Next generation technologies

16

Juergen Janek and Philipp Adelhelm

Contents

16.1 Introduction

Rechargeable lithium-ion batteries have been continually developed since their introduction by Sony in 1991. Energy density is one of the key parameters for

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J. Janek (Prof.) (✉)
Physikalisch Chemisches Institut & Laboratory for Materials Research (LaMa)
Justus-Liebig-Universitat Giessen,
Heinrich-Buff-Ring 17, 35392 Giessen, Germany
e-mail: juergen.janek@phys.chemie.uni-giessen.de

P. Adelhelm (Prof.)
Institut fuer Technische Chemie und Umweltchemie, Center for Energy and Environmental Chemistry (CEEC Jena), Friedrich-Schiller-Universitaet Jena, Philosophenweg 7a, 07743 Jena, Germany
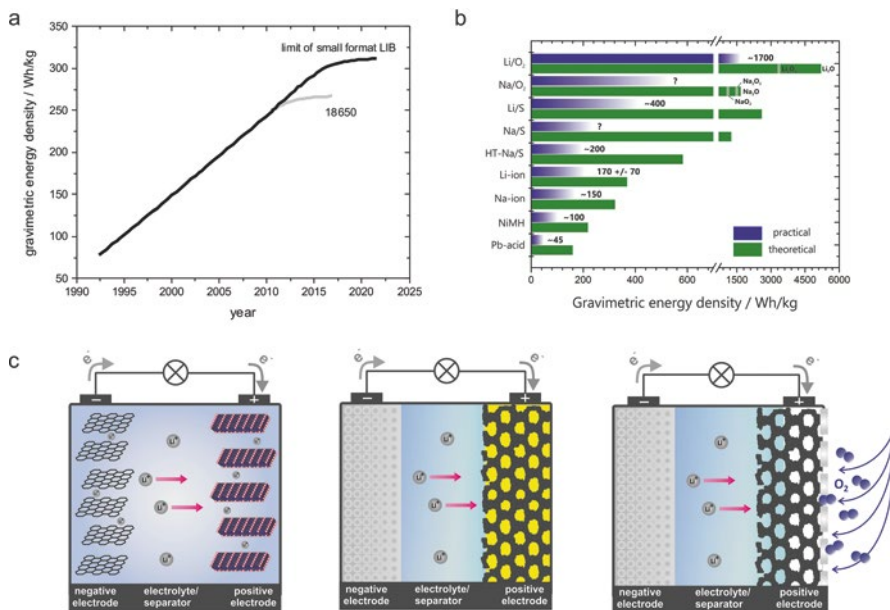e-mail: philipp.adelhelm@uni-jena.de

Fig. 16.1 (a) Chronological development of lithium-ion cells' mean practical energy densities (high energy design). Diagram after ref [1]. (b) Theoretical and (forecast) practical energy densities for different rechargeable cell systems (secondary elements). Practical energy density values are reference values only and strongly vary with the respective cell design (size, geometry, high energy, high power): Pb-acid battery (car battery, 12 V), NiMH – nickel metal hydride (cell level, AA), lithium-ion – mean value across different types (cell level), HT-Na/S – high temperature sodium/sulfur (cell level) Li/S – data from by Sion Power (cell level, pouch), Li/O$_2$ – data from by Polyplus (cell level, primary element)) (c) Comparison between the different cell concepts of conventional lithium-ion cells, metal/sulfur cells and metal/oxygen cells.

lithium-ion batteries. It was steadily increased by optimizing battery components such as electrode materials or electrolyte as well as by improving the cell construction technologies. The cell level progress during recent years is shown in Fig. 16.1. The gravimetric energy density of standard cells (18650) increased from below 100 Wh/kg to about 250 Wh/kg today. Similarly, the volumetric energy density increased from about 200 Wh/L to around 700 Wh/L, see [1].

It is obvious however, that a similar increase is not to be expected in the coming years since technology reaches its natural limits. Eventually, the electrode materials used will be the limiting parameters. Currently, carbon materials (mainly graphite) are used in anodes, while cathodes contain oxidic transition metal compounds. These are for example lithium cobalt oxide ($LiCoO_2$), Li-NCM ($Li(Ni_{1-x-y}Mn_xCo_y)O_2$), lithium iron phosphate ($LiFePO_4$), or lithium manganese oxide ($LiMn_2O_4$). The theoretical gravimetric energy density[1] for these cell types typically ranges from 350 to 400 Wh/kg.

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[1]The theoretical (gravimetric) energy density is the stored chemical energy based on the pure electrode materials' mass.

If further cell components such as electrolyte, separator, current collector, additives, and housing are taken into account, energy density typically decreases by more than 50 percent. The transition from single cell to battery[2] causes additional losses, resulting in values of 110–140 Wh/kg in electric vehicles. With today's commercial cells' values in mind, it can be predicted that a considerable energy density increase is not achievable with the conventional approaches (Fig. 16.1a and Table 16.1).

Table 16.1 Practical energy densities of a choice of lithium-ion cells compared to Li/S and Li/O$_2$ systems (manufacturer's information, cell level). Depending on size, cell geometry, and application (high-power or high-energy), energy densities show a certain range for cells with identical cell chemistry

Cell type	Type/manufacturer	$E°$ [V]	Grav. energy density [Wh/kg]	Vol. energy density [Wh/l]
C/LiCoO$_2$	Cylindrical; VL 34570 – SAFT	3.7	160	380
C/LiCoO$_2$	Prismatic; MP 144350 – SAFT	3.75	143	344
C/LiCoO$_2$	Prismatic; MP 174565 – SAFT	3.75	175	423
C/LiCoO$_2$-based	Cylindrical; ICR18650-26F – Samsung	3.7	209	581
C/LiCoO$_2$-based	Prismatic; ICP103450 – Samsung	3.7	185	415
C/LiFePO$_4$	Cylindrical; VL 45E Fe – SAFT (high energy)	3.3	156	292
C/LiFePO$_4$	Cylindrical; VL 10 V Fe – SAFT (high power)	3.3	55	122
C/LiFePO$_4$	Cylindrical; IFR18650-11P – Samsung	3.2	82	213
C/LiFePO$_4$	Cylindrical; ANR 26650 – A123 Systems	3.3	109	239
Li/S$_8$*	Prismatic; – Sion Power Corp.	2.15	350	320
Li/S$_8$*	n/a – Oxis Energy Ltd.	-	300	-
Li/O$_2$*	n/a; primary element – Polyplus	-	> 700	-

[2]Initially, the terms "cell" and "battery" had strictly different definitions. An electrochemical cell is the smallest battery unit and consists of anode, cathode, electrolyte, separator, current collector, and housing. As opposed to that, a battery consists of at least two cells connected in series or in parallel. A 12-V lead battery for instance is made of six 2-V cells. Nowadays however, a cell is often called battery also. The electrochemical processes do not differ from cell to battery and this is why the present Chapter does not differentiate between those two terms. Specifying the practical energy densities however calls for a differentiation. All practical energy density values (with the exception of lead batteries) in this Chapter refer to cells.

Currently, important approaches to maximize energy and power density by improving electrode materials are in particular (a) partially or completely substituting lithium alloys containing tin and silicon for carbon in the negative electrode and (b) increasing the positive electrode's nickel content.

Lithium-sulfur and lithium-air systems are much discussed next generation technologies and use cell chemistries considerably different from those of standard lithium-ion batteries. Developing these battery types to marketable systems in regards to gravimetric energy density would mean a great step forward when compared with the current lithium-ion technology.

Theoretical and provisional practical energy densities of both technologies are compared with conventional systems in Fig. 16.1b and Table 16.2. A lithium-air cell has a theoretical energy density of several thousand Wh/kg. This explains the fascination sparked by this cell system.

The most important reasons for the high energy density of both cell concepts are

(1) the substitution of the light elements sulfur and oxygen for the cathode's comparatively heavy transition metal compounds.
(2) the storing of more lithium per formula unit. Conventional cathode materials change the transition metal's oxidation state during the lithium's intercalation and deintercalation. Hence, maximally one lithium ion per formula unit can be stored with the redox pairs Co^{4+}/Co^{3+}, Fe^{3+}/Fe^{2+} and Mn^{4+}/Mn^{3+}. Effectively, only 0.8 lithium ions ($LiMn_2O_4$) and 0.5 lithium ions ($LiCoO_2$) respectively can be utilized per formula unit. In contrast to that, sulfur and oxygen can incorporate 2 lithium ions each per formula unit during a complete reaction.
(3) the replacement of the anode's graphite with metallic lithium in the future. However, using a pure metal anode poses challenges that have yet to be resolved, most notably the dangerous dendrite formation. The continuous electrolyte consumption induced by the reaction with the metal anode during charging and discharging is a decisive factor for cycling stability.

Moreover, the use of sulfur or oxygen as active components in batteries is also attractive considering their elemental abundance.

This Chapter takes an in-depth look at the cell chemistries of next generation technologies using Li/S and Li/O_2. It also discusses advantages and disadvantages as well as solutions for the current problems. "All-solid state batteries" become more and more interesting and are reviewed at the end of this Chapter.

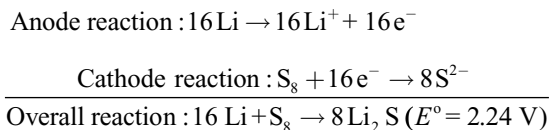## 16.2 The lithium-sulfur battery

16.2.1 Basic principle

The lithium-sulfur cell chemistry has been examined for several decades [2–4]. The reasons for this are the high energy density, the almost unlimited availability of

Table 16.2 Theoretical gravimetric (Wh/kg) and volumetric (Wh/l) energy densities w_{th} for different cell reactions

Cell type and reaction (lithium - anode)	$E°$ [V]	w_{th} [Wh/kg]	w_{th} [Wh/l]	Cell type and reaction (graphite - anode)	$E°$ [V]	w_{th} [Wh/kg]	w_{th} [Wh/l]
$\frac{1}{2}\text{Li} + \text{Li}_{0.5}\text{CoO}_2 \underset{charge}{\overset{discharge}{\rightleftarrows}} \text{LiCoO}_2$	3.9	534	2,723	$\frac{1}{2}\text{LiC}_6 + \text{Li}_{0.5}\text{CoO}_2 \underset{charge}{\overset{discharge}{\rightleftarrows}} 3\,\text{C} + \text{LiCoO}_2$	3.75	375	1,432
$\text{Li} + \text{FePO}_4 \underset{charge}{\overset{discharge}{\rightleftarrows}} \text{LiFePO}_4$	3.45	586	2,110	$\text{LiC}_6 + \text{FePO}_4 \underset{charge}{\overset{discharge}{\rightleftarrows}} 6\,\text{C} + \text{LiFePO}_4$	3.3	385	1,169
$0.8\,\text{Li} + \text{Li}_{0.2}\,\text{Mn}_2\text{O}_4 \underset{charge}{\overset{discharge}{\rightleftarrows}} \text{LiMn}_2\text{O}_4$	4.00	474	2,044	$0.8\,\text{LiC}_6 + \text{Li}_{0.2}\,\text{Mn}_2\text{O}_4 \underset{charge}{\overset{discharge}{\rightleftarrows}} 4.8\,\text{C} + \text{LiMn}_2\text{O}_4$	3.85	346	1,225
$2\,\text{Li} + \frac{1}{8}\,\text{S}_8 \underset{charge}{\overset{discharge}{\rightleftarrows}} \text{Li}_2\text{S}$	2.2	2,613	4,286	$2\,\text{LiC}_6 + \frac{1}{8}\,\text{S}_8 \underset{charge}{\overset{discharge}{\rightleftarrows}} 12\,\text{C} + \text{Li}_2\text{S}$	2.09	589	1,222
$2\,\text{Li} + \frac{1}{2}\,\text{O}_2 \underset{charge}{\overset{discharge}{\rightleftarrows}} \text{Li}_2\text{O}$	2.91	5,220	10,508	$2\,\text{LiC}_6 + \frac{1}{2}\,\text{O}_2 \underset{charge}{\overset{discharge}{\rightleftarrows}} 12\,\text{C} + \text{Li}_2\text{O}$	2.76	850	1,885
$2\,\text{Li} + \text{O}_2 \underset{charge}{\overset{discharge}{\rightleftarrows}} \text{Li}_2\text{O}_2$	2.96	3,458	7,989	$2\,\text{LiC}_6 + \text{O}_2 \underset{charge}{\overset{discharge}{\rightleftarrows}} 12\,\text{C} + \text{Li}_2\text{O}_2$	2.81	793	1,804

Conventional lithium ion cells are based on a graphite anode which forms an intercalation compound LiC_6. In contrast to this, lithium metal is the preferred anode in Li/O_2 and Li/S batteries. An improved comparability of energy densities is achieved by calculating densities with graphite and a lithium anode. When graphite is used, the cell voltage decreases about 0.15 V compared with metallic lithium. The volumetric energy densities are calculated for cells in a discharged state, i.e. densities and mass fraction of the charged products are included in the calculation.

sulfur, and its low toxicity. There have been great improvements during the last 10 or 15 years. But the technology still faces great challenges, even now. On first glance, a lithium-sulfur cell is based on reversible transformation of lithium by means of sulfur according to the following principle:
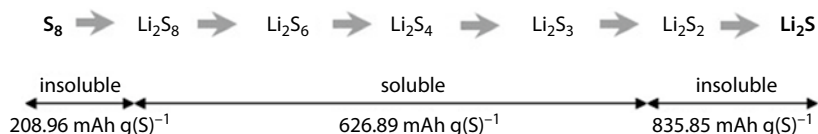
$$\text{Anode reaction}: 16\,\text{Li} \rightarrow 16\,\text{Li}^+ + 16\,\text{e}^-$$

$$\frac{\text{Cathode reaction}: S_8 + 16\,\text{e}^- \rightarrow 8\,S^{2-}}{\text{Overall reaction}: 16\,\text{Li} + S_8 \rightarrow 8\,\text{Li}_2\,S\ (E^\circ = 2.24\ \text{V})}$$

The theoretical cell voltage is calculated as $E^\circ = 2.24$ V from the Gibbs energy of this reaction ($\Delta_r G^\circ_{(25\,^\circ C)} = -432.57$ kJ/mol [Li$_2$S]). Combined with the theoretical capacity of 1,167 mAh/g (Li$_2$S), the resulting theoretical energy density is 2,613 Wh/kg (Li$_2$S). This value is several times higher than that of conventional batteries. Literature often describes the cathode reaction by itself, thus the capacity mentioned there is usually referring to sulfur. It is 1,672 mAh/g (S).

Fig. 16.2a shows a schematic diagram of a cell. A suitable cathode structure must be generated since both sulfur and the discharge product Li$_2$S are not electrically conducting. Usually, porous carbon particles with large surfaces are used as carrier material. They provide electronic contact and also ensure sufficient electrolyte accessibility. The considerable volume changes are characteristic for cell reactions. Li$_2$S ($\rho = 1.66$ g/cm^3, $V_m = 28.0$ ml/mol) has a lower density than sulfur ($\rho = 2.07$ g/cm$_3$, $V_m = 15.5$ ml/mol). Therefore, the cathode must provide enough space to compensate for a volume increase of around 80 %. In general, a sulfur cathode contains between 50 and 70 % weight percent sulfur. The remaining weight is divided among the carbon carry material and the binding agent (small amount). Carbon also needs to be added to standard cathode materials as a conducting additive, but with lower percentages. The energy densities of a lithium-sulfur cell attainable in practice are much lower than the theoretical energy densities. This is mainly due to the high carbon content and the required high porosity.

The electrolyte is made of a mixture of organic solvents and the applicable conducting salt. As opposed to standard carbonate-based solvents such as ethylene carbonate (EC)/dimethyl carbonate(DMC) with the conducting salt LiPF$_6$, the Li/S$_8$ cell in general features a mixture of dimethoxyethane (DME, C$_4$H$_{10}$O$_2$), 1,3-dioxolane (DOL, C$_3$H$_6$O$_2$), and lithium bis(trifluoromethylsulfonyl)imide (LiN(SO$_2$CF$_3$)$_2$, LiTFSI), because, at this stage, this mixture seems to be best compatible with the metallic lithium anodes.

This cell reaction seems quite simple at first glance, however if one takes a closer look it becomes very complex. Several intermediate steps for the reduction of sulfur to the sulfide ion (S^{2-}) are the reason:

S$_8$ → Li$_2$S$_8$ → Li$_2$S$_6$ → Li$_2$S$_4$ → Li$_2$S$_3$ → Li$_2$S$_2$ → **Li$_2$S**

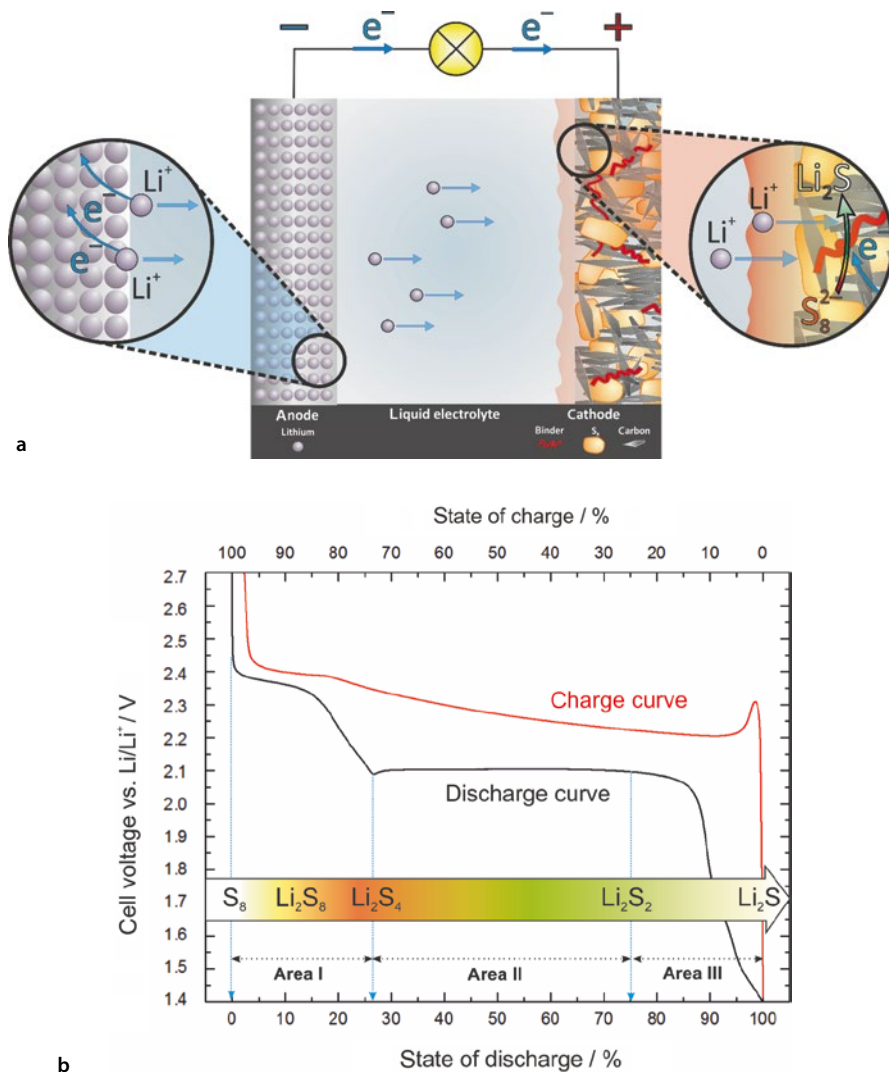| insoluble	soluble	insoluble
208.96 mAh g(S)$^{-1}$	626.89 mAh g(S)$^{-1}$	835.85 mAh g(S)$^{-1}$

Fig. 16.2 (a) Schematic diagram of a lithium-sulfur cell. Metallic lithium is the anode material. The cathode consists of a mixture of sulfur and carbon particles, which is mechanically stabilized by means of a binding agent. (b) Typical voltage profile (charging and discharging cycle) of a lithium-sulfur cell.

Most polysulfides dissolve very well in the electrolyte, hence the reaction mechanism is considerably different to that of conventional lithium-ion batteries where the reactions are pure solid state reactions. Fig. 16.3 shows polysulfide solubility in the electrolyte with the help of a demonstration. The electrolyte takes on color immediately after the beginning of the discharge reaction because of the dissolved species.
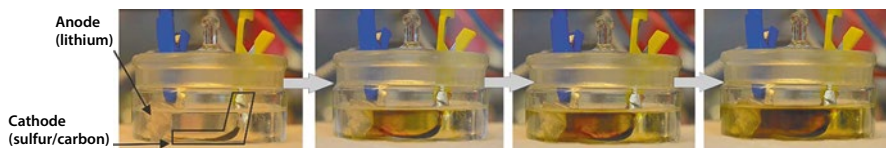
Fig. 16.3 First discharging of a lithium-sulfur cell in a glass cell. In the beginning of the reaction, soluble polysulfides are formed at the cathode from sulfur and lithium. They diffuse to the lithium anode (Section 16.2.2 – Shuttle mechanism)

It is still unsure which species emerge, how quickly the individual partial reactions take place, and how high the respective concentrations are at a specific point in time. The influence of polysulfide formation on the cell reaction can be directly seen from the discharge voltage (Fig. 16.2b). The discharging process can be divided into three areas.

In the beginning (area 1), the discharge reaction starts with the reduction of elementary sulfur S_8. Higher polysulfides such as Li_2S_8 and Li_2S_6 are formed. They dissolve in the electrolyte, which causes the discharge voltage to continually decrease. A minimum characterizes the transition to area 2. The incipient formation of solid Li_2S (Li_2S_2) phase is the reason. The required nucleation enthalpy causes an additional overvoltage and subsequently a discharging cycle minimum. Sulfur reduction continues in area 2. Aside from the solid phases, low-order soluble polysulfides (Li_2S_4, Li_2S_3) exist. Ideally, a full transition from Li_2S_2 to Li_2S takes place at the end of discharging. However, this is usually not achieved in cells. In general, 2/3 to 3/4 of theoretical capacity are reached. Reasons for this could be: insufficiently fast solid-state diffusion during the transition from Li_2S_2 to Li_2S, low electrical conductivity of Li_2S_2 and Li_2S, blocking of the porous electrode by the growing Li_2S particles, or the shuttle mechanism (Section 16.2.2). Overall, the complex cell reaction leads to two plateaus which is why the measured cell voltage slightly deviates from the thermodynamic value of 2.24 V for the direct transition from lithium and sulfur to Li_2S.

There is less knowledge on what happens when reversing the reaction. Charging features a continually increasing potential and appears to be simpler, namely by means of multiple electron transfer. Peled et al. [5] used cyclic voltammetry during the discharging process to show an incremental reduction, i.e., the voltammogramm displays several maximums. However, there was only a single maximum for the charging process (oxidation). This correlates with formation of S_8^{2-}.

Oxidation to S_8 at the end of the charging process apparently is incomplete [6, 7]. It is still unclear how much of the solid phases (S_8, Li_2S_2, Li_2S) eventually form during cell cycling and how high the share of the respective polysulfides is. Only gradually, elaborate in situ experiments shed light on cell chemistry [8, 9].

16.2.2 Shuttle mechanism

Polysulfides dissolve very well in electrolytes. This causes another lithium-sulfur cell characteristic, the so-called shuttle mechanism (Fig. 16.4). The polysulfides
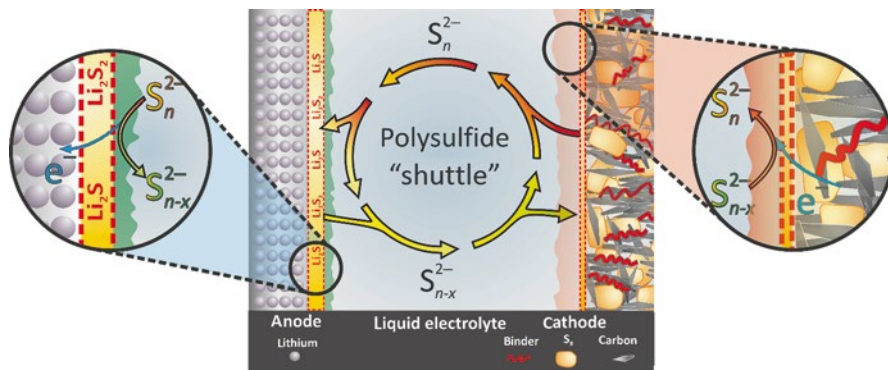
Fig. 16.4 Li/S cell shuttle mechanism during charging. The polysulfide solubility in the electrolyte causes a sulfur loss at the cathode. This reduces capacity ("fading") and eventually causes reduced cell service life. Li_2S/Li_2S_2 depositions form at the anode and cathode surface during cell cycling

S_n^{2-} that form and dissolve at the cathode, diffuse to the lithium anode and are reduced to Li_2S_2 and Li_2S.[3] Subsequent high-order polysulfide species react with these compounds and form low-order polysulfides $S_{(n-x)}^{2-}$. This means that the desired electrochemical reaction of sulfur at the cathode partly also takes place at the anode in uncontrolled fashion (chemical or electrochemical reactions both are conceivable), which negatively influences cell characteristics.

The low-order polysulfides formed at the anode diffuse back to the cathode. When the cell is discharged, these diffused species are further reduced to Li_2S_2 or Li_2S. Simply put, the cathode reaction partly takes place at the anode during the discharging process or, rather, the cell self-discharges. Both are undesirable effects decreasing capacity. In contrast to that, the diffusion to the cathode during the charging process is followed by a re-oxidation of the polysulfide species from low order to higher order. These polysulfides then diffuse to the anode again. This cycle is generally known as the shuttle mechanism. For a very strong shuttle, charging continues infinitely as the cell is "chemically short-circuited". Kumaresan et al. [10] gave a mathematical description of the discharging and charging reaction and the shuttle mechanism.

Overall, the shuttle mechanism causes a loss of sulfur active mass in the cathode leading to poor cycle life.

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[3]The polysulfide species S_n^{2-} that form at the cathode during discharging dissolve in the electrolyte there. A concentration gradient versus the anode develops, which causes the polysulfides to diffuse toward the anode. Step by step, the polysulfides are distributed in the electrolyte.

16.2.3 Long-term stabilization concepts

Currently, several concepts are tested to improve Li/S cell cycling characteristics. These concepts concern the cathode (carbon/sulfur), the electrolyte, and the anode (lithium metal). The goals especially are to limit the active mass loss, to suppress the shuttle mechanism, and to keep the cathode structures mechanically stable over a longer period of time. Hence, special carbon materials with a defined porosity are used for the cathode. They ensure sufficient electrical sulfur contact and also immobilize the polysulfide species to limit their loss in the electrolyte. A great many number of scientific papers treating these issues have been published during recent years. Nazar et al. [11] for example melt-infiltrated a special carbon (CMK-3) with a defined pore size of $d = 3$ nm with sulfur at 155 °C in their highly regarded paper (Fig. 16.5). The material showed a considerably less pronounced shuttle mechanism and a comparably stable cycling behavior at high capacities when compared to not-infiltrated samples. This is due to the material's special nanostructure.

Modifying the carbon surface with polyethylene glycol (PEG) resulted in additional improvement. Other researched carbon materials include activated carbon, carbon black, graphene, and carbon nanotubes.

It is important to note that, next to the carbon material, also the electrode preparation has a major influence on the cathode performance. Electrode sulfur surface load, layer thickness, binder content, and binder type are among significant parameters in this respect [12, 13]. Decrease in electrode layer thickness or decrease in sulfur surface load also are simple measures to improve cycling behavior. Research is also looking into polysulfide loss reduction by adding cathode additives such as Al_2O_3 or SiO_2 (polysulfide trap). Currently, a high surplus of electrolyte and lithium is still required to guarantee sufficient cycling stability. These measures however defeat the purpose of creating a high energy density battery. Therefore, there must be a balanced approach between improving individual parameters and decreasing energy density [14–18].

Another approach is to prevent the diffusion of polysulfide species to the anode. To that end, solid or gel polymer electrolytes are used as barriers [19]. Compared to liquid electrolytes, however, this material has a decreased conductivity and contacting capability that cause higher overvoltages and thus lower cell energy efficiency. Aurbach et al. [20] researched lithium anode passivation by means of the electrolyte additive $LiNO_3$. This additive forms a protective layer which effectively mitigates the parasitic polysulfide reduction a the lithium electrode. $LiNO_3$ has established itself as standard additive in lithium-sulfur battery research. However, $LiNO_3$ is continually broken down in the cell and therefore does not prevent aging, it only slows it down [21].

In addition to all of the above-mentioned cell concepts, additional approaches to create an electrochemical storage device based on lithium and sulfur compounds are currently being researched or rediscovered [22]. It seems as if sulfur can be reversibly implemented in Li^+-conducting compounds such as lithium
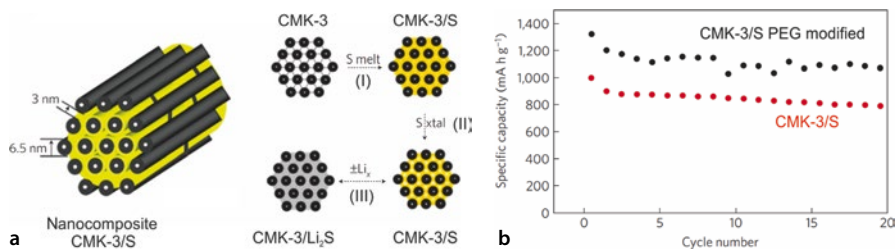
Fig. 16.5 (a) Production of a nano-structured cathode from mesoporous carbon (CMK3) and sulfur. (I) Carbon melt infiltration with liquid sulfur. (II) Sulfur cooling and crystallization (30 wt% CMK-3, 70 wt% S). (III) The volume increase that results from Li_2S formation is compensated by the carbon that provides enough free space. (b) Nanocomposite (CMK-3/S) or PEG-modified material cycling stability
(Material reproduced and modified by permission of Macmillan Publishers Ltd: Nature Materials [11], Copyright 2009)

polysulfidophosphates [23]. A different approach substitutes a liquid catholyte for the solid C/S cathode, a concept similar to that of redox-flow batteries [24]. Other approaches are: cells based on dissolved polysulfides (an approach that had been looked into several decades ago [25] and that currently enjoys a renaissance [26–28]) and the opposite, namely all-solid state batteries [29–30] in which a solid electrolyte replaces the liquid electrolyte. It remains to be proven, whether these approaches are finally more promising than the conventional cell design, however.

16.2.4 Status quo

Up to now and in spite of many different approaches, Li/S cells could not be sufficiently improved to ensure satisfying behavior with respect to all important application parameters. For example, cycle life under practical conditions is often insufficient and volumetric energy densities are lower than expected. Also, compared to lithium-ion batteries, cell reaction speed (kinetics) is still insufficient due to the usage of nonconducting species such as S_8, Li_2S_2, and Li_2S. Increased research and development efforts are therefore required to develop a mass-marketable lithium-sulfur cell. There exist however novel applications relying on high gravimetric energy densities (e.g., aerial drones). The intensified research efforts produce a high publication rate of 5 to 10 per week. In addition to the lithium-sulfur battery discussed here, a sodium-sulfur battery that operates at ambient temperatures is also conceivable [31]. So far, however, the performance of these cells still lacks behind the lithium-sulfur cells.

Oxis Energy Limited (Oxfordshire, UK) and formerly also Sion Power Corp. (Tucson, USA) developed Li/S cells for a variety of applications. Energy densities of 400 Wh/kg on the cell level (500 Wh/kg targeted for 2019) are reported yet they are not available on the free market.

16.3   The lithium-air battery

16.3.1 Basic principle

Abraham et al. in 1996 were the first to describe the function of lithium-air batteries (more precisely lithium-O_2 batteries) using non-aqueous electrolytes [32]. The main difference to standard batteries is that this cell type is an open system because – as with fuel cells – atmospheric oxygen is changed over at the cathode (Fig. 16.6). One might assume that the discharge product of an Li/O_2 cell is Li_2O, similar to fuel cells where H_2O is formed from hydrogen and oxygen. However, it is lithium peroxide (Li_2O_2) that is generally formed as a discharge product for thermodynamic reasons. Research has shown that potentially formed Li_2O is difficult to oxidize again. Metastable lithium superoxide probably develops as interstage product.

Anode reaction : $2Li \rightarrow 2\,Li^+ + 2\,e^-$	Anode reaction : $2Li \rightarrow 2\,Li^+ + 2\,e^-$
Cathode reaction : $0.5\,O_2 + 2e^- \rightarrow O^{2-}$	Cathode reaction : $O_2 + 2\,e^- \rightarrow O_2^{\,2-}$
Overall reaction : $2\,Li + 0.5\,O_2 \rightarrow Li_2O$ ($E^{\circ} = 2.91$ V)	Overall reaction : $2\,Li + O_2 \rightarrow Li_2O_2$ ($E^{\circ} = 2.96$ V)

Battery mass increases with an increasing discharge state because oxygen is introduced from the outside during discharging. This is why the described theoretical energy density of this system varies considerably. If the oxygen mass is included in the calculation, the free reaction enthalpy $\Delta_r G^{\circ}_{(25\ °C)} = -439.08$ kJ/mol (Li_2O) combined with a capacity of 1,793 mAh/g (Li_2O) results in a theoretical energy density of 5,220 Wh/kg (Li_2O) (or 1,168 mAh/g and 3,458 Wh/kg for Li_2O_2 as discharge product). Without the oxygen mass, the energy density for both reaction products is above 11,000 Wh/kg. This is similar to theoretical energy densities of standard fuels where oxygen mass is also not included in energy density calculations.

Fig. 16.6 shows that a suitable cathode structure (conductive carbon matrix covered with catalytic particles, if necessary) is required to enable the cell reaction and to provide enough free space for the resulting solid reaction products. The reaction products have a very low conductivity. This is why large-surface carbon materials (> 50 m^2/g) are generally used to ensure a homogeneous distribution of product particles that are as small as possible. Since it is difficult to specify the theoretical cathode capacity, literature specifies measured capacity as absolute (mAh) or sets it in reference to the carbon carrier material's weight (mAh/g[C]).

For operating a lithium-oxygen cell with air, several undesired side reactions with air components must be prevented by using suitable membranes. Examples are: unwanted introduction of N_2 (nitride formation, Li_3N), H_2O (hydroxide formation, LiOH), and CO_2 (carbonate formation, Li_2CO_3). Currently, no simple solutions have been found in this respect. Hence, cell chemistry research is not conducted with air,
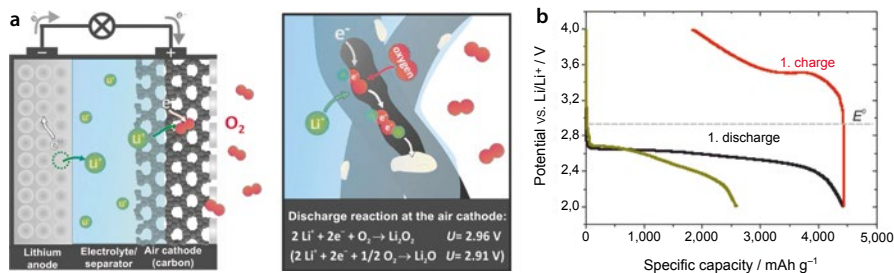
Fig. 16.6 **(a)** Schematic diagram of a lithium-air cell and electrode reaction for Li_2O_2 as the discharge product (oxygen reduction reaction, ORR). **(b)** Typical charging and discharging cycle. The displayed capacity relates to the mass of the carbon material used. The thermodynamically calculated voltage is $E° = 2.96$ V

but with oxygen. Also, cell drying-out, i.e., electrolyte evaporation from the cathode that is in contact with the atmosphere, must be prevented during operation. At the same time, lithium anode corrosion by dissolved oxygen in the electrolyte must be inhibited. In practice, this also calls for an additional protective layer. Because of the additionally required components, the attainable energy density will be much lower in practice than the theoretical values.

16.3.2   Electrolyte stability, efficiency, and reversibility

Fig. 16.6b shows a typical charging and discharging cycle of a Li/O_2 cell. The big difference between the measured discharge voltage (~2.6 V) and the charging voltage (> 3.5 V) is representative for this cell type and results in pronounced hysteresis. This is caused by high overvoltages during cell reactions, especially during the charging process (oxygen oxidation). The extent of the hysteresis scales inversely with the energy efficiency of the cell reaction which is only around 60 to 70 % for many current aprotic Li/O_2 cells. This observation led to increased catalyst usage (MnO_2, Pt, Au, etc.) and better cathode materials (activated carbon, carbon black, graphene, nanotubes, etc.) with the hope to reduce overpotentials and to improve rechargeability.

Early research results indicated complex cell reactions [33–35]. However, it was recently proven that carbonate-based electrolytes (i.e., 1 M $LiPF_6$ in propylene carbonate) that had been used until then irreversibly degrade during cell reaction [36, 37]. Instead of the desired product (Li_2O_2), a multitude of degradation products (Li_2CO_3, CO_2, H_2O, $C_3H_6[OCO_2Li]_2$, …) were accounted for. Partially, these degradation products are further degraded during charging. This is due to the reactivity of the superoxide radical ($O_2\cdot-$) which forms as an intermediate during oxygen reduction. Thus, capacity values achieved in experiments were based not only on the reversible formation and degradation of Li_2O_2, they also were a result of irreversible
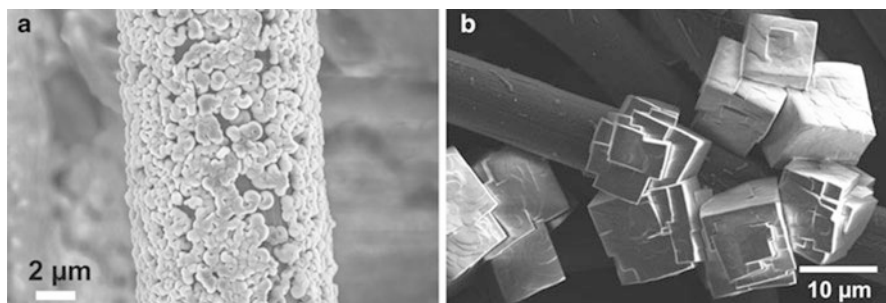
Fig. 16.7 SEM micrographs of an Li/O_2 cell cathode (*left*) and an Na/O_2 cell (*right*) after discharging. Carbon fibers were the conducting carrier material in both cases. It is clearly discernible that Li_2O_2 is present as nanoparticles, while NaO_2 forms cubic crystallites in the μm range

electrolyte degradation. Even worse, many of the suggested catalysts accelerated this degradation process even more [38].

Research focus has changed due to these results and currently is directed toward developing electrolytes with a sufficient stability. It was not possible to identify a suitable system for practical applications till now. However, cell reactions, which still are accompanied by undesired secondary reactions, can at least be better examined in glyme or DMSO based electrolytes. For example, the discharge product Li_2O_2 generally occurs as nanoscopic particles shaped as a torus (Fig. 16.7). The use of gold instead of carbon as electrode may also ease scientific examinations of the electrode reaction [39].

16.3.3 Status quo

The current Li/O_2 battery status quo without a doubt still requires more fundamental research. At present, there is no cell concept for aprotic electrolytes that is able to prove reversible formation of Li_2O_2 (or Li_2O) across several cycles without simultaneous electrolyte degradation in practice.

Recent research results make it obvious that currently the greatest challenge for commercialization is the development of chemically stable electrolytes and electrode materials. In terms of the electrolyte, additional requirements need to be fulfilled aside from chemical stability. These are: lithium-ion conductivity, oxygen solubility and diffusivity as well as suitable electrode wetting. To better determine and understand the many various secondary reactions, current research uses a great variety of analysis methods. Gas analysis or pressure monitoring during cell cycling are methods that can provide clear evidence for side reactions, for example.

A more recent approach to reducing charging overvoltages uses redox mediators such as tetrathiafulvalene (TTF), lithium iodide, or tetramethylpiperidinoxyl (TEMPO) [40–46]. Oxidation is attained through dissolved compounds in this case. During charging, these compounds themselves are electrochemically oxidized at

first, then they are reduced by Li_2O_2, which then decomposes under release of O_2. Another important aspect is the understanding of water impurities on the cell chemistry [47–51].

Surprisingly, it could be proven that a substitution of sodium for lithium makes the cell reaction much more reversible. The discharge products in this case are not nanoscopic Na_2O_2 particles however, but large sodium superoxide (NaO_2) crystallites (Fig. 16.7) [52]. A catalyst may not be required because overvoltages are very low. Compared to an Li/O_2 cell, energy density is lower (2,643 Wh/kg[Na] and 1,105 Wh/kg[NaO_2], respectively).

Li/O_2 cells not only are developed by academic institutions, but also by companies [37, 53]. Li/O_2 batteries with an aqueous electrolyte are an alternative to the non-aqueous Li/O_2 batteries discussed here [54]. In such a system, oxygen from the ambient air reacts with lithium and water to lithium hydroxide (LiOH). Very high energy densities are to be expected with this cell concept as well. It is a prerequisite however, to effectively protect the lithium anode against the aqueous electrolyte.

16.4   Challenges of using lithium metal as anode

The use of lithium metal as anode is most appealing for achieving highest energy densities.

Reversible dissolution and re-plating of lithium that are required for rechargeable batteries faces a range of difficulties and related safety concerns so far largely prevent its use in application. This is due especially to the chemical reactivity of lithium with the electrolyte as well as to the formation of dendrites during charging.

In general, lithium reacts with all known electrolytes for thermodynamic reasons. A key criteria for using lithium metal in an battery therfore is that the electrolyte forms a passivating layer that prevents further parasitic reactions. The concept of such an solid electrolyte interphase (SEI) has been introduced by Peled in 1979 [55]. The layer must be conductive to lithium ions and block electrons to achieve this. It should be mentioned that all lithium-ion batteries with graphite anode are also operated outside of the electrolyte's stability range. Caused by a reaction with the carbonate-based electrolyte (i.e., $LiPF_6$ in EC/DMC and additives), a very stable SEI is formed that has a thickness of only a few nanometers. Contrary to that, ether-based solvents such as dioxolane or glyme are preferable for metallic lithium anodes [56]. This in spite of the fact that they are irreversibly degraded over time. Creeping corrosion of the lithium electrode requires that lithium anode cell systems have to be operated with excess lithium and liquid electrolyte. This negatively impacts the energy density of the cell. It should be pointed out that especially when lithium-sulfur cells are researched in a laboratory environment, this is often done with a great excess of liquid electrolyte and lithium. This excess must be considerably reduced to achieve a marketable cell concept. Therefore, there is great need to develop suitable approaches to improve the behavior of lithium electrodes with electrolytes in general.

Next to the thermodynamic instability of lithium in contact with electrolytes, the phenomenon of dendrite formation is a key challenge. Dendrites are well known to form during metal plating and hence during charging of a battery with lithium electrode. If the dendrites grow all the way to the cathode, they would cause a short circuit in the cell resulting in thermal runaway. It is possible that the dendrites fully become detached from the anode during cycling. Then they would not be available for the electrode reaction ("dead lithium"). Cell capacity would continually decline. An excess of lithium could balance out this loss. The amount of added lithium strongly depends on the system researched and the degree of cell optimization. Earlier research with lithium anodes (MoS_2 cathode) could give some pointers in this respect. A threefold lithium excess resulted in a service life of 300 cycles [57].

The following requirements must be fulfilled to use lithium in rechargeable cells: parasitic reactions must be kept as low as possible and lithium plating should be as planar as possible, i.e., dendrite formation needs to be prevented. It might be possible to achieve these goals if a suitable electrolyte composition is developed that promotes formation of a pertinent SEI in the contact with lithium. An alternative could be coatings or membranes. These could be applied directly to the anode and may also function as separator. Another approach to prevent dendrite formation subjects the cell to mechanical pressure above the lithium yield point [58]. There is also research looking into different additives to improve lithium electrode reversibility [59–63].

If lithium cannot be used, conventional anode materials such as graphite may be used instead. This would however considerably reduce the theoretically achievable energy density (Table 16.2) to more unattractive values. This is why another approach favors silicon as anode material in Li/S cells [64–65]. Assuming formation of $Li_{4.4}Si$, the theoretical cell voltage and energy density would amount to 2.04 V and 1,863 Wh/kg (3,299 Wh/l), respectively. Another alternative is tin ($E° = 1.72$ V, 922 Wh/kg and 2,628 Wh/l, respectively) [19]. On the other hand, the use of metals such as Si or Sn as substitute is not straightforward either as the large volume expansion during lithium intercalation leads to particle cracking and poor SEI stability.

16.5   All-solid state batteries

A very recent trend is the development of rechargeable solid state batteries (SSB), often also noted as "all-solid state batteries" (ASSB) or "solid state lithium batteries" (SSLB) in order to highlight the fact that this type of battery is constructed without the typical liquid electrolyte [66–69]. The current rate of development is fast, and only some of the most important topics related to the development of SSB shall be discussed here briefly (see [67–68] for a discussion of the essential challenges).

Two major types of SSLB have to be distinguished on the basis of the cell geometry and cell charge capacity: *Thin film* SSLB (tf-SSLB) have a relatively low area

capacity in the order of 0.1 mAh/cm^2 and are typically prepared by gas phase deposition. Thin film SSB are already commercialized, but the corresponding market is yet small. Commercial tf-SSLB are usually based on single cells of the type Li/"LiPON"/LCO, i.e. contain a thin film cathode (a few μm thick) of LiCoO$_2$, a thin film solid electrolyte separator made of "LiPON" (an amorphous Li$_3$PO$_4$ film containing a few percent of nitrogen) and a lithium metal anode. Once well-functioning, tf-SSB can be run reversibly for thousands of cycles without significant degradation. Production of large scale batteries on the basis of multi-layer tf-SSB will not be cost-efficient, and therefore, the further development and use will be restricted to low-energy mobile applications (smart cards, flexible batteries for textiles, etc.).

Thick film or *large scale* SSB are still in the state of research [67–71]. Here, two general trends can be identified: In "solidified" lithium ion batteries (SE-LIB; Solid Electrolyte LIB) the liquid electrolyte is substituted by either a solid polymer or a glass-ceramic electrolyte, or a combination of both. As solid electrolytes have usually a higher density than liquid (organic) electrolytes, SE-LIB will only gain improved energy density if the use of high capacity electrodes or of high voltage cathodes are enabled. One particular development in the direction of high energy SSB would then be LiM-SSB (Lithium Metal SSB) in which a thick lithium metal anode is utilized. Due to the high specific capacity of the lithium metal anode, LiM-SSB could offer a significant jump in energy density (up to +70%), but both severe mechanical effects during metal dissolution and deposition, as well as the risk the abovementioned dendrite growth through the solid electrolyte separator have to be overcome.

Power density is considered as "Achilles heel" of SSB, as solid electrolytes are considered as comparably poor ionic conductors. This is not correct, and today already quite a number of inorganic solid electrolytes with lithium ion conductivity higher than that of liquid electrolytes have been reported, see Fig. 16.8 for comparison [72–73]. In the case of SE-LIB, authors of a recent report even suggest higher
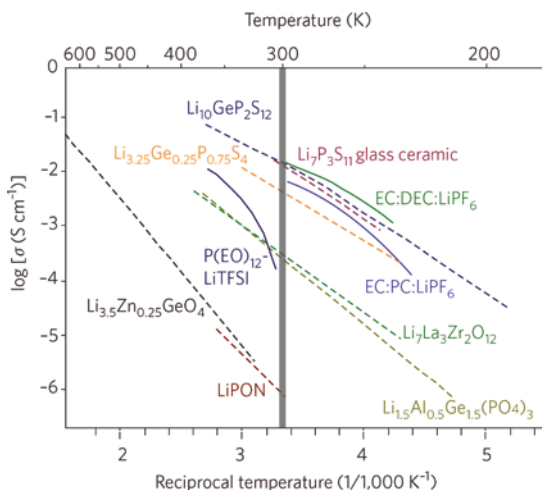

Fig. 16.8 Ionic conductivity of various solid electrolytes (Reprinted by permission from Macmillan Publishers Limited, Nature Energy, doi: 10.1038/nenergy.2016.141 (2016))

rate capability than in the case of conventional LIB [70]. This can be of great relevance for fast charging and will surely drive further research.

It is generally accepted that interface kinetics is key to SSB with sufficient performance [67–68]. Once the lithium metal anode is employed, SEI formation with the solid electrolyte will take place, as the best solid electrolytes are all thermodynamically unstable against reduction [74–75]. If the forming SEI is highly resistive, the cell impedance will increase and will reduce the energy efficiency. If the forming SEI is highly conductive it may stabilize the cell, as in the case of SEI in conventional LIB. At the cathode/solid electrolyte interface also degrading interfacial reaction may take place and may also increase the cell impedance.

In summary, solid state batteries may open an attractive avenue toward high energy and high power lithium batteries. It is too early to judge the potential commercial success, as still some critical issues have to be solved.

16.6   Outlook

Lithium-sulfur and lithium-air batteries are two of the few systems with which it seems feasible to achieve a gravimetric energy density increase compared to lithium-ion batteries. Increase in volumetric energy density is less significant however. When sulfur or oxygen are used instead of transition metal compounds, there is also hope for producing low-cost batteries provided that the need for special carbons (or alternative electrode materials) or catalysts does not increase costs.

Both systems still pose great challenges from a technological point of view. This is especially true for lithium-air systems, because no suitable aprotic electrolyte could be found up till now. Both systems require protection of the lithium metal anode from parasitic secondary reactions. Special electrolytes or protective layers are required to prevent the shuttle mechanism in Li/S systems and the anode's oxygen corrosion in Li/O_2 cells. Furthermore, dendrite formation must be averted. Also, solid, insulating reaction products develop in both cell types during cycling (S, Li_2S_2, Li_2S and Li_2O_2, Li_2O). They may block the electrode and considerably impair the cell reaction's kinetics. Therefore, it is probably necessary to use cathode structures with a suitable porosity to promote a fine (nanometer range) reaction product distribution. A lithium-air cell also requires an effective and low-cost membrane, which specifically enables oxygen transport into and from the cell. This calls for innovations on both material and cell level.

It is hard to forecast whether and, if possible, when the next generation technologies for secondary elements described here can actually be put into practice. This is due to the current development status and the very diverse requirements for different application areas. A study conducted by the Fraunhofer Institute for Systems and Innovation Research expects rechargeable Li/S_8 cells (400 Wh/kg, 100 cycles) between 2020 and 2030 and Li/O_2 cells (>300 Wh/kg, > 500 cycles) later than 2030. This shows that there are still fundamental problems to be solved. In terms of primary elements, lithium-air and similar systems may be on the market earlier than that.

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