# Ceramic Materials for Energy Applications II

Ceramic Engineering and Science Proceedings

Volume 33, Issue 9, 2012

*Edited by*
*Kevin Fox*
*Yutai Katoh*
*Hua-Tay Lin*
*Ilias Belharouak*

*Volume Editors*
*Michael Halbig*
*Sanjay Mathur*

WILEY

The American Ceramic Society

# Ceramic Materials for Energy Applications II

*A Collection of Papers Presented at the 36th International Conference on Advanced Ceramics and Composites January 22–27, 2012 Daytona Beach, Florida*

Edited by
Kevin Fox
Yutai Katoh
Hua-Tay Lin
Ilias Belharouak

Volume Editors
Michael Halbig
Sanjay Mathur




WILEY

A John Wiley & Sons, Inc., Publication

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.



***Library of Congress Cataloging-in-Publication Data is available.***

ISBN: 978-1-118-20599-0
ISSN: 0196-6219

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

# Ceramic Materials for Energy Applications II

# Preface

This proceedings issue contains contributions from three energy related symposia and the European Union–USA Engineering Ceramics Summit that were part of the 36th International Conference on Advanced Ceramics and Composites (ICACC), in Daytona Beach, Florida, January 22-27, 2012. The symposia include Ceramics for Electric Energy Generation, Storage and Distribution; Advanced Ceramics and Composites for Nuclear and Fusion Applications; and Advanced Materials and Technologies for Rechargeable Batteries. These symposia and the Summit were sponsored by the ACerS Engineering Ceramics Division. The symposium on Advanced Ceramics and Composites for Nuclear and Fusion Applications was cosponsored by the ACerS Nuclear & Environmental Technology Division.

The editors wish to thank the authors and presenters for their contributions, the symposium organizers for their time and labor, and all the manuscript reviewers for their valuable comments and suggestions. Acknowledgment is also due for financial support from the Engineering Ceramics Division, the Nuclear & Environmental Technology Division, and The American Ceramic Society. The editors wish to thank Greg Geiger at ACerS for all his effort in assembling and publishing the proceedings.

Kevin Fox, Savannah River National Laboratory
Yutai Katoh, Oak Ridge National Laboratory
Hua-Tay Lin, Oak Ridge National Laboratory
Ilias Belharouak, Argonne National Laboratory

# Introduction

This issue of the Ceramic Engineering and Science Proceedings (CESP) is one of nine issues that has been published based on content presented during the 36th International Conference on Advanced Ceramics and Composites (ICACC), held January 22–27, 2012 in Daytona Beach, Florida. ICACC is the most prominent international meeting in the area of advanced structural, functional, and nanoscopic ceramics, composites, and other emerging ceramic materials and technologies. This prestigious conference has been organized by The American Ceramic Society's (ACerS) Engineering Ceramics Division (ECD) since 1977.

The 36th ICACC hosted more than 1,000 attendees from 38 countries and had over 780 presentations. The topics ranged from ceramic nanomaterials to structural reliability of ceramic components which demonstrated the linkage between materials science developments at the atomic level and macro level structural applications. Papers addressed material, model, and component development and investigated the interrelations between the processing, properties, and microstructure of ceramic materials.

The conference was organized into the following symposia and focused sessions:

| | |
|---|---|
| Symposium 1 | Mechanical Behavior and Performance of Ceramics and Composites |
| Symposium 2 | Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications |
| Symposium 3 | 9th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology |
| Symposium 4 | Armor Ceramics |
| Symposium 5 | Next Generation Bioceramics |

| | |
|---|---|
| Symposium 6 | International Symposium on Ceramics for Electric Energy Generation, Storage, and Distribution |
| Symposium 7 | 6th International Symposium on Nanostructured Materials and Nanocomposites: Development and Applications |
| Symposium 8 | 6th International Symposium on Advanced Processing & Manufacturing Technologies (APMT) for Structural & Multifunctional Materials and Systems |
| Symposium 9 | Porous Ceramics: Novel Developments and Applications |
| Symposium 10 | Thermal Management Materials and Technologies |
| Symposium 11 | Nanomaterials for Sensing Applications: From Fundamentals to Device Integration |
| Symposium 12 | Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases) |
| Symposium 13 | Advanced Ceramics and Composites for Nuclear Applications |
| Symposium 14 | Advanced Materials and Technologies for Rechargeable Batteries |
| Focused Session 1 | Geopolymers, Inorganic Polymers, Hybrid Organic-Inorganic Polymer Materials |
| Focused Session 2 | Computational Design, Modeling, Simulation and Characterization of Ceramics and Composites |
| Focused Session 3 | Next Generation Technologies for Innovative Surface Coatings |
| Focused Session 4 | Advanced (Ceramic) Materials and Processing for Photonics and Energy |
| Special Session | European Union – USA Engineering Ceramics Summit |
| Special Session | Global Young Investigators Forum |

The proceedings papers from this conference will appear in nine issues of the 2012 Ceramic Engineering & Science Proceedings (CESP); Volume 33, Issues 2-10, 2012 as listed below.

- Mechanical Properties and Performance of Engineering Ceramics and Composites VII, CESP Volume 33, Issue 2 (includes papers from Symposium 1)
- Advanced Ceramic Coatings and Materials for Extreme Environments II, CESP Volume 33, Issue 3 (includes papers from Symposia 2 and 12 and Focused Session 3)
- Advances in Solid Oxide Fuel Cells VIII, CESP Volume 33, Issue 4 (includes papers from Symposium 3)
- Advances in Ceramic Armor VIII, CESP Volume 33, Issue 5 (includes papers from Symposium 4)

# Contents

# ANALYTICAL TECHNIQUES FOR Li-S BATTERIES

Manu U.M. Patel, Rezan DEMIR CAKAN, Mathieu MORCRETTE, Jean-Marie TARASCON, Miran GABERSCEK, Robert DOMINKO

National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia
ALISTORE-ERI, 33 Rue Saint-Leu, 80039 Amiens, France
LRCS, Université de Picardie Jules Verne, 33 Rue Saint-Leu, 80039 Amiens, France

## ABSTRACT

Lithium sulfur rechargeable batteries are foreseen to be used in electric vehicles in the near future. To enable their placement to the market we need to improve their reliability and cycling performance. This can be done by selective change of the chemical environment in the Li-S battery, including electrolyte (solvents and salts), different combinations of cathode composites and different additives. With an aim to understand differences between different chemical environments, suitable and reliable analytical techniques that can effectively monitor the changes of interest, should be developed. In this work we present two newly developed analytical techniques which are capable to detect quantitative and qualitative differences between different polysulfide species in the electrolyte. More specifically, both proposed techniques can detect the polysulfides that have diffused away from the cathode composite. With a modified 4-electrode Swagelok cell we can quantitatively determine the amount of such polysulfides, while an in-situ UV-Vis cell gives us information about the composition of these polysulfides. Combining these techniques with a classical galvanostatic cycling method could lead to a better understanding, consequently, a faster tuning of Li-S battery properties.

## INTRODUCTION

The on-going and foreseen increased electrification of the transport sector, the "electromobility" revolution is one of the major driving forces for energy storage breakthroughs. Current rechargeable Li-ion batteries for electric vehicle (EV) are capable to deliver between 100 Wh/kg and 150 Wh/kg energy density, while typical consumption of a liter of gasoline produces 2500 Wh of useful work. So there is still a factor of 15 between the energy delivered by one liter of gasoline and 1 kg of battery (e.g. the autonomy of the car with similar weight that is driven by batteries is between 5-10 times shorter than with gasoline). Hence, if we want to achieve or even approach the goal of a 500 km driving range using battery powered vehicles, we need to explore new batteries that are different from the existing Li-ion technology and that offer a real step further in the energy storage[1].

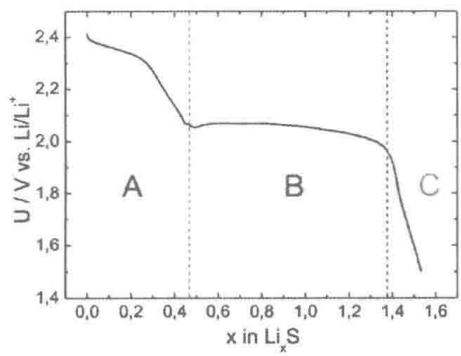
One of the possibilities is the lithium-sulfur battery technology, the principle of which has been known for several decades[2-4], however without real commercial breakthrough. In theory, Li-S battery can fulfill all the requirements of the intelligent vehicle battery system since it possesses a high volumetric (small size) and a high gravimetric (low weight) energy density. In addition, it can be produced as a flexible, environmental friendly and cost effective cell and in theory offers a safe and a reliable operation.

Elemental sulfur as a positive electrode material in combination with lithium metal as a negative electrode material offers an attractive high-energy rechargeable cell. More specifically, assuming the whole reaction to $Li_2S$, the average redx voltage and the theoretical energy values of such a cell are 2.1V and 2500W/kg (or 2800Wh/l), respectively.

One of the main reasons that the Li-S system has still not reached a wide commercial availability is the not-yet-optimized function of the cathode. Over the last two decades different directions towards improved cathode architecture and chemical compositions have been proposed. One of the strategies has been a special cell configuration where all polysulfides are solubilized – the so called catholyte cells[2]. Another strategy is the use of either a mixture of sulfur and suitable matrix to

improve the electronic conductivity or embedment of sulfur into a polymer matrix (for instance polyaniline).

The first discharge of Li-S battery and potential reactions are shown in the Figure 1. Along the high voltage plateau (2,3 – 2,4V), reduction of cyclic sulfur to the long chain polysulfides (e.g. $Li_2S_8$ and $Li_2S_6$) occurs. Further reduction progressively leads to the low voltage plateau at 2,1V and to the formation of $Li_2S_4$. The plateau at 2.1V corresponds to a 1 electron reaction per sulfur atom and to the reduction to $Li_2S_2$. Reduction of lithium disulfide to lithium monosulfide occurs in region C (Figure 1) and leads to a very fast voltage decay due to insolubility of $Li_2S$ in most of electrolytes (due to the formation of insoluble blocking layer of $Li_2S$).



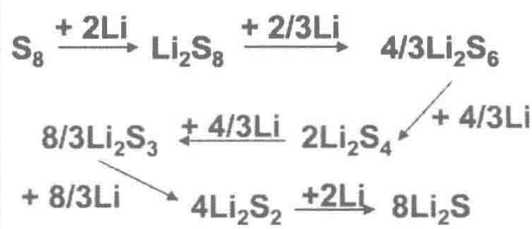




Figure 1: First discharge curve for Li-S battery and suggested reaction scheme divided into three typical regions of sulfur reduction

Regarding the chemical environment, most of polysulfides (except $Li_2S$) are soluble in electrolytes and can diffuse away from the cathode composite, thus leading to active material loss and self-discharge. Once dissolved in the electrolyte, they can move to the negative electrode (metallic lithium) and react with it, leading to a shuttle mechanism that decreases charge efficiency and leads to the formation of blocking $Li_2S$ layer on the surface of lithium. With an aim to minimize the diffusion of soluble polysulfides from the cathode composite, different strategies have been proposed. The most promising direction of cathode composite architecture is the use of mesoporous matrix with a tiny layer of sulfur dispersed on the surface of pores. Pores in this case can act as mini chambers and at least in the formation cycles the diffusion of polysulfides is reduced and postponed to later stages of Li-S battery cycling. Nevertheless, mesoporous substrate represents a high surface area substrate for sulfur impregnation. The other possible solutions how to prevent diffusion of reduced states of sulfur are the use of different electrolyte combinations or the use of different additives in the electrolyte. The common point in all of the literature reports on that matter is the lack of detailed understanding about how different changes in the chemical environment (changes in the composition and architecture of cathode composite, changes in the electrolyte formulation, etc.) affect the electrochemical performance (utilization of sulfur and discharge/charge efficiency).

Whereas most of the published works focus predminantly on the cycling behavior, efficient progress is only possible if one deeply understands the correlation between the morphological and compositional changes on one side and the electrochemistry on the other. In our recent work[6], we have proposed the use of a modified 4-electrode Swagelok cell that can be used as a reliable analytical cell for the quantitative determination of polysulfides that have diffused away from cathode composite.

## EXPERIMENTAL

Cathode composites (carbon + sulfur in 1:1 weight ratio) were prepared by infiltration of sulfur onto the carbon black (Printex XE2) surface or into the mesoporous carbon. Cathode composites were mixed with 7 wt.% of PVdF (Aldrich) and additional 8 wt.% of Printex XE2 carbon black and casted on an aluminum current collector. Electrodes with diameter 12 mm containing 2-3 mg of sulfur were pressed and dried at 90°C overnight before use.

Electrolyte solutions used in this study were 1M LiTFSI (lithium bis(trifluirimethanesulfonyl)imide) containing tetra methylene sulphone (TMS) or ethyl methyl sulphone (EMS). Electrolyte solutions with chemically synthesized polysulfides were prepared by mixing adequate amount of polysulfide powder with electrolyte solutions. Polysulfide powder was prepared by reaction of stoichiometric amounts of sulfur and lithium in ethylene glycol diethyl ether at 150°C. The denotation of polysulfides is based on the stoichiometric composition and it is not necessary to reflect exact electronic state of sulfur. Chemically synthesized polysulfides, which were used for standardization, were dissolved in electrolyte to form known concentration in the electrolyte. 1mM, 5mM, 10mM, 25mM and 50mM solutions were prepared by dissolving following $Li_2S_n$ polysulfides (n=2,…,8).

The principle of 4 electrode Swagelok cell operation was published in our previous work[6]. The cell compromises two electrochemical cells in one, where one serves as a typical battery cell using two electrode cells (a working electrode with casted cathode composite and lithium as counter and reference electrodes). The second one is built perpendicularly to the battery sandwich and placed in between two separators, where nickel or stainless steel wires can be used as a working electrode and platinum wire as a counter and as a reference electrode. Operation of two cells is in the sequence, i.e. galvanostatic discharging with a C/20 rate for 2h of Li-S battery followed by a cyclovoltametric measurement using perpendicular electrodes in the potential region between 2.5 and 1 V with a scan rate of 2 $mVs^{-1}$ and continued with galavanostatic discharging. Measurements with different concentration of $Li_2S_8$ were performed in the same way as in ordinary Li-S battery cells, except that the cathode composite did not contain any sulfur.

The cell designed for the in-situ UV-Vis measurements is based on the coffee bag cell with a sealed quartz window on one side. The cell was mounted in the UV-Vis spectrophotometer and measured simultaneously in the reflection mode during galvanostatic cycling. Charge/discharge rate was C/20 and UV-Vis spectra were measured every 15 min. Battery was built by using pressed electrode composite on the aluminum substrate, separator and ring based lithium electrode as a counter electrode. Design of ring based electrode is necessary for the detection of polysufides in the separator in the reflection mode. Electrolyte solutions with a known concentration of different polysulfides – $Li_2S_n$ (n=2-8) were used for the calibration. UV-Vis spectra were measured in the cell designed for the electrochemical measurements (cell with a quartz window), except that only a separator with a wiped 1 mL of electrolyte solution containing different polysulfides was used.

## RESULTS AND DISCUSSION

The applicability of modified 4-electrode Swagelok cell was tested first in the configuration of a blank cell (cathode composite without sulfur). The corresponding cyclic voltammogram (Fig. 2a) shows a cathodic peak at a potential bellow 0.8 V versus platinum reference electrode. Once polysulfide solution of $Li_2S_8$ and electrolyte are used, another cathodic peak appears in the potential range between 2.25V and 1.5V (Figure 2a). The height of this cathodic peak is in correlation with the concentration of $Li_2S_8$ in the electrolyte. As we showed in our previous work, the correlation is linear and in some standardized conditions it can be used for comparison of different systems. However, it cannot be used for the determination of overall quantity of polysulfides that has diffused away from the cathode composite. The cumulative (integrated) charge that corresponds to the area in the selected potential range corresponds to the reduction of only approximately 2% of polysulfides added to the

electrolyte solution. Using the blank cell, we further observed that most of the polysulfides were reduced in the first scan, as shown in Figure 2b. The integrated charge in higher cycles corresponds to less than 5 % of the charge obtained from the first scan and it can be correlated to the polysulphides diffused from the rest of separator area. Typically we found a yellow to white precipitate in the separator which was in the vicinity of the working electrode (nickel or stainless steel wire), while the wire was not covered by any visible layer.

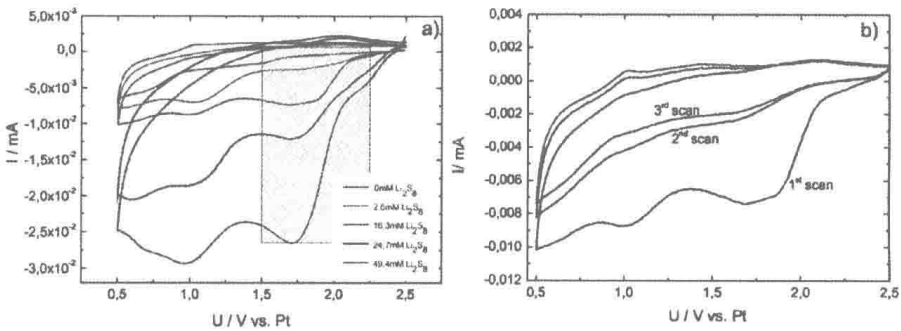



Figure 2: a) cyclic volmmograms for electrolytes in the blank battery configuration with different standards (different concentration of dissolved $Li_2S_8$) and b) consecutive three cyclic volmmogram scans for the same blank battery with standard electrolyte containing 24.7 mM $Li_2S_8$.

Application of the modified 4-electrode cell in combination with a real battery (cathode composite containing sulfur) confirmed our expectation that we can detect polysulfides during the battery operation. Cyclic volammograms were collected after every 2 hours of galvanostatical discharging in the first cycle (Figure 3).

The measured cyclic voltammograms showed evolution of the soluble polysulfides which can be scaled with the intensity of cathodic peak at approximately 1.8 V. Note that a remarkable change is only observed in the cathodic peak at 1.8 V while the second cathodic peak (at 1.3 V) remained relatively constant; the origin of the latter is not clear at the present state of the work. The maximum solubility has been detected after a change in the composition for $\Delta x=0.2$. During the next two steps it remained relatively high. Here we need to consider that we might need to reduce shorter polysulfides ($Li_2S_6$ and/or $Li_2S_4$) chains which can consume less charge that $Li_2S_8$ available in the beginning of the discharge curve. Later during the discharge, the amount of charge used for the reduction of soluble polysulfides becomes smaller which may be ascribed to a smaller diffusivity of shorter chain polysulfides and a smaller quantity of charge required for the reduction of short chain polysulfides (i.e for the reduction of $Li_2S_3$ and $Li_2S_2$).