Journal of Electroanalytical Chemistry 807 (2017) 174–180

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Influence of salt, solvents, and additives on the thermal stability of delithiated cathodes in lithium-ion batteries

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ARTICLE INFO

Keywords:
Lithium-ion battery
Solvents
Additives
Cathode
Thermal stability

ABSTRACT

The thermal stability of a fully delithiated cathode, coupled with an inorganic salt, organic solvents, and electrolyte, was evaluated with differential scanning calorimetry (DSC) to address the safety issue of lithium-ion batteries. The DSC experiments revealed that vinylene carbonate (VC)-based systems exhibit decreased thermal stability compared to other coexisting systems. The DSC analysis of the cathode and electrolyte in the presence of VC, employed as additives, confirmed the reduction in thermal stability. Our results suggested that VC additives, which have been recently employed to enhance the electrochemical performance in anodes, negatively affect the thermal properties and safety characteristics of the cathode in lithium-ion batteries.

1. Introduction

Lithium-ion batteries (LIBs) have been widely used as power sources for portable applications, such as cell phones and laptops, due to their high energy density, long cycle life, and the absence of a memory effect. In recent years, several studies have focused on the application of LIBs as power resources in large energy-storage systems, electric vehicles (EVs), and hybrid-electric vehicles (HEVs). Relatively inexpensive batteries with a high energy density and power density are required for large energy-storage systems; however, safety issues must be considered as a priority. For example, fire accidents and explosions caused by batteries of portable devices, such as mobile phones and mp3 players, have been quite frequent since 2006. Furthermore, several fire accidents of large-storage systems, such as that of Honda HEV in 2008 (Japan), cargo aircraft in 2009 (Shenzhen, China), EV bus in 2010 (Urumqi, China), EV bus in 2011 (Shanghai, China), Tesla Model S EV, and Boeing 787 Dreamliner airplane are infamous examples of accidents caused by LIB explosions [1].

The malfunction and subsequent fire or explosion of a battery originates from an increase in the internal temperature of the cell, possibly caused by misuse by the consumer, or use in high-temperature environments. The thermal increase leads to the decomposition of the solid-electrolyte interface (SEI) of the negative electrode (anode) and subsequent exothermic reaction. As a result of a thermal reaction, the separator melts, and a consequent joule heating occurs due to a short circuit between the cathode and anode. Eventually, an exothermic reaction is triggered between the cathode and electrolyte. Researchers have focused on the thermal reaction that occurs between the graphite of the commercial anode material and electrolyte, because the exothermic reaction starts with the thermal decomposition of the SEI layer on the anode. Wang et al. explored the effect of the components of the cell on the thermal decomposition of the SEI layer of the anode material by using a C80 calorimeter suitable for the investigation of thermal reactions at low temperature [2]. Kim et al. confirmed that ionic-liquid-containing electrolytes and fluoroethylene carbonate (FEC) additives can form an electrochemically and thermally stable SEI film on the graphite surface [3]. Winter et al. revealed that vinylene carbonate (VC) and FEC additives can form a resistive film that protects the

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Abbreviations: DSC, differential scanning calorimetry; VC, vinylene carbonate; LIBs, lithium-ion batteries; EVs, electric vehicles; HEVs, hybrid-electric vehicles; SEI, solid-electrolyte interface; EC, ethylene carbonate; EMC, ethyl methyl carbonate; PC, propylene carbonate; DMC, dimethyl carbonate; DEC, diethyl carbonate; GBL, gamma-butyrolactone; PEO, polyethylene oxide

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https://doi.org/10.1016/j.jelechem.2017.11.046
Received 18 August 2017; Received in revised form 15 November 2017; Accepted 15 November 2017

thermal runaway on the surface of silicon anode materials [4]. Choi et al. employed differential scanning calorimetry (DSC) to demonstrate that FEC additives can form a SEI film, which suppresses the thermal reaction and enhances the electrochemical properties owing to a low interfacial resistance on the surface of the graphite anode [5]. Other studies have focused on the thermal reactions between the cathode and electrolyte, which involve flammable organic solvents; these are the most exothermic reactions in the batteries and result in thermal runaway and fire. Early studies, however, mostly focused on the improvement of the electrochemical performance of cathodes with only brief reports about the enhancement in thermal properties of the cathode and electrolyte [6–11]. More recently, studies have been proposed on the thermal properties of cathodes and electrolytes. For instance, Wang et al. evaluated the thermal reaction between the cathode and electrolyte occurring at high temperature, investigating different organic solvents and mixed electrolytes [12]. Prakash et al. focused on the thermal stability of the $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode by utilizing ethylene carbonate (EC) and FEC as the main co-solvent [13]; Amine et al. investigated the safety issues related to the $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode with several major solvents, e.g., EC, ethyl methyl carbonate (EMC), propylene carbonate (PC), and the $LiPF_6$ salt [14].

In this study, we systematically investigated the thermal properties of a delithiated cathode, $LiPF_6$ salt, and solvents such as EMC, dimethyl carbonate (DMC), diethyl carbonate (DEC), EC, PC, gamma-butyrolactone (GBL), and VC; their coexisting systems were also studied to analyze the exothermic reactions occurring between 200 and 350 °C. In addition, we evaluated the thermal influence of the VC solvents on the cathode and electrolyte; these have been recently employed as additives to enhance the electrochemical performance of the anode for the application of LIBs.

2. Experimental

2.1. Cell fabrication and electrochemical delithiation measurements of the cathode material

The $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode material was obtained from TODA America Corporation. The cathode was fabricated by blending a slurry of 92 wt% $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ material, 4 wt% denka black, 4 wt% binder (poly(vinylidene) fluoride) in *N*-methyl pyrrolidone (NMP). The blended slurry was cast on aluminum foil. The pouch cells were assembled in a dry room with 1 M $LiPF_6$ in the EC/DMC/DEC (1:1:1 vol%) electrolyte with and without 1 or 3 vol% VC, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ electrodes and Li metal being employed as the working electrode and counter/reference electrode, respectively. A charge measurement was carried out up to 4.3 V vs. Li/Li^+ at C/10 rate to delithiate the cathodes.

2.2. DSC measurements

The organic solvents used in this work (EMC, DMC, DEC, EC, PC, GBL, and VC) were obtained from Sigma-Aldrich. DSC measurements were carried out using a TA Instruments Auto Q20 instrument. The charged cells were disassembled in an argon-filled glove box and transferred into a bottle filled with DMC to remove the electrolyte and residual salt from the cathode material. After being rinsed, the electrode was dried to remove the DMC solvent; it was then carefully scraped from the aluminum foil for the subsequent thermal analysis. In order to evaluate the thermal behavior of the pure systems (solvent, delithiated cathode, and salt) or coexisting systems of cell components (salt/delithiated cathode, salt/solvents, delithiated cathode/solvents, salt/solvents/delithiated cathode, and electrolyte with additives/delithiated cathode), 3 μl of solvent or electrolyte and 3 mg of delithiated cathode or $LiPF_6$ salt were introduced into stainless-steel high-pressure capsules and hermetically sealed. All samples were measured under nitrogen atmosphere with a heating rate of 5 °C min^{-1} at the temperature range of 40 and 350 °C. The onset temperature in this study was determined based on the intersection of the tangents of the peak with the extrapolated baseline from the DSC curve.

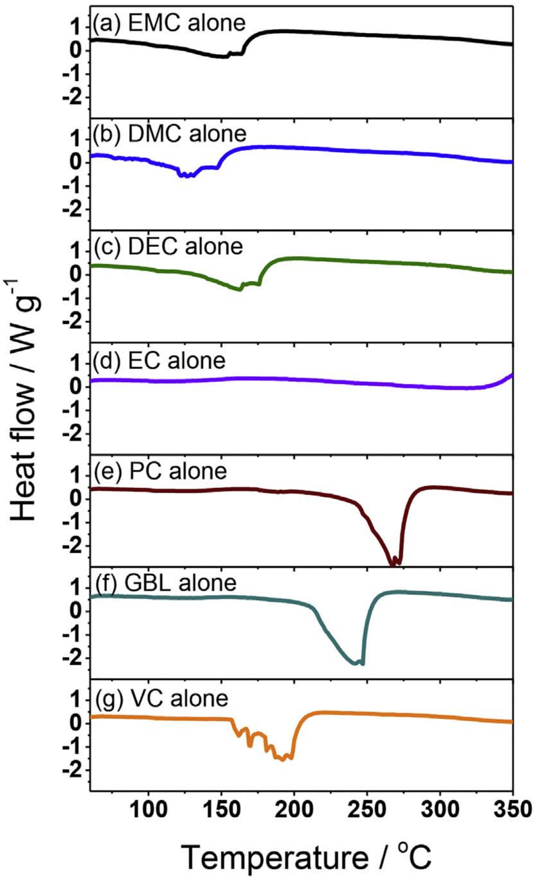

Fig. 1. DSC profiles of organic solvents.

3. Results and discussion

3.1. Thermal behavior of pure solvents, delithiated cathode, and salt

The thermal stability of the organic solvents, e.g., EMC, DMC, DEC, EC, PC, GBL, and VC during a temperature increase was evaluated with DSC; results are displayed in Fig. 1, and the thermodynamic parameters of the organic solvents (including the onset temperatures obtained from DSC) are listed in Table 1. The organic solvents employed in this study can be divided into three categories, i.e., linear carbonates (EMC, DMC, and DEC), cyclic carbonates (EC, PC, and VC), and cyclic ester (GBL). All the carbonate and lactones exhibit peaks typical of an endothermic reaction, which is attributed to their boiling process; the onset temperature of linear carbonates is generally lower than that of cyclic carbonates or cyclic ester [2,12,15–16]. These results are in good agreement with the previous DSC study on pure organic solvents materials [15,16] although this tendency exhibits discrepancy with other group [12,17]. As the DSC results in this study are well-matched with the boiling point of pure solvents, respectively, the endothermic reaction is thought to be the vaporization of pure solvents at boiling point. Linear carbonates are known to have weaker covalent bonds due to a smaller binding energy compared to cyclic carbonates and lactone-based solvents. Thus, the bonds of linear carbonates are likely to break at lower temperatures. Among the linear carbonates, which are commonly used in commercial electrolytes of LIBs, DEC exhibits the highest onset temperature; DMC shows the lowest onset temperature during the endothermic reaction. Generally, C_2H_5 or CH_3 radicals, placed at the