# Using *In Situ* Liquid Single Photon Ionization Mass Spectrometry (SPI-MS) to Probe Lithium Polysulfide Electrolyte in Motion

Aala Al Hasan[1],Jiachao Yu[2], Juan Yao[2], Vijayakumar Murugesan[2], Manjula Nandasiri[2], and Xiao-Ying Yu[2]*

[1] University of Houston, 4800 Calhoun Rd, Houston, Texas, 77004

[2] Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99352

Pacific Northwest NATIONAL LABORATORY

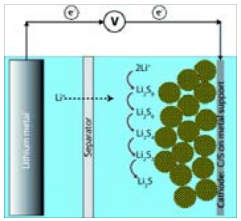
*Proudly Operated by Battelle Since 1965*

## Introduction

The solid-liquid (s-l) interface is the most common interface encountered in electrochemical systems. The s-l interface has wide applications in energy storage, catalysis, and material sciences. *In situ* studies of chemical reactions taking place on the s-l interface can further our understanding of electron transfer and link to real-world device functions under challenging conditions. Direct probing of the solid electrode and liquid electrolyte interface has been realized using a vacuum compatible electrochemical microfluidic reactor, system for analysis at the liquid vacuum interface (SALVI) with time-of-flight secondary ion mass spectrometry (ToF-SIMS)[1,2]. In this work, we extend such capability to the Advanced Light Source (ALS) vacuum ultraviolet (VUV) single photon ionization mass spectrometry (SPI-MS)[3].

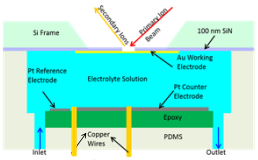
## Background

From cell phones to smart watches, the number of electronic devices have been slowly growing requiring the need of small yet powerful batteries. Due to lithium-ion batteries coming to non-existence and lacking improvement, lithium-sulfur batteries are attracting more attention in energy storage materials.

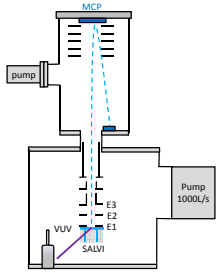



**Lithium sulfur batteries[4]**

## Experimental Setup




Schematic of the electrochemical version of the SALVI




Liquid SPI-MS schematic using SALVI

**Electrochemical SALVI**

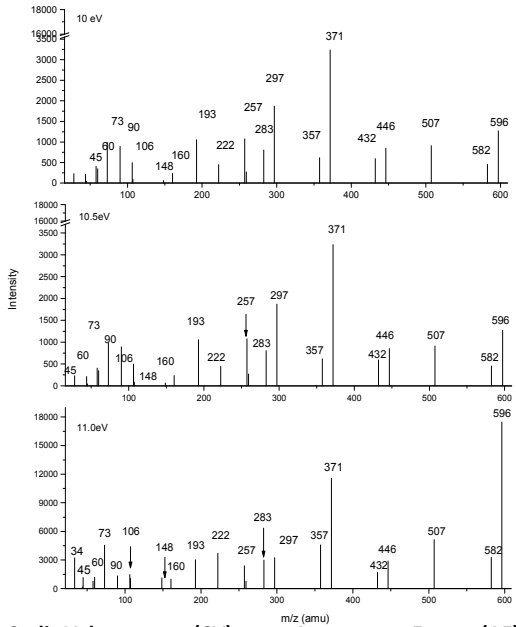
- This electrochemical (EC) SALVI is a three electrode system which includes gold (Au) working electrode (WE) and platinum reference and counter electrodes.
- The EC SALVI has been successfully used in ToF-SIMS.
- The EC SALVI was adapted to the electrode in the SPI-MS.

**Liquid SPI-MS paired with SALVI is a soft ionization technique**

- 2 µm holes drilled through the Au WE allow analysis of the electrolyte and volatile species during charge and discharge in SPI-MS.

## Results & Discussion

**Mass Spectra ($Li_2S_6$)**




**Cyclic Voltammetry (CV)** **Appearance Energy (AE)**

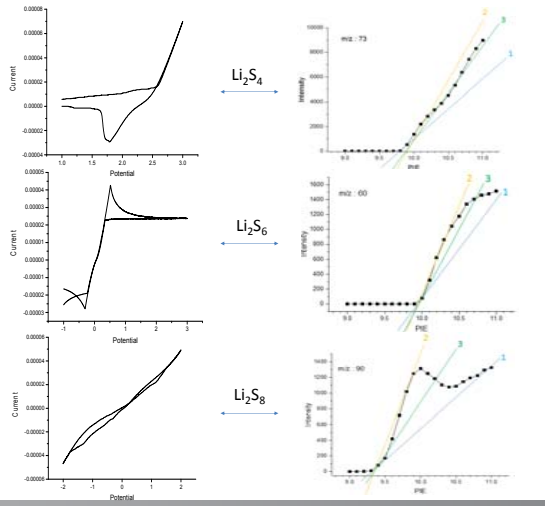



**Table 1: Possible Peak Identification and AE Values**

| m/z obs. | m/z calc. | Formula | Name | AE Value | Reference |
|---|---|---|---|---|---|
| 60 | 59.94 | $Li_4S^+$ | N/A | 9.9±0.1 | This work |
| 73 | 73 | $C_3H_5O_2^+$ | Propanoate | 9.9±0.1 | NIST webbook[5] |
| 90 | 90.12 | $C_4H_{10}O_2$ | Dimethoxyethane | 9.3±0.1 | This work |

- Mass spectra depict various peaks of interest present in the electrolyte as a result of electron transfer.
- CV is a potential dynamic electrochemical technique that helps identify the concentration of the elelctrolyte and kinetics happening at the solid-liquid interface.
- AE values were estimated using the experimental observations.

## Conclusions

- E-cell SALVI was successfully integrated with the ALS 9.0.2 beam line.
- We enabled operando electrochemistry study using SPI-MS and SALVI.
- Electron transfer of LixSy electrolytes were investigated.
- We were able to identify unique peaks of interest to the electron transfer of the $Li_xS_y$ electrolytes according to the SPI-MS mass spectra.
- Able to estimate AEs for compounds of interest using this approach.

## References

1. Liu, B., Yu, X. Y., Zhu, Z., Hua, X., Yang, L., & Wang, Z. (2014), *14*(5), 855-859.
2. Yu, J., Zhou, Y., Hua, X., Liu, S., Zhu, Z., & Yu, X. Y. (2016). DOI: 10.1039/C6CC02893D.
3. Kaiser, Ralf I., *Faraday Discuss.*, 2010, **147**, 429-478
4. Schuster, J., He, G., Mandlmeier, B., Yim, T., Lee, K. T., Bein, T. and Nazar, L. F. (2012),51:35913595, doi:10.1002/anie.201107817
5. NIST Webbook (2016). http://webbook.nist.gov/chemistry/

## Acknowledgments

- LaVon Conlin, Rachel Komorek, Shannon Fasings, Dr. Zihua Zhu, and the entire ToF-SIMS team at PNNL.
- MS3 LDRD, TIC LDRD, and the DOE BER EMSL user facility.
- LBNL collaborators Drs. Musa Ahmed , Oleg Kostko, Bo Xu, and Tyler Troy.
- Funding : DOE, STAR, and NSF

## Contact Information

Dr. Xiao-Ying Yu, xiaoying.yu@pnnl.gov
Tel: 509-372-4524

PNNL-SA-120045

### About Pacific Northwest National Laboratory

U.S. DEPARTMENT OF ENERGY

The Pacific Northwest National Laboratory, located in southeastern Washington State, is a U.S. Department of Energy Office of Science laboratory that solves complex problems in energy, national security, and the environment, and advances scientific frontiers in the chemical, biological, materials, environmental, and computational sciences. The Laboratory employs nearly 5,000 staff members, has an annual budget in excess of $1 billion, and has been managed by Ohio-based Battelle since 1965.

NSF STAR CAL POLY SAN LUIS OBISPO CSU www.pnnl.gov