

# Flame Retardant Triethyl Phosphate/Propylene Carbonate Electrolyte for Supercapacitor Applications

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The safety and charge/discharge performance of electrochemical devices is directly correlated to the property of electrolyte in these devices. Simultaneous improving the safety and charge/discharge performance of supercapacitor through electrolyte optimization has attracted wide research interests recently. In this work, we report a high-performance fire-retardant electrolyte. The electrolyte comprises of a mixed solvent of propylene carbonate/triethyl phosphate (PC/TEP) and high concentration lithium salts (5 M LiTFSI). Supercapacitor assembled with 5 M LiTFSI-TEP/PC shows a high capacitance of 27 F g<sup>-1</sup> and excellent fire-retardant property. The combination of the TEP component and high concentration LiTFSI is the key to the excellent performance of the electrolyte.

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**Keywords:** electrolyte; supercapacitor; high concentration; triethyl phosphate; fire retardant

## 1. INTRODUCTION

Supercapacitor is a highly efficient energy storage device due to its excellent rate performance and low-cost. As the widespread application of supercapacitor in our daily life, the safety performance of the supercapacitor has aroused wide concerns. Fire hazard is the most common safety accident caused by supercapacitor because of the flammability of the organic electrolyte used in supercapacitor. Lowering the flammability of the electrolyte is thus a key to improve the flammability of the supercapacitor. However, development of flame-retardant electrolyte system for supercapacitor without compromising its charge-discharge performance remains a challenge.

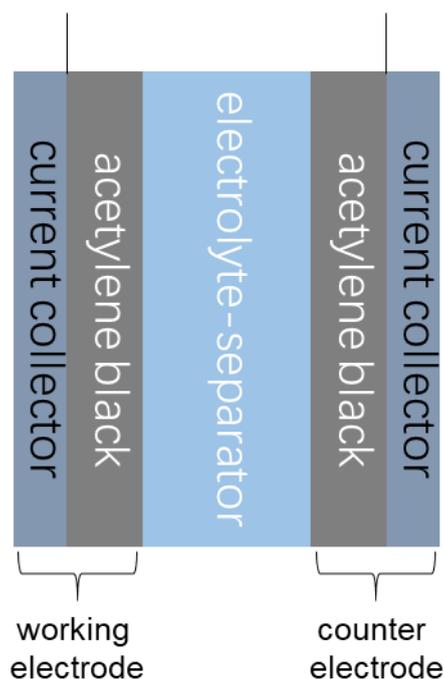
Replacing organic electrolyte with aqueous electrolyte is a possible solution to significantly improve the safety performance of electrochemical devices. For example, a series of water-based electrolyte system has been proposed recently[1-3]. Despite the fact that the use of aqueous electrolyte lower down the risk of fire accidents, electrochemical systems based on these aqueous electrolytes

normally suffer from a limited working voltage due to electrochemical water splitting. To increase the working voltage of these devices to an acceptable level for practical application, high concentration salts and tricky formation of sophisticated formation of SEI layers are required. These stringent restrictions not only result in poor rate performance but also increases the cost of the whole device, making practical use of aqueous electrolyte difficult.

Doping the conventional organic electrolyte with flame retardant species is an efficient and economically feasible approach to alleviate the risk of fire accident in electrochemical devices. Triethyl phosphate (TEP) is a cost-effective flame-retardant solvent with low-viscosity, good electrochemical stability and excellent solvating capability[4]. Recently, TEP has been demonstrated to be an efficient co-solvent in electrolyte for lithium ion battery[5-8], lithium sulfur battery[9, 10], lithium metal battery[11, 12], sodium ion battery[4], Zinc ion battery[13] and etc. In these previous reports, the favorable role of TEP for fire retardance have been clearly demonstrated. However, it was also shown that TEP might decompose and interfere the SEI formation on the electrode[10, 14]. These results suggest that successful application of TEP solvent in electrochemical device needs tailored design of the electrolyte system. Compared to the intensive research of TEP co-solvent in batteries, the use of TEP in supercapacitor is rarely explored[15, 16]. In this work, we investigated the effect of TEP in the electrolyte on the electrochemical performance of supercapacitor. TEP-containing electrolyte with different lithium salt concentration was prepared and used. We show that this novel LiTFSI-TEP/PC electrolyte displays a high electrical conductivity of 2.33 mS cm<sup>-1</sup> and a viscosity of about 24.5 cp, which benefits the enhanced electrochemical properties of supercapacitors.

## 2. EXPERIMENTS

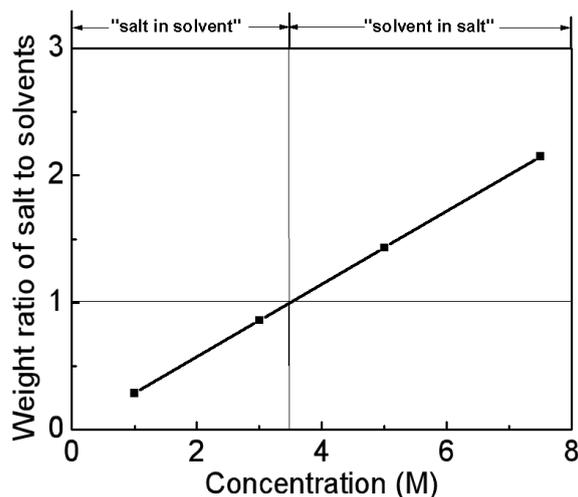
All the chemicals used in this study was purchased from Alladin Reagent Co. Ltd unless otherwise specified. The electrolyte was prepared by mixing lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in triethyl phosphate (TEP) and propylene carbonate (PC) in desired ratio in a glove box filled with argon. The viscosity and conductivity of the electrolyte was measured using a viscosity meter (FANGRUI NDJ-5S) and a conductivity meter (DDSJ-308F) at room temperature, respectively. The working electrode of the supercapacitor was fabricated by coating of slurry composed of polyvinylidene fluoride (10 wt%), acetylene black (AB, 90 wt%) onto a nickel foam, which was then dried by heating at 60 °C for 12 h. A symmetric supercapacitor was assembled using the acetylene black (AB) working electrodes and electrolyte of different LiTFSI concentration, named as AB//AB. The cyclic voltammetry(CV)curves(scan rate: 100-1000 mV s<sup>-1</sup>, shown in the figures) and electrochemical impedance curves(10<sup>-2</sup> to 10<sup>5</sup> Hz, amplitude: 5 mV)of the supercapacitor were recorded using an electrochemical working station (CHI 760, Shanghai Chenhua Co., Ltd) to investigate the electrochemical performance of the supercapacitor. In addition, the galvanostatic charge-discharge characteristics of the supercapacitor was evaluated on a Land charge/discharge instrument (Wuhan Land Electronic Co., Ltd).All the electrochemical measurements (CV and GCD) in this manuscript were performed using a two-electrode system with the AB pasted current collector (nickel foam) as both the working electrode and counter electrode (Scheme 1).



**Scheme 1.** Schematic illustration showing the configuration of the supercapacitor.

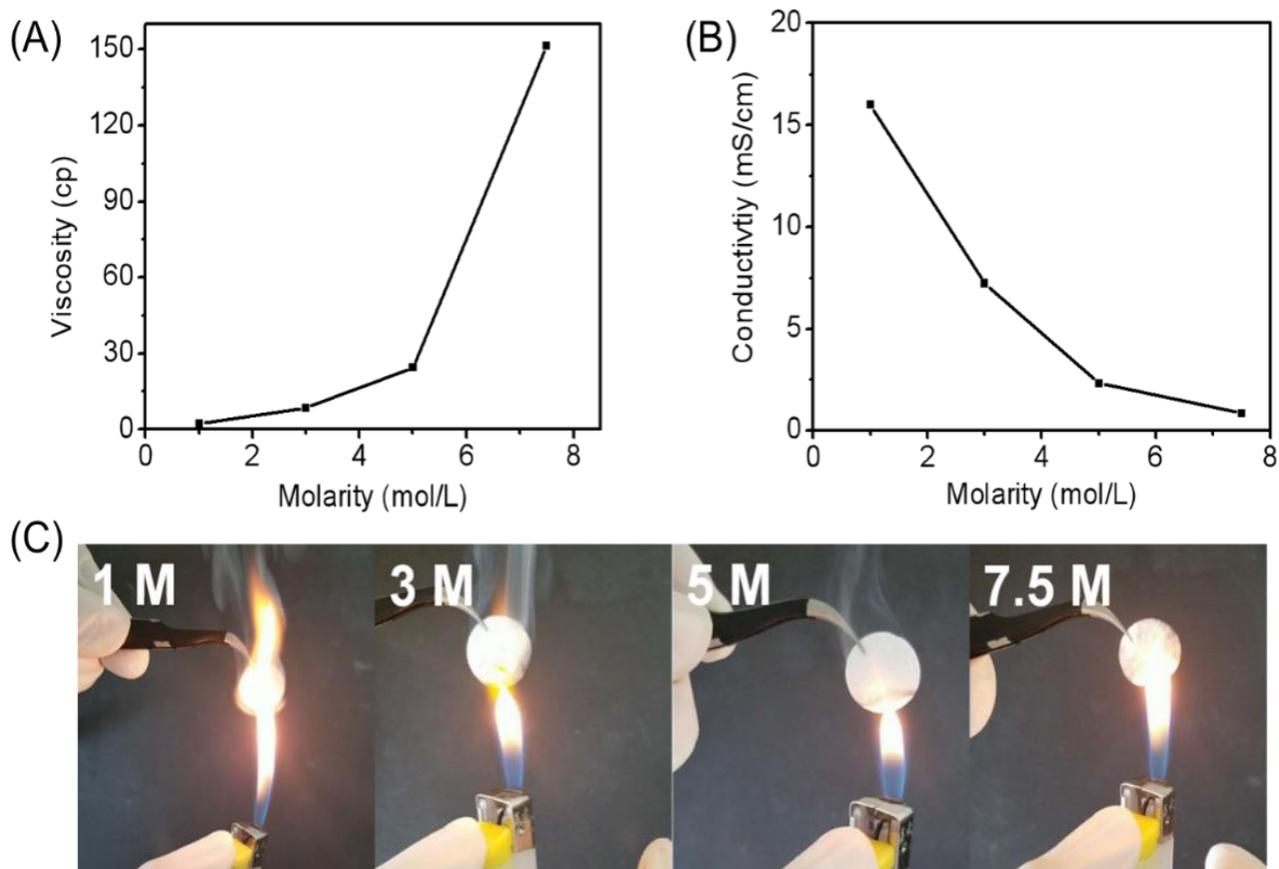
### 3. RESULTS AND DISCUSSION

Propylene carbonate (PC) is a widely used electrolyte solvent for supercapacitor due to its wide electrochemical window and good compatibility with LiTFSI. Triethyl phosphate (TEP) can be introduced into PC as a co-solvent to endow the electrolyte with fire retardant property. In general, the fire-retardant performance of the mixed solvent increases with the TEP content and insufficient doping of TEP may lead to limited flame-retardant performance of the supercapacitor. However, over-doping of TEP may lead to decomposition of TEP and subsequent performance degradation of the supercapacitor. To balance the lithium ion transfer performance and fire-retardant performance of the mixed solvent, the ratio of PC:TEP was set to be 1:1 (v/v) in this study. One attractive feature of TEP is its excellent solvation property, which can be used to obtain electrolyte with high lithium salt concentration. Considering that increasing the concentration of lithium salt in the electrolyte may improve the cycling performance of the supercapacitor, electrolyte with different lithium salt concentration ranging from 1 M to 7.5 M was prepared and tested. The concentration of the lithium salt was designed to cover both the “salt in solvent” state and “solvent in salt” state to identify the optimal lithium salt concentration in the current electrolyte system. (Fig. 1).

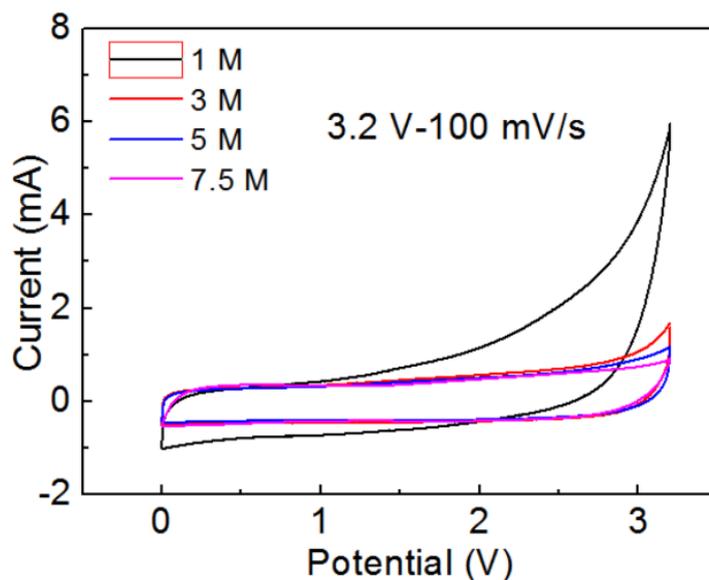


**Figure 1.** Mass ratio of salt (LiTFSI) to solvent (TEP/PC) in different concentrations of LiTFSI-TEP/PC electrolyte.

The physical characteristics of the electrolyte was firstly investigated. The concentration of LiTFSI has a great impact on the viscosity of the electrolyte. At low LiTFSI concentration of 1 M and 3 M (correspond to “salt in solvent” state), the viscosity of the electrolyte was 2.34 and 8.55 cp, respectively (Fig. 2A). The electrolyte exhibited significantly higher viscosity in the “solvent in salt” state. The viscosity of electrolyte with LiTFSI concentration of 5 M and 7.5 M reached 24.5 and 151.31 cp, respectively. The conductivity of the electrolyte was also closely related to the concentration of the electrolyte (Fig. 2B). This is because the viscosity of the electrolyte significantly influences the rate of ion transport in the electrolyte. Furthermore, the coordination strengthen between  $\text{Li}^+$  and TFSI $^-$  also varied with the concertation of electrolyte. Such a change in the coordination strengthen also led to different conductive behavior of the electrolyte. The conductivity of the electrolyte with 1 M, 3 M, 5 M and 7.5 M LiTFSI was 15.99, 7.23, 2.33 and 0.861  $\text{mS cm}^{-1}$ , respectively. The concentration of LiTFSI also had a dramatic effect on the fire-retardant performance of the electrolyte, which is characterized by the flammability test with electrolyte saturated separator. Despite the use of fire retardant TEP in the electrolyte, the separator wetted with electrolyte containing 1 M LiTFSI could be easily ignited.in the presence of open flame. The separator wetted with electrolyte containing 3 M LiTFSI was also flammable upon continuous heating. With the increase of salt concentration in the electrolyte above 5 M, the electrolyte became inflammable. The excellent fire-retardant performance of the electrolyte with high LiTFSI concentration (above 5 M) could be explained by the fact that the flammable PC solvent is protected by the surrounding LiTFSI in such a “solvent in salt” state. According to the results above, a higher LiTFSI concentration in the electrolyte lowers the conductivity of the electrolyte and enhances the safety performance of the electrolyte. An optimal LiTFSI concentration in the electrolyte should balance the ion conductive performance and fire-retardant performance of the electrolyte.



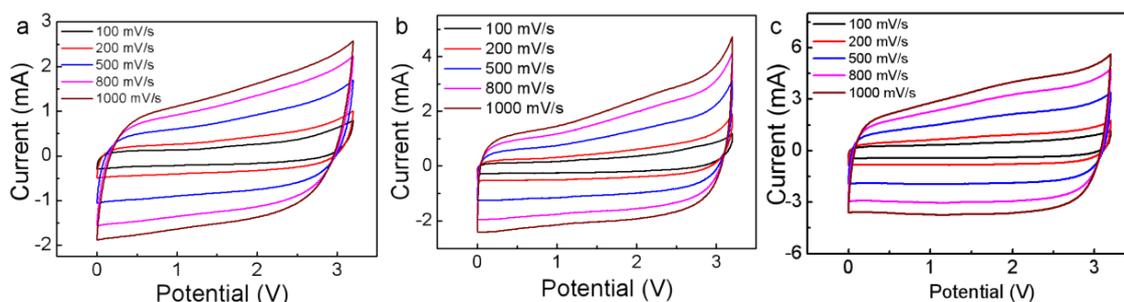
**Figure 2.** (A)Viscosity, (B) conductivity and (C) flammability of LiTFSI-TEP/PC electrolyte with different LiTFSI concentration.



**Figure 3.** CV curves of the acetylene black (AB) electrode in symmetric supercapacitor (AB//AB) assembled using LiTFSI-TEP/PC electrolyte of different concentrations in the potential range of 0 V~3.2 V (scan rate: 100 mV s<sup>-1</sup>).

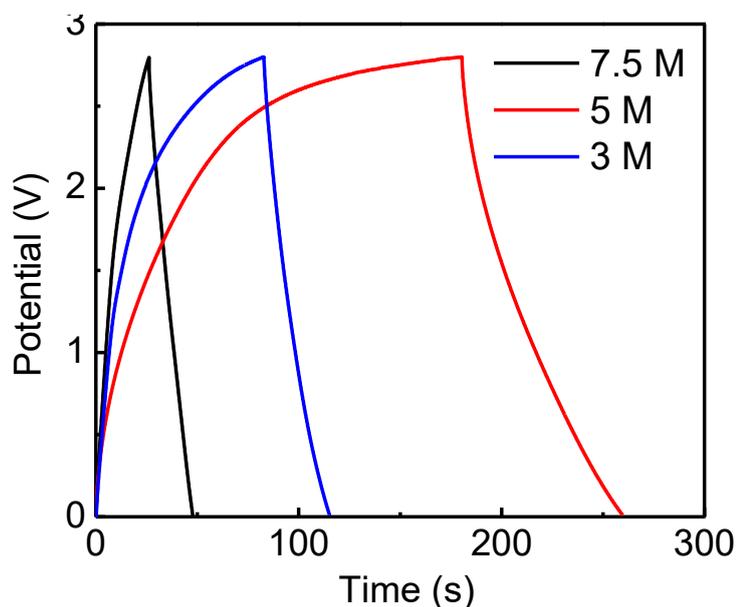
To identify the optimal LiTFSI concentration in the electrolyte system for supercapacitor application, CV measurements with the supercapacitor assembled with different electrolyte was

conducted in the potential range of 0 to 3.2 V (Fig. 3) using a two-electrode system with the acetylene black pasted electrode as both the working electrode and reference electrode. The supercapacitor with 1 M LiTFSI in the electrolyte showed strong polarization in the potential range tested. In contrast, supercapacitor assembled with electrolyte of higher LiTFSI (3 M, 5 M and 7.5 M) concentration exhibited much lower polarization, as reflected by the rectangular shape of the CV curves. In addition, the supercapacitor assembled with electrolyte of higher LiTFSI had similar capacitance. Taking all these results into consideration, electrolyte with 5 M LiTFSI was selected as the optimal electrolyte because it showed high fire retardance, low polarization and relatively low cost. In subsequent studies, all the supercapacitor was assembled with the electrolyte containing 5 M LiTFSI.



**Figure 4.** CV curves of the acetylene black (AB) electrode in symmetric supercapacitor (AB//AB) assembled with 5 M LiTFSI-TEP, 5 M LiTFSI-PC, 5 M LiTFSI-TEP/PC electrolyte (scan rate ranging from 100 mV s<sup>-1</sup> to 1000 mV<sup>-1</sup>).

The electrochemical performance of the electrolyte with 5 M LiTFSI was further studied with CV measurements at different sweep rates. For comparison, the electrolyte with single solvent (PC or TEP) was also studied. The curves of asymmetric supercapacitor with 5 M LiTFSI-TEP or 5 M LiTFSI-PC gradually deviated from rectangular shape with the increase of sweep rate, which was an indication of relatively high polarization. For the asymmetric supercapacitor prepared with 5 M LiTFSI-TEP/PC electrolyte, the CV curves maintained quasi-rectangular shape even at a high sweep rate, showing its low polarization. In addition, a larger current response was also observed, implying improved capacitance performance of 5 M LiTFSI-TEP/PC electrolyte over the electrolyte with single solvent. The enhanced electrochemical performance of 5 M LiTFSI-TEP/PC electrolyte may be resulted from the synergetic effect of the PC and TEP solvents. A composite solvent comprising both PC and TEP is advantageous due to its excellent capacitance behavior and fire-retardant performance.

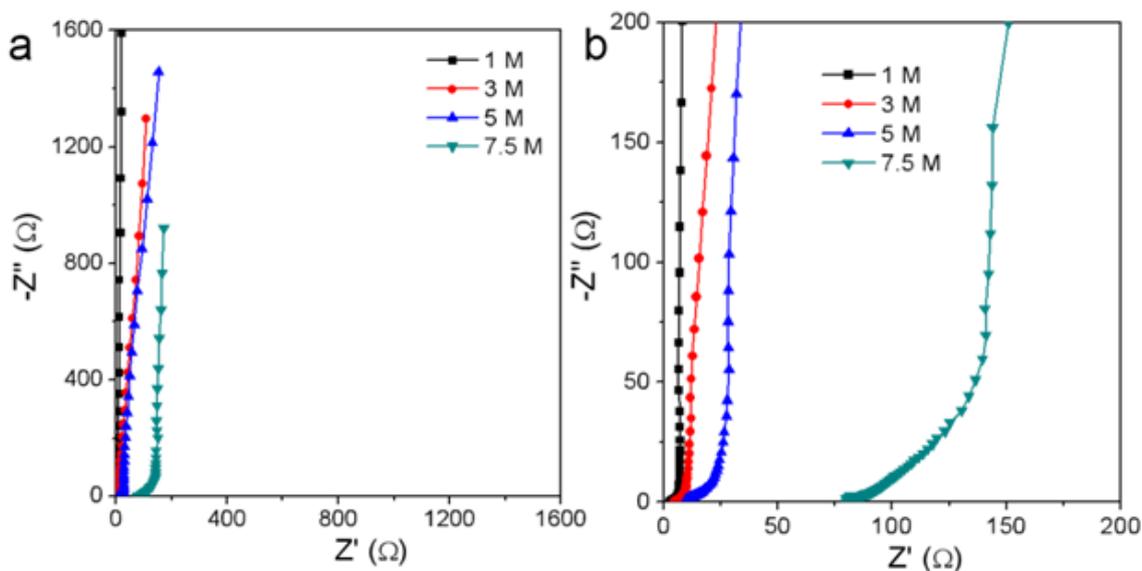


**Figure 5.** Galvanostatic charge/discharge curves of supercapacitor with different concentrations of LiTFSI in the electrolyte.

The charge-discharge performance of the supercapacitor with different electrolytes was quantified with galvanostatic charge/discharge (GCD) tests at a current density of  $0.5 \text{ A g}^{-1}$  (Fig. 5). The GCD curves of supercapacitor with 3 M LiTFSI-TEP/PC or 5 M LiTFSI-TEP/PC electrolyte showed triangular shapes, suggesting the characteristics of double-layer capacitor, which is consistent with the results of CV measurement. The specific capacitance was calculated to be 16, 27 and  $7 \text{ F g}^{-1}$  for supercapacitor with electrolyte containing 3 M, 5 M or 7.5 M LiTFSI-TEP/PC, respectively. A high Faradic efficiency close to 100% was observed for all supercapacitor. To understand the excellent electrochemical performance of 5 M LiTFSI-TEP/PC electrolyte, EIS measurements were performed. It was seen that all the impedance curves were near-perpendicular to the real axis in the low-frequency region, which was close to the behavior of ideal capacitance. The ionic resistance of the supercapacitor with different electrolyte, determined by the intersect of impedance curve with the real axis, was 2.4, 5.3, 10.2 and  $81.5 \text{ } \Omega$ , respectively, which increases with the increase of the electrolyte concentrations.

Other fire-retardant electrolyte, such as aqueous electrolyte [17], was also proposed recently for supercapacitor applications. However, such aqueous electrolyte suffers from its narrow electrochemical window, which lowers down the energy density of the supercapacitor. Although this issue can be partly solved by the use of super-concentrated electrolyte, in which the activity of water is significantly suppressed [18]. However, the use of super-concentrated electrolyte also leads to lowered ionic conductivity and thus inferior electrochemical performance. Another drawback of the water containing electrolyte is that the wetting of electrolyte with the separator is affected due to the high surface tension of water. The poor wetting between the electrolyte and the separator decreases the electrochemical performance of the electrochemical device [19]. Moreover, the electrochemical behavior of aqueous fire-retardant electrolyte on the surface of the electrode was still poorly understood. Such a lack of understanding in these fundamental issues greatly limits the use of aqueous

electrolyte. Supercapacitor with flame-retardant performance was also demonstrated with organic gel polymer electrolyte [20].



**Figure 6.** (a) Nyquist plots of supercapacitor with different concentrations of LiTFSI in the electrolyte. (b) Enlarged figure of the high frequency region.

Despite its effectiveness in improving the fire suppression, the gel polymer electrolyte suffers from low ionic conductivity and poor compatibility at the electrode-electrolyte interface. Additionally, the cost of gel polymer electrolyte is high. Alternatively, engineering the electrode may also impose inflammable property with the supercapacitor. One of such examples is the electrode consisting functionalized spongy graphene [21]. The functionalized heteroatoms, such as phosphorus and nitrogen, are the origin of its fire-retardant performance. It should also be noted that a number of other factors, such as conductivity of the electrode, should be considered in the engineering the electrode. Therefore, endowing the supercapacitor through electrode engineering is challenging. As a contrast, the electrolyte system developed herein is based on traditional organic solvent, which is compatible with a range of electrode materials (e.g. metal oxide) [22] and can enable a large electrochemical window. Therefore, we expect that the developed electrolyte system can find enormous applications.

#### 4. CONCLUSION

Fire-retardant electrolyte with propylene carbonate (PC) and triethyl phosphate (TEP) as solvents are developed. The optimal concentration of lithium salt in the electrolyte is also identified. It is demonstrated that 5 M LiTFSI-TEP/PC shows excellent fire-retardant performance and best electrochemical performance toward supercapacitor applications. The excellent fire-retardant performance of 5 M LiTFSI-TEP/PC electrolyte stems from the appropriate combination of fire retardant TEP and high concentration LiTFSI. The optimal electrochemical performance of 5 M

LiTFSI-TEP/PC electrolyte is a result of the suitable viscosity and the conductivity. It is expected that the results presented herein may provide useful guidelines for future design of electrolyte system for supercapacitor applications.

#### ACKNOWLEDGEMENT

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