BNL-107588-2015-JA

Quantitative Chromatographic Determination of Dissolved Elemental Sulfur in the Non-aqueous Electrolyte for Lithium-Sulfur Batteries

Dong Zheng[1], Xuran Zhang[2], Chao Li[1], Meaghan E. McKinnon[1], Rachel G. Sadok[1], Deyu Qu[2], Xiqian Yu[3], Hung-Sui Lee[3], Xiao-Qing Yang[3], Deyang Qu[*1]

[1] Department of Chemistry, University of Massachusetts Boston, Boston, MA 02125, USA

[2] Department of Chemistry, School of Science, Wuhan University of Technology, Wuhan 430070, Hubei, P.R. China

[3] Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA

Abstract

A fast and reliable analytical method is reported for the quantitative determination of dissolved elemental sulfur in non-aqueous electrolytes for Li-S batteries. By using high performance liquid chromatography with a UV detector, the solubility of S in 12 different pure solvents and in 22 different electrolytes was determined. It was found that the solubility of elemental sulfur is dependent on the Lewis basicity, the polarity of solvents and the salt concentration in the electrolytes. In addition, the S content in the electrolyte recovered from a discharged Li-S battery was successfully determined by the proposed HPLC/UV method. Thus, the feasibility of the method to the online analysis for a Li-S battery is demonstrated. Interestingly, the S was found super-saturated in the electrolyte recovered from a discharged Li-S cell.

Keywords: quantitative elemental sulfur analysis; Li-S batteries; HPLC-MS; Lewis basicity; non-aqueous electrolyte

[*] Corresponding Author: Tel: +1 617 287 6035; Fax: +1 617 287 6185: e-mail: deyang.qu@umb.edu

1, Introduction

As a promising candidate to meet the high energy density demand for next generation rechargeable Li batteries, the rechargeable Li-S battery has drawn a lot of attention in recent years [1]. Detailed mechanisms for the redox reactions in a non-aqueous Li-S battery are still not well understood. However, it is widely accepted that the polysulfide anions play an important role, and that elemental sulfur is the active material and the product of charge process in a Li-S battery. Therefore, quantitative analysis of polysulfide anions and elemental sulfur in the organic electrolyte of a Li-S battery is of great importance for understanding the mechanism of redox reaction and optimizing battery performance. Polysulfide anions were detected by various analytical methods, such as UV-Vis spectroscopy [2,3], electrochemical methods [4], Raman spectroscopy [5], and X-ray absorption near edge spectroscopy (XANES) [6]. Interestingly, no research work on quantitative analysis of elemental sulfur in Li-S battery has been reported, although the elemental sulfur is involved in the charge/discharge of Li-S batteries. Presumably, it results from the assumption that solid S_8 participates in the interfacial reaction before it is reduced to soluble polysulfides. The mechanism for the redox reaction of S differs in different non-aqueous electrolytes. Such difference was attributed to the formation of various kinds of dissolved polysulfide ions [7]. However, there is no evidence to preclude dissolved S from participating in the redox reaction. Reliable quantification of dissolved S in the electrolyte is a necessity to investigate the role of soluble S species in the S redox reaction. It is worth to emphasizing that UV-Vis can be used to analysis elemental sulfur in pure organic solvents, however S is hard to be identified in the solution containing polysulfide ions due to the shape of UV-Vis spectra which are too broad and overlaid on each other [8, 9]. Therefore, S can only be quantitatively analysized by UV-Vis detector after being effectively separated from the polysulfide ions.

Although the quantification of dissolved S in the electrolyte for a Li-S battery is seldom reported, high performance liquid chromatography (HPLC) is widely used to determine S in the area of environmental science and coal technology. Harmers et al. reported the quantitative analysis of elemental S on oxidized sulfide minerals through liquid extraction and HPLC analysis [10]; Yperman et al. investigated S in biodesulphurized low rank coals by a similar HPLC method with different extraction procedures [11]. Due to its non-polar nature and strong UV absorbance,

S can be effectively separated from organic solvents and inorganic salts with a reverse-phase HPLC column and detected by a UV detector. Indeed, it was reported that S was separated by a RP-HPLC column [8, 9], there was evidence that the S co-eluted with polysulfide ions. In addition, most of the HPLC studies were focused on the separation of polysulfide ions, the quantification of S was not reported to the best our knowledge.

In our recent work [12], HPLC separation was observed for elemental sulfur in electrolyte of a Li-S battery. A systematic quantification of elemental S in the common organic solvents and electrolytes of interest to Li-S batteries is reported in this paper.

2, Experimental Details

2.1, Chemicals

Elemental sulfur (Fisher Scientific), lithium metal, sodium sulfide, acetone, acetonitrile (AN), dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), ethanol, gamma-butyrolactone (GBL), pyridine(PY), hexane, diethylene glycol dimethyl ether (GDME), N-butyl-N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (BMPTFSi), HPLC grade methanol (from Sigma Aldrich), and propylene carbonate (PC), dimethoxyethane (DME), lithium bis(trifluoromethane) sulfonimide (LiTFSi), lithium perchlorate ($LiClO_4$), lithium tetrafluoroborate ($LiBF_4$), lithium trifluoromethanesulfonate ($LiCF_3SO_3$), tetraethylammonium tetrafluoroborate($TEABF_4$) (from FERRO) were purchased with the most adequate grades and used without further treatment.

2.2, Sample preparation

The standard solutions of elemental S: The stock solution was made by dissolving 0.1209g elemental sulfur in 100.00 ml DME, the molar concentration was 4.722mM. The standard solutions of 1.889mM, 0.378mM, 0.0756mM, and 0.0151mM were then made by diluting the stock solution. It is worth to emphasizing that unlike polysulfide ions which distribution change with the concentration due to the equilibrium and disproportionation, elemental S is stable in DME, therefore a series of S standard solutions can be made for a reliable calibration curve.

The elemental S saturated solutions: 0.2 g of elemental S was added into a sample vial with 5ml of target electrolyte (or organic solvent); after being sealed and shaken for 96 hours, the solution

was allowed to rest for 72 hours; the clear solution at top was used for the analysis. 34 sample solutions were made as tabulated in Table 1.

Solutions with various amounts of S and polysulfide combinations were prepared by adding different amount of Na_2S into a 0.601M elemental sulfur DME solution. The formula Na_2S concentrations were 1.884mM, 3.768mM, and 7.536mM.

Approximately 10 ml electrolyte was recovered from a 3-electrode electrochemical cell after the S cathode was fully discharged. The cathode was made of elemental sulfur loaded porous carbon (60 wt% elemental sulfur); metallic Li was used as both reference and counter electrode. 1.0M LiTFSi/DME solution was used as electrolyte. The cell was discharged at constant current of 1.6 mAg^{-1} of S from 3.37 V (OCP vs. Li) to 1.75 V.

Table 1 The list of the S saturated solutions

Sample No.	Solvent	Salt	Salt concentration
1	Acetone	N/A	N/A
2	Ethanol	N/A	N/A
3	Hexane	N/A	N/A
4	AN	N/A	N/A
5	PY	N/A	N/A
6	DMF	N/A	N/A
7	PC	N/A	N/A
8	GBL	N/A	N/A
9	DGME	N/A	N/A
10	DME	N/A	N/A
11	DMSO	N/A	N/A
12	BMPTFSi	N/A	N/A
13	AN	LiTSFi	0.1M
14	PY	LiTSFi	0.1M
15	DMF	LiTSFi	0.1M
16	PC	LiTSFi	0.1M
17	GBL	LiTSFi	0.1M
18	DGME	LiTSFi	0.1M
19	DME	LiTSFi	0.1M
20	DMSO	LiTSFi	0.1M
21	BMPTFSi	LiTSFi	0.1M
22	AN	LiTFSi	1.0M
23	PY	LiTFSi	1.0M
24	DMF	LiTFSi	1.0M
25	PC	LiTFSi	1.0M

26	GBL	LiTFSi	1.0M
27	DGME	LiTFSi	1.0M
28	DME	LiTFSi	1.0M
29	DMSO	LiTFSi	1.0M
30	BMPTFSi	LiTFSi	1.0M
31	DMSO	$LiClO_4$	1.0M
32	DMSO	$LiBF_4$	1.0M
33	DMSO	$LiCF_3SO_3$	1.0M
34	DMSO	$TEABF_4$	1.0M

All of the above samples were prepared or obtained under Argon filled glove box (both water and oxygen are less than 5ppm). All samples except the standard solutions were diluted to 0.0151 mM and 1.889 mM of S by diluting with corresponding solvent in order to reach optimal sensitivity of the HPLC measurement. All solutions were sealed in 1.5 ml HPLC sample vials before being taken out of glove box.

2.3, Instruments

An Agilent 1100 isocratic pump (from Agilent) with a 7725i Rheodyne manual injector was used to deliver methanol (purged by dry nitrogen gas) through an HPLC column at flow rate 0.75mL/min. The injection volume was 20 µL, the diode array detector (DAD) operated at 210 to 300nm range, and total HPLC running time of 15 min. The HPLC/UV chromatograms were recorded by Masslynx 4.0. Most of HPLC results were obtained by using a Luna HPLC column (from Phenomenex, C_{18}, 4.6*250mm, 5um). As the comparison of retention for elemental sulfur on different HPLC columns, three other reversed-phase HPLC columns were used: Symmetry C_{18} (from Waters, C_{18}, 4.6*250mm, 3.5um) ; Xterra MS (from Waters, C_8, 4.6*250mm, 5um); Zorbax 300SB (from Agilent, C_8, 4.6*250mm, 5um).

HPLC/(-)ESI-MS was only used to exclude the possibility of polysulfides for the minor peaks at arount 3 and 6 min. A Quattro LC mass spectrometer (triple quadrupole, from Micromass-Waters) with ESI source was operated under positive mode or negative mode. The typical source parameters were set as following: Capillary 2.50kV, Cone 20V, Extractor 0V, RF lens 0.1V, Source temperature 100°C, Desolvation temperature 250°C, nitrogen gas flow is 90LNebuliser and 600L/hr for Desolvation. For HPLC ESI/MS run, the m/z ratio from 20 to 600 was recorded

All of the electrochemical measurements were carried out using an Arbin MSTAT (Arbin instruments) controlled by MITS PRO software.

3, Results and Discussion

3.1, Analysis of Standard

Lauren et al. demonstrated that elemental S can be effectively analyzed with a reversed-phase C_{18} HPLC [13]. By comparing different reversed phase HPLC columns under the same mobile phase condition, it was found that the C_8 column didn't have sufficient retention time for elemental sulfur [13]. Similar chromatographic separation was observed in this study shown in Figure 1. In two C_8 columns, the elemental sulfur had the retention time of 4.2 min (for Zorbax 300SB) and 4.8 min (for Xterra MS). DME was eluted very close to the elemental S in both C_8 columns forming a shoulder peak superimposed on the chromatographic peak of elemental sulfur. In the two C_{18} columns, however, the elemental sulfur not only had longer retention times (11.1 min for Luna and 12.9 min for Symmetry C_{18}), but also had a baseline separation from DME solvent. Luna C_{18} column was used for the quantitative analysis of S in this study. The peaks observed at the elution time of 3-6 min were proven not to be related to polysulfide ions by an separate HPLC/(-)ESI-MS.

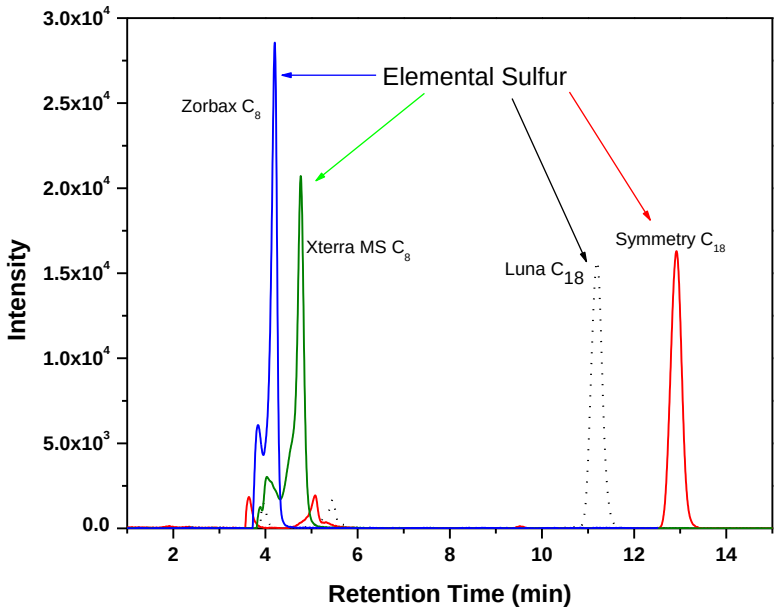

Figure 1, The chromatograms of elemental sulfur on different reversed phase HPLC columns.

Figure 2 shows the chromatograms of elemental S standards with different concentrations and the calibration curve obtained by plotting the chromatographic peak area vs. elemental sulfur concentration as shown in the inset in Figure 2. The linear range in this study was determined within 0.0151mM to 1.889mM; similar linear ranges were reported in other publications [10, 11]. The wide linear range indicates the reliability and sensitivity of this HPLC/UV method over other methods, e.g. gas chromatography (GC) [13].

3.2, Determination of solubility of elemental sulfur in different solvents and electrolytes

The solubility of elemental sulfur in different organic and inorganic media was summarized in the review by Meyer in reference 14. However the usefulness of that data was limited for Li-S batteries since most of the solvents were inadequate for Li-S electrolyte. The solubility was mainly determined by sequentially adding a solvent until the visual disappearance of solid S in the corresponding solution. Large error would be introduced which can be demonstrated in Table 2. Table 2 tabulates the solubility of three popular solvents measured by HPLC/UV and from reference 14. Although the S solubility in ethanol and hexane was in reasonable agreement, the discrepancy in acetone was extraordinary.

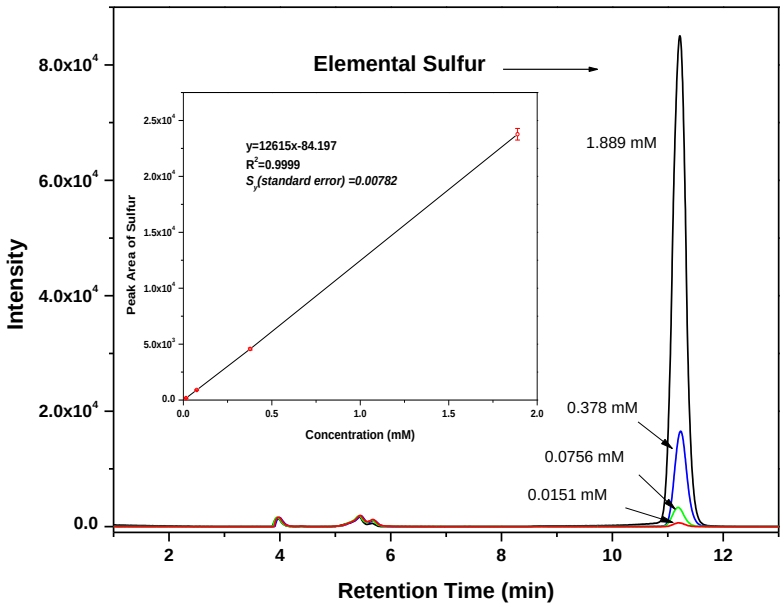

Figure 2, The calibration curve and chromatograms of different elemental sulfur standards.

The solubility of S in various solvents and the corresponding electrolytes with 0.1 M and 1 M LiTFSi determined by the HPLC/UV method is summarized in Table 3, while the solubility of S in DMSO with 1 M of different salts is tabulated in Table 4. Based on the results tabulated in tables 2-4, two observations can be found. First, in a pure organic solvent, the solubility of S is dependent on the polarity and the Lewis basicity of the solvent. The solubility of a non-polar S molecule should be higher in a non-polar solvent than that in a polar solvent [15], for example, the solubility of S in hexane is an order of magnitude higher than that in acetonitrile. The relative polarities of hexane and AN are 0.009 and 0.460, respectively [16]. The S is also more soluble in a solvent with high Lewis basicity [15], for example, the solubility of S in pyridine is about 5 times over that in DME. This is in agreement with the Lewis basicity ($SbCl_5$ affinity) of pyridine (142.3kJ mol^{-1}) and DME (83.68 mol^{-1}) [17], despite the similar relative polarity of the two solvents (0.231 for DME, and 0.302 for pyridine). However it is worth emphasizing that the relationship between the solubility of S and either polarity or Lewis basicity of a solvent is more qualitative than quantitative. Secondly, in an electrolyte solution, the solubility of S is greatly influenced by the existence of supporting salts. As the concentration of the salt in an electrolyte increases, the solubility of S decreases compared to the solubility in pure solvent. As demonstrated in Table 3, the solubility of S decreases on average 12.5% and 53.4% in the 0.1 M and 1.0 M LiTFSi electrolytes from their corresponding solvents, respectively. Table 4 demonstrated that the solubility of S is also influenced with the type of the salt. Noticeable differences in the solubility of S in DMSO with different salts at the same molar concentration can be observed in Table 4.

Table 2, Comparison of solubility of elemental S in selected solvents measured with HPLC/UV method and from reference. The reference data were recalculated in molar unit from reference 12.

Solvent	Solubility mM	Solubility mM ref. 12
Acetone	2.105	83.42
Ethanol	1.704	2.03
Hexane	7.068	6.39

Table 3, Solubility of elemental S in pure solvents and in corresponding electrolytes with different LiTFSi concentrations obtained through HPLC/UV method.

Solvent	Solubility mM, pure solvent	Solubility (mM), 0.1M electrolyte	Solubility (mM), in 1.0M electrolyte

AN	0.610	0.596	0.390
PY	48.046	28.005	15.909
DMF	5.944	5.895	2.603
PC	1.318	1.255	0.633
GBL	3.888	3.366	1.606
DGME	10.259	9.511	3.875
DME	9.957	8.963	3.994
DMSO	3.936	3.845	1.933
BMPTFSi	0.349	0.245	0.216

Table 4, Solubility of elemental S in DMSO with 1M of different salts obtained through HPLC/UV method.

Salt	Solubility (mM)
LiTFSi	1.933
$LiClO_4$	2.416
$LiBF_4$	1.768
$LiCF_3SO_3$	2.161
$TEABF_4$	2.170

3.3, Quantification of soluble S in simulated electrolytes and in electrolyte recovered from a Li-S cell

Although the HPLC/UV method is proven possible to quantify the S in organic solvents and in their corresponding electrolytes, due to the complexity of the S redox reaction [7, 18-20] e.g. the inclusion of multiple dissolved polysulfide ions, the feasibility of the method for the online electrolyte in a Li-S battery still needs to be verified. Figure 3 shows the chromatograms of the simulated electrolytes, which was made by adding various amounts of Na_2S into 0.601 mM S/DME solution. The concentrations of S in the black and simulated electrolytes are presented in Table 5. Since the added Na_2S reacts with elemental S to form different polysulfide species, the simulated electrolytes would represent the online electrolyte of a Li-S battery with all polysulfide species. Moreover the reaction between Na_2S and elemental S consumed the S, therefore the concentration of elemental S in the simulated electrolytes would be roughly proportional to the amount of Na_2S added. As clearly illustrated in Figure 3 and Table 5, the concentration of elemental S indeed decreased in corresponding to the increase of Na_2S in the simulated electrolytes. It is interesting to note that, as shown in the inset of Figure 3, the S concentration is

not exactly proportional to the amount of Na_2S added, the phenomena ought to be expected due to the complexity of S chemistry.

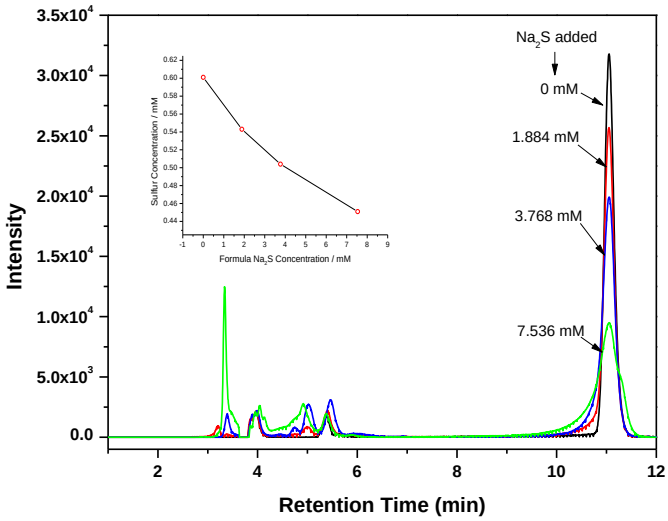

Figure 3, The chromatograms of different simulated electrolytes and blank S/DME solution. The inset shows the change of S concentration with the amount of Na_2S added.

Table 5, Concentration of elemental S in different simulated electrolytes and in blank S/DME solution.

Electrolytes	Concentration (mM)
Blank S/DME solution	0.601
Simulated electrolyte A	0.543
Simulated electrolyte B	0.504
Simulated electrolyte C	0.451

Figure 4 shows the chromatographic result of the electrolyte covered from a discharged Li-S battery. The major peak around 11 min indicates the existence of elemental sulfur in the electrolyte from the battery. The concentration of dissolved S in the electrolyte is summarized in Table 6 in comparison with concentration of S in pure DME and 1M LiTFSi/DME electrolytes. Interestingly, the elemental sulfur concentration in the electrolyte recovered from the discharged Li-S battery is higher than the saturated concentration. The hypothesis for the interesting observation is that the oversaturation of S in the discharged electrolyte was result from the

disproportionation of long chain polysulfide ions. During the S reduction reaction, S_8 gained electrons forming polysulfide species which were soluble in the electrolyte. The longer chain polysulfide ions could disproportionate to form shorter chain polysulfide ions and elemental S [18-20]. Consequently, the newly formed S molecule during the homogenous reaction could oversaturate the electrolyte, the results is consistent with that was reported by Xiao et al that the electrochemically or chemically formed elemental sulfur with largely reduced particle size can facilitate the dissolution of elemental sulfur [21]. This observation indicates that the concentration of S in the electrolyte of a Li-S battery may be much higher than expected.

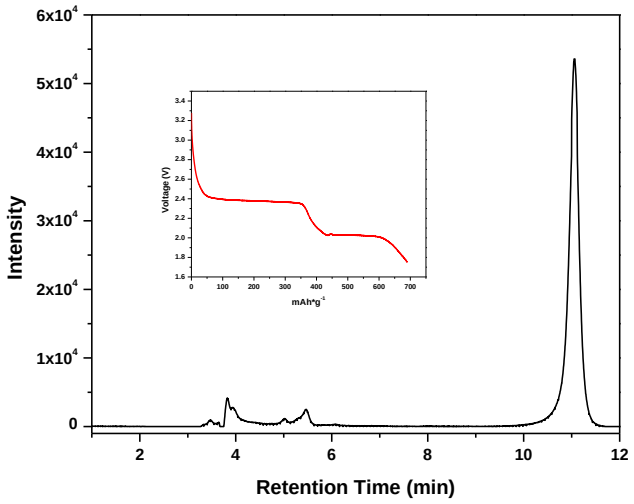

Figure 4, The chromatogram of electrolyte from discharged Li-S battery and the discharged profile of Li-S battery.

Table 6, Concentration of elemental elemental sulfur in pure DME saturated with elemental sulfur, in 1M LiTFSi/DME saturated with elemental sulfur, and in electrolyte from discharged Li-S battery.

Solutions	Concentration
DME saturated with elemental sulfur	9.957
1.0M LiTFSi/DME saturated with elemental sulfur	3.994
Electrolyte from discharged Li-S battery	16.617

4, Conclusion

In summary, a simple and effective HPLC/UV method was successfully developed for the quantification of dissolved S in the electrolyte of Li-S battery. It's found that: the solubility of elemental S is influenced by the Lewis basicity and the polarity of the solvents; the salt and its concentration in the electrolyte also has a great impact on the solubility of S; the concentration of S in the electrolyte in a Li-S battery is much higher than expected, and it may be the result of the homogenous disproportionation of polysulfides.

Acknowledgements

The authors from UMB are indebted to the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy for financial support and the work done at Brookhaven National Lab. is supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, under the program of Vehicle Technology Program, under Contract Number DEAC02-98CH10886. The work done in WUT was partially financially supported by the Fundamental Research Fund for the Central Universities China 2013-Ia-016, 2013-Ia-034, 2014-Ia-033, 2014-zy-166 and 2014-LX-B1-11.

Reference

1, X.L. Ji, L.F. Nazar, *J. Mater. Chem.* **20**, 9821(2010).

2, R. Bonnaterre, G. Cauquis, *J.C.S. Chem*. 293 (1972).

3, F. Seel, H.J. Guttler, G. Simon, A. Wiechowski, *Pure and Appl. Chem*. **49**, 45(1977).

4, G. Le. Guillanton, T.Q. Do, D. Elothmani, *J. Electrochem. Soc.* **143**, L223 (1996).

5, M. Hagen, P. Schiffels, M. Hammer, S. Dorfler, J. Tubke, M.J. Hoffmann, H. Althues, S. Kaskel, *J. Electrochem. Soc.* **160**, A1205 (2013).

6, M.A. Lowe, J. Gao, H.D. Abruna, *RSC Advances* **3**, 1957(2013).

7, R.D. Rauh, F.S. Shuker, J.M. Marston, S.B. Brummer, *J. Inorg. Nucl. Chem*. **39**, 1761 (1977).

8, C. Barchasz, F. Molton, C. Duboc, J-C Lepretre, S. Patoux, F. Alloin, *Anal. Chem.* **84**, (2012)3973.

9, A. Kamyshny, A, Goifman, J. Gun, D. Rizkov, O. Lev, *Environ. Sci. Technol.* **38**, 6633(2004).

10, M.M. Mcguire, R.L. Hamers, *Environ. Sci. Technol.* **34**, 4651(2000).

11, L. Gonsalvesh, S.P. Marinov, M. Stefanova, R. Carleer, J. Yperman, *Fuel* **90**, 2923(2011).

12, D. Zheng, D.Y. Qu, *J. Electrochem. Soc*. **161**, A1164 (2014).

13, D.R. Lauren, J.H.Watkinson, *J. Chromatogr*. **348**, 317(1985).

14, B. Meyer, *Chem. Rev*. **76**, 367 (1976).

15, J.H. Karchmer, "Analytical Chemistry of Sulfur and its Compounds, Part 1", Wiley-Interscience, 1970.

16, C. Reichardt, "Solvents and Solvent Effects in Organic Chemistry", Wiley-VCH, 2003.

17, C. Laurence, J-F Gal, "Lewis Basicity and Affinity Scales: Data and Measurement", Wiley, 2010.

18, J. Badoz-Lambling, R. Bonnaterre, G. Cauquist, M. Delamar, G. Demange, *Electrochim. Acta*, **21**, 119 (1976).

19, R.P. Martin, W.H. Doub, J.L. Roberts, D.T. Sawyer, *Inorg. Chem*. **12**, 1921 (1973).

20, N.S.A. Manan, L. Aldous, Y. Alias, P. Murray, L. J. Yellowlees, M. C. Lagunas, C. Hardacre, *J. Phys. Chem*. B, **115**, 13873 (2011).

21, J.M. Zhang, D.P. Lv, M. Gu, C.M. Wang, J.G. Zhang, J. Liu, J.Xiao, *J. Electrochem. Soc.* **160**, A2288 (2013).