A simple approach for making a viable, safe, and high-performances lithium-sulfur battery

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HIGHLIGHTS

- A safe DEGDME-LiTFSI is studied as glyme electrolyte for Li/S battery.
- The electrolyte is characterized by NMR and EIS for high energy lithium metal battery.
- Composite cathode is prepared by melting elemental sulfur into MWCNTs.
- The Li/S cell shows capacity ranging from 1300 mAh g^{-1} to 900 mAh g^{-1}.
- A practical energy higher than 400 Wh kg^{-1} is estimated for the Li/S battery.

GRAPHICAL ABSTRACT
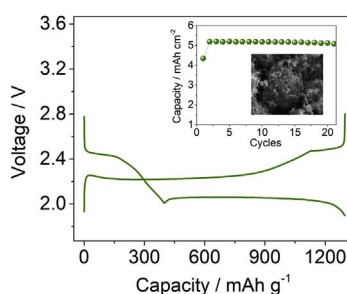
ABSTRACT

We report an electrolyte with low flammability, based on diethylene glycol dimethyl ether (DEGDME) dissolving lithium bis-trifluoromethane sulfonimidate (LiTFSI), and lithium nitrate ($LiNO_3$) for high-performances lithium/sulfur battery. Self-diffusion coefficients, conductivity, and lithium transport number of the electrolyte are obtained by nuclear magnetic resonance and electrochemical impedance spectroscopy. Interface stability, lithium stripping/deposition ability, and the electrochemical stability window of the electrolyte are determined by voltammetry and impedance spectroscopy. The tests suggest conductivity higher than 10^{-2} S cm^{-1}, lithium transport number of about 0.5, electrochemical stability extending from 0 V to 4.6 V, and excellent compatibility with lithium metal. A composite cathode using sulfur and multi walled carbon nanotubes (MWCNTs) is characterized in terms of structure and morphology by X-ray diffraction and scanning electron microscopy. The study shows spherical flakes in which the carbon nanotubes protect the crystalline sulfur from excessive dissolution, and create the optimal host for allowing the proper cell operation. The Li/S cell reveals highly reversible process during charge/discharge cycles, fast kinetic, and lithium diffusion coefficient in the sulfur electrode ranging from 10^{-12} to 10^{-10} cm^2 s^{-1}. The cell evidences a coulombic efficiency approaching 100%, capacity from 1300 mAh g^{-1} to 900 mAh g^{-1} and practical energy density higher than 400 Wh kg^{-1}.

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1. Introduction

Among the several batteries proposed during the last decades, the lithium ion battery is undoubtedly the most attractive one due to its remarkable energy and power contents [1,2]. Increasing interest on new electrochemical energy storage systems characterized by high performance has been recently triggered by the rapid spread of portable electronics, and the recent challenge of hybrid electric (HEVs), plug-in hybrid (PHEVs), and full electric (EVs) vehicles, suggested for limiting climate changes driven from excessive greenhouse gasses emission by massive use of fossil fuels [3–5]. Therefore, the emerging needs may be fulfilled by cheap, highly efficient and energetic batteries, rather than the most widespread lithium ion system in which the use of expensive $LiCoO_2$ limits the energy density to about 550 Wh Kg^{-1} with respect to the cathode mass and drastically increases the costs [6]. The lithium/sulfur battery, due to limited cost, very high theoretical capacity (1675 mAh g^{-1}) and energy density (3600 Wh Kg^{-1}), as well as environmental compatibility, appears to be one of the most suitable candidates for overcoming the intrinsic limits of common batteries [7]. The Li/S electrochemical reaction, $16Li + S_8 \leftrightarrow 8Li_2S$ [8,9], evolves between 2.4 V and 2.1 V and leads to phase changes [10] with production of several polysulfides moieties and radicals [11–13]. Unfortunately, polysulfides dissolve into the electrolytes during the discharge, shuttle between cathode and anode during charge, and directly react by electrochemical short circuit with lithium leading to low coulombic efficiency, loss of cathode mass, and fast capacity decay, particularly in organic carbonate solutions commonly used in the commercial lithium-ion battery [14]. Hence, a new classes of electrolyte mainly based on ether bond, such as dioxolane (DOL), dimethoxyethane (DME), end-capped glymes, and polyethyleneoxide (PEO), appeared to be a valid alternative for application in Li/S battery [15–17]. DOL/DME mixture containing LiTFSI salt is presently the most used electrolyte for Li/S battery, due to the high ionic conductivity promoted by the ether bond which actually drives the lithium ion transport [18]. This electrolyte is generally upgraded by the use of $LiNO_3$ as sacrificial film forming agent to stabilize the lithium/electrolyte interface [19–21], while further improvements of the cell performance may be obtained using alternative separators added by carbon to physically trap the polysulfides on the cathode side [22–24], or by metal oxides to chemically retain the polysulfides on electroactive sites of the cathode surface [25–27]. Many efforts have been devoted to develop composite cathodes combining sulfur and functional carbons, such as nano-sphere [28], carbon nanosheets [29], nanotubes [30], and mesoporous carbons [31], suitable for efficiently hosting sulfur and strongly adsorbing polysulfides during cycles. However, the most successful approaches involved very volatile and flammable DOL-DME-based electrolyte [32], or very safe but poorly conductive viscous glyme-based ones [33–35], as well as highly engineered and not particularly cost effective sulfur cathodes [36], which have led to poorly scalable Li/S cells. A comparative study focused on the determination of the most suitable thermal, transport and electrochemical characteristics of various ether-based electrolytes differing by chain length, using the lithium triflate ($LiCF_3SO_3$) salt, suggested the DEGDME glyme-based electrolyte as a promising material for application in lithium cell [17]. The study reported a proof of concept Li/S battery using a ball milled S-C composite which was preliminarily studied over 25 cycles at low current rate (C/20 = 83.75 mA g^{-1}). Therefore, we study in this work a new electrolyte based on DEGDME solvent, LiTFSI salt, and $LiNO_3$ additive, advantageously combining the high safety level of the glyme, and a high conductivity expected by the low viscosity and the high solvating ability of the short-chain DEGDME. The solution is investigated by suitably combining NMR and electrochemistry at various temperatures, and adopted as the electrolyte media in a high performance Li/S cell in combination with a S-MWCNTs composite prepared by melting commercial sulfur and MWCNTs, and cast on a carbon cloth with increasing loadings. The sulfur electrode is fully studied, and the kinetics aspects of its electrochemical process in lithium cell are originally clarified by adopting the Randles-Sevcik equation during cycling voltammetry. The improved characteristics of the electrode/electrolyte configuration here reported lead to substantial increase of the cell cycle life (to over 120 cycles), the rate capability, and the energy density. The high safety content and significant performance of the Li/S battery configuration studied in this work may actually suggest a sustainable scaling-up of an efficient high energy storage system.

2. Experimental

2.1. Materials

Diethylene glycol dimethyl ether $(CH_3OCH_2CH_2)_2O$ (Sigma-Aldrich), denoted hereafter by DEGDME, was dried before use with molecular sieves (5 Å) until the water content was below 10 ppm as measured by a 831 Karl Fischer Coulometer (Metrohm). Lithium bis-trifluoromethanesulfonimidate ($LiN(SO_2CF_3)_2$, LiTFSI) and lithium nitrate ($LiNO_3$), from Sigma-Aldrich, were separately dried under vacuum overnight at 80 °C. All the samples were subsequently handled in argon filled glove box, with oxygen and moisture content lower than 1 ppm. LiTFSI was dissolved in DEGDME using a salt to solvent ratio of 1 mol kg^{-1} to obtain the electrolyte (indicated by DEGDME-LiTFSI). The electrolyte for battery application (DEGDME-LiTFSI-$LiNO_3$) was prepared by dissolving $LiNO_3$ (film forming sacrificial additive with salt to solvent ratio of 1 mol kg^{-1}) and LiTFSI (ion conductor with salt to solvent ratio 1 mol kg^{-1}) in DEGDME. The S-carbon powder was prepared by melting elemental sulfur (Sigma-Aldrich) at 135 °C and mixing with multi-walled carbon nanotubes MWCNTs (from Sigma-Aldrich) at a 60:40 S to C weight ratio. The sample was stirred for 3 h under heating at 135 °C in order to obtain a homogeneous mixture, cooled down to room temperature and refined by mortar. The electrode slurry was prepared by mixing the S-MWCNTs-S powder, Super P Carbon conductive additive (Timcal) and polyvinylidene difluoride binder (PVdF; Solvay Solef) in 80:10:10 wt ratio, using N-methylpyrrolidone (NMP) as solvent. The slurry was cast onto carbon cloth support (GDL ELAT) by the Doctor Blade method with a wet thickness varying from 300 μm to 600 μm, in order to obtain various sulfur loadings. The electrode foils were punched into 10 mm and 16 mm disks, dried for 48 h at 60 °C under vacuum before assembling the cell in the argon filled glovebox with oxygen and water content lower than 1 ppm. The sulfur loading of the final electrodes was 2, 2.5, 3 and 4 mg cm^{-2}.

2.2. Electrolyte characterization

The self-diffusion coefficients of the ^1H, ^{19}F, and ^7Li nuclei in the DEGDME-LiTFSI electrolyte were measured by a Bruker 400 Advance III NMR spectrometer with screw-cap gastight NMR tubes in order to overcome possible evaporation along the temperature scan range from 20 °C to 70 °C. The data were collected every 10 °C for each nucleus using a double-stimulated echo sequence with pulsed field gradients (PFG) to suppress convection. The gradient pulse strength was increased linearly in 32 steps from 1 to 45 G cm^{-1}, and the gradient pulse duration (δ) was of 1.4–4 ms with a diffusion delay (Δ) of 200–400 ms. Eddy current effects were avoided by using a longitudinal eddy-current delay (LED) of 5 ms.

The self-diffusion coefficients were calculated by eq. (1):

$$I = I_0 e^{-D\gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right)} \tag{1}$$

where I is the signal integral, D is the self-diffusion coefficient, γ is the gyromagnetic ratio of the studied nucleus, g is the gradient pulse strength, δ is the gradient pulse duration and Δ is the diffusion delay. The error on the self-diffusion coefficient is about 3–5% [37].

The lithium transport number (t^+) was calculated from the self-diffusion coefficient by eq. (2):