Energy Storage Materials 50 (2022) 197–224

Contents lists available at ScienceDirect

Energy Storage Materials

journal homepage: www.elsevier.com/locate/ensm

A review on the use of carbonate-based electrolytes in Li-S batteries: A comprehensive approach enabling solid-solid direct conversion reaction

Ayda Rafie, Jin Won Kim [1], Krishna K. Sarode, Vibha Kalra [*]

Department of Chemical and Biological Engineering, Drexel University, 3141 Chestnut Street, Philadelphia 19104, USA

ARTICLE INFO

Keywords:
Carbonate electrolyte
Li-S battery
Solid-solid reaction
Single-plateau discharge

ABSTRACT

Li-S batteries have attracted great attention from academia and industry because of their high theoretical capacity and energy density, arising from the multi-electron electrochemical reactions. Although significant progress has been made to improve the capacity and cycle life of these batteries, a major challenge has been overlooked. Ether-based electrolytes, commonly used in Li-S batteries, are highly volatile and impractical for many applications. On the other hand, carbonate-based electrolytes have been used in commercial Li-ion batteries for three decades and are a natural and practical choice to replace ether-based electrolytes in Li-S batteries. The lack of attention towards the use of carbonate-based electrolytes in Li-S batteries, is in part from the irreversible reaction between carbonate solvents and polysulfides anion that results in battery shut down, when conventional material designs and strategies are employed. Here, a comprehensive and critical review of recent progress on the use of carbonate-based electrolyte is presented. Throughout this work, we provide our insight to different approaches that can mitigate the irreversible reaction between carbonate solvents and sulfur cathode. First, we introduce the solid-solid direct conversion reaction of sulfur, which enables the successful use of carbonate electrolytes in Li-S batteries. Then, we discuss the progress made on design of cathodes, engineering of electrolytes, and strategies for Li metal protection, when carbonate electrolytes are used in Li-S batteries. Furthermore, the future directions to achieve a long-term cycling Li-S battery with carbonate electrolytes is provided. We believe that this work can be a useful source to draw the attention of Li-S battery field to develop practical Li-S batteries.

1. Introduction

Fossil fuels are the main source of energy for human beings, however, they create a complex series of environmental, social and economic problems [1]. Burning fossil fuels to meet our energy needs, results in carbon dioxide emissions which along with other greenhouse gasses are responsible for long-term effects on the earth's temperature. In addition to climate change, the combustion of fossil fuels results in emission of volatile organic compounds (VOCs) and poly-aromatic hydrocarbons (PAHs), nitrogen oxides (NO_x), carbon monoxide (CO), and sulfur oxides (SO_x). Apart from the environmental and health aspects, fossil fuels are not benign, and the resources are expected to end in 40 to 150 years [2]. These reasons necessitate a global effort to explore all the means to exploit renewable energy resources such as wind, sun, and water. Although, the use of such resources seems very attractive, there is a huge obstacle, as the energy harvested from renewable resources is intermittent. To solve this challenge, development of energy storage devices becomes an essential part of future energy supply transition. Electrical vehicles (EVs) are an example of such transition, where a CO_2 emission-free transportation is realized through elimination of combustion engines. The first demonstration of EVs happened in 1830s, however, the combustion engine vehicles were still favored because of their higher energy density and lower cost [3]. In 2009, Tesla introduced a high-performance sports car and since then Li-ion batteries are being used to power EVs [4]. The new generation of these batteries such as those in Tesla model S (extended range) offer a 400-mile range travel on a single charge [5]. Despite Li-ion battery's commercialization, their theoretical energy density is limited to 570 Wh/kg for lithium cobalt oxide systems and 440 Wh/kg for lithium manganese oxide systems, based on the weight of the active material [6]. The energy density

* Corresponding author.
E-mail address: vk99@drexel.edu (V. Kalra).
[1] Current affiliation:Ertl Center for Electrochemistry and Catalyst, Gwangju Institute of Science and Technology (GIST), Gwangju, Republic of Korea.School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, Republic of Korea.

https://doi.org/10.1016/j.ensm.2022.03.015
Received 7 July 2021; Received in revised form 15 February 2022; Accepted 13 March 2022
Available online 17 March 2022

number for an internal combustion engine running with gasoline is over 12,000 Wh/kg, which clearly manifests the need for moving toward higher energy density battery systems [7]. The capacity limitation in Li-ion batteries is mainly imposed from the intercalation type metal oxides, such as $LiCoO_2$, $LiFePO_4$, etc., that are used as electrode material in these batteries. On the other hand, Lithium-Sulfur (Li-S) batteries are considered as the next candidate for commercialization, as their theoretical gravimetric energy density reaches ~2510 Wh/kg based on discharge voltage of ~2.15 V [8]. Table 1, shows the comparison between cathode materials commonly used in Li-ion batteries and the on-going research, focusing on developing suitable batteries for various applications. This table shows a clear advantage of the sulfur cathode in terms of the theoretical gravimetric capacity and energy density.

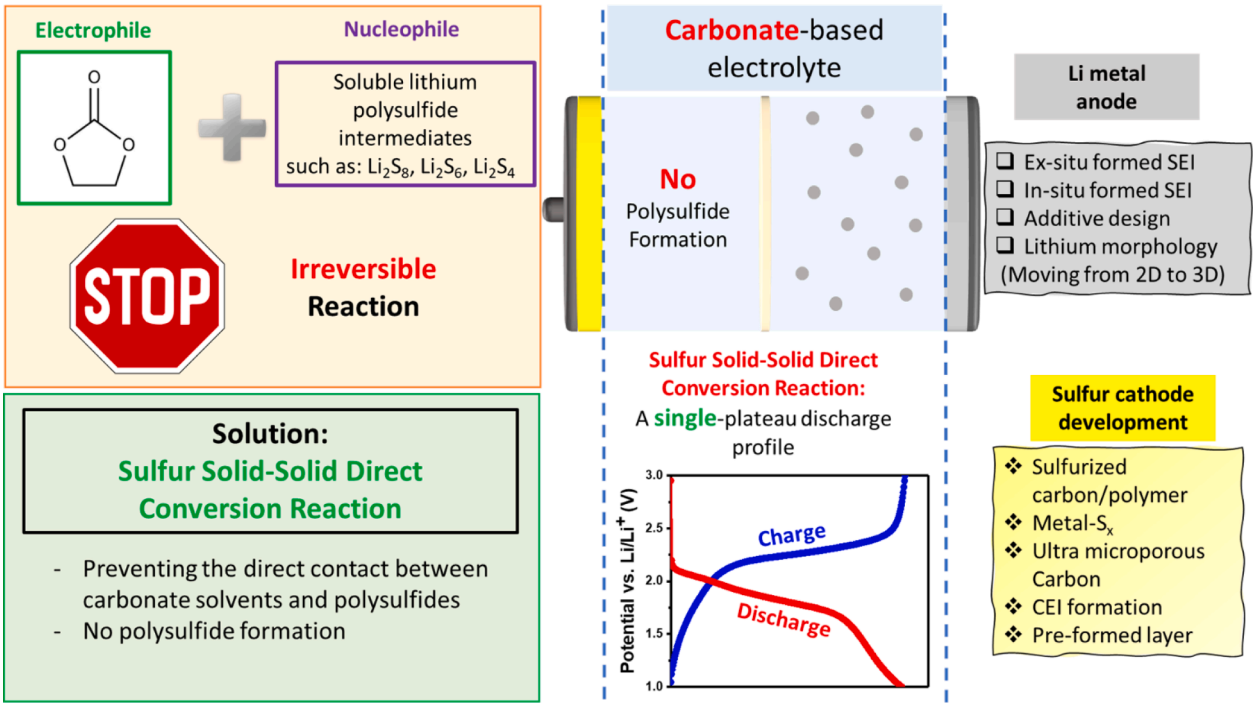
The high theoretical capacity of Li-S batteries arises from the multi-electron reactions, making them an attractive candidate to replace Li-ion batteries [8]. It is important to note that such interest in Li-S batteries has been global. For example, the European Commission has funded two projects namely, "Advanced Lithium–Sulfur Batteries for Hybrid Electric Vehicles" (ALISE) [11] and "High Energy Lithium–Sulfur Cells and Batteries" (HELIS) [12] for development of Li-S batteries [13]. These two projects are now being continued under "Lithium sulphur for SAfe road electrification" (LISA) [14]. The very high theoretical capacity offered by Li-S battery compared to commercialized Li-ion batteries, is only one of the advantages of Li-S batteries. The intense focus on development of Li-S batteries in academia and industry, also lies on the advantages of using sulfur, a benign and cheap material, as active material in cathode [8], and Li metal because of the highest theoretical capacity (3860 mAh/g) offered by this metal as anode material [15]. An important factor which makes commercialization of Li-S battery so attractive is it's potential low sell cost [13]. The Advanced Battery Consortium had targeted a Li-ion battery pack price of $150 kW/h, this price eventually dropped as a result of development, and the portable Li-ion cell price is around $100 kW/h. Similar initial estimation for a Li-S cell projects the cost to be ~$70 kW/h [3]. Moreover, based on the reported results, Li-S batteries show promising performance at lower temperature accompanied by lower weight of the Li-S cells, making them a potential candidate for applications such as unmanned aerial vehicles, space batteries or military purposes [3,13]. Some of the projects investing on the Li-S batteries in these areas are Facebook Aquila and Airbus Zephyr [16]. Despite so many advantages and potential applications of Li-S batteries there are challenges in achieving high capacity and stable cycle life for these batteries. First, sulfur as the active material is insulating (conductivity= $\sim 5.0 \times 10^{-30}$ S/cm) [17]. To enable sulfur utilization, it needs to be in close contact with a conductive host material [18]. Second, Li metal, as the anode has high reactivity towards electrolyte solvents [15,19]. As a result of the side reactions , dendrite formation not only leads to short cycle life of the battery but also is considered as a very serious safety hazard, which can lead to thermal runaway and explosion in these batteries [15,20]. Third, sulfur undergoes substantial volume change of ~80% in each cycle, as a result of lithiation/de-lithiation from elemental S_8 (density: 2.07 g/cm^3) to the discharge end product of Li_2S (density: 1.66 g/cm^3) [21]. This volume change results in mechanical instability and failure of the battery. Although there are challenges on both cathode and anode side of Li-S batteries, however, a key challenge, often overlooked, exists in the electrolytes used in these batteries. Ether based electrolytes are commonly used in Li-S batteries, because of their stability toward sulfur cathode and intermediate species formed during cycling. Elemental sulfur used in these batteries is reduced to the highly soluble lithium polysulfide intermediates (Li_2S_x, $4 \leq x \leq 8$), before finally depositing as the solid lithium sulfide (Li_2S) discharge product. Although these highly soluble intermediates can help in enhancing the reaction kinetics of the battery, however, they lead to the infamous phenomena of polysulfide shuttle, which is known to be seriously effecting Li-S battery cycling stability [22–24].

Table 1
Comparison between the capacity, average voltage and current level of development in different cathodes, the values presented are based on the active material weight [3,9,10].

Cathode material	Theoretical gravimetric capacity (mAh/g)	Experimental Capacity (mAh/g)	Average voltage (V)	Level of development
$LiCoO_2$	274	130–150	3.8	Commercialized
$LiMn_2O_4$	148	100–120	4.1	Commercialized
$LiFePO_4$	170	160–165	3.4	Commercialized
$LiCoPO_4$	167	110–130	3.24	Research
Sulfur	1675	200–1400	2.15	Research

Ether-based electrolyte, the most used electrolyte in Li-S battery research, has two main drawbacks. The first drawback is the polysulfide shuttling which results in loss of active material both in the anode and cathode side, low cycle life (explained in detail in Section 2), severe self-discharge, and short shelf-life. The other disadvantage of ether electrolytes, which is often ignored, is the safety issue related to ether solvents and lithium nitrate additive. For example, the combination of sulfur, carbon, and nitrate is reported to be the composition of an explosive (charcoal, sulfur and potassium nitrate) [25,26]. Moreover, ether-based electrolytes with $LiNO_3$ additive produce gasses and swell above ~40 °C, making them impractical because they cannot obtain the Transport of Dangerous Goods Certification [27]. These two drawbacks raise a lot of questions related to cycling and, more importantly, safety of Li-S batteries, particularly pertaining to commercialization of these batteries. The safety concerns become very important once the battery is under harsh conditions such as heating, crashing, and overcharging [28]. On the other hand, carbonate-based electrolytes have been used in commercial Li-ion batteries for over 30 years and are the first viable option to replace ether-based electrolytes in Li-S batteries [29]. Moreover, many additives used in commercial Li-ion batteries can be applied in Li-S batteries to decrease the flammability problem of liquid electrolytes [18]. However, the use of carbonate-based electrolyte in lithium-sulfur batteries has several challenges. The most important challenge is the irreversible reaction of lithium polysulfide nucleophilic species with the electrophilic carbonate solvents through nucleophilic- electrophilic substitution reaction [30,31]. This irreversible reaction shuts down the battery in the first discharge. By eliminating the formation of these intermediate species, we can achieve two goals at the same time. Firstly, the polysulfide shuttling challenge is resolved, and as a result, a stable and long cycle life could be achieved. Secondly, carbonate electrolyte as a safer and more reliable electrolyte system in terms of practical use can replace ether electrolytes. It is important to note that the first step in using carbonate electrolytes is to eliminate the direct contact between soluble polysulfide species and carbonate solvents.

In this review paper, first, we will discuss the advantages and disadvantages of using carbonate electrolytes in Li-S batteries. Then we will present detailed comparison between ether-based and carbonate-based electrolytes with discussion on the irreversible reaction mechanism between nucleophilic polysulfides and electrophilic carbonate solvents. Then with defining the "solid-solid direct conversion reaction" (SSDC) of sulfur, the single plateau potential profile, and solid to solid reaction pathways will be discussed. Later, in Section 3, we will provide a comprehensive review of the approaches on cathode modification to make the SSDC reaction possible. In Section 4, based on the literature, we will offer a possible solution to the reactivity challenges of carbonate electrolyte-based Li-S batteries through electrolyte modification. In Section 5 we will present the challenges of using Li metal anode in carbonate electrolytes, and possible solutions to those challenges will be discussed. Finally, our perspective on the future of the Li-S batteries will be given based on the progress made in current studies in making practical Li-S batteries, and suggestions for further development of cathodes, anodes and electrolytes will be presented.



Schematic 1. A brief outline of the paper.

2. Carbonate-based electrolyte and solid-solid direct conversion (SSDC) reaction of sulfur

In this section, we attempt to provide a general understanding of the working mechanism of Li-S battery in ether and carbonate electrolytes. The advantages and challenges of using carbonate electrolytes in Li-S batteries will be discussed in detail. Solid-solid direct conversion reaction of sulfur, enabling the use of carbonate-based electrolytes in Li-S batteries, will be discussed.

2.1. Advantages and challenges of using carbonate electrolytes for Li-S batteries

Various factors such as a wide electrochemical window, low volatilely, high chemical stability, high ionic conductivity, reduced flammability, and material/production cost need to be considered for practical use of electrolytes [29,32]. Carbonate-based electrolytes have been widely used in Li-ion battery industry for three decades [29]. Moreover, several additives (such as flame-redundant additives) have been already investigated and applied in carbonate-based electrolytes used in commercial Li-ion batteries [29]. Therefore, employing the commercial carbonate-based electrolytes in Li-S batteries is potentially one of the best strategies moving towards commercialization of Li-S batteries. Another prominent distinction is thermal stability to prevent an explosion. The most famous carbonate solvents in Li-ion batteries, EC, DMC, and DEC, have a higher boiling point compared to ether solvents, enabling the potential working temperature of over 100 °C [32,33]. For example, the boiling point of carbonate solvents such as EC, often used in Li-ion batteries is ~248 °C. On the other hand, the boiling point of DME and DOL ether solvents are ~84 °C and ~78 °C, respectively. This comparison shows the clear advantage of carbonate solvents over ether solvents [32]. Table 2 presents properties of the carbonate and ether solvents, used in organic electrolytes. Given that ether-based electrolytes in Li-S batteries are one of obstacles for the commercialization due to its lower boiling points [34], the application of carbonate-based electrolytes in Li-S batteries become more promising. However, despite the motivation there are significant challenges on the application of carbonate electrolytes in Li-S batteries.

Li-S batteries offer lower voltage (2.15 V) compared to their Li-ion counterparts (>3 V) [10]. In addition, Li-S batteries using carbonate electrolytes suffer from lower electrode potential compared to ether-based cells [35]. This arises from the higher dielectric constant of ethylene carbonate, EC (~90) compared to DME (~10) leading to a lower binding energy, between the first Li-ion solvation shell and the bulk electrolyte [36]. This, in turn, results in single solvation shells around the Li^+ ions (compared to the multilayer solvation shells in DME), leading to a lower change in entropy during de-solvation and consequently a lower electrode potential. Therefore, optimization of solvents used in carbonate electrolytes should be taken into consideration. The second challenge is related to the Li-metal stability in

Table 2
Properties of the commonly used ether and carbonate solvent in Li- ion and Li-S batteries [32].

Solvent	MW (g/mol)	T_m (°C)	T_b (°C)	η at 25 °C (cP)	Ɛ at 25 °C	Dipole moment (debye)	T_f (°C)	d at 25 °C (g/cm^3)
EC	88	36.4	248	1.90 (40 °C)	89.78	4.61	160	1.321
PC	102	−48.8	242	2.53	64.92	4.81	132	1.200
BC	116	−53	240	3.2	53	–	–	–
DMC	90	4.6	91	0.59 (20 °C)	3.107	0.76	18	1.063
DEC	118	−74.3	126	0.75	0.2805	0.96	31	0.969
EMC	104	−53	110	0.65	2.958	0.89	–	1.006
DMM	76	−105	41	0.33	2.7	2.41	−17	0.86
DME	90	−58	84	0.46	7.2	1.15	0	0.86
DOL	74	−95	78	0.59	7.1	1.25	1	1.06

presence of carbonate solvents [37]. The reason behind the Li metal instability is because of the instability of the SEI formed in presence of carbonate electrolytes, which leads to dendrite formation. A detailed discussion on the properties of the SEI, dendrite formation and possible solutions is presented in Section 5. Moreover, carbonate-based electrolytes are prone to decomposition even with trace number of impurities like water [38]. The most important challenge, however, is related to the irreversible reaction between the carbonate solvents and polysulfide anions, formed as a result of sulfur (S_8) reduction in Li-S batteries [31]. Without resolving this problem, the use of carbonate electrolytes in Li-S batteries is impossible. Therefore, the rest of this section is focused on providing a detailed discussion on the origin of this problem, and electrochemical pathways in presence of carbonate electrolytes compared to the ether electrolytes.

2.2. Solid-solid direct conversion reaction (SSDC) of sulfur

Two different types of electrochemical reactions have been reported in Li-S batteries [17,39-41]. In case of the commonly used ether-based electrolytes, a conventional multiphase sulfur conversion reaction, shown in Fig. 1a, is reported. As sulfur goes through multiple phase change during a cycle, two distinguished reduction peaks at ~2.3 and ~2.1 V in the cathodic scan and two oxidation peaks (sometimes a broad peak) at ~2.1 and ~2.4 V in the anodic scan are observed in the cyclic voltammetry (CV) of Li-S batteries [8,18,39]. In the discharge step, elemental sulfur (S_8) with octa-ring structure is first reduced to the soluble lithium polysulfides (LiPS, Li_2S_x, $4 \leq x \leq 8$), reflected as the first reduction peak in the range of OCV – 2.3 V. Following the first peak, high order LiPSs are further reduced electrochemically to shorter chain LiPSs (Li_2S_x, $1 \leq x < 4$) in a solid phase, shown as the second reduction peak at ~2.1 – 2.0 V. The two-step reduction can be divided into a two-potential plateau curve: an upper potential plateau (UPP) with a lower number of electron transferring reaction (<0.5 e^- per sulfur atom) and lower potential plateau (LPP) with a higher number of electron transferring reaction (>0.5 e^- per sulfur atom), as can be seen in Fig. 1b [42–44].

The reduction and oxidation processes in Li-S batteries can be divided to four main steps [46]. In region I (solid-liquid conversion), solid sulfur first reacts with Li ions, producing soluble Li_2S_8, as described in Eq. (1). The cell potential drops vertically as soon as the current is applied, this drop is then followed by the UPP at ~2.3 V (vs. Li/Li^+). In region II (liquid-liquid reduction), the high-order polysulfides, Li_2S_8, in the liquid phase are reduced to Li_2S_6 and Li_2S_4, shown in Eq. (2) and (3), respectively. At this step, the electrolyte viscosity increases due to the LiPS formation, and consequently, the potential is dropped from UPP (~2.3 V) to ~2.0 V. The next step is the nucleation and growth of solid-phase Li_2S_2, and Li_2S from the liquid phase Li_2S_4 Eq. (4) and (5). This process is reflected as LPP at ~2.0 V, and is marked as region III in Fig. 1b (liquid-solid conversion). At the end of the discharge step, the accumulation of solid-phase Li_2S final product is dominant in the cathode. In region IV, when all reduction products are fully converted, the potential sharply drops.

$$S_{8(s)} + 2Li^+ + 2e^- \rightarrow Li_2S_{8\ (l)}\ (>2.3\ V) \quad (1)$$

$$3Li_2S_{8(l)} + 2Li^+ + 2e^- \rightarrow 4Li_2S_{6\ (l)}\ (>2.3\ V) \quad (2)$$

$$2Li_2S_{6(l)} + 2Li^+ + 2e^- \rightarrow 3Li_2S_{4\ (l)}\ (2.3-2.1\ V) \quad (3)$$

$$Li_2S_{4(l)} + 2Li^+ + 2e^- \rightarrow 3Li_2S_{2\ (s)}\ (2.1-1.9\ V) \quad (4)$$

$$Li_2S_{4(l)} + 6Li^+ + 6e^- \rightarrow 4Li_2S_{2\ (s)}\ (2.1-1.9\ V) \quad (5)$$

$$Li_2S_{2(l)} + 2Li^+ + 2e^- \rightarrow 2Li_2S_{\ (s)}\ (<1.9\ V) \quad (6)$$

The mechanism of multiple redox reaction of sulfur in ether electrolytes was confirmed by many reports investigating the products at

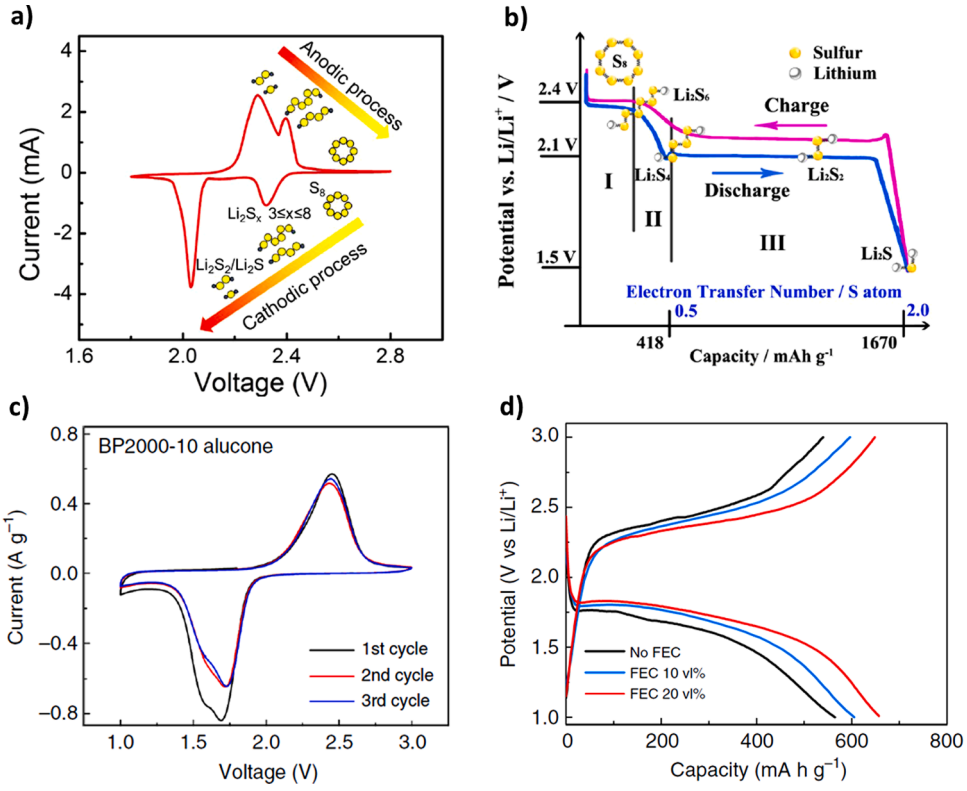


Fig. 1. Comparison of CV curves and potential profiles when a & b) ether-based electrolyte. Reproduced with permission from Kong [45]. Copyright (2017), Elsevier. Reproduced with permission from Liang [46]. Copyright (2016), Elsevier. and c & d) carbonate-based electrolyte are used in Li-S batteries. Reproduced with permission from Li [29]. Copyright (2018), Springer Nature.

various degrees of discharge and charge through a variety of *in-situ* and *operando* analysis such as X-ray diffraction (XRD), X-ray absorption pectroscopy (XAS), UV–visible absorption spectroscopy (UV–vis), nuclear magnetic resonance (NMR), and Raman spectroscopy [40,47-49].

Most Li-S studies have focused on using ether-based electrolytes because of their stability towards sulfur cathode and intermediate species, lithium polysulfides formed during cycling [10,18,50]. On the other hand, based on the literature, carbonate-based electrolytes seem to have different electrochemical reactions when used in Li-S batteries. To understand this difference, first, we take a look at the CV of sulfur cathode in these two electrolytes. Fig. 2a shows the CV of a Li-S battery in ether-based electrolytes (presented in black) and carbonate-based electrolytes (presented in red). As discussed before, when ether-based electrolyte is used, there are two peaks in the cathodic scan [41]. The two peaks are attributed to the reduction of elemental sulfur to high order lithium polysulfides (Li_2S_x, $4 \leq x \leq 8$) at ~2.3 V, followed by their further reduction to low order lithium polysulfides (Li_2S_x, $1 \leq x \leq 4$) at ~2.1 V. On the other hand, Li-S batteries with carbonate-based electrolytes suddenly shut down after the first discharge [30]. The reason behind this sudden shutdown is attributed to the reaction between the soluble LiPSs and carbonate solvents [30,31]. As seen in this figure, when carbonate-based electrolyte is used, one reduction peak at around ~2.3 V is seen. The absence of a peak in charging, in contrast to ether electrolyte, shows that the reaction in reduction step must be irreversible. Unlike the CV curve of ether-based electrolytes, reversible electrochemical reaction is not observed in carbonate-based electrolytes after the elemental sulfur is reduced to a high order polysulfides at the initial discharge step. Therefore, high order polysulfides species are involved in the irreversible chemical products. Fig. 2.b shows the cycling result of a sulfur cathode in ether-based electrolyte compared to the carbonate electrolytes, showing that the battery with carbonate-based electrolyte shuts down in the first cycle. It is well known that carbon bond to an electronegative atom such as oxygen would act as an electrophile [51]. In other words, the carbon connected to oxygen in linear and cyclic carbonate solvents is considered to be the source of electrophilicity. On the other hand, polysulfide anions are known to be strong nucleophiles [52–54]. The electrophilicity of carbonate solvents and nucleophilicity of the polysulfides anions is believed to be the main reason of such failure. To the best of our knowledge, there are only two studies that aim to understand the reason behind the irreversible reaction of sulfur and carbonate solvents [30,31]. In the first study, it is suggested that the higher order polysulfides generated in the first discharge step can easily open the ring structure of EC by attacking the carbon atom of the solvent [30]. Following a substitution and elimination reaction, the EC solvent is decomposed to ethylene glycol and thiocarbonate species (see Fig. 3a). The aliphatic carbonate species, like EMC, are also readily decomposed to the thiocarbonate, methanol, and ethanol in the same way [30]. The suggested degradation mechanism is supported with the results of NMR, FT-IR, and Raman spectroscopy on the discharge products [30-32,55]. On the other hand, carbonate solvents have both hard and soft electrophilic sites [56]. According to the "hard-soft acid-base (HSAB)" theory, polysulfides, being soft nucleophiles, should attack the soft electrophilic sites of the carbonate solvents. In the second study, such reaction mechanism is proposed (Fig. 3b) and backed up with XAS results [31]. In this regard, Zhang et al. conducted NMR studies on the SEI formed on sulfur cathode as a result of the reaction between polysulfides and carbonate [57]. This study showed that both the reactions shown in Fig. 3a and b takes place when carbonate solvents are in contact with polysulfides anions. Based on this study, we can conclude that both the mechanisms shown in Fig. 3a and 3b are responsible for the irreversible reaction between polysulfides and carbonate solvents. Therefore, carbonate-based solvents and other solvents with high electrophilicity such as ester, aldehyde, and ketone are also considered improper candidates as well. As a result, a different reaction pathway is required to enable the use of carbonate electrolytes in Li-S batteries, as discussed below.

Based on the discussion so far, we know that when ether-based electrolytes are used, sulfur undergoes a 'solid-liquid-solid' conversion reaction arising from conversion of solid S_8 to soluble LiPSs and then solid discharge product (Li_2S_2/Li_2S) [8,20,50]. These electrochemical reactions are generally reflected by two potential plateau profiles in the discharge profile of the Li-S batteries (Fig. 1b). On the other hand, Li-S batteries with carbonate-based electrolyte seem to undergo a different electrochemical reaction pathway, following the "solid-solid direct conversion reaction" of sulfur [35,58,59]. As depicted in Fig. 1c, only one reduction and one oxidation peaks are shown in the CV curves of these batteries. The conventional two plateau behavior in ether-based electrolyte, is replaced with a single plateau potential profile when the carbonate-based electrolyte is used (Fig. 1d). This different behavior implies that different solvents invoke different reaction mechanisms, and a deep understanding of the single potential plateau behavior is required. Therefore, in this review paper, we would like to emphasize a new perspective focused on the solid-solid direct conversion (SSDC) reaction of sulfur in Li-S batteries. These types of reactions can lead to a single plateau behavior of sulfur cathodes in Li-S batteries.

Recently, studies on achieving a single plateau behavior in Li-S batteries have beenspotlighted even in the cells with ether-based electrolytes. Based on the previous studies, the specific electrolyte conditions can manipulate the sulfur redox pathways [60]. By controlling the solvent reactivity and decreasing LiPSs dissolution-precipitation, a direct reduction pathway from S_8 to Li_2S_4 was achieved [60]. Eq. (7) describes such reaction pathways that eliminated the formation of Li_2S_8 and Li_2S_6 species (from Eq. (1) to Eq. (3)).

$$S_8 + 4Li^+ + 4e^- \rightarrow 2Li_2S_4 \ (\sim 2.2\ V) \quad (7)$$

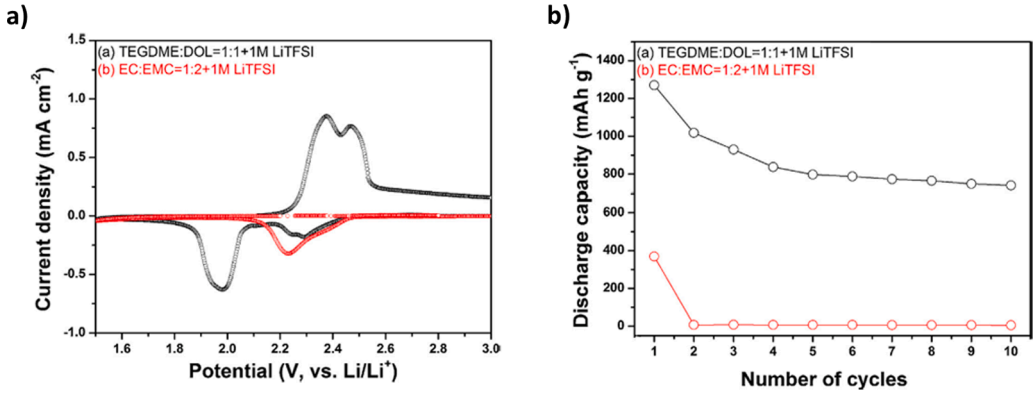


Fig. 2. a) Comparison of electrochemical behavior of the Li-S cell with carbonate-based and ether-based electrolytes, b) cycling performance of Li-S batteries in ether-based electrolyte compared to carbonate-based electrolyte. Reproduced with permission from Yim [30]. Copyright (2013), Elsevier.

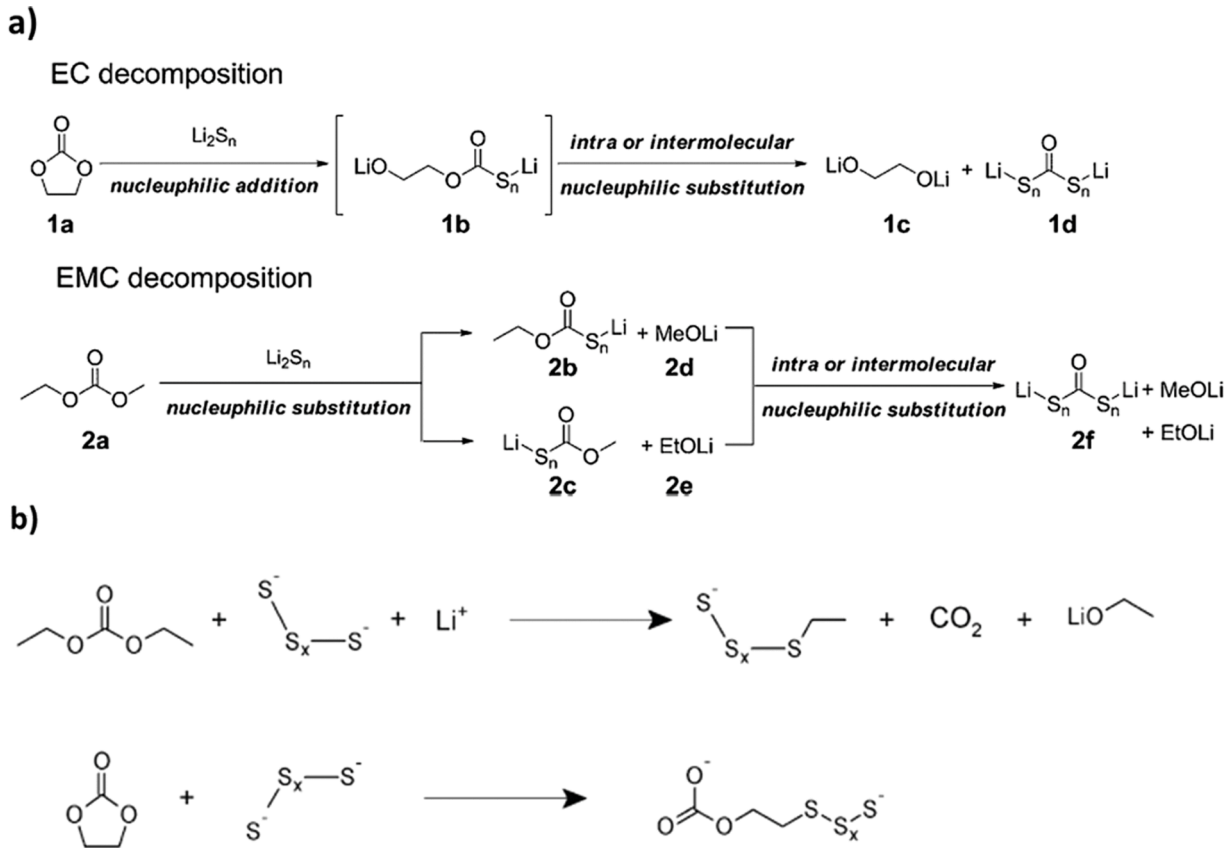


Fig. 3. Proposed reaction mechanisms between carbonate solvents and polysulfide anions in reference a) Reproduced with permission from Yim [30]. Copyright (2013), Elsevier. and b) Reproduced with permission from Gao [31]. Copyright (2011), American Chemical Society.

Lee et al. also suggested that a solvent plays an important role in introducing a direct sulfur reduction pathway [61]. They investigated the sparingly solvating system, where the solid sulfur direct reduction pathway was shown in a single potential plateau. This approach mainly aims to decrease solvent reactivity with sulfur by increasing the ratio of lithium salt to solvent. On the other hand, a single potential plateau behavior appears in all-solid-state Li-S batteries (ASS). The electrolyte in these cells is Li-ion conducting solid electrolytes, such as glass/glass-ceramics (e.g., Li_2S-P_2S_5 (Li_3PS_4)), LISICON, garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO), NASICON-type oxides, perovskite, and solid polymer [62–65]. The report by John Muldoon's group is a great example of using this type of electrolyte [66]. In this study, a ceramic electrolyte, lithium thiophosphate, was used as the solid electrolyte without adding any liquid electrolyte. A single potential plateau at ~2.0 V in the potential profiles (Fig. 4a) and a pair of redox peaks in CV curves was observed (Fig. 4b). Note that the first potential plateau at ~2.3 V was attributed to the oxidation and reduction reaction of lithium thiophosphate electrolyte in each cycle. The concept of solid-state Li-S batteries is only possible when the electrolyte is incorporated along with the cathode active material. Otherwise, addition of liquid electrolyte, to reduce the interfacial resistance between the electrodes and electrolyte, and to provide the Li^+ ion to utilize active material in cathode side, is inevitable. It is interesting to note that adding a very small amount of liquid ether electrolyte results in a conventional two plateau potential profile (Fig. 4c and 4d) [67,68].

Following these studies, we believe there are two essential requirements for using carbonate electrolytes in Li-S batteries. First, the solvent should have a relatively lower solubility of sulfur compared to ether solvents. This is because a solvent with a high sulfur solubility, such as, DME, might open the sulfur ring, leading to a lower number of electron transferring reaction (<0.5 e^- per sulfur atom) with a lower overpotential (~2.3 V vs. Li/Li^+). Second, the undesired and irreversible reaction between anionic LiPSs and carbonate solvents should be suppressed. Therefore, SSDC pathway introduced here is a general concept, and involves all the strategies that enable a solid to solid conversion of S_8 to Li_2S, reflected as a single discharge plateau. Examples of these strategies are the quasi solid-state reaction, concentrated electrolytes, sulfur composites with covalent immobilization of sulfur, and/or a combination of them.

2.3. Strategies enabling SSDC reaction in carbonate electrolytes

Despite the differences in electrochemical behavior, and advantages of carbonate-based electrolytes, there is no review paper on the use of carbonate-based electrolytes as a viable option in the commercialization of Li-S batteries. Moreover, most of the literature on the carbonate-based electrolyte in Li-S batteries focus on the perspective of material science and engineering. However, the key to overcome the technical bottleneck is to look for strategies to decrease the chemical reactivity of the nucleophilic sulfur and electrophilic carbonate solvents.

To have a direct reduction from S_8 to S_2^{2-}, a key approach is to control the interface conditions such that the sulfur atom is surrounded only by Li^+ and electrons without any carbonate solvents. The key strategy is to suppress the direct contact of sulfur species with reactive and carbonate species. This concept has been previously introduced as the" quasi solid-state" (QSS) conversion in literature, where the formation of CEI layer, as explained in detail in Section 3 of this paper, was introduced, and believed to be responsible for providing a solvent deficit environment. Here we put a step forward and introduce the SSDC reaction that covers all the scenarios leading to a controlled interface condition and therefore a single plateau discharge profile. We also believe that an optimal design of solvent in an electrolyte is vital when optimizing the interface

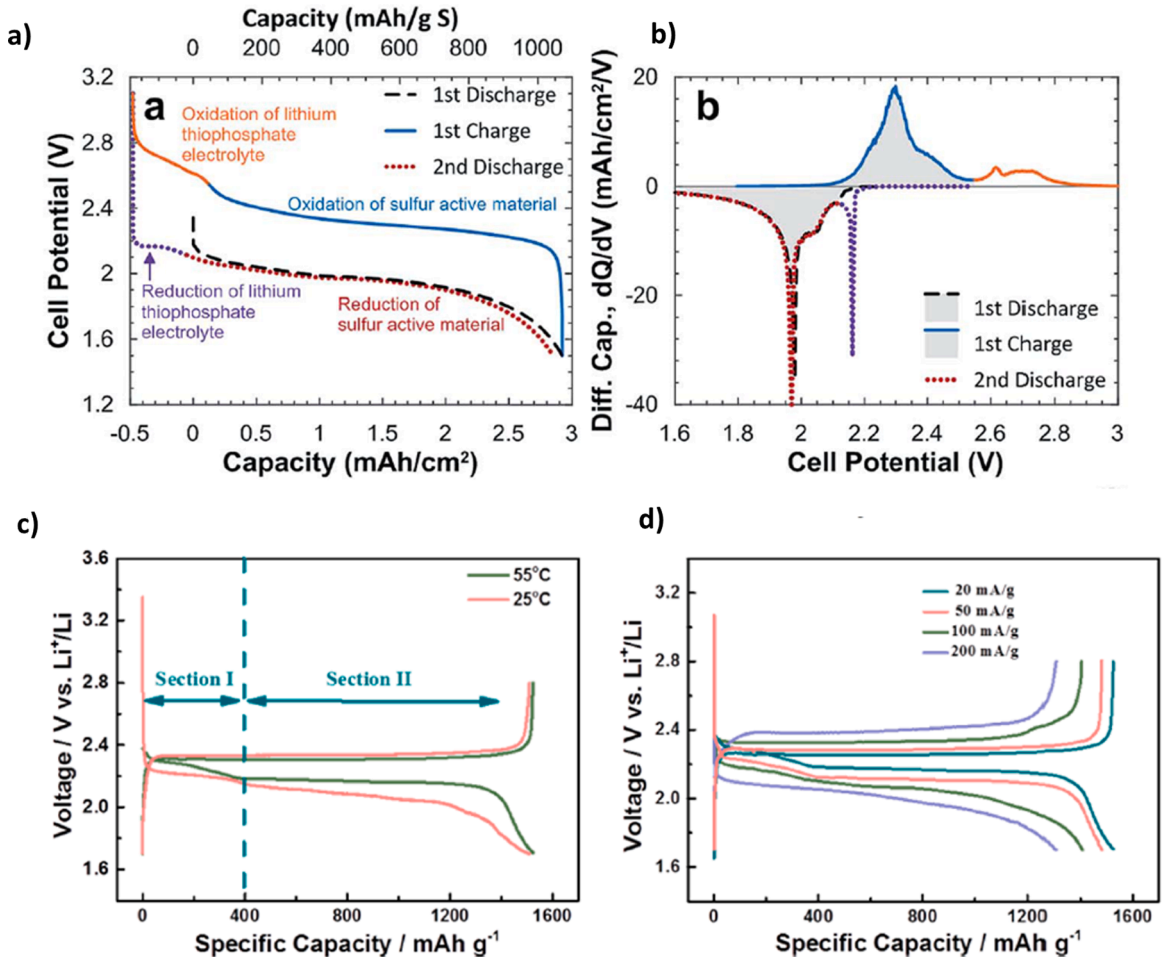


Fig. 4. a) Discharge and charge curves as a function of capacity for the S-composite/nano-crystalline Li_3PS_4 •1/2 LiI / Li cell at 60 °C. The cell was discharged at 2.28 mA/cm^2 (C/2) and charged at 0.456 mA/cm^2 (C/10) with potential limits of 1.5 V and 3.1 V, b) Differential capacities results of the cells shown in a. Reproduced with permission from Bonnick [66]. Copyright (2013), Royal Society of Chemistry. c) Discharge/charge curves of the solid-state Li-S cell at 25 and 55 °C at 20 mA/g, and d) Rate capability of solid-state Li-S cell at 55 °C. Reproduced with permission from Hao [67]. Copyright (2017), American Chemical Society.

between the electrolyte and electrodes. This is particularly important because the interface can dictate the reaction pathway and determine the electrode potential [69]. In other words, the successful use of the carbonate electrolytes in Li-S batteries relies on the strategies that can facilitate an apparent single potential plateau without the parasitic/irreversible reactions such as chemical decomposition of the carbonate species. To avoid the irreversible reactions, we believe, we should consider three strategic ways: 1- Decreasing the reactivity of sulfur by cathode modification (explained in Section 3), 2- Decreasing carbonate solvents' reactivity via an appropriately designed electrolyte (explained in Section 4), and 3- Eliminating the contact between polysulfides and solvent species.

3. Development of sulfur cathodes compatible with the carbonate-based electrolyte

As mentioned in previous sections, when a sulfur cathode is discharged, several intermediates are formed. At the dissolution step, after the octa-sulfur ring opens, the terminal sulfur (S_T^{2-}) at both ends of the nucleophilic polysulfide anions (S_x^{2-}) have a strong reactivity [70]. The soluble polysulfides formed, as strong nucleophiles, can participate in SN_1/SN_2 type reactions when electrophiles, such as carbonate solvents, are present (see Section 2 for a detailed discussion). In order to prevent such reactions and to be able to use sulfur cathodes in carbonate-based electrolytes, the formation of polysulfide anions should be limited or eliminated, or a direct contact between carbonate solvents and sulfur cathode should be avoided. For this reason, most of the literature in this area is focused on the development of sulfur cathodes to make sure irreversible reactions between LiPSs and carbonate solvents are avoided. This part will mainly focus on the different approaches introduced in the literature to decrease the nucleophilicity on the cathode side. We have categorized these approaches into four main subsections: 1) Cathodes with S-X covalent bonding, 2) Confinement approaches, 3) pre-formed layer on the sulfur cathode, and 4) other novel approaches.

3.1. Cathodes with S-X covalent bonding

Given the severe reaction between soluble LiPSs and carbonate solvents, one of the strategies to use carbonate electrolytes in Li-S batteries is to limit the formation of such intermediates. Covalent bonding is considered as one of the methods to immobilize sulfur. By covalently bonding sulfur atoms to a matrix, several different organic and inorganic compounds can be synthesized. In these cathodes, -S-S- bonds attached to the matrix will undergo the redox reaction. The covalent bonding of sulfur ensures that sulfur is embedded in a matrix and is retained on the cathode side. Several criteria can play a role in the evaluation of such cathodes. The theoretical capacity achieved in these cathodes depends on the sulfur content and it increases with the sulfur chain length in the composite [71]. The -S-S_n-S- bonds in such cathodes are electrochemically active and cleave as the cell is discharged. The sulfur chain length (n in S_n-X) in these cathodes should be optimized so that the formation of lithium polysulfides is prevented. Here, we will be discussing various

S-X composites in terms of their synthesis, electrochemical reaction pathways and challenges. This part is organized into three sections with different types of S-X materials reported in the literature where X can be: 1) a carbon atom (such as sulfurized carbon or sulfurized polymer), 2) a metal (TiS, NbS_5…), or 3) selenium/ Tellurium.

3.1.1. Sulfurized carbon/polymer composites

Sulfur as the active material in the Li-S battery normally exists in an orthorhombic S_8 structure. The crystal structure of sulfur changes from orthorhombic to monoclinic at 95 °C. Sulfur melts at 120 °C and reaches its minimum viscosity at 155 °C (often used in melt-diffusion techniques). Once the temperature reaches 159 °C (known as floor temperature), the S-S bond in the S_8 ring breaks and sulfur diradicals are formed, and ring-opening reaction (ROP) of sulfur takes place [72]. Once the sulfur diradicals are formed, sulfur polymerization will start taking place to form "polymeric sulfur" with high molecular weights [22]. If the polymeric sulfur is not stabilized, it will eventually depolymerize to form the stable S_8 ring again. The sulfur diradicals can be stabilized by unsaturated sites of inorganic compounds such as metal compounds (oxides, sulfides, carbides, and nitrides) and C—C bonds in organic moieties (thiol and nitrile group) [73]. The sulfur diradicals formed at high temperature can act as an efficient dehydrogenation agent [74]. Further increase in temperature would boil sulfur over 444 °C, which results in the formation of various chain lengths of sulfur vapor (e.g., S_2 vapor can be formed at ~850 °C) [22,75]. Fig. 5 summarizes various compounds formed from sulfur (S_8) with increasing temperature. As illustrated in this figure, the synthesis process for sulfur composites containing short-chain sulfur fragments relies on heat treatment above 200 °C. Sulfurized polymer/carbon is one of the examples of such composites, which are being widely used in Li-S batteries.

The first study on sulfurized copolymers was reported by Wang et al. in 2002 [76]. The sulfurized polyacrylonitrile (SPAN) was synthesized using sulfur as a dehydrogenating agent and by increasing the temperature of polyacrylonitrile (PAN)/sulfur to 280–300 °C [76]. Surprisingly, the SPAN cathode showed a single plateau discharge profile when gel electrolyte containing 1 M $LiPF_6$/EC-DMC was used. The general understanding in the initial studies was that the small elemental sulfur particles are embedded inside the polymer matrix and the single plateau behavior of the cell was attributed to the strong interaction between the polymer and the sulfur, preventing the dissolution of intermediate lithium polysulfides formed into the electrolyte. It is worth mentioning that PAN undergoes cyclization and carbonization reactions at high temperatures (see Fig. 6a) [77]. The reaction mechanism proposed by Wang et al. relied on the same reaction pathways when sulfur was present [78]. Later, Yu et al. showed that sulfur cannot be embedded inside the cyclized PAN ring because of size limitation (see Fig. 6b) [77]. They hypothesized that during dehydrogenation and cyclization of PAN, the sulfur diradical, formed due to the S_8 ring cleavage, can bond with carbon atoms in the polymer backbone. In fact, they believed that sulfur could accelerate the dehydrogenation of PAN and make a covalent bond with carbon atoms. This study was not only the first study to confirm the existence of C-S bond in SPAN composite, but also showed the potential use and electrochemical pathways for SPAN composite in carbonate-based electrolytes for the first time. The systematic experiments presented in this paper showed that the reaction temperature had a tremendous effect on the structure of the SPAN and the electrochemical behavior of this composite. The first discharge profile of the SPAN-300 (synthesized at 300 °C) sample showed two plateaus (~2.4 & 1.2 V), the SPAN-450 sample and SPAN-800 samples exhibited one plateau at ~1.6 V and 1.2 V, respectively, see Fig. 6c. This study introduced sulfurized polymers as cathode material in sulfur-metal batteries in presence of carbonate-based electrolyte. They proposed a two-electron transfer electrochemical reaction in the SPAN cathode (see Fig. 6b), and calculated a theoretical capacity of ~327 mAh/g for SPAN composite. Since then, several studies have been carried out on SPAN composite to understand the chemical structure, electrochemical pathways, and the effect of various experimental parameters on the performance of SPAN in Li-S batteries. In these studies, the effect of synthesis temperature and time [79–84], vapor pressure [85], grinding method [86], sulfur to PAN ratio [87], electrolyte composition [88], SPAN morphology [89–95], and kinetic characteristics of the cathode [96–99] are investigated. For a detailed literature review we encourage the readers to refer to review papers published in recent years [71,100,101].

Despite all the research on various aspects of SPAN cathode, there are still some questions and controversies which remain unanswered

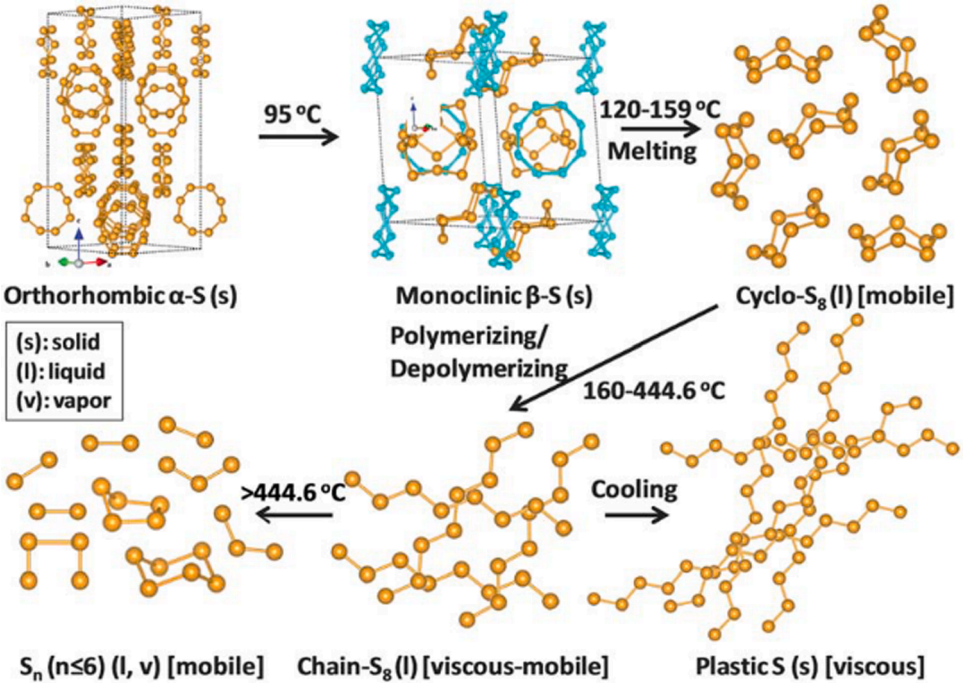


Fig. 5. Transformation of sulfur with heat treatment. Reproduced with permission from Wang [75]. Copyright (2013), Royal Society of Chemistry.

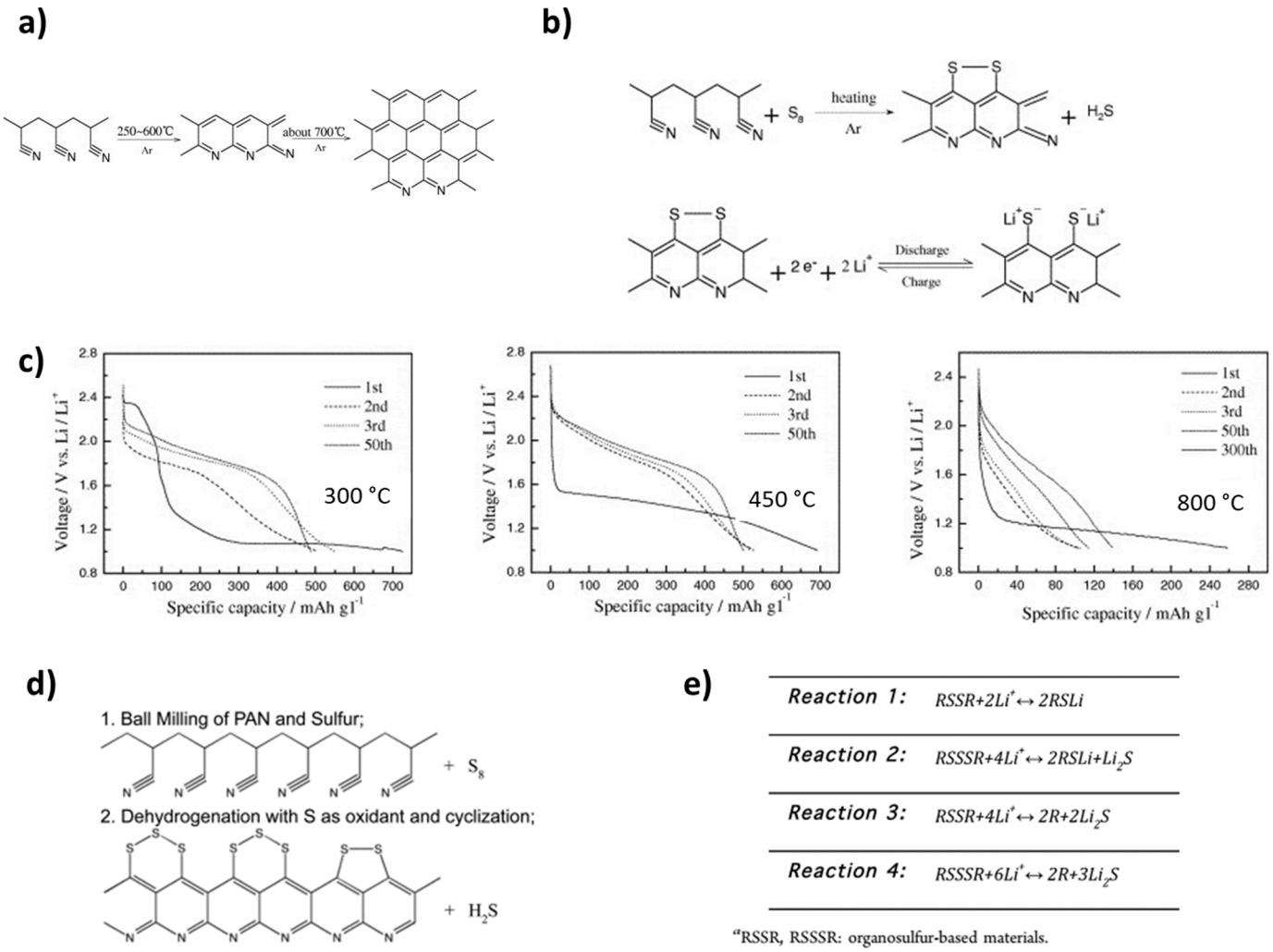


Fig. 6. a) Chemical structure change with heat treatment. Reproduced with permission from Yu [77]. Copyright (2004), Elsevier. b) Proposed SPAN structure and electrochemical reaction. Reproduced with permission from Yu [77]. Copyright (2004), Elsevier. c) Discharge profile of SPAN cathode synthesized at 300 °C, 450 °C, and 800 °C. Reproduced with permission from Yu [77]. Copyright (2004), Elsevier. d) Chemical structure proposed by Wang et al. Reproduced with permission from Wei [79]. Copyright (2015), American Chemical Society. e) Possible electrochemical reaction mechanisms for SPAN cathode. Reproduced with permission from Wei [79]. Copyright (2015), American Chemical Society.

and unclear. We hope that our review of some of the recent papers can help answer these questions: 1. *Why does the first discharge plateau of the SPAN cathode have a lower potential compared to subsequent cycles*? 2. *There are different structures reported in various studies. Which one can represent the chemical structure and electrochemical behavior of the SPAN composite in carbonate-based electrolyte*? 3. *The initial capacity of the SPAN cathodes reported in literature are often more than the theoretical capacity of sulfur (1672 mAh/g). Are there any irreversible reactions happening*?

A comprehensive study by Wei et al. proposed a covalently bound sulfur with two to three sulfur atoms connected to the polymer backbone (Fig. 6d) [79]. Moreover, they summarized all the possible reactions; and employed electrochemical and material characterization techniques to understand the real mechanism of SPAN cathode in Li-S batteries. As presented in Fig. 6e, reaction 1 suggests that the C-S bond does not break in each discharge cycle and because sulfur exists in R-S-S-R form (with short sulfur chain length), there is no formation of Li_2S. In reaction number 2, although the C-S bond does not break, the higher sulfur chain length necessities the formation of lithium organo polysulfides along with Li_2S. Reaction number 3 and 4 are based on the reversible breakage and formation of the C-S bond during discharge and charge of the SPAN cathode, respectively, where the polymer backbone and Li_2S are the discharge products of the cathode. It is interesting to note that there are reports in the literature supporting both the reaction mechanisms. On one hand, there are reports based on the C-S bond cleavage and formation in each cycle [79,102,103]. On the other hand, other reports show strong evidence that the C-S bond is stable, and the capacity originates from S-S bond breakage in such cathodes [77,91,104]. Here, we present the most recent studies wherein more sophisticated techniques such as solid-state NMR, EPR, and DFT calculations are employed to understand the structure, reaction mechanism and electrochemical properties of the SPAN cathode.

Based on the NMR results presented in Fig. 7a, two possible structures were proposed by Wang et al. (Fig. 7b-d) [105]. In these structures sulfur atoms either form bridges between the conjugated polymer backbone, or they act as side chains in the structure of the SPAN polymer. Based on the results from solid-state C-NMR, it was concluded that the $C_3N_1S_1$ unit (Fig. 7b) structure is present in the SPAN composite. — On the other hand, Li-NMR studies confirmed that the electrochemistry of SPAN cathode is different from S_8 cathode and polysulfides are not formed when SPAN cathode is used. Moreover, the solid-state N—NMR conducted in this study showed an interaction between Li^+ ion and nitrogen atom and formation of an ion-coordination bond in the polymer backbone. Aside from the comprehensive NMR and DFT results presented, we believe that the EPR experiment carried out in this paper is

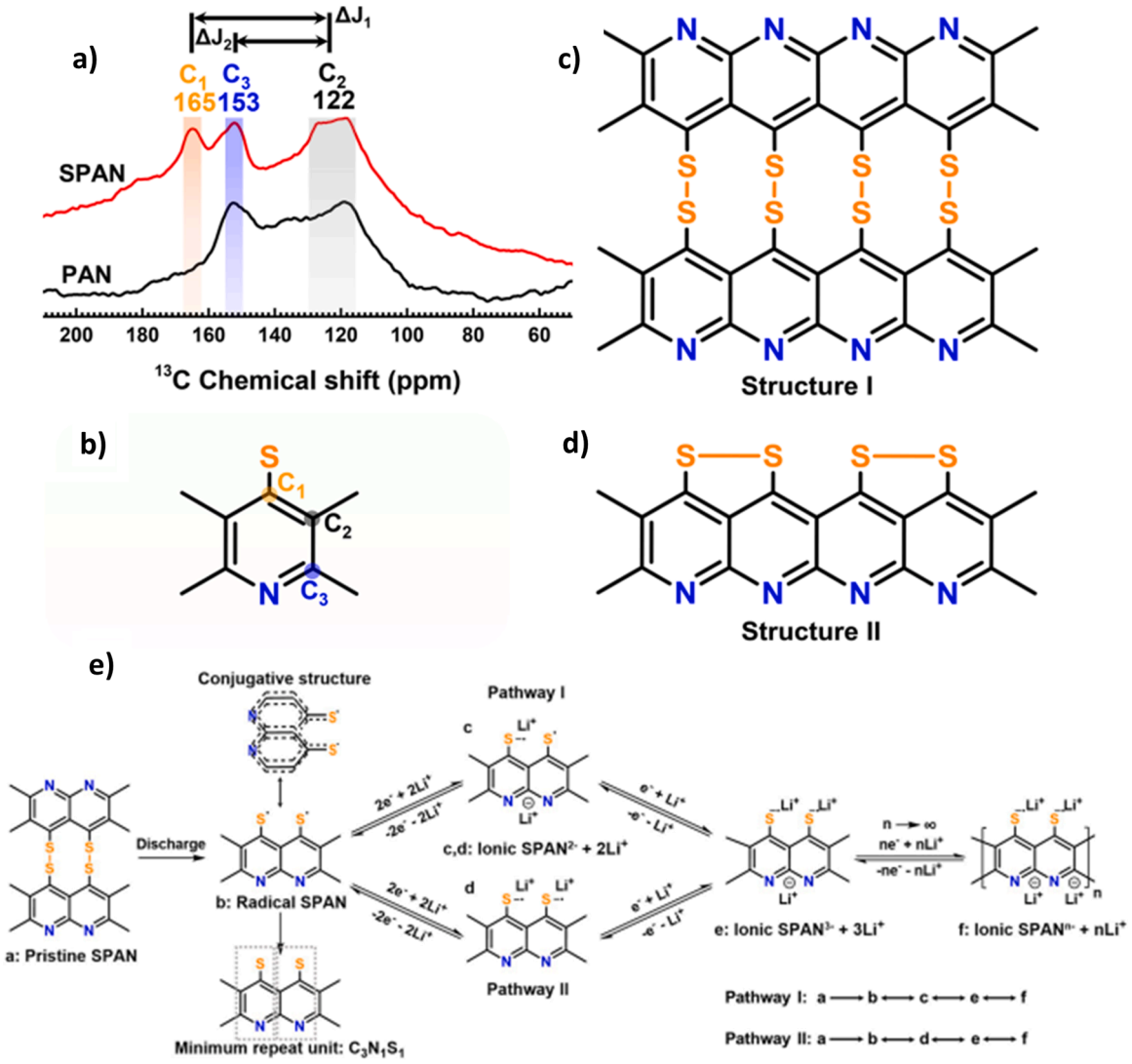


Fig. 7. a) Proposed structure of the SPAN cathode based on C-NMR spectra b) SPAN unit and the corresponding carbon location, c,d) Proposed molecular structure in this work. Reproduced with permission from Wang [105]. Copyright (2018), American Chemical Society., and e) Proposed reaction mechanism for SPAN cathode in this study. Reproduced with permission from Wang [105]. Copyright (2018),American Chemical Society.

specifically important in revealing new electrochemical pathways for SPAN-based cathodes [105]. The EPR results of the SPAN cathode at different depths of first discharge and first charge confirms the continuous cleavage of S-S bond in SPAN composite. At the end of discharge, these results confirm the redox reaction of R-S$^{\cdot}$ radicals with Li^{+} ions. The existence of the thiyl radical at the end 1st and 2nd charge cycles confirms that the SPAN does not convert back to the original state. The authors argued that the SPAN transforms to a "zigzag" shape due to the electrostatic repulsion as a result of S-S bond cleavage and the negative charge formed. This result is particularly important from two aspects: 1- The lower potential of the plateau in the first discharge can be explained, as the S-S cleavage only happens in the first discharge, requiring more energy input, and 2- It changes our insight into the reaction pathways of the SPAN cathode in Li-S batteries. The authors proposed two possible reaction mechanisms for the SPAN cathode presented in Fig. 7e, based on the EPR studies. They concluded that pathway I is more relevant electrochemical pathway for the SPAN cathode. Detailed experimental and computational approaches are further discussed in this study to prove the proposed mechanism. Moreover, using $C_3N_1S_1$ unit structure and number of Li^{+} ion interaction with sulfur diradicals and nitrogen atoms in SPAN, they presented a theoretical capacity calculation for the SPAN composite. It is worth noting that a very stable capacity of 631 mAh/g (based on the SPAN weight) after 2000 cycles is reported in this study. This study provided new insight into the structure and working mechanism of SPAN cathode in Li-S batteries. However, this work does not attempt to elucidate the reason for the existence of such small sulfur chain length. Moreover, we noticed that there is a small peak at ~160 eV in the XPS results from the discharged sample that was neglected in the paper. We believe this peak can be attributed to Li_2S in the discharged state, which suggests that either SPAN molecules with more than two bridging sulfur atoms were present, or a small amount of elemental sulfur in the SPAN was present.

Later on, a new structure was proposed (Fig. 8a) as a potential molecular structure for SPAN composite [106]. In this study the solid-state C-NMR of the SPAN cathode at the first and second discharge was compared to the pristine SPAN. Based on the analysis provided in this work, Li-C-C-Li and Li-C-N-Li are formed, contributing to the extra capacity observed in the SPAN cathode. It is important to note that these peaks do not disappear in the first charge, indicating an irreversible capacity loss after the first discharge. The same conclusion was also made from the Li-NMR of the samples which was attributed to the conjugate double-bonds energy storage mechanism. Also, the change in potential of the first plateau and subsequent discharge cycles was also attributed to the formation of Li-C-C-Li and Li-C-N-Li bonds as well. The

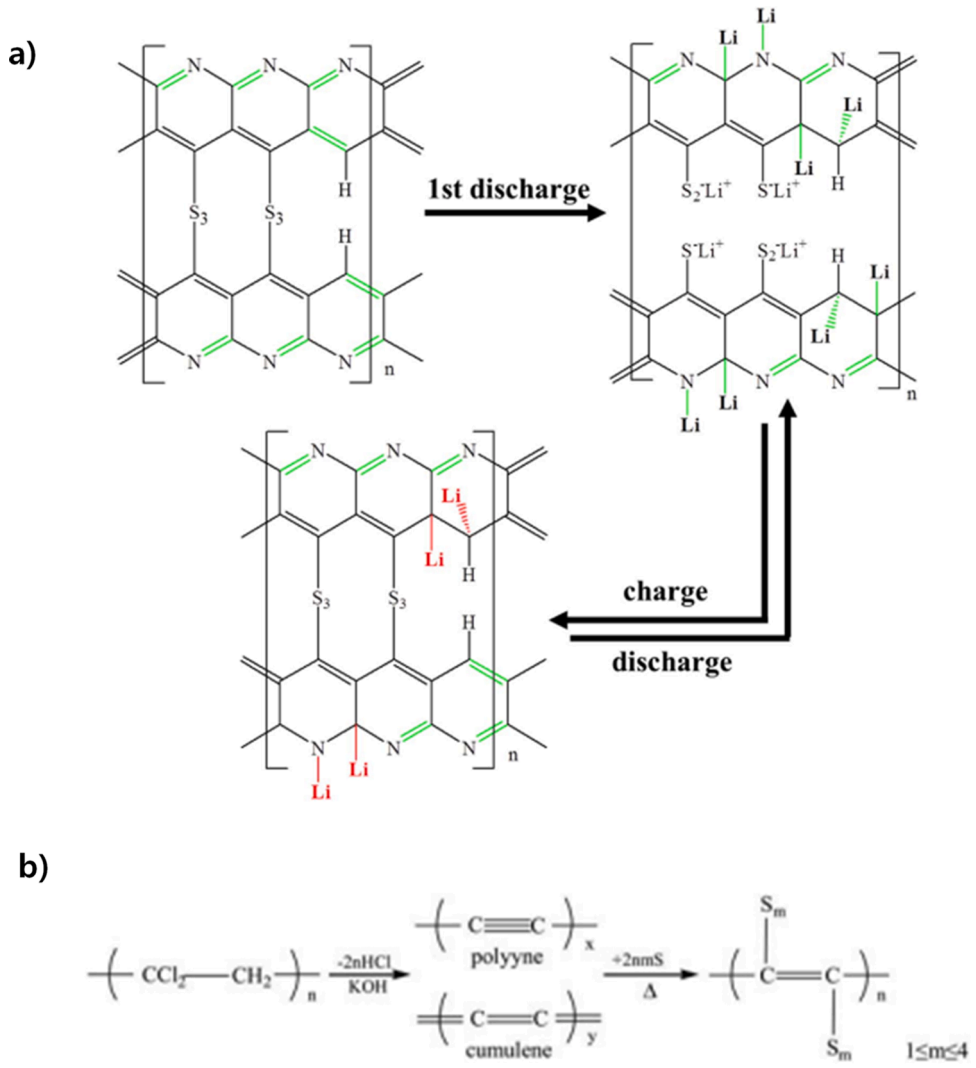


Fig. 8. a) Proposed structure of SPAN cathode based on C-NMR, Li-N.MR and XPS studies. Reproduced with permission from Jin [106]. Copyright (2018), Elsevier. and, b) Structure of carbyne polysulfide, Reproduced with permission from Duan [107]. Copyright (2013), Royal Society of Chemistry.

authors proposed that the formation of these bonds can increase conductivity and therefore lower polarization of the composite after the first discharge.

Based on the literature provided in this part, we believe that the C-S bond does not break when the battery is cycled. This can be clearly seen from the solid-state NMR results and XPS results reported by several groups [84,91,104,106]. On the other hand, it is fair to conclude that the Li_2S formation reported in most literature and elemental analysis of SPAN composite might be a result of sulfur chain length less than four in polymer backbone (i.e., R-S_x, $x<4$). Moreover, the extra capacity of the first cycle can be attributed to the conjugated polymer backbone and the formation of Li-C-N-Li at the first discharge. Based on the results, this reaction is probably irreversible. Although there are studies that attribute this extra capacity to the cathode-electrolyte interphase (CEI) formation, but unfortunately, no proof/ characterization of the formation of such CEI is presented in those studies [79]. We speculate that the CEI reported in the literature might be formed because of the reaction between small amount of elemental loose sulfur (not bound to C in the polymer) and carbonate solvent. However, such an assumption needs further investigation. Moreover, based on the literature, we can conclude that the lower potential of the plateau in first discharge compared to the subsequent discharge cycles arise from the irreversible change in the molecular structure of the SPAN cathode in the first discharge cycle, making it more conductive and accessible to the Li^+ ions in subsequent discharge cycles. Although the progress made from 2002 and the first repost of SPAN composite in the literature is significant; we believe that a comprehensive experimental study coupled with simulation is necessary to answer some of the controversies that still exist in the literature.

Based on the general understanding of the SPAN structure and electrochemical pathways discussed in previous pages, PAN polymer used in vulcanization can be replaced with polyaniline (PANI) conductive polymer [108]. The motivation behind these studies is to take advantage of the conjugated skeleton and good electrical conductivity of PANI. For example, Ma et al., fabricated SPANI composite and varied reaction temperatures of 280 to 350 °C and reported a stable capacity of 575 mAh/g_{sulfur} after 500 cycles [109]. Despite the stable cycling in carbonate-based electrolytes, there are two main questions remaining. The first question is that it is not confirmed that sulfur is embedded as short-chain sulfur, between the SPANI composite. Moreover, no conductivity measurement was carried out, this is particularly important as Nazar et al., previously argued that PANI in the voltage range used in Li-S battery is in its reduced state and highly insulating [110].

Similar to sulfurized polymers, sulfurized carbon material can also benefit from the covalent bonding between carbon and sulfur atoms and become compatible with carbonate-based electrolytes [107]. An example of this type of S-X covalent bond is the carbyne polysulfide composite material (see Fig. 8b for the structure) [107]. In this material,

the C double bond C and C triple bond C can form short-chain sulfur molecules that are covalently bound to the carbon atom. Similar to this study, Yan et al. introduces C-S and O-S bonds to CNTs by first creating oxygen-containing group and subsequently heating a mixture of CNTs and sulfur at 300 °C [111]. Luo et al. also used a similar concept by using carbon with oxygen functionalities and achieved a capacity of 508 mAh/g for 2000 cycles using carbonate-based electrolytes [112]. However, Li et al. argued that using carbon with oxygen functional groups can reduce the conductivity of the cathode and might cause undesired side reactions [113].

Although using sulfurized polymer/carbon composite material is a great method to stabilize sulfur with the formation of covalent bonding, preventing the formation of soluble lithium polysulfides and enabling the use of carbonate-based electrolytes, however, they suffer from low sulfur wt.% in their composite. These materials are limited to a maximum of ~50 wt% sulfur, considering a slurry with 80 wt% of active composite material, the wt% of sulfur in the slurry will be limited to only 40%. This becomes significantly important where a loading of more than 5 mg/cm^2 is targeted for practical applications of Li-S batteries [114–116]. This loading translates into 10 mg/cm^2 for SPAN (considering 50 wt.% of sulfur in composite) and 12.5 mg/cm^2 of slurry in a single cathode. Utilizing such a high loading of SPAN in a Li-S battery requires us to overcome challenges such as slow kinetics and electrolyte accessibility. Moreover, the amount of electrolyte required to utilize such loadings is going to be very high, signifcantly decreasing the energy density of the battery.

3.1.2. Metal-S composites

One of prominent sulfur compounds to depress the dissolution step, an envoke the SSDC reaction, is metal polysulfides (MS_x, $2 < x \leq 4$) formed by covalently bonding a short-chained PS to transition metal or inorganics. For example, amorphous MoS_3 showed SSDC reaction pattern with a single plateau potential profile and demonstrated stable cycling performance (~1000 cycles), and the possibility to achieve high areal capacity of ~2.8 mAh/cm^2 in 1 M $LiPF_6$ in EC/DEC [117]. Similarly, it is revealed that transition metal polysulfides such as amorphous FeS_4 and TiS_4, is highly suitable for introducing SSDC reaction in carbonate-based electrolytes [118,119]. Amorphous MoS_3 composite material has been used as active material in cathode, introducing the concept of "sulfur equivalent cathode materials". This concept emphasizes on the great potential of M-S composites as sulfur alternative for room temperature metal-sulfur batteries [93]. Nevertheless, the use of such transition metal-based polysulfide cathodes can decrease the gravimetric energy density of Li-S batteries due to their heavy weight.

3.1.3. Composites with selenium and tellurium

Besides the metal polysulfides, selenium and Tellurium-based polysulfides seem to be a better option to be used in Li-S batteries. Selenium has a theoretical capacity of 678 mAh/g. Despite the similarities between selenium and sulfur cathodes, selenium is a semi-conductor (conductivity: 1×10^{-3} S/cm), which leads to higher utilization and faster electrochemical kinetics compared to sulfur. Moreover, because of the higher density of Se compared to sulfur (4.809 g/cm^3 vs. 2.07 g/cm^3), Li-Se batteries can compete with Li-S batteries [120]. A promising approach to take advantage of both sulfur and selenium as cathode material is to use seleniumpolysulfide composite. This approach was introduced for the first time in 2012, showing the potential use of Se_xS_y cathodes for rechargeable Li and Na batteries [121,120]. It is worth mentioning that optimization of y to x ratio in such composites plays a vital role. Although selenium as cathode material is compatible with carbonate electrolyte, however, at higher y to x ratio, the formation of lithium polysulfides would lead to irreversible reactions with carbonate solvents [98]. For example, various S-rich $S_{1-x}Se_x$/C ($x \leq 0.1$) compounds were prepared by controlling the stoichiometric ratio of S and Se [122]. Amorphous $S_{0.94}Se_{0.06}$/C composite reported by Li et al. showed superior specific capacity of 910 mAh/g at 1 A/g over 500 cycles in carbonate-based electrolytes. Recently, a novel S@PAN/S_7Se composite was used in Li-S batteries [123]. In this work, sulfur nanoparticles are wrapped by PAN/S_7Se such that the contact between carbonate solvents and active material is limited by the Se-doped sulfurized polyacrylonitrile shells and in situ formed CEI on the PAN/S_7Se shells. As a result, this composite delivered a very high capacity of ~1100 mAh/g at 0.1 A/g with capacity retention of 77% over 500 cycles at 2 A/g.

Tellurium is another chalcogen material with enhanced conductivity compared to sulfur and selenium (2×10^{-2} S/m) [124] Fig. 9a shows a comparison between the properties of this material. Te_xS_{1-x} composites can be fabricated by heat treatment of sulfur and tellurium. Zhou et al. synthesized a composite of mesoporous carbon/sulfur/tellurium by heating the material to 550 °C for 4 h and used it as cathode material in Li-S batteries [125]. The battery delivered a reversible capacity of 485 mAh/g after 500 cycles at 1 A/g rate Fig. 9c and d shows the cyclic voltammetry and schematic diagram of CEI formation, reported in this work. They hypothesized that the reversible cycling of this composite in the carbonate-based electrolyte is a result of the CEI layer formed on the cathode. This CEI layer was formed because of the reaction between polytellurides and carbonate solvents, which prevented further contact between carbonate solvents and polysulfides/polytellrides [125].

3.2. Confinement of elemental sulfur into host material

Another approach to prevent the contact between lithium polysulfides and carbonate solvents is sulfur confinement into micropores of carbon/host material. Along with the extensive research on sulfurized polymers, the sulfur confinement approach is also widely investigated. Most of the papers in the literature focus on two points of view in the design of such cathodes: 1) molecular size of short-chain sulfur (S_{2-4}) is less than 0.5 nm, and 2) relationship between the ionic radius of carbonate species and pore size.

Based on the first viewpoint, sulfur is confined as short-chained molecules (S_{2-4}), so the formation of nucleophilic polysulfide anions is avoided [102,126-136]. Relying on this approach, various types of ultra-microporous carbon (UMPC) and sulfur composites have been investigated. The UMPC with <0.5 nm pore size is synthesized by diverse approaches. Conductive carbon is generally derived from carbonization (>700 °C) of organics such as glucose-like sources, polymers, and biomass like bamboo and coffee wastes. The activation steps to produce microporous structures involve heat treatment in the presence of KOH or CO_2. Fig. 10a shows an example of such cathodes. The microporous carbon is synthesized by pyrolyzing PVDF powder at 800 °C under N_2 for 2 h, and sulfur was incorporated into the micropores at 155 °C for 20 h under vacuum. It should be noted that the confinement of sulfur as S_{2-4} species inside the micropores in most of these papers is carried out at 155 °C (lowest viscosity of sulfur in a molten state). However, confined sulfur within 0.5 nm micropore synthesized under 300 - 400 °C might be close to a higher order of sulfur (S_6-S_8) as molecular dissociation of S_8 to S_{2-4} starts prevailing from 550 °C, even at high temperature of 600 °C only ~16% of sulfur consists of short-chain sulfur. One can also argue that the short-chain sulfur can re-form the S_8 structure after cooling down. Moreover, if the confined sulfur molecules were truly in S_{2-4} chain length, a single plateau discharge behavior should be expected in the ether-based electrolyte as well. A great review paper by Aurbach et al. discussed the reaction mechanisms of these cathodes. This group revealed that the confined sulfur within a wider micropore (1–2 nm) shows a quasi solid-state (QSS) behavior in Li-S batteries when 1 M $LiPF_6$ in FEC/DEC is used [58]. The quasi solid-state reaction mechanism was first introduced by Wang et al. as a reaction between Li^+ ions and active material under solvent deficient environment [75]. Based on this definition, Aurbach et al. put one step further and showed that the formation of CEI is another possible way to invoke the QSS mechanism. The CEI formed on the cathode prevents the direct contact between sulfur cathodes and carbonate species, minimizing the notorious and irreversible reactions. The formation of CEI in

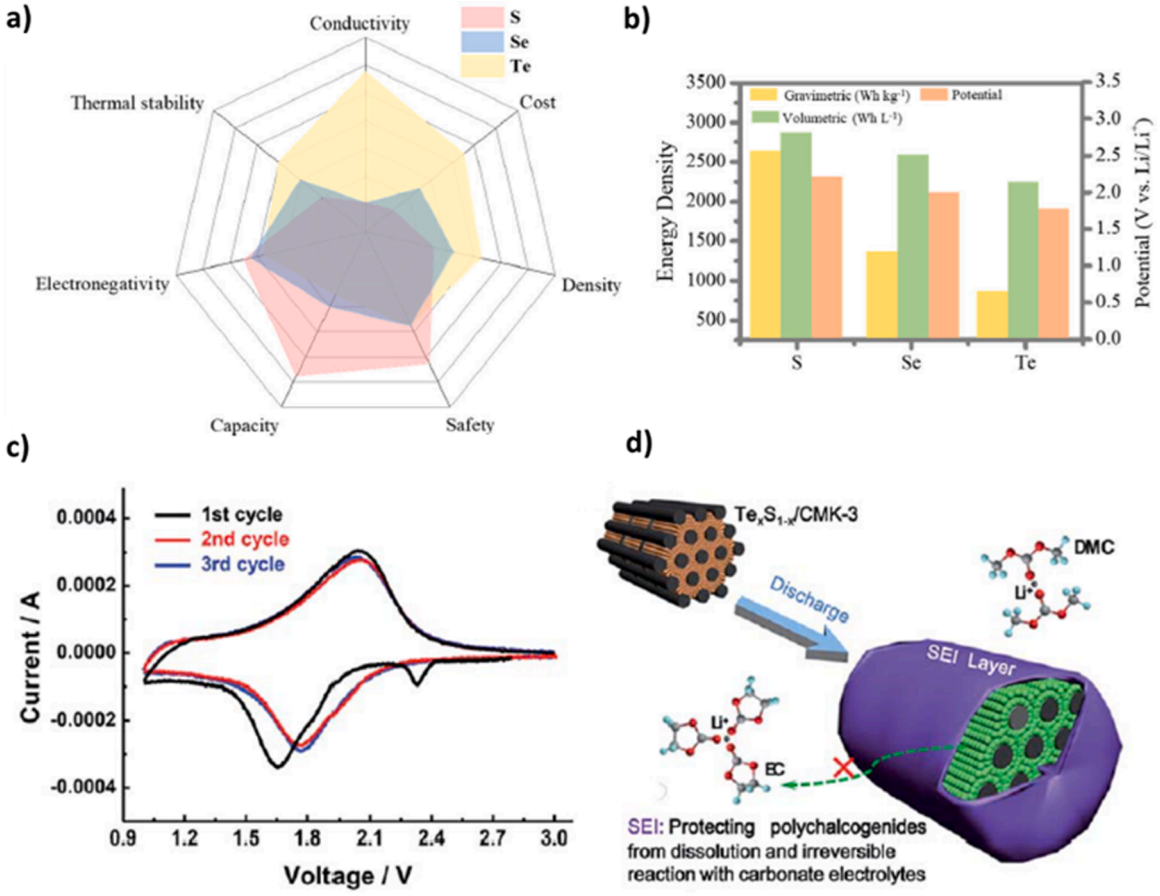


Fig. 9. a & b) Comparison between sulfur, selenium, and tellurium active material. Reproduced with permission from Chen [124]. Copyright (2020), John Wiley & Sons Ltd. c) CV curves of $Te_{0.1}S_{0.9}$ CMK-3 cathode Reproduced with permission from Sun [125]. Copyright (2018), Royal Society of Chemistry. and d) Schematic showing the CEI formation. Reproduced with permission from Sun [125]. Copyright (2018), Royal Society of Chemistry.

this paper will be discussed in detail in next section.

Although most of the literature focus on the confinement of short-chain sulfur in the microporous carbon, however, as mentioned before, there is enough reason to confirm that the sulfur confined inside micropores of carbon should be in the form of S_8. That's why the second viewpoint becomes more important. The overall idea behind this viewpoint is that the ionic radius of carbonate solvents (EC (5.74 Å) and DEC (7.96 Å) are larger than the pore size of microporous carbon [137]. In this case, micropores of carbon act as a filter to screen the carbonate solvents, and a direct contact between sulfur/polysulfide species confined in microporous carbon is avoided. Reddy et al. presented a schematic to describe this concept [138]. Fig. 10b shows a schematic illustration of the UMC-sulfur composite used in this study. Using EELS spectra of this composite, they showed that sulfur is present in the form of a linear polymeric chain aligned with the carbon lattice inside the pores of UMC. The charge-discharge profile of this cathode in 1 M LiPF6 in EC/DMC electrolyte is shown in Fig. 10c. The small plateau in the first discharge cycle is attributed to the reaction between lithium and functional groups in UMC. Based on the experiments in these papers, they concluded that a solid-liquid-solid reaction is expected in the microporous carbon where pore size exceeds 0.7 nm (see Fig. 10d). They also concluded that there are two conditions for a Quasi-solid-state reaction to take place: 1) in ultra-microporous carbon where pore size is less than 0.7 nm, and 2) in microporous carbon provided that a CEI is formed on the cathode. Most recently, our group fabricated MXene-based sulfur cathodes for Li-S batteries, with the aim to use 2D-MXene nanosheets as host to confine sulfur [191]. This work is the first study on confining sulfur in a 2D layered material. The result of this study showed that this novel cathode material triggers Li^+ ion desolvation, thereby mitigating the unwanted reaction between sulfur and carbonate solvents.

A very recent spectroscopic study using XANES profiles also confirmed that sulfur confined in microporous carbon is in form of S_8 chains [139]. The reaction mechanism in this study was investigated using operando XAS and the model presented in Fig. 10e is proposed. This model confirms that Li_2S_8 is the first discharge intermediate in the sulfur/microporous carbon composite. Despite all the research carried out to understand the reaction mechanism of sulfur confined in the carbon host, we feel there is one question that is not answered in any of these papers. In some of the studies using microporous carbon, the formation of a C-S bond is observed using XPS or FTIR [140]. However, there is no study on the role of the formed C-S bond (if any) in such studies. It should also be noted that similar to sulfurized polymer/-carbon, the weight percentage of sulfur in the confinement approach is limited to the volume of the micropores present.

Based on the SSDC reaction mechanism discussed in section two of this paper, there are two main approaches to use sulfur cathodes in carbonate-based electrolytes in Li-S batteries: the first one focuses on the nucleophilicity of lithium polysulfides and relies on the formation of X-S bond to suppresses the formation of such species. The other approach, known as the QSS reaction mechanism, focuses on eliminating contact between nucleophilic polysulfide anions and carbonate solvents. There is another approach to enable the SSDC reaction. This method relies on the *ex situ* formation of a layer on the sulfur cathode. Similar to the CEI layer (formed in situ), this method can be used to prevent the contact between carbonate solvents and polysulfide anions.

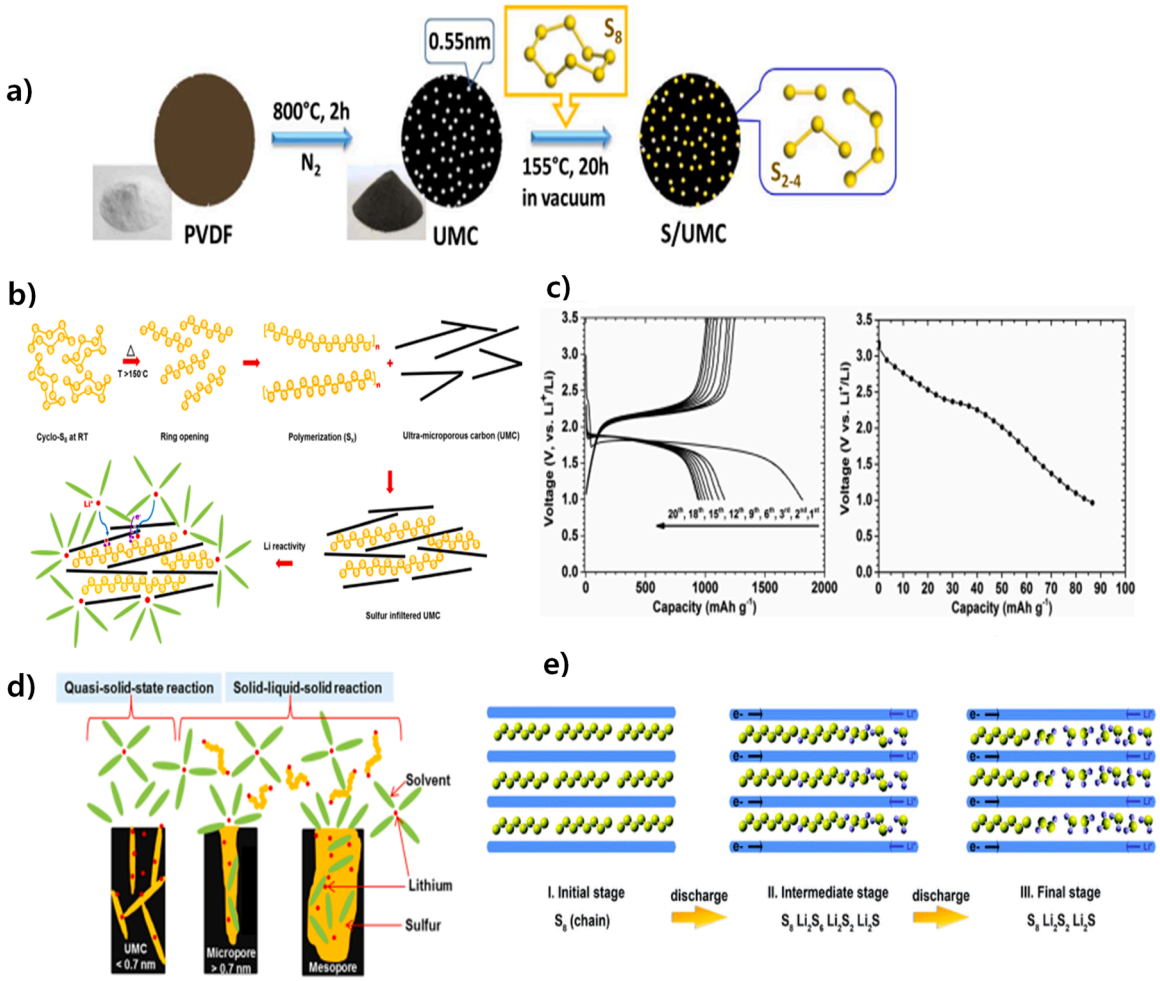


Fig. 10. a) S/UMC composite material synthesized using PVDF powder. Reproduced with permission from Zhu [141]. Copyright (2017), Elsevier. b) Schematic illustration of S/UMC composite prepared by Reddy et al., showing polymeric sulfur chain inside the UMC pores. Reproduced with Permission from Helen [138]. Copyright (2018), American Chemical Society. c) Galvanostatic discharge profile of the cathode in part b and Lithium insertion into the UMC in first discharge. Reproduced with Permission from Helen [138]. Copyright (2018), American Chemical Society. d) Schematic showing the difference between the quasi-solid-state reaction and solid-liquid-solid reaction based on the pore size of carbon used. Reproduced with Permission from Helen [138]. Copyright (2018), American Chemical Society. and e) reaction pathways for microporous carbon based on XAS. Reproduced with Permission from Xiao [139]. Copyright (2020), Royal Society of Chemistry.

3.3. Pre-formed layer on the sulfur cathode

An ex-situ formed layer on sulfur cathode can prevent the nucleophilic-electrophilic attack between lithium polysulfides and carbonate solvents. Sun et al. coated the sulfur carbon composite using a molecular layer deposited alucone layer [142]. Using this layer, they have achieved a capacity of ~870 mAh/g after 300 cycles in carbonate-based electrolytes. Fig. 11a shows a schematic of alucone coated sulfur/carbon composite. Later on, they reported a high loading of 4 mg/cm^2 with 64 wt% of sulfur in composite [29]. The battery using this composite as cathode delivered a capacity of 705 mAh/g after 300 cycles (Fig. 11b). Using *in operando* XANES spectra, they confirmed a direct conversion from sulfur to the final discharge product of Li_2S. Fig. 11c shows a schematic of the proposed mechanism for this study. Based on this schematic, Li^+ ions de-solvate because of the coating layer, preventing a direct contact between sulfur and carbonate solvents. It is worth noting that the thickness of alucone layer was controlled at 3 nm. Based on other studies reported in literature, it seems that a 3 nm coating layer on sulfur/carbon composite can allow Li^+ ion de-solvation without hindering kinetics of the reaction.

3.4. Other approaches

Recently, our group demonstrated the use of γ-sulfur, a monocilinc phase of sulfur, as active material in Li-S batteries [190]. This rare phsae of the sulfur was stabilized on a porous carbon nanofiber host at 180 °C. While the conventional two plateau behavior was observed when this cathode was used in ether-based Li-S batteries, interestingly, a single plateaue potential profile was seen when used in carbonate-based electrolytes. Given that sulfur is not confined, the authors concluded that the crystal strcuture of sulfur played an important role, therfore, XRD and XPS studies were carried out to understand the reaction mechanism. These studies showed conversion of the γ-monoclinic sulfur to Li_2S (at the end of dicharge), and back to a new monoclinice crystal phase (at the end of charge). The battery with the γ-sulfur/carbon nanaofiber cathdoe material exhibited an initial capacity of 800 mAh/g and an outstanding cycling performance, with a small 0.0375% decay rate over 4000 cycles.

Despite numerous research reports and excellent cycle stability, desiging a cathode enabling the use of carbonate-based electrolyte in Li-S batteries is challenging because of the low sulfur wt% and high amount of electrolyte. Here we would like to discuss different methods used in literature based on modification in electrolyte to enable the SSDC

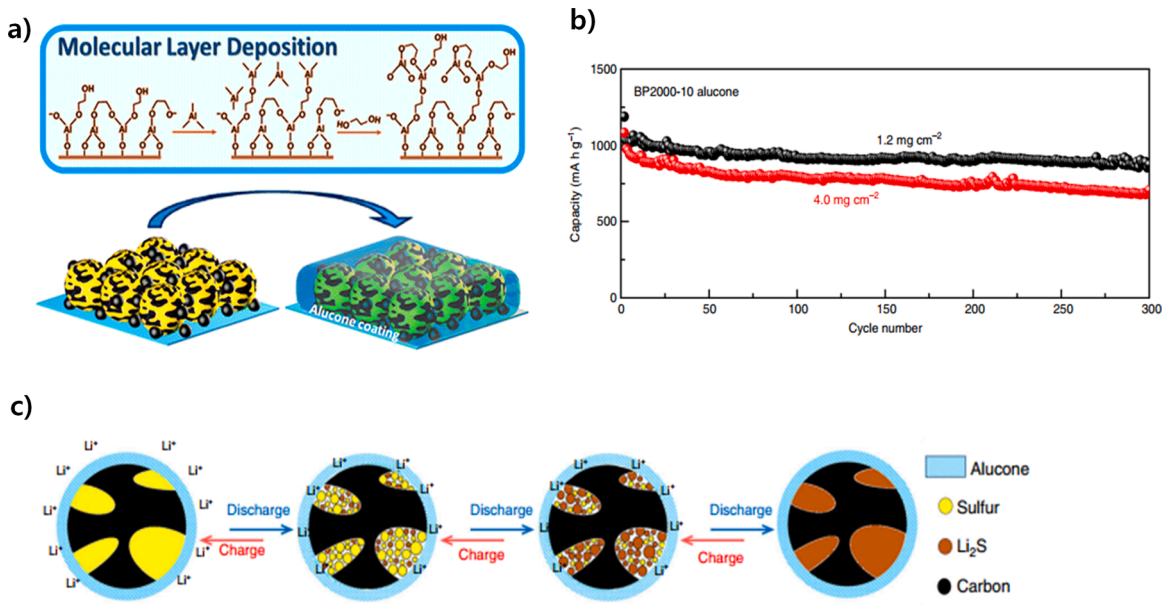


Fig. 11. a) Synthesis schematic of alucone coated C/S composite used in carbonate-based electrolyte. Reproduced with permission from Li [142]. Copyright (2016), American Chemical Society. b) Cycling stability of these cathodes with very high loading of 4 mg/cm^2. Reproduced with permission from Li [29]. Copyright (2018), Springer Nature. and c) Proposed discharge and charge mechanisms in these cathodes. Reproduced with permission from Li [29]. Copyright (2018), Springer Nature.

reaction in carbonate-based Li-S batteries.

4. Optimal electrolyte design for SSDC reaction

As discussed in section 2, a key requirement for using carbonate-based electrolytes in Li-S batteries is to suppress undesirable electrolyte decomposition by the irreversible reaction between carbonate solvents and intermediate lithium polysulfides. In non-aqueous electrolytes, terminal sulfur (S_T^{-1}) of the polysulfides, generated during discharge, is almost four times more soluble than elemental sulfur (or bridged sulfur, S_B^0) at OCV [143]. Therefore, introducing a pathway of SSDC reaction could efficiently lead to suppressing the parasitic reaction at the interface. To optimize the solvation environment in carbonate-based electrolytes, relevant strategies can be adopted from other battery systems, such as the primary Li-SO_2 chemistry and Li-air batteries. Having similar technical issues, these batteries can provide great insight into the design of electrolytes to alter the reaction pathways in Li-S batteries. An example of such studies is the distinct solvation environment observed for two different electrolytes in the Li-SO_2 battery system [144]. Using DFT calculations, the reaction pathway for two types of solvents (TEGDME and EC/DMC) was studied. In EC/DMC solvents (dielectric constant of 35.0), SO^{2-} is stabilized to form $S_2O_4^{2-}$ via dimerization reaction and there is high number of electron transfer reactions per sulfur atom. Meanwhile, in TEGDME solvent (dielectric constant of 7.8), SO^{2-} prefers to form neutral species, such as $LiSO_2$, with a smaller number of electron transfer reactions per sulfur atom. This could explain the different electrochemical pathways in different electrolytes in Li-S batteries as well; specifically comparing the conventional solid-liquid conversion in ether-based electrolytes and SSDC reaction in carbonate-based electrolytes. The discharge reaction pathways and products can alter with electrolyte solvent properties, such as donor number and dielectric constant. For a conventional ether-based solvent with a relatively low dielectric constant of ε~7 (weak electrostatic interaction), the chemical interaction of S_T^{-1} and Li^+ with a lower number of electron transfer reactions, we believe, is more favorable due to the solvent's weaker electrostatic interaction. Therefore, formation of neutral species is favored. In contrast, carbonate-based solvents with higher dielectric constant of ε~35 (strong electrostatic interaction) [145] offer a more suitable environment to stabilize the charged S_T^{-1} species, rather than the neutral species favored in ether electrolytes. In a review paper by Lu et al., on a Li-O_2 system, the authors concluded that an electrolyte with higher donor number (higher dielectric constant) shows a strong solvation effect to towards superoxide intermediate species [146]. The stabilization effect discussed earlier can increase the concentration of O_2^- which can induce electrolyte decomposition [146]. Recently, Li et al. showed the effect of dielectric constant on the polysulfide reaction pathways in Li-S batteries. Fig. 12a shows the schematic presented in this study. Their result showed the stability of charged species, such as S_6^{2-} and S_3^-, in solvents with higher dielectric constant and stability of Li_2S_8 and Li_2S_4 in solvents with lower dielectric constant [147]. Based on these two studies, and similarity of decomposition reaction between O_2^- and polysulfide anions with carbonate electrolyte, we can conclude that the donor number and dielectric constant of a solvent may be responsible for altered reaction mechanism in carbonate-based electrolyte. Furthermore, the interaction between lithium salt and solvent should be considered as a function of polysulfide interactions with Li^+ and other anion species. Using molecular dynamics and DFT calculation, several interactions among Li^+-S_x^{2-}, Li^+-solvent, and Li^+-salt anion (like $TFSI^-$) were revealed in reference [148].

We believe that the optimal solvation structure in carbonate-based electrolytes for SSDC reaction should contain i) solvents with low dielectric constant (i.e., weaker Li^+ ion solvating power), and ii) lower sulfur solubility with no direct contact between free carbonate species and PS anions (weaker interaction of PS with solvent). We believe that engineering electrolyte composition can have a tremendous effect on the electrochemical reactions occurring in Li-S cells. Moreover, it is shown that the high E/S ratio required in the Li-S batteries can be lowered by simply tuning the electrolyte composition. A simple approach to achieve this goal is to use non-solvating electrolytes. Nazar er al., used the term "non-solvent" to describe such electrolytes [149]. Fig. 12b shows a schematic explaining the reaction pathways in these electrolytes. Despite their positive effect on limiting the formation of polysulfides and their subsequent shuttle, these electrolytes suffer from kinetic problems and high polarization, which result in poor rate capability in Li-S batteries. To overcome this problem, the same group worked on sparingly solvated electrolytes (with polysulfide concentration of less than 1 mM) [61]. A comprehensive study on this concept is presented by Gallagher et al. [150]. Moreover, in a totally opposite approach, J. R. Owen's

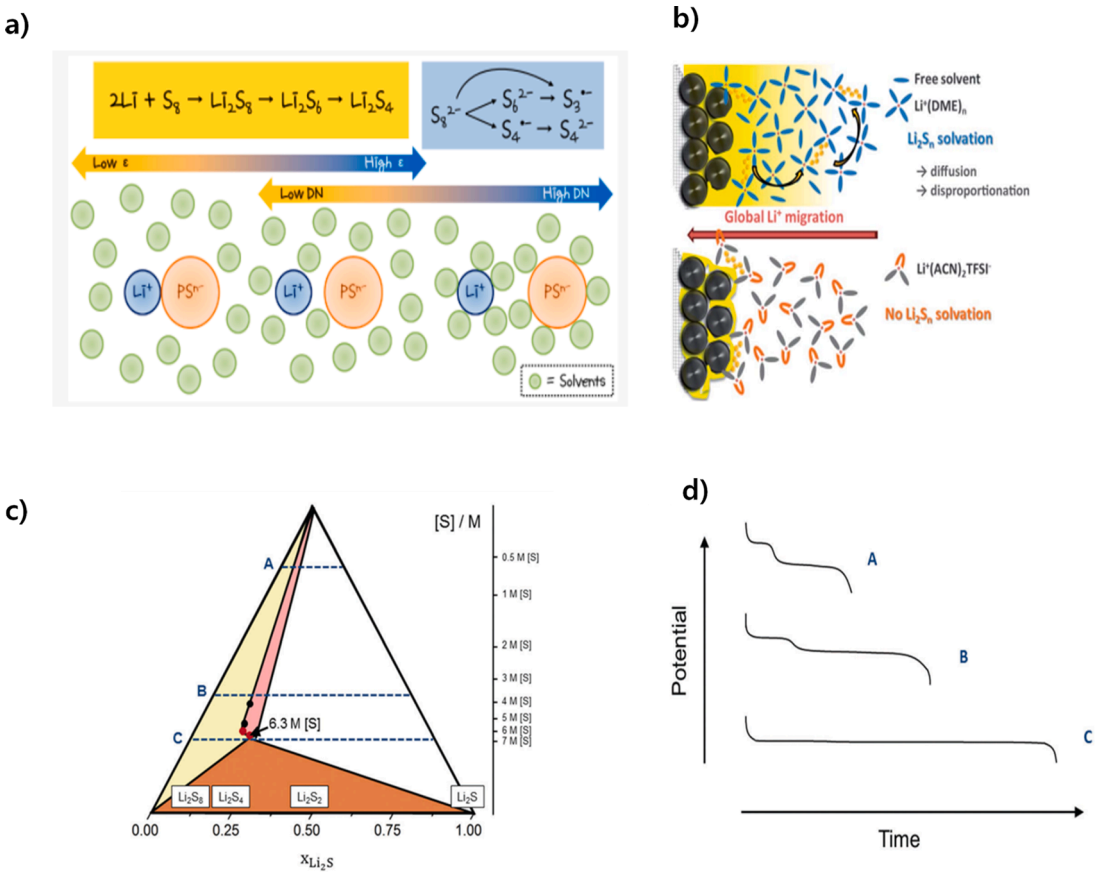


Fig. 12. a) Schematic showing solvent interaction with PSs in different solvents. Reproduced with permission from Du et al. [147]. Copyright (2020), MDPI. b) Schematic of the concept of non-solvents in Li-S batteries. Reproduced with permission from Cuisinier [149]. Copyright (2014), Royal Society of Chemistry. c) The ternary diagram showing effect of PSs concentration. Reproduced with permission from Dibden [151]. Copyright (2016), Royal Society of Chemistry. and d) Corresponding voltage profile at points A, B and C in part c. Reproduced with permission from Dibden [151]. Copyright (2016), Royal Society of Chemistry

group suggested a ternary S_8-Li_2S-electrolyte, supported by experimental data [151]. By analyzing the solution with highly concentrated polysulfides in the solution of 1 M LiTFSI in DOL, the ternary phase diagram (presented in Fig. 12c) was constructed. In this triangular phase diagram, the single-phase region at the top edge means that all solid S_8 and Li_2S are fully dissolved. When each solid component, S_8 (to the left edge) and Li_2S (to the right edge), is saturated, a bi-phase region can be found. Following the trajectory of line A, a conventional discharge profile with a distinct two plateau behavior can be expected according to Nernst equation, as depicted in Fig. 12d. With a higher polysulfide concentration in electrolyte, trajectory of line B, both upper and lower plateau may be longer. When the initial polysulfide concentration reaches to its saturation point (~6.3 M), trajectory of line C, the discharge potential will be constant according to the Nernst equation, illustrated as profile C in Fig. 12d. Based on this ternary phase diagram, SSDC reaction in Li-S batteries can be relized by reducing the amount of solvent. The explanation is in accordance with the results from reference [149], and [152]. Although the studies discussed here are all on ether-based electrolytes, however, the results can be expanded to the carbonate-based Li-S batteries as well. These studies confirm that by engineering electrolyte composition and structure, different reaction pathways could be achieved. This difference in electrochemical pathways relies on isolating the redox reaction of sulfur in the cathode from electrolyte solvents.

Based on this difference, two different approaches can be used to tune the electrolyte structure of carbonate-based electrolytes to enable SSDC reactions without modifying the electrode, e.g., using sulfurized carbon/polymer or UMC cathodes. The first approach is to use concentrated electrolytes, without presence of any free solvents to interact with sulfur cathode. The second approach is to design electrolytes which can form a stable CEI layer on sulfur cathode, preventing the contact between sulfur and carbonate solvents.

4.1. *Concentrated electrolytes*

In concentrated electrolytes, the content of free solvent (here, the reactive carbonate species) is limited. The conventional electrolyte design relies on only two factors, namely salt, and solvent chemistries. On the other hand, highly concentrated electrolytes are more complicated due to addition one more factor: concentration. By increasing the Li salt concentration, unusual physicochemical and electrochemical properties appear in these electrolytes originating from the three-dimensional solution structure. These properties are non-flammability, high rate capability, elimination of side reactions, suppression of dendrite formation, and high energy density [153,154]. Fig. 13a shows the difference between a dilute (conventional) and concentrated electrolytes. In the dilute electrolyte, each Li^+ ion is coordinated with 3–4 solvent molecules, and is surrounded by free solvents and solvent separated ion pairs [153]. On the contrary, in a concentrated electrolyte, this number is reduced to 1–2, and the salt anions enter the solvation sheath to form contact ion pairs and cation-anion aggregates. This happens because there is no free solvent available in the concentrated electrolytes. The difference in the solvation structure of the electrolytes results in different properties and different solid-electrolyte interphase (SEI) formation mechanism. The SEI formed in a dilute electrolyte is a result of solvent decomposition whereas the SEI formed in a concentrated electrolyte is a result of salt anion decomposition reaction.

Based on the previous discussion, a key strategy to use carbonate-based electrolytes relies on preventing a direct interaction between

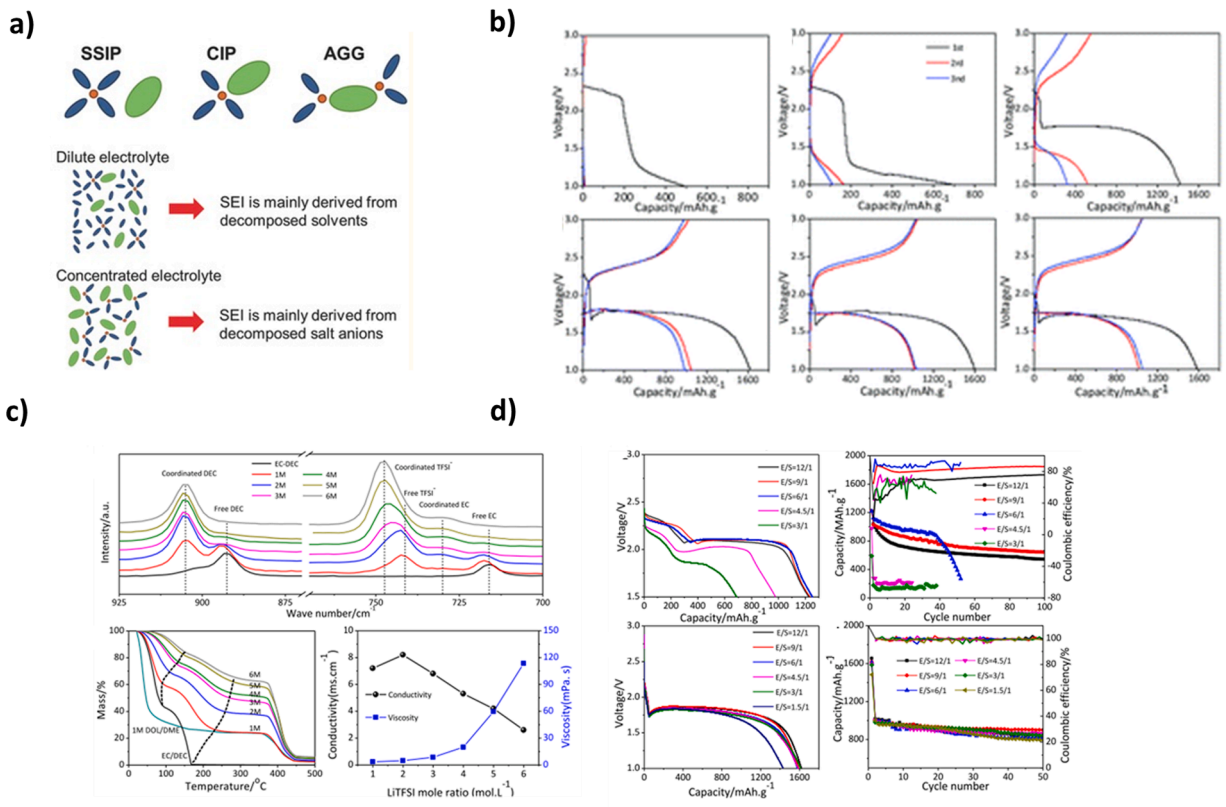


Fig. 13. a) Lithium ion solvation in dilute and concentrated electrolytes, Reproduced with permission from Zheng [153]. Copyright (2017), Wiley & Sons, Inc. b) First discharge voltage profile of cells using carbonate electrolyte with different concentration (1 M, 2 M, 3 M, 4 M, 5 M, and 6 M) of salt. Reproduced with permission from Huang [155]. Copyright (2019), Royal Society of Chemistry. c) Raman spectra of the electrolytes showing the coordination structure, TGA curves of the electrolyte in Nitrogen atmosphere, conductivity, and viscosity of the carbonate electrolytes. Reproduced with permission from Huang [155]. Copyright (2019), Royal Society of Chemistry. d) Cycling performance of Li-S batteries with varied E/S ratios at the rate of 0.2C. Reproduced with permission from Huang [155]. Copyright (2019), Royal Society of Chemistry.

the carbonate solvents and polysulfides. A report published by Huang et al., suggested that sulfur cathodes, without any modification, can be compatible with carbonate-based electrolytes when concentrated electrolytes are used [155]. This group used the commercial Ketjen black with mesopore-dominant pore structure to embed sulfur. In this cathode, sulfur is exposed to the electrolyte, therefore the soluble LiPSs irreversibly react with carbonate species triggering electrolyte decomposition (see Fig. 13b). However, they found that amount of free solvent (un-coordinated) molecules such as EC^-, DEC^- and $TFSI^-$ dramatically decreases by adding more lithium salts (increasing the salt concentration from 1 M to 6 M). As shown in Fig. 14c, Raman spectroscopy can confirm that the concentration of EC^-, DEC^- and $TFSI^-$ species is very low. Moreover, using NMR they confirmed that the peaks from ethylene glycol, and thiocarbonate, from the side reaction between carbonate solvents and the PS anions, are not present. These results indicate that modifying the coordination structure of carbonate-based electrolytes enables the use of conventional sulfur cathode, without the need to design complicated cathode structure. In addition to enabling the reversible reaction in Li-S batteries in presence of carbonate electrolyte, this paper has two other important takeaways. It is revealed that highly concentrated carbonate electrolytes with viscosity-lowering additives, such as hydroflorinated ether (HFE), can efficiently decrease the E/S ratio to 1.5 $\mu L/mg_S$ as shown in Fig. 13d. Note that a low E/S ratio is necessary to achieve higher gravimetric energy density than that of the commercial Li-ion batteries (~200 Wh/kg_{cell}) [156]. Moreover, using Li-Li symmetric test, it is shown that the concentrated electrolyte can modify lithium electrodeposition and dendrite growth. The role of concentrated electrolytes in improving Li metal performance will be discussed in Section 5. The last point we would like to make here is that the formation of a CEI layer on the cathode is shown when concentrated electrolyte is used. Using XPS, formation of thiocarbonates was confirmed; and attributed to the reaction of polysulfide formed in the first discharge with the coordinated carbonates. The presence of LiF in the CEI structure can be attributed to the decomposition of $TFSI^-$ anion. Followed by this study, Huang et al. used a CMK-3/sulfur composite, with 65 wt% of sulfur, as cathode material.. They used the concentrated electrolyte concept with LiFSI and LiTFSI dual salt dissolved in EC/DEC/FEC solvents. The XPS result presented in this study also confirmed the formation of a CEI layer on sulfur cathode [157]. In summary, by using concentrated electrolytes not only deactivation of the sulfur cathode is resolved, but also the chemical reactivity between Li metal and carbonate solvent can be suppressed. However, despite the advantages, there are still many challenges to overcome in terms of the poor ionic conductivity originating from the high viscosity, investigation of a diluent agent reducing viscosity, and most importantly the high production cost from the increased amount of salt used in the electrolyte.

Introducing diluent with low donor number and dielectric constant is a way of improving the ionic conductivity and wettability. In this regard 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE) has been used in Li-ion batteries [158,159]. Most recently He et al., developed a localized high concentration electrolyte system [160]. They showed that by reducing the activity of the free solvents in this system, the charge-discharge mechanism of the Li-S battery can be altered with a solid-solid conversion route. This required using high concentration (7 M) of salt in carbonate electrolytes. They demonstrated that by addition of an inert solvent, TTE, the concentration of salt in electrolyte can be reduced from 7 M to 1.5 M, significant increasing the ionic conductivity

of the electrolyte. In addition, they showed that in the first discharge, a CEI layer is formed on the sulfur cathode that prevents further reaction between carbonate solvents and nucleophilic anions, forcing a direct conversion from S_8 to Li_2S. The CEI formation on sulfur cathode is a major part of invoking SSDC reactions and should be discussed in more detail.

4.2. Formation of a CEI layer

A very important approach in preventing the direct interaction between carbonate species and sulfur is the formation of a passivation layer on the sulfur cathode. Although most studies refer to this layer as "SEI," here we chose to use the term "CEI" to differentiate between the coating layer formed on anode and cathode side. This concept relies on the QSS reaction, discussed in Section 3.2, as the interaction between carbonate solvents and polysulfide anions is prevented by formation of a solvent deficient environment. The role of a CEI layer is essentially the same as the preformed layer concept (see Section 3.3). However, because this layer is formed in situ, as a result of electrolyte modification, it does not require any sophisticated cathode modification, and therefore it is more practical.

D. Aurbach's group reported the positive effect of CEI formation in invoking the QSS and as a result, SSDC reactions [59]. In their first study, they used ionic liquid (IL) electrolyte with LiFSI and LiTFSI salt. They observed a single plateau discharge profile when LiFSI salt was used. It is worth mentioning that the carbon host used in this study contained pores with pore size>2 nm. Therefore, the single plateau behavior was not originated from the de-solvation of Li^+ ions as a result of using UMCs, as discussed in Section 3.2. Based on previous literature, the CEI formed was attributed to the reaction between LiFSI salt and Li_2S_2, according to the following reaction:

$$(LiFSI)_2 + Li_2S_2 \rightarrow LiNS(O_2)S - SS(O_2)NLi + 2LiF$$

It is important to note that based on results of this study, a cut-off voltage of 1.4 V is required for the CEI formation. Moreover, the authors concluded that the FSI^- anions play a significant role on CEI formation, as shown in the equation above. After a galvanostatic preformation step of CEI layer in ionic liquid-based electrolyte containing LiFSI, the cathode was tested in the carbonate-based electrolyte (propylene carbonate, PC) as well as ether-based electrolyte (Fig. 14).

Following this study, the same group showed the positive effect of fluorine-rich additives, such as FEC, on the formation of CEI layer, while many papers dealing with FEC additives in Li-S batteries have emphasized on the formation of a protecting layer on the Li metal anode [78] [79]. Table 3 shows a summary of experiments carried out by this group. This table clearly shows that several factors, such as cut-off voltage, type of salt anion, and additives, may contribute to the CEI formation. It is worth mentioning that the CEI formed in the IL electrolyte (Fig. 14b and e) is stable in carbonate-based electrolyte (Fig. 14c). However, the same CEI is not stable in the ether-based electrolyte, and a mixed behavior is observed (Fig. 14f).

Even though the approaches leading to formation of the CEI layer have still not been well understood, the role of this layer can be explained: Similar to the pre-formed layer, which works as a thin Li^+

Table 3
Summary of results from reference [58,59].

Cathode	Salt	Electrolyte type	Cut-off voltage (V)	Result
Fresh	LiTFSI	IL	1.7/1.4	Cell did not perform well
Fresh	LiFSI	IL	1.7	Cell did not perform well
Fresh	LiFSI	IL	1.4	Single Plateau was observed
Fresh	LiFSI	Carbonate (PC)	1.4	Failed in first cycle
Preformed CEI using IL	LiFSI	Carbonate (PC)	1.4	Single Plateau was observed
Fresh	LiFSI	Carbonate (PC)	0.5	Single Plateau was observed
Fresh	LiFSI	Carbonate (PC) + FEC	1	Single Plateau was observed
Fresh	LiFSI	Ether (DME: DOL)	1.4	Two Plateau was observed
Preformed CEI using IL	LiFSI	Ether (DME: DOL)	1.4	Mixed behavior observed

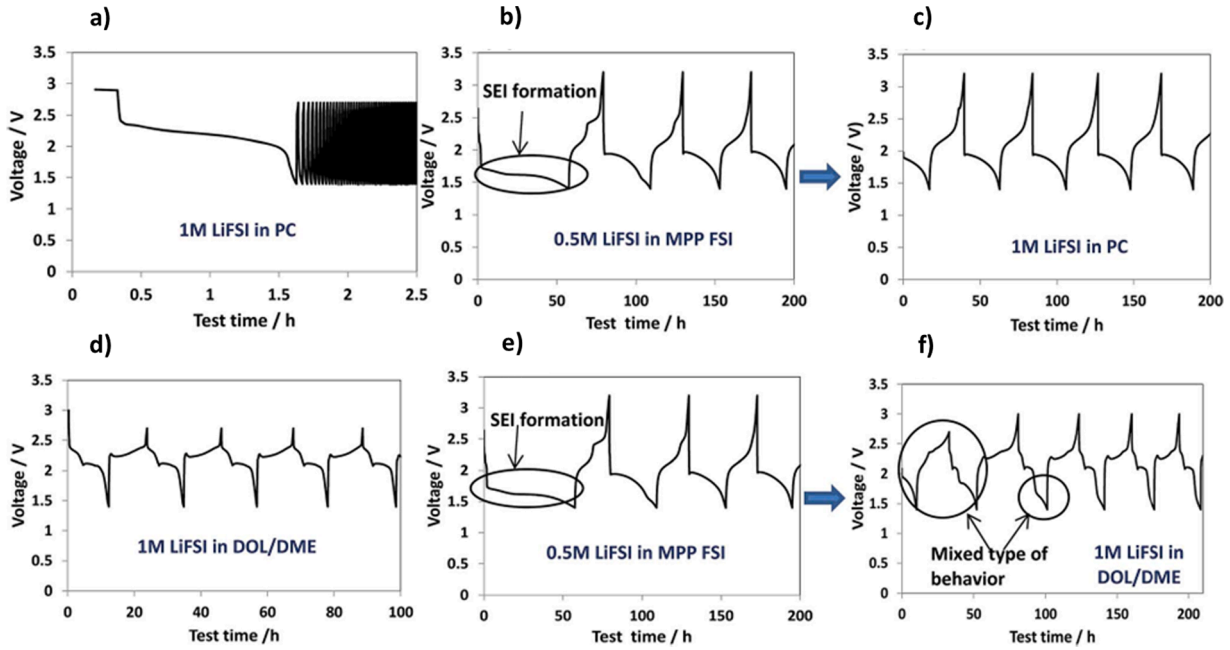


Fig. 14. a) Fresh electrode cycled in 0.5 M LiFSI in PC, b) Fresh electrode cycled in 0.5 M LiFSI in MPP FSI, c) electrode from part b cycled in PC electrolyte solution, d) Fresh electrode cycled in 1 M LiFSI in DOX/DME, and e) Fresh electrode cycled in 0.5 M LiFSI in MPP FSI, and (f) Electrode from part e cycled in DOX/DME electrolyte solution. Current density: 50 mA/g_{sulfur}, 30 °C. Reproduced with permission from Markevich [59]. Copyright (2015), Royal Society of Chemistry.

conducting membrane, the CEI can filter out the free solvent molecules. Therefore, the SSDC reaction pathway is relized since these interface structures are similar to that of solid-state electrolytes, discussed in section 2.2.

In this regard, Xia et al., also proposed a new strategy to coat the sulfur cathode by a thin layer of CEI, to prevent the reaction between carbonate solvents and polysulfides anions. They used a carbonate/ether co-solvent electrolytes, more specifically, 1 M LiTFSI in DME/DOL as the ether electrolyte and tested variety of the organic carbonate solvents such as VC, DMC, and FEC as cosolvents. They hypothesized that the solid-solid conversion reaction achieved using this electrolyte is because of the formation of in-situ CEI in the first cycle. This CEI is formed as a result of the reaction between carbonate solvents and polysulfide anions (generated in first discharge in ether electrolyte) [161].

Although these studies show the effect of CEI formed on the cathode, however, the formation mechanism, designing the optimal CEI layer, and sulfur loading amount in the carbon matrix have not been studied yet. We believe that the CEI formation can be used as a method to increase the sulfur wt% on the cathode side, but systematic experimental and fundamental modeling investigations are required to optimize this layer.

5. Lithium metal anode in carbonate electrolyte

Lithium metal is known as a "Holy Grail" electrode material for battery applications [162]. Lithium is the world's lightest alkali metal with a high theoretical capacity of ~3860 mAh/g and the lowest electrochemical potential of −3.04 V with respect to the Standard Hydrogen Electrode (SHE) (see Fig. 15a) [15,163]. The overall reaction of Li metal in Li-S batteries is:

$$Li^{+} + e^{-} \rightarrow Li$$

The challenges facing Li metal research largely arise from the highly reactive nature of the Li metal (see Fig. 15b) [73,164]. This means that lithium reacts with most solvents used in the battery; leading to two key challenges:

1 Lithium dendrite formation, which can lead to internal short circuit of the battery. This internal short circuit can cause safety hazards because of thermal runaway and electrolyte combustion, leading to cell explosion [165,166].
2 Formation of porous lithium layer, which not only increases the contact between solvents and fresh Li, but also would result in formation of an electrochemically dead Li layer. This leads to electrolyte depletion in the cell. Moreover, the dead layer formed on top of fresh lithium can make the Li^{+} ion diffusion harder, leading to increase in cell resistance. All these scenarios will eventually lead to low coulombic efficiency and large polarization in the cell [37,167].

It is worth mentioning that all the challenges presented in this section become bolder under practical conditions, where harsh currents, lean electrolyte condition, and thin Li must be used to achieve the desired high energy density Li-S batteries. Based on these challenges, it is important to effectively regulate Li deposition and minimize dendrite formation, and growth in Li metal batteries. Any negligence would result in serious safety problems and low cycle life of the battery. Although understanding of the fundamentals of nucleation, formation and growth of dendrites in Li metal batteries is critical, however, it does not fit the scope of this review paper, and the readers are encouraged to read the review paper recently published by Cheng et al. [163]. Despite severe challenges associated with the lithium metal anode, to date, there are very limited studies on stabilizing the Li metal anode specifically for Li-S batteries [164]. However, a key advantage of using carbonate electrolyte in Li-S batteries, is that we can leverage the research on stability of lithium anode in lithium metal batteries (typically with transition metal oxide-based cathodes) with commercial carbonate electrolytes owing to their compatibility with Li-ion transition-metal oxide-based cathodes. Therefore, in this section, we will review the most relevant literature and concepts related to Li metal batteries in presence of carbonate-based electrolytes; when available, we will also discuss the relevant literature from Li-S battery research. We would like to start with a brief discussion on the SEI formation, structure and composition in presence of carbonate electrolytes and then we will summarize various methods in literature to reduce lithium dendrite formation to ensure long-term and safe cycling of batteries using carbonate-based electrolytes.

5.1. SEI structure and characteristics in carbonate-based electrolytes

The concept of solid electrolyte interphase (SEI) was first introduced in 1979, as an electronically insulating layer, similar to solid electrolyte, which acts as an interphase between the metal and solution [168]; and ideally prevents further reaction between the electrode and electrolyte. The high reactivity of Li metal becomes more important in carbonate-based electrolyte compared to the commonly used ether electrolyte in Li-S batteries [169]. Thats because ether electrolytes with DME and DOL solvents form a relatively stable SEI on Li metal through the polymerization of DOL and use of $LiNO_3$ additive [20,170]. Heterogeneous deposition of lithium, dendrite nucleation and formation of mossy-like, dead lithium is believed to be related to the characteristics and the quality of the SEI formed as a result of electrolyte/Li metal reaction. It is important to note that the efficiency of the SEI layer on Li metal anode is governed by the carbonate electrolyte composition. If the SEI layer is not designed properly, the spontaneous SEI formed because of the contact between carbonate electrolyte and Li metal anode will lead to an unstable SEI. Fig. 16a shows a schematic of SEI formation in liquid electrolyte proposed by Goodenough et al. [171], using the electrochemical potential of the anode (μ_a) and cathode (μ_c), voltage

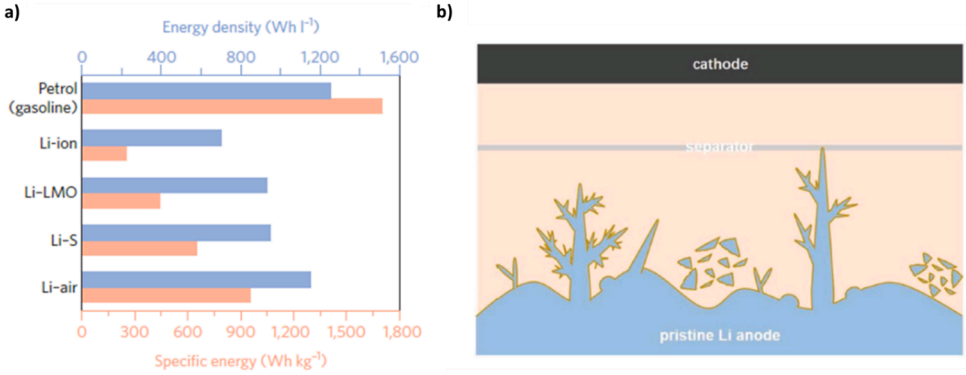


Fig. 15. a) Li metal anodes apportunities. Reproduced with permission from Lin et al. [15]. Copyright (2017), Springer Nature. and b) Schematic showing the failure mechanisms of Li metal anodes. Reproduced with permission from Guan [167]. Copyright (2018), Wiley & Sons Inc.

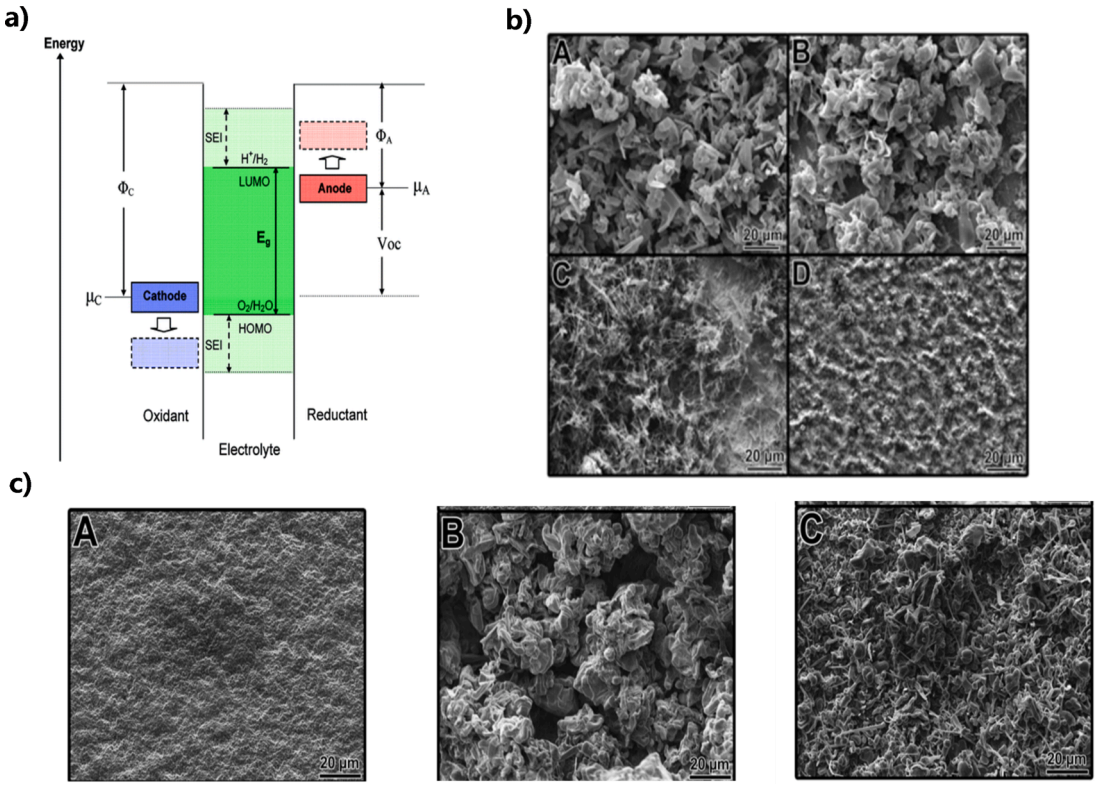


Fig. 16. a) Schematic showing the relative electron energies in a thermodynamically stable battery cell, proposed by Goodenough et al. Reproduced with permission from Goodenough et al. [171]. Copyright (2009), American Chemical Society. b) SEM images of Li deposition in presence of 1 M $LiPF_6$ salts and PC, EC, DMC and EMC solvents. Reproduced with permission from Ding [173]. Copyright (2013), The Electrochemical Society. and c) SEM images of Li deposition showing the morphology of Li deposits in 1 M $LiPF_6$ salts with VC, FEC, and VEC solvents. Reproduced with permission from Ding [173]. Copyright (2013), The Electrochemical Society.

corresponding to the lowest unoccupied molecular orbit of the electrolyte (E_{LUMO}), and voltage corresponding to the highest occupied molecular orbit (E_{HOMO}) of the electrolyte [171]. As presented in Fig. 16a, if $\mu_a > E_{LUMO}$, then the electrons on anode tend to move to the unoccupied orbital of the electrolyte. This results in reduction of electrolyte on anode, and as a result the SEI layer is formed. Due to the very high reactivity of Li metal, the formation of a stable SEI layer is beneficial as it will prevent the immediate reaction (time constant: milliseconds or less) and exposure of the bulk Li metal to the electrolyte. Because the SEI composition and morphology strongly depends on the electrolyte composition, it is important to understand the difference that solvents and salts can make on the SEI layer and long-term cycling of a Li metal battery. Aurbach et al. investigated the composition of the SEI formed in PC using FTIR and XPS [172]. They found that PC solvent can undergo a one-electron reduction reaction with Li metal followed by free radical termination reactions. Later, Ding et al., designed series of systematic experiments to investigate the difference in morphology and composition of carbonate-based electrolytes [173]. In this study, 1 M $LiPF_6$ salt was dissolved in EC, PC, DMC, EMC, VEC, VC, and FEC carbonate solvents and used as electrolyte in a Li/Cu cell, to study the morphology of the Li deposition on Cu substrate. Fig. 16b and c shows the SEM result of this study [173]. Morphology of the deposited Li on Cu substrate was found to be different in cyclic carbonates (PC and EC, Fig. 16b), compared to the linear carbonate solvents (DMC and EC, Fig. 16c). In cyclic carbonate a conformal coating of thick clusters were found, whereas in linear carbonates the deposited Li was more fibrous, and not conformal. Moreover, by comparing FEC, VC and VEC solvents, which are mainly used as additives in other studies, it was concluded that the formation of the dendrite is possibly prevented by the SEI formation in VC solvent. This was attributed to the positive effect of polymerization of VC on Li metal surface, which significantly enhances the quality of the SEI film. Moreover, the average coulombic efficiency of various solvent used in this study was calculated to be: PC (76.5%), EC (94.8%), DMC (23.6%), and EMC (7.3%). The result of this study clearly shows the advantage of using cyclic carbonate solvents, specifically ethylene carbonate, with a very high columbic efficiency. Moreover, the coulombic efficiency of the other carbonate solvents, VC (97.1%), FEC (98.2%), and VEC (97.6%), showed the potential of using such solvents as additives to enhance the cycling performance of the Li metal battery. This study showed that various salt and solvents could have a tremendous effect on the morphology and efficiency of deposited lithium. In this regard, Nuli et al. investigated the compatibility of two different carbonate electrolytes with SPAN cathode and Li metal used in Li-S batteries [174]. The Li metal plating/striping test using Li/Cu cells, cycling stability of Li-S batteries, EIS studies and the morphology of the Li metal after cycling show that the new carbonate electrolyte system with LiFSI salt in EMC/FEC carbonate electrolyte can improve the efficiency of Li metal in Li-S batteries. Fig. 17a shows the Li/Cu stripping/plating test results from this study. Based on these results, the cell lasted for 1000 cycles when 1 M LiFSI salt in EMC/FEC was used. Moreover, as shown in Fig. 17b the cycling stability of the Li-S battery is significantly enhanced in presence of 1 M LiFSI salt in EMC/FEC electrolyte. This cell achieved an outstanding discharge capacity of 1270 mAh/g after 1000 cycles at C/2 rate. We would like to emphasize that FEC additive can form stable interphase on the anode side as well as cathode side, therefore, FEC has a very positive effect on the cycling stability of Li-S batteries. Fig. 17c is the schematic from a study by Wang et al., where the effect of using FEC as cosolvent was investigated using SPAN cathode. This group reported a very stable cycling (~4000 cycles at 6C) of SPAN cathode when FEC was used as cosolvent [175]. Moreover, Fig. 17d shows the morphology of Li metal using digital images and SEM pictures with and without FEC cosolvents. This study clearly shows the importance of solvent

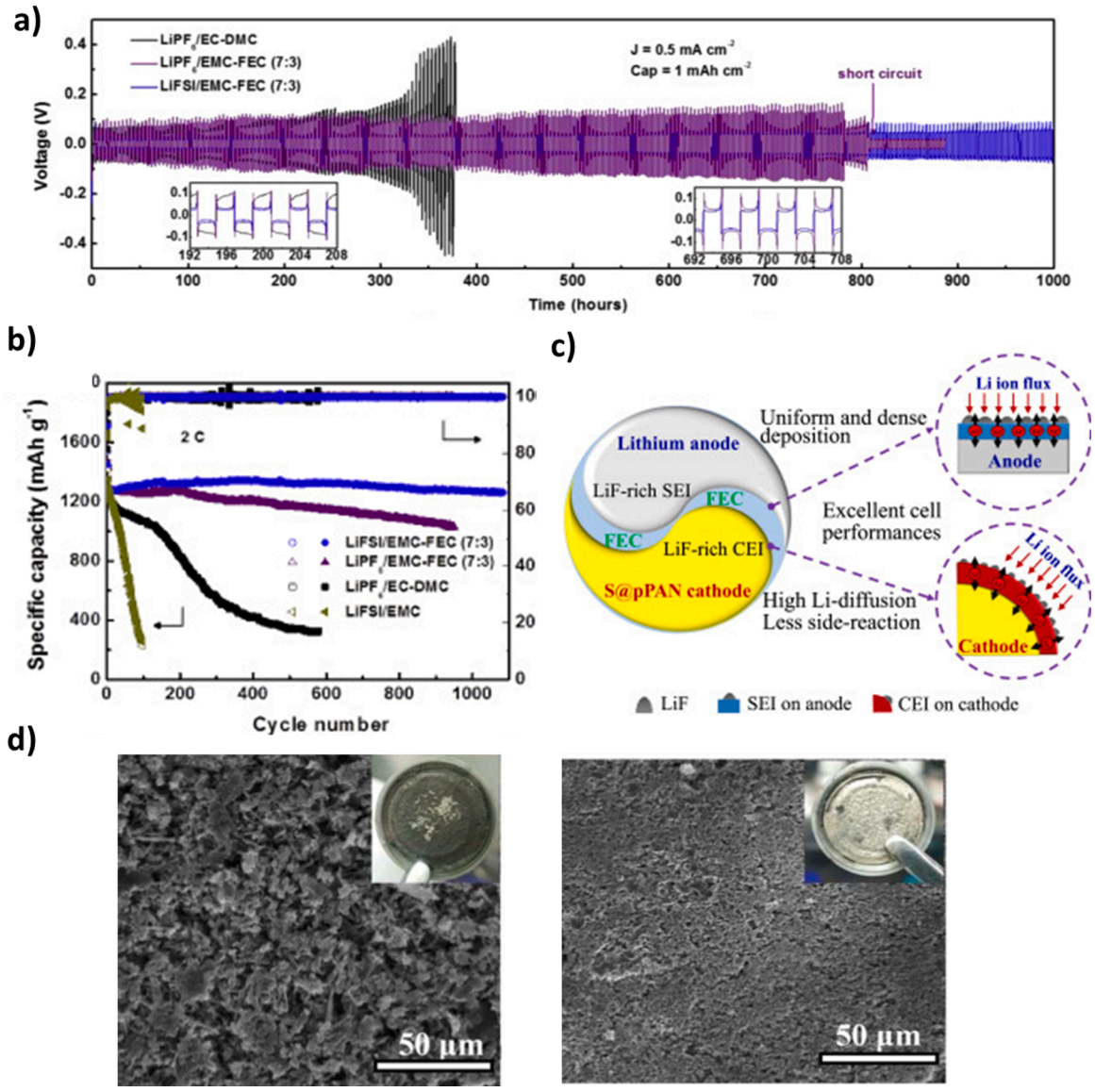


Fig. 17. a) Potential profile of Li/Li symmetric cells at 0.5 mA/cm^2, showing the effect of solvents used in carbonate electrolytes. Reproduced with permission from Chen [174]. Copyright (2018), Elsevier. b) Cycling stability performance of Li-S battery with SPAN cathode and Li metal anode in presence of different electrolyte systems. Reproduced with permission from Chen [174]. Copyright (2018), Elsevier. c) Schematic illustration showing the role of FEC cosolvent on the performance of Li-S batteries with SPAN cathode and carbonate electrolytes. Reproduced with permission from Yang [175]. Copyright (2018), Elsevier. and d) SEM and digital pictures of the Li electrodes recovered from Li/Li cells cycled at 1 mA/cm^2 after 100 cycles in EC-based electrolytes on the left and FEC-based electrolyte on the right. Reproduced with permission from Yang [175]. Copyright (2018), Elsevier.

optimization for Li-S batteries in presence of carbonate electrolytes.

So far, we have discussed the importance of solvent selection on SEI formation in carbonate electrolytes. The ideal SEI [176] [37,165] on Li metal anode must have characteristics such as: a) high ionic conductivity towards Li^+ ions, to reduce diffusion resistance, 2) negligible electronic conductivity to avoid Li deposition on SEI layer itself, 3) proper thickness, thin SEI can allow electron transfer between electrolyte and Li metal, however, it can be easily ruptured during cycling, on the other hand, a thick SEI layer might impose diffusion limitations, 4) Strong mechanical stability and flexibility to adjust to the volume changes during cycling, and 5) Stability in morphology, composition and chemical structure.

Knowing the characteristics of an ideal SEI, different techniques have been employed to increase the efficiency, reduce, and control dendrite formation. Fig. 18 summarizes the approaches used in the literature [37]. Overall, Li metal protection using SEI formation is divided to two main categories, SEI formation by electrolyte additives (in-situ), and pre-formed SEI on Li metal (ex-situ). These two approaches along with other methods will be discussed in next section.

5.2. Designing a safe, and stable Li metal anode

5.2.1. Engineering in/ex situ SEI layers

As mentioned before, the SEI formed in presence of carbonate electrolytes is not as homogenous as ether-based electrolytes [172]. Electrolyte additives can be used to form a stable SEI layer and control the reactions between Li metal and electrolyte solvents. Ideally, additives should be reduced before the electrolyte solvents to enhance the homogeneity of the SEI formed. Therefore, the additive must have lower LUMO (higher HOMO) compared to the solvents and salts used in the electrolyte [171]. These type of additives are known as self-sacrificing additives, as they are continuously consumed in each cycle, forming a protecting layer on Li metal. $LiNO_3$, commonly used in ether-based Li-S batteries, is a perfect example of such additive that can form a flexible

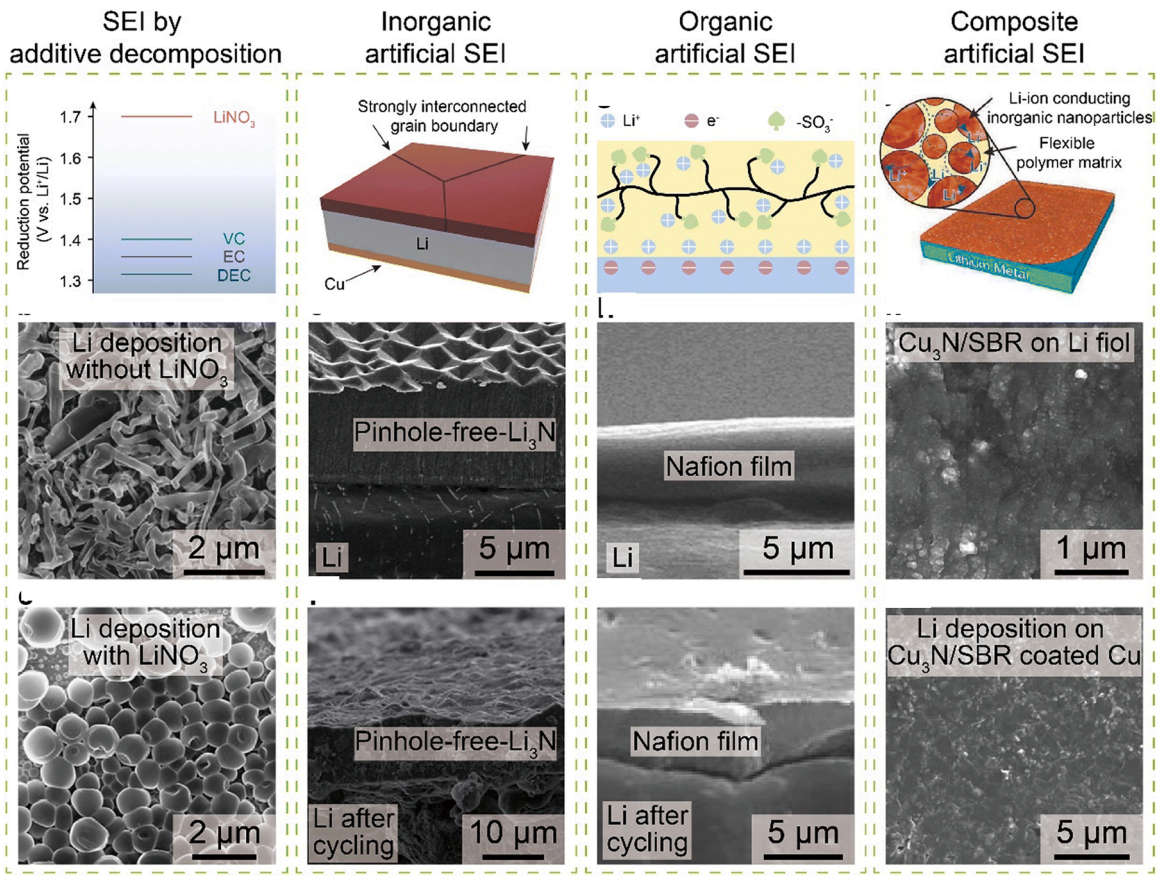


Fig. 18. Various approaches for SEI foramtion on Li metal. Reproduced with permission from Wang [37]. Copyright (2019), Springer Nature.

SEI on Li metal. Additives such as FEC and VC, commonly used in carbonate electrolytes, also belong to the category of self-sacrificing additives [177–179]. FEC can form stable SEI on Li metal and prevent the reaction between electrolyte solvent and Li metal. This happens because FEC has lower LUMO compared to carbonate solvents (−0.87 eV for FEC, vs. −0.38 eV for EC and 0 eV for DEC). To form this stable SEI, C-F bond in FEC breaks and forms LiF-rich SEI layer on Li metal. The LiF layer formed on Li metal is electronically insulating and has low diffusion energy barrier for Li ions, enhancing Li ion diffusion. On the other hand, because of the presence of unsaturated carbon double bonds in structure of VC solvent, it can easily undergo ring-opening polymerization and form SEI on Li metal. The SEI formed contains poly-vinylene carbonate, oligomeric VC, and a ring-opened polymeric form of VC. The SEI formed using these two additives can have a tremendous effect on reducing the unwanted side reaction and electrolyte depletion, and can greatly increase the coulombic efficiency. Very limited studies have been carried out using FEC, VC/ tris(trimethylsilyl) phosphite, tris(trimethylsilyl)borate (TMSB), phospourous rich additives such as dimethyl methylphosphonate (DMMP) [64], tris(2,2,2-trifluoroethyl) phosphite (TTFP) [65], triphenyl phosphite (TPPi) [66], triethyl phosphate (TEP) [51], and tris(trimethylsilyl) phosphite (TMSP) with SPAN cathode using carbonate electrolytes.

Another approach to increase the coulombic efficiency of Li metal is by forming artificial SEI via physical or chemical pre-treatment of the Li metal. The chemical pre-treatment can be achieved using different gasses such as O_2, N_2, CO_2, F_2 and SO_2. Different liquid media is also used to pre-form SEI on Li metal. For example, a stable SEI was electroplated on Li metal in LiTFSI (1.0 M)-$LiNO_3$ (5.0 wt%)-Li_2S_5 (0.02 M)-based-electrolyte [180]. Based on XPS results, composition of the pre-formed SEI layer included organic composites of $ROCO_2Li$, ROLi, and inorganic composites of Li_3N, $Li_2N_xO_y$, LiF, Li_2S_x, and $Li_2S_xO_y$. The modified Li metal was then tested in ether electrolyte using sulfur cathode and in carbonate electrolyte using NMC cathode. Coulombic efficiency of 99% for celsl using carbonate electrolyte was maintained when the pre-treated Li was used, on the other hand, coulombic efficiency of the cell with bare Li metal sharply decreased from 97% to 82%. Another example of ex-situ formed SEI is reported by Yan et al., where the artificial SEI layer is formed by simply soaking Li metal in FEC solvent [181]. Two layers are formed as a result of the reaction between FEC and Li metal. An inorganic layer (LiF, Li_2CO_3) on Li metal and an organic layer (ROLi, $ROCO_2Li$) close to the electrolyte. The inorganic layer formed on Li metal facilitates ordered nucleation and prevents dendrite formation and growth, while the organic layer formed on top of the inorganic part forms a flexible layer to prevent damages arising from battery cycling. Another approach to protect Li metal is using interlayers between separator and Li metal or physical treatment of the Li metal. Xu et al., synthesized and tested an artificial protective layer composed of poly(vinylidene-co -hexafluoropropylene) (PVDF-HFP) and LiF, and used it as an interlayer, see Fig. 19a [180]. Although the film used in this study had a very good mechanical modulus, however the addition of the interlayer to the system can increase the internal resistance of the battery. The physical pretreatment of SEI using amorphous hollow sphere carbon was carried out by Cui et al., using this artificial SEL layer, very high mechanical module of 200 GPa is achieved [182]. The thin layer of this pre-formed SEI (~20 nm) does not change the internal resistance of the battery.

5.2.2. *Other approaches*

In addition to the SEI formation approach, used to control the contact between electrolyte solvents and Li metal, other approaches have been investigated. A summary of these techniques is presented here.

Alkali cations such as Cs^+ and Rb^+ were used as additives [183]. As

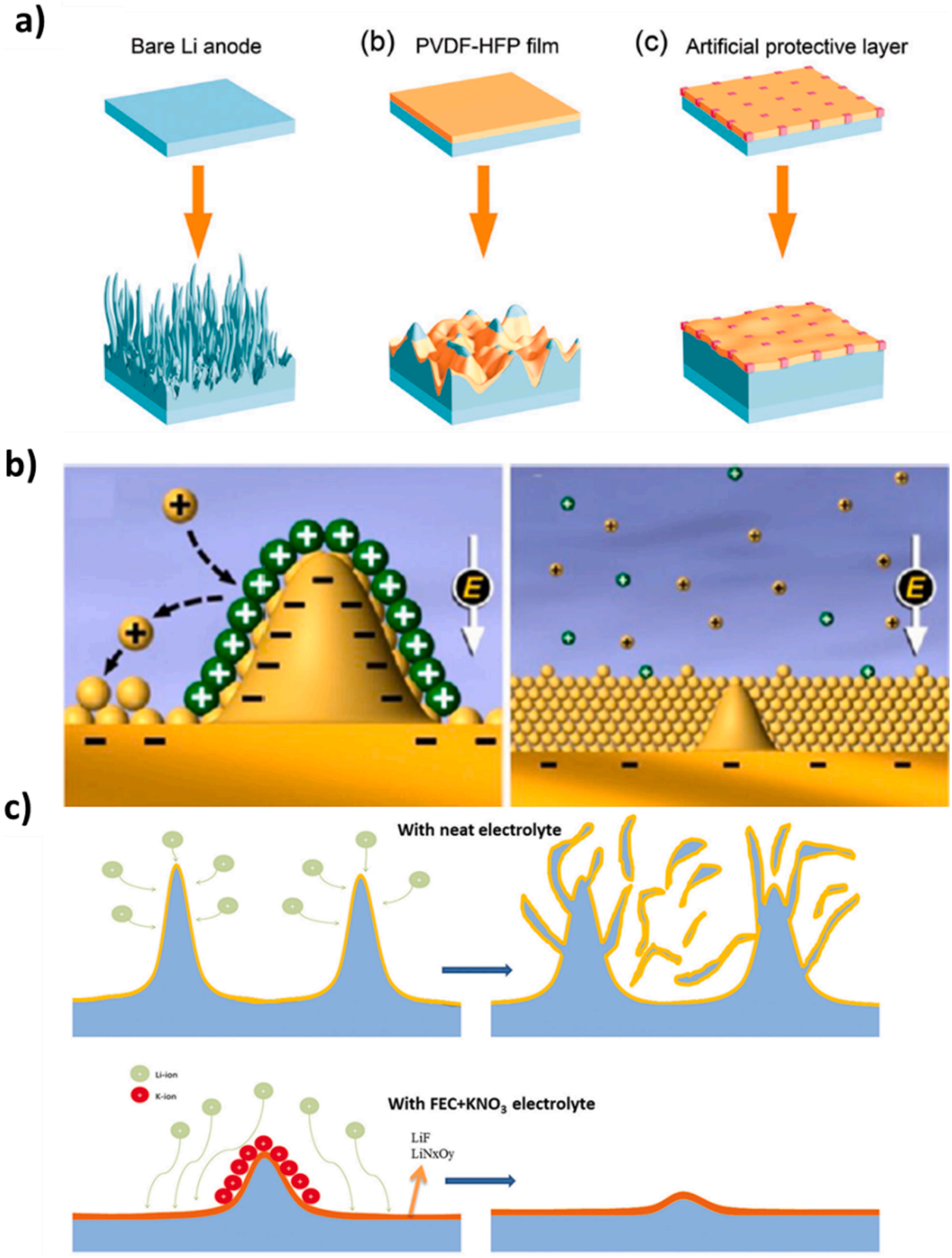


Fig. 19. a) Illustration of pre-formed SEI layer of PVDF-HFP on the Li metal. Reproduced with permission from Xu [180]. Copyright (2018), Wiley & Sons Inc. b) Schematic of Li deposition based on the self-healing electrostatic sheild mechanism. Reproduced with permission from Ding [183]. Copyright (2013), American Chemical Society. and c) Illustration of Li plating with and without FEC+ KNO_3 addiitves. Reproduced with permission from Shuai [186]. Copyright (2019), Royal Society of Chmeistry.

shown in Fig. 19b, because of their lower reduction potential compared to Li^+, they are not reduced on Li metal surface. Instead, these additives help in conformal Li deposition by "self-healing electrostatic shield mechanism". This mechanism relies on formation of a positively charged shield around the initially formed tip (dendrite), preventing further Li deposition on that tip. This forces the Li^+ ions to deposit near the initially formed tip, resulting in uniform deposition of Li metal. The metal cations used in forming the electrostatic shield is not consumed during cycling and it protects the Li tips from growing and puncturing the separator. Followed by this study, other cations such as K^+, Ca^{2+},

Ba^{2+}, Na^{+} were studied as additives to enhance the cyclability and safety of Li metal in carbonate electrolytes [184,185]. Although this method can improve the cycle life of a Li metal battery and can reduce the risk of dendrite growth, however, the reduction potential of the Cs^{+} cations are close to the Li^{+} ion [73]. For this reason, it is possible that under high current densities, Cs^{+} may co-deposit with Li^{+} ions. Moreover, although these additives can help reduce dendrite growth and facilitate uniform Li deposition in the discharge of a battery, however, the unwanted reactions between Li metal and solvents will continue to happen. For this reason, the second type of additives introduced in this section can be beneficial. The in-situ formed SEI discussed above can help in stabilizing Li metal in carbonate electrolytes. Although, as shown in Fig. 19c, an attempt by Shuai et al. was made to combine these two methods (using FEC as sacrificing additive and KNO_3 as self-healing electrostatic shield additive), however, based on the results reported, more elaborate research is required to evaluate the synergistic effect of this combination [186]. As shown in Fig. 19c, using this combination, a uniform SEI consisted of LiF and LiN_xO_y is formed on the anode. Moreover, K^{+} cations from a shield on the formed Li tip preventing dendrite growth.

Modifying Li metal morphology is another approach used in literature to enhance the cyclability of Li metal. As shown in Fig. 20, Li powder and patterned Li foil with microneedle surface can be used instead of planer Li foil [187]. The problem with this approach is that the modified morphology of Li disappears after several cycles [165]. Fig. 20b shows SEM pictures of fresh and cycled Li powder [188]. The enhanced coulombic efficiency in this study was attributed to the higher surface area of Li powder, lowering the overall current density. Although using Li powder instead of the foil prevents the formation of Li dendrites and increases the efficiency, however, the modified morphology is stable up to 100 cycles only. The SEM picture of the Li metal at 100th cycle shows that the 3D morphology of the Li metal disappears and a planer Li metal, similar to Li foil, conventionally used in batteries is achieved. Using concentrated electrolytes also helps in controlling the dendrite formation and growth. For example, Huang et al., showed the effect of concentrated electrolytes on the morphology and coulombic efficiency of Li metal [155]. Using the Li/Li symmetric cells, they showed that the concentrated electrolyte can modify Li electrodeposition and dendrite growth. Based on their results, dendrite morphology changed from needle-like to a nodule-like structure, and a flat voltage profile was observed when 6 M electrolyte was used. This led to a stable plating/striping over 1000 h The readers are encouraged to refer to the review papers such as [154] and [158] for a detailed discussion on the use of concentrated electrolytes for Li metal batteries.

As discussed above, very limited number of papers in Li-S battery field have focused on the use of carbonate electrolyte with regard to the challenges related to the Li metal. This originates from the fact that running sulfur cathode in carbonate electrolyte is challenging, as discussed in Section 2 of this paper. However, for practical applications, where high sulfur loading, high current density, and low E/S ratio are required, a comprehensive research is necessary to overcome the cycling stability challenge, and more importantly to address safety concerns related to the use of Li metal in Li-S batteries [189].

6. Concluding remarks and future perspective

In this review, we present a comprehensive summary on the use of carbonate-based electrolytes in Li-S batteries, see schematic 2. While tremendous attention has been given to ether electrolytes; carbonate electrolytes employed in commercial Li-ion batteries for three decades, are an ideal alternative candidate for commercialization of Li-S batteries. Moreover, Li-S batteries with carbonate electrolytes show stable long-term cycling. This is because the carbonate electrolytes in Li-S batteries introduce a different reaction pathway, which directly forms low-chain LiPSs without the formation of soluble long-chain LiPSs. Moreover, electrolyte additives used in carbonate electrolytes in Li-ion batteries can be directly applied to the Li-S battery technology. Therefore, there is a rising interest from Li-S battery research in academia and industry toward the use of carbonate-based electrolytes. However, despite the advantages and growing interest, there are challenges on development of Li-S batteries using carbonate electrolytes. Some of these challenges are: 1) The lower electrode potential in carbonate electrolytes compared to ether electrolytes, 2) The poor stability of the SEI formed in carbonate electrolytes leading to Li metal instability, 3) Their severe irreversible reactions with polysulfide anions. Based on these challenges we have organized this manuscript to provide a detailed discussion on the existing literature as summarized below.

The primary technical barrier in using carbonate electrolytes is the sudden degradation of cell performance originating from decomposition of carbonate solvents, via nucleophilic/electrophilic substitution reaction, with anionic polysulfides (see Section 1). We believe that there are two general requirements to suppress this reaction: 1) Reducing/eliminating the formation of soluble lithium polysulfides (cathode modification), and 2) Preventing the direct contact between sulfur cathode and carbonate solvents (electrolyte modification). In this regard, we have introduced the “solid-solid direct conversion reaction” (SSDC) of sulfur as key to successfully use carbonate-based electrolytes in sulfur batteries. Carbonate-based electrolytes may be successfully employed in Li-S batteries by modulating the electrochemical reaction pathway wherein

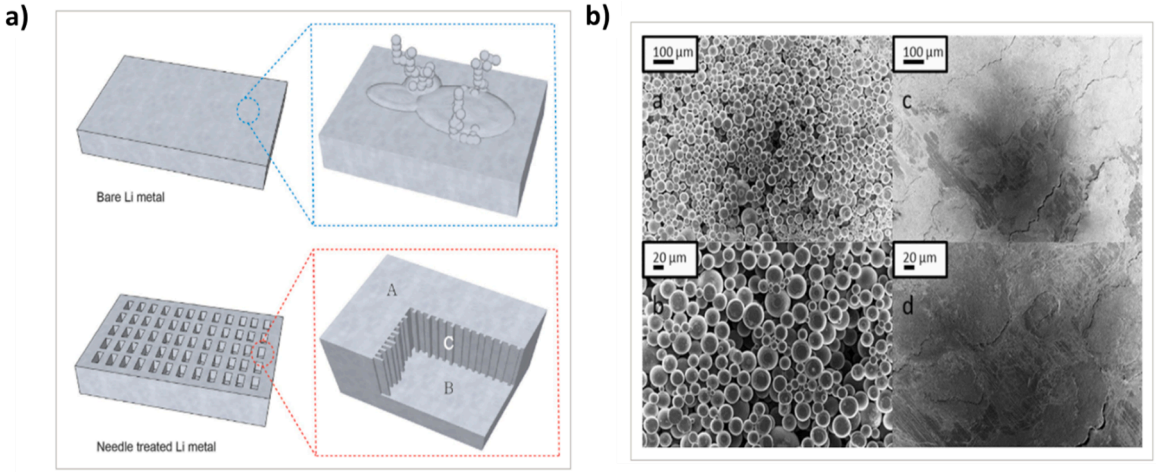
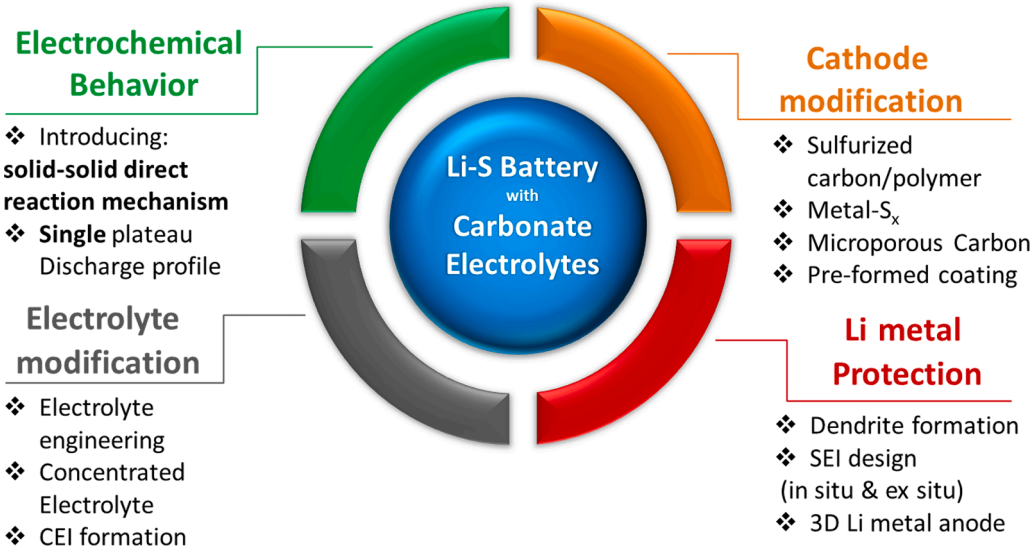


Fig. 20. a) Schemtic of Li plating-striping on bare Li metal comapred to the micro-needle treated Li metal. Reproduced with permission from Ryou [187]. Copyright (2014), Wiley & Sons Inc. and b) SEM images of Li metal powder before and after cycling. Reproduced with permission from Heine [188]. Copyright (2013), Wiley & Sons Inc.



Schematic 2. A summary of various approaches covered in this work.

the active sulfur material in the cathode is directly reduced to the short-chain LiPSs without the formation of high order LiPSs. Therefore, as a result of the SSDC reaction, the battery shows a single potential plateau during charge and discharge steps. As discussed in this paper, several modifications such as formation of S-X bonds and confinement approaches have been widely investigated to invoke the SSDC reactions. The idea behind these modifications is to immobilize sulfur atoms by covalent bonding, so that the formation of short-chain sulfur, the polysulfide formation is suppressed. Another approach used in literature is to design microporous carbon. Based on our analysis of the literature, although these two approaches enable the use of carbonate electrolytes in Li-S batteries, however, these strategies limit the maximum achievable sulfur wt% in the cathode, thereby limiting the practical achievable energy density. As a result, we believe that the majority of the work in the future must focus on the use of carbonate electrolytes with sulfur cathodes that enable high sulfur wt%, while preventing adverse polysulfide-carbonate reactions. In this regard, we propose that electrolyte modifications, such as concentrated electrolytes or optimized electrolytes with tailored properties must be pursued. Therefore, in Section 4, we emphasize on the proper selection of solvents and salts for carbonate-based electrolytes. For example, we have presented a case where the donor number and dielectric constant of the solvent is responsible for the changes in nature of the intermediate species formed. Moreover, the carbonate electrolyte used in Li-S battery field is simply adopted from Li-ion batteries. Given the differences in the working mechanism between Li-S and Li-ion batteries, the electrolyte optimization is an essential step toward employing carbonate electrolytes in Li-S batteries. It is also important to note that the electrolyte modification in terms of using high amount of salt or electrolytes with FEC additive or co-solvent impose cost concerns. Therefore, we believe that in future, the field must take a step further to integrate cathode modifications with electrolyte design to be able to achieve high energy density and low-cost carbonate-based Li-S batteries.

Finally, in the last section (Section 5) of this paper, we focus on challenges related to the anode side. We acknowledge that based on the reports in literature, carbonate electrolytes are more prone to dendrite, and formation of dead lithium compared to ether electrolytes. However, despite the growing attention in the literature to modify the cathodes for carbonate-based Li-S batteries, very limited attention has been given to the challenges related to the Li metal anode. Therefore, this section is dedicated to strategies that can increase the safety of Li-S batteries by controlling dendrite formation, based on the literature from Li metal batteries. To mitigate the undesirable reactions between the carbonate solvents and Li metal anode, designing a protective layer, ex-situ and/ or in-situ, on Li surface is recommended.

Although as discussed in this review article, the anode protection literature from Li metal batteries can be leveraged for the Li-S battery field, investigating the Li metal side, more specifically for sulfur-based lithium batteries is critical and is an important pre-requisite before Li-S batteries can be successfully commercialized.

In conclusion, the use of carbonate-based electrolytes in Li-S batteries can be considered a revolution in Li-S batteries because these electrolytes are practical and enable long-term cycling. Although there are several challenges left to be solved, we hope that this review paper draws the attention of scientists to fundamentally investigate the optimization of electrodes and electrolytes using sophisticated experiments, in-operando spectroscopic and microscopic tools, and theoretical simulation and modeling.

Funding

This work was funded by the National Science Foundation (NSF-1804374 and NSF-1938787).

CRediT authorship contribution statement

Ayda Rafie: Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **Jin Won Kim:** Writing – original draft, Supervision. **Krishna K. Sarode:** Writing – review & editing. **Vibha Kalra:** Funding acquisition, Supervision, Writing – review & editing.

Declaration of Competing Interest

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.

References

[1] C. Olson, F. Lenzmann, The social and economic consequences of the fossil fuel supply chain, MRS Energy Sustain. 3 (2016).
[2] M. Höök, X. Tang, Depletion of fossil fuels and anthropogenic climate change—a review, Energy Policy 52 (2013) 797–809.
[3] D.-C. Rezan, *Li-S Batteries: The Challenges, Chemistry, Materials, and Future Perspectives*. 2017: # N/A.
[4] E.J. Cairns, P. Albertus, Batteries for electric and hybrid-electric vehicles, Annu. Rev. Chem. Biomol. Eng. 1 (2010) 299–320.

[5] T.T. Team, Model S Long Range Plus: Building the First 400-Mile Electric Vehicle, 2020. Available from, https://www.tesla.com/blog/model-s-long-range-plus-building-first-400-mile-electric-vehicle.
[6] J. Zheng, et al., Suppressed oxygen extraction and degradation of LiNi x Mn y Co z O 2 cathodes at high charge cut-off voltages, Nano Res. 10 (12) (2017) 4221–4231.
[7] P. Kurzweil, Post-lithium-ion Battery Chemistries For Hybrid Electric Vehicles and Battery Electric vehicles, in Advances in Battery Technologies For Electric Vehicles, Elsevier, 2015, pp. 127–172.
[8] A. Manthiram, et al., Rechargeable lithium–sulfur batteries, Chem. Rev. 114 (23) (2014) 11751–11787.
[9] A. Mauger, C.M. Julien, Olivine positive electrodes for Li-ion batteries: status and perspectives, Batteries 4 (3) (2018) 39.
[10] K. Zhu, et al., How Far Away are Lithium-Sulfur Batteries from Commercialization?, 2019.
[11] J. Shepard, ALISE Project to Develop 500Wh/kg Batteries by 2019. Available from: https://eepower.com/news/alise-project-to-develop-500whkg-batteries-by-2019/.
[12] *High Energy Lithium Sulphur Cells and Batteries (HELIS)*. 2014; Available from: https://cordis.europa.eu/project/id/666221.
[13] M. Wild, G.J. Offer, Lithium-Sulfur Batteries, John Wiley & Sons, 2019.
[14] LISA Project. Available from: https://www.lisaproject.eu/.
[15] D. Lin, Y. Liu, Y. Cui, Reviving the lithium metal anode for high-energy batteries, Nat. Nanotechnol. 12 (3) (2017) 194.
[16] A. Fotouhi, et al., Lithium-sulfur battery technology readiness and applications—a review, Energies 10 (12) (2017) 1937.
[17] A. Rosenman, et al., Review on Li-sulfur battery systems: an integral perspective, Adv. Energy Mater. 5 (16) (2015), 1500212.
[18] L. Borchardt, M. Oschatz, S. Kaskel, Carbon materials for lithium sulfur batteries—ten critical questions, Chemistry 22 (22) (2016) 7324–7351.
[19] A. Singh, V. Kalra, Electrospun nanostructures for conversion type cathode (S, Se) based lithium and sodium batteries, J. Mater. Chem. A 7 (19) (2019) 11613–11650.
[20] H. Zhao, et al., A review on anode for lithium-sulfur batteries: progress and prospects, Chem. Eng. J. 347 (2018) 343–365.
[21] S. Waluś, et al., Volumetric expansion of Lithium-Sulfur cell during operation–Fundamental insight into applicable characteristics, Energy Storage Mater. 10 (2018) 233–245.
[22] R. Xu, J. Lu, K. Amine, Progress in mechanistic understanding and characterization techniques of Li-S batteries, Adv. Energy Mater. 5 (16) (2015), 1500408.
[23] S.-Y. Li, et al., Recent progress on confinement of polysulfides through physical and chemical methods, J. Energy Chem. 27 (6) (2018) 1555–1565.
[24] V. Knap, et al., Investigation of the self-discharge behavior of lithium-sulfur batteries, J. Electrochem. Soc. 163 (6) (2016) A911.
[25] K. Zhu, et al., How far away are lithium-sulfur batteries from commercialization? Front. Energy Res. 7 (2019) 123.
[26] C. Qu, et al., LiNO3-free electrolyte for Li-S battery: a solvent of choice with low Ksp of polysulfide and low dendrite of lithium, Nano Energy 39 (2017) 262–272.
[27] T. Cleaver, et al., Perspective—Commercializing lithium sulfur batteries: are we doing the right research? J. Electrochem. Soc. 165 (1) (2017) A6029.
[28] H. Fei, et al., Enhancing the safety and electrochemical performance of ether based lithium sulfur batteries by introducing an efficient flame retarding additive, RSC Adv. 6 (58) (2016) 53560–53565.
[29] X. Li, et al., A high-energy sulfur cathode in carbonate electrolyte by eliminating polysulfides via solid-phase lithium-sulfur transformation, Nat. Commun. 9 (1) (2018) 1–10.
[30] T. Yim, et al., Effect of chemical reactivity of polysulfide toward carbonate-based electrolyte on the electrochemical performance of Li–S batteries, Electrochim. Acta 107 (2013) 454–460.
[31] J. Gao, et al., Effects of liquid electrolytes on the charge–discharge performance of rechargeable lithium/sulfur batteries: electrochemical and in-situ X-ray absorption spectroscopic studies, J. Phys. Chem. C 115 (50) (2011) 25132–25137.
[32] K. Xu, Nonaqueous liquid electrolytes for lithium-based rechargeable batteries, Chem. Rev. 104 (10) (2004) 4303–4418.
[33] E.P. Roth, C.J. Orendorff, How electrolytes influence battery safety, Electrochem. Soc. Interface 21 (2) (2012) 45.
[34] Z. Xu, et al., Enhanced performance of a lithium–sulfur battery using a carbonate-based electrolyte, Angew. Chem. Int. Ed. 55 (35) (2016) 10372–10375.
[35] X. Yang, et al., Structural design of lithium–sulfur batteries: from fundamental research to practical application, Electrochem. Energy Rev. 1 (3) (2018) 239–293.
[36] H. Wang, et al., Correlating Li-Ion Solvation Structures and Electrode Potential Temperature Coefficients, J. Am. Chem. Soc. 143 (5) (2021) 2264–2271.
[37] H. Wang, et al., Lithium metal anode materials design: interphase and host, Electrochem. Energy Rev. 2 (4) (2019) 509–517.
[38] C. Sångeland, et al., Decomposition of carbonate-based electrolytes: differences and peculiarities for liquids vs. polymers observed using operando gas analysis, Batteries Supercaps 4 (5) (2021) 785–790.
[39] M. Wild, et al., Lithium sulfur batteries, a mechanistic review, Energy Environ. Sci. 8 (12) (2015) 3477–3494.
[40] J. Conder, et al., Direct observation of lithium polysulfides in lithium–sulfur batteries using operando X-ray diffraction, Nat. Energy 2 (6) (2017) 1–7.
[41] X. Huang, et al., Cyclic voltammetry in lithium–sulfur batteries—challenges and opportunities, Energy Technol. 7 (8) (2019), 1801001.
[42] M. Marinescu, T. Zhang, G.J. Offer, A zero dimensional model of lithium–sulfur batteries during charge and discharge, Phys. Chem. Chem. Phys. 18 (1) (2016) 584–593.
[43] T. Zhang, et al., Modeling the voltage loss mechanisms in lithium–sulfur cells: the importance of electrolyte resistance and precipitation kinetics, Phys. Chem. Chem. Phys. 17 (35) (2015) 22581–22586.
[44] D. Moy, A. Manivannan, S. Narayanan, Direct measurement of polysulfide shuttle current: a window into understanding the performance of lithium-sulfur cells, J. Electrochem. Soc. 162 (1) (2014) A1.
[45] L. Kong, et al., Beaver-dam-like membrane: a robust and sulphifilic MgBO2 (OH)/CNT/PP nest separator in Li-S batteries, Energy Storage Mater. 8 (2017) 153–160.
[46] J. Liang, et al., Carbon materials for Li–S batteries: functional evolution and performance improvement, Energy Storage Mater. 2 (2016) 76–106.
[47] M. Hagen, et al., In-situ Raman investigation of polysulfide formation in Li-S cells, J. Electrochem. Soc. 160 (8) (2013) A1205.
[48] H. Wang, et al., In situ NMR observation of the temporal speciation of lithium sulfur batteries during electrochemical cycling, J. Phys. Chem. C 121 (11) (2017) 6011–6017.
[49] Q. Wang, et al., Direct observation of sulfur radicals as reaction media in lithium sulfur batteries, J. Electrochem. Soc. 162 (3) (2015) A474.
[50] G. Li, et al., Developments of electrolyte systems for lithium–sulfur batteries: a review, Front. Energy Res. 3 (2015) 5.
[51] T. Soderberg, Organic Chemistry With a Biological Emphasis, University of Minnesota Morris, Morris, Minnesota, 2016.
[52] M. Ling, et al., Nucleophilic substitution between polysulfides and binders unexpectedly stabilizing lithium sulfur battery, Nano Energy 38 (2017) 82–90.
[53] A. Loch, et al., Nucleophilic Aliphatic Substitution Reactions of Propachlor, Alachlor, and Metolachlor with Bisulfide (HS-) and Polysulfides (S n 2-), Environ. Sci. Technol. 36 (19) (2002) 4065–4073.
[54] R. Steudel, T. Chivers, The role of polysulfide dianions and radical anions in the chemical, physical and biological sciences, including sulfur-based batteries, Chem. Soc. Rev. 48 (12) (2019) 3279–3319.
[55] X. Zhang, et al., Electrochemical and infrared studies of the reduction of organic carbonates, J. Electrochem. Soc. 148 (12) (2001) A1341.
[56] A.E. Rosamilia, F. Arico, P. Tundo, Insight into the hard– soft acid– base properties of differently substituted phenylhydrazines in reactions with dimethyl carbonate, J. Phys. Chem. B 112 (46) (2008) 14525–14529.
[57] Y.-Z. Zhang, et al., Microporous carbon polyhedrons encapsulated polyacrylonitrile nanofibers as sulfur immobilizer for lithium–sulfur battery, ACS Appl. Mater. Interfaces 9 (14) (2017) 12436–12444.
[58] E. Markevich, et al., on the mechanism of quasi-solid-state lithiation of sulfur encapsulated in microporous carbons: is the existence of small sulfur molecules necessary? J. Electrochem. Soc. 164 (1) (2016) A6244.
[59] E. Markevich, et al., The effect of a solid electrolyte interphase on the mechanism of operation of lithium–sulfur batteries, J. Mater. Chem. A 3 (39) (2015) 19873–19883.
[60] Q. Pang, et al., Tuning the electrolyte network structure to invoke quasi-solid state sulfur conversion and suppress lithium dendrite formation in Li–S batteries, Nat. Energy 3 (9) (2018) 783–791.
[61] C.-W. Lee, et al., Directing the lithium–sulfur reaction pathway via sparingly solvating electrolytes for high energy density batteries, ACS Cent Sci 3 (6) (2017) 605–613.
[62] X. Judez, et al., Solid electrolytes for safe and high energy density lithium-sulfur batteries: promises and challenges, J. Electrochem. Soc. 165 (1) (2017) A6008.
[63] E. Umeshbabu, B. Zheng, Y. Yang, Recent progress in all-solid-state Lithium–Sulfur batteries using high Li-ion conductive solid electrolytes, Electrochem. Energy Rev. 2 (2) (2019) 199–230.
[64] D. Lei, et al., Progress and perspective of solid-state lithium–sulfur batteries, Adv. Funct. Mater. 28 (38) (2018), 1707570.
[65] S. Kim, et al., A complex hydride lithium superionic conductor for high-energy-density all-solid-state lithium metal batteries, Nat. Commun. 10 (1) (2019) 1–9.
[66] P. Bonnick, et al., A high performance all solid state lithium sulfur battery with lithium thiophosphate solid electrolyte, J. Mater. Chem. A 7 (42) (2019) 24173–24179.
[67] Y. Hao, et al., A design of solid-state Li-S cell with evaporated lithium anode to eliminate shuttle effects, ACS Appl. Mater. Interfaces 9 (39) (2017) 33735–33739.
[68] Y. Cao, et al., A quasi-solid-state Li–S battery with high energy density, superior stability and safety, J. Mater. Chem. A 7 (11) (2019) 6533–6542.
[69] H. Schneider, et al., On the electrode potentials in lithium-sulfur batteries and their solvent-dependence, J. Electrochem. Soc. 161 (9) (2014) A1399.
[70] M. Vijayakumar, et al., Molecular structure and stability of dissolved lithium polysulfide species, Phys. Chem. Chem. Phys. 16 (22) (2014) 10923–10932.
[71] R. Fang, J. Xu, D.-W. Wang, Covalent fixing of sulfur in metal–sulfur batteries, Energy Environ. Sci. 13 (2) (2020) 432–471.
[72] W.J. Chung, et al., The use of elemental sulfur as an alternative feedstock for polymeric materials, Nat. Chem. 5 (6) (2013) 518–524.
[73] J. Yu, et al., Progress and perspective of constructing solid electrolyte interphase on stable lithium metal anode, Front. Mater. 7 (2020) 71.
[74] J. Kruželák, R. Sýkora, I. Hudec, Sulphur and peroxide vulcanisation of rubber compounds—overview, Chem. Pap. 70 (12) (2016) 1533–1555.
[75] D.-W. Wang, et al., Carbon–sulfur composites for Li–S batteries: status and prospects, J. Mater. Chem. A 1 (33) (2013) 9382–9394.
[76] J. Wang, et al., A novel conductive polymer–sulfur composite cathode material for rechargeable lithium batteries, Adv. Mater. 14 (13–14) (2002) 963–965.
[77] X.-g. Yu, et al., Lithium storage in conductive sulfur-containing polymers, J. Electroanal. Chem. 573 (1) (2004) 121–128.

[78] J. Wang, et al., Sulfur–carbon nano-composite as cathode for rechargeable lithium battery based on gel electrolyte, Electrochem. Commun. 4 (6) (2002) 499–502.
[79] S. Wei, et al., Metal–sulfur battery cathodes based on PAN–sulfur composites, J. Am. Chem. Soc. 137 (37) (2015) 12143–12152.
[80] L. Wang, et al., Analysis of the synthesis process of sulphur–poly (acrylonitrile)-based cathode materials for lithium batteries, J. Mater. Chem. 22 (41) (2012) 22077–22081.
[81] X. Yu, et al., Stable-cycle and high-capacity conductive sulfur-containing cathode materials for rechargeable lithium batteries, J. Power Sources 146 (1–2) (2005) 335–339.
[82] L. Yin, et al., A novel pyrolyzed polyacrylonitrile-sulfur@ MWCNT composite cathode material for high-rate rechargeable lithium/sulfur batteries, J. Mater. Chem. 21 (19) (2011) 6807–6810.
[83] T.N.L. Doan, et al., Binding mechanism of sulfur and dehydrogenated polyacrylonitrile in sulfur/polymer composite cathode, J. Power Sources 241 (2013) 61–69.
[84] M.A. Weret, et al., Mechanistic understanding of the Sulfurized-Poly (acrylonitrile) cathode for lithium-sulfur batteries, Energy Storage Mater. 26 (2020) 483–493.
[85] Y. Liu, et al., Effect of vapor pressure on performance of sulfurized polyacrylonitrile cathodes for Li/S batteries, RSC Adv. 6 (108) (2016) 106625–106630.
[86] A. Konarov, et al., Simple, scalable, and economical preparation of sulfur–PAN composite cathodes for Li/S batteries, J. Power Sources 259 (2014) 183–187.
[87] J. Fanous, et al., High energy density poly (acrylonitrile)-sulfur composite-based lithium-sulfur batteries, J. Electrochem. Soc. 160 (8) (2013) A1169.
[88] S. Warneke, A. Hintennach, M.R. Buchmeiser, Communication—influence of carbonate-based electrolyte composition on cell performance of SPAN-based lithium-sulfur-batteries, J. Electrochem. Soc. 165 (10) (2018) A2093.
[89] M. Frey, et al., Easily accessible, textile fiber-based sulfurized poly (acrylonitrile) as Li/S cathode material: correlating electrochemical performance with morphology and structure, ACS Energy Lett. 2 (3) (2017) 595–604.
[90] J. Xiang, et al., Facile synthesis of sulfurized polyacrylonitrile composite as cathode for high-rate lithium-sulfur batteries, J. Energy Chem. (2020).
[91] X. Huang, et al., Flexible free-standing sulfurized polyacrylonitrile electrode for stable Li/Na storage, Electrochim. Acta 333 (2020), 135493.
[92] J. Wang, et al., Hierarchical sulfur-based cathode materials with long cycle life for rechargeable lithium batteries, ChemSusChem 7 (2) (2014) 563–569.
[93] Y. Liu, et al., Highly ordered mesoporous sulfurized polyacrylonitrile cathode material for high-rate lithium sulfur batteries, J. Phys. Chem. C 121 (47) (2017) 26172–26179.
[94] Y. Liu, et al., Freestanding porous sulfurized polyacrylonitrile fiber as a cathode material for advanced lithium sulfur batteries, Appl. Surf. Sci. 472 (2019) 135–142.
[95] S. Kalybekkyzy, et al., Flexible S/DPAN/KB nanofiber composite as binder-free cathodes for Li-S batteries, J. Electrochem. Soc. 166 (3) (2019) A5396.
[96] L. Wang, et al., Kinetic investigation of sulfurized polyacrylonitrile cathode material by electrochemical impedance spectroscopy, Electrochim. Acta 56 (14) (2011) 5252–5256.
[97] Y. Liu, et al., A polysulfide reduction accelerator–NiS 2-modified sulfurized polyacrylonitrile as a high performance cathode material for lithium–sulfur batteries, J. Mater. Chem. A 5 (42) (2017) 22120–22124.
[98] A.A. Razzaq, et al., Anchoring MOF-derived CoS 2 on sulfurized polyacrylonitrile nanofibers for high areal capacity lithium–sulfur batteries, J. Mater. Chem. A 8 (3) (2020) 1298–1306.
[99] S. Li, et al., Manipulating kinetics of sulfurized polyacrylonitrile with tellurium as eutectic accelerator to prevent polysulfide dissolution in lithium-sulfur battery under dissolution-deposition mechanism, Nano Energy 60 (2019) 153–161.
[100] R. Mukkabla, M.R. Buchmeiser, Cathode materials for lithium–sulfur batteries based on sulfur covalently bound to a polymeric backbone, J. Mater. Chem. A 8 (11) (2020) 5379–5394.
[101] X. Zhang, et al., Structure-related electrochemical performance of organosulfur compounds for lithium–sulfur batteries, Energy Environ. Sci. 13 (4) (2020) 1076–1095.
[102] L. Wang, et al., Organic polymer material with a multi-electron process redox reaction: towards ultra-high reversible lithium storage capacity, RSC Adv. 3 (10) (2013) 3227–3231.
[103] S.S. Zhang, Understanding of sulfurized polyacrylonitrile for superior performance lithium/sulfur battery, Energies 7 (7) (2014) 4588–4600.
[104] J. Fanous, et al., Structure-related electrochemistry of sulfur-poly (acrylonitrile) composite cathode materials for rechargeable lithium batteries, Chem. Mater. 23 (22) (2011) 5024–5028.
[105] W. Wang, et al., Recognizing the mechanism of sulfurized polyacrylonitrile cathode materials for Li–S batteries and beyond in Al–S batteries, ACS Energy Letters 3 (12) (2018) 2899–2907.
[106] Z.-Q. Jin, et al., A new insight into the lithium storage mechanism of sulfurized polyacrylonitrile with no soluble intermediates, Energy Storage Mater. 14 (2018) 272–278.
[107] B. Duan, et al., Carbyne polysulfide as a novel cathode material for lithium/sulfur batteries, J. Mater. Chem. A 1 (42) (2013) 13261–13267.
[108] C.-H. Tsao, et al., Vulcanized polymeric cathode material featuring a polyaniline skeleton for high-rate rechargeability and long-cycle stability lithium-sulfur batteries, Electrochim. Acta 276 (2018) 111–117.
[109] J. Ma, et al., An in situ chemically and physically confined sulfur–polymer composite for lithium–sulfur batteries with carbonate-based electrolytes, Chem. Commun. 54 (100) (2018) 14093–14096.
[110] Q. Pang, et al., The importance of chemical interactions between sulfur host materials and lithium polysulfides for advanced lithium-sulfur batteries, J. Electrochem. Soc. 162 (14) (2015) A2567.
[111] J. Yan, et al., Long-life, high-efficiency lithium/sulfur batteries from sulfurized carbon nanotube cathodes, J. Mater. Chem. A 3 (18) (2015) 10127–10133.
[112] C. Luo, et al., Activation of oxygen-stabilized sulfur for Li and Na batteries, Adv. Funct. Mater. 26 (5) (2016) 745–752.
[113] X. Li, et al., Tailoring interactions of carbon and sulfur in Li–S battery cathodes: significant effects of carbon–heteroatom bonds, J. Mater. Chem. A 2 (32) (2014) 12866–12872.
[114] Q. Zhao, J. Zheng, L. Archer, Interphases in lithium–sulfur batteries: toward deployable devices with competitive energy density and stability, ACS Energy Letters 3 (9) (2018) 2104–2113.
[115] D. Eroglu, K.R. Zavadil, K.G. Gallagher, Critical link between materials chemistry and cell-level design for high energy density and low cost lithium-sulfur transportation battery, J. Electrochem. Soc. 162 (6) (2015) A982.
[116] B. Liu, et al., Revisiting scientific issues for industrial applications of lithium–sulfur batteries, Energy Environ. Mater. 1 (4) (2018) 196–208.
[117] H. Ye, et al., Amorphous MoS3 as the sulfur-equivalent cathode material for room-temperature Li–S and Na–S batteries, Proc. Natl. Acad. Sci. 114 (50) (2017) 13091–13096.
[118] A. Sakuda, et al., Amorphous metal polysulfides: electrode materials with unique insertion/extraction reactions, J. Am. Chem. Soc. 139 (26) (2017) 8796–8799.
[119] X. Li, et al., Stabilizing sulfur cathode in carbonate and ether electrolytes: excluding long-chain lithium polysulfide formation and switching lithiation/delithiation route, Chem. Mater. 31 (6) (2019) 2002–2009.
[120] A. Eftekhari, The rise of lithium–selenium batteries, Sustain. Energy Fuels 1 (1) (2017) 14–29.
[121] A. Abouimrane, et al., A new class of lithium and sodium rechargeable batteries based on selenium and selenium–sulfur as a positive electrode, J. Am. Chem. Soc. 134 (10) (2012) 4505–4508.
[122] X. Li, et al., Amorphous S-rich S 1− x Se x/C (x≤ 0.1) composites promise better lithium–sulfur batteries in a carbonate-based electrolyte, Energy Environ. Sci. 8 (11) (2015) 3181–3186.
[123] B. He, et al., Rationally design a sulfur cathode with solid-phase conversion mechanism for high cycle-stable Li–S batteries, Adv. Energy Mater. 11 (14) (2021), 2003690.
[124] Z. Chen, et al., Metal-tellurium batteries: a rising energy storage system, Small Struct. 1 (2) (2020), 2000005.
[125] F. Sun, et al., Heteroatomic Te x S 1− x molecule/C nanocomposites as stable cathode materials in carbonate-based electrolytes for lithium–chalcogen batteries, J. Mater. Chem. A 6 (21) (2018) 10104–10110.
[126] Y. Xu, et al., Confined sulfur in microporous carbon renders superior cycling stability in Li/S batteries, Adv. Funct. Mater. 25 (27) (2015) 4312–4320.
[127] S. Xin, et al., Encapsulation of sulfur in a hollow porous carbon substrate for superior Li-S batteries with long lifespan, Part. Part. Syst. Charact. 30 (4) (2013) 321–325.
[128] S. Niu, et al., Sulfur confined in nitrogen-doped microporous carbon used in a carbonate-based electrolyte for long-life, safe lithium-sulfur batteries, Carbon 109 (2016) 1–6.
[129] J. Zhou, et al., Confining small sulfur molecules in peanut shell-derived microporous graphitic carbon for advanced lithium sulfur battery, Electrochim. Acta 273 (2018) 127–135.
[130] S. Zheng, et al., High performance C/S composite cathodes with conventional carbonate-based electrolytes in Li-S battery, Sci. Rep. 4 (1) (2014) 1–7.
[131] Z. Li, L. Yin, Nitrogen-doped MOF-derived micropores carbon as immobilizer for small sulfur molecules as a cathode for lithium sulfur batteries with excellent electrochemical performance, ACS Appl. Mater. Interfaces 7 (7) (2015) 4029–4038.
[132] Q. Zhao, et al., Three-dimensional carbon current collector promises small sulfur molecule cathode with high areal loading for lithium–sulfur batteries, ACS Appl. Mater. Interfaces 10 (13) (2018) 10882–10889.
[133] D. Sun, et al., Tremella-like nitrogen-doped microporous carbon derived from housefly larvae for efficient encapsulation of small S2–4 molecules in Li-S batteries, Mater. Res. Express 6 (8) (2019), 085509.
[134] Q. Zhao, et al., 2D MXene nanosheets enable small-sulfur electrodes to be flexible for lithium–sulfur batteries, Nanoscale 11 (17) (2019) 8442–8448.
[135] J. Han, et al., A low cost ultra-microporous carbon scaffold with confined chain-like sulfur molecules as a superior cathode for lithium–sulfur batteries, Sustain. Energy Fuels 2 (10) (2018) 2187–2196.
[136] S. Xin, et al., Smaller sulfur molecules promise better lithium–sulfur batteries, J. Am. Chem. Soc. 134 (45) (2012) 18510–18513.
[137] Z. Li, et al., Insight into the electrode mechanism in lithium-sulfur batteries with ordered microporous carbon confined sulfur as the cathode, Adv. Energy Mater. 4 (7) (2014), 1301473.
[138] M. Helen, et al., Insight into sulfur confined in ultramicroporous carbon, ACS omega 3 (9) (2018) 11290–11299.
[139] Y. Xiao, et al., Operando soft X-ray absorption spectroscopic study on microporous carbon-supported sulfur cathodes, RSC Adva. 10 (65) (2020) 39875–39880.
[140] Z. Peng, et al., Graphene-based ultrathin microporous carbon with smaller sulfur molecules for excellent rate performance of lithium–sulfur cathode, J. Power Sources 282 (2015) 70–78.

[141] Q. Zhu, et al., Ultra-microporous carbons encapsulate small sulfur molecules for high performance lithium-sulfur battery, Nano Energy 33 (2017) 402–409.
[142] X. Li, et al., Safe and durable high-temperature lithium–sulfur batteries via molecular layer deposited coating, Nano Lett. 16 (6) (2016) 3545–3549.
[143] D. Zheng, et al., Quantitative chromatographic determination of dissolved elemental sulfur in the non-aqueous electrolyte for lithium-sulfur batteries, J. Electrochem. Soc. 162 (1) (2014) A203.
[144] H. Park, et al., High-efficiency and high-power rechargeable lithium–sulfur dioxide batteries exploiting conventional carbonate-based electrolytes, Nat. Commun. 8 (1) (2017) 1–10.
[145] D.S. Hall, J. Self, J. Dahn, Dielectric constants for quantum chemistry and Li-ion batteries: solvent blends of ethylene carbonate and ethyl methyl carbonate, J. Phys. Chem. C 119 (39) (2015) 22322–22330.
[146] Y. Liu, et al., Understanding and suppressing side reactions in Li–air batteries, Mater. Chem. Front. 1 (12) (2017) 2495–2510.
[147] G.-Y. Du, C.-Y. Liu, E.Y. Li, A DFT investigation on the origins of solvent-dependent polysulfide reduction mechanism in rechargeable Li-s batteries, Catalysts 10 (8) (2020) 911.
[148] N.N. Rajput, et al., Elucidating the solvation structure and dynamics of lithium polysulfides resulting from competitive salt and solvent interactions, Chem. Mater. 29 (8) (2017) 3375–3379.
[149] M. Cuisinier, et al., Unique behaviour of nonsolvents for polysulphides in lithium–sulphur batteries, Energy Environ. Sci. 7 (8) (2014) 2697–2705.
[150] L. Cheng, et al., Sparingly solvating electrolytes for high energy density lithium–sulfur batteries, ACS Energy Lett. 1 (3) (2016) 503–509.
[151] J.W. Dibden, et al., Predicting the composition and formation of solid products in lithium–sulfur batteries by using an experimental phase diagram, Chem. Commun. 52 (87) (2016) 12885–12888.
[152] X. Yu, A. Manthiram, A class of polysulfide catholytes for lithium–sulfur batteries: energy density, cyclability, and voltage enhancement, Phys. Chem. Chem. Phys. 17 (3) (2015) 2127–2136.
[153] J. Zheng, et al., Research progress towards understanding the unique interfaces between concentrated electrolytes and electrodes for energy storage applications, Adv. Sci. 4 (8) (2017), 1700032.
[154] Y. Yamada, A. Yamada, Superconcentrated electrolytes for lithium batteries, J. Electrochem. Soc. 162 (14) (2015) A2406.
[155] F. Huang, et al., Akin solid–solid biphasic conversion of a Li–S battery achieved by coordinated carbonate electrolytes, J. Mater. Chem. A 7 (20) (2019) 12498–12506.
[156] J. Robinson, et al., 2021 roadmap on lithium sulfur batteries, J. Phys. (2021).
[157] X. Chen, et al., Realizing an applicable "solid→ solid" cathode process via a transplantable solid electrolyte interface for lithium–sulfur batteries, ACS Appl. Mater. Interfaces 11 (33) (2019) 29830–29837.
[158] X. Cao, et al., Localized high-concentration electrolytes for lithium batteries, J. Electrochem. Soc. 168 (1) (2021), 010522.
[159] S. Chen, et al., High-voltage lithium-metal batteries enabled by localized high-concentration electrolytes, Adv. Mater. 30 (21) (2018), 1706102.
[160] M. He, et al., Realizing solid-phase reaction in Li–S batteries via localized high-concentration carbonate electrolyte, Adv. Energy Mater. 11 (31) (2021), 2101004.
[161] F. He, et al., Building a cycle-stable sulphur cathode by tailoring its redox reaction into a solid-phase conversion mechanism, J. Mater. Chem. A 6 (46) (2018) 23396–23407.
[162] L. Yu, et al., Enhanced stability of lithium metal anode by using a 3D porous nickel substrate, ChemElectroChem 5 (5) (2018) 761–769.
[163] X.-B. Cheng, et al., Toward safe lithium metal anode in rechargeable batteries: a review, Chem. Rev. 117 (15) (2017) 10403–10473.
[164] W.J. Chen, et al., Electrolyte regulation towards stable lithium-metal anodes in lithium–sulfur batteries with sulfurized polyacrylonitrile cathodes, Angew. Chem. (2019).
[165] S. Li, J. Yang, Y. Lu, Lithium metal anode. Encyclopedia of Inorganic and Bioinorganic Chemistry, 2011, pp. 1–21.
[166] D.-H. Liu, et al., Developing high safety Li-metal anodes for future high-energy Li-metal batteries: strategies and perspectives, Chem. Soc. Rev. 49 (15) (2020) 5407–5445.
[167] X. Guan, et al., Controlling nucleation in lithium metal anodes, Small 14 (37) (2018), 1801423.
[168] E. Peled, The electrochemical behavior of alkali and alkaline earth metals in nonaqueous battery systems—The solid electrolyte interphase model, J. Electrochem. Soc. 126 (12) (1979) 2047.
[169] W.J. Chen, et al., Electrolyte Regulation towards Stable Lithium-Metal Anodes in Lithium–Sulfur Batteries with Sulfurized Polyacrylonitrile Cathodes, Angew. Chem. 132 (27) (2020) 10821–10834.
[170] Y. Guo, H. Li, T. Zhai, Reviving lithium-metal anodes for next-generation high-energy batteries, Adv. Mater. 29 (29) (2017), 1700007.
[171] J.B. Goodenough, Y. Kim, Challenges for rechargeable Li batteries, Chem. Mater. 22 (3) (2010) 587–603.
[172] D. Aurbach, et al., Identification of surface films formed on lithium in propylene carbonate solutions, J. Electrochem. Soc. 134 (7) (1987) 1611.
[173] F. Ding, et al., Effects of carbonate solvents and lithium salts on morphology and coulombic efficiency of lithium electrode, J. Electrochem. Soc. 160 (10) (2013) A1894.
[174] Z. Chen, et al., A compatible carbonate electrolyte with lithium anode for high performance lithium sulfur battery, Electrochim. Acta 282 (2018) 555–562.
[175] H. Yang, et al., Lithium sulfur batteries with compatible electrolyte both for stable cathode and dendrite-free anode, Energy Storage Mater. 15 (2018) 299–307.
[176] K. Thanner, et al., Artificial solid electrolyte interphases for lithium metal electrodes by wet processing: the role of metal salt concentration and solvent choice, ACS Appl. Mater. Interfaces 12 (29) (2020) 32851–32862.
[177] X.Q. Zhang, et al., Fluoroethylene carbonate additives to render uniform Li deposits in lithium metal batteries, Adv. Funct. Mater. 27 (10) (2017), 1605989.
[178] H. Ota, et al., Structural and functional analysis of surface film on Li anode in vinylene carbonate-containing electrolyte, J. Electrochem. Soc. 151 (11) (2004) A1778.
[179] Y. Xu, et al., Atomic to nanoscale origin of vinylene carbonate enhanced cycling stability of lithium metal anode revealed by cryo-transmission electron microscopy, Nano Lett. 20 (1) (2019) 418–425.
[180] R. Xu, et al., Artificial soft–rigid protective layer for dendrite-free lithium metal anode, Adv. Funct. Mater. 28 (8) (2018), 1705838.
[181] C. Yan, et al., Dual-layered film protected lithium metal anode to enable dendrite-free lithium deposition, Adv. Mater. 30 (25) (2018), 1707629.
[182] G. Zheng, et al., Interconnected hollow carbon nanospheres for stable lithium metal anodes, Nat. Nanotechnol. 9 (8) (2014) 618.
[183] F. Ding, et al., Dendrite-free lithium deposition via self-healing electrostatic shield mechanism, J. Am. Chem. Soc. 135 (11) (2013) 4450–4456.
[184] Q. Xu, Y. Yang, H. Shao, Enhanced cycleability and dendrite-free lithium deposition by adding potassium ion to the electrolyte for lithium metal batteries, Electrochim. Acta 212 (2016) 758–766.
[185] J.K.S. Goodman, P.A. Kohl, Effect of alkali and alkaline earth metal salts on suppression of lithium dendrites, J. Electrochem. Soc. 161 (9) (2014) D418.
[186] Y. Shuai, et al., Highly stable lithium plating by a multifunctional electrolyte additive in a lithium-sulfurized polyacrylonitrile battery, Chem. Commun. 55 (16) (2019) 2376–2379.
[187] M.H. Ryou, et al., Mechanical surface modification of lithium metal: towards improved Li metal anode performance by directed Li plating, Adv. Funct. Mater. 25 (6) (2015) 834–841.
[188] J. Heine, et al., Coated lithium powder (CLiP) electrodes for lithium-metal batteries, Adv. Energy Mater. 4 (5) (2014), 1300815.
[189] M. Zhao, et al., Lithium–sulfur batteries under lean electrolyte conditions: challenges and opportunities, Angew. Chem. Int. Ed. (2020).
[190] R. Pai, A. Singh, M. Tang, V. Kalra, Stabilization of gamma sulfur at room temperature to enable the use of carbonate electrolyte in Li-S batteries, Comm. Chem. (2022), 17, https://doi.org/10.1038/s42004-022-00626-2.
[191] R. Pai, V. Natu, M. Sokol, M. Carey, T. Greszler, M. Barsoum, V. Kalra, Sulfur confined MXene hosts enabling the use of carbonate-based electrolytes in alkali metal (Li/Na/K)-sulfur batteries, Mat. Energy (2022), https://doi.org/10.1016/j.mtener.2022.101000.