Carbon Cage Encapsulating Nano-cluster Li_2S by Ionic Liquid Polymerization and Pyrolysis for High Performance Li-S Batteries

Liumin Suo^a, Yujie Zhu^a, Fudong Han^a, Tao Gao^a, Chao Luo^a, Xiulin Fan^a, Yong-Sheng Hu^b,
and Chunsheng Wang^{a,*}

^a Department of Chemical and Biomolecular Engineering, University of Maryland, College Park,
MD 20742, USA

Corresponding Authors* Email: cswang@umd.edu

^b National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of
Sciences, Beijing 100190, China.

Abstract

The reversibility and stability of Li_2S electrode can be improved by carbon coating on nano sized Li_2S . However, how to uniformly coat a dense layer of carbon on nano sized Li_2S is still challenge so far. Here, we utilized a novel flowable ionic liquid (1-Ethyl-3-methylimidazolium dicyanamide) as a carbon precursor to uniformly coat a dense carbon on Li_2S nano-clusters. The carbon coated nano- Li_2S cathode displays not only much high active material utilization (826 mAh/g at 0.1C) due to short lithium ion diffusion distance and low charge transfer resistance, but also long cycling stability (82% of capacity retention after 500 cycles at 1C) with near 100% Coulombic efficiency due to encapsulation of the lithium polysulfide within the carbon cage.

Keywords: lithium sulfide; ionic liquid; carbon coating; lithium-sulfur batteries

During the last two decades, lithium-ion batteries (LIBs) have achieved a great success in portable electronic devices due to their high energy density. However, with the rapidly expanding demand on high energy density batteries from clean energy storage, low emission transportation (e.g., electric vehicles), current state-of-the-art LIBs could hardly keep up with those ever-growing requirements [ENREF 1 ENREF 1](#)[1-3]. The sluggish progress is attributed to the relatively low capacity of cathode materials (<300 mAh/g)[4]. In the efforts of developing the next generation cathode, sulfur has attracted more and more attention due to its high theoretical capacity (1672 mAh/g S), low cost and environmental benignity[5-15]. [ENREF 6 ENREF 7](#)Since there is no lithium in pristine sulfur, lithium metal had to be used as the anode. Once employing metallic lithium anode, it is inevitable to face the safety issues caused by lithium dendrite formation during cycling, which limits the practical application of metallic lithium-sulfur batteries. One alternative method is to use lithium sulfide (Li_2S) as the cathode which not only can provides a high theoretical specific capacity (1166 mAh/g) but also, in contrast to sulfur electrode, can be paired with a diversity of lithium-free anodes (e.g., graphite, Si, Sn), alleviating the safety issues induced by using metallic lithium[16, 17] [ENREF 6](#). Nevertheless, the micro sized Li_2S suffers from fast capacity decay, low capacity and low Coulombic efficiency due to the long ion diffusion distance in commercial micro sized Li_2S and slow charge transfer between electrolyte and active materials[18]. Several previous studies have demonstrated that the reversibility and cycling stability of micro-sized Li_2S electrode could be improved by reducing particle size to nano-scale to shorten lithium ion diffusion distance or by carbon coating to improve electronic conductivity and enhance charge transfer[18-31]. However, it is much challenged to achieve a uniform and dense carbon coating on nano sized Li_2S , which

is critical to ensure the electronic conductivity of insulating Li_2S and structure stability during long cycle. Traditional carbon coating normally uses carbohydrate or polymer as the carbon precursor. The water is generated during decomposition of carbon precursor, which could react with Nano- Li_2S . In addition, the carbonization of polymeric precursors usually breaks down the polymeric chain and generates large amount of volatile species, resulting in porous carbon coating with impurity[32]. Recently, we successfully used an ionic liquid as a carbon precursor to form a conformal carbon coating in porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles due to the excellent fluidic properties of ionic liquid[33, 34]. As a matter of fact, the high flow ability of ionic liquid and wettability to sulfides make the ionic liquid unique carbon source for carbon coating on nano- Li_2S .

In this work, a high fluid ionic liquid (IL) (1-Ethyl-3-methylimidazolium dicyanamide) [Emim]- $[\text{N}(\text{CN})_2]$ is utilized as a novel carbon precursor to form uniform and dense carbon cage coating on Li_2S nano-cluster. Firstly, the ionic liquid is penetrated into agglomerated Nano- Li_2S particle and is polymerized at low temperature and then carbonized at a high temperature. Due to the oxygen-free nature of [Emim]- $[\text{N}(\text{CN})_2]$ (with chemical formula of $\text{C}_8\text{H}_{11}\text{N}_5$), H_2O will not generate during its decompositions in inert atmosphere, which effectively avoids the side reaction between Li_2S and H_2O in pyrolysis process. Secondly, strong **Coulombic** interaction between cation and anion makes IL nearly non-volatile, thus, which is favorable for crosslinking reaction under pyrolysis conditions and thereby increasing carbon yield and carbon density[35, 36], meanwhile the high mobility of [Emim]- $[\text{N}(\text{CN})_2]$ is easy to achieve sufficient immersion with Li_2S particle and IL, which is beneficial to form an uniform carbon coating on Li_2S subsequently. The high fluid, non-volatile IL carbon precursor for carbon coating combines the

advantages of simple operation, easy obtainment and high yield in solid-state carbonization reaction and conformal coating in chemical vapor deposition (CVD) [20].

Experimental section

Material synthesis

Nano-Li₂S was prepared by a one step in-situ chemical reduction method and the whole experiment was conducted in an argon (Ar)-filled glove box[37]. Firstly, sulfur is dispersed into tetrahydrofura (THF) solvent by strong mechanical agitation to make a 0.5 mol/L (20 mL) suspension. Then 1/8 (2.5 mL) of reductant (1 mol/L Li(CH₂CH₃)₃BH in THF) was slowly introduced into the suspension under magnetic stirring and the solution became dark-brown. And, after waiting for 10min, the residual 7/8 (17.5 mL) of reductant was slowly added into the solution drop by drop. After 24 hours of reaction, the solution was centrifuged, and the precipitate was collected and washed for three times. The final nano-Li₂S was prepared by vacuuming above precipitate for one hour at room temperature and then heating at 90 °C for two hours in Ar atmosphere. A proportion of ILs ([Emim]-[N(CN)₂]) from BASF corporation and Nano-Li₂S (50 uL:100 mg) is shocked by vortex mixer to make high viscosity IL and Li₂S mixing uniformly, then heat the mixture by two steps (350 °C for 0.5h and 600 °C for 0.5 h) in Ar atmosphere to carbonize the IL.

Characterizations and electrochemical Measurements

X-ray diffraction patterns were recorded on D8 Advance X-ray diffraction (Bruker), with Cu K-alpha radiation in the 2-theta ranging from 10 to 90 and all samples were assembled in airtight specimen holder ring (Bruker) in Ar filled glove box. Raman measurements were performed on a Horiba Jobin Yvon Labram Aramis using a 532 nm diode-pumped solid-state laser, attenuated to

give $\sim 900\ \mu\text{W}$ power at the sample surface and all samples were placed between two slide glasses and sealed by adhesive tape in Ar filled glove-box. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were examined in a Hitachi S-4700 (Japan) operating at 10 kV and in a JEOL (Japan) 2100F field emission respectively.

The electrode was fabricated by compressing cathode (Micro- Li_2S , Nano- Li_2S and C-Nano- Li_2S), carbon black, poly(vinylidene difluoride) (PTFE) in weight ratio of 6:3:1 onto a stainless steel grid (200 mesh) for electrochemical performance measurement and the mass load of electrode is about $2.5\sim 3\ \text{mg}/\text{cm}^2$. The CR2032-type coin cells were assembled with the electrode, pure lithium foil as counter electrode and a glass fiber separator in an Ar-filled glove box. The electrolyte is LiTFSI in DOL (50 vol%)- DME (50 vol%) with the ratio of salt (mol): solvent (L) of 7mol/1L as our previous paper[15]. The galvanostatic measurements were carried out on a Land BT2000 battery test system (Wuhan, China) at room-temperature. The Cyclic voltammetry (CV) was carried out on CHI 600E electrochemical workstation.

Results and discussion

Scheme 1 schematically shows the detailed preparation of carbon coating nano-sized Li_2S (C-Nano- Li_2S). First, the as-synthesized Nano- Li_2S is mixed with [Emim]-[N(CN) $_2$] at room temperature by vortex mixer. Then, the homogeneous mixture is heated to 350°C and 600°C under Ar atmosphere to realize the carbonization of [Emim]-[N(CN) $_2$] through the two stages of polymerization and carbonization process. During the polymerization of cation [N(CN) $_2$] $^+$ at low temperature of 350°C , the [Emim]-[N(CN) $_2$] shrinks and breaks the agglomerated nano- Li_2S into a few nano- Li_2S clusters, while the amorphous polytriazine networks are dynamically formed on

the surface of nano-Li₂S clusters at the same time. When the temperature further increases to 600°C (the second stage), the amorphous polytriazine out-layer pyrolysis into rectangular dense carbon cage and encapsulate the inner Li₂S nano-clusters.

The carbon coating are confirmed by TEM images of nano-sized Li₂S (Nano-Li₂S) and carbon coated nano-sized Li₂S (C-Nano-Li₂S) (Figure 1). The Nano-Li₂S has needle-like morphology and has aggregated into large particles (Figure 1a and 1b). After carbon coating, the aggregated Nano-Li₂S breaks into about 100 nm with rectangular shape and is confined by the carbon cage (Figure 1c and 1d). The thickness of carbon coating is about 5nm as shown in Figure 1e. The SAED pattern in Figure 1f reveals the crystal structure of Li₂S, with the first six rings are indexed to the (111), (200), (220), (311), (222), (400) reflections of Li₂S phase. For carbon coated S nanoparticles, yolk-shell structure is required since the enough free space has to be reserved for 76% volume expansion during initial lithiation[8, 38]. However C-Nano-Li₂S is in full lithiation (expanded) state, simple conformal carbon coating rather than complicated yolk-shell is enough for maintaining the structure stability due to no stress/strain generating in whole lithiation/delithiation process (Figure 1g). Thus, the electrochemical performance of Nano-Li₂S coated by IL-pyrolysis is expected to have stable cycling stability.

Figure 2a shows the XRD patterns of Nano-Li₂S, C-Nano-Li₂S and commercial Micro-Li₂S (50 um particle size). The SEM image of commercial Micro-Li₂S is shown in Figure S1. As shown in Figure. 2a, Nano-Li₂S is in crystal structure without any detectable impurity (the bump at ~20° is due to the airtight sample holder). The XRD pattern of C-Nano-Li₂S is the same as that of Nano-Li₂S, confirming that no any side reaction between Li₂S and products generated from the pyrolysis process of the oxygen-free [Emim]-[N(CN)₂] (C₈H₁₁N₅) precursor. As expected, the half-peak widths of Nano-Li₂S and C-Nano-Li₂S significantly increase compared to the XRD

pattern of commercial Micro-Li₂S due to the size effects. The natures of coated carbon and lithium sulfide were characterized using Raman spectra (Figure. 2b). The Raman spectra of C-Nano-Li₂S in the range of 200 ~ 1200 cm⁻¹ is the same as commercial Micro-Li₂S and Nano-Li₂S. The two additional broad peaks at 1334 cm⁻¹ and 1600 cm⁻¹ for C-Nano-Li₂S is attributed to carbon since the carbon produced by pyrolysis of IL also shows similar peaks. The peak at 1334 cm⁻¹ (D-band) is usually associated with the vibrations of carbon atoms with dangling bonds forth in-plane terminations of disordered graphite, and the peak at 1600 cm⁻¹ (G-band) (corresponding to the E_{2g} mode) is closely related to the vibration in all *sp*₂ bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphene layer. The intensity ratio of the D- to G- band (I_D/I_G) could further reflect the relative disorder and degree of graphitization of carbon. In this case, the intensity of D-band peak is stronger than G-band, indicating that the generated carbon is more disordered. To detail understand the nature of coated carbon, a bulk carbon synthesized by pyrolysis of IL was characterized using scanning electron microscopy (SEM) (Figure. S2) and XRD (Figure. S3). As shown in Figure. S2, the pyrolysis of IL can form a dense carbon without any noticeable cracks, which could effectively encapsulate the inside intermediate lithium polysulfide and avoid the shuttle effect when it coated on nano-Li₂S particles. XRD pattern in Figure. S3 shows that the pyrolysis-generated carbon is partially graphitized, in which the broad peaks at 26 and 44 degree were corresponding to (002) and (100) of graphite. “The carbon-yield during the pyrolysis of [Emim]-[N(CN)₂] was estimated by measuring the weight difference before and after carbonization of [Emim]-[N(CN)₂] in Ar under the same heat treatment condition as for [Emim]-[N(CN)₂]/Nano-Li₂S composite. The carbon-yield of [Emim]-[N(CN)₂] is 20 wt%. Since the ratio of ILs ([Emim]-[N(CN)₂]) to Nano-Li₂S is

50uL:100 mg, we can estimated the carbon content in C-Nano-Li₂S composite using equation below:

Carbon content = carbon yield × IL volume × IL density / carbon yield × IL volume × IL density + Li₂S). The carbon content was determined as 10% ($20\% \times 50\text{uL} \times 1.06\text{g/cm}^3 / 20\% \times 50 \times 1.06 + 100\text{mg} = 9.6\%$).

In order to further prove the effect of carbon coating by [Emim]-[N(CN)₂], we tested the electrochemical performances of commercial Micro-Li₂S, Nano-Li₂S and C-Nano-Li₂S (Figure 3). Figure 3a shows the charge-discharge curves of commercial Micro-Li₂S, Nano-Li₂S and C-Nano-Li₂S at a rate of 0.1C (117 mA/g-Li₂S) after the first cycle activation process (0.02C) (~23 mA/g-Li₂S), and the first charge-discharge profile of C-Nano-Li₂S at 0.02C is presented in Figure S4. Compared with Micro-Li₂S and Nano-Li₂S, C-Nano-Li₂S shows a much higher utilization of active material, as indicated by the large difference in lithiation capacities, which are 826.1 mAh/g for C-Nano-Li₂S, 608.4 mAh/g for Nano-Li₂S and 162 mAh/g for micro-sized commercial Li₂S. The capacity of C-Nano-Li₂S is calculated by the total weight of cathode. The significant increase in capacity for C-Nano-Li₂S could be contributed to much high specific surface area, high electronic conductivity and short lithium diffusion distance, which facilitate the lithiation/delithiation kinetics and increase the utilization of Li₂S. Figure. 3b shows the cycling stability of C-Nano-Li₂S, Nano-Li₂S and Micro-Li₂S at 0.1C (~ 117 mA/g), which presents that C-Nano-Li₂S maintains 78.5% of initial capacity after 50 charge/discharge cycles which is much higher than that (51.8%) of Nano-Li₂S. Meanwhile, the long-term cycling stability of C-Nano-Li₂S at a high rate of 1C (1166 mA/g-Li₂S) is also shown in Figure 3c. As shown in Figure 3c, a reversible capacity of 439.5 mAh/g-Li₂S (calculated based on Li₂S) or 630.8 mAh/g-S (calculated based on S) could be achieved even at a high rate of 1C after the

initial activation process (0.1C). Moreover, high capacity retention of 82% could be achieved after 500 cycles with a Coulombic efficiency near 100%. C-Nano-Li₂S also shows high rate capacity as demonstrated in Figure 3d. It exhibits capacities of 856 mAh/g, 691 mAh/g, 537 mAh/g, 365 mAh/g, and 251 mAh/g at current rates of 0.1, 0.2, 0.5, 1, and 2 C. When the current density is reduced back from 2 C to 0.1 C, the capacity is almost fully recovered, indicating the robust rate stability of the C-Nano-Li₂S electrode. This significant improvement on electrochemical performances of C-Nano-Li₂S is attributed to the unique core-shell structure of C-Nano-Li₂S, which could effectively reduce cycling decay caused by large volume change between Li₂S and S and inhibit the shuttle reaction induced from the dissolution of high-order polysulfide. Meanwhile, carbon coating-layer as a cage inhibits nano-particle agglomeration induced by redistribution of active material during the cycles.

Conclusion

In summary, we developed a facile and effective carbon coating method by utilizing high fluid ionic liquid (IL) (1-Ethyl-3-methylimidazolium dicyanamide) [Emim]-[N(CN)₂] as a novel liquid phase carbon precursor. In virtue of the unique oxygen-free chemical formula and physicochemical properties of [Emim]-[N(CN)₂], we successfully prepare to achieve nano-scale carbon cage encapsulating Li₂S nano-clusters (Nano-Li₂S) by designing two heat treatment steps. This method combines the advantages of solid-state reaction (simple operation, easy obtainment and high yield) and chemical vapor deposition (CVD) approach (coating uniformity and entirety). Compared with commercial Micro-Li₂S and pure Nano-Li₂S, C-Nano-Li₂S electrode displays much higher Li₂S utilization in virtue of short lithium ion diffusion distance in nano-sized particle and low charge transfer by carbon coating. More importantly, the formed core-shell structure is able to enhance electrode stability for long-term cycling by entrapping the lithium

polysulfide within the carbon cage. The nano-clusters Li_2S encapsulated in carbon cage exhibited a high capacity (826 mAh/g at 0.1C) and high capacity retention after 500 cycles (82% at 1C) with near 100% Coulombic efficiency.

Scheme 1. The schematic of preparing carbon cage encapsulating nano-clusters Li₂S composite

Figure 1. TEM images of a) and b) Nano-Li₂S; c), d) and e) C-Nano-Li₂S; f) Selected area electron diffraction (SAED) pattern of the particle shown in d); g) Schematic of the delithiation and lithiation process in carbon-coated Nano-Li₂S with cage-like structure.

Figure 2. a) X-ray diffraction patterns and b) Raman spectra

Figure 3. Comparison of electrochemical performance of different Li_2S samples (Micro-sized Li_2S purchasing from Aldrich, Nano- Li_2S , and C-Nano- Li_2S), all the capacity calculated based on the weight of C/ Li_2S . a) the typical charge-discharge profiles at 0.1C after the first cycle activation (charge to 3.8V) at 0.02C; b) cycling life and Coulombic efficiencies at C/10 after activation for 1 cycle at 0.02C; c) long cycling life and Coulombic efficiency of C-Nano- Li_2S at a high rate (1C) after the first cycle at 0.1C; d) rate capability of C-Nano- Li_2S .

Acknowledgment

The authors gratefully acknowledge the support of DoE ARPA-E (DEAR0000389). We also acknowledge the support of the Maryland NanoCenter and its NispLab. The NispLab is supported in part by the NSF as a MRSEC Shared Experimental Facility.

Supporting Information.

Details of material Synthesis the synthesis, characterization, electrochemical measurements. Additional figures of SEM and XRD.

References

- [1] J.M. Tarascon, M. Armand, *Nature*, 414 (2001) 359-367.
- [2] M. Armand, J.M. Tarascon, *Nature*, 451 (2008) 652-657.
- [3] B. Dunn, H. Kamath, J.-M. Tarascon, *Science*, 334 (2011) 928-935.
- [4] C.X. Zu, H. Li, *Energy & Environmental Science*, 4 (2011) 2614-2624.
- [5] X. Ji, L.F. Nazar, *Journal of Materials Chemistry*, 20 (2010) 9821-9826.
- [6] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.-M. Tarascon, *Nature Materials*, 11 (2012) 19-29.
- [7] C. Huang, J. Xiao, Y.Y. Shao, J.M. Zheng, W.D. Bennett, D.P. Lu, S.V. Laxmikanth, M. Engelhard, L.W. Ji, J. Zhang, X.L. Li, G.L. Graff, J. Liu, *Nature Communications*, 5 (2014).
- [8] Z.W. Seh, W. Li, J.J. Cha, G. Zheng, Y. Yang, M.T. McDowell, P.-C. Hsu, Y. Cui, *Nature Communications*, 4 (2013).
- [9] N. Jayaprakash, J. Shen, S.S. Moganty, A. Corona, L.A. Archer, *Angewandte Chemie-International Edition*, 50 (2011) 5904-5908.
- [10] C.D. Liang, N.J. Dudney, J.Y. Howe, *Chemistry of Materials*, 21 (2009) 4724-4730.
- [11] B. Zhang, X. Qin, G.R. Li, X.P. Gao, *Energy & Environmental Science*, 3 (2010) 1531-1537.
- [12] L.W. Ji, M.M. Rao, H.M. Zheng, L. Zhang, Y.C. Li, W.H. Duan, J.H. Guo, E.J. Cairns, Y.G. Zhang, *Journal of the American Chemical Society*, 133 (2011) 18522-18525.
- [13] J.C. Guo, Y.H. Xu, C.S. Wang, *Nano letters*, 11 (2011) 4288-4294.
- [14] H.L. Wang, Y. Yang, Y.Y. Liang, J.T. Robinson, Y.G. Li, A. Jackson, Y. Cui, H.J. Dai, *Nano letters*, 11 (2011) 2644-2647.
- [15] L. Suo, Y.-S. Hu, H. Li, M. Armand, L. Chen, *Nature Communications*, 4 (2013).
- [16] J. Hassoun, B. Scrosati, *Angewandte Chemie-International Edition*, 49 (2010) 2371-2374.
- [17] Y. Yang, M.T. McDowell, A. Jackson, J.J. Cha, S.S. Hong, Y. Cui, *Nano letters*, 10 (2010) 1486-1491.
- [18] Y. Yang, G. Zheng, S. Misra, J. Nelson, M.F. Toney, Y. Gui, *Journal of the American Chemical Society*, 134 (2012) 15387-15394.
- [19] S. Jeong, D. Bresser, D. Buchholz, M. Winter, S. Passerini, *Journal of Power Sources*, 235 (2013) 220-225.
- [20] C. Nan, Z. Lin, H. Liao, M.-K. Song, Y. Li, E.J. Cairns, *Journal of the American Chemical Society*, 136 (2014) 4659-4663.
- [21] F. Wu, A. Magasinski, G. Yushin, *Journal of Materials Chemistry A*, 2 (2014) 6064-6070.
- [22] K. Cai, M.K. Song, E.J. Cairns, Y. Zhang, *Nano letters*, 12 (2012) 6474-6479.
- [23] Z. Lin, Z. Liu, N.J. Dudney, C. Liang, *Acs Nano*, 7 (2013) 2829-2833.
- [24] S. Zheng, Y. Chen, Y. Xu, F. Yi, Y. Zhu, Y. Liu, J. Yang, C. Wang, *Acs Nano*, 7 (2013) 10995-11003.
- [25] Y. Fu, Y.-S. Su, A. Manthiram, *Advanced Energy Materials*, 4 (2014) n/a-n/a.
- [26] Z.W. Seh, H. Wang, N. Liu, G. Zheng, W. Li, H. Yao, Y. Cui, *Chemical Science*, 5 (2014) 1396-1400.
- [27] Z.W. Seh, H. Wang, P.-C. Hsu, Q. Zhang, W. Li, G. Zheng, H. Yao, Y. Cui, *Energy & Environmental Science*, 7 (2014) 672-676.
- [28] Y. Fu, C. Zu, A. Manthiram, *Journal of the American Chemical Society*, 135 (2013) 18044-18047.

- [29] M. Nagao, A. Hayashi, M. Tatsumisago, *Journal of Materials Chemistry*, 22 (2012) 10015-10020.
- [30] J. Liu, H. Nara, T. Yokoshima, T. Momma, T. Osaka, *Chemistry Letters*, 43 (2014) 901-903.
- [31] F. Wu, H. Kim, A. Magasinski, J.T. Lee, H.-T. Lin, G. Yushin, *Advanced Energy Materials*, 4 (2014).
- [32] C.H. Hou, X.Q. Wang, C.D. Liang, S. Yiacoumi, C. Tsouris, S. Dai, *Journal of Physical Chemistry B*, 112 (2008) 8563-8570.
- [33] L. Zhao, Y.S. Hu, H. Li, Z. Wang, L. Chen, *Advanced materials*, 23 (2011) 1385-1388.
- [34] Z. Ding, L. Zhao, L. Suo, Y. Jiao, S. Meng, Y.-S. Hu, Z. Wang, L. Chen, *Physical Chemistry Chemical Physics*, 13 (2011) 15127-15133.
- [35] J.S. Lee, X. Wang, H. Luo, S. Dai, *Advanced materials*, 22 (2010) 1004-+.
- [36] J.P. Paraknowitsch, J. Zhang, D.S. Su, A. Thomas, M. Antonietti, *Advanced materials*, 22 (2010) 87-92.
- [37] J.A. Gladysz, V.K. Wong, B.S. Jick, *Tetrahedron*, 35 (1979) 2329-2335.
- [38] W. Zhou, Y. Yu, H. Chen, F.J. DiSalvo, H.D. Abruna, *Journal of the American Chemical Society*, 135 (2013) 16736-16743.

Dr. Liumin Suo received his Ph.D. in condensed matter physics in 2013 at Institute of Physics, Chinese Academy of Sciences. He is currently postdoctoral Research Associate in University of Maryland, College Park, USA. His research interests focus on energy storage devices including electrode materials, electrolyte and electrochemistry for rechargeable batteries (rechargeable Lithium ion and lithium metal batteries).

Dr. Yujie Zhu received his B.S. degree in Chemical Engineering from Tsinghua University, and earned his Ph.D. degree in Chemical and Biomolecular Engineering in 2013 from University of Maryland, College Park (UMCP). He is now a postdoctoral research associate in Professor Chunsheng Wang's research group at UMCP. His research focuses on development of electrochemical techniques for phase transition electrode materials, investigation of charge/discharge process for single particle systems by in-situ transmission electron microscopy, and electrode materials synthesis for lithium-/sodium-ion batteries.

Mr. Fudong Han received his B.S. and M.S. degree in Materials Science and Engineering from Shandong University, and is currently a Ph.D. student at Department of Chemical and Biomolecular Engineering at University of Maryland, College Park. His research focuses on all-solid-state lithium-ion batteries with the aim to minimize the interfacial resistance between the electrodes and electrolyte.

Mr. Tao Gao received his bachelor degree in Automotive Engineering and M.S. degree in Mechanical Engineering both in Tsinghua University. He is currently a P.h.D student majoring in Chemical Engineering in University of Maryland. His research interest is kinetics study of energy materials and electrochemical techniques for characterization of electrochemical energy system

Dr. Xiulin Fan received his Ph.D. in Materials Science and Engineering from Zhejiang University in 2012. He is currently a postdoctor at University of Maryland-College Park. His research interests are novel nanostructured materials and their application in energy storage and conversion devices including lithium-ion batteries, sodium-ion batteries and hydrogen storage.

Dr. Yong-Sheng Hu is a professor at the Institute of Physics, Chinese Academy of Sciences (IOP-CAS). He received his Ph.D. at IOP-CAS with Prof. Liquan Chen in 2004, and then moved to Max Planck Institute for Solid State Research as postdoctoral fellow in the Prof. Joachim Maier's Department. After a short stay at Prof. Eric McFarland's group in the University of California at Santa Barbara, he joined IOP-CAS in 2008 and is working on advanced materials and technology for long-life grid-scale stationary batteries. He was recently named amongst Thomson Reuters Highly Cited Researchers in the field of Materials Science in 2014.

Dr. Chunsheng Wang is an Associate Professor in the Chemical & Biomolecular Engineering at the University of Maryland. He received Ph.D in Materials Science & Engineering from Zhejiang University, China in 1995. Prior to joining University of Maryland in 2007, he was an assistant professor in Department of Chemical Engineering at Tennessee Technological University (TTU) in 2003-2007 and a research scientist in the Center for Electrochemical System and Hydrogen Research at Texas A&M University in 1998-2003. His research focuses on rechargeable batteries and fuel cells. He has published more than 110 papers in peer-reviewed journals. His work has been cited form more than 4200 times with H-index of 36. His work on lithium batteries have been featured in *NASA Tech Brief*, *EFRC/DoE newsletter*, *C&EN* etc. Dr. Wang is the recipient of the A. James Clark School of Engineering Junior Faculty Outstanding Research Award in the University of Maryland in 2013

A high fluid ionic liquid (IL) (1-Ethyl-3-methylimidazolium dicyanamide) is utilized as a novel carbon precursor to form uniform and dense carbon cage coating on Li₂S nano-cluster. It is shown that carbon uniformly coated on nano aggregated Li₂S to form nano core-shell structure (100 nm) exhibited high capacity (826 mAh/g at 0.1C), long cycling life and high capacity retention of 82% after 500 cycles at 1C with near 100% Coulombic efficiency.