Review Article
Gravimetric and volumetric energy densities of lithium-sulfur batteries

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Lithium-sulfur (Li-S) batteries receive considerable attention as a potential alternative to lithium-ion batteries (LIBs) due to their high theoretical gravimetric energy density (E_g). However, their volumetric energy density (E_v), which is also very important for practical applications is often neglected to emphasize their superior gravimetric energy density. In this review, we will try to provide a realistic and balanced perspective on the E_v of Li-S batteries. To calculate E_v, we establish a model based on a commercial pouch cell configuration, which allows one to evaluate the effect of various cell parameters. The requirements for Li-S batteries to be competitive against commercial LIBs in terms of E_v are proposed. Higher E_v for Li-S batteries could be expected by further balancing the sulfur loadings and sulfur utilization while reducing the electrode porosity as well as the amount of inactive additives in cathode. In particular, based on the calculated E_v values of recent works, we highlight the recent progress in both coin and pouch cells.

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Introduction

Li-S batteries [1–3] are regarded as a potential candidate for next-generation batteries with high energy density. Based on the electrochemical reaction $S_8 + 16Li \leftrightarrow 8Li_2S$, sulfur possesses a theoretical capacity of 1672 mAh g^{-1}, almost ten times of that of the commercial cathode materials for LIBs such as $LiCoO_2$, $LiFePO_4$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) and $LiNi_xCo_yMn_{1-x-y}O_2$ (NCM) (140–180 mAh g^{-1}) [4–6]. By coupling with a Li metal anode, the theoretical E_g and E_v of Li-S batteries can reach to 2500 Wh kg^{-1} and 2800 Wh L^{-1}, respectively. Unfortunately, the commercialization of Li-S batteries is hindered by several major challenges: (i) Both sulfur and its discharge product lithium sulfide (Li_2S) are intrinsically poor electrical and ionic conductors, resulting in a low sulfur utilization and poor rate performance. (ii) The soluble intermediate species, long-chain lithium polysulfides Li_2S_n ($4 \leq n \leq 8$), can freely migrate between the cathode and anode, causing fast capacity decay and poor Coulombic efficiency. In order to address (i) and (ii), the introduction of conducting materials [7,8] and/or sulfur host materials [9,10] with high surface area into sulfur electrodes have been proposed. Moreover, sufficient amount of electrolyte and excessive void space for electrolyte access are also required for achieving high sulfur utilization, which significantly sacrifice the energy density. (iii) The SEI film formed on Li anode is unstable upon cycling, leading to the continuous consumption of Li and electrolyte. Consequently, the use of excessive amount of Li and electrolyte is required, further reducing the E_g and E_v of the full cell.

All the aforementioned inactive additives counteract the advantage of Li-S batteries in energy density. So far, at the pouch cell level, the practical E_g of Li-S batteries can achieve 350 Wh kg^{-1} with a cycling life of 100 cycles. The Li-S cell manufacturers such as Sion Power and Oxis Energy expect that E_g of 400∼600 Wh kg^{-1} can be reached, twice of that of the state-of-the-art LiBs in the near future, but an E_v of only ∼700 Wh L^{-1} [11]. However, E_v is crucial for practical applications especially for the electric vehicles and portable electronic devices. Therefore, it is quite urgent and worthy to evaluate the latest researches to gain more insight on the E_v of Li-S batteries. In this review, we first establish a model for calculating E_v based on a commercial cell configuration. The effect of various cell parameters on E_v is also evaluated to provide us theoretical guidance to improve E_v. Furthermore, we discuss the recent progress on improving the E_v of Li-S batteries from the viewpoint of both sulfur cathode and Li anode.
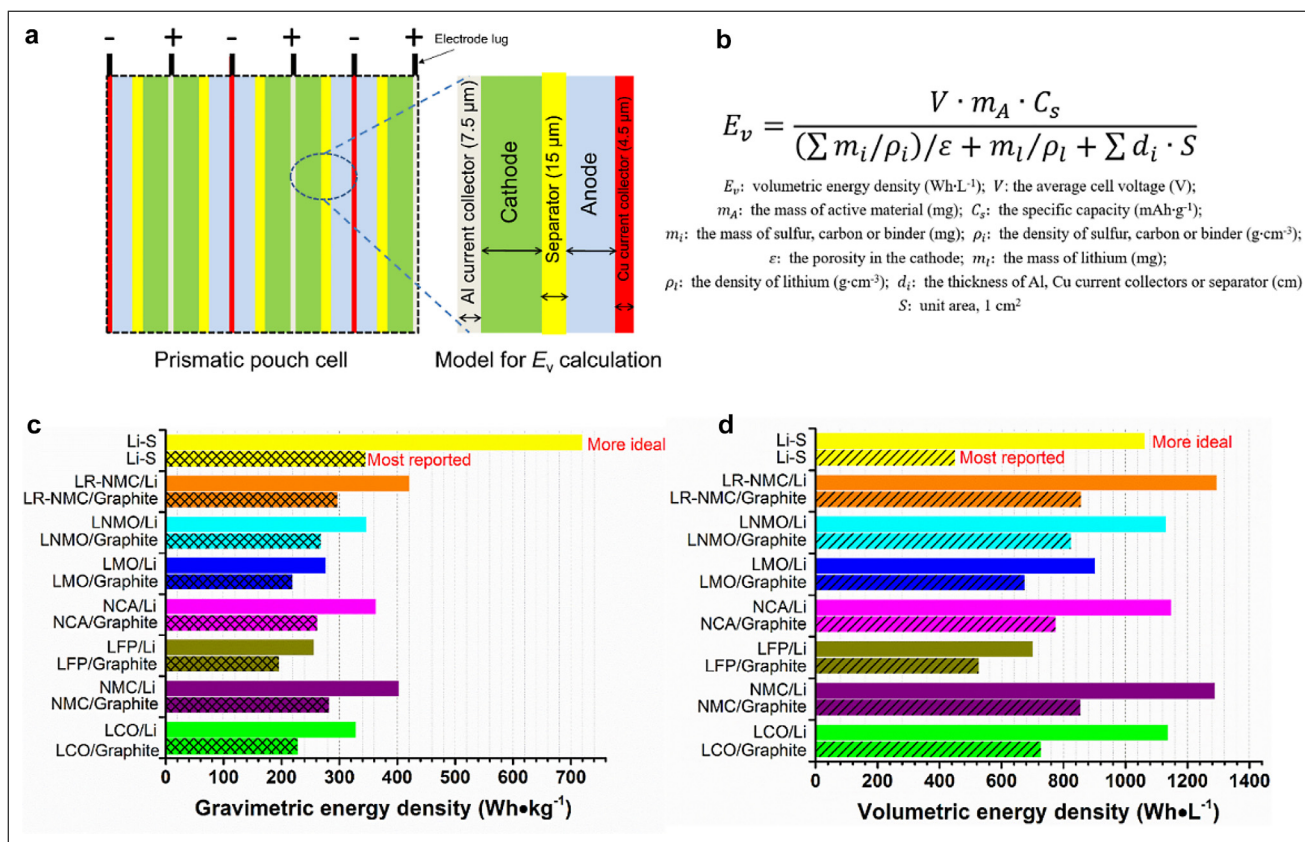
(a) Simplified schematic of a pouch Li-S cell and the corresponding model for the calculation of the volume energy density (E_v); (b) The equation used to calculate E_v; Calculated gravimetric (c) and volumetric energy densities (d) of Li-ion batteries and Li-S batteries.

Model for estimating the practical volumetric energy density

In our model, the packaging materials are not taken into account as the fractional volume of packaging materials is negligible in a multi-electrodes pouch cell. Figure 1a presents a schematic of a prismatic pouch cell. To simplify the calculations, we use a sandwich-structured model consisting of Al (7.5 μm) and Cu (4.5 μm) foils, separator (15 μm), lithium foil, and sulfur cathode. Regarding the thicknesses of the current collectors, we use half of the thicknesses of the foils in our model due to the widely used double-side coating technology industrially. Moreover, we assume that the cathodes are composed of sulfur, carbon, binder (5 wt%), and interspaces in/between them (described as porosity (ε)). In particular, when calculating E_v, we also assume no excess electrolyte is used in the Li-S cells but just filling the interspaces in the sulfur cathode and separator. This assumes the Li-anode is fully dense and develops no porosity or thickness change of its own, which is of course overly optimistic. Based on the above assumptions, we can calculate E_v and E_g using the equation shown in Figure 1b and Supplementary Equa-

tion (1), respectively. Various parameters used for the calculation are summarized in the Supplementary Information. The estimated E_v and E_g values for lithium-ion batteries (LIBs) and Li-S batteries are shown in Figure 1c and d, respectively.

According to our estimations, the commercially available LIBs using graphite anodes may deliver E_g in a range of 197–297 Wh kg^{-1}. The main advantage of Li-S batteries compared to LIBs is obvious from Figure 1c with E_g values of 720 Wh kg^{-1} (in more ideal case) and ~350 Wh kg^{-1} (most reported). We expect that further optimization could boost E_g to a level beyond 500 Wh kg^{-1}, which exceeds the lithium-rich NMC//Li-metal anode (421 Wh kg^{-1}). As shown in Figure 1d, the commercially available LIBs can provide E_v ranging from 540 to 815 Wh L^{-1} with a graphite anode, and the values can be further increased to 737–1300 Wh L^{-1} when partnered with a Li anode. A relatively ideal E_v value of Li-S cells as high as 1017 Wh L^{-1} can be obtained assuming the sulfur content (S%) = 70% (all sulfur contents are weight percentage), sulfur loading = 10 mg cm^{-2}, the porosity in cathode = 30% and Li excess amount = 50%.

Figure 2
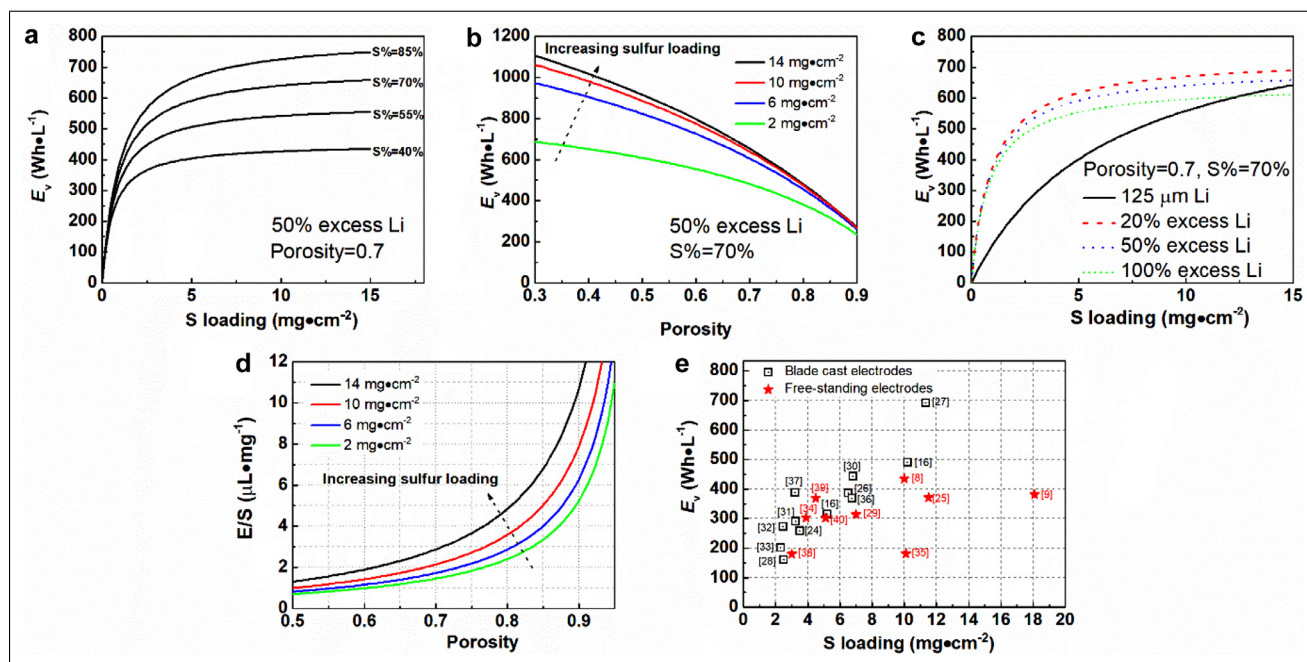
Relationship between cell parameters and E_v. (a) E_v as a function of areal sulfur loading at different sulfur contents; (b) E_v as a function of porosities in electrodes at different sulfur loadings; (c) E_v as a function of areal sulfur loading at different lithium excess amounts; (d) E/S as a function of electrode porosity at different sulfur loadings assuming that electrolyte fills out all the void spaces in the sulfur cathode and separator; (e) E_v values calculated from references [8,9,16••,24••–40]. Fixed parameters for different calculations are shown in the corresponding figures.

However, most of the E_v values calculated from references are around 400 Wh L^{-1}, falling behind the LiFePO$_4$//C battery (540 Wh L^{-1}). Due to the high volume fraction of void space and inactive carbons in sulfur electrode, and the use of excessive lithium anode, the E_v of Li-S batteries is much lower than the ideal value. As a result, their E_v is often not mentioned to emphasize their superior E_g in most of the previous literatures. In our review, we will focus on establishing the relationship between various electrode parameters and E_v, and determine the requirements for Li-S batteries to be competitive vs to the commercial LIBs in E_v.

Factors influencing the volumetric energy density

For all the following calculations, we assume that the specific capacity of sulfur is 1000 mAh·g^{-1} with 2.1 V discharging voltage. Other fixed parameters for different calculations are shown in the corresponding figures. In Figure 2a and b, we plot the projected E_v vs. sulfur loading under different sulfur contents and lithium-excess levels. It is apparent that a sulfur loading < 2 mg cm^{-2} may lead to an extremely low E_v even with an extremely high-sulfur content ratio of 85%, suggesting that a high-loading sulfur electrode is critical for achieving high E_v, which is in agreement with previous analysis [11]. Notably, with the increase of the sulfur loading, E_v values in Figure

2a and b reach an asymptotic limit. Therefore, the sulfur loading of electrodes should be maintained at a high level with the consideration of the sulfur utilization. Moreover, the sulfur content is another factor which has a significant impact on the E_v. As shown in Figure 2a, with the increase of sulfur content from 40% to 85%, there is nearly a twofold increase in E_v for sulfur loading higher than 2 mg cm^{-2}. For the most reports to date, a wide range of sulfur contents was reached from 32% [12] to 80% [13] for sulfur/carbon cathodes and from 32% [14] to 64% [15–18] for sulfur/carbon/metal oxides cathodes, respectively. Although the high sulfur content is critical to engineering Li-S batteries with high E_v, special attention must be paid to balancing the sulfur utilization and sulfur content, especially for high loading cathodes.

Furthermore, E_v is also very sensitive to the electrode porosity. As illustrated in Figure 2b, E_v decreases rapidly with increasing porosity. With a porosity of $\varepsilon = 0.30$ ($\varepsilon = 0.25$–0.4 for for commercial LIBs cathodes [19,20]), in the best case scenario, a maximum E_v of 1060 Wh L^{-1} could be reached for Li-S batteries at a sulfur loading of 14 mg cm^{-2}. However, since the actual electrode porosity is usually around 0.7 [21], it is expected that E_v of Li-S cells will likely reach ~600 Wh L^{-1} with ≥6 mg cm^{-2} sulfur loading, 70% sulfur content, 70% cathode porosity, and 50% excess Li. In contrast, the degree of Li

excess has a relatively small effect on E_v (Figure 2c). However, there will be an overestimate in E_v values when the sulfur loading is below ~11 mg cm^{-2} because there is difficulty in fabricating thin Li foils in practice. Therefore, it is more realistic to assume a constant thickness of 125 μm for the Li foils (Figure 2c). Moreover, the electrolyte volume/sulfur weight ratio (E/S, μL mg^{-1}) is significantly more important when characterizing Li-S cells than LIBs because excessive electrolytes are often required for supporting appropriate polysulfide dissolution to achieve high sulfur utilization. We established the relationship between E/S ratio and ε with the assumption that the volume of electrolyte is equal to that of the void spaces in the sulfur cathode (i.e. no air pores after electrolyte wetting) and separator (Figure 2d). The required E/S ratio increases rapidly as the porosity increases. Regarding the most reported $\varepsilon \approx 0.7$, the estimated E/S ratio is around 2 μL mg^{-1} which results in a significant underestimate of the electrolyte amount. Zheng *et al.* [22] discussed the basic requirements for getting reproducible Li-S battery data and proposed an optimized E/S ratio of ~20 μL mg^{-1}. Zhang reported [23] that an E/S ratio of 10 μL mg^{-1} was optimum. Such high E/S ratios will significantly compromise both E_g and E_v. In summary, decreasing ε, E/S ratio, Li excess amount as well as increasing the sulfur content at high loadings while guaranteeing high sulfur utilization will be important for improving E_v and E_g.

Recent progress in improving the volumetric energy density of Li-S batteries

The aforementioned discussion provides us with a theoretical relationship between the cell parameters and E_v. In this section, we will focus on recent experimental progress in coin cells and pouch cells toward high E_v of Li-S batteries.

Coin cells

Based on our model, we calculate E_v values for some recent works tested in coin cells (Figure 2e). Notably, we do not take into account the electrolyte amount in our model, which will lead to some overestimate in E_v. According to current collectors and fabrication methods for sulfur cathodes, we categorize the electrodes into blade-cast and free-standing electrodes. Blade-cast electrodes based on Al foil current collectors are the most reliable architectures for practical applications owing to their rolling processability and the mature industrial plants for large-scale fabrication. The biggest issue for the blade-cast electrodes is the poor infiltration of electrolyte in the rolled electrodes, in spite of the effectiveness of rolling in decreasing the electrode porosity. By carefully balancing the rolling pressure (0.9 MPa) and the sulfur loading (3.5 mg cm^{-2} sulfur), Lv *et al.*'s research [24••] yields an E_v of 248 Wh L^{-1} based on our model (Figure 3a). Using an *in situ* cross-linked binder, Nazar's group [16••] developed a crack-free and com-

pact high loading electrode featured by the low electrolyte/sulfur ratio of 3.5 μL mg^{-1} and high areal capacity of 14.7 mAh cm^{-2} (Figure 3b). According to our calculation, a high E_v of 476 Wh L^{-1} can be reached. Most recently, Mao *et al.* reported a promising method to increase E_v, by partially replacing porous carbon with metal-organic framework (MOF) particles, a high-density MOFs/CNTs-based sulfur electrode was fabricated with 11.33 mg cm^{-2} sulfur loading and only ~ 80 μm thickness leading to a high E_v of 663 Wh L^{-1} based on the model discussed above, which is comparable to that of the commercial Li-ion batteries [27••] (Figure 3f). In addition, another promising approach for improving the E_v for blade-cast electrodes is to realize higher tap density of electrodes by partially replacing the high surface area carbon materials with polar inorganic compounds such as metal oxides [18,41–43], sulfides [18,41–43], and carbides [44].

With a high volumetric fraction of carbon (typical >60 vol%) and poor electrolyte immersion in thick sulfur electrodes, the high-sulfur-loading sulfur electrodes fabricated via routine slurry-casting procedure always suffer from brittle-fracture problem and exhibit low sulfur utilization with poor rate performance. In this context, freestanding sulfur electrodes, which use 3D porous carbon collectors such as carbon papers, foams, films, cloths, and so on as current collectors, represent a facile approach to fabricating high-sulfur-loading electrodes (Figure 3c). Compared with the Al foil collector, the 3D porous carbon matrices provide plentiful internal space for electrolyte immersion and continuous pathways for electron transportation, which decrease the energy barriers for the conversions between S and Li$_2$S, and thus enhance the sulfur utilization and rate capability [45]. As a result, freestanding electrode architecture is proper for thick electrodes (up to 1000 μm based on the reports in Figure 3e) with a high loading of active materials. To our knowledge, a maximum of sulfur loading (61.4 mg cm^{-2}) has been attained [46]. Free-standing sulfur electrodes could be fabricated by infiltrating of the active materials (sulfur, polysulfides or Li$_2$S) onto the carbon matrices [47] (Figure 3d) or loading the active materials (or their precursors) during the assembling process of the electrodes (Figure 3e) [48••]. With a simple stacking or layer-by-layer strategy, the areal loading of free-standing sulfur electrodes could be easily multiplied to extremely high level without obvious-specific capacity loss (Figure 3e) [25••,49••]. However, high-loading electrodes with high-specific capacity do not always lead to the high E_v of Li-S batteries, due to the high porosity of carbon-based free-standing electrode usually required considerable uptake of the electrolyte to wet the whole sulfur cathodes. Moreover, despite the numerous advantages of free-standing sulfur electrodes, a high implementation cost is still needed for their mass production, which greatly counteract the cost advantage of Li-S batteries.

Figure 3
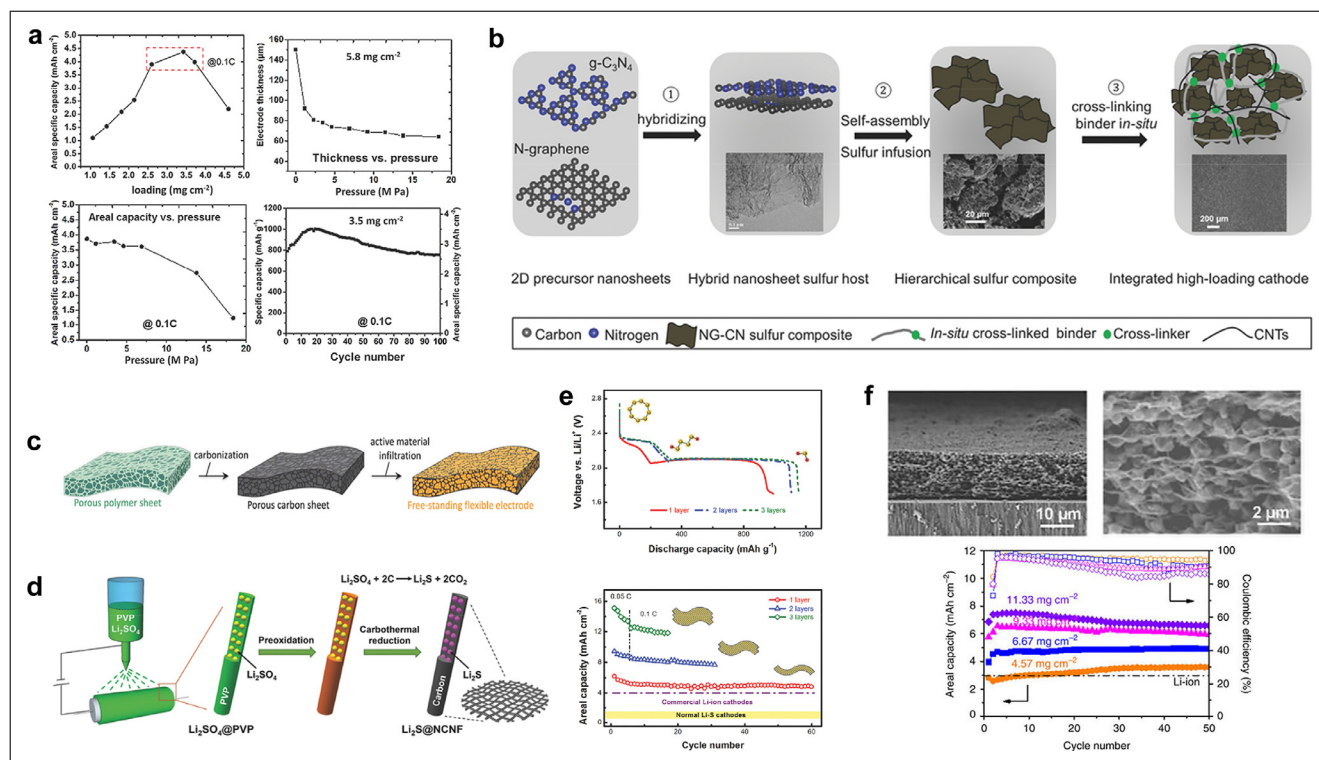
Various types of sulfur cathodes with high volumetric energy density. (a) The electrode thickness and areal capacity under different rolling pressure [24••]; (b) Schematic of the fabrication process of a highly compacted high loading sulfur electrode using an *in situ* cross-linked binder to achieve a high E_v [16••]; (c) Schematic illustration for the typical fabrication of the free-standing sulfur electrodes, including the formation of free-standing porous carbon sheet, and the infiltration of the active material [47]; (d) Schematic illustration for the *in situ* encapsulation of Li$_2$S in a freestanding carbon paper [48••]; (e) Galvanostatic discharge curves and cycling performance of stacked free-standing sulfur electrodes [25••]; (f) A hierarchical porous interpenetrated MOFs/CNTs conductive network for loading up to 11.33 mg cm^{-2} sulfur, yielding a very high E_v [27]. Reproduced from refs [24, 16, 47, 48, 25, 27] with permission from Wiley-VCH and Nature Publishing Group
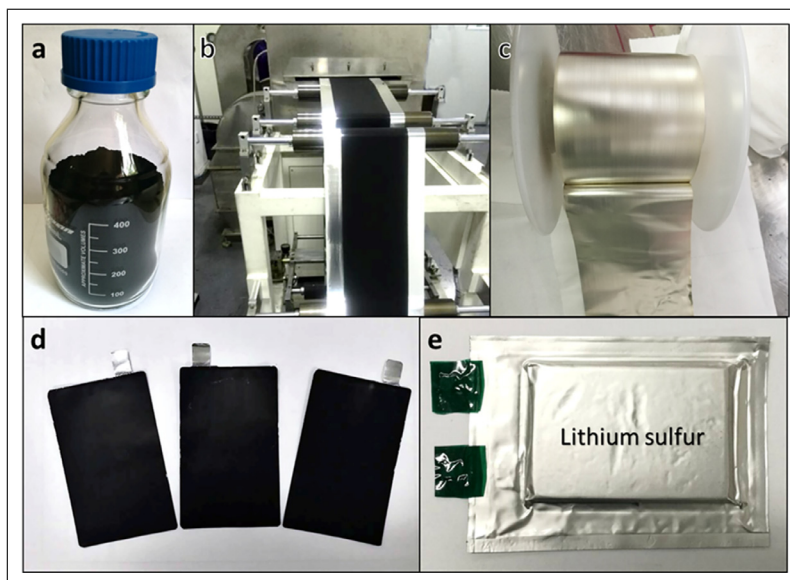
Pouch cells

Despite the remarkable progress achieved on the laboratory scale, the Li-S battery is in their infancy of practical applications. In 2014, Sion Power announced their Li-S batteries with an E_g of 350 Wh kg^{-1} successfully assisted the 11-days flight of a solar/battery powered aircraft (Zephyr 7) in winter. But no details on the cycle life and volumetric energy density were provided [50]. Another manufacturer of Li-S batteries, Oxis Energy, developed a Li-S battery with an E_g of 300 Wh kg^{-1} in 2016, which could successfully be cycled for 80 cycles, however, its E_v is only <200 Wh L^{-1}, much lower than that of commercial LIBs [51].

To accelerate the translation of basic-research results to commercially viable cells, we investigated pouch-typed Li-S cells in lab. Figure 4a shows the image of sulfur-carbon powder (88% sulfur content). For the slurry preparation, a water-based binder (LA132) and Super-P conductive carbon were used. Typically, the thickness of the double-side-coated cathode is 250–300 μm. The sulfur loading ranges from 4.5 to 6.5 mg cm^{-2} with 75% sulfur content. According to our model, the porosity of the electrode is calculated to be 71–76%. The electrolyte/sulfur ratio is 3 μL mg^{-1} in our case. The thickness of the lithium foil used is 150–200 μm corresponding to 200% excess. (Here, no Cu current collector is used, and the lithium foil works as double-sided anode). Its E_v is ∼300 Wh L^{-1}. It is noted that some electrolyte is pumped out from the stacked electrode to the empty part of the package during discharge and pumped back into the electrode in the following charging process. The movement of the electrolyte might be caused by the volume change of sulfur electrode during the discharge/charge processes. However, this phenomenon disappeared after several cycles possibly because of the high porosity mossy lithium after cycling which can store the electrolyte pumped out from the cathode.

This paper has mainly discussed the E_v for the Li-S batteries with elemental sulfur cathodes. Another type of lithium sufur batteries with sulfur composite cathodes in-

Figure 4

Photos of Li-S pouch cell components. (a) Sulfur-carbon composites; (b) Coated cathode; (c) Lithium metal foil; (d) Double side cathode; (e) Self-made Li-S pouch cell.

cluding S@pPAN, small-sulfur@meso-carbon might not well match with the aformentioned E_v calculation model [52,53]. These sulfur composite cathode materials in which sulfur are mono-dispersed in conductive matrix exhibit excellently compatiblility with carbonate electrolyte, and the sulfur electrodes survive under high rolling pressure and high cathode loading, similar to commercial Li-ion electrodes. However, the sulfur contents of these types of sulfur composites which are generally relatively low, ca. 45% or less, is one of the main factors affecting the E_v of this type of Li-S batteries.

Concluding remark

The analysis in the present review provides some strategies and criteria for achieving high E_v of Li-S batteries. The results indicate that to be comparable to the commercial LIBs ($\sim$600 Wh L^{-1}) in E_v, a Li-S cell should employ a cathode with an areal sulfur loading of $\geq$6 mg cm^{-2}, a sulfur content of $>$70%, and an electrode porosity of $<$70%, and a specific capacity of $>$1000 mAh g^{-1}, and an anode with $<$50% excess of Li metal. Based on the established relationship between cell parameters and E_v, higher levels could be expected by further balancing the sulfur utilization, areal sulfur loading and electrode porosity. Although the E_v of a Li-S battery may not be much higher than current LIBs due to the intrinsic low density of both sulfur and lithium, recent progress has shown great promise in advanced electrode designs in both coin and pouch cells.

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