



Short communication

A multi-electron redox mediator for redox-targeting lithium-sulfur flow batteries



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- A redox-targeting Li-S flow battery (RTLSFB) which uses only single redox mediator.
- Dimethyl trisulfide (DMTS) is a multi-electron redox mediator for Li-S reactions.
- A RTLSFB with improved sulfur utilization and cycle stability.
- DMTS is better used as a redox mediator than as a catholyte.

ARTICLE INFO

Keywords:

Lithium flow battery
Lithium-sulfur flow battery
Dimethyl trisulfide
Redox mediator
Redox-targeting

ABSTRACT

The lithium-sulfur flow battery (LSFB) is a new addition to the rechargeable lithium flow batteries (LFBs) where sulfur or a sulfur compound is used as the cathode material against the lithium anode. We report here our evaluation of an organic sulfide - dimethyl trisulfide (DMTS), as 1) a catholyte of a LFB and 2) a multi-electron redox mediator for discharging and charging a solid sulfur cathode without any conductive additives. The latter configuration is also known as the redox-targeting lithium-sulfur flow battery (RTLSFB). The LFB provides an initial discharge capacity of 131.5 mAh g_{DMTS}^{-1} (1.66 Ah L^{-1}), which decreases to 59 mAh g_{DMTS}^{-1} (0.75 Ah L^{-1}) after 40 cycles. The RTLSFB delivers a significantly higher application performance - initial discharge capacity of 1225.3 mAh g_{sulfur}^{-1} (3.83 Ah L^{-1}), for which 1030.9 mAh g_{sulfur}^{-1} (3.23 Ah L^{-1}) is still available after 40 cycles. The significant increase in the discharge and charge duration of the LFB after sulfur addition indicates that DMTS is better used as a redox mediator in a RTLSFB than as a catholyte in a LFB.

1. Introduction

The accelerated growth of portable electronic products, electric vehicles, and smart grids has greatly increased the demand for battery-based energy storage devices [1–3]. While rechargeable lithium-ion batteries (LIBs) have been filling the demand for the past several decades [4], their limited energy density due to the constraints in the intercalation chemistries of the cathode (e.g. $LiCoO_2$) and anode (e.g. graphite) materials, is a technical concern [5,6]. A transition from intercalation chemistry to conversion chemistry is necessary to increase the battery energy density [7]. Elemental sulfur, as a lightweight two-electron conversion cathode material, offers a high theoretical specific capacity of 1675 mAh g^{-1} . Sulfur is also abundant in nature, low cost and environmentally benign. When sulfur is coupled to metallic lithium, the resulting Li-S battery can provide 2600 Wh kg^{-1} of energy density, about tenfold the energy density of the LIBs, making it an appealing alternative for the next-generation high energy-density

rechargeable batteries [8–10]. However, the electrically insulating property of sulfur and its discharge products (Li_2S_2 , Li_2S), and the redox-shuttling of soluble polysulfide intermediates between the two electrodes during charge and discharge (“the polysulfide shuttle”), result in low sulfur utilization, low coulombic efficiency and rapid capacity fading. Significant progress has been made in the last decade to address these issues, and the most common approach is sulfur immobilization within various host materials [11–20]. Manthiram and co-workers extended the concept to include lithium polysulfides as the cathode material, and stored them as adsorbed species in a porous electrode. Significantly improved sulfur loading and cycle stability were claimed [21]. Dissolved lithium polysulfides can also be used as a recirculating catholyte in a flow battery, as shown by the work of Chiang and co-workers [22]. These studies demonstrated the viability of using sulfur-based cathode materials or polysulfides for the development of Li-S batteries.

There are still technical challenges. For static Li-S batteries, the

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highly insulating property of sulfur requires the use of a conductive host material and/or a conductive additive in excess, resulting in a loss of energy density. For Li-S flow batteries (LSFBs), the deposition of insoluble discharged products ($\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$) on the porous carbon current collector can reduce battery life by flow channel blockage. The Cui group proposed a compromise solution by reducing the battery operating voltage window. The formation of $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ was averted and capacity was constant for 2000 cycles. The penalty was the decrease of the discharge capacity to 210 mAh g^{-1} [23]. Very recently, we demonstrated a redox-targeting lithium-sulfur flow battery (RTLFSB) where two single-electron redox mediators were used to respectively discharge and charge a sulfur/polymer composite [24], based on the principle of redox-targeting [25]. The tandem use of two redox mediators which are air and moisture sensitive was an inconvenience. In this study, we present a new RTLFSB design, where dimethyl trisulfide (DMTS, $\text{CH}_3\text{SSSCH}_3$) is used as a multi-electron redox mediator to discharge and charge a sulfur/activated carbon felt (S/ACF) composites. Liquid DMTS was previously used as the cathode material of a static Li-S battery [26]. We observed that it has redox potentials which are well-matched for targeting the S/ Li_2S conversion in Li-S batteries. We therefore envisaged the possibility of using DMTS to replace the dual redox mediators in RTLFSBs. The experimental measurements corroborated our expectation - a significant improvement of the flow battery performance was shown by using DMTS as a single two-electron redox mediator.

2. Experimental

2.1. Chemicals and materials

Lithium foil (99.9%, 0.75 mm thickness), sublimed sulfur (99.5%), lithium bis(trifluoromethane sulfonimide) (LiTFSI, $\geq 99\%$), lithium nitrate (LiNO_3 , 99.99%), tetraethylene glycol dimethyl ether (TEGDME, $\geq 99\%$), 1-methyl-2-pyrrolidinone (NMP, 99.5%), dimethyl trisulfide (DMTS, $\geq 98\%$) and sodium hydroxide (NaOH, $\geq 98\%$) from Sigma-Aldrich; carbon disulfide (CS_2 , $\geq 99.9\%$) from Acros Organics; carbon felt (CF, ≥ 99.9 , 5 mm in thickness) from HCS Scientific & Chemical Pte Ltd, and Toray carbon paper from Alfa Aesar, were used as received other than TEGDME, where molecular sieves were used to remove residual water before use.

2.2. Preparation of standard electrolyte and DMTS catholyte

The standard electrolyte for lithium flow battery (LFB) and redox-targeting lithium sulfur flow battery (RTLFSB) was 1.0 M LiTFSI and 0.4 M LiNO_3 in TEGDME. The DMTS catholyte for LFB and RTLFSB was prepared by dissolving 1.0 M LiTFSI, 0.4 M LiNO_3 and 0.1 M DMTS in TEGDME.

2.3. Preparation of activated carbon felt (ACF)

Activated carbon felt (ACF) was prepared by activating CF with NaOH at high temperature. In brief, a CF was first punched into 12 mm diameter round discs, and immersed into a NaOH solution (40 wt%) for 12 h. The alkali-treated carbon discs were oven-dried at 100°C for several hours to remove the residual water, and then heated at 800°C for 2 h in flowing N_2 in a tube furnace. The activated carbon discs were rinsed with distilled water for several times and vacuum-dried at 100°C .

2.4. Preparation of free-standing S/ACF composites

Free-standing S/ACF composites was prepared by a simple dissolution-heat treatment process. Sublimed sulfur was first dissolved in CS_2 to a concentration of 10 mg ml^{-1} . The as-prepared ACF was then submerged into the S/ CS_2 solution. After slow evaporation of CS_2 , the

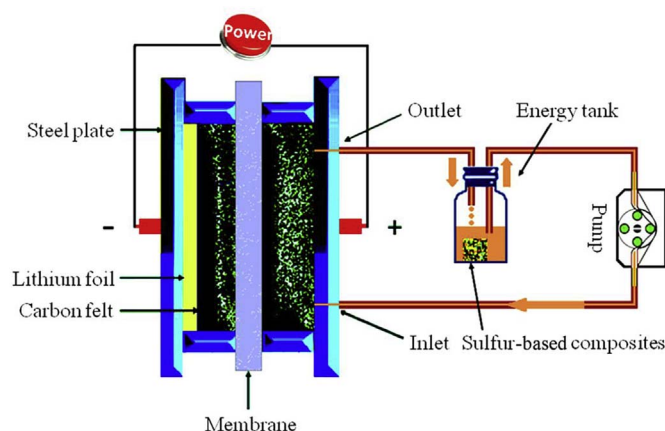


Fig. 1. Schematic of the experimental RTLFSB.

sulfur-impregnated S/ACF was transferred to an Ar-filled PTFE autoclave; and heated at 155°C for 12 h. Free-standing S/ACF composites was harvested after cooling to room temperature.

2.5. Electrochemical measurements

Coin cells (CR2025) were used for the cyclic voltammetry (CV) measurements of DMTS catholyte and S/ACF composites. The cell for measuring the CV of DMTS catholyte was assembled using a Li foil anode, a Celgard-2325 membrane separator, and a Toray carbon paper imbibed with 0.05 ml of DMTS catholyte as the cathode. For the CV measurement of S/ACF composites, the free-standing S/ACF composites was first ground into a fine powder. A homogeneous slurry containing the ground S/ACF powder (60 wt%), Super P carbon (30 wt%) and PVDF (10 wt%) was drop-cast on an aluminum foil current collector. All cells were assembled in the same Ar-filled MBRAUN glove box. Voltammograms were measured by an Auto Lab FRA2 type III electrochemical system at 0.2 mV s^{-1} . The cells were discharged and charged galvanostatically at 1.0 mA cm^{-2} , using a Neware BTS-5V battery tester.

2.6. Structure and morphology characterization

The structure and morphology of the CF, ACF, and S/ACF composites before and after cycling were examined by X-ray diffraction (XRD; Bruker D8) and field emission scanning electron microscopy (FESEM; JEOL JSM-6700F). The ^1H NMR spectra of the pristine DMTS, reaction intermediates and products at different depths of discharge were measured by Nuclear Magnetic Resonance Spectroscopy (NMR, Bruker AVANCE III HD 500 MHz).

3. Results and discussion

Fig. 1 shows the schematic of the RTLFSB. Two stainless steel plates with a centered circular recess and an active contact area of $\sim 3.14 \text{ cm}^2$ are used as the cathode and anode end plates. On the left-hand side of the electrochemical cell is a “hybrid” anode formed by stacking a Li foil with a carbon felt (CF), which buffers the lithiation and delithiation reactions [27]. The anode compartment is injected with the standard electrolyte of 1.0 M lithium bis(trifluoromethane sulfonimide) (LiTFSI) and 0.4 M lithium nitrate (LiNO_3) in tetraethylene glycol dimethyl ether (TEGDME). LiNO_3 is introduced as an electrolyte additive to inhibit the passivation of metallic Li by the polysulfide shuttle [28]. The “hybrid” anode is separated from the cathode compartment by two Celgard-2325 membranes. The cathode is also occupied by a CF, the pores of which are the flow channels for the recirculating catholyte. The energy tank to the right of the electrochemical cell stores the DMTS catholyte and the

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