



# In Situ formation of pentafluorophosphate benzimidazole anion stabilizes high-temperature performance of lithium-ion batteries



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## ARTICLE INFO

### Article history:

Received 2 March 2014

Received in revised form 9 May 2014

Accepted 9 May 2014

Available online 19 May 2014

### Keywords:

Benzimidazole

Anion

Lithium ion battery

Solid electrolyte interface

Lewis acid-base reaction

## ABSTRACT

Lithium salts play a critical role in initiating electrochemical reactions in Li-ion batteries. Single Li ions dissociate from bulk-salt and associate with carbonates to form a solid electrolyte interface (SEI) during the first charge-discharge of the battery. SEI formation and the chemical stability of salt must both be controlled and optimized to minimize irreversible reactions in SEI formation and to suppress the decomposition of the salt at high temperatures. This study synthesizes a new benzimidazole-based anion in the electrolyte. This anion, pentafluorophosphate benzimidazole, results from a Lewis acid-base reaction between the benzimidazole anion and PF<sub>5</sub>. The new pentafluorophosphate benzimidazole anion inhibits the decomposition of LiPF<sub>6</sub> by inhibiting PF<sub>5</sub> side reactions, which degrade the SEI, and lead to the formation of LiF and HF at high temperatures. In addition, the use of the pentafluorophosphate benzimidazole anion results in the formation of a modified SEI that is able to modify the battery's performance. Cyclic voltammetry, scanning electron microscopy, differential scanning calorimetry, electrochemical impedance spectroscopy, as well as charge-discharge and X-ray photoelectron spectroscopy measurements have been used to characterize the materials in this study. The formation of the pentafluorophosphate benzimidazole anion in the electrolyte caused a 14% decrease in the activation energy for ionic diffusion, a 19% increase in capacity at room temperature, and led to a well-maintained battery performance at 60 °C, compared with an electrolyte only cell used in conjunction with the anion of PF<sub>6</sub><sup>-</sup>.

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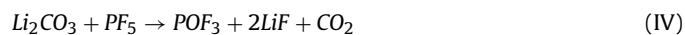
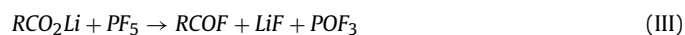
## 1. Introduction

Lithium-ion batteries are a widely used rechargeable power source for portable electronic devices. In addition to these applications, Li-ion batteries are now being used to power electric vehicles (EVs) and hybrid electric vehicles (HEVs). However, low durability at high-temperatures is a critical downside affecting the battery life in EVs and HEVs. Typically, EV or HEV batteries must operate at a wide range of temperatures (including  $\geq 60$  °C). Currently, the majority of Li-ion batteries perform poorly at high temperatures due to decomposition of Li salt. LiPF<sub>6</sub>, the most widely used salt in commercial batteries, provides excellent ionic conductivity and a wide electrochemical window. However, high-temperature applications accelerate the generation of HF and PF<sub>5</sub> and in doing so destroy the battery's infrastructure, including its solid electrolyte interface (SEI), electrode materials, and current collectors [1,2].

LiPF<sub>6</sub> is used to dissolve into mixed carbonate solvents, such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) [3,4], where it easily dissociates into single Li ions (Li<sup>+</sup>) and PF<sub>6</sub><sup>-</sup> due to the high dielectric constant of carbonates [5]. However, LiPF<sub>6</sub> suffers thermal stability problems, resulting in facile decomposition leading to side reactions at temperatures above 60 °C, as shown in Equation (I) [1,6,7]:

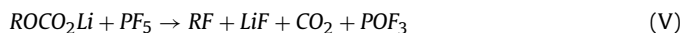


The product of PF<sub>5</sub> (i.e., Lewis acid) catalyzes HF and LiF formation owing to PF<sub>5</sub> reacting with the SEI in the presence of moisture. The following reactions trigger the formation of insulators (LiF, POF<sub>3</sub>, and RCOF), thereby increasing the interfacial impedance and corroding the current collector according to the reactions expressed in Equations (II)–(V) [1].



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Based on these equations,  $\text{LiPF}_6$  is critical, and its chemical composition must be stabilized. According to previous research [8,9],  $\text{PF}_5$  can easily accept a lone pair from a Lewis base. Several methods have been studied that inhibit  $\text{PF}_5$  generation by replacing the  $\text{LiPF}_6$  with a new salt, or that maintain the  $\text{LiPF}_6$  structure by adding electrolyte additives [1,10]. LiBOB was proposed as a salt candidate to resolve the problem of thermal stability. Wang *et al.*, showed that batteries containing LiBOB exhibit greater charge-discharge capacity at elevated temperatures than batteries containing  $\text{LiPF}_6$ . However, compared with  $\text{LiPF}_6$ , LiBOB exhibits lower ionic conductivity [11].  $\text{LiBF}_4$  has been introduced as a candidate salt because of its high thermal stability, although it is affected by low ionic conductivity [5,12]. Both LiBOB and  $\text{LiBF}_4$  exhibit a superior thermal performance due to the absence of  $\text{PF}_5$  formation and reduced HF production during high-temperature cycling. Several studies have discussed the application of electrolyte additives in high-temperature applications. Vinyl EC (VEC), by suppressing  $\text{CO}_2$  evolution at high temperatures, has been proposed as a means to improve battery performance at  $50^\circ\text{C}$  [13]. Trimethyl phosphite and trimethyl phosphate have been reported as offering improved thermal stability and battery performance due to the formation of SEI on the cathode's surface [14,15]. However, the results of the above studies have been questioned; thus, the low ionic conductivity problem together with SEI formation, when  $\text{LiPF}_6$  is used remains unresolved.

In this study, a novel benzimidazole-based Li salt was successfully synthesized and shown to be able to play a critical role in forming the new SEI, while maintaining the chemical stability of  $\text{LiPF}_6$  due to the Lewis acid-basic reaction. This article discusses the effects of the Li benzimidazole salt that was used as an electrolyte additive in a Li battery system, and details the measurements taken at elevated temperatures.

## 2. Experiment

### 2.1. Materials and the Preparation of Lithium Benzimidazole

Lithium benzimidazole was synthesized using a deprotonation method between benzimidazole (Alfa Aesar Company) and LiOH (Sigma Aldrich) [16]. Tetrahydrofuran (THF) was dried prior to use. To prepare the Li benzimidazole, benzimidazole (0.2 M) was stirred with LiOH (0.4 M) and then placed into THF solvent for 24 h in a three-necked round bottomed flask. After stirring, the slurry was filtered and placed in a vacuum at  $80^\circ\text{C}$  overnight before use. The resulting Li benzimidazole was characterized using nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry and differential scanning calorimetry (DSC).

For the NMR measurement, the Li benzimidazole was prepared by dissolution in d-DMSO. The DSC sample was prepared on a high-pressure gold plate—prior to scanning from room temperature to  $300^\circ\text{C}$  (at  $5^\circ\text{C s}^{-1}$ ). The graphite anode comprised 93 wt% meso-carbon microbeads (MCMBs), 3 wt% vapor-grown carbon fibers (VGCFs) as a conductive additive, and 4 wt% PVDF as a binder.

### 2.2. Preparation of electrolyte

Two electrolytes were prepared for the experiments. Sample A was 1 M lithium hexafluorophosphate ( $\text{LiPF}_6$ ) in EC: DEC (1:1 in volume), while Sample B was identical to Sample A, except for the addition of 0.1 wt% Li benzimidazole. The battery fabrication and electrolyte preparation were performed inside the glove box under an Ar gas atmosphere to avoid interference from moisture effect.

### 2.3. Instrumentation

The ionic conductivities were measured using electrochemical impedance spectroscopy (EIS) (Biologic VMP3) from 100.0K–0.1 Hz with an AC amplitude of 5 mV, at temperatures from  $25$ – $90^\circ\text{C}$ . The equipment was controlled using EC-Lab electrochemical software (Biologic, Inc.). Temperature-dependent conductivities were obtained by placing the electrochemical cell in an oven. The impedance spectra exhibited depressed semicircles at high frequencies and slanted lines at low frequencies. The resistance was determined based on an extrapolation of the intercept of the slanted line and the real axis of each impedance spectra plot [imaginary ( $Z''$ ) versus real ( $Z'$ )]. The specific ionic conductivity  $\sigma$  was obtained from  $\sigma = l/AR$ , where the distance between the two stainless electrodes  $l = 0.5$  cm. For the stainless electrode, the measured area  $A = 1$  cm<sup>2</sup>, and  $R$  is the measured resistance ( $\Omega$ ). The compatibility of the electrolytes with the stainless electrode was determined using EIS analysis under open-circuit conditions at various temperatures.

Ionic conductivity measurements, at various temperatures, were used, to determine the activation energy of the electrolyte from an Arrhenius plot.

$$\ln \sigma = -\frac{Ea}{RT} + \ln A$$

$$\text{slope} = -\frac{Ea}{R}$$

The electrochemical stability of the electrolytes was measured using cyclic voltammetry (CV) (Biologic VMP3) between 3.00 and 0.01 V at a scan rate of 0.1 mV/s, using a three-electrode cell that comprised stainless steel working and counter electrodes (1.0 cm<sup>2</sup>), a Li reference electrode with the electrolyte filling the space between the working and the counter electrodes.

The EIS was performed using a Biologic VMP3 from 100 M to 0.01 Hz with an AC amplitude of 5 mV at  $25^\circ\text{C}$ . All of the EIS measurements were performed using a half cell (CR2032) comprising carbon and Li metal electrodes (area = 1.0 cm<sup>2</sup>) in a 100% state of discharge (SOD).

The charge-discharge test was conducted using the constant current-constant voltage (CC-CV) mode with a voltage range of 0.005 to 3.000 V at 0.1 C/0.1 C, measured using a U-bic battery tester. Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) were used to observe the MCMB electrode's morphology after a Pt coating (in the glove box) onto the electrode at an accelerating voltage of 15 kV using an LEO-1530 microscope. Before any observations were made, the specimens were disassembled and washed with DMC in a dry room, and then dried overnight in a vacuum. The samples were placed into a custom-built high vacuum stainless steel holder to transfer the anode electrodes from the dry room to the SEM instruments. The SEI was not influenced by the graphite's treatment before assembling and drying the cell.

The surface and depth profile composition of the electrode were determined using X-ray photoelectron spectroscopy (XPS) (PHI, 1600S) to evaluate the SEI composition. The sputtering rate was set at 1 s per 1 nm of thickness. For the SEM, EDS, and XPS sample preparation, the MCMB electrode was removed from the cell and washed three times using DMC. The MCMB electrode was dried overnight in a vacuum before use. All of the sample preparations were performed in an Ar-filled glove box to avoid moisture.

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