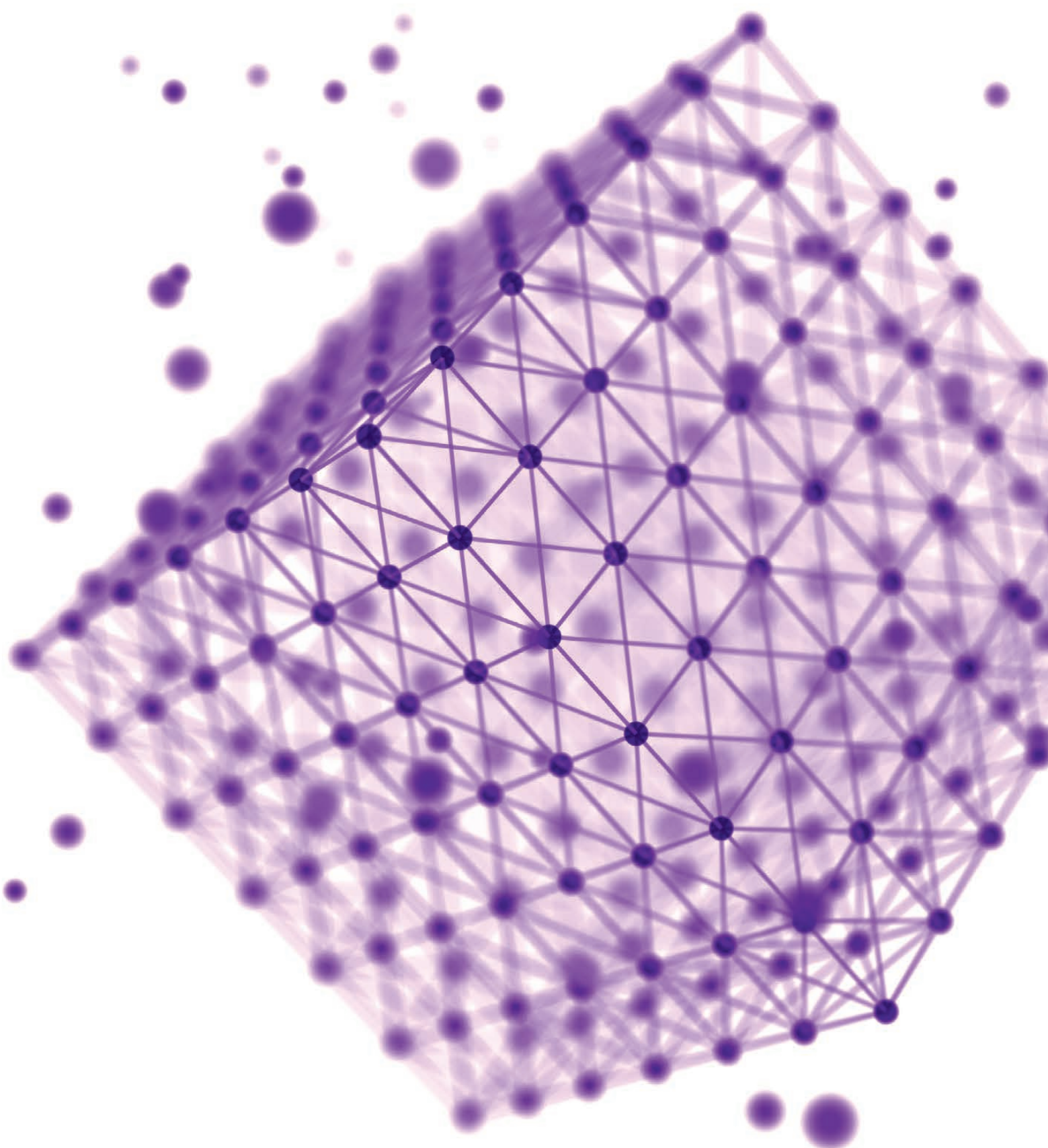


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A Short Review on Advanced Battery Materials Research at Nazarbayev University, Kazakhstan



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Lithium-ion batteries (LIBs) are receiving tremendous attention and further development due to their leading performance characteristics among other rechargeable batteries available on the market. A variety of cathode materials have been developed to satisfy increasing demands for next generation power sources. LIBs are moving to their next generation forms such as the all-solid-state batteries, thin film and microbatteries. In order to overcome the safety, cost and performance drawback of existing LIBs, various batteries “beyond” LIBs with very promising performance have been intensively studied such as lithium-sulfur batteries, as well as the lithium-based batteries with aqueous electrolytes. In this work we provide a short review of state in lithium-sulfur batteries, lithium-based microbatteries and lithium-ion aqueous batteries, as well as the works done in these directions by our Research Group at Nazarbayev University, Kazakhstan.

1. Introduction

Wide implementation and rapid technological advances in electric transport, renewable energy production and portable electronics encouraged tremendous growth of the market of rechargeable batteries. However, existing battery technologies cannot fully satisfy the performance requirements of the above applications and even restrict the implementation of next generation devices due

to limited energy and power. Therefore, great attention is paid to development of new materials for next generation batteries and/or improving existing battery materials. It should be noted that so called ‘all solid state’ batteries became one of the hottest hot topics of battery research due to their advantages such as safety and compactness combined with higher energy and power density. Such batteries are considered as very suitable especially for electric transport application as well

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as for portable electronics.

At the same time, when considering large scale application such as renewable energy storage the battery materials cost environmental friendliness become one of the most critical criteria to choose from various battery chemistries. From this point of view, lithium-sulfur batteries (Li-S) are considered as one of the most promising technologies due to a very high theoretical capacity of sulfur, and abundant availability of sulfur, which mainly comes as a side product of oil and gas industry.

Battery safety is the main concern especially when the batteries should be scaled up or used for stationary applications such as renewable energy or industry/household energy backup. Along other battery systems, those based on aqueous electrolytes become the most beneficial from the safety and cost effectiveness points of view. The combination of the advantages of lithium-ion batteries with water based electrolyte could be the best solution for such applications.

In this paper we present a short review of some problems existing in the abovementioned battery systems, and provide the information on potential solutions based on the research in our Battery Group at Nazarbayev University in Kazakhstan. International collaboration with the research group in Japan is very critical especially considering the leading role of Japan in this field. We have strong collaboration in battery field with the Laboratory of Prof. Kiyoshi Kanamura from Tokyo Metropolitan University, several companies including SuperOx Japan and Hohsen Inc., and would like to expand it. The authors thank the Furukawa Batteries Co., Ltd for this invitation and a great chance to introduce our research via the Journal of the Furukawa Battery, which will enhance and further strengthen our collaboration with the battery research community of Japan.

2. Development of microbatteries for microelectronics

Numerous miniature electronic gadgets needing independent micropower sources will be connected to the internet as the world enters the Internet of Things (IoT) era. The most suitable on-chip power sources for IoT-enabled microelectronic devices are thought to be all-solid-state thin-film lithium/lithium-ion microbatteries (TFBs), which combine thin-film manufacturing and solid-state battery architecture^{1), 2)}. TFBs, on the other hand, are still in their infancy and need fresh developments in materials, production, and structure to perform better than commercialized lithium-ion batteries. One of the directions of the battery group at Nazarbayev University is focused on prototyping lithium-ion microbatteries (LIMBs) that are ultra-thin, high cycle life, variable in shape and form, stackable and durable at high/low temperatures. In order to develop the microbatteries meeting the current requirements of microelectronics, the thin-film materials without any additives/binders for implementation as cathodes, anodes as well as electrolytes are fabricated and studied (Fig. 1). The main methods used are a glove-box system with magnetron sputtering and thermal evaporator equipment as well as regular methods such as the spin-coating and electrodeposition. Studies for positive electrodes, lithium cobalt oxide (LiCoO₂)³⁾, other nickel-containing metal oxides (LiNiMnCoO₂ (NMC), LiMn_{1.5}Ni_{0.5}O₄ (LMNO)⁴⁾, low voltage cathodes CuS⁵⁾ were conducted. The obtained monolithic LiCoO₂ thin film cathode delivered the stable specific capacity of around 120mAh g⁻¹. The cracking problem of NCM material is solved by building the gradient structured film that is achieved by sputtering the NCM magnetron targets with different Ni content. As for anode, the successfully developed

negative electrodes are pure sputtered Si^(6)~9), electrodeposited Ni₃Sn₄^(10), 11), and thermally-evaporated monolayered lithium and multilayered Li-Sn films. All the anodes retain a high reversible specific capacity (Si – around 1,500mAh g⁻¹, both Ni₃Sn₄ and Li-Sn – 800mAh g⁻¹) and good cycling stability. The solid electrolytes, being interlayers between electrodes, should provide high ionic conductivity and be electrochemically stable^(1), 2). The sputtered films of Li₃PO₄ in N₂ (LiPON)⁽¹²⁾, sputtered/spin-coated Li_{1+x}Al_xTi_{2-x}(PO₄)₃, Li₇La₃Zr₂O₁₂ and Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ reached the ionic conductivity within 10⁻⁵ – 10⁻⁶S cm⁻¹. In addition to fabricating separate parts of LIMBs,

integration of them into one whole battery is quite a complicated process requiring the matching of material properties at the interfaces in order to have an unhindered flow of ions and electrons. Based on the preliminary studies, the thin film microcell was constructed with the best matching materials according to the scheme presented in Fig. 1.

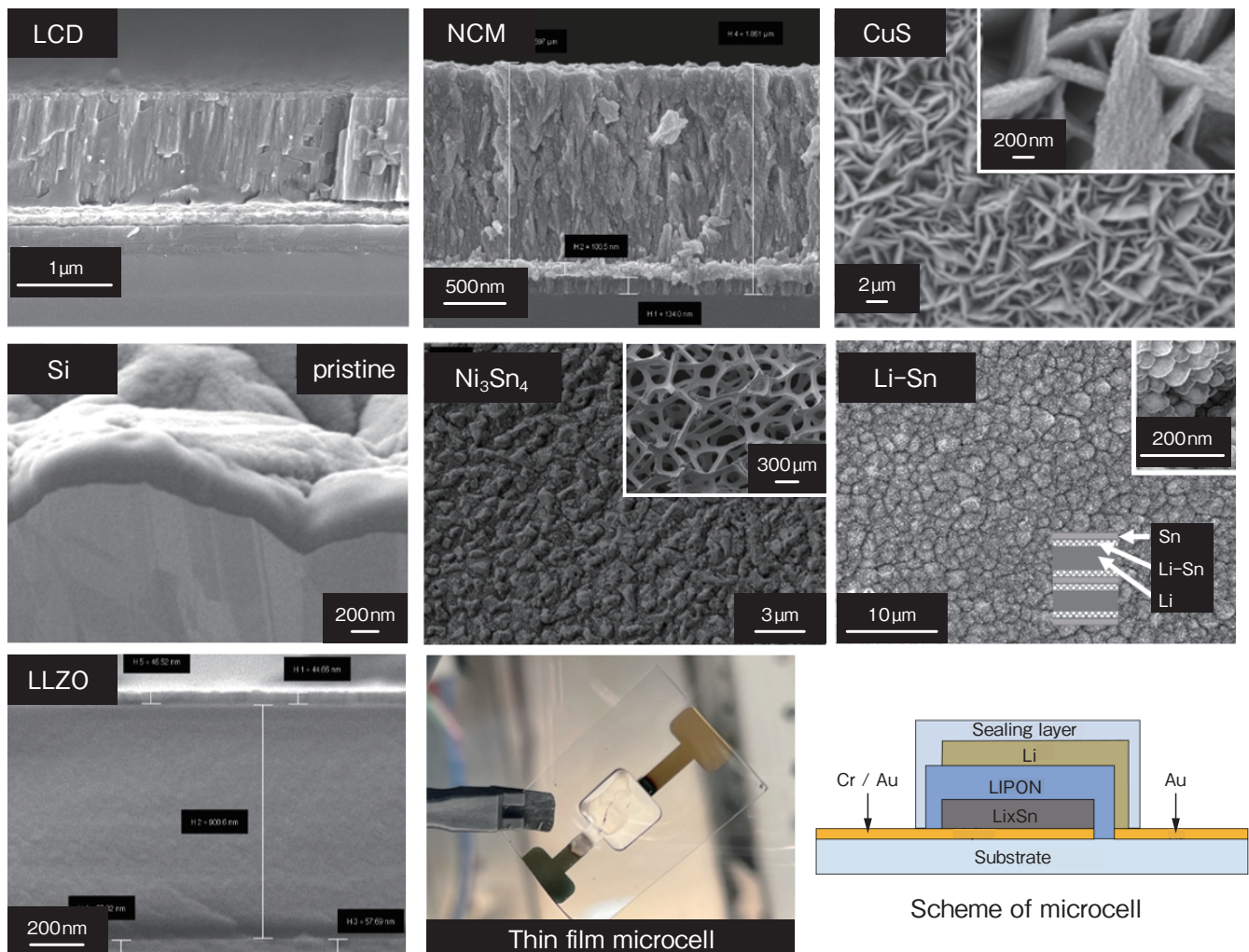


Fig. 1 The thin film materials developed at NU^(3)~12)

3. Advances in lithium-sulfur batteries

Lithium-sulfur batteries (LSB) are recognized as next-generation energy storage systems given their high theoretical specific capacity ($1,675 \text{mAh g}^{-1}$) and theoretical energy density ($2,600 \text{Wh kg}^{-1}$)¹³. Sulfur as a cathode material is attractive due to its abundance, low cost, and non-toxicity¹⁴. However still there exist “hot” problems which limit their practical use, in particular, (1) poor electrical conductivity of sulfur and its discharge products resulting in cell's resistivity increase; (2) cell's volume expansion during charge/discharge cycling due to the large difference in densities of sulfur and its species leading to electrodes structural damage; (3) the so-called polysulfide shuttle effect mainly associated by the dissolution of lithium polysulfides (LiPs) in organic electrolytes and their diffusion to the anode side resulting in loss of the active material^{15, 16}.

To overcome these issues, several strategies, including the combination of porous carbon with metal oxides^{17)~25)}, the design of transition metals-based catalysts^{26)~28)}, fabrication of free-standing composite cathodes^{29)~31)}, and current collectors^{32), 33)}, preparation of gel and solid polymer electrolytes^{18), 34)} and modification of commercial separators^{35), 36)} were developed by our Research Group.

The nanosized nickel magnesium oxide ($\text{Mg}_{0.6}\text{Ni}_{0.4}\text{O}$) is a promising material for LSBs due to its strong LiPs absorbing ability and catalytic activity in Li/S redox reaction. Initially, nanosized $\text{Mg}_{0.6}\text{Ni}_{0.4}\text{O}$, prepared by self-propagating high temperature synthesis (SHS), demonstrated poor electrochemical performance as a sulfur host with a reversible capacity of only 850mAh g^{-1} at 0.1C ¹⁷. However, further research^{18), 19)} demonstrated the tremendous effect of $\text{Mg}_{0.6}\text{Ni}_{0.4}\text{O}$ as an additive to conductive polymer (PAN and PANI) based hosts on the cell's electrochemical performance.

In particular, the $\text{S}/\text{Mg}_{0.6}\text{Ni}_{0.4}\text{O}/\text{PAN}$ cathode delivered a reversible capacity of $1,223 \text{mAh g}^{-1}$ at 0.1C , while for the $\text{S}/\text{Mg}_{0.6}\text{Ni}_{0.4}\text{O}/\text{PANi}$ cathode this value was $1,448 \text{mAh g}^{-1}$ at 0.1C . Additionally, the effect of various metal oxides (ZnO , $\text{Fe}/\text{Co}_3\text{O}_4$, $\text{Co}_3\text{O}_{4-x}$, Fe_3O_4 , TiO_2 , TiO_{2-x}) and their combinations with nanostructured carbons demonstrated superior electrochemical performance due to strong affinity of metal oxides to polar LiPs^{20)~25)}. Particularly, the highly dispersed ultra-fine ZnO nanocrystals anchored on the 3D conductive polypyrrole matrix (S-3DOMPPy@ZnO , Fig. 2 (a), (b) demonstrated long-term cyclability of 794.5mAh g^{-1} at 0.1C (300 cycles, Fig. 2 (c)) and remarkably enhanced rate capability (515.6mAh g^{-1} at 2C ²⁰). The 3D porous microspheres obtained by spray-drying process consisted of nanosized sulfur particles and nitrogen-doped oxygen deficient N-TiO_{2-x} nanorods supported by reduced graphene oxide exhibited stable cycle performance at 1C over 300 cycles with a 700mAh g^{-1} specific capacity with 0.09% per cycle capacity decay²⁵⁾. The advantage of using composites of carbon with metal oxides is the simplicity of their synthesis (hydrothermal method, spray-drying process), which allows controlling the particle's size and shape and their uniform distribution over the supporting matrix.

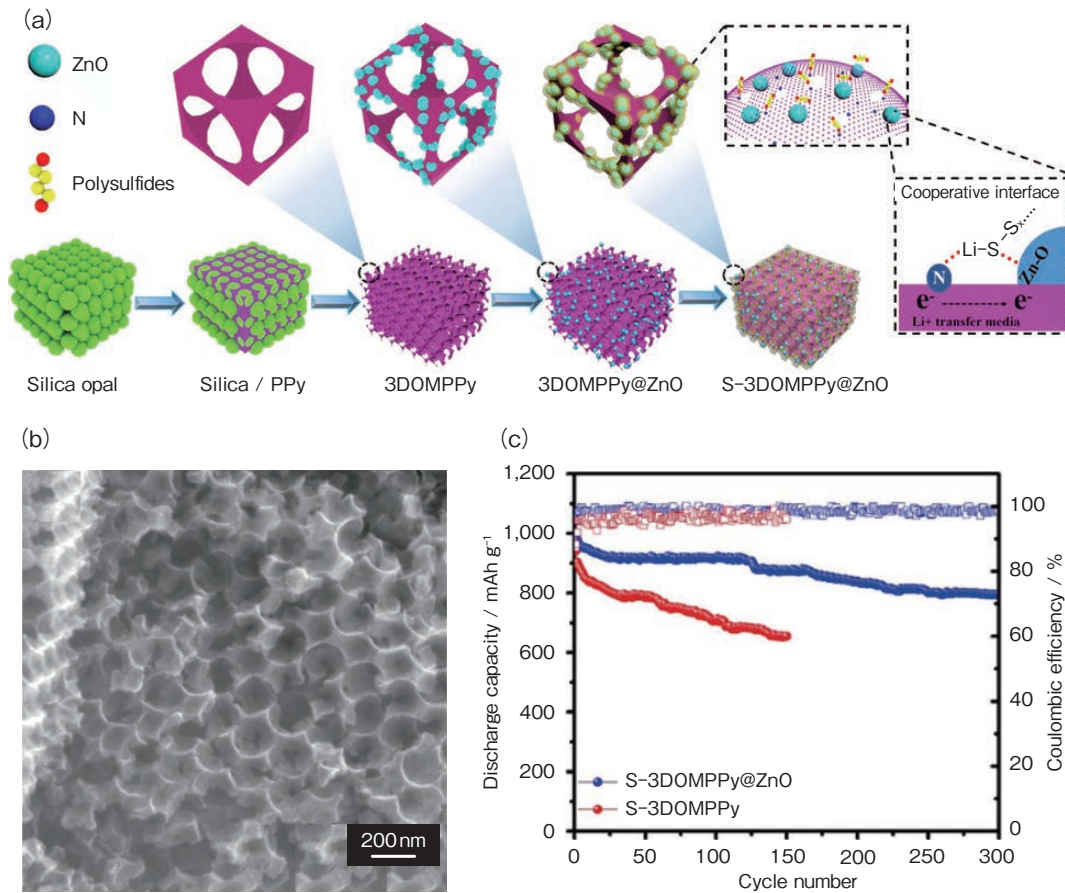


Fig. 2 (a) Schematic of preparation procedure of 3DOMPPy@ZnO and S-3DOMPPy@ZnO; (b) SEM image of 3DOMPPy@ZnO and (c) Cycle performance of S-3DOMPPy@ZnO and S-3DOMPPy electrodes²⁰⁾

To facilitate the kinetics of sulfur conversion to LiPs, the effective catalytic metal nanoparticles and their phosphides were designed. Transition metals like Ni, Co, and Fe are more advantageous than others (for ex. noble metals) because of their low price and abundance. For instance, in¹⁹⁾ the Ni/Ni₂P@C hollow heterostructure microsphere applied as a functional sulfur host delivered a high initial discharge capacity of 1,187.3 mA h g⁻¹ at 0.2C, notable rate capability of 716.9 mA h g⁻¹ at 3C and excellent reversible capacity of 636.6 mA h g⁻¹ over 300 cycles at 1C. Further, the reported CoNi@porous N-doped carbon fibers²⁶⁾ delivered a discharge capacity of 828 mA h g⁻¹ at 5C with a capacity decay of less than 0.019% per cycle over 1,500 cycles. Thus, the highly polar and electrocatalytically active transition metal-based

additives improve the interaction with polar LiPs and exhibit enhanced catalysis performance, which results in good electrochemical performance of the batteries and long cycling life.

As an alternative to the modified host materials, free-standing cathodes receive much attention due to their good flexibility, low thickness, and lightweight. These cathodes exclude the use of a metal current collector and binder, which decrease the total weight of the battery and increase its total gravimetric capacity. The prepared by simple vacuum-filtration method S/DPAN/MWCNT free-standing cathode utilized the synergistic effect of pyrolyzed PAN to covalently bind sulfur with a uniform distribution and excellent electrical conductivity of MWCNT with superior mechanical properties which resulted in high capacities of

1,450mAh g⁻¹ at 0.2C and 930mAh g⁻¹ at 2C²⁹. Furthermore, Kalybekkyzy et al.³³ demonstrated the effectiveness of the electrospinning method for the fabrication of sulfur-based cathodes (Fig. 3 (a), (b)). In particular, the lightweight electrospun CNFs with the high surface area served as a structured current collector for the sulfur cathode, which allowed the load of the larger sulfur amount to the matrix compared to the conventional Al foil. The carbonized at 800°C PAN CNFs-based current collectors delivered the initial discharge capacity of 1,620mAh g⁻¹ at 0.1C and maintained a reversible capacity of 1,104mAh g⁻¹ at the 100th cycle.

Starting with pure CNFs as a current collector, the research is focused on functionalization of nanofibers with the metal compounds. One of the research projects was based on the all-purpose

3D current collector with CoNi-N-doped polymer carbon fiber (CoNi@PNCFs) synthesized from metal acetates and PAN²⁶. Co and Ni nanoparticles on the surface of nanofibers demonstrated the synergistic catalytic effect of Co and Ni in LiPS conversion and the Li₂S precipitation experiments on the surface of PNCFs (Fig. 4). Moreover, CoNi@PNCFs was utilized as a current collector for Li, and Li-S battery assembled with S/CoNi@PNCFs cathode and Li/CoNi@PNCFs anode exhibits a high reversible specific capacity of 785mAh g⁻¹ and long cycle performance at 5C (capacity fading rate of 0.016% over 1,500 cycles).

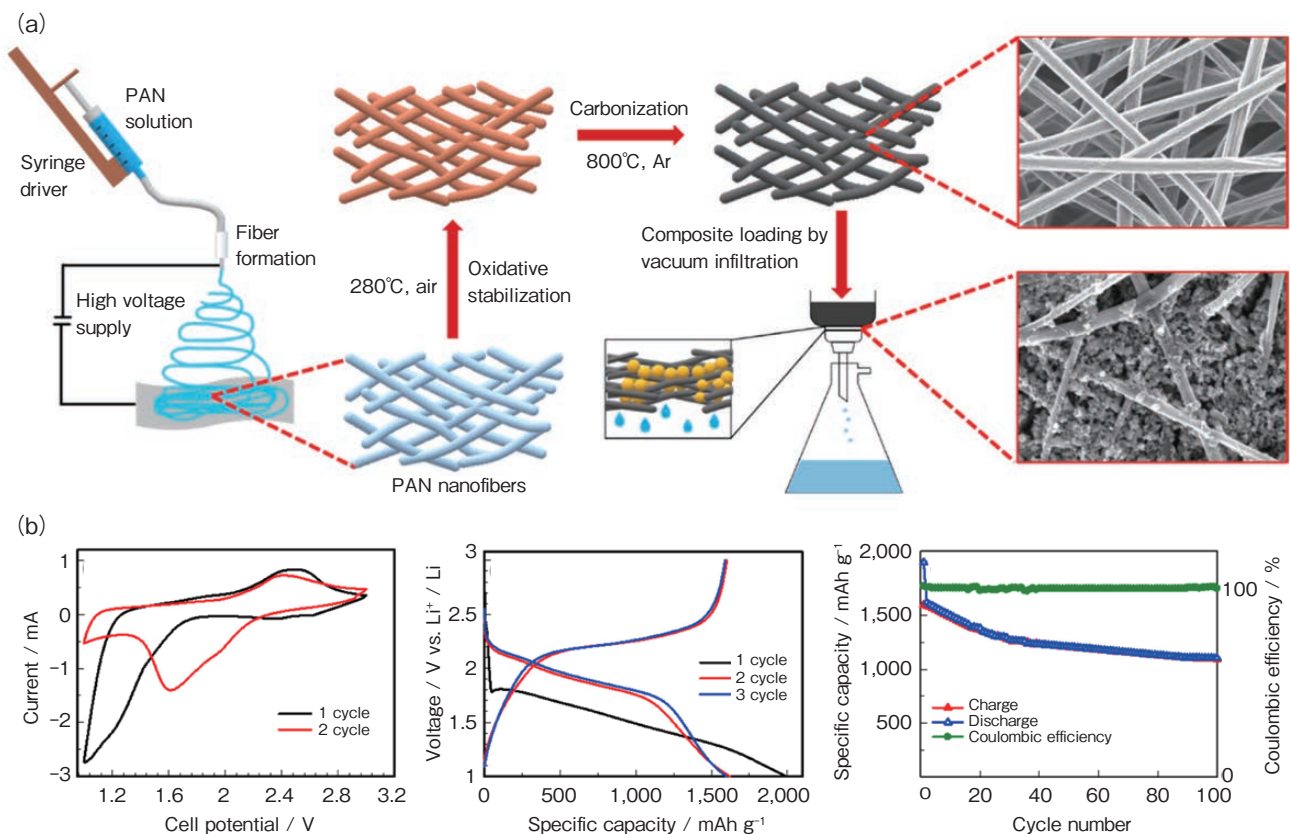


Fig. 3 (a) Scheme of carbon nanofiber fabrication and sulfur-based cathode preparation and (b) electrochemical performance of the sulfur composite on cPAN CNFs at 0.1C³³

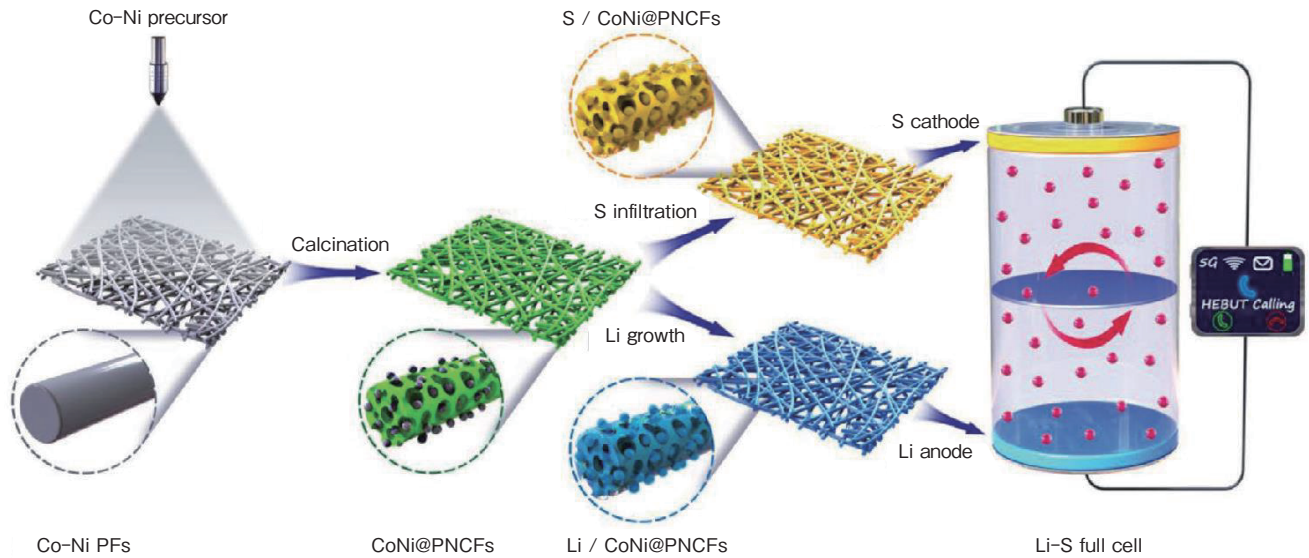


Fig. 4 Schematic diagram of synthetic procedures of CoNi@PNCFs electrode and an electronic watch powered by Li-S full cell²⁶⁾

One of the research directions is based on the development of gel polymer electrolytes to limit dissolution of polysulfides. PVDF-HFP/PMMA/MMT polymer membrane with rich pore structure and strong ability to absorb liquid electrolyte in excess of 67wt% was utilized as an electrolyte with S/PAN/Mg_{0.6}Ni_{0.4}O composite cathodes (Fig. 5 (a))³⁷⁾. The Li-S GPE cells exhibited rather high initial specific discharge capacity, maintaining 1,071mAh g⁻¹ reversible discharge capacity after 100 cycles at 0.1C, along with a high coulombic efficiency close to 100%. Another work was based on the analysis of 1M of LiTFSI in PVDFHFP/PMMA/SiO₂ polymer electrolyte with sulfur/graphene nanosheets (S/GNS) composite³⁴⁾. The GPE exhibited a pore-rich structure, a high ability to absorb liquid electrolyte exceeding 71wt%, and a high ionic conductivity at ambient temperature (Fig. 5 (b)). The Li|GPE|S cells exhibited a high initial specific discharge capacity and maintained a reversible discharge capacity of 413mAh g⁻¹ after 50 cycles at 0.2C, along with a high coulombic efficiency. The system could deliver reversible capacity of 316mAh g⁻¹ even

at 1C.

Dissolution of polysulfides upon cycling of the sulfur cathode and their diffusion through the separator membrane is a major factor which deteriorates performance and safety of Li-S batteries. In this regard, modification of separators with functional nanocoatings are designed to suppress the shuttle effect. Mentbayeva et al.³⁵⁾ developed ultrathin, light-weight polyelectrolyte-clay layer-by-layer assemblies as versatile nanocoatings on the polypropylene (PP) separator (Fig. 6 (a)). The use of weak polyelectrolytes (polyethyleneimine, PEI, and polyacrylic acid, PAA) and montmorillonite (MMT) or halloysite (Hal) clay nanoparticles enabled full control over mass and charge balance of polyelectrolyte/clay film components, which was critical for achieving ion selectivity and reduction of the polysulfide diffusion. As a result, deposition of 450nm MMT-based coatings at pH 3 and 6 lead to an increase in electrolyte uptake, delayed the lithium dendrite growth and enhanced the discharge capacity of the cell to 690mAh g⁻¹ for coated PP separator over 200 charge-discharge cycles at 0.5C.

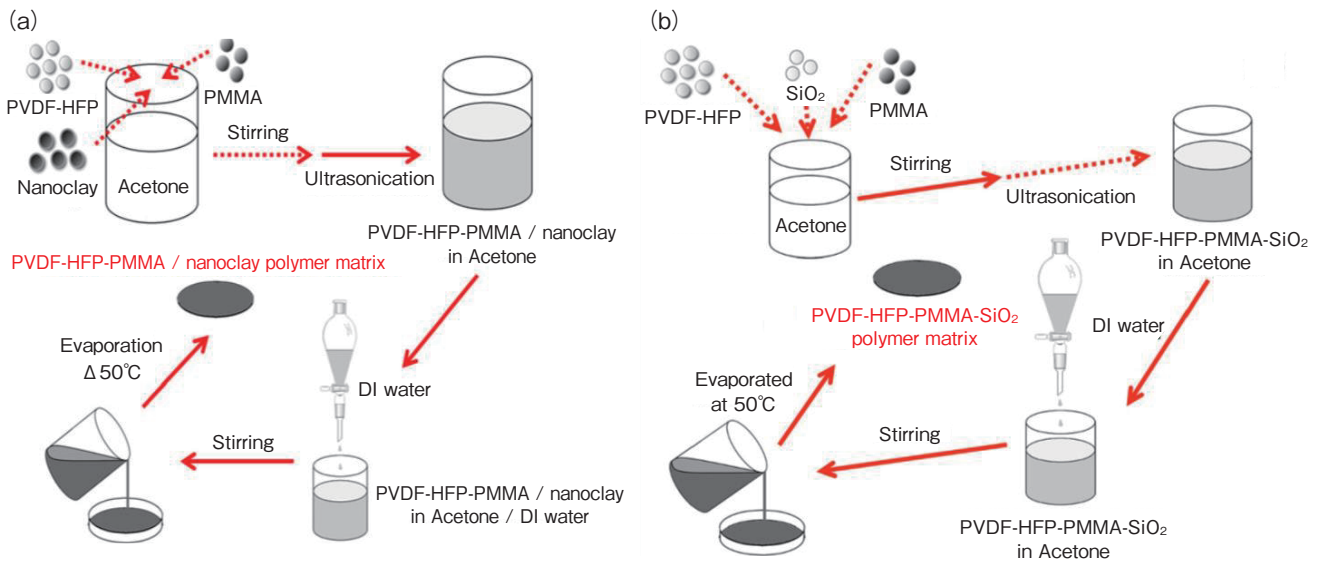


Fig. 5 Schematics of the preparation of (a) PVDF-HFP/PMMA/MMT polymer matrix³⁷⁾ and (b) PVDF-HFP/PMMA/SiO₂ polymer matrix³⁴⁾

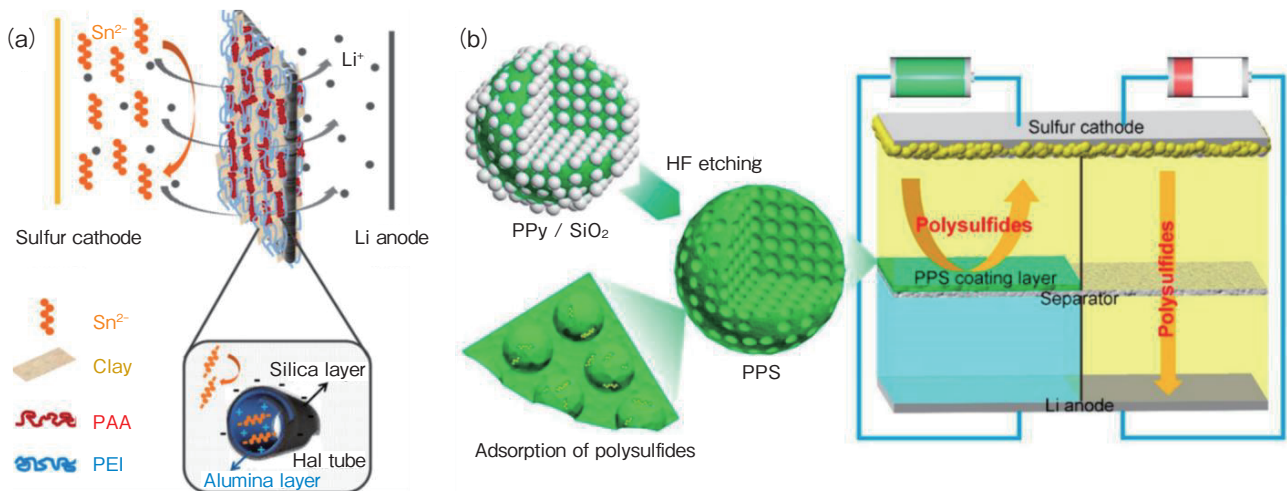


Fig. 6 (a) Illustration of the polysulfide shuttle effect suppression by a (PEI/Clay/PAA)-coated separator²⁷⁾. (b) Schematic of PPS structural characteristics and Li-S cell with PPS-modified separator³⁶⁾

Another work was based on the modification of separator with porous polypyrrole sphere (PPS) which was prepared by using silica as hard-templates (Fig. 6 (b))³⁶⁾. PSS coating could efficiently reduce the polarization of sulfur cathode and efficiently immobilize polysulfides. When tested in the lithium-sulfur battery, it exhibited a high capacity of 855mAh g⁻¹ after 100 cycles at 0.2C, and delivered a reversible capacity of 507mAh g⁻¹ at 3C, showing excellent

electrochemical performance.

The ongoing research in the design of cathode materials for LSBs is mainly focused on the substitution of the widely investigated expensive carbon nanomaterials (graphene, CNTs, CNFs) by abundant and cheap graphene-like porous carbon that can be obtained by the processing of biomass waste (rice husk, walnut shell), which is beneficial from both economic and scientific-practical points of view. This carbon is presented by high surface

area (more than $2,200\text{m}^2\text{g}^{-1}$), pronounced micro- and mesoporosity, excellent electrical conductivity and large amount of loaded sulfur. Moreover, this type of carbon can be easily modified by heteroatom doping (N, B, S) or by addition of metal oxide, metal sulfides, metal phosphate nanoparticles, MOFs and MXene. This strategy of combination of bio-derived carbon with a polar additives can result in synergistic effect, in which highly porous and electrically conductive carbon is able to physically adsorb LiPs, while the polar additives on its surface can enhance the chemical binding of LiPs by the composite.

4. Rechargeable aqueous batteries

Due to global climate change and resource depletion caused by the use of fossil fuels, the search for alternative sustainable energy sources has become a major focus of research around the world. Sustainable energy resources such as solar and wind have entered the global spotlight, triggering the search for reliable, low-cost electrochemical energy storage. An ideal energy-storage device that is characterized by high capacity, fast charge/discharge capability, safety, environmental friendliness, and low cost is of vital importance for today's society. Among the various options, lithium-ion batteries (LIB) are currently the most attractive candidates due to their high energy density, and foothold in the marketplace.

However, safety of LIBs is one of the major issues which is not solved as yet due to the high risk of flammability of organic electrolytes and the thermal runaway caused by the reactivity of electrode materials with electrolytes. In addition, the cost of LIBs is high as summarized in **Table 1**. Adopting LIBs technology to aqueous system could solve the mentioned disadvantages, providing a high performance inexpensive and

very safe energy storage system. Therefore rechargeable aqueous Li-ion batteries (RALB) are promising alternatives for large scale applications, which could solve several challenges of LIB in terms of safety, low cost manufacturing conditions, huge improvement of electrolyte conductivity, power improvement, environmentally friendliness, and recycling conditions.

Table 1 Comparison of battery technology costs³⁸⁾

	LIB	RALIB	Lead-acid battery
Battery cost (USD/KWh)	600	170	170
Working Voltage (V)	3.0	1.2	2.0
Cycle life (numbers)	2,000	1,000	1,000
Efficiency (%)	100	100	50-95
Energy density (Wh/KG)	100-350	40-60	30-40
Lifetime cost (USD/KWh)	0.30	0.17	0.23

In 1994, Dahn and co-workers proposed the first ARLB prototype using LiMn_2O_4 and VO_2 as positive and negative electrodes, respectively³⁹⁾. In which metal-ions are intercalated into or extracted from the active materials upon charge/discharge processes, identical to that of organic systems. It is therefore referred to as the “rocking chair” type or “intercalation-chemistry” type (**Fig. 7 (a)**). Since then, significant progress has been made in this intriguing area with more electrochemical redox couples being identified, more insights into fundamental chemistry being gained, and new battery chemistries are explored.

More recently, hybrid design via coupling an intercalation cathode with a metal anode (**Fig. 7 (b)**) or combining an intercalation anode with a metal oxides/ sulphide (**Fig. 7 (c)**), was introduced in the aqueous rechargeable hybrid battery (ARHB) with the appearance of a new class of aqueous hybrid batteries systems such as $\text{LiMn}_2\text{O}_4//\text{Zn}$ ⁴⁰⁾, $\text{Na}_{0.44}\text{MnO}_2//\text{Zn}$ ⁴¹⁾, $\text{Na}_{0.61}\text{Fe}_{1.94}(\text{CN})_6\text{A}_{0.06}//\text{Zn}$ (A indexed as vacancy)⁴²⁾, $\text{Ni}(\text{OH})_2//\text{TiO}_2$ ⁴³⁾, and $\text{Co}_x\text{Ni}_{2-x}\text{S}_2//\text{TiO}_2$ ⁴⁴⁾. Differ from the “rocking

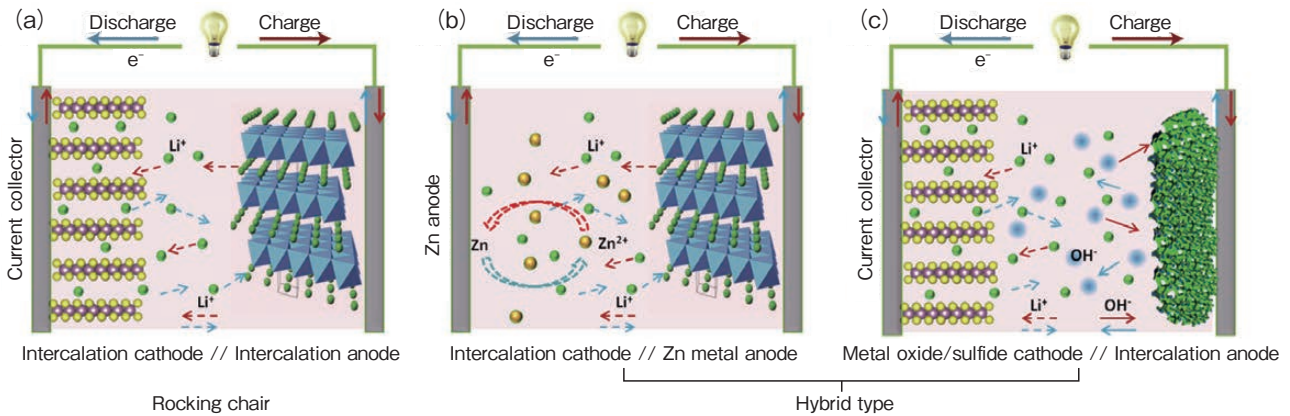


Fig. 7 Schematic illustration of “rocking chair” and “hybrid type” aqueous rechargeable batteries⁴⁵⁾

chair” type batteries, these batteries operate based on two reversible electrochemical redox processes involved in anode and cathode parts separately, and the charge/discharge mechanism in one or two electrodes is not guest ion intercalation/de-intercalation (Fig. 7 (a)). Instead, it can be the reaction of Zn²⁺ deposition-dissolution (Fig. 7 (b)) and/or proton-induced oxidization/reduction (Fig. 7 (c)). The electrolyte here acts as conducting ions and cooperates with the electrodes to store energy rather than being used as the simple supporting media in “rocking chair” type batteries. Here are denoted them as “hybrid chemistry” type batteries with abbreviation as ARHB. These hybrid systems enrich the existing RALBs chemistry and open up a new research era for high-performance RALBs design.

In aqueous batteries, various types of metals can be selected as the anode, such as aluminum⁴⁶⁾, iron⁴⁷⁾, magnesium⁴⁸⁾, or zinc⁴⁸⁾ (Fig. 8). Among these different metals, zinc is the most suitable to be used in ARHBs due to its low redox potential, good reversibility, high over-potential for hydrogen evolution in an acidic environment, large specific capacity, good corrosion resistance, and cost-effectiveness^{48), 49)}. Hence, many aqueous batteries, especially alkaline batteries, utilize zinc metal as the anode.

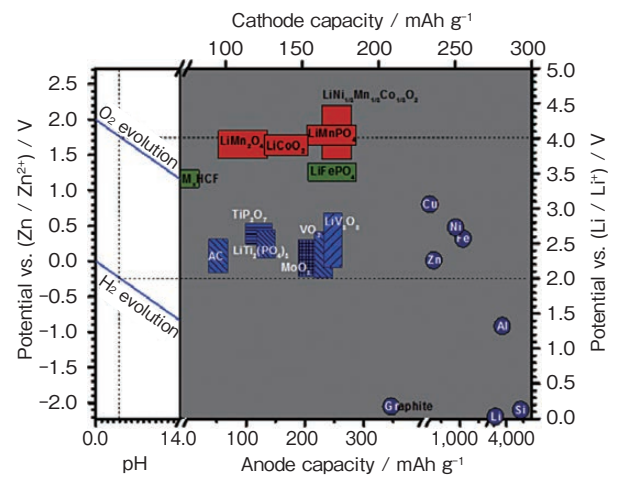


Fig. 8 Potential vs. pH stability diagram. Main insertion materials studied as positive and negative electrodes in aqueous rechargeable lithium-ion batteries⁵⁹⁾

Although the 4V materials such as LiMn₂O₄^{50)~52)}, LiMnPO₄⁵³⁾, LiCoO₂^{54)~56)} or LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂^{57), 58)} were reported in RALBs, their potential plateaus in aqueous media are close to water decomposition potential as shown in Fig. 8. Under these conditions, the oxygen evolution along with the dissolution of the metal ions from the positive electrode could not be avoided.

Our group developed a novel Rechargeable Aqueous Zn/LiFePO₄ with a mild acidic electrolyte with high efficiency and long-term cyclability^{59), 60)}. It relies on a high ionic conductivity with sufficient amounts of Zn²⁺ ions

for efficient cyclability of zinc anode and Li^+ ions for reversible insertion/extraction in the host cathodic material. The electrochemical reaction can be expressed as follows:



During the charge process, Li ions are extracted from LiFePO_4 at positive electrode (1.2V vs Zn^{2+}/Zn) and Zn^{2+} deposition at negative electrode (0V vs. Zn^{2+}/Zn). Upon discharge zinc metal loses electrons and dissolves in electrolyte, while on positive electrode Li ions insert into LiFePO_4 matrix (Fig. 9).

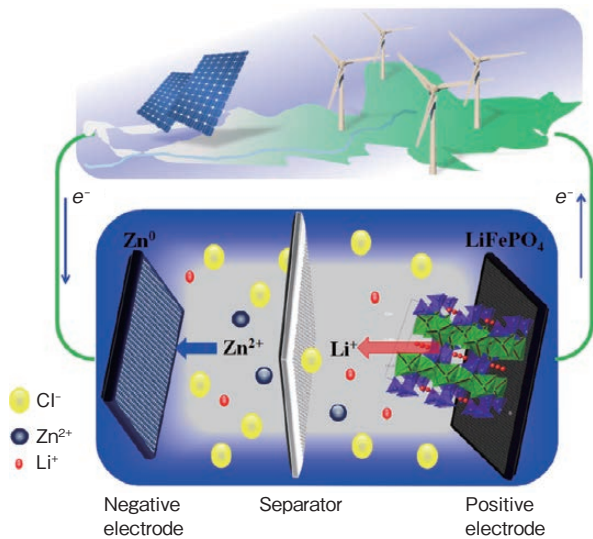


Fig. 9 Schematics of mechanism of Zn/LiCl-ZnCl₂/LiFePO₄ aqueous battery during the charge step⁵⁹⁾

Main electrochemical performance of the developed Zn/LiCl-ZnCl₂/LiFePO₄ system is presented in Fig. 10. Rate capability performance (Fig. 10 (a)) shows that the specific capacity gradually decreases with the current density increase. After extremely high C-rate (60C), the capacity is fully recovered when the cycling rate is switched back to 0.6C, indicating that along with superior rate capability, the battery system possesses a very high reversibility and

electrochemical stability⁶⁰⁾. The Zn/LiFePO₄ battery illustrated stable cycling properties (Fig. 10 (b)). The initial discharge capacity was slightly reduced from 120mAh g⁻¹ to 100mAh g⁻¹ at 6C with stable capacity retention even after 400 cycles. In addition, a laboratory prototype was designed and tested (Fig. 10 (c)). Zn/LiFePO₄ battery offers an exceptional safe, low cost, long cycling life, and high energy and power density energy storage for large-scale applications.

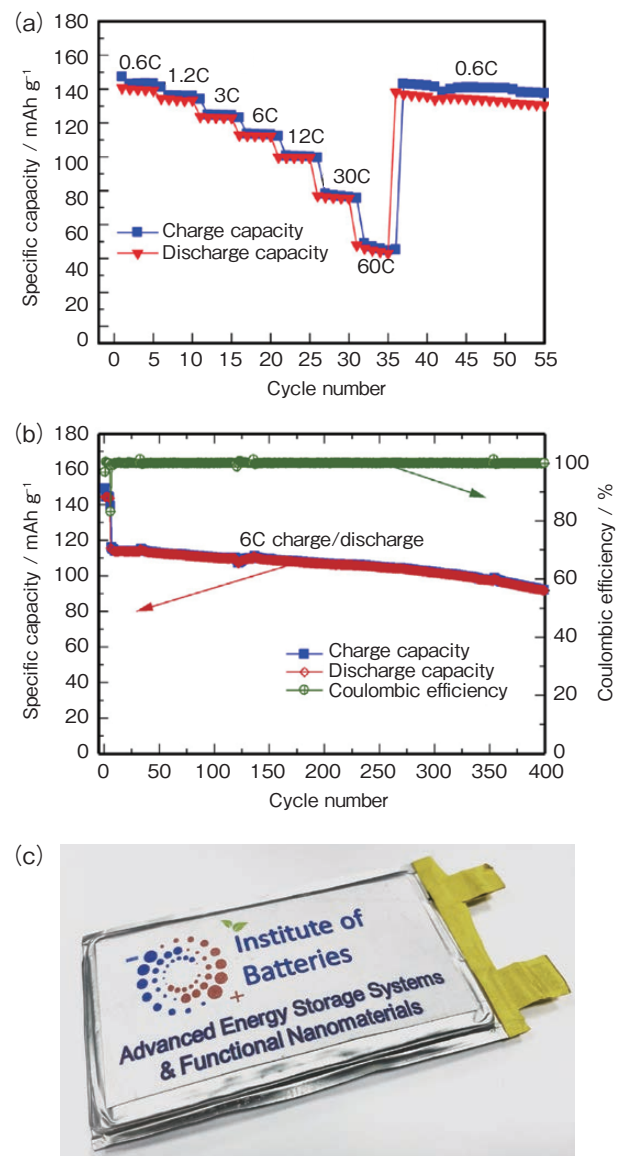


Fig. 10 (a) Rate-capability and (b) cycle performance at 6C of Zn/LiFePO₄ battery with binary LiCl-ZnCl₂ electrolyte (c) Zn/LiFePO₄ pouch cell⁵⁹⁾

5. Conclusion

In this paper we discuss some existing issues limiting the development of rechargeable batteries, and review the research activities towards resolving these obstacles in some of the ‘hottest’ areas of rechargeable battery research, namely, microbatteries, lithium-sulfur batteries, and aqueous lithium-ion batteries, conducted at our Research Group at Nazarbayev University, Kazakhstan, led by Prof. Zhumabay Bakenov. The authors strongly believe that this introduction review paper will be useful for the readers of the Journal of the Furukawa Battery Co., Ltd., expanding potential collaboration works with the battery and materials researchers in Japan, along with providing the information in the above mentioned remarkably research active and important areas of battery development.

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リチウム硫黄電池用硫黄極への チタン酸リチウム添加による特性向上

Improvement of Lithium Sulfur Batteries
by Adding Lithium Titanate to Sulfur Electrode

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The application of ceramic materials is effective in improving the performance of lithium sulfur batteries. Here we show the application of lithium titanate as the ceramics material for the sulfur electrode. As the application methods of lithium titanate, an adding of lithium titanate into the sulfur electrode and the formation of a lithium titanate layer on the surface of the sulfur electrode are investigated. In the adding of lithium titanate into the sulfur electrode, sulfur utilization and cycle ability were improved by a simple method of the adding lithium titanate to the sulfur electrode. In the formation of the lithium titanate layer on the surface of the sulfur electrode, sulfur utilization was improved when the sulfur loading was increased. The application of lithium titanate to the sulfur electrodes is found to be effective in improving the performance of the lithium sulfur batteries.

1. はじめに

スマートフォンをはじめとする小型電子機器に加え、電気自動車やスマートグリッドなどの電源としてリチウムイオン二次電池が使用されている。用途の拡大に伴い、安価で高性能なリチウムイオン二次電池の開発が求められている。現行のリチウムイオン二次電池の正極には、 LiCoO_2 、 LiMn_2O_4 、 LiFePO_4 、 $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ などのセラミックス材料が使用されている。これらは遷移金属の酸化還元反応を利用する正極材料であり、優れた出力特性やサイクル特性を示す。しかしながら、使用可能な容量が 200mAh g^{-1} 程度に制限されてしまうため、高容量正極材料の適用が電池性能向上の一つの手段といえる。当社では正極の高容量化を目的に高い理論容量をもつ硫黄を活物質として用いるリチウム硫黄電池について研究してきた。

リチウム硫黄電池は、全固体電池やリチウム金属

負極電池などと同様にポストアリチウムイオン二次電池のひとつとして注目されている。リチウム硫黄電池は正極に硫黄を使用することを特長としており、硫黄の理論容量が $1,672\text{mAh g}^{-1}$ と既存の正極材料に比べて高い値を示すことから、高エネルギー密度を有する電池設計が期待できる。また、硫黄は汎用元素であり、既存の正極材料に含まれるコバルトなどの高コストなレアメタルを含まないため、電池コストの削減が期待できる¹⁾。

リチウム硫黄電池の実現には、多くの課題がある。中でも、硫黄の絶縁性とレドックスシャトル現象は早急に解決する必要がある。硫黄の低い電子伝導やイオン伝導により、電池の内部抵抗が大きくなり、レート特性などの観点で不利になる。硫黄の特性改善にむけて、硫黄と炭素を複合化するなどの検討が行われている²⁾。一方、レドックスシャトル現象とは、充放電過程で生成する中間生成物の多硫化リチウムが電解液に溶出し、負極上での還元と正極上での酸化を繰り返すことであり、これによりサイクル特性などの電池特性が大きく劣化することが報告されている。レドックスシャトル現象の抑制方法

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として、多硫化リチウムの電解液への溶解、および拡散の制御をすることが重要であり、電解液種³⁾やセパレータ⁴⁾など様々な解決方法が検討、報告されている。

本研究では、セラミックス材料をリチウム硫黄電池へ適用する方法に注目した。セラミックス材料のリチウム硫黄電池への適用はこれまでに様々な研究グループから報告されており、セパレータへのセラミックスの塗工⁵⁾、硫黄極へのセラミックス粉末の添加⁶⁾などが行われており、セラミックスの有する多硫化リチウムの吸着特性や、セラミックス粒子による多硫化リチウムの拡散の物理的抑制などにより、サイクル特性をはじめとする電池特性の向上が報告されている。セラミックス材料としては、酸化アルミニウム、酸化マグネシウムや酸化チタンなどの適用が報告されているが、我々はチタン酸リチウム(Li₄Ti₅O₁₂、LTO)に着目した。チタン酸リチウムは、リチウムイオン電池の負極として用いられている材料であり、同時に多硫化リチウムの吸着効果を有することが知られており、リチウム硫黄電池の硫黄支持体としての適用などが検討されている^{7,8)}。また、チタン酸リチウムは還元状態で電子伝導性を有するため、他のセラミックスに比べ、電極内の電子伝導性の面での性能向上も期待できる。さらに、チタン酸リチウムは、1.55V(vs. Li/Li⁺)で充放電し、175mAh g⁻¹の容量を有し、かつ、優れたサイクル特性を示す材料である点から、硫黄極の充放電電位範囲内でチタン酸リチウムの容量も利用することができるため、他のセラミックス材料の添加に比べ、実容量の増加という観点でも性能向上が期待できる。

本報では、チタン酸リチウムの硫黄極への適用方法とその効果について調査した結果を報告する。

2. 実験

2.1 硫黄炭素複合粉末の調製

活物質である硫黄炭素複合粉末は、炭素材料へ硫黄を溶融含浸することにより調製した。ケッチェンブラック(KB)と硫黄(S)粉末を重量比30:70で秤

量し、乳鉢中で十分に混合した後に、Ar雰囲気下で155℃、12時間の熱処理を施すことでKBとSを複合化し、活物質である硫黄炭素複合粉末(KBS)を調製した。この時、熱重量分析により熱処理後のKBとSの比率に変化がないことを確認した。

2.2 チタン酸リチウムを添加した硫黄極の作製

硫黄極は硫黄合材スラリーを集電箔上に塗工することで作製した。正極活物質であるKBS、添加剤であるチタン酸リチウム、導電助剤であるアセチレンブラック(AB)、バインダーであるカルボキシメチルセルロース(CMC)とスチレンブタジエンラバー(SBR)を85:0:10:3:2、84:1:10:3:2、83:2:10:3:2、80:5:10:3:2、75:10:10:3:2、65:20:10:3:2の重量比で蒸留水中で混練、分散することで、硫黄合材スラリーを調製した。調製した硫黄合材スラリーをカーボンコートアルミ箔上に塗工し、真空乾燥処理を施すことでチタン酸リチウムを添加した硫黄極を作製した。

2.3 チタン酸リチウム/硫黄極複層電極の作製

チタン酸リチウム/硫黄極複層電極は硫黄合材スラリーとチタン酸リチウム合材スラリーを集電箔上に順に塗工することで形成した。硫黄極層はKBS、AB、CMCとSBRを重量比85:10:3:2で秤量し、蒸留水中で分散、混練して得られた硫黄合材スラリーをカーボンコートアルミ箔上に塗布、乾燥することで作製した。また、チタン酸リチウム層は、チタン酸リチウム、AB、ポリビニルフッ化ビニリデンを90:5:5の重量比でN-メチルピロリドン中で混練、分散し、硫黄極上に塗布し、真空乾燥処理を施すことで、硫黄極層の上に形成した。このようにしてチタン酸リチウム層/硫黄極層/集電体の構造を有するチタン酸リチウム/硫黄極複層電極を作製した。

2.4 リチウム硫黄電池の作製

正極にはそれぞれ作製した硫黄極を、対極には厚み600μmのリチウム金属を使用した。セパレータにはポリイミド製のセパレータを使用した。電解液

は、リチウム塩であるリチウムビストリフルオロメタンスルホニルイミド (LiTFSI) と溶媒のスルホラン (SL) をモル比1:2で混合することで調製した⁹⁾。それぞれの材料を Ar 雰囲気グローブボックス内で 2032 型コインセル中に設置し、かしめにより密閉することでリチウム硫黄電池を作製した。

3. 結果

3.1 硫黄極内へのチタン酸リチウムの添加

図1にはチタン酸リチウムを添加した際の各組成における充放電曲線の比較を示す。硫黄のローディング量は 0.7mg cm^{-2} に固定して試験を実施した。充放電曲線から、チタン酸リチウムの添加量の増加に応じて、電池過電圧の減少、及び 2V 付近の硫黄の容量成分が大きくなっていることを確認した。また、1.5V 付近に注目すると、チタン酸リチウム由来の酸化還元容量成分が認められ、チタン酸リチウムの添加量に比例して容量成分が長くなっていることが確認された。これらの結果より、チタン酸リチウムの添加は、内部抵抗の抑制、硫黄の利用率向上に加え、チタン酸リチウムの酸化還元による電池の実容量の増加にも寄与することを確認した。表1は、初期放電から得られた硫黄の重量当たりの容量と、合材電極の重量当たりの容量を示す。チタン酸リチウムの添加量が増えるほど硫黄の重量当たりの容量が増加する傾向が確認された。一方、合材電極の重量当たりの容量の比較では、添加量が増えるほど合材電極内の硫黄の割合が減少するため、20wt.% のチタン酸リチウムを添加した場合、未添加の電極よりも容量が減少したことから、2-10wt.% の添加が適当であることが示唆された。

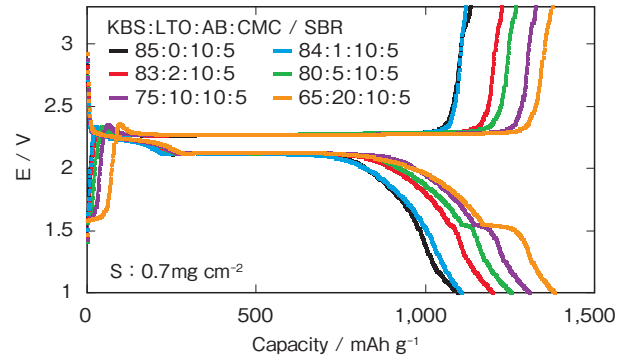


図1 チタン酸リチウムの添加量による初期充放電特性比較
Fig. 1 Comparison of initial charge and discharge curves by amount of lithium titanate additive

表1 チタン酸リチウムの添加量に対する硫黄の重量当たりの容量及び合材電極重量当たりの容量
Table.1 The capacity per weight of sulfur and the capacity per weight of composite electrode against the amount of lithium titanate additive

KBS:LTO:AB:CMC/SBR	硫黄の重量当たりの容量	合材電極重量当たりの容量
85 : 0 : 10 : 5	1,097mAh g ⁻¹	652mAh g ⁻¹
84 : 1 : 10 : 5	1,107mAh g ⁻¹	639mAh g ⁻¹
83 : 2 : 10 : 5	1,200mAh g ⁻¹	697mAh g ⁻¹
80 : 5 : 10 : 5	1,255mAh g ⁻¹	702mAh g ⁻¹
75 : 10 : 10 : 5	1,306mAh g ⁻¹	685mAh g ⁻¹
65 : 20 : 10 : 5	1,381mAh g ⁻¹	628mAh g ⁻¹

図2は添加剤なしの硫黄極、チタン酸リチウムを10wt.%添加した硫黄極、及び比較として、一般的なセラミックス材料である $\gamma\text{-Al}_2\text{O}_3$ を10wt.%添加した硫黄極の 30°C 、0.1Cにおけるサイクル特性の比較を示す。添加なし、 $\gamma\text{-Al}_2\text{O}_3$ 添加、チタン酸リチウム添加の各電極の50サイクル時の容量維持率は、それぞれ72.9%、74.8%、80.3%であり、未添加の電極よりセラミックスを添加する方が優れ、 $\gamma\text{-Al}_2\text{O}_3$ とチタン酸リチウムの比較においては、チタン酸リチウムを添加したものが高い容量維持率を示した。チタン酸リチウムを添加した場合、初期の容量劣化が大きく抑制されており、結果としてサイクル特性の向上につながったと考えられる。この初期の容量劣化が抑制された要因の一つに中間生成物であるリチウムポリスルフィドが電解液へ溶解および拡散することを抑制したことが考えられる。 Li_2S_8 をジオキソラン/ジメトキシエタン混合溶媒に溶解

することで調製した Li_2S_8 溶液中に、 $\gamma\text{-Al}_2\text{O}_3$ およびチタン酸リチウムを浸漬した様子を図3に示す。図3から分かる通り、 $\gamma\text{-Al}_2\text{O}_3$ 、及びチタン酸リチウムを浸漬することで溶液の色が薄くなっていることから、各々のセラミックスがリチウムポリスルフィドを吸着したこと、特にチタン酸リチウムが優れた吸着特性を示すことが推察できる。リチウムポリスルフィドの吸着特性により、レドックスシャトルや、硫黄極実容量低下が抑制され電池特性が向上したと考えられる。

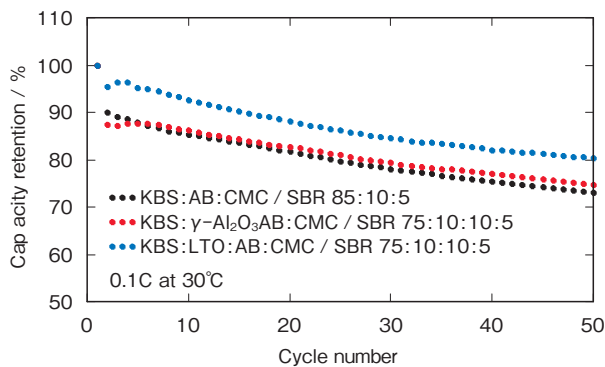


図2 リチウム硫黄電池のサイクル特性
Fig. 2 Cycle performances of lithium sulfur batteries

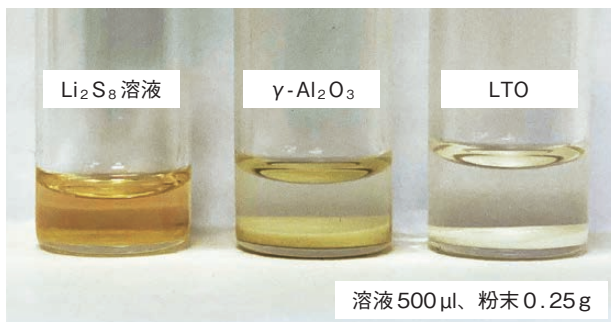


図3 Li_2S_8 へのセラミックスの浸漬
Fig. 3 Immersion of ceramics in Li_2S_8 solution

図4には60°Cでの充放電試験結果を示す。チタン酸リチウムの添加がない場合、数サイクル後に充電電位が一定の数値から上昇しない挙動が確認された。これはレドックスシャトル現象や、リチウム金属のデンドライト析出による微小短絡が原因として考えられ、高温環境で溶解しやすくなったリチウムポリスルフィドが原因で生じたと推察される。一方

で、チタン酸リチウムを添加した硫黄極では、30サイクルまで安定な充放電挙動を示す。これはチタン酸リチウムのリチウムポリスルフィド吸着特性が顕著に現れた結果であり、チタン酸リチウムの添加がリチウム硫黄電池の高温特性にも効果があることが示唆された。

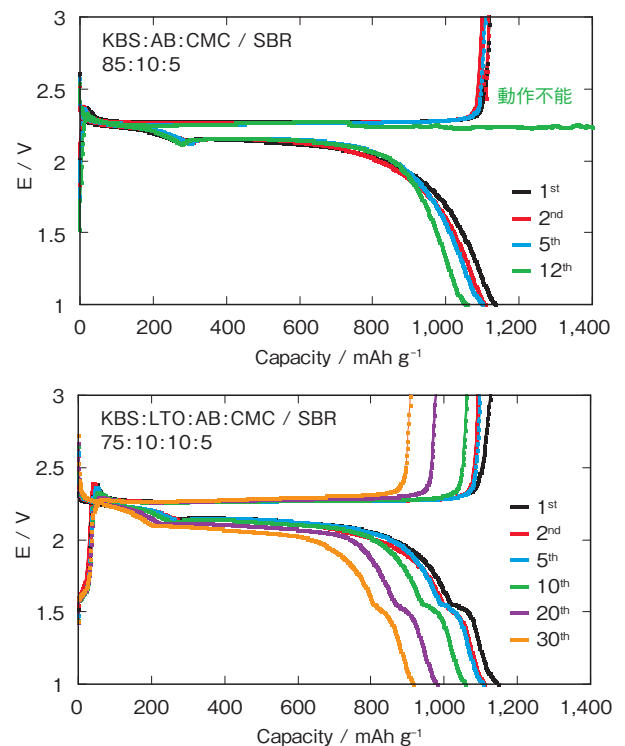


図4 チタン酸リチウムの添加の有無による60°Cでのリチウム硫黄電池の充放電曲線
Fig. 4 Charge and discharge curves of lithium sulfur batteries with or without lithium titanate additive at 60°C

3.2 チタン酸リチウム/硫黄極複層電極の特性評価

図5 (a) は硫黄のローディング量を 1.6mg cm^{-2} とした硫黄極の充放電曲線を示す。図1に示す電極に比べ硫黄ローディング量が大きいため、過電圧が増大し容量が減少している。図5 (b) は硫黄のローディング 1.6mg cm^{-2} の硫黄極上にチタン酸リチウム層を形成した複層電極の充放電曲線を示す。放電プラトーは2.3V、2.1V、1.5Vの3段確認され、2.3Vと2.1Vのプラトーが硫黄の還元由来し、1.5V付近のプラトーはチタン酸リチウムの還元由来すると思われる。2.3V、2.1Vの容量が増加しているこ

とから、チタン酸リチウム層を導入することで、硫黄の利用率が向上したといえる。加えて、チタン酸リチウムの容量成分も確認されたことから、硫黄極上に形成したチタン酸リチウムも充放電可能であることが示唆された。図6にはチタン酸リチウム層の有無による放電深度ごとのナイキストプロットの変化を示す。放電開始から3時間は抵抗の変化に大きな差は見られないが、放電時間が4時間以降になると、チタン酸リチウム層を形成した複層電極の抵抗増大が抑制されていることが確認された。この抵抗増大の抑制により2.3V、2.1Vの硫黄由来の容量が増加したと考えられる。抵抗増大が抑制された理由として、リチウムポリスルフィドを吸着するチタン酸リチウム層が存在することにより、放電過程で生じるリチウムポリスルフィドの電解液への拡散が抑制され、電解液の劣化や、活物質の減少を抑制できたためであると考えられる。

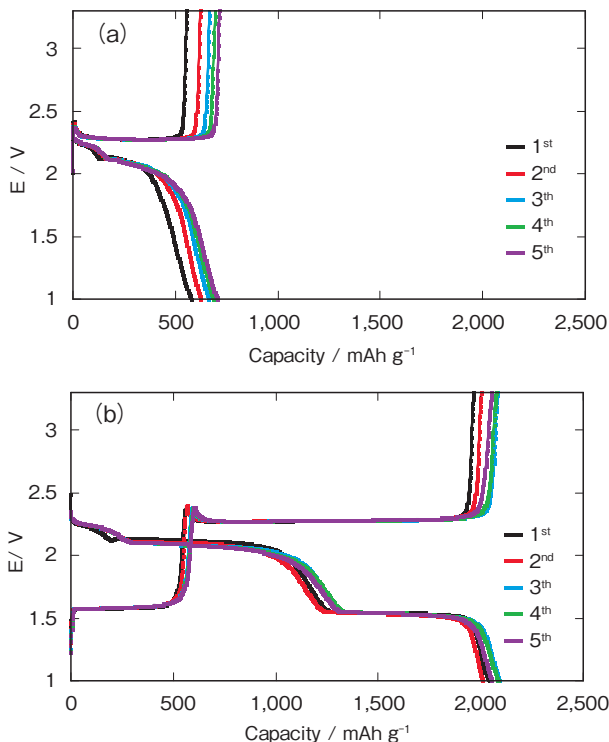


図5 (a) 硫黄極と (b) チタン酸リチウム/硫黄複層電極の充放電曲線
Fig. 5 Charge and discharge curves of lithium sulfur batteries with (a) sulfur electrode or (b) lithium titanate/sulfur multilayer electrode

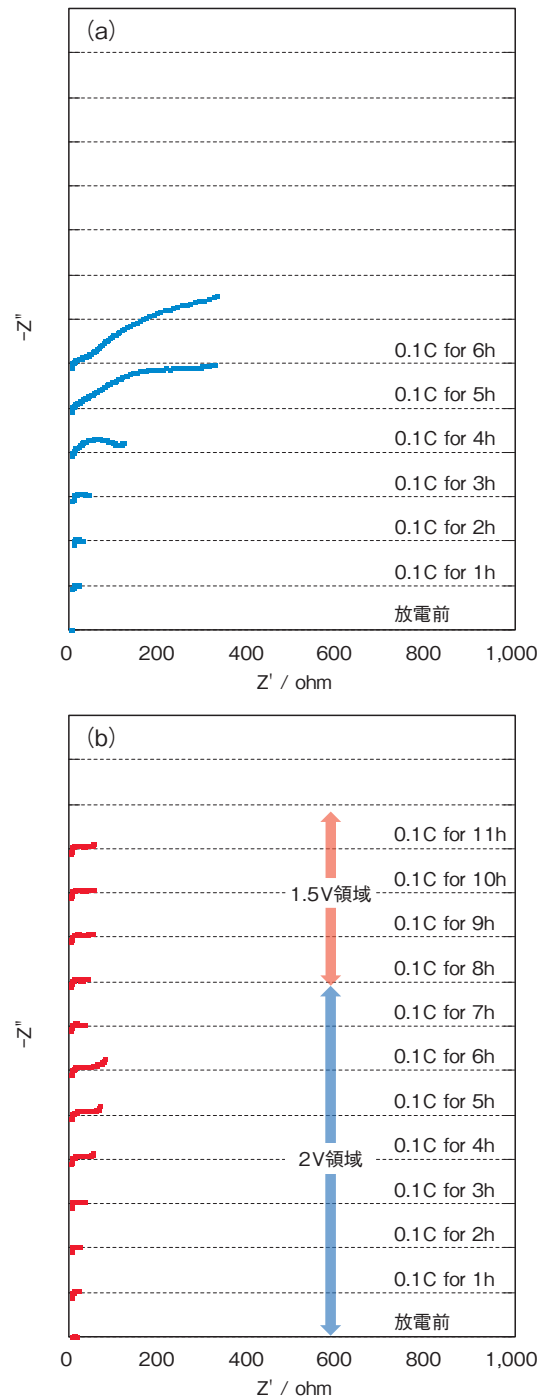


図6 (a) 硫黄極と (b) チタン酸リチウム/硫黄複層電極の放電深度ごとのナイキストプロット
Fig. 6 Nyquist plots of lithium sulfur batteries with (a) sulfur electrode and (b) lithium titanate/sulfur multilayer electrode at each depth of discharge

また、図5 (b) の1.5V領域での放電容量が、1.5V領域での充電容量に比べ大きくなっていることから、1.5Vの放電プラトーではチタン酸リチウムの放電に加え、硫黄の還元も進行しているものと考えら

れる。図7 (a) には満充電状態のチタン酸リチウム電極の外観を示す。一方、図7 (b) には満充電状態のチタン酸リチウム電極を硫黄極と接触させた後のチタン酸リチウム電極の外観を示す。満充電状態のチタン酸リチウム電極は黒色であるのに対し、硫黄極と接触させた後のチタン酸リチウム電極は白色であった。チタン酸リチウムは少量の充電状態で黒色に変化することから、白色である硫黄極接触後のチタン酸リチウムは満放電状態であることが推察できる¹⁰⁾。この結果から、充電状態のチタン酸リチウム電極と硫黄極が物理接触することで、チタン酸リチウム電極から硫黄極へ容易にリチウムイオンが移動すると考えられる。そのため、チタン酸リチウム層を形成した硫黄極においては、チタン酸リチウムの還元電位でチタン酸リチウムの還元する過程と、還元したチタン酸リチウムから未反応の硫黄へリチウムイオンが移動し硫黄が還元する過程が同時に進行することで放電容量が増加したと考えられる。上記の結果から、硫黄極表面へのチタン酸リチウム層の形成は硫黄の利用効率向上に効果があると推察できる。

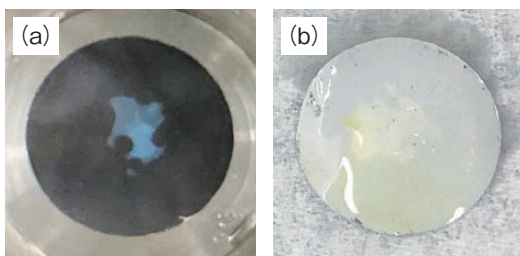


図7 (a) 満充電状態のチタン酸リチウム電極と (b) 硫黄極接触後のチタン酸リチウム電極

Fig. 7 Photographs of (a) full charged lithium titanate electrode and (b) full charged lithium titanate electrode after contact with sulfur electrode

4. まとめ

リチウム硫黄電池用の硫黄極へのチタン酸リチウムの適用を検討した。チタン酸リチウムの適用方法として、硫黄極へのチタン酸リチウムの添加と、硫黄極表面へのチタン酸リチウム層の形成を検討した。チタン酸リチウムの添加では、硫黄極スラリーへのチタン酸リチウムの添加という簡便な手法で、硫黄の利用効率向上やサイクル特性が改善した。硫黄極表面へのチタン酸リチウム層の形成では、硫黄のローディング量が増加した場合でも、硫黄の利用効率向上が確認された。また、チタン酸リチウムの添加は、他のセラミックス材料の添加に比べ、チタン酸リチウムが容量を有するため、電池容量の観点でも、非常に興味深い材料であることが明らかになった。

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Finite Element Simulation of Deformation of Battery Electrodes

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A common failure mode of lead-acid batteries is related to corrosion-induced electrode deformations. For a better understanding of these phenomena, our study proposes a simulation model for the analysis of these undesired deformations. First, the underlying chemical and electrochemical mechanisms behind the expansion are discussed, and an approach is proposed to model the mechanics of expansion. Next, material behavior is demonstrated using uniaxial tensile tests. Finally, a finite element model is built for the mechanical analysis of the battery cell.

1. Introduction

Lead-acid batteries can be subject to several modes of failure. Among these, there is the undesired deformation of electrode plates, especially positive ones. This may result in a short-circuit (due to a positive plate touching the negative electrode assembly, sometimes even ripping the separator bag), in the separation of the positive active material (PAM) from the lead material of the grid or an accelerated demolition of the structure of the active material^{1),2)}. In any of these cases, the battery cell fails or has a reduced capacity. Fig. 1 and Fig. 2 illustrate this on electrodes aged in a typical battery aging test.

Extending the lifespan of lead-acid battery cells through design is a complex process, requiring a detailed understanding of underlying chemical (electrochemical) and physical (electric, mechanical, thermal) processes. In the literature, there is a limited number of studies on electrode corrosion^{3)~6)}. Also, there is a number of simulations on various

aspects of lead-acid batteries, but not on their mechanical behavior. The authors haven't found any simulation studies about corrosion-induced deformation of battery electrodes.

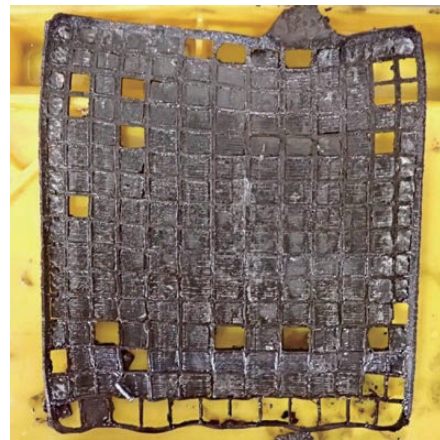


Fig. 1 In-plane deformation of a positive electrode



Fig. 2 Out-of-plane deformation of positive plates

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The aim of the present work is to build a mechanical simulation model for the deformation of lead-acid battery electrodes, providing a tool to complement other design principles for improved batteries.

2. Expansion model

Deformations in the battery are thought to be caused by the expansion of developed materials during the preparation and operation of the electrode plates. In the present study, expansion of the positive grids due to the oxidation of the lead material is dealt with. Volume change (“breathing”) of a well-prepared positive active material (PAM) during the charge-discharge process tends to be neglectable. Therefore, it is left out of our considerations.

During battery operation, one of the main electrochemical processes occurs on the positive electrode. It is the transformation of PbO_2 to PbSO_4 during discharge, which is converted back to PbO_2 during recharge. This is the process related to energy storage.

However, an inherent process of charge is the surface oxidation of the positive electrode lead grid. This process creates a non-stoichiometric material of lead and oxygen, denoted here by PbO_x , with an increasing oxygen concentration towards the active material, as Fig. 3 shows. This is called “corrosion layer”.

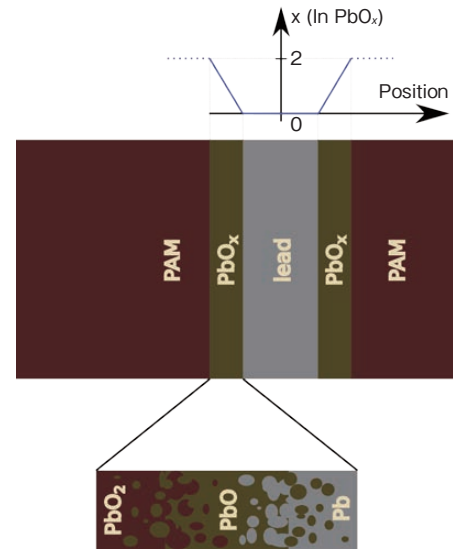


Fig. 3 A proposed understanding of corrosion layers (PbO_x in the figure)

From a mechanical point of view, the principal effect caused by this material transformation is volumetric expansion: if the volume of one mole of lead is considered 100%, that of one mole of PbO is between 123 and 130% (depending on the ratio of allotropic forms of PbO), and that of one mole of PbO_2 is between 121 and 138% (also depending on the ratio of allotropic forms)⁷.

The main effect on grid deformation is caused by the expansion of the corrosion layer during its formation, which is thought to happen as follows:

- before formation, material in immediate contact with PAM can be considered to be lead;
- after the start of electrochemical processes, corrosion layer starts to form;
- corrosion layer volume is larger than the volume of lead, which means the transformed layer needs more space and will tend to expand;
- during this expansion, it exerts mechanical force/stress on the materials it is in contact with. These materials include the grid metal, and this force causes its deformation.

The expansion of the corrosion layer occurs

gradually, depending on the x value in PbO_x : it is smaller near the lead grid (where x is small) and larger near the PAM (where x is near 2).

The thickness of this corrosion layer is estimated to be in the 10–100 micrometer range (based both on experimental results and theoretical considerations).

A similar corrosion layer is also considered to form on the surface of the grid in contact with the sulfuric acid solution. It is assumed to have the same mechanical behavior as the layer between PAM and grid lead.

For simulation purposes, it is advantageous to simplify the above model. This is detailed in Section 4, which also illustrates the above idea.

It is also to be mentioned that corrosion-induced deformation has not been experimentally observed on negative electrodes. Thus, the negative electrodes are considered not to deform by themselves, only by the contact force from the positive ones.

3. Constitutive modeling of materials

There are multiple options to manufacture lead grids, e.g. punching from a rolled sheet, casting etc. For *rolled lead materials*, earlier work has been performed⁸⁾ and its result is used. However, *cast lead* is expected to have a different behavior. The reason for this is not only its slightly modified composition, but also the different production technology, resulting in a different internal structure of the material. Therefore, cast lead requires new measurements. On the other hand, its behavior is expected to be isotropic.

Uniaxial tensile experiments have been performed using the technique described earlier in⁸⁾. It consists of loading the sample with a displacement and then holding this displacement constant and letting the sample relax (see Fig. 4

for an illustration). This procedure is used because it is thought to show the long-term behavior of the material as much as possible with reasonably short tests; the processes in the battery, in which we are interested, are also happening on a long time scale.

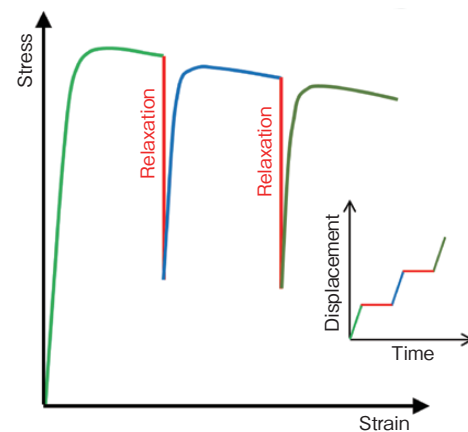


Fig. 4 Displacement load and stress-strain response in the uniaxial tensile experiment⁸⁾

Fig. 5 presents a typical force-displacement curve for a cast grid material sample.

Another thought is given to the *stress-strain behavior of the corrosion layer*: although it is present in the structure in a small amount, its stiffness determines the strength of the expansion effect.

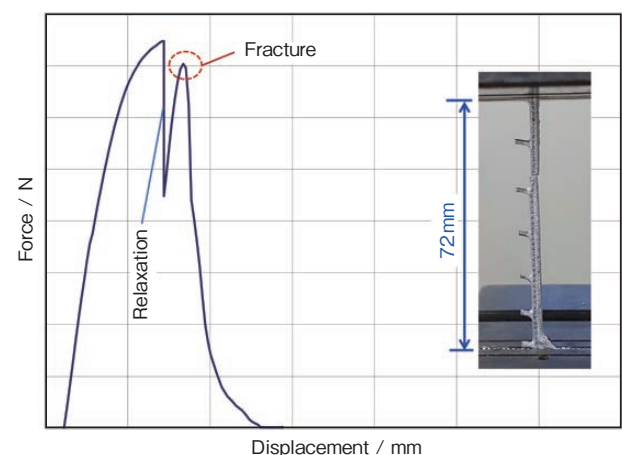


Fig. 5 Measured force-displacement behavior of a selected piece of a cast grid

PbO is a stiff and brittle material compared to Pb; corrosion layer is considered to be a mixture between lead and lead-oxides. Thus, its material properties are assumed to be between those of lead and its oxides. In our case, it is achieved by using a plastic modulus much larger than for lead.

For the corrosion layer, the same elastic modulus value is used as for lead. There are two reasons for this: on one hand, there is no reliable data of it; on the other hand, a different value after transformation is expected to cause numerical problems.

4. Finite element model

In this Section, the finite element model of a battery cell is described briefly.

As mentioned in Section 2, *expansion modeling* should be simplified for simulation purposes. The main reason for this is that in numerical modeling, it is often difficult to handle small and large dimensions together; here, the corrosion layer is very thin compared to the grid dimensions (10–100 μm magnitude vs. 100mm magnitude), and could still be split to further layers, very challenging to model. Therefore,

- corrosion layer is considered a single layer, and is expanded uniformly (neglecting the change of its composition through thickness), or
- expansion modeling is simplified further, expanding the PAM material instead of corrosion layer. Note that the physical meaning of this model is questionable, but it is expected to lead to simulation results faster.

Fig. 6 shows a detail of a model geometry with corrosion layer. It can be seen that corrosion layer thickness (100 micrometers in this case) is much smaller than any other dimension in the model.

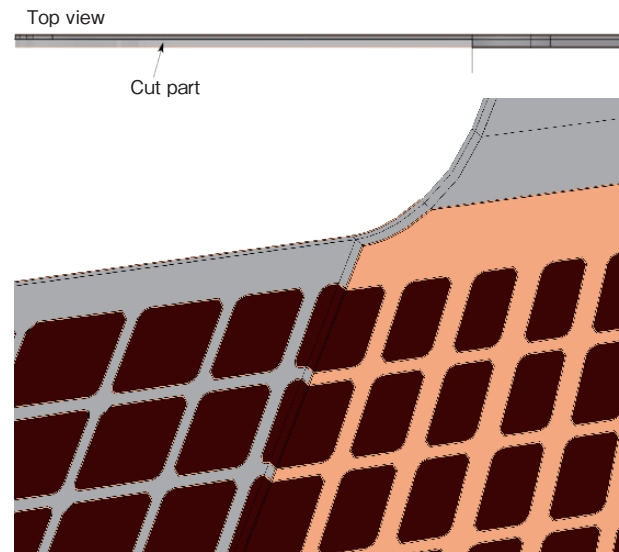


Fig. 6 Illustration of a model including a corrosion layer (both in the PAM window and on the grid surface). Grey=lead, brown=PAM, orange=corrosion layer

Volume of the corrosion layer is increased gradually, uniformly and isotropically during the simulation (i.e. by the same amount everywhere and in all directions).

The model is made using the *COMSOL finite element package*⁹⁾. It consists of volumetric (solid) elements, and uses uniquely the structural mechanics interface – no thermal, electric or chemical phenomena are modeled here. A quasi-stationary model is used, which means that, although expansion is applied gradually, inertia effects are not taken into account: the deformation process is assumed to be very slow.

Fig. 7 shows the *geometry* of an 8-electrode finite element model, with 4 positive and 4 negative electrodes. As mentioned earlier, positive electrodes are expanded using a uniform expansion of the corrosion layers (both in the PAM windows and on the grid surface), situated as shown in Fig. 6. Negative electrodes only deform due to contact with positive ones, they have no other source of shape change.

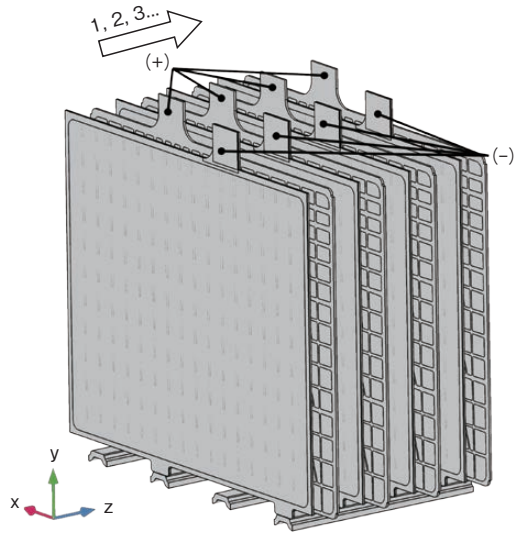


Fig. 7 Finite element model illustrated

Contact between the electrodes is taken into account, as well as electrode contact with the bottom of the container of the cell and with the cell walls (in the z direction). Along x , cell walls are considered to be reasonably far (in reality, they are often in contact with separator bags but not too much with the lead grids themselves).

Material models used for the lead materials come from experiments (see Section 3). The positive grid is made of a rolled material, modeled using Hill's anisotropic yield criterion¹⁰. The material of the negative grid is a cast one, modeled using the usual, isotropic von Mises plasticity (Section 3).

Mesh is a 3D mesh with prismatic elements, generated from a planar mesh. A positive electrode uses approximately 700,000 elements. This mesh is shown in Fig. 8 to give an idea about its general shape.

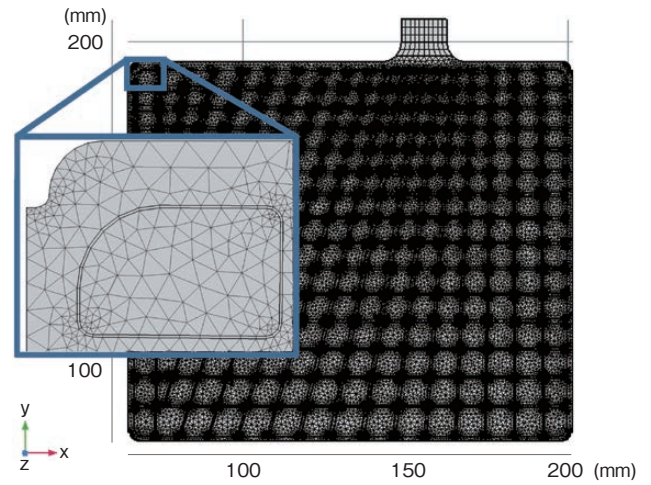


Fig. 8 Mesh of the positive electrode including a corrosion layer in the PAM windows

The models are in test use now. In the followings, some results obtained with them are presented.

5. Finite element results

In this Section, sample finite element results are shown.

Using expansion caused by the corrosion layer, two-electrode models have been run so far.

Typical deformed shape of the positive electrode is shown in Fig. 9. Earlier experimental analysis (on larger, production-scale battery cells) suggests that the external dimensions of the electrode are expected to enlarge by a few percents; in contrast, this simulation predicts enlargements a magnitude smaller.

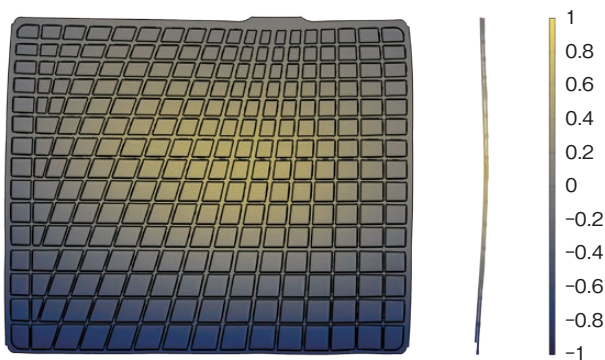


Fig. 9 Deformed shape of the positive electrode and side section of both electrodes (10x displacement magnification). Color shows out-of-plane displacement in arbitrary units

A reason for this difference can be the constitutive model of the corrosion layer. In this calculation, its stress-strain curve was the same as that of lead. As mentioned in Section 3, it is thought that in reality, the value for plastic modulus is higher than that. Therefore, simulation has been repeated with higher hardening moduli.

Fig. 10 shows the outer contours of the resulting electrode shapes in different cases. It can be seen that, as expected, a stiffer corrosion layer leads to larger, more realistic deformations. Therefore, this is a logical direction for the following steps in refining the simulation.

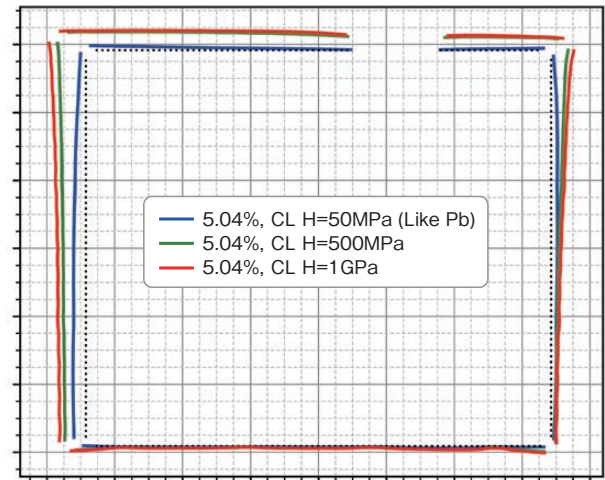


Fig. 10 Deformed shape of the positive electrode with stiffer corrosion layer behavior (10x displacement magnification)

Larger cell models, with more electrodes, have also been run. However, they use the simpler expansion model described in Section 2, the PAM expansion model, due to model size reasons.

Fig. 11 illustrates results from this type of model, using 11 electrodes. This shows the further potential in this work.

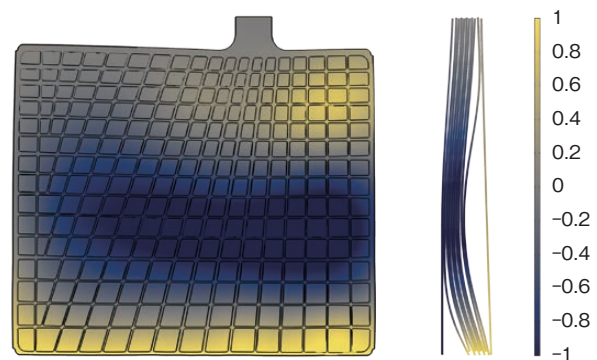


Fig. 11 Deformed shape of the first positive electrode and side section of all electrodes in an 11-electrode model (no displacement magnification). Color shows out-of-plane displacement in arbitrary units

6. Conclusions

In the present study, a mechanical finite element model was proposed for the description of lead-acid battery electrode deformations. Results obtained with it are presented as illustrations. After further development, it is expected to provide applicable results, and aid the design process of future battery electrodes. This would result in batteries with a longer lifespan, better reliability and lower price.

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EN規格LN1形蓄電池 トヨタ自動車株式会社様に採用

Adoption of 345LN1 Lead Acid Battery for
TOYOTA MOTOR CORPORATION

この度、トヨタ自動車株式会社様が2022年5月に発売された新型BEV (Battery EV) である“bZ4X”に、当社のLN1形蓄電池をご採用頂きました。本車両は、トヨタ自動車様のBEV「bZ (beyond Zero) シリーズ」の第一弾車種で、「ゼロを超えた価値」を目指した車両です。当社のLN1形蓄電池がその一翼を担い、価値提供の一助になることを強く期待します。

本製品は、2015年からプリウスに搭載している「345LN1」の改良品となっています。欧州のEN (European Norm) 規格及び、トヨタ自動車様の要求を満足したEN蓄電池です。

LN1以外にも、サイズの異なるEN蓄電池を開発・販売しており、これまで培った技術と実績を織り込んだ高品質、高安全性の電池となっています。

概要を以下に示します。

1. 製品名及び外観*1

345LN1形蓄電池



345LN1形蓄電池外観

2. 主な特長

①安全に配慮した設計

- ・液口栓を設け、使用中の液減りに対して精製水の補充が可能な構造としました。
- ・防爆フィルターを採用し、外部で発生した火花（スパーク）による引火爆発を防ぐ構造となっています。
- ・液面線を設け、側面から液面の確認が可能な構造としました。

②車両の使用用途に合わせた最適設計

- ・電動車に補機用途として搭載した際に、長寿命が期待できる電池設計となっています。
- ・正/負極板、セパレータ、電解液の設計を見直し、高性能な電池を開発いたしました。

3. 要項表

電圧 (V)	20時間率容量 (Ah)	外形寸法 (mm)*2			液入質量 (約kg)
		総高さ	幅	長さ	
12	45	190	175	175	11.8

* 1、2 外観、外形寸法はEN規格 (EN-50342) に準拠

(自動車生産統括部 技術部 飯田峻司)

Energy Storage System (電力貯蔵システム) 実証試験について

Verification Test of Energy Storage System for Reduction of CO₂ Emission

近年、「脱炭素社会の実現」に向けて再生可能エネルギー（以下、再エネ）の普及が求められており、再エネから生み出される電力を効率的に貯蔵・供給することが課題となります。当社は、2025中期経営計画の中で、Energy Storage System（電力貯蔵システム、以下ESS）など「脱炭素ソリューションビジネスに挑戦する」ことを重点施策として掲げています。従来蓄電池や電源装置など「製品の単品売り」を主なビジネスとしてきましたが、新たに「システム」や「サービス」の提供に加え、総合的にお客様のエネルギーに関する問題を解決する「ソリューションビジネス」に事業領域を広げていくことを目指しています。

ESSの市場投入に先駆けて、本年10月に当社の今市事業所に太陽光発電（以下、PV）併設型のESS実証システムを立ち上げ、試験運用を開始しました。実証試験で得られたデータ・知見を基にお客様のニーズに応える満足度の高い「システム」や「サービス」の開発に活用してまいります。

1. ESS実証システムの概要

ESS実証システムは、PV電力の有効利用、および自家消費によるCO₂排出量の削減を目的としています。ESS実証システムは、今市事業所の事務棟に設置したPVパネルと蓄電池を組み合わせる構成となっています。使用するPCS（パワーコンディショナ）は自立運転機能を備えており、停電時にはBCP（Business Continuity Plan）対策の一環として事務棟へ電力を供給します。また、V2X^{*1}対応充放電装置を設置しており、電気自動車などと電力の相互供給を行うことが可能となっております。

2. 今後の計画

今後は、システム運用を通じてPV電力を無駄なく蓄電池に貯蔵し、消費電力量の削減＝CO₂排出量の削減とBCP対策を両立させるシステム運用の知見を習得していく予定です。また、ESSの設計・工事・運用までの全工程の課題、問題点の抽出を行い、2024年度の商品化を目標に取り組んでまいります。



ESS実証システムの外観

*1 V2Xとは、Vehicle to Everythingを意味しており、V＝電気自動車などとH＝住宅（V2H）、B＝ビル（V2B）、G＝電力網（V2G）の全てをつなぎ、電力の相互供給を行うことができるシステムを表します。

安全で長時間の飛行が可能な ドローン用高エネルギー密度電池の開発

Development of High Energy Density Lithium-ion Batteries for Drone

当社は、国立研究開発法人 新エネルギー・産業技術総合開発機構（以下NEDO）が実施するロボット・ドローンが活躍する省エネルギー社会の実現プロジェクト（Drones and Robots for Ecologically Sustainable Societies project（以下、DRESSプロジェクト））助成事業において、当社従来品に比べ、優れた精度を持つ高精度残量計とドローンの飛行距離に直結する高出力・高容量のドローン用インテリジェントリチウムイオン電池パックを開発しました。

1. DRESSプロジェクトについて

小口輸送の増加や積載率の低下などエネルギー使用の効率化が求められる物流分野や、効果的かつ効率的な点検を通じた長寿命化による資源のリデュースが喫緊の課題となるインフラ点検分野において、無人航空機やロボットの活用による省エネルギー化の実現が期待されています¹⁾。

本件は、物流、インフラ点検、災害対応等の分野で活用できる無人航空機及びロボットの開発を促進するとともに、社会実装するためのシステム構築及び飛行試験等を実施するNEDOのプロジェクトです。

2. 開発製品の概要

2.1 技術的なポイント

ドローン用蓄電池に求められる出力特性（セル連続放電5C以上）を維持したまま、エネルギー密度を向上させるために、主に充電電圧の高電圧化と内部抵抗低減を図りました。その結果、エネルギー密度（Wh/kg）を約20%増加させることに成功しました。

本成果はドローンの飛行時間に直結し、現行品と比較し、飛行時間を約20%増加させることに繋がりました。



図1 開発したインテリジェントリチウムイオン二次電池

2.2 ドローンへの搭載と飛行試験結果

2022年2月、本テーマにて開発されたインテリジェントリチウムイオン二次電池を、ドローン実機へ搭載し飛行試験を行いました。この飛行試験により、今回開発した電池が、当初の開発目標（飛行距離10km）を達成できていることを確認しました。



図2 搭載した電池と飛行試験の様子

トピックス 安全で長時間の飛行が可能なドローン用高エネルギー密度電池の開発

3. 今後の展開

ドローンの用途拡大が見込まれる中で、今後は社会実装に向けたドローンの社会順応性が求められると考えられます。当社では、これらの背景を踏まえて、ドローン市場から安全性・信頼性の高い電池が求められると考え、保護機能を持つインテリジェントリチウムイオン二次電池と専用充電器を製品化し、今日まで供給し続けてきました。

今回開発された技術により、安全性・信頼性は兼ね備えながら、従来の電池よりも『ドローンをより遠くまで飛ばす』、『ドローンでより重たいものを運ぶ』といった、ドローンを社会実装するために必要

なニーズに応えることができると考えています。今後も本技術の製品への適用を目指して、開発を進めていきます。

4. 謝辞

この成果は、NEDOの助成事業により得られたものです。

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https://www.nedo.go.jp/activities/ZZJP2_100080.html
(参照2022-10-07)

表1 開発品の仕様

項目	単位	現行品	開発品
単セル公称容量	Ah	9.8	11
単セル重量	g	172	167
単セルエネルギー密度	Wh/kg	211	255
単セル最大出力密度	W/kg	1250	1600
バック動作電圧範囲	V	36 ~ 50.4	36 ~ 53.4
バック公称電圧	V	44.4	46.3
バック公称容量	Wh (Ah)	435 (9.8)	510 (11.0)
バック連続最大出力	W	1400	1700
バック重量	kg	約2.6	約2.6
バックエネルギー密度	Wh/kg	167	200

※製品の仕様とは異なります。

ドローン/ロボット用 インテリジェントリチウムイオン二次電池の 展示会出展

Exhibiting Intelligent Lithium-ion Secondary Battery
for Drones and Robots

当社は、2022年6月21日～23日に幕張メッセで開催されたJapan Drone 2022（第7回）（主催：一般社団法人 日本USA産業振興協議会、通称JUIDA）及び2022年6月1日～4日にSORA 札幌コンベンションセンターで開催されたロボティクス・メカトロニクス講演会2022 in Sapporo（主催：一般社団法人 日本機械学会 ロボティクス・メカトロニクス部門）に出展しました。

1. Japan Drone 2022

Japan Drone 2022には、187社・団体が出展し、3日間で延べ17,021人の来場者が訪れました（主催者発表）¹⁾。

Japan Drone 2022は国内最大のドローンの展示商談会で、当社としては昨年に続き2度目の出展となります。古河電池ブランドとして昨年新たなスタートを切った「ドローン/ロボット用インテリジェントリチウムイオン二次電池パック、充電器」を展示し、安全・安心/取扱いが容易/高出力という特長を兼ね備え、国産という強みをアピールしました。

バッテリーメーカーで唯一の展示のため多くの来場者があり、たくさんのお客様に当社製品を見て頂くことができました。



図1 会場風景 (Japan Drone 2022)



図2 ドローン用インテリジェントリチウムイオン二次電池パック (Japan Drone 2022)



図3 ドローン用インテリジェントリチウムイオン二次電池パック 充電器 (Japan Drone 2022)

トピックス ドローン/ロボット用インテリジェントリチウムイオン二次電池の展示会出展

2. ロボティクス・メカトロニクス 講演会 2022 in Sapporo

ロボティクス・メカトロニクス 講演会 2022 in Sapporoには、企業の参加が30件（うちブース出展は24件）/論文の発表が1,209件（うちオーラルセッションが68件）ありました（主催者発表²⁾）。

ロボティクス・メカトロニクス 講演会は、ロボットに関する学術講演会であり、多くの企業の研究者や大学関係者が参加しています。今回、ロボットの技術開発関係者への認知度向上を狙って出展を行いました。

ロボットが利用される分野は大変広範囲に及び、日々新しい技術が生み出されています。ロボットの電動化において、開発の早い段階から当社バッテリーを検討いただけるよう、企業の研究開発者やロボット研究者に当社のロボット用バッテリーを訴求しました。

本出展により大学、研究機関、企業などの関係者に当社技術を広く知ってもらうことができました。

参考文献

- 1) Japan Drone, “Japan Drone 2022”, 一般社団法人日本UAS産業振興協議会 (JUIDA), 2022年7月11日
<https://ssl.japan-drone.com/> (参照 2022-10-07)
- 2) ロボティクス・メカトロニクス 講演会 2022 in Sapporo, 一般社団法人 日本機械学会 ロボティクス・メカトロニクス部門, 2022年10月2日
<https://robomech.org/2022/> (参照 2022-10-07)



図4 出展ブース
(ロボティクス・メカトロニクス 講演会 2022 in Sapporo)



図5 会場風景 (ロボティクス・メカトロニクス 講演会 2022 in Sapporo)

富山工場の紹介

TOYAMA FACTORY

1. はじめに

2021年4月1日付でマクセル(株)より積層ラミネート型リチウムイオン二次電池事業を承継し、当社いわき事業所 富山工場が誕生しました。

事業承継の目的

- ・リチウムイオン電池の技術展開・用途拡大の推進
- ・両社が培ってきた技術力・研究開発力の融合による競争力強化

富山工場はJR富山駅より約16km離れた富山市八尾町に立地しています。富山工場の敷地面積は11,493m²、晴れた日は立山連峰が一望できる環境です。

また、八尾町が誇る「おわら風の盆」は全国的にも有名な行事で、毎年9月に行われる祭りの時期は全国から集まった観客を魅了します。



富山工場 (2021年4月1日に承継)

2. 電池および電池パックの生産

富山工場では、主にドローンおよびロボット用のバッテリーパックに内蔵するセル(単電池)とバッテリーパックの生産を行っています。ドローンの用途を見ると農業、物流、点検などがあり、ロボットについても医療、介護、サービスなど様々な分野でバッテリーパックが使用されています。



(ドローン用)



(ロボット用)

リチウムイオン二次電池バッテリーパック

3. 安全第一の風土醸成

工場を円滑に操業するためには安全が何よりも優先されます。富山工場では、毎週全員で『労働災害KYT』、『交通安全KYT』を実施しています。

4. 将来事業への育成

リチウムイオン二次電池事業を当社の将来事業のひとつに育成するため、今後、設備増強の投資を行い、生産能力を現在の2倍に引き上げる計画です。

お客様からの要望にお応えするため、安全で高品質な新製品の上市を行うと共に、社会の強靱なインフラ構築に貢献できるようリチウム事業統括部全員で業務を遂行して参ります。

(リチウム事業統括部 業務企画部 麻原隆広)

FLHシリーズに新機種追加 (FLH1220SL)

The New Additional Model of FLH Series (FLH1220SL)

1. 背景

小形制御弁式鉛蓄電池はその利便性の良さから通信機器、非常用照明設備、コンピュータ及び防犯システム機器などのバックアップ用電源として幅広く採用頂いております。この市場のニーズには、高温雰囲気での使用や電池交換サイクル延長などがあり、長寿命化が望まれていました。当社ではこれらのニーズに応えるため、25℃、0.25C₂₀A放電において、期待寿命約13年を有するFLHシリーズ (2Ah～65Ah 6品種) を既に商品化しております。この度、更なる高温雰囲気下における長寿命化の市場ニーズがあり、FLHシリーズの新機種として35℃、0.25C₂₀A放電において、期待寿命約10年 (25℃換算期待寿命約20年相当) を有するFLH1220SL型蓄電池 (2Ah/20HR) を開発し、FLHシリーズに追加しましたので、その概要について紹介いたします。

2. 特長

- 長寿命
極板、電解液、電槽、蓋などの最適化を図ることにより、0.25C₂₀A放電において、35℃で従来品の約1.5倍となる10年の期待寿命を実現しました。その結果、蓄電池の交換回数が減少し、これまで以上にランニングコストの低減が可能となりました。
- 安全性
これまで同様、電槽樹脂に難燃樹脂 (UL94 V-0) を採用し、焼損防止など、安全性を高めております。極板の伸びによる電槽割れを防止するため、伸びスペースを十分に確保しております。
- 現行品との互換性
現行品のFLH1220Sと外形寸法、端子の互換性があります。



FLH1220SL型蓄電池外観

表1 FLH型蓄電池の概要

型式	公称電圧 (V)	定格容量 (Ah)	外形寸法 (mm)				質量 (約g)
			総高	箱高さ	幅	長さ	
FLH1220S	12	2	91	89 ± 2	25 ± 1	150 ± 1	850
FLH1220SL	12	2	91	89 ± 2	25 ± 1	150 ± 1	900
FLH1270	12	7	102	94 ± 2	65 ± 1	151 ± 1	2,800
FLH12150	12	15	169	167 ± 2	76 ± 2	181 ± 2	5,900
FLH12240L	12	24	127	125 ± 2	166 ± 2	175 ± 2	9,300
FLH12400	12	40	172	170 ± 2	165 ± 2	197 ± 2	16,000
FLH12650	12	65	177	175 ± 2	166 ± 2	350 ± 2	24,500

(産業機器生産統括部 産業機器技術部)

ストリングセンサI/Fユニットの紹介

Introduction of String Sensor Interface Unit

1. 背景

サイクルユース向けBMU (Battery Monitoring Unit) では、ストリングセンサと呼ばれる、組電池の総電圧・総電流を測定するセンサを使用しています。

ところが、従来使用していたセンサが廃版となり、後継センサの通信仕様が従来のRS232CからCAN (Controller area network) に変更となりました。

検討の結果、後継センサの採用は必須であり、CAN-LAN変換機能をもっている機器、SIU (String sensor interface unit) を開発することとなりました。

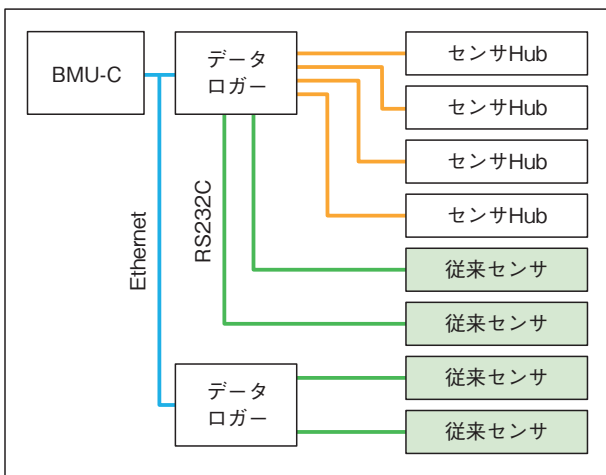


図1 従来のBMUシステム構成図

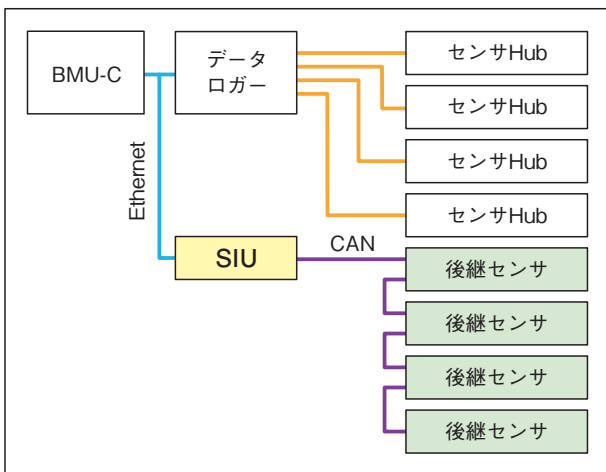


図2 SIUを採用したBMUシステム構成図

2. 特長

ストリングセンサ改版対応以外に以下の特長を有しています。

- ①最大12式のストリングセンサを接続可能
- ②ストリングセンサ計測データを100ms周期で収集
- ③各ストリングセンサ毎に最新10データをバッファリングすることで突発的な欠測に対応 (BMU-Cの計測周期は1～10s)
- ④最大2台のBMU-Cと接続可能
- ⑤OSSの積極的利活用による開発コスト低減

3. 諸元

表1 SIU諸元

項目・仕様			
環境条件	使用温度範囲	-20～70 (°C)	
	使用湿度範囲	20～80 (% RH)	
外形寸法	W 125 × H 136.5 × D 67.5 (mm)		
冷却方法	自然空冷		
取付方法	DIN レール		
接続I/F	Ethernet	RJ 45	
	入力電源端子	ネジ接続方式	
	ストリングセンサ接続端子	ネジ接続方式	
電気的特性	入力電圧	定格	DC 24 (V)
		許容範囲	DC 18～36 (V)
	出力電圧	DC 24 (V)	
	消費電力	最大 10 (W)	
機能仕様	プロトコル変換機能	UDP ↔ CAN	
	CAN bus CH数	2	
	接続可能台数	BMU-C MAX	2台
		ストリングセンサ MAX	6台 / CH
	計測周期	100 (ms)	

鉄道車両用アルカリ蓄電池 「AH5MC/AH8MC形」のご紹介

New Alkaline Storage Battery “AH5MC/AH8MC Type”
for Rolling Stock

「AH5MS形」、「AH8MS形」蓄電池について、この度「AH5MC形」、「AH8MC形」蓄電池へモデルチェンジしますのでご紹介いたします。

「AH5MS形」、「AH8MS形」蓄電池は2002年に発売され、鉄道車両の無線用、緊急用電源などに使用されています。後継となる「AH5MC形」、「AH8MC形」蓄電池は極板やセパレータといった電池の中核となる部品をベストセラーであるMTシリーズより採用し、高性能、省メンテナンス化を図っています。

1. 特長

① 高性能化

実容量が向上し、高率放電性能、低温放電性能も同等以上になります。

② 補水間隔の延長

MTシリーズと同様に水消費の少ない極板を使用しているため補水間隔が延長します。



③ 小形・軽量

「AH5MS形」、「AH8MS形」と同寸法で、同等の質量を維持しています。

2. 性能

環境温度25℃で「AH5MC形」、「AH8MC形」蓄電池は「AH5MS形」、「AH8MS形」蓄電池と比べ、 $0.2C_5A$ (5時間率)～ $2.0C_5A$ (0.5時間率)の範囲で放電容量が約15%向上し、放電電圧も同等以上です。0℃を下回る低温環境下でも放電容量、出力が向上しています。

3. 外観および主な仕様

摘要	前機種		後継機種	
形式	AH5MS	AH8MS	AH5MC	AH8MC
外観				
蓄電池容量 (Ah / 5 HR)	5	8	5	8
質量 (約 kg)	0.40	0.45	0.40	0.45
公称電圧 (V)	1.2			
寸法 (約 mm)	総高	177		
	幅	61		
	長さ	27		

FB 古河電池株式会社

<https://www.furukawadenchi.co.jp/>

本社・支店

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関西支社	〒541-0048	大阪府大阪市中央区瓦町4-2-14(京阪神瓦町ビル9F)	TEL.06-7634-7551
関西支社 四国支店	〒760-0023	香川県高松市寿町1-1-12(パシフィックシティ高松5F)	TEL.087-811-5980
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九州支社 中国支店	〒730-0051	広島県広島市中区大手町2-11-2(グランドビル大手町8F)	TEL.082-240-8001

事業所・工場

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いわき事業所	〒972-8312	福島県いわき市常磐下船尾町杭出作23-6	TEL.0246-43-0080
エフビー工場	〒321-2331	栃木県日光市針貝字茅場1066-22	TEL.0288-26-8061
富山工場	〒939-2376	富山県富山市八尾町福島5-88	TEL.076-455-3411

