Journal of Electroanalytical Chemistry 808 (2018) 293–302

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

# Enhanced performance of the electrolytes based on sulfolane and lithium difluoro(oxalate)borate with enhanced interfacial stability for $LiNi_{0.5}Mn_{1.5}O_4$ cathode

Hongming Zhou[a,b], Demin Xiao[a], Chengjie Yin[a], Zhaohui Yang[a], Kaiwen Xiao[a], Jian Li[a,b,*]

[a] *School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, China*
[b] *Hunan Zhengyuan Institute for Energy Storage Materials and Devices, Changsha, Hunan 410083, China*

## ARTICLE INFO

*Keywords:*
Lithium difluoro(oxalate)borate
Sulfolane
Interfacial stability
Decomposition
Passivation

## ABSTRACT

The electrolytes based on lithium difluoro(oxalate)borate (LiODFB) and sulfolane (SL) including LiODFB-ethylene carbonate (EC)/dimethyl carbonate (DMC) and $LiPF_6$-EC/DMC as the references have been studied on electrochemical performance and interfacial stability in Li/$LiNi_{0.5}Mn_{1.5}O_4$ cells. LiODFB-containing electrolytes show outstanding electrochemical stability within 5.5 V due to the passivation phenomenon on the cathodes, while $LiPF_6$-containing electrolytes undergo continuous decomposition beyond 4.5 V. The initial charge/discharge profiles and cyclic voltammetry (CV) curves prove that the cell with LiODFB-SL/DMC(2:1 by vol.) electrolyte has lower degree of polarization and better reversibility. The cathode with LiODFB-SL/DMC(2:1 by vol.) electrolyte displays the best cycling performance and the cathode with $LiPF_6$-EC/DMC(1:1 by vol.) electrolyte displays the worst cycling performance. AC impedance shows that the cell cycling with LiODFB-SL/DMC(2:1 by vol.) electrolyte has much smaller resistance of charge transfer on cathode/electrolyte interface than the cell cycling with LiODFB-EC/DMC(1:1 by vol.) electrolyte. The characterization of the cathode surfaces indicates that a more homogeneous and compact passivation layer forms on the cathode cycling with LiODFB-SL/DMC(2:1 by vol.) electrolyte to greatly improve the interfacial stability for the reason that SL motivates the passivation reaction of LiODFB and itself participates the formation of the passivation layers. Therefore, LiODFB-SL/DMC(2:1 by vol.) is a promising electrolyte for $LiNi_{0.5}Mn_{1.5}O_4$ cathode.

## 1. Introduction

The aggravation of environmental pollution consequences and the enhancement of people's environmental protection awareness make green energy products play an increasingly important role in daily life. As a result, electric vehicles (EVs) and hybrid electric vehicles (HEVs) have become one of the mainstream travel tools in recent years. In spite of this, EVs and HEVs still cannot completely replace fuel vehicles so far mainly because of the short continuation of the power provided by lithium ion batteries. Therefore, there is an urgent demand for lithium ion batteries with higher energy density [1,2]. Apart from cathode materials with higher specific capacity, cathode materials with high operating voltage are also effective alternatives to improve the energy density of lithium ion batteries [3,4]. Spinel $LiNi_{0.5}Mn_{1.5}O_4$ cathode with high voltage plateau at around 4.7 V (vs. $Li/Li^+$) has attracted great attention since it was first systematically studied by J. R. Dahn et al. [5–7]. Due to serious capacity fading especially at elevated temperature caused by the Jahn-Teller distortion of $Mn^{3+}$ [8] and no competitiveness with other common commercial cathode materials such as $LiCoO_2$ and $LiFePO_4$ in terms of energy density [9,10], spinel $LiMn_2O_4$ cathode has not gotten further application. With Ni substituting Mn partially based on $LiMn_2O_4$, $LiNi_{0.5}Mn_{1.5}O_4$ obtains a stable structure and improved cycling life for the reason that the redox process occurs on the Ni site, which prevents the generation of the $Mn^{3+}$ and the related Jahn-Teller distortion [11]. The wonderful high operating potential at around 4.7 V vs. $Li/Li^+$ endows $LiNi_{0.5}Mn_{1.5}O_4$ cathode with higher energy density (650 $Wh \cdot kg^{-1}$), compared with common commercial cathodes $LiCoO_2$ and $LiFePO_4$ [9,10]. Besides, there are three dimension paths for $Li^+$ diffusion in spinel structure and owing to this, $LiNi_{0.5}Mn_{1.5}O_4$ cathode exhibits great rate performance and power density [12].

Although $LiNi_{0.5}Mn_{1.5}O_4$ with high energy density and high power density has been considered to be a promising cathode for the next generation of lithium ion batteries used in automotive field, its high operating voltage brings great challenges to its application for imposing great stresses on the conventional $LiPF_6$/carbonates-based electrolytes.

---

[*] Corresponding author at: School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, China.
*E-mail address:* ziliao2000@126.com (J. Li).

https://doi.org/10.1016/j.jelechem.2017.12.040
Received 25 June 2017; Received in revised form 12 November 2017; Accepted 14 December 2017

The widely used lithium salt $LiPF_6$ suffers serious decomposition ($LiPF_6 = LiF + PF_5$) when the voltage reaches to 4.5 V, which leads to abnormal charge/discharge process and very low capacity and coulomb efficiency [13,14]. What's worse, as a strong Lewis acid, $PF_5$ reacts immediately with any $H_2O$ inside the batteries to form HF ($PF_5 + H_2O = 2HF + POF_3$). HF is disastrous to cathode materials, cathode aluminum current collector and even the stable and conductive solid electrolyte interphase (SEI) films that have formed on anodes [15]. The oxidation potential of the pure carbonate solvents is $> 5.0$ V, but the transition metal ions from the cathode materials catalyze the oxidation reaction and accelerate the decomposition of the carbonates at lower potential [16]. The inorganic species such as LiF, $Li_xPO_yF_z$ and $Li_xPF_y$ resulting from the decomposition of $LiPF_6$ as well as the organic species such as polyethers and polycarbonates resulting from the decomposition of carbonates (mainly ethylene carbonate (EC) and propylene carbonate (PC)) deposit on the cathodes to form the films that increase internal resistance of batteries but have no much benefit for the stability of the cathode/electrolyte interfaces [13,14,17]. Thus, the development of the electrolytes that can withstand high operating voltage is necessary for the commercial application of $LiNi_{0.5}Mn_{1.5}O_4$ cathode.

In recent years, lithium difluoro(oxalate)borate (LiODFB), first reported as a lithium salt by Sheng Shui Zhang in 2006 [18], has been favored by researchers on high voltage lithium ion batteries for possessing some superior characteristics. Unlike $LiPF_6$, there is no generation of HF when the decomposition of LiODFB occurs [19]. LiODFB also participates in the formation of SEI films on anodes and suppresses the reactivity of lithiated graphite toward the electrolytes [20]. More importantly, LiODFB can passivate cathode aluminum current collector [21] and facilitate the formation of cathode electrolyte interphase (CEI) passivation layers at high potential [22]. It was reported that typical high voltage cathode material $LiCoPO_4$ exhibited higher reversible charge/discharge capacity and better cyclic stability using LiODFB-containing electrolyte [23]. Several studies demonstrated that LiODFB as lithium salt in ionic liquid-based electrolytes had positive effects on the performance of $Li/Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ and Li/MCMB cells. The results indicated that LiODFB could be preferably oxidized during charging and reduced during discharging and the reaction products piled up to form passivation layers on the surfaces of electrodes to ensure the good electrochemical performance of the cells [24,25].

The instability of conventional carbonate solvents on the surfaces of high voltage cathodes cannot be ignored and to solve it, finding favorable solvents is a problem that must be overcome. A lot of researches have been done to match high voltage cathodes with compatible organic solvents. Among these results, the function of sulfones in improving the performance of electrolytes is very worthy of attention. The oxidation potential of sulfones is over 5.0 V according to theoretical and experimental studies [26,27]. Angell et al. [28] reported that 1 M $LiPF_6$ in ethylmethyl sulfone (EMS)/dimethyl carbonate (DMC) (1:1 by wt.) mixed electrolyte performed very well (97% capacity retention after 100 cycles with 99–100% coulomb efficiency) at $LiNi_{0.5}Mn_{1.5}O_4$ cathode and also at $Li_4Ti_5O_{12}$ anode. Abouimrane et al. [29] expounded that in a cell with $LiNi_{0.5}Mn_{1.5}O_4$ electrode and 1 M $LiPF_6$ in sulfolane (SL) as electrolyte, the capacity reached 110 $mAh{\cdot}g^{-1}$ at C/12 rate and when SL was blended with ethyl methyl carbonate (EMC), $Li_4Ti_5O_{12}/LiNi_{0.5}Mn_{1.5}O_4$ cell delivered initial capacity of 80 $mAh{\cdot}g^{-1}$ and cycled well for 1000 cycles at 2C rate. The lower flammability of sulfones than carbonates can significantly improve the safety of lithium ion batteries. However, the high viscosity of sulfones greatly decreases the ionic conductivity of electrolytes and the $Li^+$ migration velocity and stable SEI films cannot form on anodes [30], which are the obstacles for the further application of sulfones in electrolytes.

To find a type of electrolyte that can be perfectly compatible with $LiNi_{0.5}Mn_{1.5}O_4$ cathode, not only suitable lithium salts but also matched solvents should be applied. In this work, LiODFB was chosen as the lithium salt due to the advantages for high voltage batteries. Meanwhile, SL was used as the main solvent and to reduce the viscosity, linear carbonate DMC was added as the co-solvent. A series of electrolytes with different proportions including LiODFB-EC/DMC and $LiPF_6$-EC/DMC as the references were systematically researched on electrochemical performance and interfacial stability in $Li/LiNi_{0.5}Mn_{1.5}O_4$ cells. The results were discussed in detail.

**Table 1**
Composition of the electrolytes.

| No. | Lithium salts | | Solvents (volume ratio) | | |
|---|---|---|---|---|---|
| | LiODFB | $LiPF_6$ | SL | EC | DMC |
| 1 | 1 M | | 3 | | 1 |
| 2 | 1 M | | 2 | | 1 |
| 3 | 1 M | | 1 | | 1 |
| 4 | 1 M | | | 1 | 1 |
| 5 | | 1 M | | 1 | 1 |

## 2. Experimental

### 2.1. Preparation of electrolytes

LiODFB (battery degree) was provided by Hunan Zhengyuan Institute for Energy Storage Materials and Devices. $LiPF_6$ (battery degree) was purchased from Morita Chemical. SL (99%), EC (99%) and DMC (99%) were purchased from Aladdin and each of them was dried by 0.4 nm molecular sieves for at least 24 h before use until the moisture content was controlled below 20 ppm determined by Mettler Toledo C20 Coulometric KF Titrator. All the electrolytes were prepared in an argon-filled glove box (Universal 1500/750/900, Mikrouna (China) Co., Ltd., moisture content $< 1$ ppm, oxygen content $< 1$ ppm) and the composition of each electrolyte is listed in Table 1.

### 2.2. Assembly of coin cells

To investigate the electrochemical stability of electrolytes by linear sweep voltammetry (LSV), the test devices were assembled into CR2032 coin cells. Al foil and Li sheet were used as cathode and anode respectively and Celgard 2400 was applied as separator. The electrolytes used were shown in Table 1. The test devices were assembled in the argon-filled glove box.

The compatibility of $LiNi_{0.5}Mn_{1.5}O_4$ cathode and the electrolytes was studied using $Li/LiNi_{0.5}Mn_{1.5}O_4$ coin cells (CR2032). The cathodes were prepared by mixing 80 wt% active material, 10 wt% carbon black and 10 wt% polyvinylidene fluoride (PVDF) in *N*-methyl-pyrrolidone (NMP) to form homogeneous slurry. The slurry was then cast on Al foil and dried at 120 °C for 12 h under vacuum. With Li sheet as anode and Celgard 2400 as separator, $Li/LiNi_{0.5}Mn_{1.5}O_4$ coin cells (CR2032) were assembled in the argon-filled glove box. The electrolytes used were shown in Table 1.

### 2.3. Characterization of electrolyte properties

Ionic conductivity of the electrolytes was measured by DDS-11A conductivity meter from 25 °C to 85 °C. Viscosity of the electrolytes was measured by AR2000EX rheometer with the temperature range of 25 °C to 85 °C.

The LSV tests were performed by an electrochemical workstation (CHI660D) with a three electrodes system and Al foil was used as working electrode and Li sheet was applied as counter electrode and reference electrode. The scan rate was 1 $mV{\cdot}s^{-1}$ and the potential range was from open circuit potential to 6.5 V.