Molecular insights into ether-based electrolytes for Li-FeS$_2$ batteries

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ABSTRACT

Lithium-FeS$_2$ is an attractive chemistry for rechargeable lithium batteries because of its high theoretical energy density ~1313 Wh kg^{-1}. However, fast capacity fade is generally observed in this system due to the irreversible dissolution of active materials (polysulfide ions, Fe ion etc.) into the electrolyte. This work investigates the effect of ethereal electrolyte solvents' structure on its solvating power of Li-polysulfides and eventually on the cycling stability of rechargeable Li-FeS$_2$ cells. Methyl t-butyl ether (MTBE), a high carbon/oxygen ratio ether, is studied and compared with the standard 1,2-dimethoxyethane (DME):1,3-dioxolane (DOL) ether couple as electrolyte solvent for Li-FeS$_2$ and similar chemistries. The higher level of non-polar character and the additional steric hindrance in MTBE both endow it with significantly lower solvating capability and lower solubility of Li-polysulfides than DME:DOL. This is predicted by quantum chemical calculation and verified by experiments. In electrochemical test, MTBE solvent helps to significantly improve the cycling stability of the Li-FeS$_2$ cell. Post-cycling material analysis and impedance tests both indicate that this is due to the alleviated active material dissolution and re-deposition on the lithium anode. Similar improvement is also observed in the Li-CuS cell case. Although the ionic conductivity of the electrolyte is also affected by this new solvent and MBTE cannot yet be a satisfactory solution, our study presents important guidance in designing future electrolyte for Li-FeS$_2$ battery.

1. Introduction

The electrochemical energy storage systems, especially the Li-ion batteries, have played a key role in the proliferation of portable electronics and communication devices in the last 20 years [1,2]. In addition, the integration of Li-ion batteries into the private-owned and the public transport vehicles to help minimizing the carbon footprint of the energy consumptions has also seen preliminary successes [3]. However, in both of the markets, the demand for batteries with higher energy density, shorter charge time (high power), longer cycle life, and at the same time lower manufacturing cost is ever increasing. The great efforts dedicated to the optimization of the Li-ion battery technologies based on transition metal oxide cathodes and graphite anodes have been consistently improving the commercial cells from year to year, but it is also realized that such important parameters as energy density is approaching its ceiling as defined by the cathode-anode couple. In this spirit, a lot of research effort has also been drawn into the exploration of the new electrode chemistries with much higher theoretical gravimetric and volumetric capacities and energy densities. For instance, our understanding of the promising new anode materials, such as silicon and tin, has been improved significantly in the last decade, and

some of these new anode materials are already being incorporated into the commercial cells [4,5]. However, the research on new cathode chemistries beyond intercalation-based lithium transition metal oxides (LiMO$_2$) seems to be more challenging. The new cathode candidates include transition metal oxides, sulfides and fluorides etc. [6]. These materials generally work at the potentials lower than LiMO$_2$, but their comparatively huge specific capacity is more than enough to turn the overall comparison around. Unfortunately, because in most cases they react with lithium by conversion mechanism that involves significant structure rearrangement, their reversibility and long-term cyclability suffer and their application in commercial cells seems unrealistic. FeS$_2$ (pyrite), an earth-abundant and low cost material, is an interesting and attractive example amongst these candidates because each formula of FeS$_2$ can react with 4 Li (4e$^-$ transfer) to deliver a high gravimetric capacity of 894 mAh g^{-1} [7]. This material has already been used as the cathode for primary lithium batteries such as Energizer, and the thermal batteries at the high operating temperature for military applications [8]. But there is not much success in developing room-temperature (RT) rechargeable Li-FeS$_2$ cells, most likely due to the poor cycle life of FeS$_2$. The main reason for the inferior cyclability of FeS$_2$ in a lithium cell probably lies in its reaction mechanism, which is

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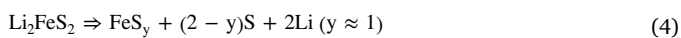yet to be fully understood, but generally described by the following processes [7]:

Discharge:

$$2Li + FeS_2 \Rightarrow Li_2FeS_2 \qquad (1)$$

$$2Li + LiFeS_2 \Rightarrow Fe + 2Li_2S \qquad (2)$$

Charge:

$$Fe + 2Li_2S \Rightarrow Li_2FeS_2 + 2Li \qquad (3)$$

$$Li_2FeS_2 \Rightarrow FeS_y + (2-y)S + 2Li \ (y \approx 1) \qquad (4)$$

Currently the common belief is that the system evolves into a FeS_y and Sulfur hybrid system after the first recharge. Sulfur is notorious for its poor cyclability due to its tendency to form a myriad of polysulfides (S_n^{2-}) intermediates during lithiation that dissolve into most polar solvents and lead to the gradual loss of active material in the cathode [9]. In addition, the Fe dissolution from FeS_2 during cycling has also been observed and seems to become exacerbated in the presence of excess sulfur [10]. Based on these considerations, it is vital to slow down or even fully stop the dissolution kinetics of FeS_2 in a lithium cell so that long-term cyclability can be achieved.

Following the hypothesis that the active material dissolution is the key factor in deciding FeS_2 cell cycle life, we can expect the cyclability issue to become aggravated when FeS_2 is processed into nano-structures to enhance its power performance and efficiency in Li-FeS_2 cells. Therefore, several efforts have been reported in the synthesis and processing of nano-FeS_2 into different forms with surface protection layers to physically encapsulate the FeS_2 particles, and the improvement in the cycle life is evident in each of these studies [11–15]. As another key component in this dissolution phenomenon, electrolyte deserves equal level of emphasis. Ethereal solvent (DME:DOL(1:1,v/v)) based electrolyte system seems to work much better than carbonate systems and the most recent results on Li-FeS_2 cells have been published with the former. However, the Li-FeS_2 cells using the ether based electrolyte generally still do not show satisfactory cyclability, since polysulfides are known to dissolve facilely into DME:DOL combination in the lithium-sulfur batteries. Apparently, other solvent systems, such as fluorinated ether [16], ionic liquid solvent [17], and solvent in salt concept [18], that have been demonstrated to work well in Li-S systems all deserve a trial in Li-FeS_2 cells. In the work by Lee et al., the ionic liquid solvent indeed significantly improves the cycle life of Li-FeS_2 couple [19]. The same research group also disclosed the concept of using a flexible solid state fast Li-ion conductor as separator for the Li-FeS_2 cell and showed improvement [20]. These two works demonstrated the role that electrolyte plays in determining the cycling stability of the Li-FeS_2 cell. The success of the use of ionic selective membrane as a separator in enhancing cycle life in Ref. [20] also indicated that the degradation processes probably involve the interaction between lithium anode and the dissolved species from the cathode.

In this manuscript, we study another group of potential electrolyte solvents ─ high carbon/oxygen ratio (C/O ratio) ethers [21], comparatively with the most commonly used DME:DOL combination in the Li-FeS_2 cell system. Our goal is to understand the influence of ether solvent's structure on the electrolyte's solvating power towards the reaction intermediates, primarily Li-polysulfides, and eventually on the long-term stability of Li-FeS_2 couple in continuous electrochemical reactions. The lessons learned in this study can also be extended to other cathode candidates amongst transitional metal sulfides (CuS, NiS, CoS_2 etc.).

2. Experimental methods

2.1. Electrolyte characterization

Methyl tert-butyl ether (MTBE) (Sigma Aldrich), methyl butyl ether (MBE) (Sigma Aldrich), 1,2-dimethoxyethane (DME) (BASF), 1,3-dioxolane (DOL) (BASF), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, BASF) were used as received without further purification. All of the preparation and measurement were performed in argon-filled glovebox (O_2, $H_2O < 0.5$ppm). To synthesize polysulfide, 0.5 M (equivalent to 4 M sulfur) Li_2S_8 solution was first prepared by mixing 0.46 g Li_2S and 2.24 g sulfur in DOL:DME = 1:1 (v/v) mixed solvent at 55 °C under magnetic stirring for 48 h under argon. The solvent was then evaporated by first isolating the vial containing the solution within an enclosure where excess activated carbon was situated on the side to absorb the ether vapor until the solution becomes too viscous to flow. A vacuum of 10^{-1} mbar was then applied over the viscous solution to extract residue ether solvent for another 48 h. The obtained Li_2S_8 in solid form was then mixed with MTBE, MBE and DME:DOL (1:1,v/v), respectively. In every case, the weight of Li_2S_8 was in excess and the solvent was 10 mL. The 3 mixtures were stirred vigorously at room temperature for 48 h. The solubility of Li_2S_8 in MTBE and MBE was measured by weighing the remnant after drying the filtered supernatant in the Li_2S_8/MTBE and Li_2S_8/MBE mixture. Solubility of LiTFSI in MTBE and DME:DOL (1:1,v/v) was measured by putting excess LiTFSI into them under magnetic stirring until significant amount of LiTFSI was observed to be non-dissolvable after 48 h of mixing. Again, the concentration of the filtered supernatant was measured and recorded as the solubility of LiTFSI. Ionic conductivity measurement of different electrolytes was performed at 0 °C, 10 °C, 20 °C, and 30 °C with a conductivity meter (YSI 3100, cell constant 1 cm^{-1}).

2.2. Electrochemical testing

FeS_2 (Sigma Aldrich, average particle size = 20–50 µm), CuS (Alfa Aesar) and Sulfur (S) (Alfa Aesar) were used as received without modifications. Electrode slurries were made by mixing 60 wt% active materials (FeS_2, CuS or S) with 30 wt% Super C65 (IMERYS) and 10 wt% PVDF binder (Alfa Aesar) in 1-Methyl-2-pyrrolidinone (NMP). The slurry was casted onto aluminum foil using a doctor blade and dried in a fume hood under continuous dry air flow (dew point < −40 °C) for 24 h before it was transferred into an oven to be heated at 50 °C for another 24 h to eliminate residual solvent and moisture. The average loading of active materials in different electrodes was ~1.2 mg cm^{-2}. 2032 coin cells were assembled by using electrodes prepared above as working electrode and a lithium disk as both counter and reference electrode, with 2 layers of Celgard (2325) separator in between to prevent shorting. Electrolytes used in the study were 1.0 M LiTFSI in MTBE and 1.0 M LITFSI in DME:DOL (1:1,v/v), which will be clearly indicated in the results and discussion. The electrochemical tests were done with a Bio-logic potentio-stat (VMP3). Cycling tests for FeS_2 and S electrodes were performed only at 0.2C galvanostatically between 1.0 V and 2.6 V, while two windows 1.0–2.6 V and 1.8–2.6 V were used for CuS electrodes. Rate test was performed with Li-FeS_2 cells. 3 discharge rates 0.5C, 1.0C and 2.0C were applied with the same voltage window (1.0–2.6 V), but the charge rate was kept at 0.2C. Li-FeS_2 cell impedance was measured after cell assembly, after the 1st cycle in the fully charged state and after 100th cycle in the fully charged state. The cell was allowed to rest for 1 h before each spectrum was collected. The measurement was done by applying voltage perturbation amplitude of 5 mV and the frequency was varied from 7 MHz to 50mHz.

2.3. Materials characterization

XRD of raw materials were done with Rigaku Ultima III X-Ray diffractometer. Morphology and composition of the lithium surface