

Multidentate ether-induced reconfiguration of solvation structure in non-flammable phosphate electrolytes for wide-temperature application in lithium-ion batteries

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Abstract

Conventional carbonate electrolytes fail to meet the requirements for lithium-ion batteries (LIBs) with wide temperature range and high safety. Diethyl ethylphosphonate (DEEP) has excellent flame retardancy and a wide temperature range (-83 to 198°C), which holds promise for developing a non-flammable electrolyte for wide-temperature application in LIBs. However, its limited compatibility with graphite electrodes and slow ionic transport capability must be addressed for effective application. Herein, we introduce diethylene glycol dimethyl ether (DEGDME) to reconfigure the solvation structure of DEEP-based electrolyte and further enhance its ion transport capacity. The film-forming additives enable the electrolyte to preserve 98% capacity retention after 150 cycles for Li||Graphite cells. The non-flammable DEEP-based electrolytes modified with DEGDME enable improved low-temperature performance with achieving 71% 50th-cycle retention of Graphite||LiFePO₄ cells at -20°C. This work introduces a new strategy for designing non-flammable phosphate electrolytes, enabling the reliable and safe application of LIBs across a wide temperature range.

1. Introduction

Lithium-ion batteries¹⁻⁴ (LIBs) deliver energy efficiently, safely and reliably across a wide temperature range, which is decisive for the performance of portable electronic devices and electric vehicles operating in complex environments. However, the commercial electrolytes^{5,6} are primarily composed of flammable carbonate solvents, which pose significant safety risks^{7,8} under conditions such as thermal abuse or external damage. Moreover, carbonate electrolytes' performance in extreme cold or high-temperature conditions remains suboptimal. Introducing flame retardant additives^{9,10} or developing entirely non-flammable alternatives^{11,12}, can mitigate the risk of electrolyte combustion and enhance the safety of LIBs. Among them, diethyl ethylphosphonate (DEEP) stands out for its exceptionally wide liquid phase range^{13,14} (-83 ~ 198°C), thus offering the potential to develop a wide-temperature and non-flammable electrolyte. Nevertheless, as a type of phosphate ester, DEEP also has some drawbacks. The reduction products^{15,16} of phosphate esters exhibit limited electron shielding capacity, which diminishes the protective role of solid electrolyte interphase (SEI) and greatly increases the irreversible capacity of the cycling process. Additionally, the strong interaction^{15,17} between the phosphate molecule and Li⁺ will make the de-solvation difficult, thereby deteriorating the electrochemical performance^{18,19} of LIBs.

The introduction of film-forming additives^{17,20} is an effective strategy for inhibiting solvent decomposition in phosphate electrolytes during the cycling process. However, as the film-forming additives gradually decompose, the reversible capacity of LIBs continues to degrade. Additionally, the design strategies^{5,21-24} involving high concentration and diluted high concentration electrolytes also face similar challenges, including high costs and low ionic conductivity, which impede the practical implementation of phosphate ester flame-retardant electrolytes. In recent years, researchers¹⁵ proposed a new approach to address these issues by constructing a dynamically stable solvation structure using ethylene carbonate (EC), thereby improving the stability of the graphite electrodes. Despite these

advancements, the electrochemical performance^{15,21} of LIBs with phosphate electrolytes remains unsatisfactory under the conditions of high discharge rates ($> 1\text{C}$) or temperatures below -20°C . In contrast, ether electrolytes^{25,26} are typically characterized by high ionic conductivity and low viscosity, offering advantages for low-temperature and rate performance. More importantly, diethylene glycol dimethyl ether (DEGDME), with its multidentate coordination and spatially flexible molecular properties, can reconstruct the solvation structure of the DEEP-based electrolyte and enhance its ion transport capacity. However, ether solvents are less compatible with graphite anodes and tend to be flammable. By leveraging the benefits of these two formulations, it is possible to accelerate the transport of Li^+ in the electrolyte and enhance the electrochemical performance of the cells.

Herein, this study proposes the introduction of DEGDME, an ether solvent^{27,28} that can form multidentate coordination with Li^+ , into the DEEP electrolytes. This modification is expected to reconfigure the PSS of Li^+ . Specifically, due to its multidentate coordination and spatially flexible molecular properties, DEGDME simultaneously weakens the interaction between DEEP and Li^+ , thus enhancing both the ionic conductivity and Li^+ transport number, thereby improving the low-temperature and rate performance of $\text{Li}||\text{Graphite}$ cells. Based on these assumptions, the DEEP-based nonflammable electrolyte enables a capacity retention of 98% after 150 cycles and a charging specific capacity of $310\text{ mAh}\cdot\text{g}^{-1}$ at 1C for $\text{Li}||\text{Graphite}$ cells. In particular at -20°C , the $\text{Graphite}||\text{LiFePO}_4$ cells also remain a capacity retention of 71% during 50 cycles, significantly enhancing the practical applicability of phosphate electrolytes at low temperatures. The work blazes a feasible pathway to formulate non-flammable phosphate electrolytes for wide-temperature application in LIBs.

2. Result and Discussion

2.1 Characteristics of DEEP-DEGDME electrolyte

Scheme 1. Conceptual diagram of advantages and defects of phosphate electrolyte and ether electrolyte. Physical properties of phosphate esters and carbonate esters are listed in the Supplementary Table 1.

To validate the design concept illustrated in Scheme 1 for developing a non-flammable DEEP-based electrolyte that can utilize the advantages of both electrolyte types while affording wide-temperature operation, DEEP and DEGDME are roughly blended and lithium bis(fluorosulfonyl)imide (LiFSI) salts are employed as the basis for our investigation. The binding energies of various solvent molecules with Li^+ are investigated by density functional theory (DFT) simulations. The results (Fig. 1a) indicate that DEGDME exhibits a binding energy of -3.57 eV with Li^+ , whereas DEEP displays a binding energy of only -2.74 eV , suggesting that DEGDME demonstrates a higher coordination potential with Li^+ resulting from its multidentate coordination. Incorporating DEGDME into phosphate ester-based electrolytes is expected to produce a more compact solvation sheath structure due to DEGDME's smaller molecular size and its multidentate coordination^{27,28}, which facilitates spatial folding (Fig. 1b). A smaller solvation

sheath size formed by the involvement of ether oxygen^{29,30} may reduce the energy barrier for ion migration, leading to faster ion conduction. Consequently, modifying DEEP electrolytes with DEGDME is theoretically feasible.

Figure 1 | Design concepts and molecular characteristics of DEGDME. **a** Electrostatic potential mapping of DEEP, Li⁺-DEEP, DEGDME and Li⁺-DEGDME structures. **b** Schematic diagram of the PSS of Li⁺ before and after the introduction of DEGDME. **c** Initial charge/discharge process with D₂G₂, D₂E₂G₂ and D₂E₂G₂T_{0.5} electrolytes for Li||Graphite cells. **d** Rate performance for Li||Graphite half-cells with D₂E₂G₂T_{0.5} and D₂E₂G₂F_{0.5} electrolytes. The corresponding electrolyte formulations in this paper are also listed in Supplementary Table 2.

Then, the compatibility of graphite electrodes in DEEP-DEGDME electrolyte (LiFSI: 2DEEP: 2DEGDME by molar ratio, denoted as D₂G₂) was evaluated by galvanostatic cycling experiments. The Li||Graphite cells (Fig. 1c and Fig. S1) exhibit a prolonged discharge plateau (~ 1.1 V) and a low charging specific capacity (~ 87 mAh·g⁻¹). And the Li||Graphite cell was disassembled after 5 cycles, and the graphite electrodes were removed for optical observation (Fig. S2a) and X-ray diffraction (XRD) testing (Fig. S2b). The graphite electrode post-cycling shows obvious peeling phenomenon, while the XRD pattern proves that the crystal structure of the graphite electrode is severely damaged. These findings suggest that solvent molecules intercalate into the graphite lattice^{31–33}, leading to a high irreversible capacity of the cell. Clearly, compatibility with graphite electrodes cannot be achieved only by these two solvents, making the introduction of a new solvent essential for addressing this issue.

EC has a high relative dielectric constant (~ 89) and excellent film-forming ability^{15,19}, which facilitates the dissociation of lithium salt and enhances electrolyte compatibility with graphite electrodes, making it a suitable choice for our designed electrolyte system. After introducing EC into the electrolyte (LiFSI: 2DEEP: 2EC: 2DEGDME by molar ratio, denoted as D₂E₂G₂) system, the assembled Li||Graphite half-cells (Fig. 1c and Fig. S3a) exhibits enhanced initial charging specific capacity with 110 mAh·g⁻¹ compared to the configuration without EC. Considering that the electrolyte still does not support reversible charging and discharging of the cells, the additives should be further explored to address this issue. And it's reported 1,3,2-dioxathiolane 2,2-dioxide^{20,34} (DTD) can participate in SEI film formation to improve the compatibility of graphite electrode and enhance the low-temperature performance of the cell, making it an optimal choice. After adding DTD, the Li||Graphite half-cells (Fig. 1c and Fig. S3b) with the electrolyte (LiFSI: 2DEEP: 2EC: 2DEGDME: 0.5DTD by molar ratio, noted as D₂E₂G₂T_{0.5}) achieve a high initial Coulombic efficiency of 87%, comparable to that of conventional carbonate electrolytes^{35,36}. These experiments demonstrate that the introduction of EC and DTD successfully enables reversible intercalation and deintercalation processes of Li⁺ in graphite electrodes within the DEEP-DEGDME electrolyte. To verify DEGDME's efficiency in enhance the rate performance of DEEP-based electrolytes, DEGDME in the D₂E₂G₂T_{0.5} electrolyte is replaced with the methyl 2,2,2-trifluoroethyl carbonate (FEMC) solvent. The charging specific capacity (Fig. 1d) of the cell using the electrolyte (LiFSI: 2DEEP: 2EC:

2FEMC: 0.5DTD by molar ratio, denoted as $D_2E_2F_2T_{0.5}$) in 1C is only $147 \text{ mAh}\cdot\text{g}^{-1}$, which is well below the performance of the $D_2E_2G_2T_{0.5}$ electrolyte with $298 \text{ mAh}\cdot\text{g}^{-1}$. A series of experiments demonstrates that the DEEP-DEGDME electrolyte can achieve good compatibility with graphite and significantly improve rate performance of the cells, thereby validating the original concept outlined in Scheme 1.

2.2 Composition of electrolyte formulations

Figure 2 | Electrochemical properties of different electrolytes. **a** Rate performance of Li||Graphite half-cells with $D_2E_2G_xT_{0.5}$ electrolytes in different molarities DEGDME solvents. **b** Percentage of charging specific capacity of electrolyte at different charging rate to charging specific capacity at 0.1C. **c** Cyclic voltammetry curves of the $D_2E_2G_2T_{0.5}F_2$ electrolyte in the range of 0.01-2V at 0.1 mV s^{-1} . **d** Rate performance and **e** cycling performance of the Li||Graphite cells in RCE and $D_2E_2G_2T_{0.5}F_2$ electrolytes.

To achieve optimal electrochemical performance, the DEGDME content was further optimized. The Li||Graphite half-cells with electrolytes (LiFSI: 2DEEP: 2EC: x DEGDME: 0.5DTD by molar ratio, denoted as $D_2E_2G_xT_{0.5}$) in different molar ratios of LiFSI to DEGDME were assembled and tested (Fig. 2a) for rate capability. The results indicate that the highest charging specific capacity was achieved with a LiFSI to DEGDME molar ratio of 1:2 at 1C, yielding a specific capacity with $315 \text{ mAh}\cdot\text{g}^{-1}$. Further increasing the DEGDME's content leads to a decline in charging specific capacity. The impact of DEGDME's content on rate performance is further assessed by calculating the percentage of charging specific capacity at different rates, relative to their 0.1C charging specific capacity (Fig. 2b). Notably, at a LiFSI to DEGDME molar ratio of 1:2, the Li||Graphite half-cells delivers the highest charging specific capacity at 0.5C, 1C and 2C, corresponding to 91%, 85% and 52% of its specific capacity at 0.1C.

Considering the flame retardancy of the designed electrolyte and accommodating to the “~1M” design principle^{37–40}, the FEMC was further added to regulate the electrolyte's concentration, aiming to enhance the flame retardancy of the electrolyte. Therefore, it's determined that the electrolyte has an optimal molar ratio of LiFSI: DEEP: EC: DEGDME: DTD: FEMC of 1:2:2:2:0.5:2 ($\sim 1.0 \text{ mol L}^{-1}$, denoted as $D_2E_2G_2T_{0.5}F_2$). Meanwhile, 1M LiPF₆-EC/DMC/EMC (volume: 1:1:1, denoted as RCE) electrolyte is used as a control for electrochemical performance comparison. The cyclic voltammetry measurements (Fig. 2c) show distinct oxidation and reduction peaks with 0.01 V and 0.26 V, without any decomposition peaks. In the initial charge/discharge curves, the Li||Graphite cell with $D_2E_2G_2T_{0.5}F_2$ electrolyte exhibits the initial charging specific capacity of $362 \text{ mAh}\cdot\text{g}^{-1}$ and a Coulombic efficiency of 87% (Fig. S4). These findings indicate that Li⁺ can undergo reversible intercalation and de-intercalation of the graphite electrode. The cells of two electrolytes (Fig. 2d and Fig. 2e) are compared in terms of their long-term cycle performance and rate performance. The Li||Graphite half-cells with $D_2E_2G_2T_{0.5}F_2$ electrolytes slightly exceed that of RCE in terms of charging capacity at various rates, marking a significant advancement for phosphate electrolytes. Additionally, after 150 cycles, Li||Graphite half-cells with $D_2E_2G_2T_{0.5}F_2$ also retains 98% of initial specific capacity.

2.3 Physical and chemical properties of electrolyte

The physical properties and solvation structure of the $D_2E_2G_2T_{0.5}F_2$ electrolyte were characterized before the full-cell testing for electrochemical performance. In the self-extinguishing experiment (Supporting Video 1 and 2 and Fig. 3a), the self-extinguishing time of RCE reaches 87 s g^{-1} , while that of the $D_2E_2G_2T_{0.5}F_2$ electrolyte is 0 s g^{-1} . This result indicates that the designed electrolyte is non-flammable, thus offering enhanced safety compared to the carbonate electrolyte. To investigate the role of DEGDME in DEEP-based electrolytes, the electrolyte (LiFSI: 2DEEP: 2EC: 2FEMC by molar ratio, denoted as $D_2E_2F_2$) without DEGDME was also used for comparison. As known in Fig. 3b, the ionic conductivity of three electrolytes was also measured. Among them, the ionic conductivity of the $D_2E_2F_2$ electrolyte is 1.4 mS cm^{-1} at -20°C and 6.1 mS cm^{-1} at 30°C , whereas that of $D_2E_2G_2T_{0.5}F_2$ is 2.3 mS cm^{-1} and 8.5 mS cm^{-1} , and its conductivity is close to 1.0 mS cm^{-1} at -40°C . Meanwhile, the ionic conductivity of the $D_2E_2G_2T_{0.5}F_2$ electrolyte is only slightly lower than that of the RCE in all temperature range. These results suggest that DEGDME's ability to facilitate ion transport in the DEEP-based electrolyte is a key factor in enhancing its rate performance and indicate the potential application of $D_2E_2G_2T_{0.5}F_2$ at low temperatures.

Fig. 3 | Physical and chemical characteristics of different electrolytes. a Self-extinguishing time of RCE and $D_2E_2G_2T_{0.5}F_2$ electrolytes. **b** The ionic conductivity at different temperatures **c** Li^+ transport number and **d** fitting results for the activation energy of the charge transfer process in Graphite||Graphite symmetric cells of RCE|| $D_2E_2G_2T_{0.5}F_2$ and $D_2E_2G_2T_{0.5}F_2$ electrolytes.

Next, Li^+ transport number and activation energy of the charge transfer impedance during de-solvation process, were measured and analyzed to assess the contribution of Li^+ to conductivity and the difficulty of de-solvation in different electrolytes, which are crucial for evaluating the ion transport behavior of electrolytes. Therefore, the next two metrics of three electrolytes were further tested and fitted. Comparing the $D_2E_2F_2$ electrolyte with the $D_2E_2G_2T_{0.5}F_2$ electrolyte, the Li^+ transport number (Fig. 3c and Fig. S5a-c) of the electrolyte increases from 0.46 to 0.52, and the activation energy⁴¹ of the charge transfer impedance during de-solvation process (Fig. 3d and Fig. S5d-i) decreases from 0.557 eV to 0.538 eV, which are better than those of the RCE. And after 50 cycles, the cells (Fig. S6a and Fig. S6b) with the $D_2E_2G_2T_{0.5}F_2$ electrolyte also have a lower SEI and charge transfer impedance. These results suggest that the cells with the $D_2E_2G_2T_{0.5}F_2$ electrolyte will experience lower polarization during charging and discharging, thereby enhancing cell's performance at low temperatures and high rates.

2.4 Characterization of electrolyte solvation structure

Figure 4 | Raw data and fitting results of Fourier infrared spectra. The FIR raw data of **a** $\text{P}=\text{O}$ vibrations **b** $\text{C}=\text{O}$ vibrations and **c** $\text{C}-\text{O}-\text{C}$ vibrations in different electrolytes. **d** Coordination numbers of anions and solvent molecules in different electrolytes.

When the strength of the solvent-Li⁺ interaction changes, the vibrational frequencies of the corresponding functional groups of molecules in the infrared spectrum (IR) also shift. Therefore, infrared absorption spectroscopy can be used to observe the vibrational features of each solvent molecule and anion functional group, providing insight into the solvation behavior of the electrolyte. As shown in Fig. 4a-c and Fig. S7, the P = O, C = O, C-O-C and S-F/S-N vibrations correspond to DEEP, EC and DEGDME solvents and anions, respectively. Compared with the electrolyte (LiFSI: 2DEEP: 2EC by molar ratio, denoted as D₂E₂) without DEGDME, the percentage of DEEP-Li⁺ clusters in the D₂E₂G₂ electrolyte decrease from 83–73%, while the percentage of EC-Li⁺ clusters decreased from 64–45%, with around 40% of DEGDME-Li⁺ clusters. These results suggest that the introduction of DEGDME weakens the interaction strength between Li⁺ and both DEEP and EC, leading to a reconfiguration of the Li⁺ solvation structure and aligning with the conclusion shown in Fig. 1b. On the other hand, the addition of DTD and FEMC to the D₂E₂G₂ electrolyte do not significantly alter the PSS of Li⁺, which is consistent with prior expectations.

The coordination number of different particles in the electrolytes can be calculated by fitting the peak areas in the infrared spectrum and the corresponding moles. Based on the infrared fitting results for each solvent/ion, the coordination number of the different electrolytes was determined (Fig. 4d). In the D₂E₂G₂, D₂E₂G₂T_{0.5} and D₂E₂G₂T_{0.5}F₂ electrolytes, the PSS of Li⁺ contains not only DEEP but also significant amounts of EC and DEGDME. This result indicates that the likelihood of direct interaction between DEEP and Li⁺ reduces, thereby minimizing DEEP decomposition and optimizing its de-solvation behavior. To further investigate the interfacial behavior of DEGDME, X-ray photoelectron spectroscopy (XPS) of the graphite electrode was conducted after cycling to assess the reductive decomposition product of the electrolyte. As known in Fig. S8a-e, the addition of DEGDME into the D₂E₂ electrolyte led to an increase in the O content, while the amounts of C, F and P either decrease or remain unchanged. This result suggests significant decomposition of DEGDME at the interface. Additionally, after the introduction of DTD, the S content significantly increases, and the O content decreases notably, indicating that DTD decomposition contribute to the formation of perfect SEI and reduces DEGDME decomposition, which are consistent with the former experimental results (Fig. S3b).

2.5 Electrochemical performance of full cells

The electrochemical of graphite anodes in D₂E₂G₂T_{0.5}F₂ electrolyte has been verified, and the cycling and low-temperature performance of Graphite||LiFePO₄ full cells in this electrolyte will be tested below. In order to improve the interfacial stability of the D₂E₂G₂T_{0.5}F₂ electrolyte towards the cathode, 5 wt. % vinylene carbonate (VC) and 3 wt. % lithium difluoro(oxalato)borate (LiDFOB) additives were added to the electrolyte (denoted as LPE). The Li||LiFePO₄ half-cells assembled in the DPE electrolyte exhibits higher specific capacity (Fig. 5a) compared to those with the RCE, indicating that the DEGDME-modified phosphate electrolyte system provides better rate performance than the carbonate electrolyte. After 150 cycles, the LiFePO₄ half-cells (Fig. 5b) afford a capacity retention of 93% using the LPE electrolyte, demonstrating excellent compatibility with the cathode.

Fig. 5 | Electrochemical performance of full cells. **a** Rate performance and **b** the cycling performance of the Li||LiFePO₄ half-cells in RCE and DPE. **c** Rate performance and **d** the cycling performance for the Graphite||LiFePO₄ full cells with RCE and DPE. (2.8-3.7 V, N/P=1:1.1). **e** Discharge curves and **f** specific capacity of the Graphite||LiFePO₄ full cells in DPE (2.8-3.7 V, N/P=1:1.1) at 25 °C, 0 °C, -20 °C and -40 °C. **g** Cycling performance for Graphite||LiFePO₄ full cells in RCE and DPE at -20 °C.

The rate and cycling performance are further evaluated in the Graphite||LiFePO₄ full cells, where the full cells with the DPE electrolyte still outperform the RCE system in terms of rate performance (Fig. 5c). After 120 cycles at 1C, the full cells with the DPE electrolyte (Fig. 5d) maintain a capacity retention of 70% and higher average Coulombic efficiency (99.3%), compared to 62% and 99.1% for the RCE system, respectively. More critically, cell's performance at low temperatures is evaluated to leverage the wide operating range of DEEP-based electrolyte. As shown in Fig. 5e, the discharge platform of the cell at 0 °C is nearly identical to that of 25 °C, while a significant drop is observed at -20 °C. The specific capacity of the full cells (Fig. 5f) is 141 mAh·g⁻¹, 115 mAh·g⁻¹, 90 mAh·g⁻¹ and 46 mAh·g⁻¹ at temperatures of 25 °C, 0 °C, -20 °C and -40 °C, respectively. Additionally, when comparing the 0.1C cycling performance (Fig. 5g) of full cells assembled with DPE and RCE at -20 °C. The cells with RCE consistently show a specific capacity of below 40 mAh·g⁻¹, while those with DPE achieve 90 mAh·g⁻¹ and even retain 71% of its initial capacity after 50 cycles. In addition to evaluating low-temperature performance, differential scanning calorimetry^{7,42} (DSC) was conducted on two of the electrolytes (Fig. S9). The results reveal that the RCE exhibits a pronounced heat absorption peak at 176.6 °C, indicating that the RCE undergoes significant vaporization or decomposition at this temperature. In contrast, the DPE electrolyte shows a much smaller heat absorption peak at 235.5 °C, demonstrating its superior thermal stability and underscoring its suitability for high-temperature applications.

3. Conclusion

In conclusion, the design of a non-flammable electrolyte with a wide temperature range using DEEP and DEGDME is proposed. However, the compatibility of these two solvents with graphite electrodes poses a challenge. Fortunately, the introduction of EC and DTD can address the challenge. And the Li||Graphite cell in the designed electrolyte retains 98% of their initial capacity after 150 cycles. As envisioned, the introduction of DEGDME enhances the rate performance of DEEP-based electrolyte. Subsequent studies show that this improvement is due to the multidentate coordination and spatial folding structure of DEGDME, which reconfigures the solvation structure of DEEP and accelerating its ion transport. Compared to carbonate electrolytes, this electrolyte allows improved cycling performance at -20 °C for Graphite||LiFePO₄ full cells and higher vaporization temperatures. Thus, the use of DEGDME-modified DEEP electrolytes can significantly improve rate performance and enable their use in LIBs across a wider temperature range, promoting the development of non-flammable phosphate electrolytes.

4 Methods

The LiFSI (99.5%) was sourced from Guangzhou Tinci High-Tech Materials Co., Ltd., while LiPF₆ (99.5%), LiDFOB (99.5%) and FEMC (99%) were acquired from Suzhou Duoduo Chemical Technology Co., Ltd. The EC (99.9%), DMC (99.9%) and EMC (99.9%) were obtained from Capchem Technology Co., Ltd., and the VC (99%) from Aladdin, and DEEP (99%) from Beijing Jintong Letai Chemical Products Co., Ltd. All chemicals were dried by molecular sieve before using.

The Graphite, LiFePO₄ and lithium metal foil (400 μm) were supplied by BTR New Material Group Co., Ltd., Jiangsu Chunlan Clean Energy Research Institute Co., Ltd., and Tianjin Zhongneng Lithium Industry Co., Ltd., respectively. And the carboxymethyl cellulose (CMC) and polyvinylidene fluoride (PVDF) binder were obtained from Aladdin. For the preparation of the graphite anode, a slurry was made of the graphite active material, Super P and CMC with a mass ratio of 8:1:1, and it was subsequently applied onto copper foil and dried at 90°C for 12 hours, yielding the graphite anode with an active-materials loading of approximately 2–3 mg cm⁻². And the LiFePO₄ cathode was made similarly, using PVDF as the binder and aluminum foil as the substrate. After drying at 110°C for 12 hours, the resulting LiFePO₄ electrodes achieved an active-materials loading of 3–4 mg cm⁻².

Declarations

Data availability

The data that support the findings of this study are enclosed in the supplementary material or are available from the corresponding author upon reasonable request.

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Schemes

Scheme 1 is available in the Supplementary Files section.

Figures

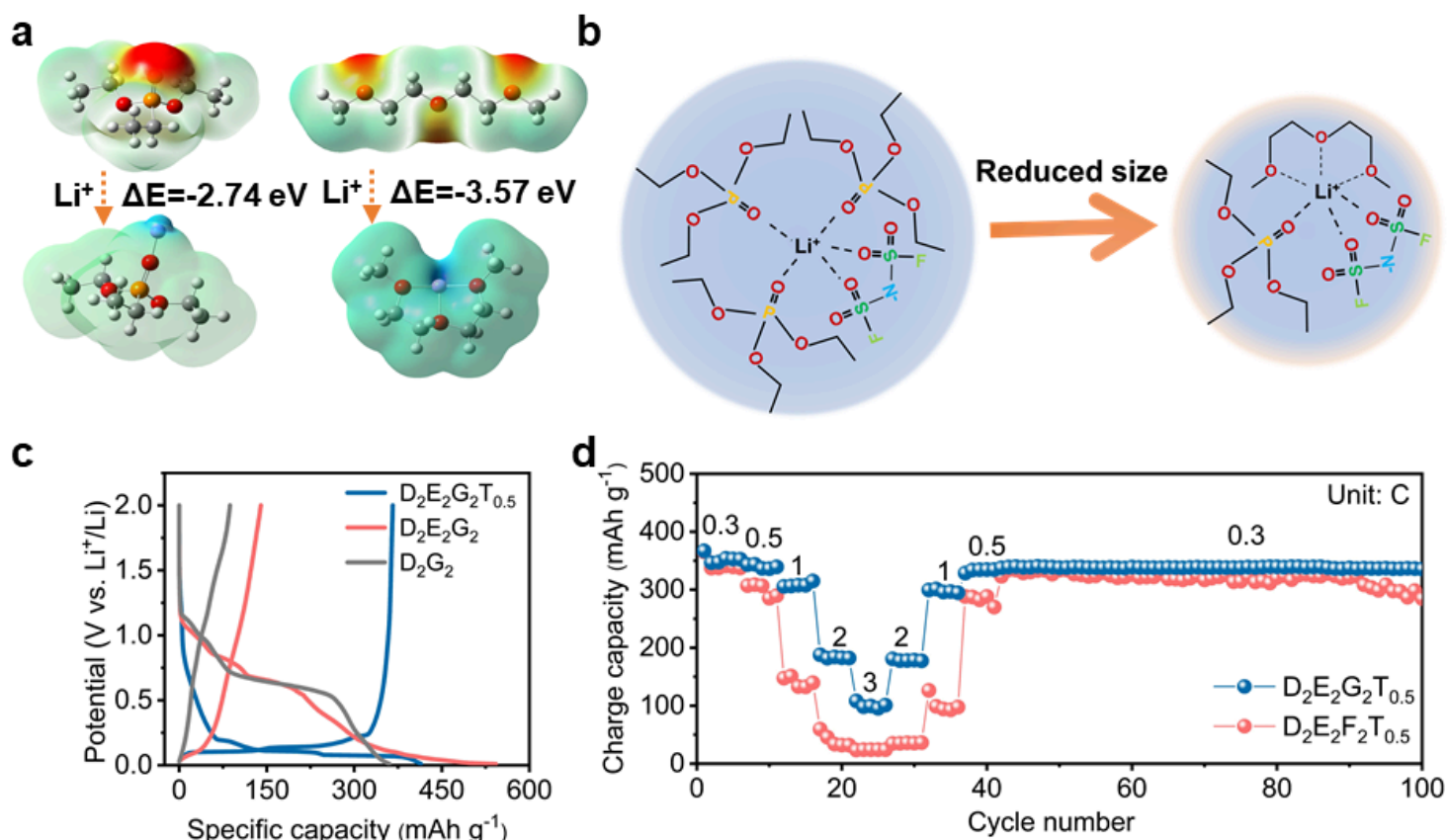


Figure 1

Design concepts and molecular characteristics of DEGDME. **a** Electrostatic potential mapping of DEEP, Li^+ -DEEP, DEGDME and Li^+ -DEGDME structures. **b** Schematic diagram of the PSS of Li^+ before and after the introduction of DEGDME. **c** Initial charge/discharge process with D_2G_2 , $\text{D}_2\text{E}_2\text{G}_2$ and $\text{D}_2\text{E}_2\text{G}_2\text{T}_{0.5}$ electrolytes for $\text{Li}||\text{Graphite}$ cells. **d** Rate performance for $\text{Li}||\text{Graphite}$ half-cells with $\text{D}_2\text{E}_2\text{G}_2\text{T}_{0.5}$ and $\text{D}_2\text{E}_2\text{G}_2\text{F}_{0.5}$ electrolytes. The corresponding electrolyte formulations in this paper are also listed in Supplementary Table 2.

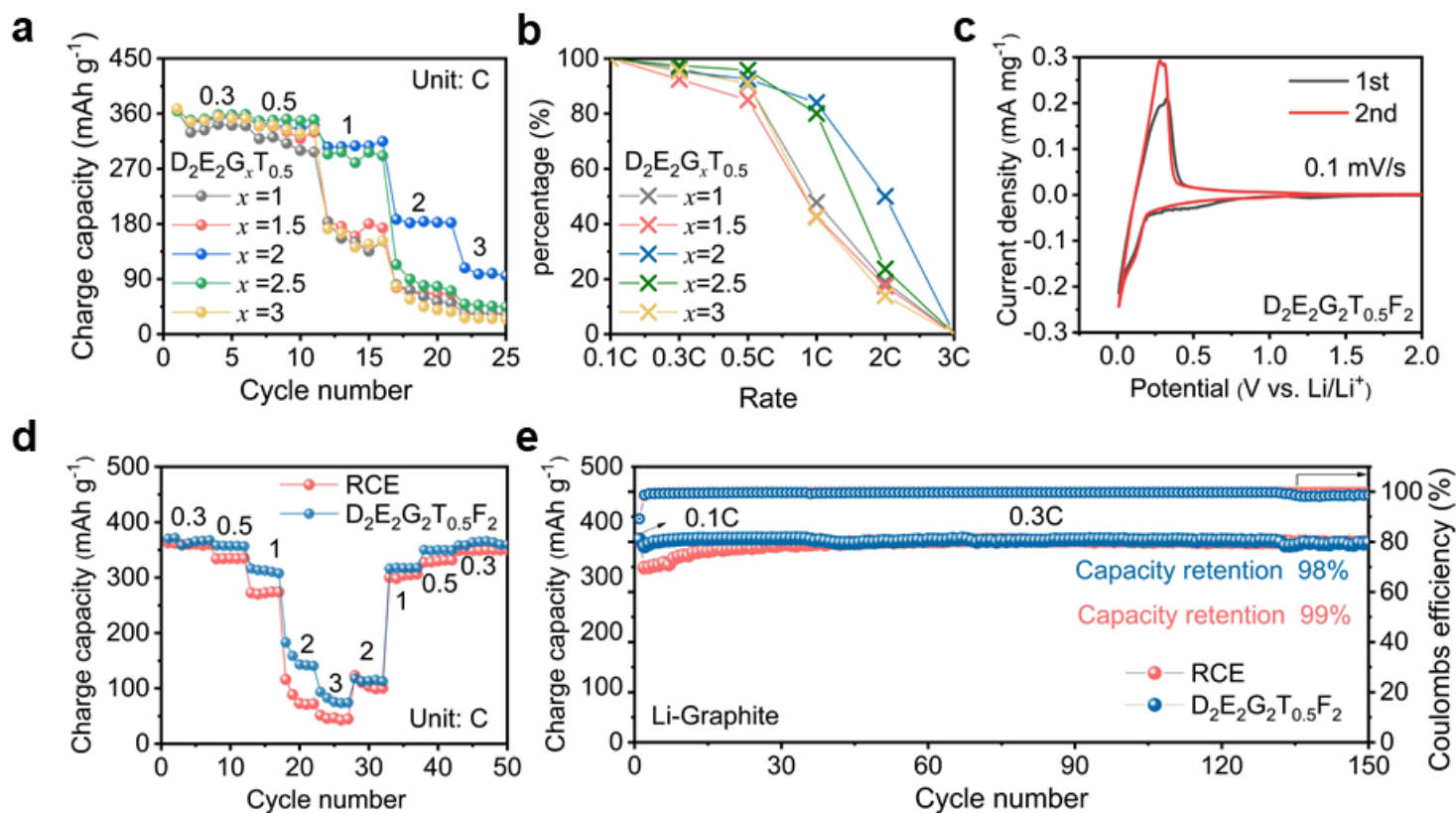


Figure 2

Electrochemical properties of different electrolytes. **a** Rate performance of $\text{Li}||\text{Graphite}$ half-cells with $\text{D}_2\text{E}_2\text{G}_x\text{T}_{0.5}$ electrolytes in different molarities DEGDME solvents. **b** Percentage of charging specific capacity of electrolyte at different charging rate to charging specific capacity at 0.1C. **c** Cyclic voltammetry curves of the $\text{D}_2\text{E}_2\text{G}_2\text{T}_{0.5}\text{F}_2$ electrolyte in the range of 0.01-2V at 0.1 mV s^{-1} . **d** Rate performance and **e** cycling performance of the $\text{Li}||\text{Graphite}$ cells in RCE and $\text{D}_2\text{E}_2\text{G}_2\text{T}_{0.5}\text{F}_2$ electrolytes.

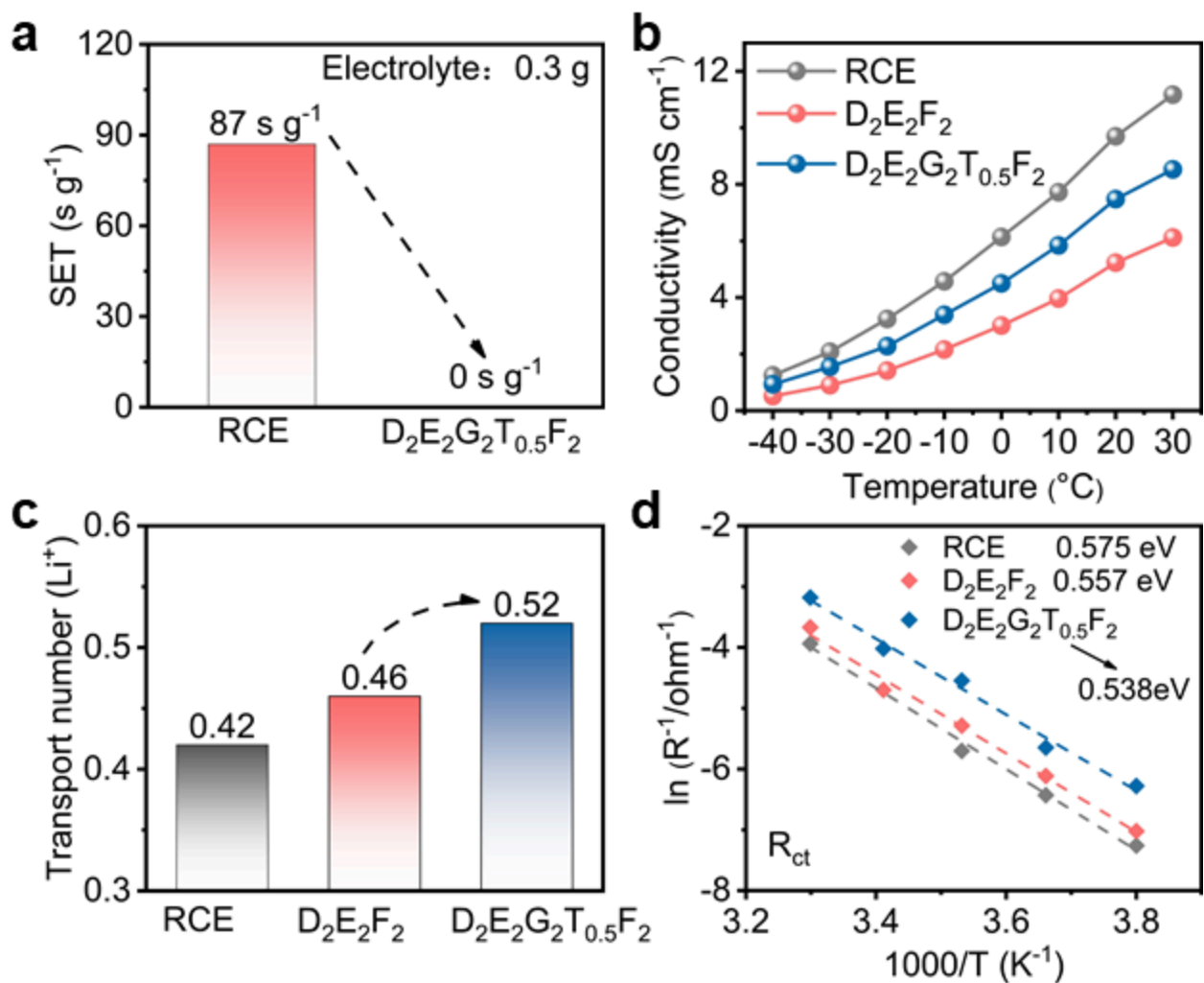


Figure 3

Physical and chemical characteristics of different electrolytes. **a** Self-extinguishing time of RCE and $\text{D}_2\text{E}_2\text{G}_2\text{T}_{0.5}\text{F}_2$ electrolytes. **b** The ionic conductivity at different temperatures **c** Li^+ transport number and **d** fitting results for the activation energy of the charge transfer process in Graphite||Graphite symmetric cells of RCE|| $\text{D}_2\text{E}_2\text{G}_2\text{T}_{0.5}\text{F}_2$ and $\text{D}_2\text{E}_2\text{G}_2\text{T}_{0.5}\text{F}_2$ electrolytes.

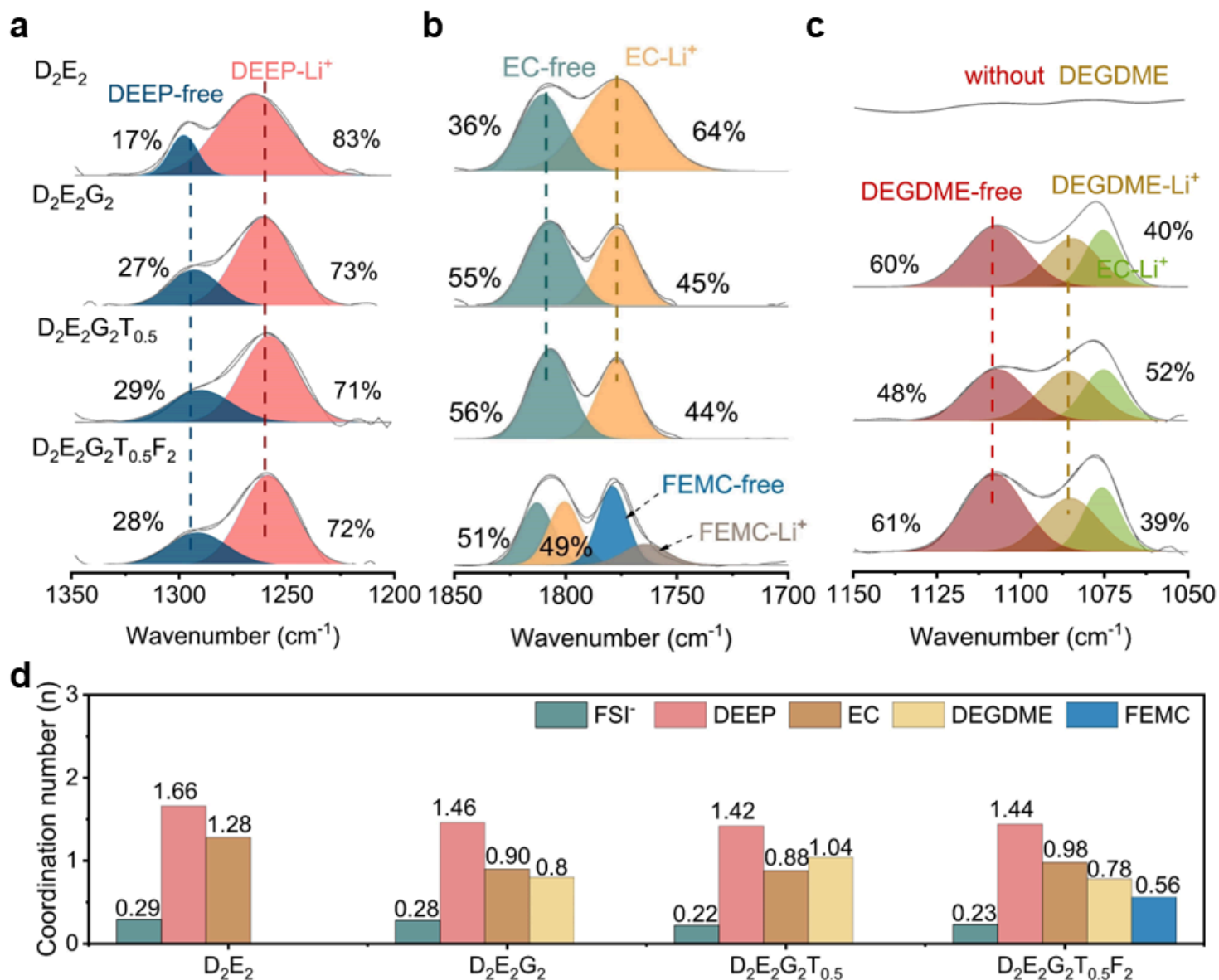


Figure 4

Raw data and fitting results of Fourier infrared spectra. The FIR raw data of **a** P=O vibrations, **b** C=O vibrations and **c** C-O-C vibrations in different electrolytes. **d** Coordination numbers of anions and solvent molecules in different electrolytes.

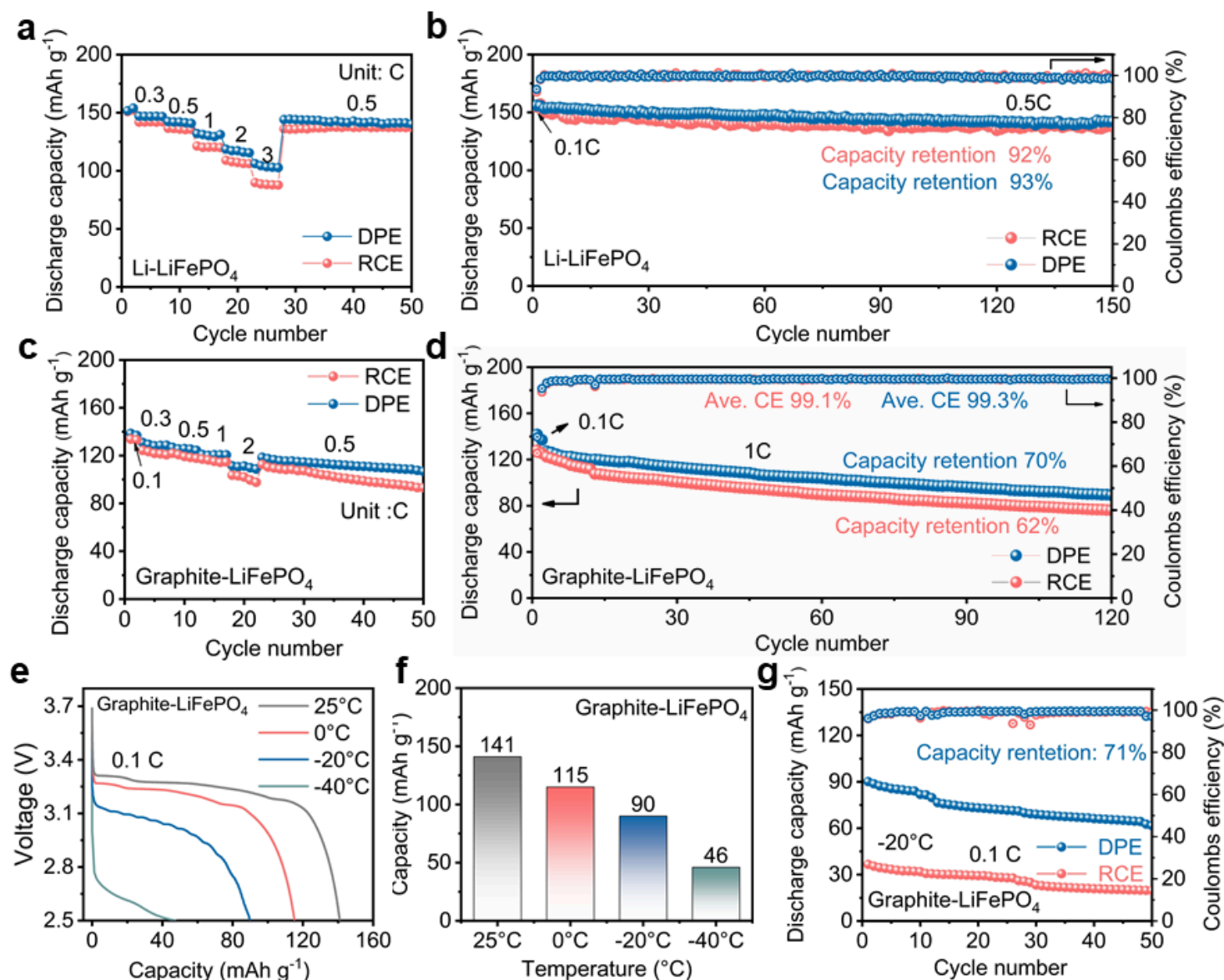


Figure 5

Electrochemical performance of full cells. **a** Rate performance and **b** the cycling performance of the Li||LiFePO₄ half-cells in RCE and DPE. **c** Rate performance and **d** the cycling performance for the Graphite||LiFePO₄ full cells with RCE and DPE. (2.8-3.7 V, N/P=1:1.1). **e** Discharge curves and **f** specific capacity of the Graphite||LiFePO₄ full cells in DPE (2.8-3.7 V, N/P=1:1.1) at 25 °C, 0 °C, -20 °C and -40 °C. **g** Cycling performance for Graphite||LiFePO₄ full cells in RCE and DPE at -20 °C.

Supplementary Files

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- [image1.png](#)
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