下一代能源存储技术及其关键电极材料

杨 泽 张 旺 沈 越 袁利霞 黄云辉*

(华中科技大学材料科学与工程学院, 材料成型与模具技术国家重点实验室, 武汉 430074)

摘要: 由于能源危机与环境问题, 全球能源的消耗正逐渐从传统化石能源转向其它清洁高效能源。高效清洁能源的存储是电动汽车和智能电网的关键技术, 对新能源、新材料和新能源汽车国家战略新兴产业的发展具有重要意义。锂离子电池是目前广泛应用的一种能源存储器件。电动汽车和智能电网对能量密度、功率密度、循环寿命和成本等方面的要求越来越高, 传统的锂离子电池面临巨大挑战, 发展下一代能源存储技术迫在眉睫。高能量密度的锂硫电池和锂空气电池, 低成本、高安全性的室温钠离子电池受到了越来越多的关注。本文简要总结了近年来锂硫电池、锂空气电池和钠离子电池及其关键电极材料的研究进展, 并对这些新型能源存储技术存在的问题和未来的前景做出了分析和展望。

关键词: 能源存储; 锂硫电池; 锂空气电池; 钠离子电池

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Next-Generation Energy Storage Technologies and Their Key Electrode Materials

YANG Ze ZHANG Wang SHEN Yue YUAN Li-Xia HUANG Yun-Hui*

(State Key Laboratory of Material Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, P. R. China)

Abstract: In response to energy shortages and environmental concerns, global energy consumption is transitioning from a reliance on fossil fuels to multiple, clean and efficient power sources. Energy storage is central to the development of electric vehicles and smart grids, and hence to the emerging nationally strategic industries. Today, lithium-ion batteries (LIBs) are among the most widely used energy storage devices in daily life, but they face a severe challenge to meet the rigorous requirements of energy/power density, cycle life and cost for electric vehicles and smart grids. The search for next-generation energy storage technologies with large energy density, long cycle life, high safety and low cost is vital in the post-LIB era. Consequently, lithium-sulfur and lithium-air batteries with high energy density, and safe, low-cost room-temperature sodium-ion batteries, have attracted increasing interest. In this article, we briefly summarize recent progress in next-generation rechargeable batteries and their key electrode materials, with a particular focus on Li-S, Li-air, and Na-ion batteries. The prospects for the future development of these new energy storage technologies are also discussed.

Key Words: Energy storage; Lithium-sulfur battery; Lithium-air battery; Sodium-ion battery

1 Introduction

Increasing huge markets in hybrid electric vehicles (HEVs), electric vehicles (EVs), and large-scale solar/wind energy storage require electrochemical devices with large energy density, long

cycle life, high safety, and low cost. The electrode materials are crucial to the next-generation energy storage technologies. In a near future, lithium-ion batteries (LIBs) with energy density $\geq 200 \text{ Wh} \cdot \text{kg}^{-1}$ and power density $\geq 3000 \text{ W} \cdot \text{kg}^{-1}$ are desired, while the ac-

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*Corresponding author. Email: huangyh@hust.edu.cn; Tel: +86-27-87558241.

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ceptable cost should be lower than $2 \text{ RMB} \cdot \text{Wh}^{-1}$ for EVs and $1 \text{ RMB} \cdot \text{Wh}^{-1}$ for energy storage in electric grid. To achieve high-capacity LIBs, Li-rich $\text{Li}_2\text{MnO}_3 \cdot \text{LiMO}_2$ ($M = \text{Co}, \text{Ni}, \text{Mn}, \text{etc.}$), high-voltage spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and layered oxides $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ (NCM) or $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$ (NCA) with high Ni content are attractive as cathode materials, and high-capacity silicon and Si-C composites are potential as anode materials¹⁻⁴.

As the new electrochemical devices, Li-S batteries (LSBs) and Li-air batteries (LABs) have been paid more and more attention due to their higher energy densities than LIBs⁵. Among them, LSBs are believed to be closest to the practical application, but low utilization and poor conductivity of S, cycle performance, high self-discharge, and safety issue of Li anode are the main problems to hinder the application⁶. Electrode materials as well as electrolyte are still crucial for the development. For large-scale energy storage, safety, and cost are the most important issues. At this point, aqueous sodium-ion batteries (SIBs) become more and more attractive in recent years⁷. With some potential cathode and anode materials have been discovered, it can be expected that industrial market of SIBs will come soon, which maybe bring a revolution in energy storage technologies. In this article, we briefly summarize the recent development in LSBs, LABs, and SIBs. Moreover, we propose our prospects for the future development of these new energy storage technologies.

2 Lithium-sulfur batteries

LSBs operate by reduction of elemental S to Li_2S during discharge. The two-electron conversion reaction gives rise to high theoretical capacity of $1675 \text{ Ah} \cdot \text{kg}^{-1}$ and energy density of $2650 \text{ Wh} \cdot \text{kg}^{-1}$, which are almost 6 times larger than those of the state-of-the-art LIBs^{5,8}. Therefore, the Li-S system has a great potential to afford a traveling distance of 500 km for EVs.

Although LSBs have high theoretical energy density, sulfur hasn't been recognized as a good electrode material for quite a long time. Elemental sulfur is a highly insulating material ($\sim 5 \times 10^{-30} \text{ S} \cdot \text{cm}^{-1}$ at 25°C). On the other hand, S_8 can generate lithium polysulfides with different chain lengths (Li_2S_n , $2 \leq n \leq 8$). The reduction level of S_8 is closely related with the solvent used. Cyclic or linear ethers with ethoxy repeating units, which show high solubility for the polysulfide, have been widely used as solvents in the electrolytes. The sulfur cathode in such solvents can achieve a high reversible capacity more than $1300 \text{ mAh} \cdot \text{g}^{-1}$, which is very close to the theoretical capacity of sulfur. But meanwhile, LSBs suffer from shuttle reaction caused by the soluble intermediate polysulfides Li_2S_n ($n > 2$) (see Fig.1). This parasitic process leads to low coulombic efficiency, severe self-discharge and rapid loss of active materials. The final result is the poor cycle life of Li-S battery. Therefore, on one hand the "solid-liquid-solid" process of the sulfur cathode promise the electrochemical accessibility and high utilization of the sulfur, but on the other hand it also brings huge challenge for the cycle stability of

YANG Ze, received his PhD from Huazhong University of Science and Technology (HUST). He is now a postdoctoral researcher in University of Houston. His research interest focuses on cathode materials for lithium-ion and sodium-ion batteries.

ZHANG Wang, received his BSc degree from Huazhong University of Science and Technology (HUST) in 2012. He is now a PhD candidate in HUST. His research interest focuses on rechargeable lithium-oxygen batteries.

SHEN Yue, received his BSc, MSc and PhD from Peking University. He was a visiting student in Georgia Institute of Technology from 2008 to 2010. He then worked as a postdoctoral researcher in Huazhong University of Science and Technology in 2011. He is now an associate professor at HUST. His research interests mainly focus on lithium rechargeable batteries.

HUANG Yun-Hui, received his BSc, MSc, and PhD from Peking University. In 2000, he worked as a postdoctoral researcher in Peking University. From 2002 to 2004, he worked as an associate professor in Fudan University and a JSPS fellow at Tokyo Institute of Technology, Japan. He then worked in the University of Texas at Austin for more than three years. In 2008, he became a chair professor of materials science in Huazhong University of Science and Technology. He is now the dean of the School of Materials Science and Engineering. His research group works on batteries of energy storage and conversion. For details please see the lab website: <http://www.sysdoing.com.cn>.

YUAN Li-Xia, received her PhD at Wuhan University in 2007. She worked as a postdoctoral researcher in Tsinghua University from 2007 to 2009. She is now an associate professor at HUST. Her research interests mainly focus on lithium rechargeable batteries.

the battery. This dilemma makes the development and practical application of LSBs very difficult.

2.1 Sulfur cathodes based on “solid-liquid-solid” electrode process

Before 2009, many research works focused on clarifying the dissolution reaction mechanisms of the discharge products, mixing sulfur with conductive materials to improve the conductivity of the cathode, modifying electrolyte for alleviating the dissoluble loss of polysulfides in liquid electrolytes, and developing advanced binders for more stable electrode structure. Most of the attempts tackled the problems at the macroscopic scale, but the main problems in LSBs still exist. In recent years, the nanotechnology brings a new opportunity for LSBs to improve capacity, power, and cycle stability. The pioneering work was carried out by Nazar's group in 2009: they used ordered mesoporous carbon to immobilize the sulfur species within nanochannels⁹. The S/CMK-3 composite, coated with an additional thin polyethylene glycol (PEG) layer, delivered an exceptionally high initial reversible capacity of $1320 \text{ mAh} \cdot \text{g}^{-1}$ along with a remarkably enhanced cyclability. After then, more and more carbon-based materials with different porous structures were investigated as sulfur-supporting matrices¹⁰. Meanwhile, the polymers, especially the conductive polymers were also widely employed as sulfur hosts or to construct some hybrid nanostructures¹¹. From these, some new cell configurations were also derived, *e.g.* inserting carbon interlayer between the separator and the electrode¹². The interlayer works as a barrier to restrain the diffusion of the dissolved polysulfides. When locating on the cathode side, it can confine the polysulfides within the cathode; while on the anode side, it can cut off the contact of the polysulfide and the Li anode. More recently, a new strategy, entrapping polysulfides within the host in the cathode *via* chemical process, was reported; some metal oxides (MnO_2 ¹³, Ti_4O_7 ^{14,15}), metal organic frameworks (MOFs)¹⁶, MXene nanosheets (Ti_2C)¹⁷ can be used as such kinds of hosts.

Whether the various S/C and S/polymer composites in which polysulfides are immobilized *via* physical absorption, or the newly achieved chemical hosts, it is difficult to capture the dissolved polysulfides completely. Here the “solid-liquid-solid” electrode process of sulfur plays a decisive role. We take the discharge process as an example. The dissolved polysulfides that are formed

Fig.1 Scheme of a Li-S battery

at the beginning of the discharge encounter two kinds of forces: one is the physical or chemical absorption between the hosts and the S_n^{2-} ($n > 2$), which prevents S_n^{2-} ($n > 2$) from diffusing to the bulk electrolyte and to the Li anode; the other is the force caused by the concentration difference and by the electric field between the anode and the cathode, which drives the S_n^{2-} ($n > 2$) to move to the anode. These two kinds of forces are opposite, and the former is stronger than the latter; their balance can be obtained through material design. Even so, the diffusion of S_n^{2-} ($n > 2$) to the anode cannot be inhibited completely due to the volume change of the sulfur species during the lithiation/delithiation. As shown in Fig.2, during the first half of the discharge, solid S_8 is converted to S_n^{2-} ($n > 2$), which is easily dissolved into the electrolyte. The spaces within the nanopores of the carbon matrix occupied by the solid S_8 will be filled by the liquid electrolyte that contains the dissolved S_n^{2-} ($n > 2$). As the discharge reaction continues, solid $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ appear, and the electrolyte penetrates over the micro-domain constructed by the porous carbon or other conductive matrix. Although the interaction between S_n^{2-} ($n > 2$) and the host can capture most of the S_n^{2-} ($n > 2$) ions, part of the S_n^{2-} ($n > 2$) ions will inevitably escape from the “carbon cage” along with the repeated “liquid $\rightarrow$ solid” phase change. As long as the “solid-liquid-solid” mechanism operates, to completely prevent the loss of S_n^{2-} ($n > 2$) is almost impossible.

2.2 Sulfur cathodes based on “solid-solid” electrode process

Among the various nanostructured sulfur composites, S/microporous carbon composites look very special. Unlike most S-based cathodes that cannot work well in the carbonate-based electrolyte owing to high reactivity between the nucleophilic polysulfide anion and carbonyl groups¹⁸, S/microporous carbon composites show great adaptability to the electrolytes. Such composites can work well with the carbonate-based electrolytes, which is even better than in the ether-based electrolytes. However, this type of cathode system shows a single lower-voltage discharge plateau and a strong dependence on sulfur loading. When the S content keeps under some level, the composite cathode can achieve excellent cycle stability; at this moment, even a little more sulfur may dramatically reduce the cycle capacity. Guo *et al.*¹⁹ proposed that the sulfur confined in the micropores exists in small molecular forms like S_{2-4} due to the space limitation, which avoids the formation of soluble long-chain polysulfides (Li_2S_n , $n > 4$). Li *et al.*²⁰ further confirmed that it is the carbon micropores with small enough space that prevent the penetration of the solvent molecules and promote the lithiation/delithiation in sulfur in a

Fig.2 Illustration of the electrode process for sulfur cathode

solid-solid process, and hence effectively avoid the irreversible chemical reactions between the polysulfides and carbonate, and restrain the dissolution of the polysulfides into the electrolytes. Interestingly, the S/microporous carbon composite exhibits a charge-discharge characteristic with outstanding cycle stability, which is quite similar to the recently-reported S/polyacrylonitrile (PAN) composite²¹. The S/PAN composite can also work well in the carbonate electrolyte and also exhibits a single discharge plateau located near 1.7 V (vs Li/Li⁺). Although the distribution and present forms of sulfur in the S/PAN system are still unclear, it seems that S/PAN also operates with a solid-solid mechanism, similar to the S/microporous carbon composite.

2.3 Perspective

With the aid of nanotechnology, Li-S batteries stand an opportunity to exceed the limitation by the “solid-liquid-solid” electrode process. So far two systems can successfully work *via* the “solid-solid” process that can achieve both high sulfur utilization and long cycle life. But unfortunately, both the microporous carbon and the PAN polymer matrix can only achieve low sulfur loading. Thus the advantage of high energy for the LSBs cannot come into true.

With the development of LSBs, the researchers start to pay attention to the real energy density in addition to the sulfur utilization and the cycle life. Almost all the data of specific capacity currently reported were calculated only based on the mass of sulfur. In fact, even in a “solid-liquid-solid” system, the high sulfur utilization and/or long cycle life were used to be attained with low sulfur content in the cathodes (usually < 60%) and low sulfur loading (usually < 2 mg · cm⁻²). Gao *et al.*²² estimated that a Li-S battery does not have the opportunity to exceed the traditional LIBs in the volumetric energy density unless the S content in the cathode exceeds 70%. On the other hand, complicated synthesis routes and/or expensive raw materials are often used to get excellent electrochemical performances, which not only increase the cost of LSBs, but also make the industrial production very difficult. In this regard, there is an urgent need to develop a facile approach to prepare high-loading sulfur cathodes with high sulfur content.

Although the main shortcomings that limit the practical application of LSBs still exist, we believe that in the long run the problems related to the sulfur cathode can be solved eventually. The key point is to find a balance between high energy density and long cycle stability. The interface uncertainty, safety, and engineering difficulties related to the lithium anode are also big challenges for this secondary battery system. The reaction between the polysulfides and lithium anode counteracts the lithium dendrite growth greatly, but sacrifices energy-bearing materials and makes the growth and evolution of solid electrolyte interface (SEI) on lithium surface more seriously. For LSBs that operate by a “solid-liquid-solid” mechanism, the electrolyte composition changes with state of charge (SOC), while the composition, thickness and densification of the SEI on the Li surface may also affect the electrolyte. Currently, almost all the sulfur cathodes or

the lithium anodes in the reports were tested on “half cells”, thus the counter electrode always has excess lithium. Due to the dissolution of the intermediate polysulfides, the relationship between cathode and anode for LSBs is more closely than that for other lithium rechargeable batteries. Therefore, we must consider the cathode together with the anode in LSBs. For practical application, full cells, in which the active materials are carefully calculated and well matched, are needed to be designed to solve the problems or to find the chances buried in the half cells. It is the time to reexamine the electrochemical performances of the sulfur cathode on the condition with S content and loading close to the actual situation.

3 Lithium-air batteries

Among the major types of “beyond lithium” rechargeable batteries, lithium-air batteries have almost the highest theoretical specific energy density. Since its invention in 1996, the research in LABs has experienced a decade of low ebb and another decade of exponential growth. Recently, it seems that the future of LABs becomes controversial. Gallagher and his co-workers²³ analyzed some models and calculated the key parameters of future LAB full cells, and then concluded that LAB “is both higher risk technically and less likely to be attractive to automakers commercially than a closed battery system utilizing a lithium metal negative and an advanced metal oxide positive”. However, any future is not always predictable. Their model is based on the existing cognition. The configuration of the real future LAB may be something very different from the current model. In the following contents, we will discuss the major problems and possible solutions of LABs in detail.

3.1 Cathode chemistry

The LAB (in Fig.3) contains lithium anode and oxygen cathode. The oxygen cathode is usually porous, which includes some catalyst for oxygen reduction.

The chemical reactions are illustrated in Fig.4. The cathode reaction is generally described as:

The formation and decomposition of Li₂O₂ are multi-step and multi-phase interfacial reactions. At least 4 phases are involved: cathode material (mainly carbon), electrolyte, solid Li₂O₂, and

Fig.3 Scheme of a lithium air battery

Fig.4 Process of LAB cathode chemistry

oxygen. The detailed mass and electron transferring processes have been extensively investigated in recent years²⁴. Now novel methods are under development to improve the capacity and reversibility of the LAB cathode²⁵.

The beginning of the discharge is a one-electron reduction reaction:

Then the LiO_2 may be transformed into Li_2O_2 via two possible routes:

One route is through a surface mechanism. The LiO_2 is simply further reduced on the carbon surface to form a Li_2O_2 layer. The formed Li_2O_2 itself is an effective catalyst to catalyze the oxygen reduction reaction. So the newcome oxygen molecules may be oxidized at the Li_2O_2 /electrolyte interface. This mechanism is dominant in the electrolyte with low donor number (DN) or acceptor number (AN) solvent. The other route is through a solution mechanism. In the electrolyte with high DN or AN solvent, the LiO_2 may be dissolved in the electrolyte^{26,27}. Then the LiO_2 molecules may chemically react with each other and form toroid-like Li_2O_2 particles away from the carbon surface. The solution mechanism usually leads to higher capacity. So the DN and AN should be carefully considered when developing novel electrolytes²⁸.

In the charging process, however, to realize the complete oxidation of Li_2O_2 is more challenging. Since Li_2O_2 is solid, the solid-solid contact is a major problem. It is generally believed that the part of Li_2O_2 in direct contact with carbon will be oxidized firstly. After that, there is no possible route for the electron transfer between the rest of the Li_2O_2 particles to the carbon surface. Thus, large charging overpotential is very common in LABs. At high potential (> 4.0 V) in oxygen atmosphere, the electrolyte or carbon will also be oxidized. How to completely oxidize Li_2O_2 while lowering the charging potential is the most critical issue in the cathode chemistry of LABs.

3.2 Cathode catalysts

As we know, the role of the catalyst in the discharge/charge process is very different from fuel cells. It should be pointed out that the LAB catalysts do not need to break the O—O bond. The kinetic overpotential in LAB is usually very small. Thus, minimizing the cell impedance is more important than reducing the kinetic overpotential to develop high-current Li-air batteries²⁹.

As for the solid catalyst for oxygen evolution reaction (OER), the situation is more complicated. There are many reports working on decreasing the charging potential of LABs, but there is no convincing explanation on the catalytic mechanism for the solid OER catalysts with poor Li_2O_2 -catalyst contact. Interestingly, some studies argue that what the conventional OER catalyst catalyzes is not the decomposition of Li_2O_2 but the decomposition of the electrolyte or carbon³⁰.

A promising way to solve the charging problem is to use some redox mediators to help the electron transfer between Li_2O_2 and carbon. These compounds are oxidized at the cathode surface, and then diffused to the Li_2O_2 particles to oxidize the Li_2O_2 . Since the first report by Bruce *et al.*³¹, many compounds have been investigated as the redox mediators for LAB cathodes³². An ideal redox mediator should have a redox potential slightly higher than 3 V, high solubility and diffusion coefficient. In addition, its stability with superoxide is also very important for the cycle life. Currently designing such compounds has become a very hot topic. It is anticipated that the charging potential will be depressed to lower than 3.3 V with a proper redox mediator.

3.3 Cathode architecture

The cathode architecture is of crucial importance for the mass/electron transfer and Li_2O_2 accommodation. Until now, there isn't a uniform protocol to evaluate the cell performances reported by different research groups due to different mass loadings, current collector structures, and electrochemical test methodologies³³. A lot of cathodes with ultra-high specific capacity ($> 10000 \text{ mAh} \cdot \text{g}^{-1}$) have been reported³⁴. But we should notice that those data were mostly calculated with ultra-light loading of carbon material, which are not practically meaningful. In fact, we need to consider other parameters to objectively estimate the performance of the LABs cathode. For example, it is more reasonable to consider the weight of the catholyte which is 10 times heavier than the carbon together when we calculate the specific capacity. Furthermore, by considering the oxygen diffusion, thick cathode has problems to effectively use its inner part. So it is not reasonable to simply compare the specific capacities of LABs cathodes with different loadings. If we can realize a LAB cathode with a capacity of $500 \text{ mAh} \cdot \text{g}^{-1}$ based on the weight including the catholyte and a loading comparable to the conventional LIB cathode ($> 20 \text{ mg} \cdot \text{cm}^{-2}$), it would be satisfactory enough for the next-generation

batteries with high energy density.

To realize high-capacity LAB cathodes with high loading, we need to carefully consider the oxygen diffusion problem. In general, the diffusion rate of oxygen in gas phase is 4 orders of magnitude higher than in liquid phase. Thus, the cathodes that are partly wetted by the catholyte are preferred³⁵. It should be pointed out that it is the electrolyte's nature that fulfills the pores in the LAB cathode due to the capillary effect. Thus, we need to put our effort to fabricate a cathode with hierarchical pores. At the same time, the dosage of electrolyte needs to be precisely controlled to achieve optimal electrochemical performance. Another approach is to use gel cathodes with small chinks and pores. According to some modeling studies³⁶, in order to fully release the capacity of the inner part of the LAB cathode, the distance between the oxygen diffusion pores inside the cathode should be in the order of tens of microns. In our opinion, the future development of cathode architecture should consider more the electrolyte/carbon composite structure instead of the simplex carbon structure.

3.4 Anode protection

To protect the lithium anode in oxygen atmosphere is actually the most challenging issue for LAB development. We all know the lithium dendrite problem during cycling. In addition, for LABs, the contaminations such as H₂O, CO₂, O₂, and even N₂ may react with lithium anode and cause serious performance decay. If we use redox mediators in the cathode, it is also necessary to make sure that the oxidized redox mediator does not diffuse to the lithium anode side to cause the phenomenon of self-discharge. Some solvents that are good for cathodes are also reactive to lithium metal³⁷. To solve the above problems, a highly selective separator is desirable, which can conduct Li ions but block any other molecules. At this point, a Li-ion conductive glass ceramic may be a choice³⁸. However, its bristle nature makes it only suitable for laboratory researches. Graphite, silicon and other LIB anode materials are also available in LAB. The safety problem induced by lithium dendrite is solved after using these LIB anode materials^{39,40}. However, these LIB anode materials couldn't provide Li-ions as lithium anode, that means the anode should presents as lithiation state or the discharge product Li₂O₂ should pre-exist in the battery before cycling.

3.5 Full cell designing

Most of the current studies on LABs are based on half cells. How to make a practical full cell is still a big challenge. Some pioneering researchers have made a pouch-type LAB full cell⁴¹. It is a single layered structure and may operate in ambient air. Its energy density is around 340 Wh · kg⁻¹. The problem is that it cannot be recharged back. In other reports, the researchers have designed more complicated multi-layered structures with corrugated cathode current collectors as channels to induce oxygen into the cathode⁴². But those designed LABs are mostly models instead of real batteries. Overall, the structure of the future LAB full cell, especially the structure of oxygen channels, is still uncertain.

Whether the LAB is going to be an open system or closed system is also under debate. An open LAB can use the oxygen

directly from the outside air, but it is necessary to use a filter to eliminate the harmful contaminants in the air. A closed LAB, on the other hand, is placed in a tank filled with high-pressure pure oxygen. For the battery chemistry, the closed system should be better, but the safety is a problem. With introduction of high-pressure pure oxygen, the tank containing organic solvent and alkaline metal together looks like a bomb. Recent researches show that the LAB cathode chemistry can tolerate some H₂O or CO₂^{43,44}. Thus, if we can well solve the anode protection, it is still possible to develop a LAB with open configuration.

3.6 Perspective

LABs have drawn much attention in recent years all over the world. Many people are concerning how long it will take to make the LABs commercialized, or it is ever impossible. According to the current reports, it is true that LABs still have a long way to go. Since the problems in LABs are becoming clearer, we believe that the researchers may have better ideas to solve them. Although the LABs cannot present charge/discharge curves as reversibly as LIBs, they are still potential as options for backup of power source or range-extending technique for electrical vehicles. In a near future, with the cycling problems solved, the people may design and fabricate some commercialized primary LAB devices with higher energy density than other rechargeable batteries.

4 Sodium-ion batteries

The sodium-ion batteries can be traced back to the late 1970's as well as LIBs^{45,46}. Recently, people have realized that lithium shortage will be an obstacle if LIBs are extensively used in HEVs, EVs and power grid⁴⁷. Sodium, which is far more abundant than lithium (0.02%), is the sixth abundant element in the earth's crust (2.3%)⁴⁸. The abundance brings much lower prices of Na compounds than the Li counterparts, such as Na-containing electrode materials and electrolyte salts. In addition, using aluminum current collector rather than copper can further reduce the cost⁴⁸. Due to the abundant resource and low cost, SIBs have been reevaluated and the investigations are accelerating in recent years.

4.1 Comparison with Li-ion batteries

The mechanism of SIBs is also a "rocking-chair" process, which is similar to LIBs (see Fig.5). Generally, Na-interaction compounds are used as electrode materials for migration of Na ions across the electrolyte to store energy. Although SIB technology inherits the LIB principle, the energy density of SIBs cannot compete with LIBs. First, the molar mass of Na is higher than Li, which leads to a lower theoretical capacity. For example, LiFePO₄ has a theoretical capacity of 170 mAh · g⁻¹ while NaFePO₄ only 154 mAh · g⁻¹. It also results in heavier electrolyte salt, such as LiPF₆ and NaPF₆. Secondly, the redox potential of sodium ($E_{\text{Na}^+/\text{Na}}^0 = 2.71 \text{ V vs SHE}$ (standard hydrogen electrode)) is 0.3 V lower than that of lithium ($E_{\text{Li}^+/\text{Li}}^0 = 3.04 \text{ V}$), indicative of less capacity and fewer anode options. Thus the capacity between 0 and 0.3 V (vs Li/Li⁺) will be excluded, and the anode materials with redox potential in this range cannot be used in SIBs. Thirdly, SIBs and LIBs show different interaction/deinteraction chemistry.

Fig.5 Schematic illustration of a typical $\text{Na}_2\text{Ti}_3\text{O}_7/\text{Na}_3\text{V}_2(\text{PO}_4)_3$ Na-ion battery

For example, with the same NASICON host, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ can afford all three Li ions but $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ can only afford two Na ions⁴⁹. As a result, Na-ion batteries are not an alternative technology to current Li-ion batteries owing to its lower energy density. Considering the abundant resources and low cost feature, Na-ion batteries can focus on price sensitive and energy density insensitive field, such as grid storage and fluctuating renewable energies storage like solar and wind energy.

4.2 Typical cathode and anode materials

For large-scale application in energy storage, the electrode materials require abundant resource, easy synthesis, safety, high efficiency and long cycle stability⁷. Hitherto, many compounds have been found to be potential as SIB electrode materials. For example, layered oxide electrode materials are also popular in SIB, such as P2- $\text{Na}_{2/3}\text{Fe}_{1/2}\text{Mn}_{1/2}\text{O}_2$, O3- $\text{Na}_{0.9}[\text{Cu}_{0.22}\text{Fe}_{0.30}\text{Mn}_{0.48}]\text{O}_2$ ⁵¹, honeycomb structured $\text{Na}_3\text{Ni}_2\text{SbO}_6$ ⁵² and NaCrO_2 ⁵³. Although the extensive research exhibit much performance improvement, low operating voltage, poor cyclability, sodium deficiency and high polarization are major obstacle in the future⁵⁴. Alluaudite $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$ is a rising star discovered by Nazar's group⁵⁵. It delivers a capacity of $102\text{mAh} \cdot \text{g}^{-1}$ with a potential of 3.8 V (vs Na/Na^+) corresponding to $\text{Fe}^{3+}/\text{Fe}^{2+}$. Its energy density is even comparable to LIB cathode LiMn_2O_4 and LiFePO_4 . NASICON-type sodium phosphates like $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{V}_2\text{O}_{2x}(\text{PO}_4)_3\text{F}_{3-2x}$ are also candidates as cathode materials⁵⁶⁻⁵⁸. With carbon coating, superior rate capability and long cycle can be achieved readily. However, toxicity of vanadium is the drawback for practical application. Very recently, a large family Prussian blue analogues, such as $\text{Na}_4\text{Fe}(\text{CN})_6$ and $\text{Na}_2\text{Mn}_2(\text{CN})_6$, have been proven available for SIB cathode materials^{59,60}, they have drawn increasing interest due to excellent performance, low cost and easy synthesis. Tuning the transition metal redox couples may greatly enlarge the family and provide more choices to optimize the performance. As for anode, the commercial LIB anode material graphite cannot be used in SIBs directly due to the bigger Na-ion radius. The carbonaceous materials, such as hard carbon and expanded graphite, are good candidates for SIBs⁶¹⁻⁶³. The main problem for such anodes is low

efficiency which consumes a lot of Na ions during the first cycle. Some alloys like [P, Sb] can also serve as anode materials for SIBs⁶⁴⁻⁶⁹; they deliver high capacity, but suffer large volume change during charge and discharge, leading to a poor cyclability. Organic electrode materials, are different from the inorganic ones, but their features are still not very clear⁷⁰⁻⁷². Among the above electrode materials, layered compounds, Prussian blue analogues and carbonaceous materials are much attractive due to the low cost, which deserve further investigations.

4.3 Aqueous Na-ion batteries

Aqueous Na-ion batteries amplify the low cost advantage of SIBs. Moreover, the aqueous SIBs are safe and environmentally friendly, which make them to be potential as stationary energy storage systems. To reach large-scale energy storage level, capital cost per cycle should be at least lower than the cost of generating electricity. It can be calculated by the following equation⁷³:

$$\text{Capital cost per cycle} = \frac{\text{Capital cost}}{[\text{Energy (kWh)} \times \text{Life (cycle)} \times \text{Efficiency}]} \quad (3)$$

It can be understood that reducing the capital cost and enhancing energy density and cycle life are effective to get low capital cost per cycle. It must be pointed out that the energy density is not sensitive for large-scale application but it also needs to be improved. To achieve equivalent energy, low capacity electrode will cost more inactive battery components such as conducting agent and current collector. The prices of these components are usually much higher than sodium electrode materials themselves. The fledgling aqueous SIBs only deliver an energy density of around $10-20\text{Wh} \cdot \text{kg}^{-1}$, but the energy densities of their rivals, such as Ni-metal hydride, Ni-Cd, and lead-acid batteries, are generally higher than $30\text{Wh} \cdot \text{kg}^{-1}$. The low energy density of aqueous SIBs will limit their application areas and also lead to increased cost with current battery design. Developing low-cost and high-performance SIB systems including cathode/anode materials, current collectors and battery design is the main concern. There are limited choices in electrode material selection when considering the chemical stability in water and water splitting in the electrolyte with specific pH value. Many electrode materials have been investigated for aqueous SIBs, but most of them suffers low capacity (such as $\text{Na}_{0.44}\text{MnO}_2$, $\text{Na}_{0.44}(\text{Mn}_{0.44}\text{Ti}_{0.56})\text{O}_2$, $\text{Cu}_x\text{Ni}_{1-x}\text{HCF}$), dissolution (like Prussian blue analogues), H_2 evolution ($\text{NaTi}_2(\text{PO}_4)_3$), high cost (active carbon), side reaction with O_2 ($\text{NaTi}_2(\text{PO}_4)_3$) or proton co-insertion (layered structured materials)⁷. For the aqueous SIBs, the first step is to greatly increase the energy density up to at least $30\text{Wh} \cdot \text{kg}^{-1}$, comparable to the lead-acid batteries; then we should further optimize the other properties like cycle life, cost, etc. If the above goals are achieved, the aqueous SIBs are really close to commercial applications, which may be ideal substitutes for the lead-acid batteries.

4.4 High-temperature Na-ion technology

High-temperature Na-ion technology is represented by sodium-sulfur and sodium-metal halide batteries^{48,74}. In the Na-S batteries, active materials are molten, and the solid state electrolyte β -alumina exhibits a conductivity as high as $0.1\text{S} \cdot \text{cm}^{-1}$ at 270°C –

350 °C. During discharge, Na⁺ ions are produced and migrate through the β -alumina electrolyte to the cathode to form Na-polysulfides. Na⁺ ions can move back reversibly to the anode during charge. Na-S batteries are expected to serve as stationary energy storage system due to their large energy density, high coulombic efficiency, flexible cycling, and low maintenance requirement, but the safety is a challenge. Possibility of the ceramic fracture, immature sealing technology, active molten sodium and sulfur may cause potential safety hazard. The safety problems should be solved before practical application for the high-temperature Na-ion technology.

4.5 Perspective

Room-temperature SIBs are still in an early stage now. The cathode/anode materials and even the battery design (especially the aqueous system) all need to be exploited. Fortunately, rich experiences gained from the LIB technology can guide the investigations of SIBs. Owing to lower energy density, SIBs cannot compete with LIBs in the market of portable electronics and EVs, but they are suitable for large-scale energy storage. For example, the aqueous SIBs are more attractive to achieve large-scale energy storage goal as compared with the non-aqueous and high-temperature Na-ion technology owing to more safety and lower cost. For the non-aqueous SIBs, the market orientation remains unclear. The flammable organic electrolyte will cause safety hazard, which limits the application in large scale energy storage. The awkward situation is also due to lower energy density than their Li-ion cousins and higher cost than their aqueous brothers. For the non-aqueous SIBs, since the energy density can be almost comparable to the conversional LIBs, their development goal is to reach the requirements for application in EVs or HEVs. But it is a very difficult task; even LIBs cannot completely satisfy the requirements of high energy density.

5 Summary

In summary, since the limitation of energy density for Li-ion batteries is believed to about 300 Wh·Kg⁻¹ in practical applications, next-generation rechargeable batteries with higher energy density such as Li-S and Li-air batteries should be urgently developed for the purpose of practical applications in EVs or HEVs. On the other hand, cheap and safe room-temperature Na-ion batteries are desirable to meet the demands of large-scale energy storage for electric grid. Here, some common technologies need to be captured, including key electrode materials, fabrication techniques of cell, module and system, and some mechanisms related to electrochemical process, capacity decay and safety. Of course, from laboratory-level research to mass production, there is a long way to go. But we believe that such next-generation rechargeable batteries should have a bright future, which will bring about a huge market and promote the developments of new energy and electric vehicles.

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