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Short communication

A novel high temperature stable lithium salt ($Li_2B_{12}F_{12}$) for lithium ion batteries

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ABSTRACT

Basic properties and battery performances of the novel high temperature stable lithium salt ($Li_2B_{12}F_{12}$, Dilithium Dodecafluorododecaborate; Li_2DFB) were studied using a Mn-based cathode and anode composed of a hard carbon and graphite mixture. The effect of co-solvents (mainly linear carbonate in electrolyte formulation of PC/EC/co-solvent (5/30/65 vol% mixture)) on conductivity, viscosity, charge–discharge capacities, rate performance, temperature performance, cycle life and storage life at 60 °C was investigated. Conductivity of Li_2DFB electrolyte increased with reducing its viscosity by changing co-solvent and increasing the volume of the higher dielectric solvent. Li_2DFB electrolytes showed comparable discharge capacity and columbic efficiency against $LiPF_6$ electrolyte. Li_2DFB electrolytes improved the storage life and cycle life of a Mn-based cell at 60 °C.

1. Introduction

Improving the life and high temperature stability of lithium ion batteries is a key to realizing their application in EV (electric vehicles), HEV (hybrid electric vehicles) and plug-in HEV [1–3]. There are several factors affecting the battery degradation. These include metal ion dissolution from the cathode material, aluminum dissolution of the current collector, decomposition and deposition of electrolyte on the anode and gas generation from electrolyte decomposition [4,5]. Many approaches have been taken to develop novel electrolyte additives to establish a functional and stable SEI (solid electrolyte interface) film s on the electrodes and to protect against undesired reactions. Some examples of additives include VC (vinylene carbonate) [6,7], VEC (vinyl ethylene carbonate) [8,9], VP (vinyl pyridine) [10], LiBOB (lithium bis(oxalato)borate) [11,12], and LiDFOB (lithium difluoro(oxalato)borate) [13]. The SEI film plays an important role to improve the battery life, but it cannot prevent degradation of the bulk electrolyte, especially the lithium salt.

The most commonly used salt in lithium ion batteries, $LiPF_6$ decomposes thermally above 80 °C and generates HF by reaction with residual H_2O in organic electrolytes. $LiN(SO_2CF_3)_2$ and $LiN(SO_2CF_2CF_3)_2$ are thermally stable up to 400 °C and do not react with H_2O easily. Thus, these salts were considered to be most promising candidates for overcoming the instability of $LiPF_6$. But, a high reactivity against the cathode has prevented the use of these compounds as bulk electrolyte salts in commercial lithium ion batteries [14,15]. Many of these salts were based in organic chemistry. We introduced a novel inorganic chemistry based lithium salt, $Li_2B_{12}F_{12}$, Dilithium Dodecafluorododecaborate; Li_2DFB, for lithium battery use. Similar to $LiN(SO_2CF_3)_2$ and $LiN(SO_2CF_2CF_3)_2$, Li_2DFB features good thermal stability up to 400 °C and is chemically and moisture stable. Unfortunately, Li_2DFB has an issue of poor conductivity and rate performance relative to $LiPF_6$ due to its large anion size compared to $LiPF_6$. Thus, the study and development of the capable formulations for Li_2DFB are needed to introduce it into the industry. This work presents a systematic formulation study of electrolytes containing Li_2DFB salt and PC/EC/co-solvent mixtures (5/30/65 vol%) on some physicochemical properties and cell performance including initial charge–discharge capacities, columbic efficiency, rate performance, temperature performance, storage life and cycle life at 60 °C using a Mn-based cathode and a graphite/hard carbon mixed anode cell.

2. Experimental

2.1. Electrolyte preparation conductivity measurement

Li_2DFB was synthesized and purified at Air Products and Chemicals, Inc., having more than 99.8% in purity and less than 20 ppm water in dry solid [16]. The Li_2DFB was stored in an Ar-filled glove box before use. Battery grade electrolyte solvents and pre-mixed solutions were provided by Kishida Chemical K.K. Electrolytes were prepared by dissolving required amount of lithium salt with pre-mixed solution in a glove box. The electrolytes investigated in this

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Table 1
Studied electrolyte formulations including slat concentration and additives.

Electrolyte	Solvents vol%	Salts mol L^{-1}	Additives wt%
F1 (DMC)	PC/EC/DMC = 5/30/65	Li_2DFB = 0.4 $LiPF_6$ = 0.1	VC = 2 PS = 1
F2 (EMC)	PC/EC/EMC = 5/30/65	Li_2DFB = 0.4 $LiPF_6$ = 0.1	VC = 2 PS = 1
F3 (DEC)	PC/EC/DEC = 5/30/65	Li_2DFB = 0.4 $LiPF_6$ = 0.1	VC = 2 PS = 1
F4 (GBL/DEC)	PC/EC/GBL/DEC = 5/30/30/35	Li_2DFB = 0.4 $LiPF_6$ = 0.1	VC = 2 PS = 1
$LiPF_6$ control	PC/EC/DEC = 5/30/65	$LiPF_6$ = 1.27	VC = 2 PS = 1

study are summarized in Table 1. PC (propylene carbonate) and EC (ethylene carbonate) were chosen as high dielectric constant solvents. Four different co-solvent combinations were selected to investigate the formulation effect on electrolyte properties and cell performance, i.e. DMC (dimethyl carbonate), EMC (ethyl methyl carbonate), DEC (diethyl carbonate) and GBL (γ-butyrolactone). A 0.4 M concentration for Li_2DFB was chosen to get maximum conductivity. $LiPF_6$ was used an additive for passivating the aluminum current collector. VC (vinylene carbonate) and PS (propane sultone) were added to prevent electrolyte reduction during formation cycling and to form proper SEI (solid electrolyte interface) film [17].

The ionic conductivity of the electrolyte were measured with the formulation did not include the additives using TOA CM 30 V conduct meter at 3 kHz and 25 °C.

2.2. Cell preparation and cell performance evaluations

7 cm × 7 cm size pouch cells were assembled using a cathode composed mainly of lithium manganese oxide, an anode comprised of 50 wt% graphite and 50 wt% hard carbon, and a 25 μm thick polypropylene separator. The cells were charged to 3 V at 0.1*C*, then kept at open circuit state for 8 h. The cells were then charged up to 4.2 V with 0.2*C* and kept at 4.2 V for 8 h as constant voltage charging using a TOACAT 3100 battery tester (Toyo system). The rate performance at varying temperature was measured with 0.2, 0.5, 1.0 and 2.0*C* at 25, 50, 0 and −10 °C. The cells were charged up to 4.2 V for 100% SOC (state of charge) and then stored at 60 °C for storage test. The SOC 100% charge–discharge cycle life test was performed under the condition of 4.2 V charging CC–CV with 1*C* and 2.7 V discharging with 1*C* at 60 °C.

3. Results and discussion

3.1. Electrolyte properties

Fig. 1 shows the chemical structure of Li_2DFB calculated by molecular orbital method (Spartan, DTF 6-311G base set). Li_2DFB has a symmetrical cage structure and possesses two Li ions. This salt needs a two step equilibrium for dissociation as shown in equations (1) and (2) as shown in Fig. 2. This salt is not like other salts used in lithium batteries such as $LiPF_6$ and $LiBF_4$ which have only has one dissociation step. The energy differences (En) between association and dissociation states were estimated from MO calculations as well. The energy E1 for first step dissociation of Li_2DFB (126 kcal mol^{-1}) is smaller than the value (E3) for $LiPF_6$ (132 kcal mol^{-1}), indicating that this first step dissociation of Li_2DFB is similar to $LiPF_6$. While the energy E2 for second step dissociation of Li_2DFB (192 kcal mol^{-1}) is larger than these energy values, indicating that the second step dissociation of Li from Li_2DFB is significantly more difficult than the first step dissociation and $LiPF_6$. These considerations suggested that Li^+, $LiDFB^-$, and DFB^{2-} must exist and $LiDFB^-$ may be the dominant component in Li_2DFB electrolyte.

Fig. 3 shows the conductivity of Li_2DFB electrolytes as a function of their reciprocal viscosity. Among the formulations composed of linear carbonate as co-solvent, the conductivity showed good linear relationship to the reciprocal viscosity. Due to the lower molecular weight of the co-solvents F1 (DMC) formulation must have a larger number of co-solvent molecules than other Li_2DFB electrolytes. This together with the lowest intrinsic viscosity of DMC, compared with

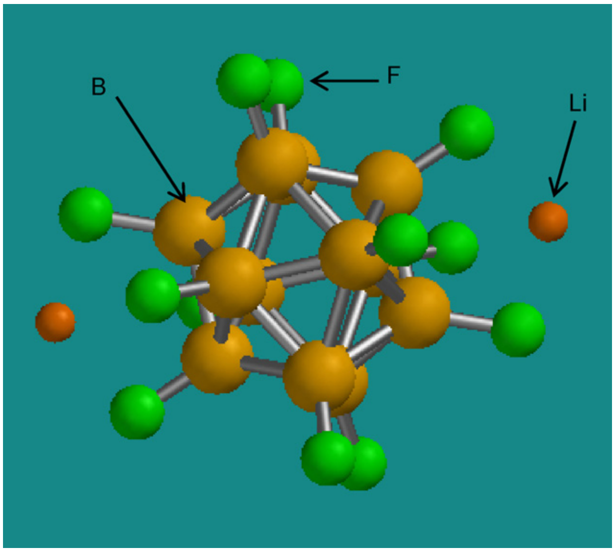
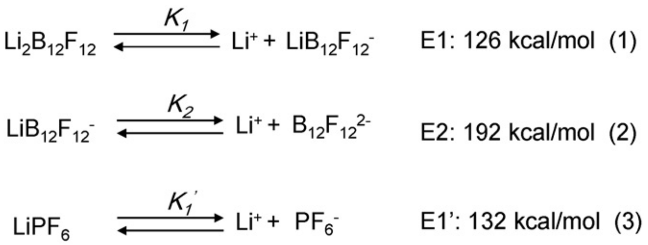


Fig. 1. The structure of Li_2DFB salt simulated by MO method.



$$Li_2B_{12}F_{12} \underset{}{\overset{K_1}{\rightleftharpoons}} Li^+ + LiB_{12}F_{12}^- \quad \text{E1: 126 kcal/mol} \quad (1)$$

$$LiB_{12}F_{12}^- \overset{K_2}{\rightleftharpoons} Li^+ + B_{12}F_{12}^{2-} \quad \text{E2: 192 kcal/mol} \quad (2)$$

$$LiPF_6 \overset{K_1'}{\rightleftharpoons} Li^+ + PF_6^- \quad \text{E1': 132 kcal/mol} \quad (3)$$

Fig. 2. The equilibrium equations for Li_2DFB and $LiPF_6$, energy difference between salt and dissociated state was calculated by MO method.

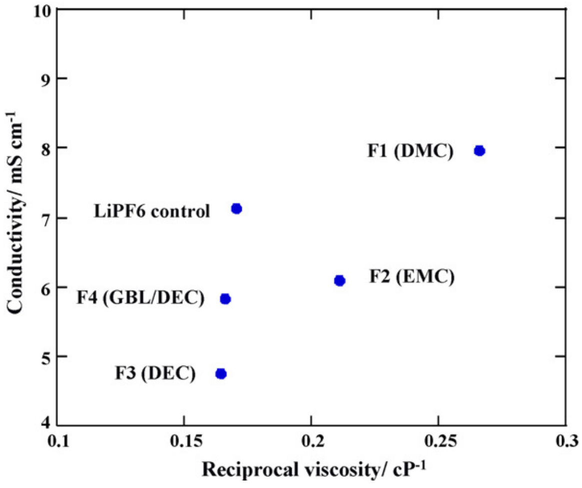


Fig. 3. The conductivity of electrolyte as a function of reciprocal viscosity.