

A novel Et_4NBF_4 and LiPF_6 blend salts electrolyte for supercapacitor battery

Shengqi Liu · Suqin Liu · Kelong Huang ·
Jiansheng Liu · Yongkun Li · Dong Fang ·
Hongmei Wang · Yufei Xia

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Abstract Electrolytes of 1 M blend salts (LiPF_6 and tetraethylammonium tetrafluoroborate, Et_4NBF_4) have been investigated in supercapacitor battery system with composite LiMn_2O_4 and activated carbon (AC) cathode, and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode. The results obtained with the blend salts electrolytes are compared with those obtained with cells build using standard 1 M LiPF_6 dissolved in ethylene carbonate+dimethyl carbonate+ethyl (methyl) carbonate (EC+DMC+EMC, 1:1:1 wt.%) as electrolyte. It is found that the blend salts electrolyte performs better on both electrochemical and galvanostatic cycling stability, especially cycled at 4 C rate. When the concentration of LiPF_6 is 0.2 M and Et_4NBF_4 is 0.8 M, the capacity retention of the battery is 96.23% at 4 C rate after 5,000 cycles, much higher than that of the battery with standard 1 M LiPF_6 electrolyte, which is only 62.35%. These results demonstrate that the blend salts electrolyte can improve the galvanostatic cycling stability of the super-capacity battery. Electrolyte of 0.2 M LiPF_6 +0.8 M Et_4NBF_4 in EC+DMC+EMC (1:1:1 wt.%) is a promising electrolyte for (LiMn_2O_4 +AC)/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Keywords Blend salts electrolyte · Supercapacitor battery · Et_4NBF_4 · (LiMn_2O_4 +AC)/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Introduction

The supercapacitor battery, which is a kind of combination of Li-ion battery and supercapacitor, has attracted many researchers to do studies on it due to their high energy density and long cycle life. While researches on electrolyte for this system are rare, lithium salt/carbonate-based electrolytes are still commonly used electrolytes in supercapacitor batteries [1]. It is known that electrolyte plays an important role in the performance of batteries and in the supercapacitor battery system of (LiMn_2O_4 +activated carbon (AC))/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$, double-layer capacitor and lithium-ion battery are combined in one unit cell. However, using pure LiPF_6 or pure LiBF_4 as electrolyte, the part of double-layer capacitor cannot be delivered very well and the capacity density is not high [1, 2]; trace amounts of reaction byproducts, such as HF, LiF, and POF_3 will be produced after long cycle life, which can attack the battery electrodes [3, 4].

Recently, tetraethylammonium tetrafluoroborate (Et_4NBF_4) have been reported and tested as electrolyte salt both in Li-ion batteries and non-aqueous supercapacitors [5, 6]. The advantages associated to the use of Et_4NBF_4 include high ionic conductivity and low viscosity [7]. Another key feature of this salt is that it can form solid electrolyte interface (SEI) film on the surface of electrode to protect active materials when used for lithium-ion battery [8]. Et_4NBF_4 is much fit for the application of supercapacitor battery electrolyte because it can provide plenty of ions for the part of electrostatic adsorbing–desorbing and form SEI film to protect LiMn_2O_4 electrode [9, 10]. Li^+ for the

S. Liu · S. Liu (✉) · K. Huang · H. Wang · Y. Xia
College of Chemistry & Chemical Engineering,
Central South University,
Changsha 410083 Hunan, China
e-mail: shengqi211@163.com

J. Liu · Y. Li
Guangzhou Tinci Materials Technology Co., Ltd,
Guangzhou 510006, China

D. Fang
Key Lab of Green Processing and Functional Textiles of New
Textile Materials, Ministry of Education, School of Material
Science and Engineering, Wuhan Textile University,
Wuhan 430073 Hubei, China

part of Li intercalation/deintercalation are required. Considering blend salts can improve some electrochemical performances [11–14], blend Et_4NBF_4 and LiPF_6 are adopted in our study.

The previous work about Et_4NBF_4 was mainly focus on supercapacitor, whereas the influences of blend salts (Et_4NBF_4 blend with LiPF_6) for supercapacitor battery, such as $(\text{LiMn}_2\text{O}_4+\text{AC})/\text{Li}_4\text{Ti}_5\text{O}_{12}$, were not reported or elaborated [5, 7]. In this paper, five electrolytes containing different concentration of LiPF_6 and Et_4NBF_4 in ethylene carbonate (EC)+dimethyl carbonate (DMC)+ethyl (methyl) carbonate (EMC; 1:1:1 wt.%) are prepared, which was tested using a $(\text{LiMn}_2\text{O}_4+\text{AC})/\text{Li}_4\text{Ti}_5\text{O}_{12}$ supercapacitor system by electrochemical behavior and galvanostatic cycling performance. It is proved that with the blend salts electrolyte, this supercapacitor battery system possesses the advantages of high capacity and long life.

Experimental

Electrolytes and electrodes preparation

LiPF_6 was produced by Kantodenka Co., Ltd (Japan). Et_4NBF_4 was purchased from Stella Chemifa Corporation Osaka (Japan). EC, DMC, and EMC were provided by Guangzhou Tinci Materials Technology Co., Ltd (China). The electrolytes were prepared by dissolving blend salts (LiPF_6 and Et_4NBF_4) in a mixture of EC, DMC, and EMC (1:1:1 wt.%). The percentage of 1 M LiPF_6 and 1 M Et_4NBF_4 is 12.6 and 16.4 wt.%, respectively. Detailed composition of the electrolytes was summarized in Table 1. All electrolytes were prepared in an argon-filled glove box. Water and free acid contents of the electrolytes were controlled below 20 ppm, which were examined by 831 KF Coulometer and 877 Titrino plus, respectively.

Cathodes were fabricated by doctor blade casting of slurry containing 20 wt.% LiMn_2O_4 powder, 60 wt.% activated carbon, 10 wt.% SP carbon powder, 3 wt.% carboxy methylcellulose, and 7 wt.% styrene–butadiene rubber dissolved in distilled water onto the current collector

(21 μm thick Al foil, flying electronic materials Co., Ltd. Shenzhen). The surface area of the supporting material was 28,160 mm^2 (40×352 mm) and the active material was 5.435 g.

Anodes were prepared using polyvinylidene difluoride as binder. A paste was prepared by mixing 80 wt.% $\text{Li}_4\text{Ti}_5\text{O}_{12}$, 10 wt.% SP carbon powder and 10 wt.% binder in *N*-methylpyrrolidone onto the Al foil current collector. The surface area of the supporting material was 31,816 mm^2 (41×388 mm) and the active material was 1.618 g.

The theoretical capacity ratio of the positive and negative electrodes was close to 1:1.1. This balancing ratio was calculated considering 140 mAh g^{-1} specific capacity for LiMn_2O_4 , 170 mAh g^{-1} specific capacity for $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and 30 mAh g^{-1} specific capacity for AC [15]. The capacity density was calculated using the active material mass of positive electrodes.

Electrochemical measurements

To evaluate the electrochemical stability of electrolyte, the samples were tested by linear sweep voltammetry (LSV; working electrode, Pt (surface area, 0.0707 mm^2); counter and reference electrodes, metallic lithium foil) at a scan rate of 1 mV s^{-1} . The experiments were carried out using a CH Instrumental Electrochemical Workstation (CHI650B).

Using composite LiMn_2O_4 and AC cathode and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode for 063048-type batteries, the charge–discharge cycling tests of $(\text{LiMn}_2\text{O}_4+\text{AC})/\text{Li}_4\text{Ti}_5\text{O}_{12}$ were performed on BS 9300R (Qingtian Guangzhou) between 0.8 and 2.8 V at a constant current. Galvanostatic cycling performance tests were divided into two modes: charge–discharge at 0.8 C rate and charge–discharge at 4 C rate. All these experiments were carried out at room temperature.

Results and discussion

Linear sweep voltammograms of the electrolytes

LSVs of Pt electrode using different electrolytes are displayed in Fig. 1. As shown in this picture, the decomposition voltage of the electrolyte with pure LiPF_6 was 4.6 V, a little higher than that of the electrolyte with pure Et_4NBF_4 , which was only 4.25 V. The electrolyte composed of 0.5 M LiPF_6 and 0.5 M Et_4NBF_4 in EC+EMC+DMC=1:1:1 (wt.%) performed best, there was a little electrolyte decomposition till 5.1 V. With the molar ratio of Et_4NBF_4 increasing, the stability of the electrolyte went up first and then down. The results suggest that the electrochemical stability of the blend salts electrolyte is better than that of the pure salt electrolyte. In other words, blend salts electrolyte used for supercapacitor batteries at high voltage is more suitable.

Table 1 Detailed composition of the electrolytes

No.	Solvent	Blend salts (molar ratio)	
		LiPF_6/M	$\text{Et}_4\text{NBF}_4/\text{M}$
1	EC+DMC+EMC 1:1:1 (wt.%)	1	0
2		0.8	0.2
3		0.5	0.5
4		0.2	0.8
5		0	1

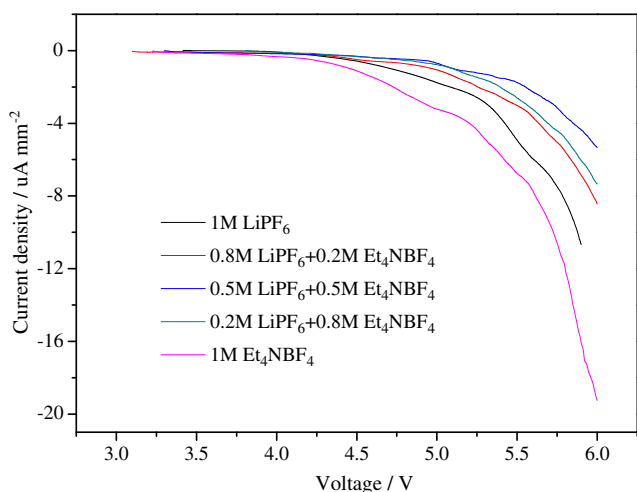


Fig. 1 LSVs of different electrolytes at a scan rate of 1 mV s^{-1}

The analysis of galvanostatic charge–discharge behavior

Figure 2a–b shows a whole charge–discharge process of supercapacitor battery ($\text{LiMn}_2\text{O}_4+\text{AC}$)/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with different electrolytes at 0.8 and 4 C rate, respectively. From Fig. 2, we can see that there was no obvious voltage plateau in these curves. At 0.8 C rate, the process of charge mainly composed of two parts: the voltage increased rapidly below 2.55 V, which indicates ion adsorption/desorption (on active carbon) energy storage; the voltage increased slowly between 2.55 and 2.8 V which is the means of the Li-intercalation/deintercalation energy storage (Fig. 2a) [2]. However, the current of charge–discharge increased to 4 C rate (Fig. 2b). The difference between the two ways of energy storage was not so significant because the electric double-layer energy storage combined with Li-

intercalation/deintercalation energy storage was better. When the current for charge and discharge is high, the Li^+ can reach the active material rapidly. It can be concluded that the formation of electric double layer can improve Li^+ to pass through the interface and participate in the reaction of Li intercalation/deintercalation.

Figure 3 shows the galvanostatic cycling stability of the supercapacitor battery system ($\text{LiMn}_2\text{O}_4+\text{AC}$)/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at a constant current of 0.8 and 4 C with different electrolytes. In Fig. 3a–b, the capacity retention increased obviously with the increase of Et_4NBF_4 concentration. When the charge–discharge rate changed from 0.8 to 4 C, the capacity retention increased from 90.3% to 96.23% with the electrolyte of 0.2 M $\text{LiPF}_6+0.8 \text{ M Et}_4\text{NBF}_4$ after 5,000 cycles. The capacity of the supercapacitor battery with a standard of 1 M LiPF_6 is not high mainly due to the part that the supercapacitor cannot perform very well: lithium ions take part in the reaction of Li intercalation/deintercalation on electrodes; by contrast, ions participate in the reaction of electric double-layer electrostatic adsorbing–desorbing which has less supercapacitor capacity [2]. The result illuminates that with the addition of Et_4NBF_4 , enough ions take part in the reaction of electric double-layer electrostatic adsorbing–desorbing and lead to a capacity increase. Ionica-Bousquet et al. have demonstrated that the presence of BF_4^- anion can improve the cycle stability in both batteries and supercapacitors due to the protective shuttle effect [16]. With the increase of Et_4NBF_4 concentration, the effect of BF_4^- gets more obvious and the galvanostatic cycling stability becomes better. When the current of charge–discharge is high, the two ways of energy storage combine better and lead to capacity retention increase.

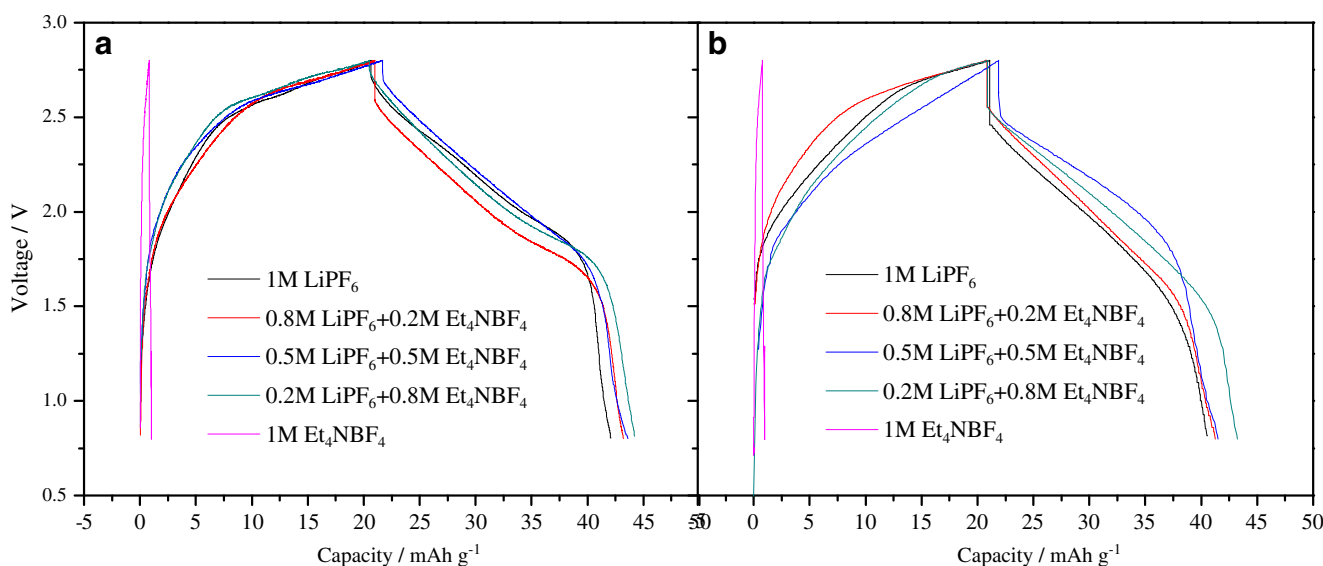


Fig. 2 Galvanostatic charge–discharge curves at 0.8 C rate (a) and 4 C rate (b) of the first cycle

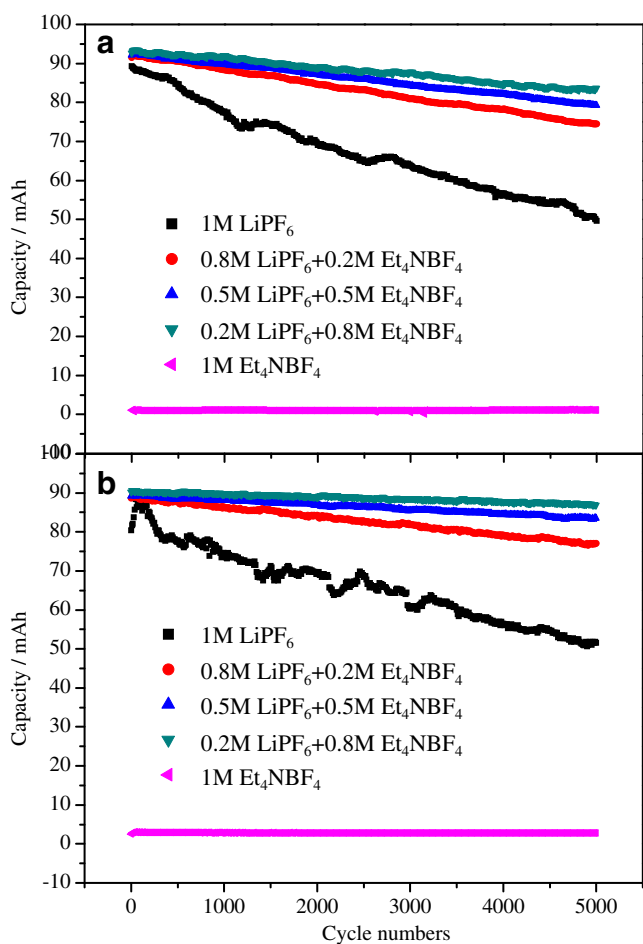


Fig. 3 Galvanostatic cycling stability of (LiMn₂O₄+AC)/Li₄Ti₅O₁₂ at 0.8 C (a) and 4 C (b)

Conclusions

A novel blend salts (Et₄NBF₄ and LiPF₆) electrolyte for supercapacitor battery (LiMn₂O₄+AC)/Li₄Ti₅O₁₂ has been investigated in EC+EMC+DMC (1:1:1 wt.%) solution. The LSV shows that the blending of LiPF₆ and Et₄NBF₄ is more stable at high voltage than the pure salt-based electrolyte system. In the test of galvanostatic cycling performance, cells assembled with the blend salts electrolyte perform better in terms of energy density and galvanostatic cycling stability after testing at room

temperature as compared to those assembled using the LiPF₆-based standard electrolyte. This confirms that the blend salts LiPF₆ and Et₄NBF₄ can obviously affect the performances of the supercapacitor battery. The LiPF₆/Et₄NBF₄ ratio of 0.2:0.8 M is the best choice for (LiMn₂O₄+AC)/Li₄Ti₅O₁₂ battery, the capacity retention reaches 96.23% after 5,000 cycles at 4 C rate. It can be concluded that the electrolyte with LiPF₆/Et₄NBF₄ ratio around 0.2:0.8 M exhibits the best characters of high capacity and long life with (LiMn₂O₄+AC)/Li₄Ti₅O₁₂ supercapacitor battery system.

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