Electrochemical performance of sulfone-based electrolytes in sodium ion battery with NaNi1/3Mn1/3Co1/3O2 layered cathode

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ABSTRACT
Introduction: Sulfolane (SL), having an edge of low melting point over other sulfones, has been adopted as an electrolyte co-solvent for lithium-ion battery (LIB), as it exhibits high stability against oxidation and combustion while not causing much side effects to the battery electrochemistry. It is therefore expected that SL may serve as a safety-enhancing agent in sodium-ion battery (SIB). To evaluate the effect of SL content on the behavior of common carbonate-based sodium electrolytes as well as the compatibility of SL-based electrolytes with NaNi1/3Mn1/3Co1/3O2 (NaNMC) cathode, mixtures of 0, 10, 20, 30 or 50% vol. SL and each of the following, EC:PC 1:1 vol. (EP11), ECDMC 1:1 vol. (ED11), EC:PC:DMC 1:1:3 vol. (EPD113) and EC:PC:DMC 3:1:1 vol. (EPD311), with or without 1M NaClO₄, were studied with regard to both inherent properties and performance in NaNMC half-cells. Methods: Solvent flammability was evaluated via the self-extinguishing time (SET) and ignition time indexes. Conductivity and viscosity were respectively measured by Electrochemical Impedance Spectroscopy (EIS) and Ostwald method. Electrochemical techniques, i.e. Cyclic Voltammetry (CV) and Galvanostatic Cycling with Potential Limitation (GCPL), were used to test the sodium-ion battery performance. Results: A moderate amount of SL (typically below 30% vol.) proved to enhance both electrolyte non-flammability and self-extinguishing behavior, while maintaining an acceptable compromising rate in viscosity and conductivity. Amongst 30%-SL electrolytes, EPD311-based ones allow the best Na⁺ diffusion when combined with NaNMC cathode in sodium half-cell configuration. The corresponding system gives satisfactory performance: initial specific capacity of 97 mAh.g⁻¹, 92% capacity retention, and above 90% reversibility after 30 cycles at C/10 rate. Conclusion: SL can be used as a stabilizing co-solvent for SIB, but its content should be limited to below 30% vol. to ensure its effectiveness. Key words: sulfolane, electrolyte Na-ion battery, non-flammable, self-extinguishing time, ignition time

INTRODUCTION
Sodium-ion battery (SIB) has recently emerged as a promising alternative to the prevailing lithium-ion battery (LIB), due to its better sustainability and suitability for large-scale applications, e.g. electric vehicles and grid storages. Similar to its lithium predecessor, SIBs generally suffer from unguaranteed fire safety that arises from high volatility and flammability of the commonly used electrolyte solvents, i.e. organic carbonates. Introducing a co-solvent with low vapor pressure and high burn-resistance, such as ionic liquids, sulfolanes and phosphates, proved to be a promising solution for this problem, as previously shown. Sulfolone compounds are well-known for their excellent stability towards oxidation, including oxidative combustion. Besides, due to high polarity arising from the two S-O bonds, they are able to allow good salt solvation and high charge-transport number. And although sulfolones are generally unable to form a protective layer on commonly-used graphitic anodes, it was discovered recently that the use of appropriate anode binder, Li salt and electrolyte additive may help. The only real limitation that prevents most sulfolones from being attractive as an ambient-temperature electrolyte co-solvent for LIB (as well as SIB in the future) is their point. Being one of the rare examples of low-melting sulfolones, sulfolane (SL, also known as tetramethylene sulfone) has unsurprisingly received much interest from the LIB community, either as an electrolyte solvent, co-solvent or additive. As expected, SL exhibits desirable properties for a safe electrolyte solvent: wide liquid range (melting point Tm = 27.5°C and boiling point Tb = 285°C), high flash point (Tf = 165°C) and high dielectric constant (ε = 60 at 25°C). The stability-related advantages have also been well-demonstrated to be inheritable to SL-based electrolytes without much compromise in electrochemical capability. For example, 1M LiPF₆ in SL:EMC

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1:1 vol., while being about 20 times less flammable than its counterpart (EC:EMC 3:7 vol.), was still able to work well in a LiNi0.5Mn1.5O4/Li4Ti5O12 full-cell, even after 1000 cycles at 2C rate. More recently, Kurc et al. showed that solutions of various Li salts in SL solvent, with or without a small amount of vinyl carbonate additive, exhibited comparable flash point to SL and remained finely stable after 20 cycles working in LiNO3 half-cell at up to C/2 rate.

Considering the analogies between LIB and SIB, we expect that SL acts as a powerful co-solvent for SIB electrolyte. To evaluate the effects of SL on the behavior of carbonate-based sodium electrolytes and estimate the appropriate SL content, we investigated the mixtures of 0, 10, 20, 30 or 50% vol. SL with each of the four common carbonate combinations, namely EC:PC 1:1 vol. (EP11), EC:DMC 1:1 vol. (ED11), EC:PC:DMC 1:1:3 vol. (EPD113) and EC:PC:DMC 3:1:1 vol. (EPD311), either in the absence (applied in flammability tests) or presence (all other tests) of 1M NaClO4. Important parameters of SL-contained electrolytes, including SET, ignition time, viscosity and conductivity, as well as their dependence of SL content were determined. We also managed to figure out a favorable range for SL content although the optimal value has yet to be concluded. The electrolytes with favorable SL content were then tested and compared in terms of electrochemical performance in NaNi1/3Mn1/3Co1/3O2 (NaNMC) half-cell.

**METHODS**

**Electrolyte and cathode composite preparation**

Carbonate solvents including ethylene carbonate (EC), dimethyl carbonate (DMC), propylene carbonate (PC), sulfolane (SL) and NaClO4 were purchased from Sigma-Aldrich (St. Louis, MO, USA) with high purity (> 99.0%) and stored in glove box under argon atmosphere ([H2O] < 10 ppm). Carbonate mixtures (EP11, ED11, EPD113 and EPD311) were first prepared by mixing the components, then mixed with 0, 10, 20, 30 or 50% vol. SL; 1M NaClO4 was finally added. At the end of each step, the mixtures were stirred for 8-12 hours. NaNi1/3Mn1/3Co1/3O2 was synthesized by co-precipitation method. The hydroxide precursor Ni1/3Mn1/3Co1/3(OH)2 was prepared by dripping 10 mL of 3M aqueous solution of Ni(NO3)2, Co(NO3)2 and Mn(CH3COO)2 following the stoichiometric ratio into 25 mL of 4M NaOH solution. The reacting system was kept at 50°C and stirred at 300 rpm for 15 hours. The product was then filtered at low pressure and washed by distilled water until pH became neutral. The powdered Ni1/3Mn1/3Co1/3(OH)2 was then dried under vacuum at 100°C for 15 hours. A homogeneous mixture of hydroxide product and Na2CO3 (5% excess) was calcined following a three-step solid state process: 500°C for 6 hours, 900°C for 36 hours, and then quenching immediately in Argon filled glove box.

Cathode composite was prepared by mixing 80% wt. NaNMC powder, 15% wt. carbon C65 (Timcal) and 5% wt. PTFE binder (Sigma-Aldrich). The resulting paste was laminated and then cut into 10-mm-diameter round disks. Both processes were carried out in glove box.

**Flammability test**

All flammability tests were performed on electrolyte solvents (carbonate-SL mixtures, without salt) only. Solvent flammability was assessed via two parameters: the self-extinguishing time (SET) and the ignition time. In the SET measurement (Figure 1a), a fixed amount of solvent immobilized on a 14-mm-diameter piece of Whatman paper was exposed to a burner for 3 s at the distance of 13 cm to trigger ignition. The time the sample continues to burn after removal from the flame, i.e. the SET, was recorded and normalized against solvent mass (as proposed by Xu et al.11). Regarding the ignition time measurement (Figure 1b), the solvent (100 µL, unless otherwise stated) was placed on a metallic container and ignited from the distance of 10 cm and the inclination angle of 45° vs. vertical. The time it takes to form a sustainable flame was recorded and regarded as the solvent ignition time. All reported SETs and ignition times are average values calculated from the results of 5 experiments.

**Conductivity and viscosity measurements**

Electrolyte ionic conductivity was determined by Electrochemical Impedance Spectroscopy (EIS) recorded on Bio-Logic VSP3 instrument in the frequency range of 10 Hz to 1 MHz. Sample (0.5 mL each) were placed in a dip-type glass cell of known cell constant (CDC749 conductivity cell, radiometer, and distance between Pt electrodes (fixed at 4 mm). The samples were kept at the desired temperature for 120 minutes prior to measurement. Viscosity determination was conducted on an Ostwald CANON 150 viscometer (Canon, Tokyo, Japan). Sample temperature was adjusted by a controlled-temperature chamber.
Electrochemical analysis

Electrochemical techniques were performed on BioLogic MGP2 instrument using Swagelok half-cell with Na metal foil (Aldrich, battery grade) as anode, glass microfiber paper (Whatman, GF/D) soaked in one of the concerned SL-based electrolytes as separator, and as-prepared NaNMC composite as cathode. Cell assembly was conducted in glove box. Cycling Voltammetry (CV) was carried out in the voltage range of 2 V – 4 V vs. Na, at various scan rates ranging from 0.01 to 0.20 mV.s\(^{-1}\). From the slope of \(I_p\) (peak current) vs. \(v^{1/2}\) (square root of scan rate) plot, \(\text{Na}^+\) diffusion coefficient \((D_{\text{Na}})\) values were calculated using Randles-Sevcik equation:

\[
I_p = (2.69 \times 10^5)n^{3/2}A\sqrt{D_{\text{Na}}C_{\text{Na}}v^{1/2}}
\]

where \(I_p\) is the peak current (A), \(n\) is the number of charge transferred, \(A\) is the electrode area (0.785 cm\(^2\)), \(D_{\text{Na}}\) is \(\text{Na}^+\) diffusion coefficient (cm\(^2\).s\(^{-1}\)), \(C_{\text{Na}}\) is the \(\text{Na}^+\) concentration of the cathode (mol.cm\(^{-3}\)), and \(v\) is the scan rate (V.s\(^{-1}\)). Cycling test was performed at C/10 rate and also in the voltage range of 2 V – 4 V vs. Na.

RESULTS

Figure 2 expresses the dependence of solvent SET values upon SL content. In general, with the addition of SL, SET values initially decreased to reach a minimum at around 20% to 30% vol. SL, before sharply rising up. This suggests that while SL, at a reasonable content, does exhibit flame-retardant effects, its presence in excessive amount may be detrimental to the solvent self-extinguished behavior. It was also noted that SET values of DMC-rich solvent families, i.e. ED11- and EPD113-based ones, tended to be lower than those of other families.

The ignition time values of pure SL are shown in Table 1. In order to verify the relationship between ignition time and sample amount, we included SL samples of different volumes (from 100 to 500 \(\mu\)L) in our experiment. The results indicate that regardless of sample volume, a sustainable flame was formed after around ten seconds of ignition, indicating that ignition time is an intensive property. Accordingly, ignition time values may be reported in second(s) without further normalization. Moreover, from those data, the ignition time of pure SL was found to be 10.22±0.38 s, which is superior to that of traditional carbonate solvents. It is therefore not surprising that the ignition time values of all concerned solvent families increased 1.5 – 2 fold with the addition of the first 10% vol. SL, and continues rising with further increase in SL content, as can be seen in Figure 3.

Figure 4 shows the viscosity and ionic conductivity at 35°C of various carbonate-SL electrolytes as a function of their SL content. In all cases, the viscosity exhibits a positive correlation towards SL content, while the ionic conductivity, as expected, follows an opposite trend. Another point worth considering is that despite not standing out in terms of fluidity, 1M NaClO\(_4\) in EPD311 + SL demonstrates good ionic
The ability of 30%-SL electrolytes to facilitate Na\(^+\) intercalation kinetics in NaNMC half-cell was tested to provide a preliminary evaluation of their feasibility in SiB. Figure 5 shows the multi-scan-rate CV curves of NaNMC cathode in our 30%-SL electrolytes. Except for the EPD113-based system, which decomposed only after the first scanning cycle, the other three electrolytes are compatible with NaNMC material as their CV profiles reveal clear and relatively reversible redox peaks. That being said, because EPD311-based electrolyte allows highest Na\(^+\) diffusion coefficient at most redox events, as evidenced in Table 2, it apparently outperforms the other system. Accordingly, we tested the charge-discharge performance of NaNMC in 1M NaClO\(_4\) in EPD311 + 30%SL electrolyte. As shown in Figure 6, the system demonstrates an initial discharging capacity of 97 mAh.g\(^{-1}\), along with 92% capacity retention after 30 cycles at C/10 rate.
The Coulombic efficiency remains steady at around 90-95% throughout the test.

DISCUSSION

The addition of SL has significant impacts on the overall behavior of traditional carbonate-based electrolytes. On the one hand, SL can greatly reduce the solvent flammability and, thus, the battery fiery hazards, if its content lies within a specific range (around 30% vol.). Considering SL low volatility and flammability, it is expectable that increasing SL content results in better SET and ignition time indexes. Although this is mostly the case at low SL content, one should notice that the solvent self-extinguishing nature started to decline when the SL content exceeds a threshold value and is presumably large enough for the combustion of SL to be triggered. It is likely that flame-resistant substances, such as SL, EC and PC, are
Figure 5: CV curves of NaNMC half-cell using 1M NaClO₄ in mixture of 30% vol. SL and (a) ED11, (b) EP11, (c) EPD113 and (d) EPD311, as electrolyte. Scan rates were 0.01, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.16 and 0.20 mV s⁻¹. The peak names (I<sub>p;A1</sub>, I<sub>p;c1</sub>, …) are shown for the purpose of peak identification. Except EPD113-based electrolyte, the others work well with NaNMC material.

Figure 6: Voltage vs. capacity (a) and capacity vs. cycle number (b) plots for NaNMC half-cell using 1M NaClO₄ in EPD311 + 30% vol. SL as electrolyte. The cycling performance is relatively stable at C/10 rate.
able to sustain their flame for a long time once they
get ignited, as their combustion rate is reasonably low
and the heat loss during combustion is thus limited.
In this way, the aforementioned low SET values of
DMC-rich solvents as well as other similar observa-
tions reported in previous studies can also be ex-
plained. On the other hand, SL inevitably thickens
the electrolyte solutions and, as a result, compromises
their ionic conductivity to a certain extent. However,
the conductivity loss corresponding to the addition
of up to 30% vol. SL remains at around 20%-30%.
We believe that such a sacrifice is practically accept-
able and may barely interfere with the battery per-
formance, given that the rate determining step of \( \text{Li}^+ \)
intercalation process is usually the diffusion through
the cathode-electrolyte interface (CEI) and/or within
the solid electrode, rather than the ionic conduction
in liquid phase. In brief, the results of flammability
tests as well as viscosity and ionic conductivity mea-
surements suggest that the addition of a moderate SL
amount, i.e. below 30% vol., is generally favorable to
improve the safety profile of our electrolytes.
Amongst tested electrolytes, the EPD113-based one
is the one with the most subjects, as well as the only
one that underwent oxidative decomposition during
cycling test with NaNMC material. Although high
DMC content clearly signifies the low anodic stability
of EPD113-based electrolyte, its oxidation at such a
low voltage as 4 V vs. \( \text{Na}^+ /\text{Na} \) is unexpected and may
result from direct exposure to the catalytic transition
metals in cathode material. A comparison between
\( \text{Na}^+ \) diffusion coefficients in the other three systems
reveals that the EPD311-based is the most compat-
ible with NaNMC material, suggesting that either too
low or too high DMC content in the electrolyte (as
in EP11- and ED11-based ones, respectively) is not
ideal in terms of promoting \( \text{Na}^+ \) diffusion kinetics.
The underlying reason has yet to be fully investigated,
but we believe that it can be associated with the ef-
fects of different CEI behaviors. Cycling test results
confirm that the EPD311-based electrolyte/NanMC
half-cell works well at regular cycling rate to give typ-
ical NaNMC charge-discharge profile as well as high
specific capacity, capacity retention and cycling re-
versibility.

CONCLUSIONS AND PERSPECTIVE
Carbonate-SL electrolytes were investigated in terms
of their inherent properties as well as their electro-
chemical performance in NaNMC half-cell. In gen-
eral, increasing SL content in the range of 0-30% vol.
proportionally reduces the electrolyte fire hazard at an
acceptable expense of conductivity drop, based on the
SL-case. SL compromises both the battery safety and
performance aspects. Amongst 30%-SL electrolytes,
the EPD311-based one exhibits the best compatibility
with NaNMC material. Their combination operated
smoothly at C/10 rate, yielding 97 mA\( \text{h} \cdot \text{g}^{-1} \) discharg-
ing capacity, above 90% reversibility and 92% capac-
ity retention after 30 cycles. It is suggested to test the
compatibility, including interfacial electrochemistry,
\( \text{Na}^+ \) intercalation kinetics and cycling performance,
of carbonate-SL electrolytes towards SIB anode as well
as other cathode materials. This helps to ensure and
diversify their applicability in full SIB cells.

ABBREVIATIONS
SL: sulfolane
SIB: sodium-ion battery
LIB: lithium-ion battery
EC: ethylene carbonate
PC: propylene carbonate
DMC: dimethyl carbonate
EP11: EC:PC 1:1 vol.
ED11: EC:DMC 1:1 vol.
EPD113: EC:PC:DMC 1:1:3 vol.
EPD311: EC:PC:DMC 3:1:1 vol.
NaNMC: Na\( \text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\)\( \text{O}_2 \)
SET: self-extinguishing time
\( D_{\text{Na}^+} \): diffusion coefficient of \( \text{Na}^+ \) ion
CEI: cathode-electrolyte interface

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

AUTHORS’ CONTRIBUTION’S
All the authors contribute equally to the paper includ-
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REFERENCES
1. Ponrouch A, Monti D, Boschin A, Steen B, Johansson P, Palacin
MR. Non-aqueous electrolytes for sodium-ion batteries.
Journal of Materials Chemistry A, Materials for Energy and
Sustainability. 2015;3(1):22–42. Available from: 10.1039/
C4TA04428B.
2. Che H, Chen S, Xie Y, Wang H, Amine K, Liao XZ, et al. Elec-
trolyte design strategies and research progress for room-
temperature sodium-ion batteries. Energy & Environmental
Science. 2017;10(5):1075–101. Available from: 10.1039/C7EE00524E.
3. Hess S, Wohlfahrt-Mehrens M, Wachtler M. Flammability of Li-ion battery electrolytes: flash point and self-extinguishing time measurements. Journal of the Electrochemical Society. 2015;162(2):3084–97. Available from: 10.1149/2.0121502jes.

4. Arbizzani C, Gabrielli G, Mastragostino M. Thermal stability and flammability of electrolytes for lithium-ion batteries. Journal of Power Sources. 2011;196(10):4801–5. Available from: 10.1016/j.jpowsour.2011.01.068.

5. Jin Z, Wu L, Song Z, Yan K, Zhan H, Li Z. A New Class of Phosphates as Co-Solvents for Nonflammable Lithium Ion Batteries Electrolytes. ECS Electrochem Lett. 2012;1(4):55–8. Available from: 10.1149/2.007203eel.

6. Abouimrane A, Belharouak I, Amine K. Sulfone-based electrolytes for high-voltage Li-ion batteries. Electrochemistry Communications. 2009;11(5):1073–6. Available from: 10.1016/j.elecom.2009.03.020.

7. Xu K. Electrolytes and interphases in Li-ion batteries and beyond. Chemical Reviews. 2014;114(23):11503–618. PMID: 25351820. Available from: 10.1021/cr500003w.

8. Zhang T, de Meatza I, Qi X, Paillard E. Enabling steady graphite anode cycling with high voltage, additive-free, sulfolane-based electrolyte: role of the binder. Journal of Power Sources. 2017;356:97–102. Available from: 10.1016/j.jpowsour.2017.04.073.

9. Zhang T, Porcher W, Paillard E. Towards practical sulfolane based electrolytes: choice of Li salt for graphite electrode operation. Journal of Power Sources. 2018;395:212–20. Available from: 10.1016/j.jpowsour.2018.05.077.

10. Kurc B. Sulfolane with LiPF6, LiNTf2 and LiBOB as a nonflammable electrolyte: working in lithium-ion batteries with a LiNiO2 cathode. International Journal of Electrochemical Science. 2018;13:5938–55. Available from: 10.20964/2018.06.46.

11. Xu K, Ding MS, Zhang S, Allen JL, Jow TR. An attempt to formulate nonflammable lithium ion electrolytes with alkyl phosphates and phosphazenes. Journal of the Electrochemical Society. 2002;149(5):622–6. Available from: 10.1149/1.1467946.