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Accelerating Rate Calorimetry and electrochemical study of imidazolium ionic salts based on 2,5-di-tert-butyl-1,4-dimethoxybenzene used as additives in Lithium-ion batteries for overcharge protection

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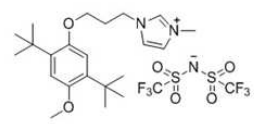
Lithium-ion batteries (LIB) are now the most promising energy storage technology for electric vehicles (EVs), hybrid electric vehicles (HEV) and plug-in hybrid electric vehicles (PHEV).[1] Their excellent cycle life, high volumetric and gravimetric energy density and their adaptability to various applications has encouraged numerous researchers to investigate the large application possibilities of LIB.[2] However, battery packs and LIBs cells are very susceptible to any overcharge abuse. The overcharge of lithium-ion batteries may result in chemical and electrochemical reactions involving the various battery components; an increase in gas with the release of gas; or an increase in temperature that can cause an out of control accelerated reaction. These consequences are not suitable in systems that dissipate heat poorly such as a LIB pack. In order to protect Li-ion cells from overcharge, one of the best solutions, among the many reported, is to use redox shuttles.[3]

Redox shuttles are electroactive species that enable overcharge protection by carrying excess charge current between the two electrodes in a cell under conditions of overcharge. They can be used as additives to the electrolytes of LIB. Ideally, redox shuttle for LIB overcharge protection are reversibly oxidized at a potential slightly higher (~ 300 mV) than the cathode's end of charge potential. Several redox-shuttles that have been dissolved in common organic solvents have been reported in the literature.[3,4] Moreover, when the benefit of redox shuttle protection can be incorporated into ionic liquids,[5] the LIB safety is expected to be improved. The improvement originates from the excellent thermal properties of ionic liquids and their high chemical stability. In order to use these additives in LIB, an investigation of the thermal stability of these molecules is required.

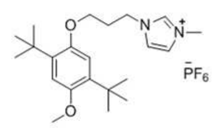
One of the best techniques to evaluate the thermal stability of such elements is Accelerating Rate Calorimetry (ARC). This method consists of testing the materials in adiabatic conditions, similar to that in actual LIB pack where the heat generated from an eventual exothermic reaction is not well dispersed, resulting in the build-up of heat in a concentrated area leading to a possible cascading thermal event.

In this report, two imidazolium-based ionic liquids incorporating 2,5-di-tert-butyl-1,4-dimethoxybenzene were studied; (DDB-EMIm-TFSI: compound **1**) and 2,5-di-tert-butyl-1,4-dimethoxybenzene imidazolium hexafluorophosphate (DDB-EMIm-PF6: compound **2**).Their electrochemical behaviour in Lithium-ion cells and their thermal properties within the ARC were investigated.

Electrochemical tests in standard lithium-ion coin cells show promising results for these compounds in overcharge conditions. Also, as expected, their thermal stability was found to be comparable to ionic liquids. Figure 1 shows the ARC profile of self-heating-rate (SHR) of compound 2 that shows no evidence of an exothermic event until 340ºC, which is well above that of the thermal instability of common lithium-ion anode and cathode materials. In this presentation, we will provide further details on the electrochemical and thermal properties of these redox shuttles, including a comparison of the thermal stability of common cathode materials in electrolytes with or without these redox shuttle molecules.



Compound 1



Compound 2

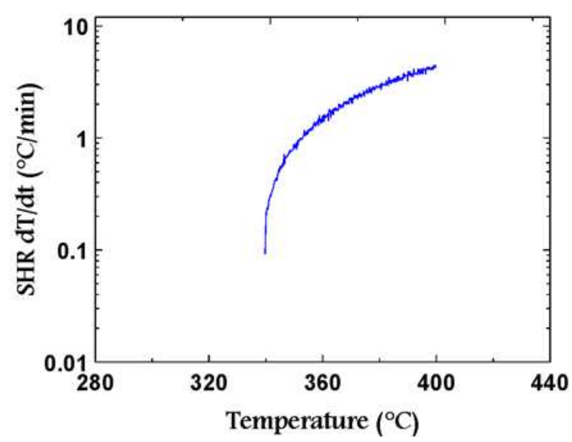


Figure 1. ARC SHR profile of 100 mg of pure compound **2**.

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