https://doi.org/10.1595/205651317X696243

Johnson Matthey Technol. Rev., 2017, **61**, (4), 308–310

JOHNSON MATTHEY
TECHNOLOGY REVIEW

www.technology.matthey.com

Lithium Sulfur Batteries: Mechanisms, Modelling and Materials Conference

Recent advances in lithium-sulfur batteries research

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Lithium Sulfur: Mechanism, Modelling and Materials (Li-SM^3) was organised by Oxis Energy Ltd, UK, Imperial College London, UK, and the Joint Center for Energy Storage Research (JCESR), USA. It was held at the Institution of Engineering and Technology (IET), Savoy Place, London from 26th–27th April 2017. More than 150 researchers from around the world attended this event, 44 of them delivered talks and about 30 people presented their posters. A significant number of delegates from the private sector were present at this event including representatives from Airbus Defence and Space, France; Arkema, France; Daimler/Mercedes, Germany; LG Chem, South Korea; National Aeronautics and Space Administration (NASA) Jet Propulsion Laboratory, USA; Renault, France; Sony Corporation, Japan; Toyota, Japan and Umicore, Belgium.

Electrochemistry

Matthew Lacey (Uppsala University, Sweden) gave a talk about water-based electrodes and more particularly about the effects of polyethylene oxide (PEO) as an electrolyte additive or as a binder. His group prepared a carbon-sulfur material by melting carbon (Ketjenblack® EC-600JD) and sulfur under air at 150°C. For the water based electrode they added C65 and 4:1 PEO:polyvinylpyrrolidone (PVP). PEO swells and locally changes the solvent system to the benefit of polysulfide (PS) solubility and kinetics. PVP is soluble but forms an insoluble complex with Li_2S_x. Ketjenblack® is the most challenging carbon adhesion-wise but shows the best electrochemical performance. 1000 mAh g^{-1} was obtained for 50 cycles using electrodes with a S loading of 2 mg cm^{-2}. Their conclusion is that PEO:PVP is a suitable water-based binder for electrodes based on highly porous C black.

Diana Golodnitsky (Tel Aviv University, Israel) gave a talk about the strategies to impede PS shuttle by using barrier membranes between cathode and separator or by depositing a thin barrier over them. Toray and SGL carbon papers are the barrier membranes used which are also electrochemically active. Cells containing these barrier membranes delivered high S utilisation and excellent columbic efficiency, which suggests that the PS shuttle has been reduced. Electrodes or cathodes deposited with thin PEO-XC72 or lithium tin phosphorous sulfide (LSPS)-PEO based layers also showed this positive effect. However, the cells with barrier layers had capacity fading problems.

Markus Hagen (Fraunhofer Institute for Chemical Technology (ICT), Germany) studied electrolyte decomposition. This decomposition is monitored by fitting a pressure sensor and applying mass spectroscopy (MS) to a LiS cell. The pressure increases during discharge due to the release of gases such as carbon disulfide (CS_2) and nitrogen, produced by the decomposition of the electrolyte. N_2 gas is produced due to the decomposition of lithium nitrate ($LiNO_3$) in the electrolyte, an additive which is widely used to suppress the PS redox shuttle. In contrast, electrolytes without it did not show any N_2 gas evolution; therefore, the speaker concluded that $LiNO_3$ is not beneficial since it promotes decomposition of the electrolyte.

Characterisation Techniques

Alice Robba (French Alternative Energies and Atomic Energy Commission (CEA), Innovation Laboratory for the Technologies of New Energies and Nanomaterials (LITEN), France) gave an interesting talk about Li_2S particle size influence on the first charge working mechanism of lithium sulfide (Li_2S) based Li-ion batteries. In order to overcome the safety issue with the use of Li metal in a LiS system, her group used Li_2S as a positive electrode and silicon as a negative electrode. Replacing S_8 by Li_2S as the active material allows the use of a safer negative electrode. However, S_8 and Li_2S have different conductivity and solubility properties. The focus of the work presented was the effect of Li_2S particle size on the charge mechanism of Li_2S based Li-ion batteries. When Li_2S was prepared by electrodeposition (nano-Li_2S), two plateaus were visible for S_8 evolution (≈2.3 V and 2.45 V). However, when commercial Li_2S (micro-Li_2S) was used, a huge difference was seen in the electrochemical signature. In order to understand this difference between nano-Li_2S and micro-Li_2S, the respective batteries were analysed by *operando* X-ray absorption and emission spectroscopies coupled with *operando* X-ray diffraction. When nano-Li_2S was used, a smaller polarisation and a smaller activation barrier for Li_2S oxidation were observed. *Operando* studies showed a very nice PS evolution and a complete disappearance of Li_2S. However, when micro-Li_2S was used, a higher polarisation was seen upon charging and there was no PS detection while E>3.3 *vs.* Li/Li^+. There was consumption of Li_2S but never a total disappearance and there was an early appearance of S. Therefore, Robba's conclusion was that use of nano-Li_2S is better because the polarisation can be lowered and there is a smaller 'activation' barrier for Li_2S oxidation.

Céline Barchasz (CEA LITEN) gave an overview of different types of LiS systems. In a Li-ion/S system the cathode initially contains Li_2S and the anode is graphite, which has better cyclability since the parasitic reactions involving Li metal anode are prevented. In a catholyte cell, comprising a high concentration (7 M) of PS in electrolyte, a special current collector with vertical C fibres is used. However the specific energy is limited to only <180 Wh kg^{-1} due to the limited solubility of PS. For encapsulated S in a C micropore system a pseudo-solid-state reaction takes place, where the signature of the galvanostatic discharge curve is different from the conventional Li/S_8 cell (1). Barchasz also talked about the tomography studies done in her group. An *ex situ* X-ray phase contrast tomography technique (2) was used to characterise the evolution of the cathode morphology upon cycling and to track the loss of S from the conductive C network. A special cell was used for the *operando* X-ray absorption tomography which consists of an aluminium can that houses the Li-metal anode, a separator containing electrolyte and a C paper as the cathode. The solid S_8 was initially placed over the C paper, which disappears during discharge and redistributes throughout the cathode during the subsequent charging sequence. The images were two-dimensional (2D) cross sections of the cell and each constituent material was shown in a different grey-scale.

Due to their high stability with no risks of vaporisation and leakage, solid-state batteries are a promising alternative to liquid electrolytes. Jessica Lefevr (Technical University of Denmark) gave a talk about solid electrolytes for LiS systems based on lithium borohydride ($LiBH_4$), which is an interesting salt for LiS due to its light weight and its electrochemical stability. While the orthorhombic phase (*Pnma*) is stable at room temperature and has a low ionic conductivity (10^{-5} mS cm^{-1} at 30°C), the hexagonal phase ($P6_3/mmc$), which is stable above 110°C, has a much higher ionic conductivity (1 mS cm^{-1} at 120°C). Confinement of BH_4 in mesoporous silicon dioxide (SiO_2) allows fast ionic conductivity even at room temperature. *Operando* X-ray diffraction, tomography and Raman spectroscopy measurements were used to understand the electrochemistry and improve the batteries' performance.

Deyang Qu (University of Wisconsin Milwaukee, USA) reported an *in situ* characterisation technique in which electrolyte retrieved from the cell at different states of charge (SOC) were analysed using high performance liquid chromatography (HPLC) and MS. 4-(dimethylamino)benzoyl chloride (3) is added to the electrolyte prior to HPLC and MS measurements, in order to prevent the dissolved PS in them from undergoing disproportionation reactions. HPLC is used to separate different PS and MS is used to identify their speciation. Based on the *in situ* HPLC and MS results Qu has proposed reaction mechanisms for both discharge and charge processes. According to him, the two plateaus characteristic of the charge and discharge curves arise due to the equilibrium between different PS ions.

Applications

For aerospace applications, gravimetric energy density is more important than the volumetric energy density. NASA and Airbus are currently using LiS technology and both gave a talk about the importance of the research in this field. The challenge is still to have higher S loading ($m_{(S)}$ = 13 mg cm^{-2} ideally).

The Zephyr aircraft is a high-altitude long-endurance unmanned aerial vehicle that holds the world record for the longest flight duration of any aircraft: 14 days non-stop. It has been in development since 2004 and uses LiS batteries to store the energy captured by its solar panels and power the aircraft at night. Sarah Bassett (Airbus Defence and Space) gave a talk about the model 'Zephyr T' that is under development. This model will provide communications and internet connectivity to developing world countries without the need for installing expensive infrastructure on the ground. She insisted on the need for ultra-lightweight batteries and explained why LiS is perfect for this application.

Conclusion

LiS batteries are a most promising candidate for the next generation of electrical energy storage. They are made of cheap and abundant elements and they have a theoretical specific energy of *ca.* 2500 Wh kg^{-1} or 2800 Wh l^{-1}, which is much higher than that of Li-ion batteries (**Figure 1**). Yet their cycling stability shows limitations and scaled production technologies need to be established to meet cost targets.

The LiSM[3] was a very interesting conference where many issues with LiS were discussed. LiS is of interest where light weight is important such as in aircraft. The main current research activity is to control the PS *via* the development of new separators and new electrolyte formulations. Anode protection was often mentioned as a key challenge (often in the conclusions slide) but no one gave a talk about it. Very little was about the cathode preparation. Engineering is also crucial for the development of this technology.

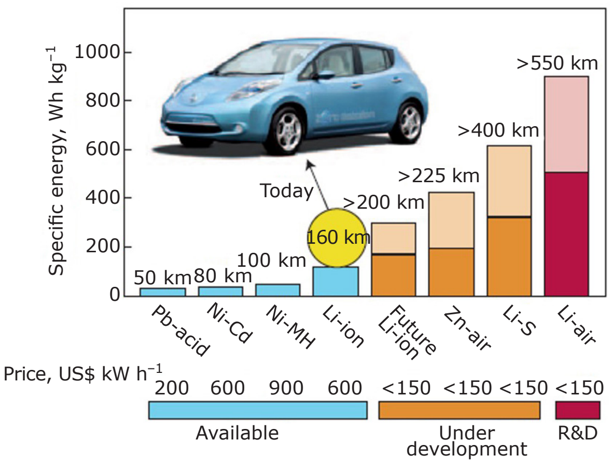

Fig. 1. Practical specific energies for some rechargeable batteries, along with estimated driving distances and pack prices (Reprinted by permission from Macmillan Publishers Ltd: *Nature Materials* (4), copyright (2012))

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The Reviewer

After a Masters in Materials Science at Université de Montréal, Canada, and a PhD in electrochemistry at Université de Picardie Jules Verne, France, working on the optimisation of the negative electrode based on silicon for Li-ion battery applications, Amina Touidjine went to the United Nations Environment Programme (UNEP) in Geneva, Switzerland, to do a traineeship on chemical waste management. She joined Johnson Matthey in October 2016 where she is currently working on LiS battery technology.

