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Benzotriazole as an electrolyte additive on lithium-ion batteries performance

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ABSTRACT

Liquid electrolyte consisting of 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) and 0.1 wt% benzotriazole (BzTz) is studied in $LiCoO_2$//graphite battery system at room temperature. Benzotriazole addition introduces excellent electrochemical stability (5.6 V vs Li) and good ionic conductivity properties at room temperature. Also, this electrolyte shows good cycling performance and better discharge capacities at high C-rates relative to the pristine electrolyte. Furthermore, the additive allows the formation of a good solid electrolyte interphase (SEI) per cyclic voltammetry (CV) examination. These specialized properties make this liquid electrolyte ideal for high power and high voltage applications.

Introduction

It is an undisputed fact that lithium-ion batteries (LIBs) are currently the main source of power for portable electronics [1]. The future application of lithium-ion batteries for high energy and power devices like electric vehicles and hybrid electric vehicles is so promising and arouses so much optimism, it continues to drive the development of new materials in this engineering field [1–3]. Most traditional LIBs employ $LiPF_6$ salt in alkyl carbonate and ester solvents as electrolytes due to its good ionic conductivity and electrochemical stability [4,5]. However, the generation of HF and PF_5 under high temperature conditions and in the presence of minute amounts of moisture is problematic [6–8]. Several alternatives have been proposed by researchers around the world to make up for the inadequacies of $LiPF_6$ [9–11]. LiFBMSI and LiFAP are some alternatives that can be used though the former exhibits lower ionic conductivity [10,12,13]. Some proposed salts, like $LiBF_4$ and LiBOB, are more stable at high temperatures due to the absence of PF_5; thus, they produce far less or no amount of HF due to their superior water tolerance properties [10]. Unfortunately, the aluminum corrosion effect (in the case of LiTFSI, LiFSI) considerably limits their commercial applications [10]. Aromatic compounds have played vital roles as electrolyte additives for lithium-ion batteries [14,15]. Benzotriazole has been used as an antifreeze and corrosion-inhibiting agent in several systems, while succinonitrile has been used as a versatile additive in polymer electrolyte systems [16–18]. Due to the high polarity of these bases, the dissolution of salts in electrolytes becomes possible, allowing for high conductivities and transference numbers. Another beneficial property of these bases is their ability to stabilize salts over a wide range of temperature, which improves cell performance. For example, Sylvia et al. attempted to capitalize on this Lewis-acid property by introducing benzimidazole in its lithium salt form as an additive; this material binds to PF_5 in the electrolyte to reduce $LiPF_6$ decomposition [15]. By forming ion complexes with electrolyte salts (e.g., PF_6^-), aromatic additives like benzimidazole can stabilize electrolyte salts such as $LiPF_6$, thereby curbing recurring side reactions in electrolytes. Research has revealed that

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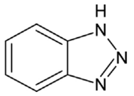
PF_5, like all Lewis-acids, is able to accept lone pairs of electrons. This additive has been shown to help improve the high-temperature performance of cells [15].

Herein, we investigated the properties of benzotriazole (structure provided below) as a $LiPF_6$ salt-stabilizing additive in an EC/DMC solvent for lithium-ion batteries.



This study reports on 0.1 wt% BzTz as an electrolyte additive for lithium-ion batteries. We investigated its performance using cyclic voltammetry (CV), electrochemical impedance, charge/discharge, linear sweep voltammetry (LSV), cycling tests, SEM, and EDX. Also the cycle life performance of this additive was tested in an old electrolyte (1 M $LiPF_6$ EC/DMC) which had been kept in a glove box for over a year.

Experimental

Materials

A 1 M $LiPF_6$ ethylene carbonate (EC)/dimethyl carbonate (DMC) electrolyte solution was purchased from Pannax, benzotriazole (BzTz), *N*-methyl-2-pyrrolidone, and polyvinylidene fluoride (PVDF) were obtained from Sigma Aldrich, and $LiCoO_2$ and graphite were supplied by Kokam Co.

Electrode and coin cell preparation

The electrode materials consisted of $LiCoO_2$ or graphite active materials, vapor-grown carbon fibers (VGCFs), and a polyvinylidene fluoride (PVDF) binder mixed at a ratio of 80:10:10 wt%. These were coated on aluminum and copper current collectors, respectively. To prepare the electrodes, a 10 w/v% solution of PVDF binder in *N*-methyl-2-pyrrolidone (NMP) was prepared and stirred for about 6 h. Then, a calculated volume of this solution was pipetted into a mortar along with an 80:10 ratio mixture of the active materials ($LiCoO_2$ or graphite) and VGCF, and mixed to form a fine slurry. NMP was evaporated at 80 °C and the electrodes were further dried in a vacuum oven at 60 °C for 48 h before use. In an argon-filled glove box, 2032 coin-type cells were assembled and fed with the 1 M $LiPF_6$ EC/DMC electrolyte and the 1 M $LiPF_6$ EC/DMC electrolyte containing 0.1 wt% BzTz.

Electrochemical analysis

The ionic conductivities of the electrolytes were measured using an Autolab PARSTAT 12/30 potentiostat/galvanostat FRA (frequency response analyzer) instrument over a frequency range of 1 Hz–1 MHz on platinum electrodes. Ionic conductivity values were deduced by calculations based on the first point of resistance values recorded on the Nyquist plots of impedance. The stability windows of the electrolytes were determined using nickel working electrodes and lithium metal as the reference and counter electrodes between 3 V and 6 V at a scan rate of 1 mV s^{-1}. Charging/discharging were performed at cut-off voltages of 3.0 V and 4.2 V with a charging rate of 0.1 C and discharging rates of 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, 5 C, and 10 C. To analyze the morphological structures of the electrode surfaces, field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDX) analyses of the cathode and anode surfaces were conducted after cycling in the electrolytes. To do this, the cells were disassembled and the electrode surfaces were washed with DMC solvent to get rid of excess electrolyte salts. The electrodes were then dried in a vacuum oven overnight before being analyzed. To monitor the resistive components of the cells, electrochemical impedance scans of the cells were taken after setup and then again after cycling. An Autolab PASTAT 12/30 potentiostat/galvanostat FRA was used again over the same frequency range (1 Hz–1 MHz). Finally, using this same instrument, cyclic voltammograms (CV) of the electrolytes were collected at a scan rate of 1 mV s^{-1} over a potential range of 0–3 V using graphite/lithium half cells.

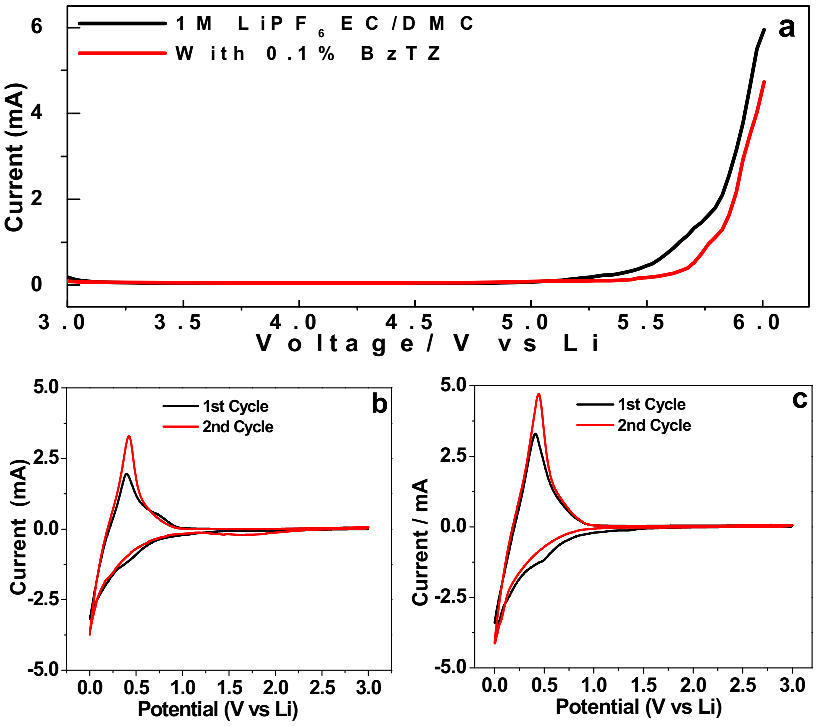


Fig. 1. (a) LSV of the electrolytes and the cyclic voltammograms of (b) the primary electrolyte and (c) the benzotriazole-containing electrolyte.