank you for your important questions. To distinguish the influence of ESP-driven preferential adsorption from other factors such as viscosity or wettability, we measured the viscosity of both bare DMF (1 M LiFSI/DMF) and the 3G7F electrolytes and their contact angles on the porous cathode. Viscosity measurements were performed using a rheometer (Anton Paar Physica MCR 301) in our laboratory. Due to the inherently low viscosities of both electrolytes, their values were below the instrument's detection limit, indicating minimal viscosity-related influence on overall cell performance. In addition, as shown in Figure below, both electrolytes exhibited excellent wettability with contact angles of 15.8° for bare DMF electrolyte and 17.8° for the 3G7F electrolyte, respectively. The small difference confirms that wettability is not the dominant factor behind the improved performance of Li-CO₂ cells using the 3G7F electrolyte. Moreover, the excellent wettability of these electrolytes reflected by small angles could ensure effective infiltration into porous electrodes and favorable ion transport.^[1,2] These results confirm that the enhanced interfacial reaction kinetics and battery performance in the 3G7F electrolyte are primarily governed by ESP-driven molecular interactions, rather than differences in viscosity or wettability.

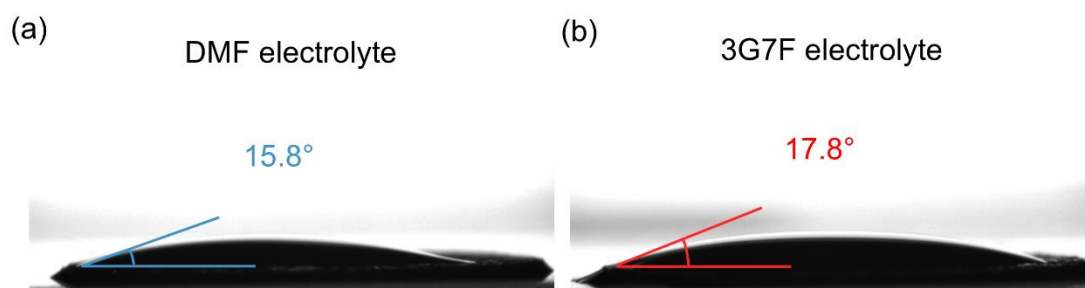


Figure. The contact angles of a) bare DMF (1 M LiFSI/DMF) and b) 3G7F electrolytes on porous cathodes.

References:

- [1] Kube, A., Bienen, F., Wagner, N., Friedrich, K.A., Wetting behavior of aprotic Li-Air battery electrolytes. *Adv. Mater. Interfaces* **9**, 2101569 (2022).
- [2] Liu, S., Vongsvivut, J., Wang, Y., Zhang, R., Yang, F., Zhang, S., Davey, K., Mao, J., Guo, Z.,

Reply to Reviewer 2

Overall comment: In this manuscript, the authors report a decoupled electrolyte design that stabilizes the electrolyte/cathode interface in Li-CO₂ batteries while preserving high ionic conductivity. Combining theoretical calculations with in-situ and ex-situ characterizations, they demonstrate that the TEGDME-rich interfacial environment suppresses DMF-related side reactions and enhances Li₂CO₃ reversibility. The findings are well supported and offer valuable insights into electrolyte and interface engineering for metal-gas batteries. Overall, I recommend minor revisions before publication in *Nat. Commun.*

Reply: Thank you very much for your excellent suggestions. We have added the relevant discussions and corrected the mistakes in the revised manuscript according to your kind comments. We sincerely hope that the manuscript will meet with your approval after revision.

Comment 1: Please add more description of the abbreviations IHL and OHL in the Figure 1 caption for clarity to readers unfamiliar with EDL structure.

Reply: Thank you for your valuable suggestion. We have added some descriptions of the abbreviations IHL and OHL in the **Figure 1** caption in the revised manuscript (Page 4, lines 4-15):

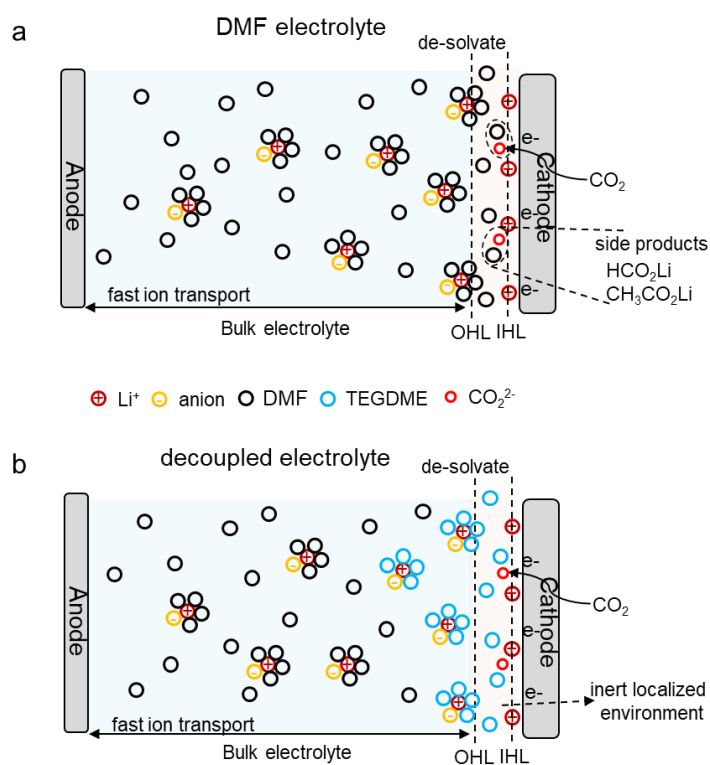


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interfacial stability and the formation of SEI layers. The OHL is positioned farther from the electrode surface than the IHL and primarily comprises solvated cations.^[20-22] (a) In the bare DMF electrolyte, side reactions between DMF and CO_2^{2-} on the cathode surface result in the formation of irreversible side reaction products ($\text{HCO}_2\text{Li}/\text{CH}_3\text{CO}_2\text{Li}$). (b) The inert, TEGDME-rich localized environment near the cathode surface in the decoupled electrolyte inhibits side reactions, enhancing interfacial stability and maintaining high conductivity in the bulk electrolyte.

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Comment 2: The asterisk * used to mark side reaction products should be explained in the Figure 2g caption.

Reply: Thank you for this important suggestion. The relevant explanation has been added in the **Figure 2g** caption in the revised manuscript.

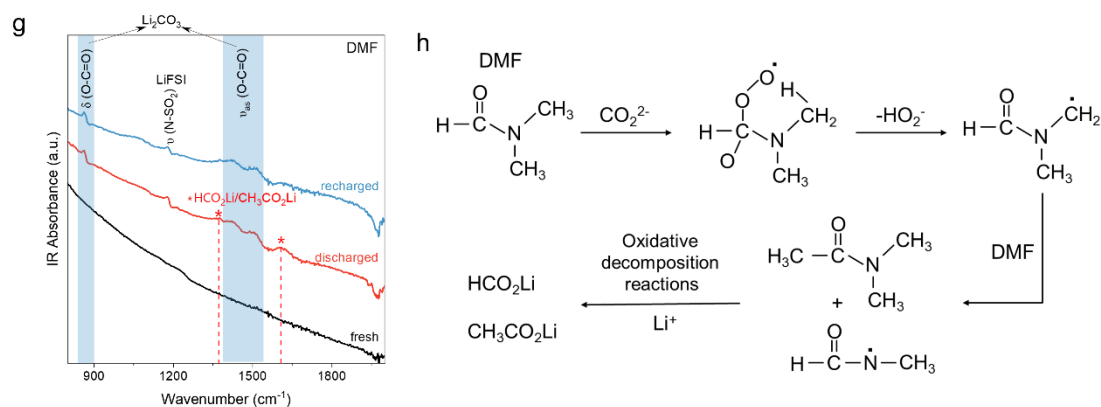


Figure 2. (g) *Ex-situ* FTIR spectra observed on the fresh cathode before cycling and the cathode discharged and recharged in the DMF cell. The discharge product Li_2CO_3 is marked by blue. The side reaction products ($\text{HCO}_2\text{Li}/\text{CH}_3\text{CO}_2\text{Li}$), marked with red asterisk (*), result from the irreversible side reaction between DMF and the intermediate CO_2^{2-} radicals during discharge. The detailed reaction mechanism is illustrated in Fig.2h. (h) The mechanism for side reactions between DMF and CO_2^{2-} during discharge.^[19]

Comment 3: The radar plot in Fig. 3a compares co-solvent candidates. A brief explanation of how the $|\text{ESP}_{\text{min}}| - \text{ESP}_{\text{max}}$ value reflects the solvent's coordination strength with Li^+ ions should be presented in the main text.

Reply: Thank you for your insightful comment. To clarify the influence of $|\text{ESP}_{\min}| - \text{ESP}_{\max}$ on the coordination strength of solvents, we have added more explanation (Page 9, lines 14-21) in the revised manuscript, as shown below:

Second, TEGDME exhibits strong coordination ability with Li^+ ions, as indicated by the largest disparity between the absolute values of the lowest ESP ($|\text{ESP}_{\min}|$) and the highest ESP ($|\text{ESP}_{\max}|$) (Fig. 3b) and further supported by comparative data in Supplementary Fig. 11. For a solvating solvent, $|\text{ESP}_{\min}|$ should be higher than $\text{ESP}_{\max}$, ($|\text{ESP}_{\min}| > \text{ESP}_{\max}$), and a larger difference between these values corresponds to stronger coordination strength with cations.^[25,39,40] Thus, in the decoupled TEGDME/DMF electrolyte, TEGDME preferentially enters the Li^+ solvation shell over DMF.

25. Wu, Y., Hu, Q., Liang, H., Wang, A., Xu, H., Wang, L., He, X., Electrostatic potential as solvent descriptor to enable rational electrolyte design for lithium batteries. *Adv. Energy Mater.* **13**, 2300259 (2023).

39. Rustomji, C.S., Yang, Y., Kim, T.K., Mac, J., Kim, Y.J., Caldwell, E., Chung, H., Meng, Y.S., Liquefied gas electrolytes for electrochemical energy storage devices. *Science* **356**, eaal4263 (2017).

40. Zhang, G., Zhang, T., Zhang, Z., He, R., Wang, Q., Chi, S.S., Cui, Y., Gu, M.D., Liu, Z., Chang, J., Wang, C., High-energy and fast-charging lithium metal batteries enabled by tuning Li^+ -solvation via electron-withdrawing and lithiophobicity functionality. *Nat. Commun.* **16**, 1-12 (2025).

Comment 4: In the theoretical calculation section, the manuscript mentions ESP values obtained via Gaussian. Please specify the level of theory and whether geometry optimizations were performed prior to ESP mapping, to ensure reproducibility.

Reply: Thank you for your kind comments. We have specified the level of theory and provided relevant information in the Theoretical calculation section in the Supplementary Information.

The analysis of MD trajectories (i.e., mean square displacement and diffusion coefficient) was performed using standard tools within GROMACS. Density functional theory (DFT) was used to investigate several Li solvation structures observed from the MD simulations. DFT calculations were implemented using the Vienna ab-initio simulation package (VASP) with the core and valence electronic interactions being modelled using the projector augmented wave (PAW) method. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation function was employed. Molecular orbital energy levels (i.e., lowest unoccupied molecule orbital (LUMO) and highest occupied molecular orbital (HOMO)) and different species interactions in solution were calculated using VASP with a kinetic energy cut-off of 500 eV and a single Gamma k-point. Gaussian was used to obtain the electrostatic potential (ESP) of Li solvation structures. In this work, the solvation structures were taken from the MD simulations and underwent further DFT geometry optimization before the ESP calculations were performed. DFT calculations were conducted using Gaussian with B3LYP (Becke, 3-parameter, Lee–Yang–Parr) functional with 6-31G(d,p) basis set. And the geometry optimization was performed prior to the ESP mapping.

Comment 5: In Supplementary Fig. 19 and 21, the MD snapshots show solvent distributions under different charge states. A brief discussion of the applied surface charge density ($\pm 1.8 \mu\text{C cm}^{-2}$) would help readers better understand the simulation conditions.

Reply: Thank you for your excellent comment. The details of the applied surface charge density ($\pm 1.8 \mu\text{C cm}^{-2}$) have been added to the Theoretical calculation section in the Supplementary Information.

A layer of carbon electrode, with an area of $1.7812 \times 10^{-13} \text{ cm}^2$, was introduced at the bottom and top of the electrolyte, to consider the effect of charged surface on the solvent and salt distribution at the interface. A total of 680 C atom was used, and a total charge of +2 and -2 (making the simulation box neutral) was considered for bottom and top electrodes, in which every atom uniformly charged. For considering the effect of charged surface, we then evaluated the changes in electrolyte distribution near the surface. The charge density of the surface can be calculated using the following equation.

Conversion of electron charge to Coulombs:

$$\text{Charge} = (n, (\text{unit in } e^{-1})) / (6.2415 \times 10^{19}, (\text{unit in } e^{-1}\text{C})) = 2 e^{-} / 6.2415 \times 10^{19} = 3.2044 \times 10^{-19} \text{ C}$$

Surface area of the carbon electrode:

$$\text{Area} = 4.26 \text{ nm} \times 4.181 \text{ nm} = 17.81 \times 10^{-14} \text{ cm}^2 = 1.7811 \times 10^{-13} \text{ cm}^2$$

Charge density calculation:

$$\text{Charge/Area} = 3.2044 \times 10^{-19} \text{ C} / 1.7812 \times 10^{-13} = 1.8 \mu\text{C cm}^{-2}$$

Comment 6: In Fig. 6a-b, the authors correlate the intensity of C-N peaks in the C 1s and N 1s spectra with improved catalytic property toward Li_2CO_3 decomposition. A brief explanation of how C-N species in the SEIs function catalytically during charge/discharge processes should be added for better understanding.

Reply: Thank you for your valuable suggestion. To improve reader understanding, we have included relevant discussion in the revised manuscript (Page 15, lines 2-13).

It is widely known that the high charging potential and large polarization in Li- CO_2 batteries are mainly caused by the sluggish oxidation kinetics of the discharge product Li_2CO_3 at the cathode/electrolyte interface.^[57,58] With the same catalyst (rGO), the improved CO_2 reaction kinetics and reduced overpotential observed in DMF-based electrolytes compared to others may be attributed to the catalytic effects of SEI compositions towards Li_2CO_3 decomposition. As explored in our previous work,^[34] *in-situ* formed C-N species in SEI layers could provide strong adsorption sites for CO_2 , $^*\text{CO}_2^{2-}$, and Li_2CO_3 , facilitating charge transfer from C-N species at the interface to $^*\text{CO}_2^{2-}$ during discharge and from Li_2CO_3 to the interfacial N sites of C-N species during charge, thereby building a bidirectional fast-reacting bridge for CO_2 reduction and evolution reaction kinetics and effectively alleviating the accumulation of Li_2CO_3 residuals. Thus, XPS was employed to analyse the chemical compositions of SEI layers formed on the cycled cathodes in the 3G7F cell (after 5 cycles, **Supplementary Fig. 28**).

Comment 7: Please carefully check the reference list to ensure all citations are presented in correct numerical order and with accurate formatting. Reference 2 cites the year 2024 but Chem. Rev. 104 was published in 2004.

Reply: We are sorry to offer the incorrect formatted reference of *Nature Communications*. We have carefully checked and corrected the reference formats in the revised manuscript. For example,

2. Xu, K., Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. *Chem. Rev.* **104**, 4303-4418 (2004).
4. Meng, Y.S., Srinivasan, V., Xu, K., Designing better electrolytes. *Science* **378**, eabq3750 (2022).
5. Zhang, W., Zhang, F., Liu, S., Pang, W.K., Lin, Z., Guo, Z., Chai, L., Regulating the reduction reaction pathways via manipulating the solvation shell and donor number of the solvent in Li-CO₂ chemistry. *Proc. Natl. Acad. Sci. U.S.A.* **120**, 2219692120 (2023).
66. Bai, P., Ji, X., Zhang, J., Zhang, W., Hou, S., Su, H., Li, M., Deng, T., Cao, L., Liu, S., He, X., Formation of LiF-rich cathode-electrolyte interphase by electrolyte reduction. *Angew. Chem. Int. Ed.* **61**, e202202731 (2022).

Reply to Reviewer 3

Overall comment: *This manuscript presents the design of a decoupled electrolyte for Li-CO₂ batteries, focusing on enhancing interfacial stability and maintaining high ionic conductivity simultaneously. By incorporating TEGDME into a DMF-based electrolyte, the authors effectively suppress DMF-related side reactions, thereby promoting Li₂CO₃ reversibility and extending battery cycle life. The combination of theoretical calculations and characterizations provides a comprehensive understanding of electrolyte composition and interfacial structure during cycling. The work is well-structured and demonstrates significant potential for advancing electrolyte design strategies for metal-gas batteries. Minor revisions are recommended before acceptance in Nat. Commun.*

Reply: Thank you very much for your insightful comments and positive opinion on our manuscript. We have carefully revised the manuscript according to your suggestions.

Comment 1: *In Fig. 2f, the rate performance data are presented, but the specific values for each current density are not clearly stated. Please add these values in the figure caption or main manuscript to facilitate a more quantitative comparison.*

Reply: Thank you for your valuable suggestion. The relevant discussions have been added in the revised manuscript (Page 7, lines 8-11).

Additionally, the DMF cell demonstrated superior rate capability (**Fig. 2f** and **Supplementary Fig. 2**), with a significantly reduced charging potential compared to DMSO and TEGDME cells across all current densities, suggesting a lower energy barrier for CER.

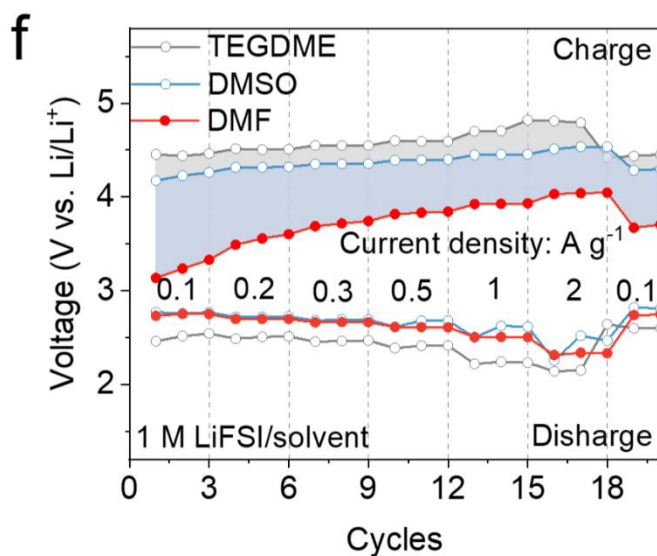
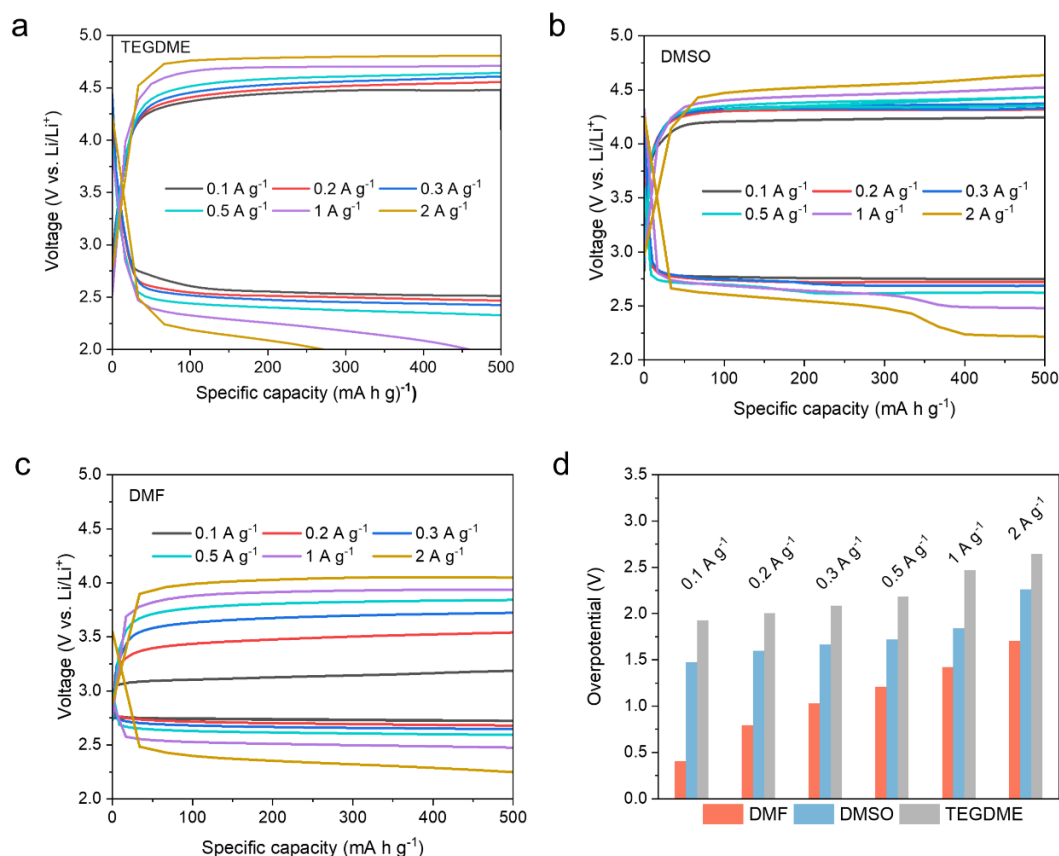


Figure 2. (f) Rate performance at various current densities from 0.1 to 2 A g⁻¹.



Supplementary Fig. 3. Rate performance of Li-CO₂ cells. Discharge-charge profiles of the (a) TEGDME, (b) DMSO, and (c) DMF cells, (d) Comparison of overpotential at various current densities from 0.1 to 2 A g⁻¹.

Note: the DMF cell exhibits a much lower overpotential of 0.4 V at 0.1 A g⁻¹, while the DMSO and TEGDME cells delivers higher overpotentials of 1.47 V and 1.9 V, respectively. Even at a high current density of 2.0 A g⁻¹, the overpotential of the DMF cell remains as low as 1.7 V, whereas those of the

DMSO and TEGDME cells increases to 2.2 V and 2.6 V, respectively. Notably, at both 1.0 and 2.0 A g⁻¹, the discharge voltage of the DMSO cell suffers a sharp drop from 2.6 to 2.2 V, and the TEGDME cell fails to reach the preset discharge capacity. In contrast, the DMF cell keeps a stable discharge voltage plateau until the cut-off capacity is achieved.

Comment 2: *The ESP values are critical to the proposed mechanism. Please specify the Gaussian basis set and functional used to ensure reproducibility in the computational method.*

Reply: Thank you for this important comments. To ensure reproducibility, we have provided relevant information in the Theoretical calculation section in the Supplementary Information.

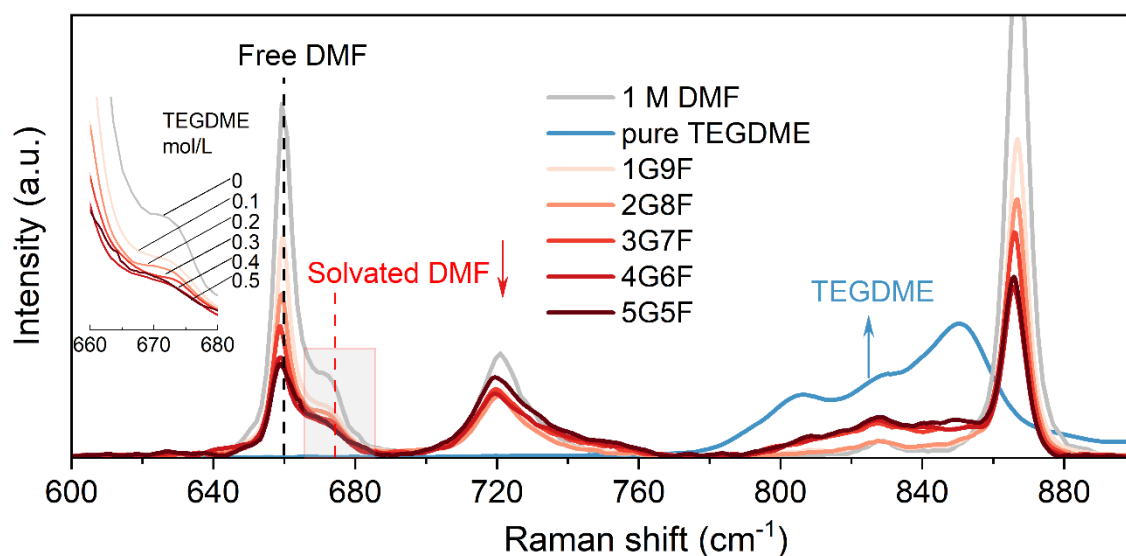
The analysis of MD trajectories (i.e., mean square displacement and diffusion coefficient) was performed using standard tools within GROMACS. Density functional theory (DFT) was used to investigate several Li solvation structures observed from the MD simulations. DFT calculations were implemented using the Vienna ab-initio simulation package (VASP) with the core and valence electronic interactions being modelled using the projector augmented wave (PAW) method. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation function was employed. Molecular orbital energy levels (i.e., lowest unoccupied molecule orbital (LUMO) and highest occupied molecular orbital (HOMO)) and different species interactions in solution were calculated using VASP with a kinetic energy cut-off of 500 eV and a single Gamma k-point. Gaussian was used to obtain the electrostatic potential (ESP) of Li solvation structures. In this work, the solvation structures were taken from the MD simulations and underwent further DFT geometry optimization before the ESP calculations were performed. DFT calculations were conducted using Gaussian with B3LYP (Becke, 3-parameter, Lee–Yang–Parr) functional with 6-31G(d,p) basis set. And the geometry optimization was performed prior to the ESP mapping.

Comment 3: *The Raman spectra in Supplementary Fig. 14 indicate distinct shifts with increasing TEGDME content. An explanation of how these shifts correlate with changes in Li⁺ solvation structures should be included to enhance the understanding of the observed differences.*

Reply: Thank you for your insightful suggestions. We have provided the relevant discussions to the revised manuscript as shown below (Page10, lines 7-19):

It is found that introducing TEGDME into DMF-based electrolytes reduces the participation of DMF in the Li⁺ solvation shells. As shown in **Supplementary Fig. 14**, both ¹H and ¹³C NMR spectra exhibit pronounced downfield shifts in the peaks corresponding to DMF in the 3G7F electrolyte compared to those in the bare DMF electrolyte. These shifts suggest reduced electron density around DMF molecules, which is attributed to the weakened interaction between DMF and Li⁺.^[47,48] To further investigate the differences in solvation structures between bare DMF electrolyte and decoupled electrolyte, Raman spectra analyses and MD simulations were conducted. Raman spectra (**Supplementary Fig. 15**) reveal that as the volume ratio of TEGDME increases up to 30% (denoted as 3G7F), the O=C–N bending vibration of solvated DMF at 675.9 cm⁻¹ is significantly weakened, while the characteristic peaks of TEGDME become more pronounced compared to those at lower TEGDME concentrations (10% and 20%).^[49] This change in solvation structures has a positive effect on battery performance, as demonstrated by the discharge-charge profiles of Li-CO₂ cells, in which the cell employing the 3G7F

electrolyte delivered stable, flat discharge/charge plateaus and a low overpotential of ~ 1 V (Supplementary Fig. 16). Furthermore, radial distribution function (RDF) calculations show that in the 3G7F electrolyte, the peak of Li-O (TEGDME) bond presents a higher intensity and a shorter distance (2.02 Å) compared to that (2.06 Å) of Li-O (DMF) bond, as shown in Supplementary Fig. 17. Specifically, the coordination number of DMF decreases from 2.2 in the bare DMF electrolyte to 1.4 in the 3G7F electrolyte (Supplementary Fig. 18).



Supplementary Fig. 15. Raman results for the electrolytes. Raman spectra of pure TEGDME solvent, the bare DMF electrolyte (1 M LiFSI/DMF), and decoupled electrolytes in the range of 600-900 cm^{-1} . The decoupled electrolytes composed of TEGDME and DMF in volume ratios of 1:9, 2:8, 3:7, 4:6, and 5:5 are denoted as the 1G9F, 2G8F, 3G7F, 4G6F, and 5G5F electrolytes, respectively.

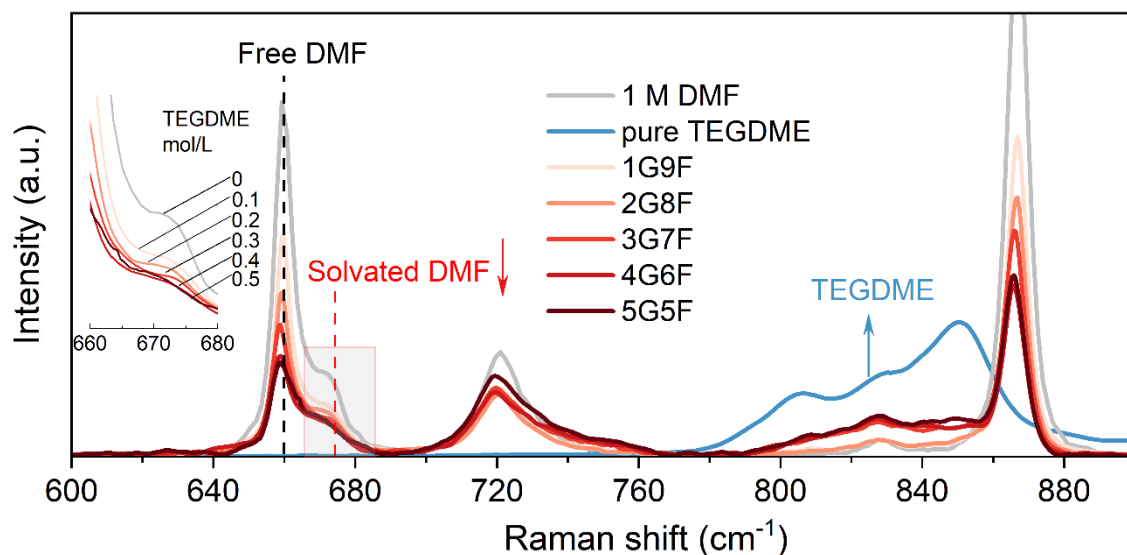
Note: The Raman peak corresponding to O=C–N bending and N–CH₃ stretching was observed at 663.3 cm^{-1} , which is assigned to free DMF solvent molecules. With the addition of LiFSI, the new peak appeared at a higher frequency of 675.9 cm^{-1} , indicating the participation of DMF in the solvation shell (solvated DMF).^[5] As the volume ratio of TEGDME increases to 30%, the intensity of TEGDME peaks become significantly more pronounced compared to their lower intensity in the 1G9F and 2G8F electrolytes.

Comment 4: The decoupled electrolyte is presented as a mixture of DMF and TEGDME, but the rationale for selecting the optimal volume ratio of 3:7 is not fully discussed. Please address how other ratios (e.g., 1:9, 5:5) impact electrochemical performance to provide a more comprehensive perspective on electrolyte composition design.

Reply: Thank you for your valuable comments. The electrolyte compositions and corresponding cycling performances for other DMF/TEGDME ratios have been provided in both the main manuscript and Supplementary Information.

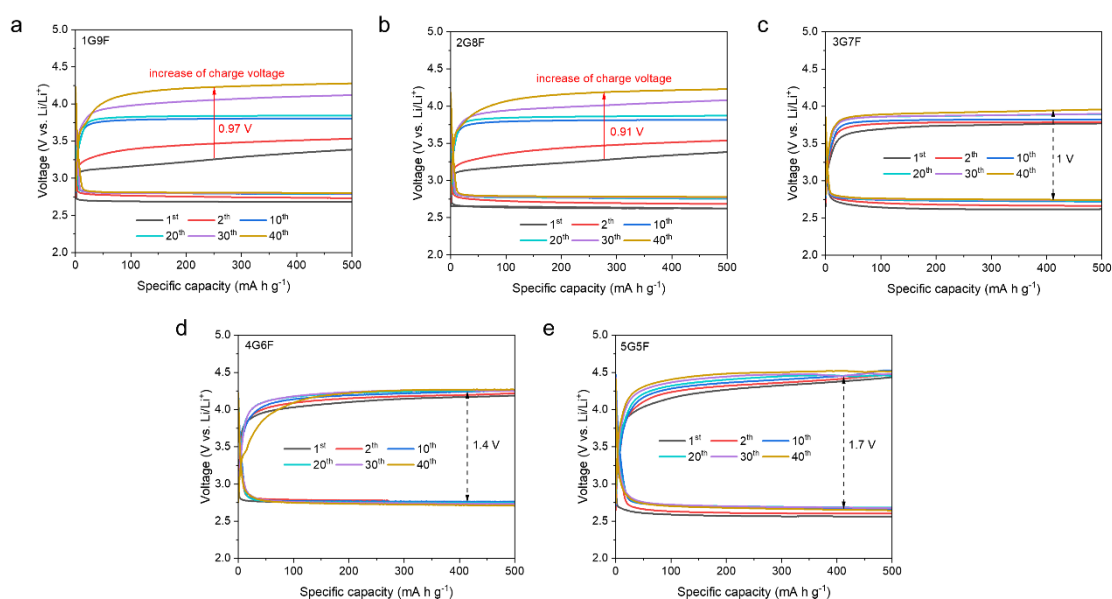
To further investigate the differences in solvation structures between bare DMF electrolyte and decoupled electrolyte, Raman spectra analyses and MD simulations were conducted. Raman spectra (Supplementary Fig. 15) reveal that as the volume ratio of TEGDME increases up to 30% (denoted as 3G7F), the O=C–N bending vibration of solvated DMF at 675.9 cm^{-1} is significantly weakened, while the characteristic peaks of TEGDME become more pronounced compared to those at lower TEGDME

concentrations (10% and 20%).^[49] This change in solvation structures has a positive effect on battery performance, as demonstrated by the discharge-charge profiles of Li-CO₂ cells, in which the cell employing the 3G7F electrolyte delivered stable, flat discharge/charge plateaus and a low overpotential of ~1 V (Supplementary Fig. 16).



Supplementary Fig. 15. Raman results for the electrolytes. Raman spectra of pure TEGDME solvent, the bare DMF electrolyte (1 M LiFSI/DMF), and decoupled electrolytes in the range of 600-900 cm⁻¹. The decoupled electrolytes composed of TEGDME and DMF in volume ratios of 1:9, 2:8, 3:7, 4:6, and 5:5 are denoted as the 1G9F, 2G8F, 3G7F, 4G6F, and 5G5F electrolytes, respectively.

Note: The Raman peak corresponding to O=C–N bending and N–CH₃ stretching was observed at 663.3 cm⁻¹, which is assigned to free DMF solvent molecules. With the addition of LiFSI, the new peak appeared at a higher frequency of 675.9 cm⁻¹, indicating the participation of DMF in the solvation shell (solvated DMF).^[5] As the volume ratio of TEGDME increases to 30%, the intensity of TEGDME peaks become significantly more pronounced compared to their lower intensity in the 1G9F and 2G8F electrolytes.



Supplementary Fig. 16. Discharge-charge profiles of Li-CO₂ cells using decoupled electrolytes at 0.1 A g⁻¹ in the first 40 cycles: (a) 1G9F, (b) 2G8F, (c) 3G7F, (d) 4G6F, and (e) 5G5F electrolytes.

Note: When the volume ratio of TEGDME is 10% or 20%, the cells still exhibited a noticeable increase in charge voltage, gradually rising from 3.2 V to 3.5 V at the 10th cycle and further to 4.2 V at the 40th cycle. This reflects poor electrolyte stability at low TEGDME concentrations. With further increasing the volume ratio of TEGDME to more than 30%, the discharge/charge voltage can retain a stable flat plateau with the initial potential over 40 cycles.

Comment 5: Several key findings, such as LUMO energy values for TEGDME and DMF, are discussed but not directly presented in the main manuscript. Please add a brief reference to the Supplementary Figure or Table in the relevant sections.

Reply: Thank you for your kind comment. To enhance clarity, the **Supplementary Table 3** has been included to present the LUMO energy values for TEGDME and DMF in the Supplementary Information. We have added the relevant discussion in the revised manuscript (Page 12, lines 15-17).

Furthermore, TEGDME after desolvation has a higher LUMO energy value (-0.53 eV, **Supplementary Fig. 22 and Table 3**) than DMF (-0.73 eV), indicating TEGDME is more stable than DMF.

Supplementary Table 3. LUMO and HOMO energy values for free FSI⁻ anions, TEGDME molecules and DMF molecules. Color scheme of molecules: C, light blue; H, white; O, red; N, navy; S, yellow; F, pink.

	LUMO energy value (eV)	HOMO energy value (eV)
FSI ⁻	-0.202	-4.1324
TEGDME	-0.53	-5.7
DMF	-0.7297	-5.79

Comment 6: In Fig. 6, the XPS analysis highlights C-N species as key catalytic components in the SEI. However, Fig.6 only compare the XPS results of cycled cathodes in the DMSO and decoupled electrolytes. To provide a more comprehensive understanding of SEI formation across different electrolyte systems, the XPS analysis for C-N species in the DMF-only electrolyte should be compared with these electrolytes.

Reply: Thank you for your valuable comments. We have provided XPS and EDS analysis results for the cathodes after 5 cycles in Li-CO₂ cells using the bare DMSO, bare DMF, and 3G7F electrolytes in the revised manuscript, as shown below:

Thus, XPS was employed to analyse the chemical compositions of SEI layers formed on the cycled cathodes in the 3G7F cell (after 5 cycles, **Supplementary Fig. 28**). To evaluate the effect of C-N species content on enhancing the reversibility of Li₂CO₃ and reducing overpotential, the cathodes cycled in the DMSO and DMF cells were used for comparison. In the N 1s XPS spectra (**Fig. 6a**), the peak corresponding to C-N species at 399.9 eV exhibited significantly higher intensity in both the bare DMF and 3G7F cells,^[34,59,60] due to the catalytic effect of C-N species in facilitating CRR and CER reactions,

thus contributing to the reduced overpotential (~ 1 V). In contrast, only a small peak associated with C-N species can be observed for the DMSO cell, correspondingly, the DMSO cell delivered a relatively larger polarization (1.62 V). Meanwhile, the C 1s XPS spectra (Fig. 6b) reveal that the 3G7F cell, with a higher content of C-N species, enabled the complete decomposition of Li_2CO_3 , unlike the DMSO cell, which remained a large amount of Li_2CO_3 residuals.^[35] These observations confirm the critical role of C-N species in promoting Li_2CO_3 decomposition and governing battery reaction kinetics. The positive correlation between C-N species and the reversibility of Li_2CO_3 was further proved by X-ray absorption near-edge spectroscopy (XANES). After 5 cycles (Fig. 6c), the 3G7F cell exhibited no Li_2CO_3 residuals, consistent with a stronger peak of C-N species,^[34,61] indicating superior reversibility of Li_2CO_3 , reduced battery overpotential, and improved cycling performance. In contrast, the DMSO cell showed a distinct peak of Li_2CO_3 residuals and a low content of C-N species, leading to sluggish battery kinetics.^[62] In addition to C-N species, the most distinguishing difference between the DMSO cell and DMF-based cells (bare DMF and 3G7F) lies in the content of FSI-derived SEI components. The peaks at 56.2 eV in the Li 1s spectra (Fig. 6d) and 685.5 eV in the F 1s spectra (Fig. 6e), assigned to LiF, present significantly stronger intensities in the DMF-based cells compared to the DMSO cell.^[63] This suggests that the SEI layers formed in the DMF-based cells contain more LiF. Additionally, other inorganic species, such as Li_2SO_4 and Li_2SO_3 , also show higher contents in the DMF-based cells (Supplementary Fig. 29).^[5] This indicates that the SEI layers in the DMF-based electrolytes are primarily formed through anion-induced decomposition, as FSI⁻ is the only fluorine source.

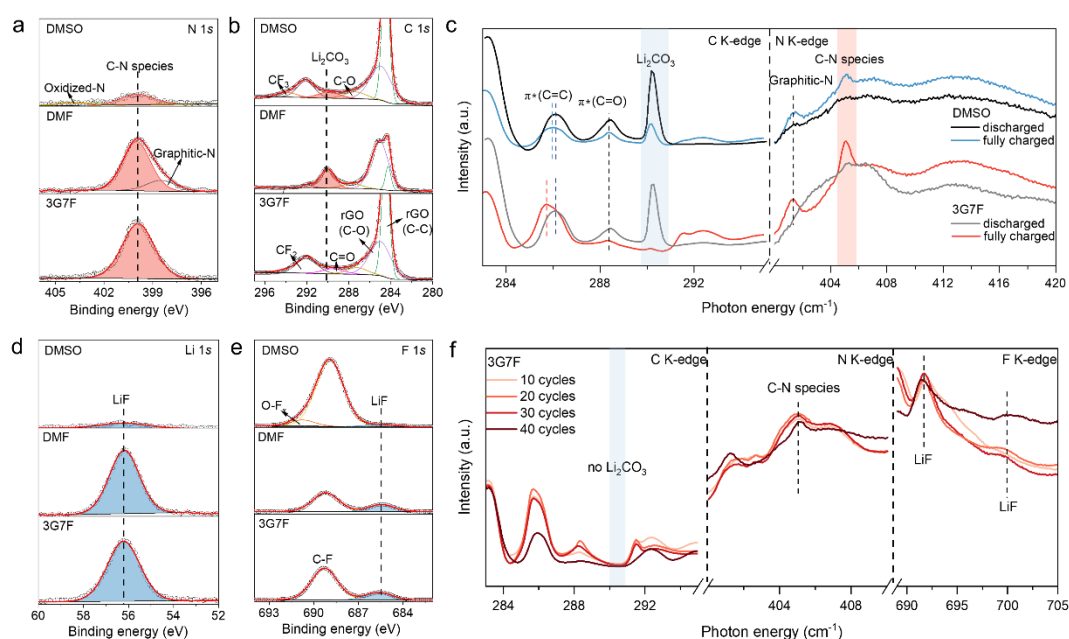
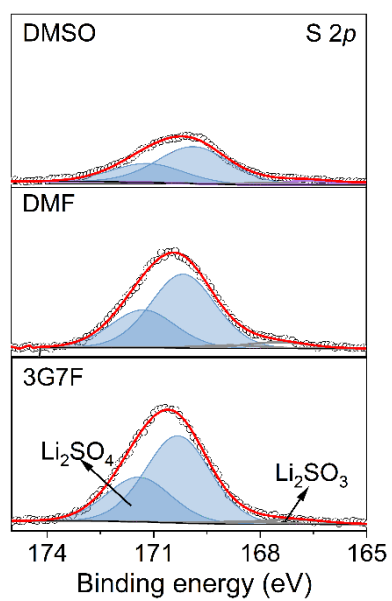


Figure 6. Characterization of the SEI composition on cathodes cycled in Li- CO_2 batteries. (a) N 1s, (b) C 1s, (d) Li 1s, and (e) F 1s XPS spectra for the cathodes after 5 cycles (fully charged state) in the cells using the bare DMSO, bare DMF, and 3G7F electrolytes. Notably, Li_2CO_3 residuals in the bare DMF electrolyte (Fig. 6b) was caused by side reaction products that decompose at lower charging voltage, as discussed in previous sections. (c) C K-edge and N K-edge XANES spectra for the cathodes discharged and after 5 cycles (fully charged state) in the DMSO and 3G7F cells, respectively. (with the peaks at 285.4, 288.6, and 291.7 eV corresponding to $\pi^*(\text{C}=\text{C})$, $\pi^*(\text{C}=\text{O})$, and $\sigma^*(\text{C}=\text{C})$, respectively). (f) C K-edge, N K-edge, and F K-edge XANES spectra for the cathodes after prolonged cycling (10, 20, 30, and 40 cycles, fully charged state) in the 3G7F cell. (The intense peak at 692 eV and a small post

peak at 700 eV are assigned to LiF.)



Supplementary Fig. 29. S 2p XPS spectra for the cathodes after 5 cycles (fully charged state) in the bare DMSO, bare DMF, and 3G7F cells.