

Sulfolane as a co-solvent for carbonate-electrolytes in lithium-ion batteries using a LiMn_2O_4 cathode

Phuong Hue Luu¹, Phuong Hue Tran¹, Hoang Van Nguyen^{1,2}, An Le Bao Phan³,
Oanh Hoang Nguyen¹, Man Van Tran^{1,2}, Phung My Loan Le^{1,2}, Thanh Duy Vo^{2*}

¹Department of Physical Chemistry, Faculty of Chemistry, University of Science, Vietnam National University, Ho Chi Minh City,
227 Nguyen Van Cu Street, Ward 4, District 5, Ho Chi Minh City, Vietnam

²Applied Physical Chemistry Laboratory, Faculty of Chemistry, University of Science, Vietnam National University, Ho Chi Minh City,
227 Nguyen Van Cu Street, Ward 4, District 5, Ho Chi Minh City, Vietnam

³University of Maryland, Virginia, United States, College Park, Maryland State, USA

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Abstract:

In this study, we aimed to evaluate the effect of sulfolane (SL) as a co-solvent in conventional carbonate-based electrolytes and its compatibility with a LiMn_2O_4 (LMO) cathode. The amount of SL was varied from 10 to 50 vol.% in an EC-DMC mixture (1:1 vol. ratio) within a 1.0-M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt. The thermal properties of the electrolytes were studied using thermogravimetric analysis (TGA). Solvent flammability was measured via self-extinguishing time (SET) and ignition time indexes while viscosity was gauged by the Ostwald method. Ionic conductivity was evaluated by electrochemical impedance spectroscopy (EIS). Electrochemical techniques such as cyclic voltammetry (CV) and galvanostatic cycling with potential limitation (GCPL) were carried out to evaluate battery performance with the selected electrolytes. The results indicated that an increasing proportion of SL leads to an enhancement of the thermal and oxidation stability of the electrolytes. At 20-vol.% SL and below, the as-synthesized electrolytes exhibited a high ionic conductivity of 7.45 mS.cm^{-1} (25°C) and enabled LMO to deliver a specific capacity of 103 mAh.g^{-1} with a capacity retention of 92% after 20 cycles at C/10 rate. Due to such favourable properties, SL can be used as a co-solvent in EC-DMC systems to enhance the safety of lithium-ion batteries under high voltage conditions.

Keywords: conductivity, electrolytes, lithium-ion batteries, sulfolane, viscosity.

Classification number: 2.2

1. Introduction

Sulfolane (SL), also known as thiolane 1,1-dioxane, is a sulfur-organic compound with a highly polar double bond $\text{S}=\text{O}$ as shown in Fig. 1.

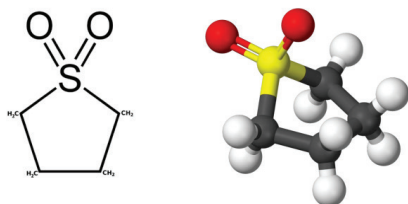


Fig. 1. Chemical formula and structure of SL.

The key features of SL are good thermal stability (decomposed at 220°C), high ignition temperature of 528°C , high flash point (FP) of 165°C , excellent oxidation resistance (above 5.0 V vs. Li^+/Li), and high polarity (water solubility of 1.266 g.l^{-1} at 20°C) [1, 2]. Owing to these advantages, SL derivatives have been considered promising electrolytes for high working potentials and the improvement of lithium-

ion battery safety. Specifically, Xu's group utilized pure SL as a non-carbonate solvent with a cathode material of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ for half and full-cell tests and obtained a capacity of about 110 mAh.g^{-1} in the first 10 cycles [3]. However, SL-based electrolytes have high viscosity and an inability to stabilize solid electrolyte interphase layers on the surface of a graphite anode. Indeed, SL has been often used in combination with carbonate-based electrolytes like diethyl carbonate (DEC), dimethyl carbonate (DMC), and ethylene carbonate (EC) to improve the electrochemical properties of electrolytic mixtures [4]. In particular, Cai, et al. (2017) [5] added 2 vol.% SL to 1.0 M $\text{LiPF}_6/\text{EC-DMC}$ (1:1) and demonstrated that the SL additive enabled oxidation resistance as well as enhanced the charge-discharge performance of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC111)/graphite batteries. As a result, the solution containing SL had an oxidation potential up to 5.0 V (vs. Li^+/Li), 4.25 V higher than electrolytes without SL. Furthermore, the long-term cycling stability of electrolytes containing SL was significantly improved in specific capacity and Coulombic efficiency as well. Abouimrane, et al. (2009) [6] tested the

*Corresponding author: Email: vodthanh@hcmus.edu.vn

ignition of the two electrolytes 1.0-M LiPF₆/EC-EMC (3:7) and 1.0 M LiPF₆/SL-EMC (1:1) exposed to a 1200°C flame in the air. The EC electrolyte ignited vigorously within 2 s while the electrolyte containing SL needed about 45 s to become weakly flamed, which indicates significantly reduced flash points. Highly concentrated sulfone-based electrolytes with lithium bis(fluorosulfonylimide) were recently suggested for a high voltage cathode such as LiNi_{0.5}Mn_{1.5}O₄ or LiCoPO₄ because of synergistic interphase (CEI/SEI) in LiF [3]. Ren, et al. (2018) [7] also worked on localized high-concentration sulfone-based electrolytes and found lithium-metal cells with high efficiency.

Herein, our work aims to investigate the thermal properties, physico-chemical, and electrochemical properties of SL substitution in 1:1 EC-DMC-based electrolytes as well as their compatibility to the high voltage cathode material LiMn₂O₄ (LMO).

2. Experimental

2.1. Preparation of electrolytes and physico-chemical characterization

SL, EC, DMC, and LiTFSI were purchased from Sigma-Aldrich with high purity (>99%) and stored inside an Argon filled-glovebox with controlled oxygen and water concentration less than 5 ppm.

The electrolytes were prepared by dissolving a lithium salt in mixtures of EC: DMC: SL (EDS) at different volume ratios and was kept stirring for 12 h in the glovebox. The composition of the prepared electrolytes is described in Table 1.

Table 1. The solvent composition of prepared electrolytes.

Abbreviation	vol.% EC	vol.% DMC	vol.% SL	C _{LiTFSI} (M)
EDS550	50	50	0	1
EDS541	50	40	10	1
EDS532	50	30	20	1
EDS523	50	20	30	1
EDS514	50	10	40	1
EDS505	50	0	50	1

The weight loss of as-prepared electrolytes at different temperatures were analysed by TGA between 0°C and 600°C with a heating rate of 10°C.min⁻¹ in an N₂ atmosphere on a thermal analysis LABSYS Evo (Setaram, France).

SET is widely applied to assess the fired resistance of electrolytes. In a typical measurement, a fixed amount of solvent was immobilized on a 14-mm diameter Whatman separator piece then exposed to a burner for 3 s. The distance between a burner and sample was 13 cm. The SET value (s/g) was recorded by measuring the burning time of sample after removal from the flame source, which was then normalized with solvent mass [8]. Each as-prepared sample was measured 3 times in order to get an average value.

The absolute viscosity of the electrolyte solution was determined by an Ostwald viscometer (Canon, Japan) using the following equation:

$$\eta = K.d.t \quad (1)$$

where K is a viscometer constant ($K=0.035$), d is the electrolyte's density, and t is the time it takes for the electrolyte to flow entirely through the capillary of the viscometer. The sample temperature was adjusted by a temperature-controlled chamber.

The specific ionic conductivity of an electrolyte solution is calculated by the following equation:

$$\kappa = \frac{L}{S} \cdot \frac{1}{R} = K \cdot \frac{1}{R} \quad (2)$$

where κ is the specific conductivity (S/cm), K is the cell constant (cm⁻¹), R is resistance of the solution (Ω), S is the surface area of the Pt electrode (cm²), and L is the distance between two electrodes (cm). To measure the electrolyte resistance, 0.5 ml of as-prepared solution was added into a dip-type glass conductivity cell (CDC749 conductivity cell, Radiometer) and then kept at the desired temperature for 120 min before each measurement. The conductivity cell was connected to an electrochemical device VSP (Biologics, France) to perform the measurement. A 10-mV AC potential was applied to the cell over a frequency range of 10 mHz to 1 MHz. The cell was initially calibrated using a 0.1 M KCl solution at 25°C to measure the K value.

2.2. Coin cell assembling and electrochemical performance

The cathode slurry was prepared by mixing commercial LMO material (MTI, USA), conductive carbon AB/graphite (Japan) and PVDF-HFP (10% in N-methyl pyrrolidone or NMP) as a binder in a mass ratio of 80:15:5. The as-prepared slurry was cast on aluminium foil, dried at 80°C for 15 h in vacuum, and finally cut out in 14-mm diameter circles.

Electrochemical measurements were conducted on the electrochemical device MPG-2 (Biologics, France). CV sweeping was performed to determine the electrochemical window of the electrolytes using a 1.0-ml three-electrode cell consisting of Pt wire and Ni grid as the working electrode and counter electrode, respectively. The reference electrode was an Ag wire embedded in a solution of 0.01 M AgNO₃ + 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile.

3. Results and discussion

3.1. Thermal properties of the electrolytes

In Fig. 2, the samples containing DMC revealed three weight loss stages based on the evaporation temperature of the three pure solvents in the mixture. Specifically, the first stage is the evaporation of DMC at 90°C. The second stage at 243°C could be involved with the evaporation of both EC and SL because their boiling temperatures are quite

close ($T_b=243^\circ\text{C}$ and 270°C for EC and SL, respectively). Finally, the weight loss step at 430°C consists of both SL evaporation and the decomposition of the LiTFSI salt. The weight loss percentages of these electrolytes and the corresponding onset temperature are detailed in Table 2. The practical boiling temperature values obtained from thermogravimetric curves closely coincided with those of the pristine solvents [9, 10].

Overall, the non-DMC electrolyte EDS505 shows only two mass loss stages at 243°C and 430°C that correspond to EC-SL evaporation and LiTFSI decomposition, respectively. This electrolyte also exhibits relatively high thermal stability (up to 270°C) due to the absence of the volatile solvent DMC ($T_b=90^\circ\text{C}$).

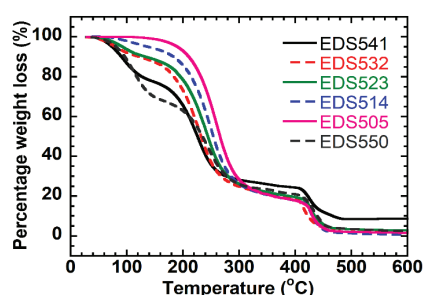


Fig. 2. Thermogravimetric curves of EC:DMC:SL+1 M LiTFSI with different volume ratios between SL and DMC.

In contrast, when adding SL to the EC-DMC electrolytes, the temperature associated with the first weight loss decreases sharply. Typically, the decomposition temperature of EDS550 (0 vol.% SL) and EDS523 (30 vol.% SL) are 112°C and 94°C , respectively. This could be attributed to different solvent polarization, for example, DMC has poor polarity ($\epsilon=3.20$) while the polarity of EC and SL ($\epsilon_{\text{EC}}=90$, $\epsilon_{\text{SL}}=43$) are strong [10, 11], which leads to micro-phase separation in these electrolyte systems. The samples with increasing SL amount in the electrolyte, namely, EDS541, EDS532, and EDS523, exhibited lower thermal stability owing to significant micro-phase separation. Interestingly, with an SL amount higher than 40 vol.%, the sample EDS514 reveals the first weight loss temperature higher than the other ones. This increase is ascribed to the hysteresis of DMC evaporation due to the significant increase of viscosity.

Table 2. The onset temperature at different stages of weight loss of SL mixed carbonate-based electrolytes.

Electrolyte	$T_{\text{onset}} (^\circ\text{C})$			Weight loss (%)		
	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3
EDS550	112	244	428	31.4	44.0	20.0
EDS541	98	227	426	27.2	50.6	16.3
EDS532	96	230	428	21.4	59.9	16.5
EDS523	94	235	426	12.1	67.6	17.1
EDS514	109	250	428	7.5	74.7	17.2
EDS505	-	266	427	-	80.4	16.8

Besides, the effect of SL on the flammability of electrolytes was evaluated by the value of SET in Table 3. The addition of a moderate amount of SL (≤ 20 vol.%) in the carbonate mixtures enhances their thermal stability. With the increase of SL content from 0 to 20 vol.%, the self-extinguishing time of the electrolytes reduced from 45 to 32 s.g $^{-1}$. When a small amount of SL was added to the electrolyte, the volatile DMC that had separated from the mixture ignited first, which lead to a combustion occurring in the gas or vapor phase followed by immediate self-extinguishing. Despite SL's high evaporation temperature and flash point compared to EC and DMC, low concentrations of SL had a negligible contribution to the combustion property of the electrolytes.

Table 3. SET values of SL-mixed electrolyte systems.

Electrolyte	% vol. SL	SET (s.g $^{-1}$)
EDS550	0	45
EDS541	10	34
EDS532	20	32
EDS523	30	59
EDS514	40	63
EDS505	50	67

When increasing the SL content from 30 to 50 vol.%, the SET value rose from 59, to 67 s.g $^{-1}$. As a fire-retardant, SL has a slow rate of ignition and low heat generation, which minimizes the amount of heat radiating to the surrounding environment. Indeed, SLs are mostly difficult to burn; however, once it was burnt, the fire lasted a very long time. This phenomenon has been similarly observed in previous studies [8, 11].

3.2. Viscosity and ionic conductivity of the electrolytes

The density, viscosity, and ionic conductivity of the carbonate electrolytes mixed with different vol.% SL are presented in Table 4. Ionic conductivity is one of the most critical properties of the application of electrolytes to Li-ion batteries. As shown in Fig. 3, two opposite directions of conductivity could be observed when increasing the SL content.

Figure 3 shows the relationship between ionic conductivity and viscosity for all the electrolytes. As SL content increases, the density and viscosity of these mixtures rose due to the high density and viscosity of SL ($d_{\text{SL}}=1.6$ g.cm $^{-3}$) compared with that of DMC and EC solvents ($d_{\text{DMC}}=1.069$ g.cm $^{-3}$, $d_{\text{EC}}=1.32$ g.cm $^{-3}$). The electrolyte EDS505 with 50 vol.% SL and no DMC solvent had the highest viscosity of 22.6 mPa.s.

The conductivity first increased with increasing SL content from 0 to 20 vol.%, then suddenly decreased with more SL content. The complicated change in conductivity can be explained by the combination of two factors: ionic solvation and viscosity. In principal, the high dielectric constant of SL ($\epsilon_{\text{SL}}=43.3$) could improve the solvating ability

of the solvent mixtures and reduce ion-ion interaction, resulting in enhanced lithium-ion mobility under the effect of electric fields. In parallel, due to the high viscosity of SL compared to EC and DMC, SL amounts greater than 20 vol.% significantly increase the viscosity of electrolytes, which mitigates lithium-ion mobility and dominates the effect of ion solvation. Thus, the ionic conductivity was totally penalized at high SL content. The sample EDS532 that contains 20 vol.% SL exhibited the highest conductivity (7.45 mS.cm^{-1} at 25°C). The viscosity and ionic conductivity need to be optimized in these carbonate-based electrolytes when adding SL.

Table 4. Density, viscosity, ionic conductivity, and oxidation limit potential (E_{ox}) of SL-based electrolytes.

Mixture	Density (g.cm^{-3})	Viscosity (mPa.s)	Ionic conductivity (mS.cm^{-1})	E_{ox} (V) vs. Li^+/Li
EDS550	1.196	6.38	4.82	4.57
EDS541	1.215	7.52	6.10	4.68
EDS532	1.234	10.40	7.45	4.72
EDS523	1.254	15.88	5.37	4.77
EDS514	1.273	20.93	3.22	4.89
EDS505	1.291	22.62	2.03	4.97

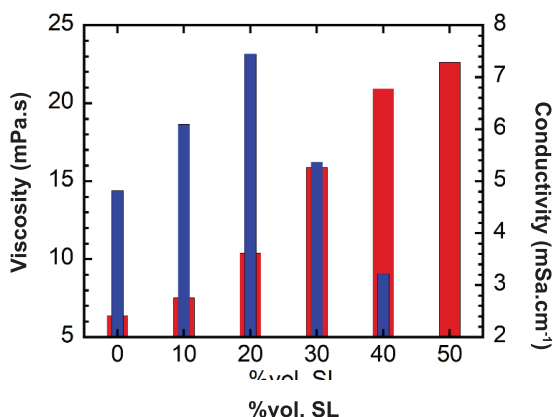


Fig. 3. Relationship between ionic conductivity and viscosity of SL-based electrolytes.

3.3. Electrochemical stability of the electrolytes

Cyclic voltammograms were performed to determine the oxidation stability of the SL-based electrolytes in the range 3.5–5.6 V (Fig. 4). The oxidation limit potential of the electrolytes were determined in the forward scan where the current reaches 0.0025 mA. The oxidation limit potential of the electrolytes containing SL reaches about 4.8 V vs. Li^+/Li , which is superior to conventional carbonate solvents or electrolytes containing only EC-DMC (EDS550). The oxidation stability rose quickly as SL content was gradually increased. Therefore, the highest electrochemical oxidation (E_{ox}) value of about 5.0 V belongs to the EDS505 electrolyte containing 50 vol.% SL (Table 4).

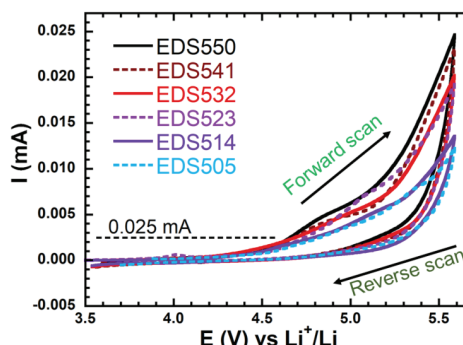


Fig. 4. Cyclic voltammograms of SL-mixed carbonate solvents + 1 M LiTFSI electrolytes.

3.4. Cycling performance of Li/LMO half-cell in the prepared electrolytes

Samples EDS532 and EDS523 with 20 and 30 vol.% SL were selected for cycling tests in a Li|LMO half-cell and compared to the cell with non-SL electrolyte (EDS550). Charge-discharge profiles of the cells showed two small plateaus at about 3.9 V and 4.1 V with a small shoulder corresponding to the two-step embedding and removal of lithium ions in different stages of the electrochemical reaction, which are also consistent with the CV curves. According to Fig. 5, EDS532 reveals the highest capacity of about 103 mAh.g^{-1} (theoretical capacity is 148 mAh.g^{-1}) and its Coulomb efficiency reaches over 95%, indicating a good compatibility between cathode materials and the investigated electrolytes.

In terms of discharge capacity, the LMO cell with the EDS532 electrolyte shows the best value at the first cycle and remains at 95 mAh.g^{-1} after 20 cycles. Both EDS550 and EDS523 have the same initial reversible capacity of 95 mAh.g^{-1} . While the capacity of EDS550 decreased to less than 85 mAh.g^{-1} after only 5 cycles, that of EDS523 remained around 90 mAh.g^{-1} . After the fifth cycle, EDS523 demonstrated a linear decrease in discharge capacity. In contrast, EDS550 showed a stable range for only 8 cycles, then continuously decreased at the same rate as EDS523 to 75 mAh.g^{-1} after 20 cycles.

Regarding Coulombic efficiency, all electrolyte systems showed various degrees of fluctuation from mild (EDS523) to high (EDS550) and remained at over 90% through 20 cycles.

The primary factor determining the discharge capability of EDS550 is ionic conduction and solvation phenomena. The sample with the lowest dielectric constant and highest DMC proportion, like EDS550, showed the electrolyte weakly solvated Li^+ resulting in low ionic conductivity and low specific discharge capacity. In the SL-based electrolyte, the highest dielectric constant of SL compared to other solvents is beneficial to ion dissociation leading to an increase of mobile Li^+ ions. However, its high viscosity penalizes the

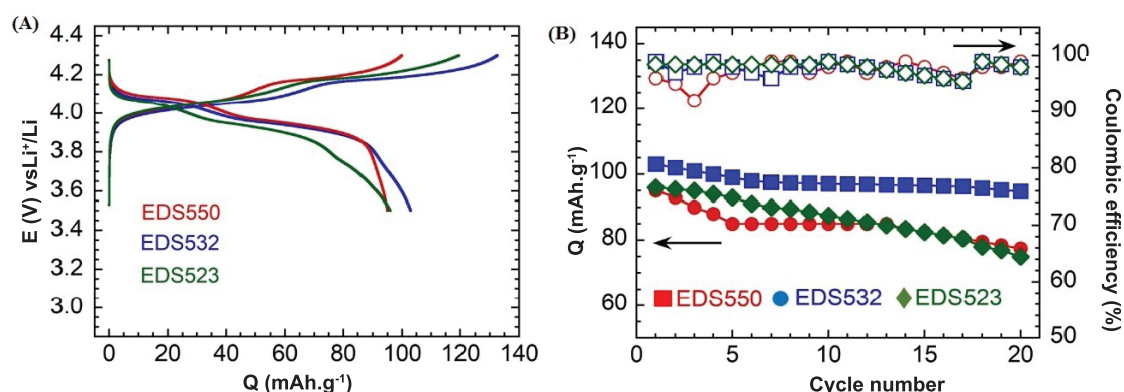


Fig. 5. First charge-discharge profiles (A) and plot of capacity and Coulombic efficiency against cycle number (B) of half-cells containing EDS550, EDS523 and EDS532 electrolyte.

movement of Li^+ ions, which means a decrease of charge mobility rate and discharge ability. Indeed, the EDS523 with 30 vol.% SL shows a linear decrease in capacity due to high viscosity resulting in hindered ionic mobility.

With an average proportion of SL (about 20 %wt.), EDS532 show a good stability after 20 cycles. The capacity loss is as low as 8%, and the Coulombic efficiency ranges from 100 to 93%.

4. Conclusions

We have studied electrolytes with different vol.% of SL in EC-DMC (1:1)/1.0 M LiTFSI. The electrolytes are thermally stable up to 100°C and their thermal stability increased with increasing SL content. The SL addition significantly enhanced the flammability resistance of the carbonate-based electrolytes. The oxidation limit of the electrolyte systems enlarged to 4.8 V vs. Li^+/Li . Although SL addition increased the viscosity of the electrolytes, the optimized amount of SL could be as low as 20 vol.% to reach the highest ionic conductivity for a mixed SL-carbonate electrolyte. Thus, the EDS532 sample exhibited the highest capacity (103 mAh.g^{-1}) and the most stable cycling after 20 cycles (efficiency above 90%).

CRedit author statement

Phuong Hue Luu: Conceptualization, Methodology, Software; Phuong Hue Tran: Data curation, Writing-Original draft preparation; Hoang Van Nguyen: Visualization, Investigation; An Le Bao Phan: Software, Validation; Oanh Hoang Nguyen: Software, Validation; Man Van Tran: Writing and Reviewing; Phung My Loan Le: Conceptualisation, Methodology and Writing; Thanh Duy Vo: Writing - Reviewing and Editing.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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