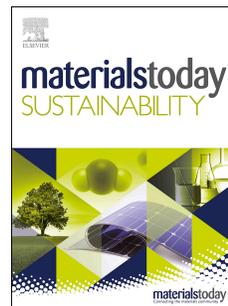


Journal Pre-proof

Review of Electrolyte Strategies for Competitive Dual-ion Batteries

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1 **Abstract**

2 The development of potential substitutes for lithium-ion batteries has attracted
3 considerable attention in recent years due to the scarcity of lithium sources and the
4 urgent demand for energy storage systems. Remarkably, dual-ion batteries (DIBs)
5 based on a particular intercalation mechanism of anions exhibit great promise as
6 next-generation batteries with high operating voltage, low cost, and high safety.
7 However, research on DIBs is still in its infancy, and many fundamental issues, such
8 as limited energy density, structural failure, sluggish kinetics, and electrolyte
9 deposition, must be understood more comprehensively to explore high-performance
10 electrolytes and electrodes and establish stable redox electrochemistry. In this review,
11 we summarize the current mechanisms and challenges of DIBs to address and
12 alleviate these issues. Among various critical components of DIBs, electrolytes are
13 receiving considerable attention because they provide the basic operating environment
14 and participate in the energy storage process. Several electrolyte strategies, including
15 high-concentration, hybrid ion, functional additive, and solid-state strategies, have
16 been proposed. These strategies have been demonstrated to not only improve the
17 properties of electrolytes, but also to deliver superior battery performance. Therefore,
18 a comprehensive overview of electrolyte strategies is presented and discussed in detail
19 for the future development of DIBs.

20 **Keywords:** dual-ion batteries, anion intercalation, electrolyte, strategies

21

1 **Introduction**

2 Developing large-scale energy storage systems is essential to assist the utilization of
3 intermittent renewable and clean energy sources, such as solar, tidal, and wind energy,
4 which are regarded as potential technologies that can alleviate the problems of fossil
5 fuel shortage and global warming.[1-3] As one of the most important energy storage
6 devices, advanced batteries are considered promising candidates for satisfying the
7 requirements of high cycle efficiency, flexible design, low cost, and various power
8 and energy features.[4, 5] Meanwhile, commercial lithium-ion batteries (LIBs) have
9 been successfully used in consumer electronics and electric vehicles.[6, 7] However,
10 LIBs exhibit difficulty in accomplishing large-scale energy storage applications with
11 low cost, high energy density, and long service life due to the low natural abundance
12 of lithium resources (0.0065 wt% in the Earth's crust) and the unrealized intrinsic
13 high capacity.[8, 9] Additional, LIBs also suffer from significant problems in terms of
14 their safety due to the toxicity and flammability of organic electrolytes, which even
15 frequent fires and explosions.[10, 11] In this context, the development of
16 next-generation superior and safe batteries with high energy density for inexpensive
17 energy storage systems is necessary to meet the continuously increasing electric
18 storage demands.[2, 6]

19 In recent years, considerable effort has been exerted to pursue “beyond lithium-ion”
20 technologies in numerous academies and companies. Therein, dual-ion batteries
21 (DIBs) have elicited widespread interest as a novel promising alternative for
22 large-scale energy storage due to their low cost, which is attributed to the use of

1 graphite as the cathode in most DIBs; high working voltage (>4 V), which is larger
2 than that of LIBs (3.3–3.7 V); and environmental friendliness.[12-19] In contrast to
3 conventional LIBs, the DIBs simultaneously provide the intercalation of anions into
4 the cathode materials and storage of cations in the anode materials upon charging.
5 Obviously, both cations and anions can act as active species in the DIBs, resulting in
6 enhanced capacity. Although as a new battery system, the DIBs has a long and
7 distinctive history. Rüdorff and Hofmann first discovered the phenomenon of anion
8 (HSO_4^-) intercalation in graphite in 1938.[20] In 1989, McCullough et al. propose a
9 concept of graphite DIBs with graphite acting as anode and cathode in their
10 patents.[21] Afterward, in the following decades, the DIBs achieve a series of
11 progress based on the anion-insertion mechanism. For example, a high-concentration
12 electrolyte is required in DIBs, leading to more usage of electrolyte salts. Therefore,
13 alkali metals salts (Na[22, 23], K[24-26], and even Ca[27, 28] salts) are developed to
14 substitute lithium salts and reduce cost. Additionally, in recent years, high-capacity
15 alloy materials (e.g., aluminum[29-31], tin[22], and silicon[13, 32]) can be directly
16 used as anodes for DIBs. This feature not only reduces costs but also facilitates
17 pairing with a graphite cathode to increase energy density and relieve the safety
18 problem. Consequently, with different combinations of electrolytes and electrode
19 materials, DIBs will have various configurations and even develop other systems
20 (such as halogen conversion–intercalation mechanism[33] and reverse DIB[34]) to
21 meet different requirements and provide more powerful next-generation batteries.
22 Although progress has been attained, the practical application of DIBs is still hindered

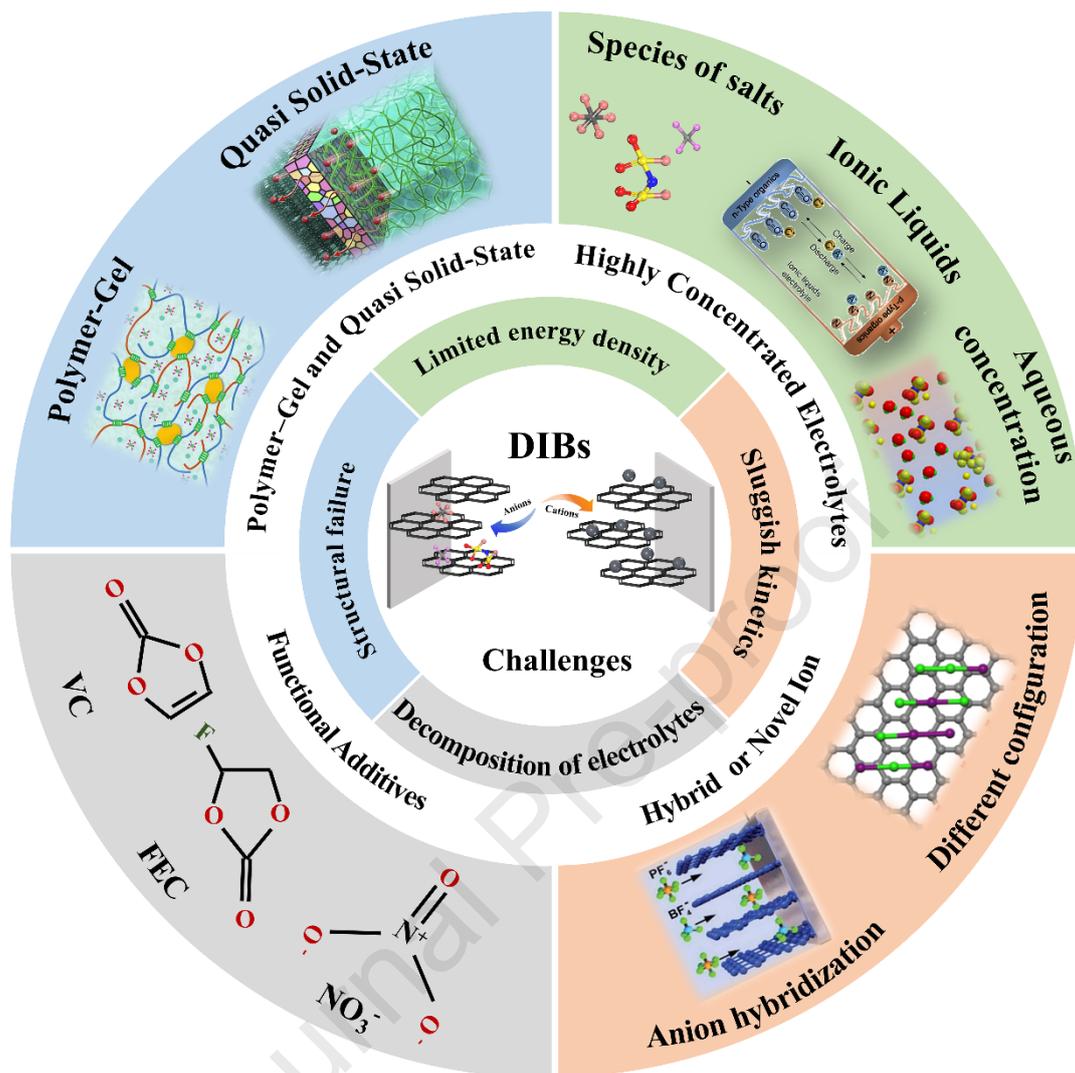
1 by unfavorable issues.[18]

2 Lately, considerable research effort still has been demonstrated to explore the
3 electrochemical mechanisms of DIBs and improve their electrochemical performance
4 through various designs and developments of electrode materials and electrolytes.

5 However, DIBs still face several challenges, such as limited energy density, structural
6 failure, sluggish kinetics, and electrolyte decomposition. One of the key reasons for
7 such problems is the inappropriately large anions of electrolyte salt that limit
8 intercalation capability into the host structure, resulting in slow diffusion kinetics and
9 even causing serious damage to the structure. In a high-voltage operating environment,
10 an electrolyte undergoes decomposition, decreasing the lifetime and stability of DIBs.

11 The properties of a battery, such as electrochemical stability, working voltage,
12 Coulombic efficiency (C_{eff}), and even its reaction mechanism, are affected by the
13 species and properties of electrolyte that provides the basic operating environment.

14 Moreover, the electrolyte in DIBs also acts as the active material in the
15 electrochemical energy storage process. Therefore, electrolyte improvement strategies
16 have received tremendous attention. Electrolytes play a key role in electrochemical
17 energy storage systems and could affect the performance of batteries through simple
18 design [35, 36]. This review intends to summarize electrolyte strategies from the
19 perspective of solving the issues of DIBs and improving their electrochemical
20 performance (Fig. 1). We hope that this review can assist researchers who are working
21 on optimizing electrolytes and promoting the development of DIBs.



1

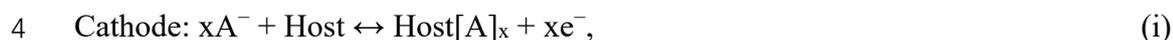
2 **Fig. 1.** Overview of electrolyte strategies for DIBs, including highly concentrated
 3 electrolytes, hybrid or novel ion in the electrolytes, functional additives, and
 4 polymer-gel and quasi solid-state electrolytes. The inserted graphics are adapted with
 5 permission from refs [64], [71], [77], [80], [93], and [96].

6 1. Mechanisms and Challenges of DIBs

7 1.1 Reaction Mechanisms

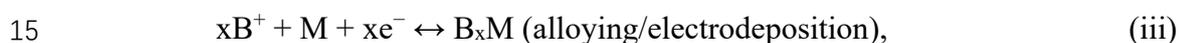
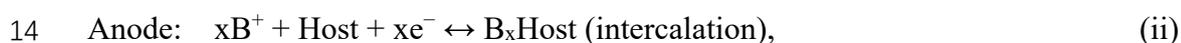
8 Here, we summarize various reaction mechanisms of DIBs (Fig. 2). Compared with
 9 LIBs, DIBs have characteristic working mechanisms that are based on the
 10 intercalation of anions into cathodes. Cathodes typically use materials that can

1 reversibly store anions, such as graphite, organic materials, and metal-organic
 2 frameworks (MOFs). This phenomenon is called anion intercalation storage. The
 3 corresponding reaction during charging can be expressed as follows:



5 where A^- anions include fluoro-based anions (PF_6^- , AlF_4^- , and BF_4^-), imide-based
 6 anions (FSI^- , TFSI^- , FTFSI^- , and BETI^-), AlCl_4^- , ClO_4^- , and DFOB^- . In particular,
 7 tremendous research effort is being exerted to understand the formation mechanism of
 8 graphite intercalation compounds (GICs) after the intercalation of anions.

9 Meanwhile, similar to LIBs' anodes, various materials can act as anodes when
 10 reversible cationic reactions, such as the intercalation, alloying/electrodeposition, or
 11 conversion of cations, can be accomplished by using them. These materials will
 12 combine with anion-intercalation cathodes to construct DIBs. The reactions of anodes
 13 during charging that have been studied thus far include

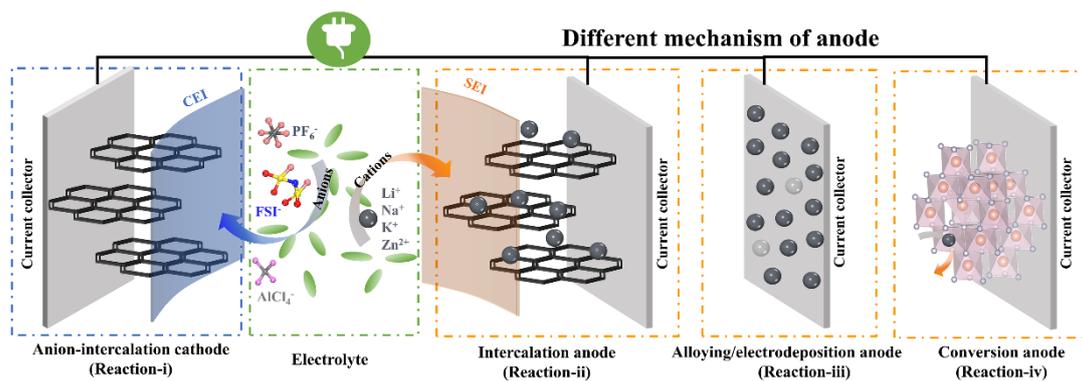


17 where B^+ cations include metal cations (Li^+ , Na^+ , K^+ , Ca^{2+} , Al^{3+} , etc.), ionic liquid
 18 (IL)-based cations (EMIC^+ , Pyr_{14}^+ , and PP_{14}^+) and so on. M is a metal or metallic
 19 element; and R is O[37, 38] and S[39, 40]. In early work, dual-graphite batteries

1 (DGBs) have motivated the study of the so-called dual-intercalation mechanism with
2 graphite as cathode and anode. These systems, which use reactions (i) and (ii), are
3 regarded as promising types of DIBs due to element abundance, environmental
4 benefits, and excellent cycling performance. Studies on alloying anode materials with
5 reactions (i) and (iii) have been increasing, with a similar process to that of LIBs in
6 releasing the potential ability of their naturally high theoretical capacity. Unexpectedly,
7 aluminum foil can be used as current collector and anode; this practice not only
8 reduces cost but also lessens the weight in recent research.[41] If M is the same
9 element as the B⁺ cation, then the B⁺ metal ions will be electrodeposited onto the
10 metal foil and the cations will be intercalated simultaneously into the cathode. In a
11 special example, Al₂Cl₇⁻ anion can generate a reversible electrochemical reaction to
12 deposit aluminum metal onto the anode from the chloroaluminate-based ILs after the
13 reaction.



15 which can be regarded as DIBs along with AlCl₄⁻ cation in a graphite cathode. As
16 another type of anode material, conversion anode materials, such as transition metal
17 oxides (e.g., MnO₂ and Nb₂O₅), are scarce for DIBs due to sluggish diffusion kinetics
18 and low cycling stability, even if they provide high safety by avoiding metal dendrite.



1

2

3 **Fig. 2.** Schematics of intercalation, alloying/electrodeposition, and conversion
 4 processes on the anode side and intercalation processes on the cathode side of DIBs
 5 during charge process.

6

7 1.2 Challenges of DIBs

8 In recent years, research on DIBs has focused on the development of novel cathode
 9 and anode materials, the exploration of reaction mechanisms, and the optimization of
 10 electrolyte systems. Considerable achievements have been reported in these aspects.
 11 However, specific issues/challenges remain and must be understood deeply in the
 12 following sections to achieve high performance in DIBs.

13 Limited energy and power density

14 As an alternative energy storage device, DIBs must guarantee high energy and power
 15 density to realize practical applications. The achievement of DIBs with the highest
 16 capacity depends on various factors, including the properties of individual electrolyte
 17 components, carbonous-based materials, and type of anions. Nevertheless, the “real”

1 energy density of DIBs has been criticized because electrolytes always need to be
2 considered as active materials due to anion/cation intercalation, leading to a limited
3 overall energy density.[42, 43] The overall energy density of lithium-based graphite
4 DIBs (GDIBs) is affected by the limited effect of the electrolyte (Fig. 3a).[44] The
5 negative effects of other inactive electrolyte components (e.g., solvents and additives)
6 will further decrease the energy density of DIBs. Therefore, it is necessary to
7 emphasize the contribution of electrolytes to energy density to avoid overestimation.

8 On the basis of the intercalation staging mechanism of anions, a graphite cathode has
9 a limited capacity ($<200 \text{ mAh g}^{-1}$), even with the maximum staging that requires high
10 operating potentials ($>5.0 \text{ V}$ versus Li/Li^+) and different cation species (Fig.
11 3b).[44-46] Consequently, a calculated specific capacity of only 140 mAh g^{-1} was
12 obtained at Stage I of a series $\text{C}_{16}(\text{PF}_6)_x$, but with an unstable capacity of $\sim 70 \text{ mAh g}^{-1}$
13 and above 5.5 V versus K^+/K .[47] For FSI^- anion intercalation into graphite, Stage 1
14 of $\text{C}_6(\text{FSI})_x$ exhibited 134% interlayer expansion (Fig. 3c), and the calculated specific
15 capacity only reached $\sim 180 \text{ mAh g}^{-1}$ (Fig. 3d).[26] Moreover, the different properties
16 of various carbon, such as crystallinity, surface area, and particle size, exerted a
17 significant effect on electrochemical PF_6^- intercalation from carbonate-based
18 electrolytes, exhibiting limited electrochemical performance.[48] Furthermore,
19 different anions, such as AlCl_4^- , BF_4^- , FSI^- , TFSI^- , FTFSI^- , ClO_4^- , and DFOB^- ,
20 demonstrated limited energy density, requiring the development of novel cathode
21 materials and optimizing the electrolyte for capacity and energy improvements.

1 Energy and power density are also affected by anode materials that store cations
2 reversibly through different mechanisms, such as intercalation,
3 alloying/electrodeposition, and conversion. Among intercalation anode materials, the
4 typical graphite only provides limited theoretical capacity (LiC_6 : 372 mAh g^{-1} , KC_8 :
5 279 mAh g^{-1}) and unstable intercalation between Na^+ and graphite interlayers.[49]
6 Other carbonaceous materials (soft carbon and hard carbon), transition metal oxides
7 (TiO_2 and Nb_2O_5), and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ also exhibit relatively low capacity and slow
8 reaction kinetic due to limited active sites. Alloying-type and conversion anode
9 materials can form compounds during the electrochemical process, proving their
10 extremely high specific capacity. However, the huge volume expansion and structural
11 change provide insufficient reaction kinetics, hindering the development of high
12 energy and power density. Although they have a reaction mechanism similar to that of
13 LIBs, anode materials in DIBs must offer excess capacity and fast anion intercalation
14 to meet harsh requirements for enhancing energy and power density. [12, 14, 50]

15 **Structure damage of cathode materials during intercalation/deintercalation**

16 The structural damage of cathode materials is an inevitable problem in nearly all
17 intercalation materials in DIBs. With the intercalation of large anions, the
18 electrochemical process causes the huge volume expansion and exfoliation of cathode
19 materials, resulting in the failure of batteries. Researchers have studied the
20 mechanisms and processes of the intercalation of anions into graphite interlayers, that
21 is the staging mechanism due to the balance between van der Waals forces in

1 graphene interlayers and ionic repulsion between and within anionic layers.[44] At the
2 lower stage, the graphite shows a higher charge storage capacity corresponding to the
3 higher intercalant anion concentration, that provides an in-depth understanding of the
4 optimization of the structural properties of cathode materials.[46] Another intractable
5 problem is anion desolvation, which requires overcoming the desolvation energy to
6 isolate anions and avoid the co-intercalation of solvent molecules (Fig. 3e).[51] Once
7 solvent molecules co-intercalate into the graphite interlayer during the repeat
8 electrochemical process, the structural damage and failure of cycling life will be
9 accelerated (Fig. 3f).[52] Therefore, the achievement of the structural stability of
10 electrodes must be optimized, including the exploitation of novel intercalation
11 cathodes and adaptive electrolytes, to facilitate the highly reversible
12 intercalation/deintercalation of anions.

13 **Insufficient reaction kinetics of anode materials**

14 To date, intercalation cathode materials are promising candidates that allow fast
15 kinetic to realize the fast-charging ability of DIBs. However, low-capacity
16 intercalation anode materials cause the slow storage kinetics problem in solid-state
17 ion diffusion due to the high kinetic barrier of no-lithium bulky cations (Na^+ : 1.02 \AA^2
18 and K^+ : 1.38 \AA^2). The match between cations and intercalation anode materials has
19 become the key to achieving fast kinetics. The most widely used anode materials are
20 transferred to alloy-type and conversion-type materials due to their special high
21 capacity. During cycling, however, the electrode suffers from the repeated phase

1 transformation and recovery of structure, resulting in a large volume change (such as
2 280% for $\text{Li}_{15}\text{Si}_4$,[53] 420% for $\text{Na}_{15}\text{Sn}_4$ [54], and 360% for K_2Sn [12]) and
3 pulverization issues. Meanwhile, the electrolyte is continuously consumed with the
4 formation of the solid electrolyte interphase (SEI) and its by-products. These issues
5 result in poor performance rate and mismatch with the cathode materials in reaction
6 kinetics. Therefore, structure design is apparently a feasible strategy for enhancing
7 slow reaction kinetics.

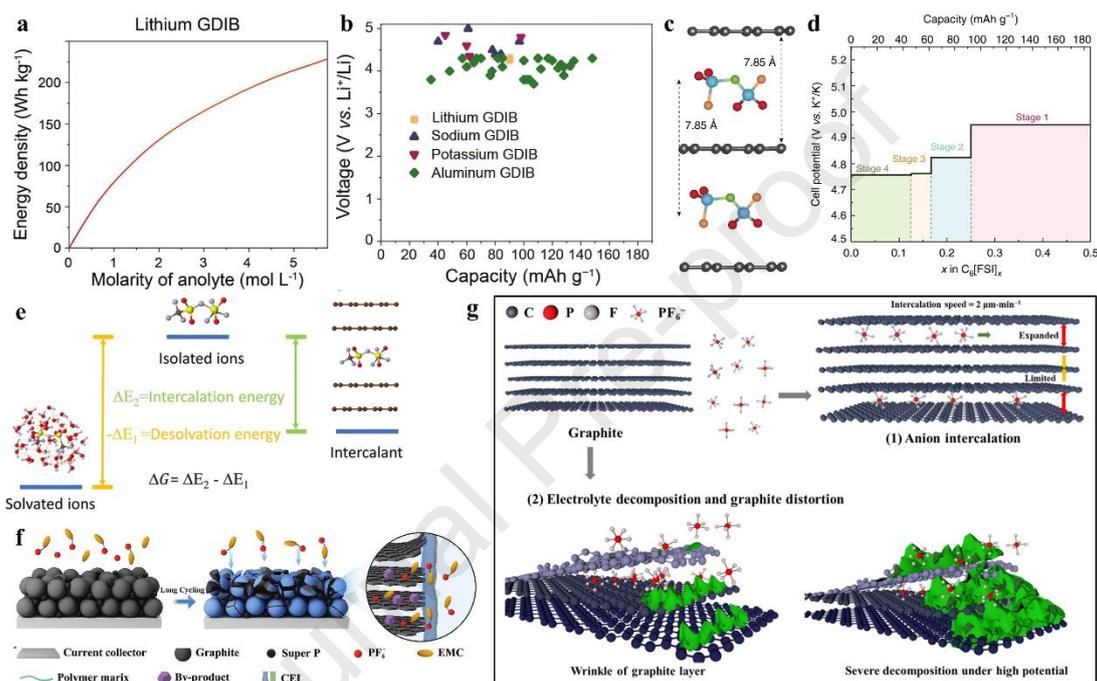
8 **Decomposition and consumption of electrolytes**

9 In contrast with LIBs, the electrolyte in DIBs not only act as the basic environment
10 for transporting ion but also as active materials that is critical to achieving the
11 chemical energy storage process. A high potential (above 4.0–4.5 V versus Li/Li^+)
12 occurs due to the anion's intercalation, inevitably resulting in the decomposition of
13 the electrolyte components and detrimental side reactions that consume the electrolyte
14 (Fig. 3g).[52, 55] Ensuring a stable electrochemical window poses a challenge at a
15 high voltage.[56] In addition, the formation of unstable SEI can degrade electrolyte
16 components and decrease C_{eff} . The irreversible intercalation of anions and cations in
17 the electrode materials will consume the isolated ions, causing capacity fading, which
18 is a major failure mechanism.[43]

19 **2. Electrolyte Optimization for Circumventing These Issues**

20 Many effective strategies have been developed to circumvent the issues discussed

1 above, such as the structural design of electrodes (nano, doping, or coating designs)
 2 and the exploration of novel organic cathodes, special 2D layered anodes, and
 3 superior electrolyte systems. In this section, we discuss the strategy of electrolyte
 4 optimization and its consequent advantages in electrochemical performance.



5
 6 **Fig. 3.** (a) Cell-level energy density of lithium GDIBs composed of LiFSI in
 7 EC/DMC as an electrolyte [44]. (b) The comparison of the average discharge voltage
 8 and the capacity of graphite cathodes in various GDIBs [44]. (c) Schematic of FSI⁻
 9 anion intercalated into graphite for stage 1 (n=1) [26]. (d) Calculated voltage profile
 10 of FSI⁻ anion intercalation into graphite as a function of the molar ratio between FSI⁻
 11 and C (i.e., x in C₆[FSI]_x) [26]. (e) Schematic of energy barriers between solvated
 12 ions, isolated ions, and intercalant state, corresponding to the desolvation process and
 13 intercalation process of anions insertion into graphite [51]. (f) Schematic illustration
 14 of the EMC co-intercalation behavior comparison in DIBs [52]. (g) A model showing
 15 the surface reaction and anion intercalation mechanism in graphite [55].

16

1 2.1 Highly Concentrated Electrolytes

2 The anions in an electrolyte can be considered active materials; hence, the
3 concentration of electrolyte plays an important role in the ion storage mechanism. As
4 previously reported, the electrochemical performance of DIBs, including its energy
5 density and working potential, is improved by the utilization of highly concentrated
6 electrolytes. Ishihara et al.[57] explored the influence of PF_6^- anion concentration in
7 ethylene carbonate (EC)/diethyl carbonate (DEC). The 3.7 M LiPF_6 in low-viscosity
8 dimethyl carbonate (DMC) obtained a significant increase in capacity of 100 mAh g^{-1} .
9 Placke et al.[58] reported that DIBs exhibited enhanced capacity and C_{eff} with an
10 increase of LiPF_6 concentration in DMC or ethyl methyl carbonate (EMC) (Fig. 4a).
11 However, as shown in Fig. 4b, the ionic conductivity of the electrolyte decreases with
12 an increase in salt concentration, while solution viscosity increases.[59] This
13 condition exerts an adverse effect on obtaining high-performance DIBs. In addition, a
14 high-concentration electrolyte is infeasible with the limited solubility of NaPF_6 and
15 KPF_6 ($<1 \text{ M}$).

16 Imide-based salts (e.g., FSI^- and TFSI^-) are used to further achieve
17 high-concentration electrolytes. Tong et al.[60] recently increased the concentration of
18 electrolytes and finally developed a 7.5 M LiFSI in an EC/DMC system. In this
19 electrolyte, the capacity and reversibility of DIBs were evidently enhanced, exhibiting
20 91.5% C_{eff} and 97.0 mAh g^{-1} discharge capacity in the aluminum anode (Fig. 4c). The
21 high concentration of electrolyte increased oxidation stability and formed the LiF-rich

1 layer during the electrochemical process, indicating a long cycling life of over 500
2 cycles with a capacity retention of 96.8 %. Similarly, an oxidation potential of 6.44 V
3 was achieved with the excellent oxidative stability of tetramethylene sulfone (TMS).
4 The compatibility and integral structure of the aluminum negative electrode were
5 improved with the formation of the LiF-rich SEI layer.[15] Furthermore, sodium- and
6 potassium-based concentrated electrolytes demonstrated that the 2.55 M NaTFSI
7 electrolyte[23] in trimethyl phosphate achieved nearly 100% C_{eff} after 750 cycles and
8 a stable SEI to reduce the decomposition of the electrolyte. Meanwhile, the 5.0
9 M-class KFSI in EC/DMC[26] and TMS[61] display a high energy density of 207 Wh
10 kg^{-1} and 130 Wh kg^{-1} , respectively.

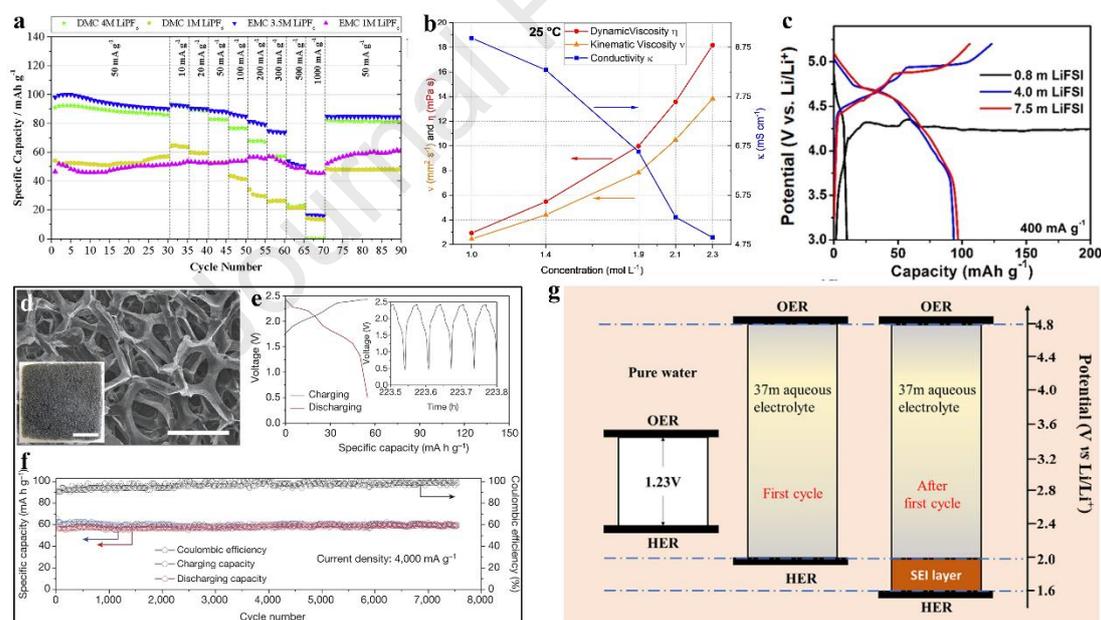
11 Notably, ILs possess broad electrochemical stable windows and high thermal stability,
12 and they have been identified as promising candidates for DIBs.[62-64] In addition, a
13 composition of entirely anions and cations will directly intercalate/deintercalate into
14 anodes and cathodes.[65, 66] For example, AlCl_3 -EMIC is widely used as an
15 electrolyte in aluminum-based DIBs, exhibiting remarkable electrochemical
16 performance.[66-69] Lin et al.[66] reported the new aluminum-based DIB system
17 with an open frame graphitic structure that displays a discharge plateau of ≈ 2 V (Figs.
18 4d and 4e). As shown in Fig. 4f, this battery obtained a specific discharge capacity of
19 ≈ 60 mAh g^{-1} with $\approx 97\%$ C_{eff} after 7500 cycles, accompanying its fast rate capability
20 and long cycling stability. Recently, in the IL $\text{Pyr}_{14}\text{TFSI}$ with LiTFSI active salt, Fan
21 et al.[70] systematically investigated the effects of the electrolyte concentration
22 gradient on DIB performance. However, better cycling stability (300 cycles) and

1 higher capacity ($\sim 94 \text{ mAh g}^{-1}$) were obtained in 1.5 M LiTFSI, while capacity
2 decreased to $\sim 89 \text{ mAh g}^{-1}$ with 2M LiTFSI due to the high viscosity. Consequently,
3 selecting the appropriate concentration is critical to obtain optimum compatibility.

4 As an extreme example, an extremely concentrated aqueous electrolyte ($>20 \text{ M}$),
5 called the “water in salt” electrolyte, was explored due to the enlarged electrochemical
6 stable window. Li et al.[71] compared the difference in potential window among 22
7 M-LiTFSI, 30 M-LiFSI, and 37 M-9LiFSI-LiTFSI electrolytes. In this bisalt aqueous
8 electrolyte, oxidation potential expanded to 1.6–4.8 V (versus Li/Li⁺) after the first
9 cycle, and the battery delivered a high specific capacity of 72 mAh g^{-1} with over 100
10 cycle stability (Fig. 4g). Wrogemann et al.[72] developed a hybrid
11 aqueous/nonaqueous electrolyte (21 m LiTFSI in H₂O + 9.25 m in DMC; 1:1, w/w).
12 In this system, a stage 2 acceptor-type graphite intercalation compound of TFSI⁻
13 anions was formed from an aqueous-based electrolyte, while a protective SEI based
14 on the nonaqueous solvent was achieved, providing good cycling stability and a high
15 safety energy storage system.

16 Furthermore, an aqueous concentration electrolyte can also be used in multivalent
17 metal ion-based DIBs (e.g., Zn²⁺ and Mg²⁺). As an economical raw material, ZnCl₂
18 salt was used to explore an extremely concentrated 30 M electrolyte by Guo et al.[73]
19 The DIBs provided increased oxygen evolution reaction potential to allow the
20 reversible intercalation of anions, exhibiting stable cycling that retained a capacity of
21 82 mAh g^{-1} after 800 cycles. Zhu et al.[74] reported a saturated 4.5 M Mg(NO₃)₂

1 aqueous electrolyte that used a polyaniline (PANI) cathode. With the enrichment of
 2 Mg^{2+} cations, the proton transfer mechanism was prohibited to exhibit excellent
 3 stability over 10000 cycles and rate performance (33% capacity retention at 500C).
 4 This concentrated electrolyte concept opens a viable route to help achieve a high
 5 electrochemical stability window and high energy density. However, the use of a
 6 concentrated electrolyte may typically result in high viscosity and low ionic
 7 conductivity, producing unsatisfactory rate performance in practice. Furthermore, the
 8 prices of concentrated electrolytes are higher than those of dilute electrolytes. These
 9 factors may hinder the large-scale application of concentrated electrolytes.



10
 11 **Fig. 4.** (a). Illustration of the C-rate dependent specific discharge capacities for a
 12 lithium metal/graphite dual-ion cell using different electrolytes at an operating
 13 temperature of 20 °C [58]. (b) Change of kinematic (orange) and dynamic (red)
 14 viscosities and ionic conductivities (blue) of all five electrolytes at 25 °C with
 15 increasing LiPF_6 concentration [59]. (c) The galvanostatic charge/discharge curves of

1 Li-graphite half-cell with 0.8 m, 4.0 m, and 7.5 m LiFSI [60]. (d) A scanning electron
2 microscopy image showing a graphitic foam with an open frame structure; scale bar,
3 300 μm . Inset, photograph of graphitic foam; scale bar, 1 cm [66]. (e) Galvanostatic
4 charge and discharge curves of an Al/graphitic-foam pouch cell at a current density of
5 4,000 mA g^{-1} [66]. (f) Long-term stability test of an Al/graphitic foam pouch cell over
6 7,500 charging and discharging cycles at a current density of 4,000 mA g^{-1} [66]. (g)
7 Illustration of expanded electrochemical window of 1.6-4.8 V [71].

8

9 **2.2 Hybrid or Novel Ions in the Electrolytes**

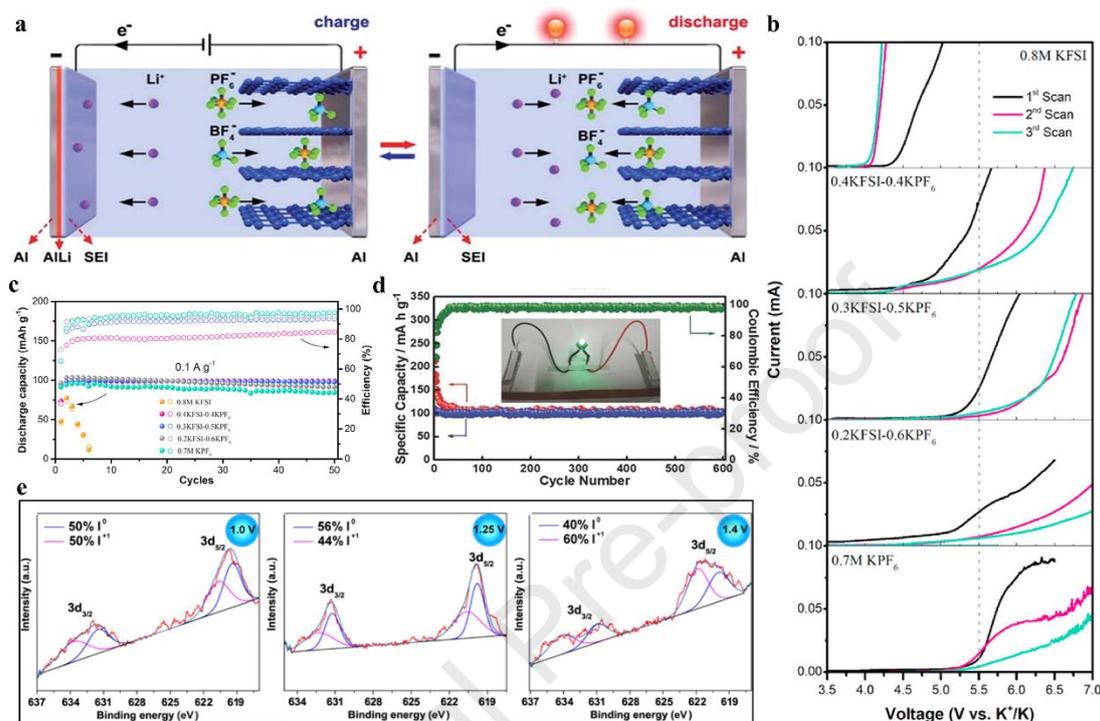
10 In DIBs, the anions can take part in the energy storage process, being the key factors
11 to affect the performance of batteries. Different anions are predicted to enhance the
12 diffusivity, reversibility, and chemical stability of electrolytes, solving the issues of
13 DIBs.[75, 76] In general, anions with a smaller ionic radius are preferentially selected
14 to enhance ion diffusion kinetics and decrease the structure changes of cathode
15 materials, such as PF_6^- , BF_4^- , AlF_4^- , and FSI^- . Shin et al.[77] reported a
16 co-intercalation strategy with PF_6^- and BF_4^- anions in the hybridization electrolyte
17 (Fig. 5a). As an appropriate content, 5% LiBF_4 can alleviate volume expansion and
18 sluggish diffusion kinetics. Therefore, these DIBs exhibited a higher capacity of 97.8
19 mAh g^{-1} , a higher rate performance with a capacity of 90.5 mAh g^{-1} at 15C, and over
20 500 cycles cycling stability at 5C. Similarly, Tan et al.[78] utilized the dual-anion
21 intercalation of FSI^- and PF_6^- to boost performance. PF_6^- could avoid electrolyte
22 deterioration through the formation of a fluorine-rich cathode–electrolyte interphase
23 (CEI). Meanwhile, FSI^- could enhance rate and long-cycling performance through

1 exceptional charge transfer kinetics (Figs. 5b and 5c). As a special anion, AlF_4^- was
2 utilized with PF_6^- to enhance energy storage and protect the aluminum anode for
3 high-performance DIBs.[79] The DIBs with complex anions (PF_6^- and AlF_4^-) could
4 realize a high specific capacity of $\approx 100 \text{ mAh g}^{-1}$ with a $\approx 99\%$ C_{eff} over 600 cycles
5 (Fig. 5d). In general, the hybridization of anions in the electrolyte exhibits a facile
6 strategy to participate in the energy storage process and accomplish high performance.

7 The intercalation behavior of different anions should be investigated to help achieve
8 better electrochemical performance with novel anions in various systems. Huang et
9 al.[51] investigated the intercalation process and energy conversion of several anions
10 (BF_4^- , TFSI^- , and Otf^-) in an aqueous battery. They determined that a high
11 intercalation potential could be achieved by the stabilization window of the TFSI^-
12 electrolyte because of the match difference between intercalation energy and
13 hydration energy. By contrast, BF_4^- and Otf^- could not exhibit satisfactory potential.

14 The DIBs based on the TFSI^- anions delivered an ultrahigh voltage of 2.2 V in an
15 aqueous electrolyte with a large capacity of 120 mAh g^{-1} . Guo et al.[80] reported the
16 oxidation of iodine on graphite electrode surface and the intercalation of novel $[\text{ICl}_2]^-$
17 anions at higher charging potential during the charging process (Fig. 5e).
18 Consequently, the DIBs with graphite cathode delivered a high capacity of 291 mAh
19 g^{-1} with 85% C_{eff} due to the high reversible intercalation of the $[\text{ICl}_2]^-$ anions.
20 Therefore, selecting suitable ions and exploring novel anions are critical for obtaining
21 high-performance batteries. However, the nature of anions dominated the
22 compatibility with the electrodes and the coordination with cations, which requires a

- 1 detailed and complex characterization for better utilization of hybrid or novel ions
- 2 strategy in the electrolyte.



- 3
- 4 **Fig. 5.** (a) Schematic illustration of the aluminum-graphite tri-ion battery
- 5 configuration configuration and charging/discharging mechanism [77]. (b) LSV of
- 6 different electrolyte systems using tungsten plate as cathode at a scan rate of 2 mV s^{-1}
- 7 [78]. (c) cycling performance using graphite as cathode [78]. (d) The cycling
- 8 performance and coulombic efficiency for over 600 cycles [79]. (e) XPS spectra of
- 9 the graphite electrode during electrochemical reactions. XPS iodine 3d core-level
- 10 spectra at 1.0, 1.25, and 1.4 V during the charging process, respectively [80].

11

12 2.3 Functional Additives in Electrolytes

- 13 The development of suitable electrolyte additives (including the solvents and salts)
- 14 can stabilize the electrode-electrolyte interface and limit the oxidative decomposition

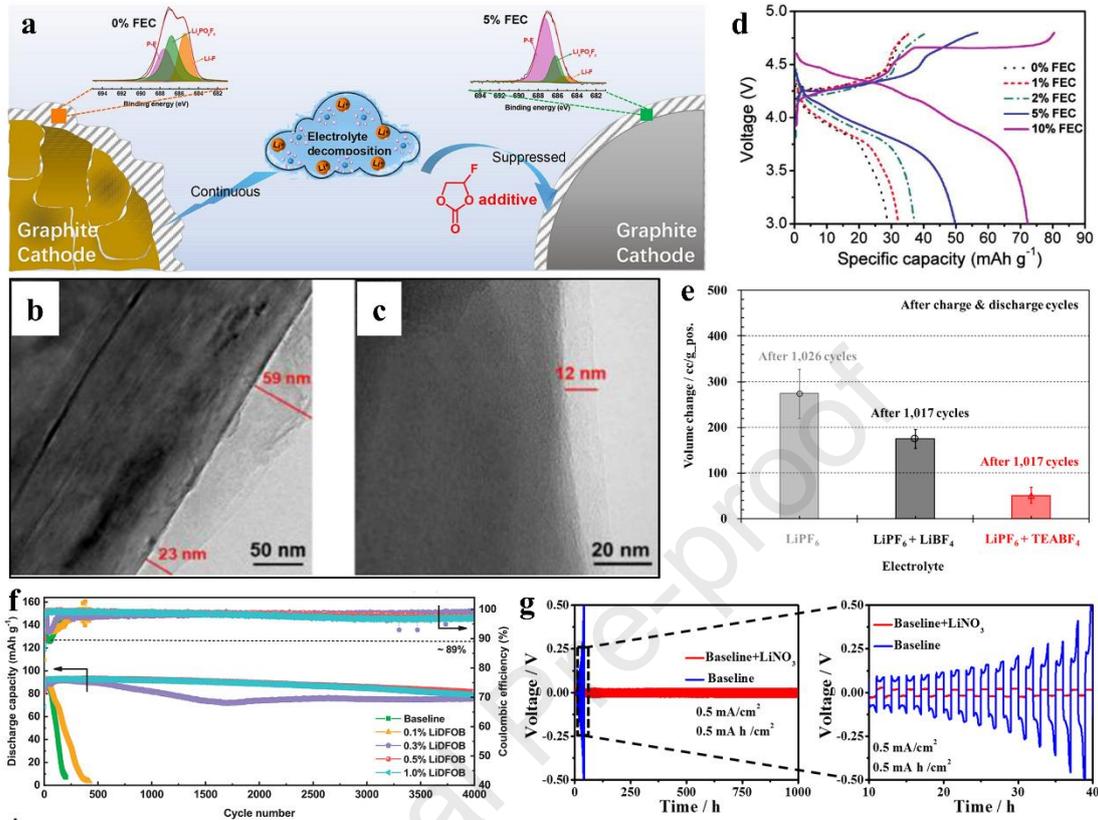
1 of the electrolyte under high voltage, improving the working voltage to obtain high
2 energy density and solve related issues in DIBs. The choice of additive mostly helps
3 improve the ionic conductivity of the electrolyte and form a stable SEI/CEI layer that
4 further achieves electrochemical performance and structural stability of electrode
5 materials. Typically, fluorine solvents and salts are added to the electrolyte to produce
6 a superior interface between the electrode and the electrolyte. For example, Wang et
7 al.[81] demonstrated the influence of fluoroethylene carbonate (FEC) additive on
8 cathode interface (Fig. 6a). As shown in Figs. 6b and 6c, 5% FEC introduced a stable
9 and homogeneous CEI with less LiF and suppressed the decomposition of electrolytes,
10 achieving an excellent cycle stability of 5000 cycles with a high $\sim 99\%$ C_{eff} .
11 Simultaneously, the FEC additive could reduce self-discharge with a smaller voltage
12 drop for practical applications. In an IL of the LiTFSI/Py₁₄TFSI system, 10% FEC
13 could induce a stable SEI film to protect the aluminum foil anode and prevent
14 pulverization during the Al-Li alloying/dealloying process; meanwhile, the DIBs
15 exhibited an 80 mAh g⁻¹ discharge capacity with 90% C_{eff} (Fig. 6d).[70] By lowering
16 the hardness of the electrolyte, the use of TEA⁺ cation additive could suppress gas
17 formation and volume change, increasing reversible capacity and cycle stability after
18 1017 cycles by using the Li₄Ti₅O₁₂ anode (Fig. 6e).[82]

19 Moreover, vinylene carbonate (VC), as a common additive for forming high-class SEI,
20 was utilized for DIB systems.[83-86] Wu et al.[38] reported adding 3% VC to the
21 electrolyte (4 m LiPF₆-EMC) to provide a stable interfacial film and suppress
22 electrolyte decomposition. The results were confirmed through a characterization of

1 online continuous flow differential electrochemical mass spectrometry. Meanwhile,
2 the addition of 2% VC to the electrolyte could effectively improve stability through
3 the SEI layer on the surface of the aluminum electrode, protecting the Al-Li alloying
4 process.[41] However, an appropriate concentration of VC in the electrolyte is key to
5 achieving superior electrochemical performance due to the fast capacity decay of low
6 VC content and the low coulombic efficiency of high VC content, which must be
7 adjusted in accordance with the DIBs systems.[53]

8 Furthermore, various additional types of additives may be used to increase the
9 electrochemical performance of DIBs for practical applications. Wang et al.[87]
10 recently reported that the addition of LiDFOB to the electrolyte of 3M LiPF₆ in EMC
11 could inhibit undesirable side reactions and stabilize the graphite cathode against
12 structural deterioration or exfoliation due to the formation of a robust and durable CEI
13 in situ on the graphite surface (Fig. 6f). Therefore, the DIBs demonstrated a long
14 cycling behavior of over 6500 cycles at 1000 mA g⁻¹ with a capacity retention of
15 92.4%. In a 4 M LiPF₆-EMC electrolyte with 3 vol% VC, the LiNO₃ additive was
16 used to refine the lithium deposition and achieve a low overpotential (<30 mV) and
17 over 1000 h long cycle of the symmetric cell (Fig. 6g).[88] With a stable SEI film, the
18 lithium-graphite DIBs displayed a cycling behavior of over 1000 cycles with a
19 capacity retention of 81% at 5C. For the conventional and suitable B-, P- or F-
20 containing additives (such as LiDFOB[89], triallyl phosphate[90], and FEC[81]), the
21 suitable content of additives can provide a superior electrode-electrolyte interface,
22 further helping to improve battery performance, but the content needs to be carefully

1 controlled.



2

3 **Fig. 6.** (a) Schematic illustration of the engineering cathode-electrolyte interface of
 4 graphite with FEC additive [81]. TEM images of graphite electrodes at the fully
 5 charged state after 200 cycles in electrolyte with (b) 0% FEC and (c) 5% FEC [81]. (d)
 6 Charge-discharge curves of the Al-MCMB DIBs in 1.0 m LiTFSI/Py₁₄TFSI
 7 electrolytes with different FEC contents from 0 to 10 wt% FEC at 2 C [70]. (e) The
 8 volume of DIB using LiPF₆ electrolyte after 1026 cycles, LiPF₆ + LiBF₄ electrolyte
 9 and LiPF₆ + TEABF₄ electrolyte after 1017 cycles in charge and discharge cycle test
 10 at 20 °C [82]. (f) cycle performance and CE of graphite||Li cells with 0% (baseline),
 11 0.1%, 0.3%, 0.5%, and 1.0% (wt%) LiDFOB-containing electrolytes [87]. (g) Cycling
 12 performances of Li||Li symmetric cells without or with LiNO₃ additives at current
 13 densities of : 0.5 mA cm⁻² with a fixed capacity of 0.5 mAh cm⁻² [88].

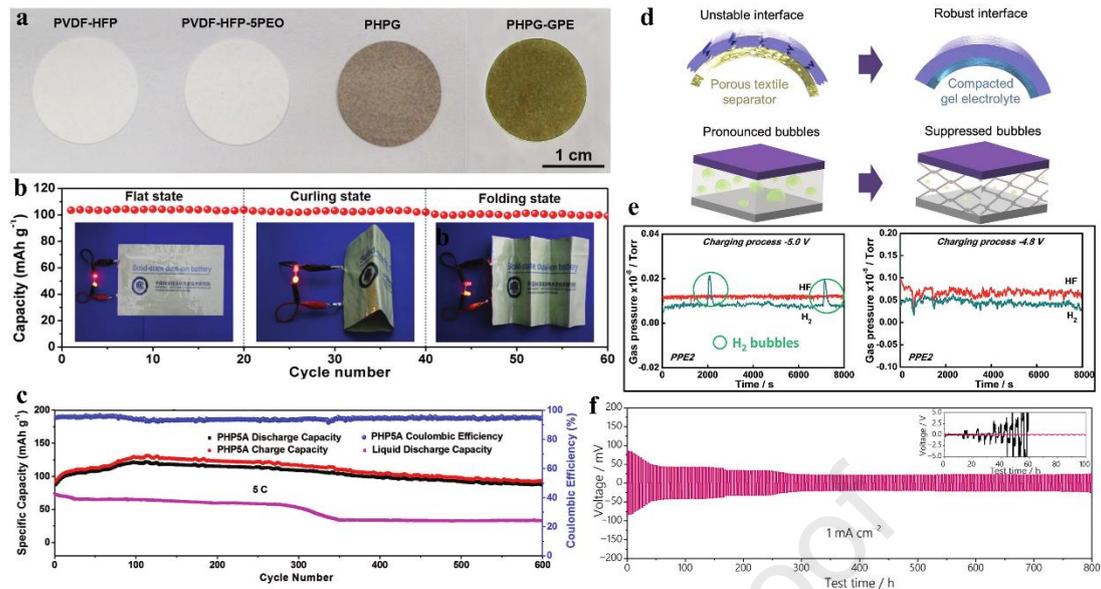
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15 2.4 Polymer-Gel and Quasi Solid-state Electrolytes (SSEs)

1 In DIBs, SSEs have been expected to address the critical issue of liquid electrolytes
2 and enhance the energy density, cycling stability, and safety of batteries because they
3 can suppress the dendrite growth process of the metal anode and compensate for the
4 material volume change during charging and discharging. Typically, gel polymer
5 electrolytes (GPEs) combine liquid electrolytes and different polymer matrices that
6 possess high ionic conductivity, a superior interface of electrode/electrolyte, and
7 outstanding mechanical properties (e.g., porosity and flexibility).[91, 92] Meanwhile,
8 the efficient transportation of anions and high oxidation stability of GPEs are
9 promising for DIBs to mitigate the challenge. Chen et al.[93] recently reported a
10 polymer electrolyte with a PVDF-HFP structure co-doped with poly(ethylene oxide)
11 and graphene oxide (GO) as polymer matrix and a 4M LiPF₆ in EMC with 2%VC as
12 the liquid electrolyte (Fig. 7a). The prepared polymer electrolyte presented a 3D
13 porous network with an improved ionic conductivity of $2.1 \times 10^{-3} \text{ S cm}^{-1}$ with 1 wt%
14 GO, which was favorable for a 2000 long cycling life at a high current density of 500
15 mA g⁻¹. Meanwhile, the structure could exhibit a negligible change in electrochemical
16 performance, indicating good flexibility with different curve states and high thermal
17 stability at different temperatures (Fig. 7b). Similarly, Xie et al.[16] reported that
18 based on PVDF-HFP, Al₂O₃ as inorganic fillers was cross-linked to form a quasi SSE,
19 which possessed a conductivity of $1.3 \times 10^{-3} \text{ S cm}^{-1}$. The flexible electrolyte facilitated
20 the fast ionic migration of anions and cations, exhibiting 600 cycles at 5C and a high
21 capacity of 96.8 mAh g⁻¹ (Fig. 7c). Yu et al.[94] explored GPEs aluminum-based
22 DIBs. They utilized the GPEs to release strain and boost the robust

1 electrode/electrolyte interfaces for enhancing stability and suppressing the
2 by-products of gas in SSE (Fig. 7d). With the presence of GPEs, the aluminum-based
3 DIBs delivered a capacity of 120 mAh g^{-1} and superior properties of flexibility and
4 thermal stability.

5 Wang et al.[95] reported a microporous gel electrolyte that exhibited outstanding
6 properties, such as high ionic conductivity and mechanical strength. The PPEs
7 reduced H_2 gas generation and prevented the corrosion of the aluminum foil anode,
8 benefiting the superior electrode/electrolyte interface (Fig. 7e). Another
9 multifunctional GPE was reported for high-performance sodium-based DIBs.[96]
10 This quasi SSE exhibits low-resistance and stable SEI to suppress the growth of
11 sodium dendrite, enabling a uniform sodium deposition during 800 h of cycling with
12 FEC and PS components (Fig. 7f). A high oxidative resistance of 5.5 V and a high
13 ionic conductivity were accomplished through an appropriate structure and
14 composition design to deliver a capacity of 78 mAh g^{-1} after 1000 cycles. In
15 conclusion, the utilization of gel polymer electrolytes can significantly improve the
16 reversible capacity and cyclability of DIBs as an effective strategy. However, the poor
17 diffusion kinetics and low ionic conductivities of GPEs and quasi SSEs need to be
18 greatly improved for the better performance and functionalization.



1
 2 **Fig. 7.** (a) Optical photographs of the as-prepared PVDF-HFP, PVDF-HFP-5PEO,
 3 PHPG membrane, and the PHPG-GPE after soaking electrolyte [93]. (b) Cycling
 4 performance of the flexible PHPG-DIB under flat, curling, and folding state at 2C.
 5 Insets are the optical photographs of the flexible PHPG-DIB under different states
 6 which all light up two LEDs in series [93]. (c) Cycling stability of the SDIBs based on
 7 quasi SSEs and conventional liquid electrolyte for 600 cycles at 5 C [16]. (d) Schemes
 8 for demonstrating the electrode-electrolyte interfaces: unstable interface based on
 9 porous separator in the liquid-state batteries and robust interface based on the GPE
 10 electrolyte in the solid-state batteries and the production of gases in the two
 11 prototypes of batteries [94]. (e) The in situ gas partial pressure of the dual-ion battery
 12 with gel electrolyte during the charging process (charged -5.0 V and -4.8 V) [95]. (f)
 13 Voltage profiles of the Na||Na symmetric cells using 0.5 M NaPF₆-PC:EMC (black
 14 line shown in the inset) electrolyte and GPE (pink line) at 1.0 mA cm⁻² with a cut-off
 15 capacity of 2 mAh cm⁻² [96].

17 4 Summary and Perspective

18 DIBs demonstrate great promise as next-generation energy storage batteries. However,

1 a series of issues still need to still be solved before practical application. Here, we
2 summarize the current challenges underlying this field to address these issues. Given
3 the importance of electrolytes in DIBs, which cannot only provide the basic operating
4 environment but can also participate in electrochemical reactions as active materials,
5 electrolyte-based solution strategies are highlighted in this review. The application of
6 high-concentration, hybrid ion electrolyte, additives, and gel electrolyte are briefly
7 introduced; and the optimization results are discussed. Although satisfactory results
8 have been achieved in enhancing the electrochemical performance of DIBs through
9 the electrolyte strategies described earlier, significant effort should still be exerted in
10 the following aspect for further progress.

11 First, the solvent structure of the electrolyte should be considered and regulated. The
12 fact that anions and cations cannot exist entirely as isolated ions is frequently
13 overlooked, affecting their important role as active materials in DIBs. The effects of
14 different types of solvents and solutes, various additives, and various concentrations
15 of salt are unclear. Therefore, systematically characterizing the desolvation process is
16 essential to gain insight into the relationship between ions and solvents. Desolvation
17 directly affects fundamental properties, including ionic conductivity, diffusion
18 coefficients, and reaction mechanisms, which are essential for exploring new
19 electrolyte systems. In addition, the exploration of high solubility and novel
20 electrolyte salts should be strengthened to improve electrochemical performance in
21 accordance with practical needs, such as unsatisfactory capacity and poor reaction
22 kinetics. Co-solvent electrolytes (e.g., organic–water and IL–water), as a new type of

1 electrolytes, are a potential trend for establishing low-cost and high-concentration
2 systems. We believe that the development of suitable salts and solvents should be
3 based on the challenges of DIBs to construct stable electrode-electrolyte interfaces,
4 avoid excessive side reactions, and achieve stable electrode structures for high C_{eff}
5 and long cycling performance. As the safe, low-cost, and environmentally friendly
6 electrolytes, aqueous electrolytes are more conducive to the advantages of DIBs.
7 However, for meeting the high-voltage requirement of DIBs, the unsatisfactory
8 electrochemical stability of aqueous electrolyte need to be expanded and adjusted
9 with the various functional additives (e.g., organic liquids: DMSO, methylurea,
10 alcohols, glycerol, and TEP or organic solids: PEG, urea and glucose). The
11 exploration of aqueous electrolytes is a promising strategy for the improvement of
12 DIBs. Finally, gel electrolytes are also promising electrolytes that suppress dendrites
13 and volume changes and provide superior mechanical strength and flexibility, which
14 are necessary for utilizing high-capacity alloying and alkali metal (lithium, sodium,
15 and potassium) anodes. As a facilitated method, ionic conductivity can be improved
16 by selecting different polymers and electrolyte salts, and the working voltage window
17 can be extended by introducing electrolytes with high decomposition voltage (e.g.,
18 high-concentration electrolytes and ILs). Therefore, studying alternative gel
19 electrolytes for DIBs is also promising.

20 Although DIBs have demonstrated encouraging advantages, real commercialization
21 still has a long way to go. Therefore, summarizing possible strategies as much as
22 possible is necessary to deepen the understanding of uncertain issues and realize the

1 application of DIBs in the future.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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