Journal of Power Sources 391 (2018) 113–119

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Hybrid electrolytes incorporated with dandelion-like silane–Al_2O_3 nanoparticles for high-safety high-voltage lithium ion batteries

Hewei Xu[a,b], Junli Shi[a,***], Guosheng Hu[b], Ying He[a], Yonggao Xia[a,*], Shanshan Yin[a], Zhaoping Liu[a,**]

[a] Advanced Li-ion Battery Engineering Laboratory and Key Laboratory of Graphene Technologies and Applications of Zhejiang Province, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Zhejiang 315201, PR China

[b] Institute of Macromolecules & Bioengineering, North University of China, Taiyuan 030051, China

HIGHLIGHTS

- Hybrid electrolytes containing liquid electrolyte and silane-Al_2O_3 are proposed.
- Hybrid electrolytes show high ionic conductivity and are flame retarded.
- 5 V batteries show enhanced cycling stability and rate capacity.
- Nail-penetration tests indicate enhanced battery safety with hybrid electrolytes.

ARTICLE INFO

Keywords:
Lithium ion battery
Safety
Nanoparticle
Hybrid electrolyte

ABSTRACT

One of the crucial challenge for developing high safety and high voltage lithium ion batteries is to find a reliable electrolyte system. In this work, we report a kind of hybrid electrolytes, which are used for high-voltage lithium ion batteries and are expected to be able to effectively enhance the battery safety. The hybrid electrolytes are obtained by incorporating silane-Al_2O_3 (Al_2O_3-ST) into liquid electrolyte, which combines the merits of both solid electrolyte and liquid electrolyte. The Al_2O_3-ST nanoparticles help to increase lithium-ion transference number and to enhance battery safety, while liquid electrolyte contributes to high ionic conductivity. The cycling stability and rate capacity of $LiNi_{0.5}Mn_{1.5}O_4$/Li batteries are improved by using the hybrid electrolytes. Nail-penetration tests indicate that $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$/graphite battery with hybrid electrolyte owns obviously enhanced safety than that using traditional liquid electrolyte. This work provides new insight on electrolyte design for high-safety high-voltage lithium ion batteries.

1. Introduction

With the development of society, environment protection and energy conservation is attracting more and more attention. As one of the most popular chemical power sources, lithium ion battery (LIB) owns relatively high energy density, long cycle life and low environment impact, and is now a research hotspot due to its promising application as power sources for hybrid electric vehicles (HEVs) and plug-in HEV (PHEV) [1]. However, for high power usage, LIBs with higher energy density and higher level of safety are still urgently required [2].

Electrolyte, as one of the most important part of LIBs, largely influences battery performances and safety. Currently, liquid electrolyte still dominants the commercial LIB market since they are low cost, easy to prepare and owns high ionic conductivity [3]. However, the highly flammable character of the electrolyte solutions usually helps to aggravate battery thermal runaway and leads to dangerous conditions, such as fire and even explosion. Now, researchers have tried to use electrolyte additives (flame retardants) to suppress electrolyte flammability. Previous studies on this subject mainly focus on phosphate esters [1,4–8], phosphite compounds [9,10], phosphazene [11] and halogenated organic compounds [8,12] and the other [13] in liquid lithium ion batteries (LIBs). Phosphorus flame retardant additives such as, triethyl phosphate (TEP) [5], hexamethyl phosphoramide (HMPA), trimethyl phosphate (TMP) and 4-isopropyl phenyl diphenyl phosphate

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: shijunli@nimte.ac.cn (J. Shi), xiayg@nimte.ac.cn (Y. Xia), liuzp@nimte.ac.cn (Z. Liu).

https://doi.org/10.1016/j.jpowsour.2018.04.060
Received 27 October 2017; Received in revised form 18 March 2018; Accepted 15 April 2018
0378-7753/

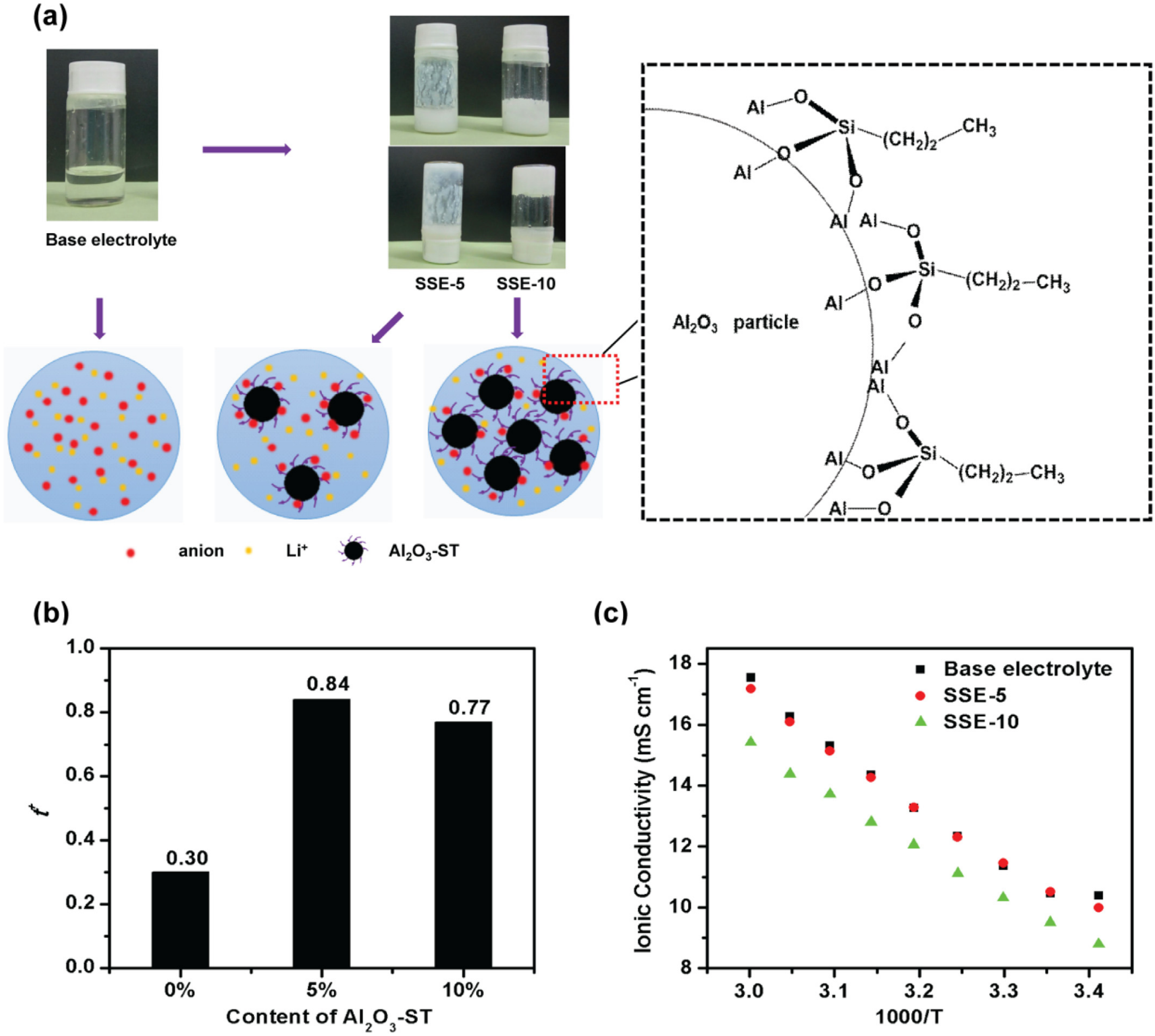

Fig. 1. (a) The photographs and the solution state schematic diagram of base electrolyte, electrolyte SSE-5 and SSE-10. (b) The lithium-ion transference number (t^+) of different electrolytes. (c) Temperature dependence of ionic conductivity of different electrolytes. Temperature range: 25–60 °C.

(IPPP) [1] have been proved to reduce the flammability of the liquid electrolytes. Unfortunately, some of the flame retardants have negative effects on battery performances due to their reactivity with the electrode materials in Li-ion cells.

Ionic liquids exhibit low vapor pressure and own good thermal, chemical and electrochemical stability, which have a promising application in high-voltage LIBs. Ionic liquid based electrolytes tend to be non-flammable when used as electrolytes in LIBs, and thus is favorable to enhance battery safety [14–19]. The $LiTFSI/PYR_{13}TFSI/PYR_{13}FSI$ electrolyte was reported to have an electrochemical stability window up to 5 V (vs. Li/Li^+). Meanwhile, NMC/graphite full batteries using the electrolyte solution showed good cycling performance [18]. The electrochemical stability window of $LiFSA/[Pyr_{1,1O1}][FSA]/OE2pyps$ electrolyte solution was reported to be higher than 5 V (vs. Li/Li^+) [19]. However, despite the above mentioned advantages, ionic liquid based electrolytes usually suffer from relatively lower ion conductivity, poor electrode/electrolyte compatibility and high cost of manufacturing.

Solid-state electrolyte is a potential candidate for high safety high energy storage systems, because it could overcome most of the safety issue encountered by using liquid electrolyte, such as leakage, volatilization and so on [20]. However, despite considerable interest in solid-state batteries, many challenges still remain in both manufacturing and fundamental understanding of this technology. For example, the ionic conductivity of solid polymer electrolytes are usually too low for battery operation at room temperature [21,22]. While, although inorganic solid electrolytes, like $Li_7P_3S_{11}$ and $Li_{10}GeP_2S_{12}$ [23], have comparable room temperature ionic conductivity with typical liquid electrolytes, the main drawbacks lie in their poor thermodynamic stability [24] and interphase problems [25].

Developing hybrid electrolyte is now considered to be a new strategy to overcome the above challenges. Gel [26–28] and slurry electrolytes [29] have been reported. However, non-uniform dispersion of the inorganic part is deemed to be a main limitation. Besides, although some electrochemical performances could be obviously improved, safety issue is still remained to be further addressed. In this