Li-S Batteries

The Challenges, Chemistry, Materials and Future Perspectives

Editor
Rezan Demir-Cakan

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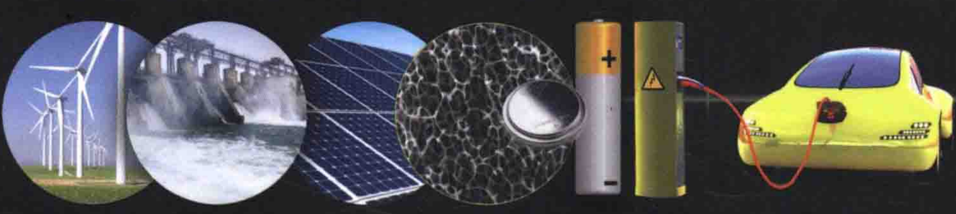
Lithium-sulfur (Li-S) batteries give us an alternative to the more prevalent lithium-ion (Li-ion) versions, and are known for their observed high energy densities. Systems using Li-S batteries are in early stages of development and commercialization however could potentially provide higher, safer levels of energy at significantly lower cost.

In this book the history, scientific background, challenges and future perspectives of the lithium-sulfur system are presented by experts in the field. Focus is on past and recent advances of each cell compartment responsible for the performance of the Li-S battery, and includes analysis of characterization tools, new designs and computational modeling. As a comprehensive review of current state-of-play, it is ideal for undergraduates, graduate students, researchers, physicists, chemists and materials scientists interested in energy storage, material science and electrochemistry.



World Scientific
www.worldscientific.com
Q0074 hc

ISBN 978-1-78634-249-2
9 781786 342492

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Published by

World Scientific Publishing Europe Ltd.
57 Shelton Street, Covent Garden, London WC2H 9HE
Head office: 5 Toh Tuck Link, Singapore 596224
USA office: 27 Warren Street, Suite 401-402, Hackensack, NJ 07601

Library of Congress Cataloging-in-Publication Data
Names: Demir-Cakan, Rezan, editor.
Title: Li-S batteries : the challenges, chemistry, materials and future perspectives / edited by Rezan Demir-Cakan (Gebze Technical University, Turkey).
Description: New Jersey : World Scientific, 2017.
Identifiers: LCCN 2016049015 | ISBN 9781786342492 (hc : alk. paper)
Subjects: LCSH: Lithium sulfur batteries. | Electric batteries. | Selenium cells. | Lithium cells. | Sodium compounds. | Electrochemistry.
Classification: LCC TK2945.L58 L5278 2017 | DDC 621.31/2424--dc23
LC record available at https://lccn.loc.gov/2016049015

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Desk Editors: Anthony Alexander/Mary Simpson

Typeset by Stallion Press
Email: enquiries@stallionpress.com

Printed in Singapore

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Preface

Energy storage is one of the main challenges of our century. Rapid societal and industrial developments dictate energy consumption, which is foreseen to grow by 56% by 2040. However, most energy sources are scarce and cause an obvious environmental impact on climate, with global warming potentially resulting in a temperature increase of 4–6°C by 2100. New storage technologies are therefore needed if more renewable energy sources are to be employed on the electrical grid; likewise, the electrification of the transport industry also requires more economical and higher energy storage systems. The need for energy storage requires a range of solutions, including batteries which are always a choice between energy, power, cost and life cycle capacity.

Lithium-ion (Li-ion) batteries have played a crucial role in the development of such energy storage technologies since their first launch by Sony in 1991. Although today lithium-ion batteries are used in most portable electronic devices and electrical vehicles (EVs), they are capable of delivering a limited gravimetric energy density, 100–200 Wh/kg, which cannot fulfill the goal of replacing combustion engines, while 1 kg of gasoline provides around 44,000 kJ/kg (~12,000 Wh/kg). Considering the differences between the fuel tank size of a combustion engine (around 60 L) and the weight of a battery pack of an electrical vehicle (could reach up to 500 kg), the running time of a car powered by batteries alone is still between 5 and 10 times shorter than with gasoline. Thus, if we want to achieve or even approach the goal of longer driving ranges using battery powered vehicles, we need to explore new batteries which are different from existing Li-ion technology and which offer further innovation in energy storage.

One of the possibilities is lithium–sulfur (Li–S) battery technology, the principle of which has been known for almost five decades, but which until now has failed to be commercialized. Theoretically, Li–S batteries can meet all the requirements of the intelligent vehicle battery system since they possess a high volumetric and gravimetric energy density. The advantage of Li–S batteries in terms of capacity and price in comparison with Li–ion technology is clear and must be carefully investigated in order to provide evidence for market adoption.

With extensive research in the past decade, the field is evolving rapidly, with successes in the laboratory in terms of long cycling stability and high rate performances. However, the commercial application of Li–S batteries is still facing barriers of the complexity of manufacturing thick electrodes, utilization of high sulfur, minimizing electrolyte/sulfur ratio or use of Li metal anode.

This first book provides the reader with an excellent review and analysis of the current rechargeable Li–S battery research. Starting with a brief history of Li–S batteries and underlining the challenges, this book introduces the past and recent improvements for each cell compartment; namely the sulfur cathode, the Li metal anode and the electrolyte which are equally responsible for the limited performance of modern Li–S cells. Moreover, new designs of Li–S batteries with a Li metal-free anode, catholyte concept as well as characterization tools for fundamental understanding and modeling of Li–S batteries have been addressed.

The authors of this book are strongly engaged in research for the progress of Li–S batteries and concentrate on the fundamental understandings of the cells while attacking the challenges found therein. As the editor, I would like to acknowledge all of the authors for their outstanding contributions to this book.

Rezan Demir-Cakan,
Istanbul, August 2016

About the Editor

Rezan Demir-Cakan graduated from Yildiz Technical University, Chemical Engineering Department and obtained her master degree from the same university. After spending one year in Cambridge/UK, she moved to Berlin/Germany to start her PhD work. She received her PhD at the Max Planck Institute of Colloids and Interfaces in the group of Professor Markus Antonietti in 2009. Thereafter, she joined Laboratoire de Réactivitéet Chimie des Solides in Amiens/France as a post-doctoral researcher working mainly on lithium–sulfur batteries under the supervision of Professor Jean-Marie Tarascon and Dr. Mathieu Morcrette.

Most of the studies of Dr. Demir-Cakan were devoted to energy related subjects. She received several prestigious awards including "the Japan Carbon Award for PhD Student" offered by the Japan Carbon Society in 2008, "Young Investigator Award" in 2012 from IMLB in South Korea, Science Academy's "Young Scientist Award" in 2015, "the L'Oréal-UNESCO For Women in Science" in 2016.

Since August 2012, Rezan Demir-Cakan has been working as an Associate Professor at the Gebze Technical University in Turkey running her own battery research group in Turkey which incorporates the application of materials chemistry towards sustainable chemical and energy technologies.

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Contents

Chapter 1

Introduction to Rechargeable Lithium–Sulfur Batteries

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1.1. Introduction and History of Lithium–Sulfur Batteries

1.1.1. Introduction

Rapid societal development and economic growth dictates the use of energy sources which are mostly based on fossil fuels. However, fossil fuels are neither continuous nor environmentally benign, leading to negative consequences in the environment caused by human energy needs. It is projected that the carbon dioxide (CO_2) emissions will cause global warming resulting in a 4–6°C temperature raise by 2100.[1] Likewise, fossil fuel depletion has been identified as a future challenge since it is foreseen that oil reserves will be terminated within the next 40 years while coal and natural gas may last at most for another 150 years.[2] Hence, researchers are responsible for realizing new ideas on how to exploit renewable energy resources such as wind, water or sun in the most efficient manner without causing any further ecological calamities. However, most renewable energy sources are intermittent; thus, energy storage is one of the essential components of the forthcoming energy supply system to make use of renewable energy sources with fluctuating power output.[3]

Technological demands for higher capacity and cost-effective energy storage options provide an incentive for exploration of alternative electrochemical energy storage systems. Technologies that can provide economic growth as well as CO_2 emission-free transportation by replacing the internal combustion engines with electric traction should be highlighted. Providing required flexible electricity generation and demand between daytime and night are highly important for grid operation.

New energy politics has led to the energy storage subject especially battery technologies becoming an important topic due to the development of mobile applications (i.e. electrical vehicles (EVs) or cellular phones). Over the past 25 years, Li-ion batteries (LIBs) played a crucial role in the development of such energy storage technologies. Today LIBs are used in 90% of rechargeable portable electronic devices. Although great improvements have been accomplished, and while active research for further developments continue, current Li-ion technologies provide a limited gravimetric energy density (100–150 Wh/kg for a full system) which cannot compete with either fulfilling the goal of replacing combustion engines or meeting large mass energy storage backup dictated by solar farms or wind turbine plants. For instance, EVs powered by LIBs result in an inadequate driving range (160–200 km) (Figure 1.1). Therefore, more drastic approaches are necessary to go beyond this limit and to accomplish "The Holy Grail" of a 500 km driving range at low cost, without the need for hybridization with conventional internal combustion engines.

Earth abundant sulfur is one alternative to reach such goals. Lithium–sulfur (Li–S) batteries offer around three fold increase in energy density compared with present Li-ion technologies. Li–S battery configuration operating at room temperature represents a valuable option as it can provide low equivalent weight, high capacity (1672 mAh/g), low cost (about $150 per ton) and environmentally benign factors. All these characteristics cannot be accomplished with current Li-ion technology.

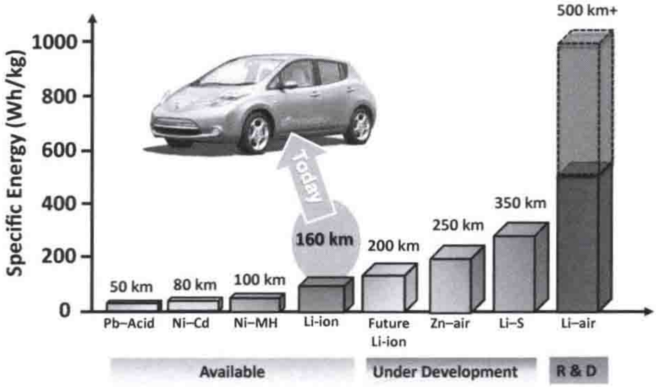

Figure 1.1 Practical, specific energies for some rechargeable batteries, along with estimated driving distances.

Source: Reproduced with permission from Ref. 1.

1.1.2. History of Li–S batteries

The history of Li–S chemistry dates back to early 1960s (even prior to the advent of rechargeable Li batteries).[4] With the patented work of Herbert and Ulam in 1962, sulfur was proposed as positive electrode and Li (or alloy of Li) as negative electrode in electric dry cells and storage batteries. Electrolyte was identified to be alkaline or alkaline-earth perchlorate, iodide, sulfocyanide, bromide, or chlorate dissolved in a primary, secondary or tertiary saturated aliphatic amine. Four years later, Herbert filed another patent,[5] which was a continuation in part of their previous patent,[4] with the electrolyte solution preferably consisting of a selected Li salt dissolved in a propyl, butyl or amyl amine. Preferably isopropyl amine was utilized as the solvent. In the same year, Rao[6] patented high-energy density metal–sulfur batteries. Electrolyte consisted of cations of light metals or ammonium ions and anions of tetrafluoroborate, tetra-chloroaluminate, perchlorate or chloride salts which were dissolved in organic solvents. The solvents were propylene carbonate, y-butyrolactone, NzN-dirnethylformamide or dimethylsulfoxide and the cells were cycled between the voltages 2.52 and 1.16 V vs. Li. Later on, in 1970, Moss and Nole,[7] represented a patent for the battery employing Li and sulfur electrodes with non-aqueous electrolyte. More information regarding the patent landscape of Li–S batteries, with analyzed and categorized total of 760 patent families, can be found in Ref. 8.

Although the concept of Li–S batteries is not new and was already intensively researched, the topic was inhibited because of missing exploitable results of the early studies.[9] Following the pioneering work published by Nazar *et al.*[10] in 2009, the topic was revisited and attracted drastic research interest in the field. The subsequent development of Li–S rechargeable batteries is enormous and has very high publication dynamic. The literature reports of research and review papers database from the Web of Science have shown results of over 2500 papers containing the phrase "lithium sulfur batteries" (Figure 1.2(a)), papers with more than 70,000 citations, showing the importance of this field of research (Figure 1.2(b)).

A detailed analysis of the literature studies for Li–S batteries and their topic distribution can be seen in Figure 1.3. Most of the works were devoted to the design of host matrices for sulfur impregnation and formulation of cathode composite electrode (detailed information can be found in Chapter 2). Besides all these attempts to control polysulfide dissolution with the help of different cathode architectures, recently many efforts have been performed to find suitable and effective adsorption/absorption of polysulfides within the composite cathode.

Apart from these confinement strategies, some reports have proven that those polysulfides are beneficial for the cell life. Xu *et al.*[11] have showed that the self-healing of Li–S batteries could be developed in the presence of polysulfide containing electrolyte by creating a dynamic equilibrium between the dissolution and precipitation of Li polysulfides at the electrode interfaces. Thus, research in the field of Li–S batteries is slightly moving from those sulfur confinements to the use of chemically synthesized dissolved polysulfides either in static condition or redox flow configuration.[12–14] Alternatively, those polysulfides are even employed as electrolyte additives for improved cycling performances.[11,15,16] More information regarding the use of polysulfide, either as electroactive component or electrolyte additives can be found in Chapter 3.

An important progress during this period was the identification of the electrolyte formulation suitable for the Li–S batteries. Many solvent/salt combinations were suggested including, sulfone based,[10,14] dimethyl sulfoxide,[17] dimethylformamide,[18] dimethoxyethane,[19] tetraethylene glycol dimethoxyethane,[20] ionic liquid,[21] mixture of those mentioned solvents at different ratios,[22] PEO polymer electrolytes,[23] or dioxolane[24] which is now