

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

COMMUNICATION

TPPi as Flame Retardant for Rechargeable Lithium Batteries with Sulfur Composite Cathodes†

Hao Jia^a, Jiulin Wang^{*a}, Fengjiao Lin^a, Charles W. Monroe^b, Jun Yang^a, Yanna NuLi^a

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Triphenyl phosphite (TPPi) is adopted as a flame retardant to improve the safety of rechargeable lithium batteries with sulfur composite cathodes. The thermal stability of electrolyte is obviously enhanced after the addition of TPPi, which also plays a positive impact on the electrochemical influence of Li/S batteries as well. TPPi facilitates the formation of SEI, resulting in a smaller interfacial impedance and a better rate performances. An addition of TPPi about 5 wt.% obviously reduces the polarization voltage, stabilizing the cycle performance of the battery, which indicates that TPPi with optimized addition is a favorable additive in conventional liquid electrolyte for rechargeable Li/S with high performances and good safety.

Lithium ion batteries demonstrate a great promising as power sources for electrical vehicles, and energy storage devices for smart grid, solar and wind stations. Because of active electrode materials and flammable organic electrolyte, the safety of lithium ion batteries is a very important issue during their practical applications. Recently secondary lithium-sulfur (Li/S), as one of most promising batteries, have been investigated intensively due to their high theoretical capacity, low cost and non-toxicity.¹ However, Li/S also suffers more serious threats of safety issues compared to lithium ion batteries. Three main factors influencing the safety performances of Li/S are presented as follows: the formation of lithium dendrites in batteries using inevitable lithium anode and dendrites are the cause of battery dysfunction and heat emission;^{2,3} liquid electrolytes applied in batteries are highly volatile and inflammable, under high temperature circumstances electrolytes tend to react with both anodes and cathodes, generating even more heat in batteries, causing thermo runaways;⁴ insulator sulfur with conductive agents (usually acetylene black) are combustible, bringing hazard to the system.⁵

In our previous works, the safety issue of sulfur cathodes has been significantly improved by combining elemental sulfur with non-flammable polyacrylonitrile (PAN).⁶ However, the traditional electrolytes with carbonates or ethers are highly flammable which might cause safety hazards when the cells are misused. In the traditional lithium ion batteries, the thermal stability and electrochemical performance of conventional electrolytes have been reported to be enhanced

by flame retardants. The most explored flame retardants used in batteries can be categorized into the following divisions: alkyl phosphate,⁷⁻⁹ fluorinated alkyl phosphate,¹⁰ ionic liquid,¹¹ and phosphazene.¹² Most of flame retardants obviously enhanced the safety of lithium ion batteries. However, flame retardants also caused bad impacts in some extends on lithium ion batteries' electrochemical performances, for example, destroying cycling stability or deteriorating power rate properties. The ideal flame retardants which completely resolve the safety of batteries and at the same time have no bad impact on battery's electrochemical performances are still under investigations.

Triphenyl phosphite (TPPi) is the chemical compound with the formula $P(OC_6H_5)_3$, as shown in Fig. S1. This colorless liquid with the viscosity of $17.7 \text{ mm}^2 \text{ s}^{-1}$ at $20 \text{ }^\circ\text{C}$ is the ester of phosphorous acid and phenol, which generates phosphates and retards the combustion at the case of heating. In this work, TPPi was adopted as flame retardant additive for traditional electrolyte to not only enhance carbonates' thermal properties but also improve the electrochemical performances of rechargeable Li/S batteries.

The thermal properties of blank electrolyte and functional electrolytes with different doses of TPPi were characterized via DSC as shown in Fig. 1 (a). For blank electrolyte, the thermolysis temperature is about $266 \text{ }^\circ\text{C}$, which shifts to about $275 \text{ }^\circ\text{C}$ after 10 wt. % TPPi addition. The thermal stability of electrolytes coupled with cathode as a whole was also investigated as shown in Fig. 1 (b). The thermolysis temperature is pushed $20 \text{ }^\circ\text{C}$ higher, demonstrating an enhanced thermal stability. DSC tested in a sealed pan without pinhole shows similar results (Fig. S2). Since such a small dose of TPPi is incapable of bringing significant changes of heat capacity to the system, the change in heat flow indicates that the pyrolysis reaction is efficiently suppressed by TPPi. When heated above the pyrolysis temperature, TPPi generate free radicals (such as $PO\bullet$), which are able to actively capture other free radicals emitted by the burning electrolyte (usually $H\bullet$ and $\bullet OH$), to retard the reaction.¹² Besides, metaphosphoric acid, polyvinylidene acid, along with other phosphorous compounds produced in this process form oxygen-proof layer that helps distinguish the flame on the surface of the combustible materials.¹³

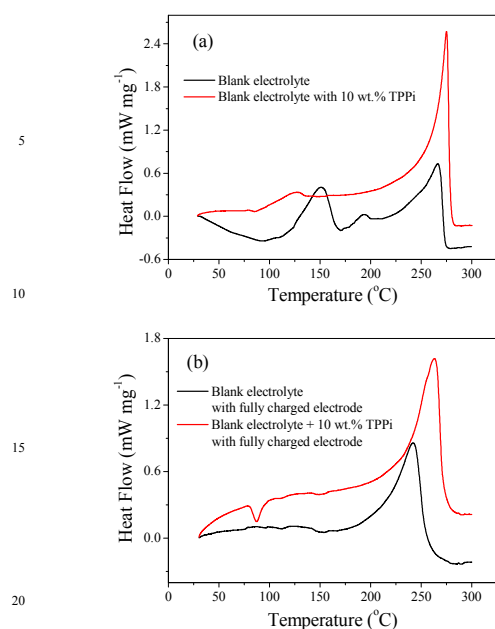


Fig.1 (a) DSC profiles of electrolytes, in which black line indicating blank electrolyte 1M LiPF₆/EC+DMC (1:1, v/v) and red line indicating blank electrolyte with 10 wt. % TPPi additive; (b) DSC profiles of electrolytes with fully charged sulfur cathodes, in which black line indicating blank electrolyte and red line indicating blank electrolyte with 10 wt. % TPPi additive. Electrolytes were sealed in an aluminum pan in the glove box. A pinhole was punched on the pan prior to the DSC testing.

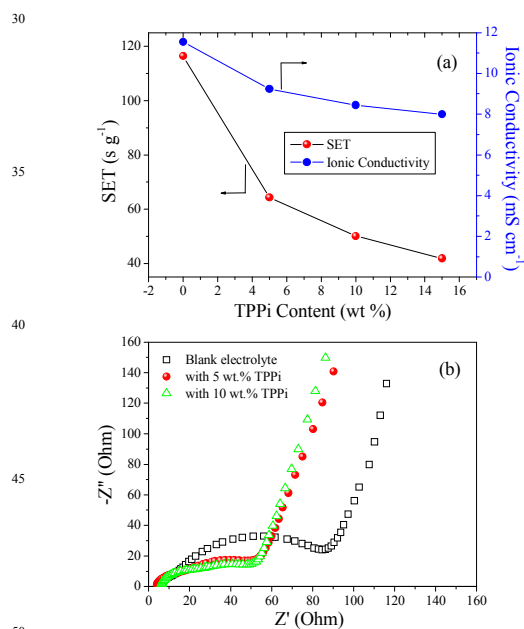


Fig. 2 (a) Effects of TPPi addition on SET and ionic conductivity; (b) Impedance spectra (at fully charged state) of the cells with the electrolytes containing 0, 5 and 10 wt.% TPPi.

The influence of TPPi on conductivity is shown in Figure 2(a). The conductivity of the electrolytes decreases with the increase concentration of TPPi due to its high viscosity. With three equivalent phenyls in its molecule, the polarity of TPPi

is weak, hindering the disassociation of LiPF₆, resulting in a lower conductivity. However, electrolytes with TPPi demonstrated lower interfacial impedances. After fully charged in the 2nd cycle at 0.1 C, the electrochemical impedances of these batteries were tested by AC impedance. As is shown in Figure 2(b), the impedances of electrolytes diminish after adding TPPi. It is possibly attributed to the rich phenyl structure of TPPi which facilitated the formation of SEI,¹⁴ enabling a faster lithium ion transportation.¹⁵ The mechanism concerning the formation of SEI is still not thoroughly elucidated as it varies in different systems. It is commonly accepted that SEI formation in all these systems involves a reductive decomposition of electrolyte components (solvents, salts, additives).¹⁴ TPPi which is consist of three reductive phenoxies which probably promote the formation of SEI and induce lower interfacial impedance. The addition of TPPi does not affect the electrochemical windows of the electrolyte, and benefits to the plating/stripping of Li metal on the anode.

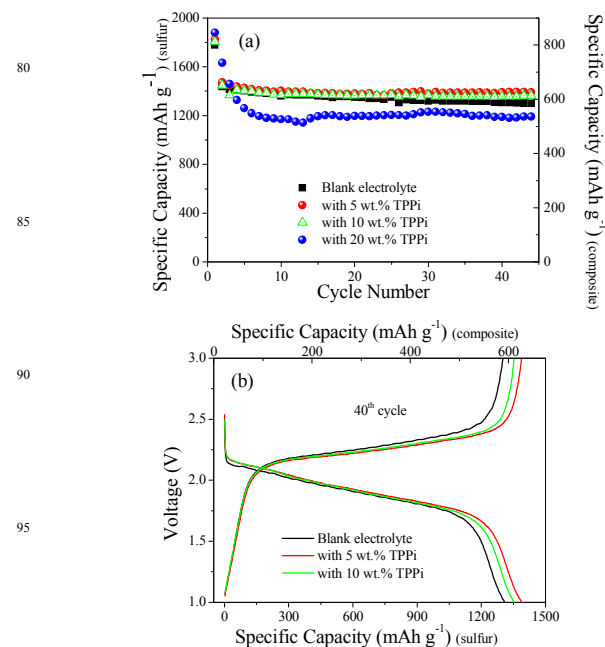


Fig.3 (a) Cycle performances at 0.5C, except for the cell with 20 wt.% TPPi which was initially activated at 0.06 C for 3 cycles, then 0.5C for the following cycles; and (b) charge/discharge profiles in 40th cycle of the cells with the electrolytes containing 0, 5 and 10 wt.% TPPi at 0.1 C.

Figure 3(a) presents a comparison among batteries using electrolytes with different TPPi contents. It should be noted that the sulfur contents in the composite materials were ca. 45 wt.% determined by elemental analysis and the specific capacities in this paper were calculated based on the whole weight of the composite materials including pyrolyzed PAN matrix and pure sulfur, noted as the units of (mAh g⁻¹)_(composite) and (mAh g⁻¹)_(sulfur) in the figures, respectively. After 45 cycles, the capacity retention rates of these batteries are 90.4% for normal electrolyte, 94.5% for functional electrolyte containing 5 wt.% TPPi and 94.2% for that containing 10

wt.% TPPi, respectively. Batteries using electrolytes with 20 wt.% TPPi however demonstrated relatively lower capacities. When the concentration of TPPi reached 20 wt.%, the high viscosity of TPPi decreases the ionic conductivity of electrolyte, and even influences the intimate contact between electrolyte and cathode material, and deteriorates Li⁺ transfer in the their interface. Fig. 3(b) shows that the polarization voltage profiles after TPPi additions. Batteries using electrolytes doped with 5 wt.% TPPi manifest the smallest polarization voltage. It can be inferred that when the concentration of TPPi is constrained around 5 wt.%, the contradictory effects brought by TPPi in electrolyte conductivity and interface impedance reach an optimal level.

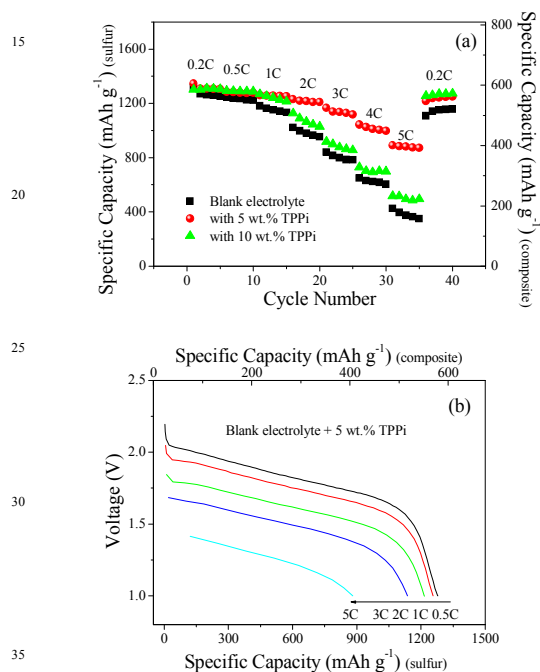


Fig.4 (a) Rate performances of the cells with and without TPPi additive; discharge profiles for the PAN-S composite electrodes at different rate in (b) blank electrolyte + 5 wt.% TPPi.

The rate performance of S-PAN cathode also benefits from TPPi's presence. Batteries with different TPPi contents are recharged and discharged at different rates varying from 0.2C to 5C. Batteries with normal electrolytes are more sensitive to rate variations. As shown in Figure 4(a), in low rate zone (<1C), the differences among three electrolytes are negligible. Significant discrepancy emerged in high rate zone, where the capacity of batteries with blank electrolytes faded to 160 mAh g⁻¹ (5C), while 5 wt.% TPPi doped batteries maintained a capacity of 400 mAh g⁻¹ (5C). 5% TPPi doped batteries illustrates the best rate performances, a fact which coincides with the recharge/discharge pattern that 5 wt.% TPPi reduces the polarization voltage most significantly. Similar to normal ones, batteries with 10 wt.% TPPi additive also suffer a rapid capacity loss at high rate. As the current increases, the rate performance of the batteries would be primarily determined by the transportation of lithium ion in electrode, interface, and electrolytes. Electrolyte with 10 wt.% TPPi possesses high

viscosity which hinders fast lithium ion transportation in electrolytes and deteriorates the rate performances. All batteries with TPPi addition recover well from high rate test, indicating that the reversibility of the electrodes is well preserved by TPPi. The effect of 5 wt.% TPPi addition on discharge voltage at different rates is shown in Fig.4 (b). Under the same rate, PAN-S cathode demonstrates a higher discharge voltage and a larger capacity when doping TPPi. The initial voltage of regular batteries decreases from 2.1 V (0.1C) to 1.7 V (2C) (Fig. S2) whereas that of batteries with additives sustains at 1.85 V as shown in Fig.4 (b), benefiting from the formation of SEI with less impedance. Since the interface is enhanced, lithium became more readily to enter the internal structure of the electrodes, resulting in a low polarization voltage and insensitivity to rate variation.

In summary, safety is a very important issue for rechargeable batteries and here TPPi's was successfully adopted as flame retardant in rechargeable lithium batteries with PAN-S composite cathode. Despite its shortages such as high viscosity and weak polarity, TPPi is applicable as an additive in the traditional electrolyte to enhance its thermal stability and improve the electrochemical performance of Li/S batteries. The optimal content of TPPi is around 5 wt.%, with which the batteries show the small polarization voltage, good rate performance and stable cycle performances.

This work is financially supported by the National Natural Science Foundation of China (51272156, 21333007) and SJTU-UM joint research project.

Notes and references

^aSchool of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R. China. Fax: (+86)-21-54747667; Tel: (+86)-21-54745887; E-mail: wangjiulin@sjtu.edu.cn.

^bDepartment of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, USA

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

- P. G. Bruce, S.A. Freunberger, L.J. Hardwick, J.-M. Tarascon, *Nat. Mater.*, 2011, **11**, 19.
- O. Crowther, A.C. West, *J. Electrochem. Soc.*, 2008, **155**, A806.
- C. Monroe, J. Newman, *J. Electrochem. Soc.*, 2003, **150**, A1377.
- T. Ohsaki, T. Kishi, T. Kuboki, N. Takami, N. Shimura, Y. Sato, M. Sekino, A. Satoh, *J. Power Sources*, 2005, **146**, 97.
- J. Wang, J. Chen, K. Konstantinov, L. Zhao, S. Ng, G. Wang, Z. Guo, H. Liu, *Electrochimica acta*, 2006, **51**, 4634.
- F. J. Lin, J.L. Wang, H. Jia, C.W. Monroe, J. Yang, Y.N. NuLi, *J. Power Sources*, 2013, **223**, 18.
- X. Xia, P. Ping, J.R. Dahn, *J. Electrochem. Soc.*, 2012, **159**, A1834.
- R. Shibutani, H. Tsutsumi, *J. Power Sources*, 2012, **202**, 369.
- Y. Shigematsu, M. Ue, J. Yamaki, *J. Electrochem. Soc.*, 2009, **156**, A176.
- G. Nagasubramanian, C.J. Orendorff, *J. Power Sources*, 2011, **196**, 8604.
- J. Choi, Y.-K. Sun, E.-G. Shim, B. Scrosati, D.-W. Kim, *Electrochimica Acta*, 2011, **56**, 10179.
- T. Tsujikawa, K. Yabuta, T. Matsushita, T. Matsushima, K. Hayashi, M. Arakawa, *J. Power Sources*, 2009, **189**, 429.
- E. P. Roth, C. J. Orendorff, *Electrochem. Soc. Interface*, Summer 2012, 45.
- M. Inaba, Y. Kawatate, A. Funabiki, S.-K. Jeong, T. Abe, Z. Ogumi, *Electrochimica Acta*, 1999, **45**, 99.
- M. Winter, R.J. Brodd, *Chem. Rev.*, 2004, **104**, 4245.