Journal of Power Sources 392 (2018) 60–68

Contents lists available at ScienceDirect

Journal of Power Sources

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

Development of wide temperature electrolyte for graphite/ $LiNiMnCoO_2$ Li-ion cells: High throughput screening

Janak Kafle[a], Joshua Harris[a], Jeremy Chang[a,b], Joe Koshina[b], David Boone[b], Deyang Qu[a,*]

[a] Department of Mechanical Engineering, College of Engineering and Applied Science, University of Wisconsin Milwaukee, Milwaukee, WI, 53211, USA
[b] Johnson Controls, Inc, 5757 N Green Bay Avenue, Milwaukee, WI, 53209, USA

HIGHLIGHTS

- The methodology for High throughput screening was introduced.
- Li-ion electrolyte with wide temperature was developed.
- Homogenous SEI layer was found to be critical.

ARTICLE INFO

Keywords:
Li-ion battery
Low temperature electrolyte
Solid electrolyte interphase

ABSTRACT

In this report, we demonstrate that the low temperature power capability of a Li-ion battery can be substantially improved not by adding commercially unavailable additives into the electrolyte, but by rational design of the composition of the most commonly used solvents. Through the detail analysis with electrochemical impedance spectroscopy, the formation of a homogenous solid electrolyte interface (SEI) layer on the carbon anode surface is found to be critical to ensure the performance of a Li-ion battery in a wide temperature range. The post mortem analysis of the negative electrode by XPS revealed that all the electrolyte compositions form similar compounds in the solid electrolyte interphase. However, the electrolytes which give higher capacities at low temperature showed higher percentage of LiF and lower percentage of carbon containing species such as lithium carbonate and lithium ethylene di-carbonate. The electrolyte compositions where cyclic carbonates make up less than 25% of the total solvent showed increased low temperature performance. The solvent composition with higher percentage of linear short chain carbonates showed an improved low temperature performance. The high temperature performances were similar in almost all the combinations.

1. Introduction

Lithium ion batteries (LIB) are considered as the state-of-art electrochemical energy storage devices used in consumer electronics, electric vehicles and space exploration [1–4]. Fast charging and discharging, long calendar life (> 10 years), long cycle life and operation over a wide temperature range (−30° C to + 60° C) are some of the important properties desired in batteries for vehicle applications [5–8]. The recent rapid proliferation of start-stop technologies can shut down the engine at stop and restart it when the car starts to move. Start-stop implementation is an economic solution to reduce fuel consumption and emissions, and a practical way to enable the automakers to satisfy more stringent government emission regulations. In the near future, start-stop may be extended to micro-hybrid applications in which the regenerative braking technology boosts energy harvesting and a more robust battery provides the energy to keep useful features like air conditioning running where a start-stop cars may not. Clearly, more and more loads will be put on the on-board batteries. Therefore, an auxiliary Li-ion battery system with a higher voltage e.g. 24 V and 48 V is needed to provide the extra energy. A state-of-art LIB, even with its superior high energy density and rate capability, lacks the high power ability at low temperature; for example at −30 °C a LIB can hardly crank the vehicle engine. Most of recent electrolyte research has been focused on the high voltage aspect in order to take the advantage of high voltage cathode materials. However, wide temperature electrolyte is equally important especially in vehicle applications. In this engineering study, we aim to develop a Li-ion battery system which can not only crank a vehicle at −30 °C without compromising high temperature performance, but also can be “dropped-in” to mass production. Therefore, all the chemicals including electrode materials and

* Corresponding author.
E-mail address: qud@uwm.edu (D. Qu).

https://doi.org/10.1016/j.jpowsour.2018.04.102
Received 31 October 2017; Received in revised form 16 March 2018; Accepted 28 April 2018

electrolyte materials are commercially available on a mass production basis. The objective was achieved through a high-throughput experimental method.

A commercial LIB consists of a graphite anode, transition metal oxides or phosphates (such as $LiCoO_2$, $LiNiMnCoO_2$, $LiFePO_4$ etc.) cathodes and a non-aqueous electrolyte. A typical non-aqueous electrolyte system consists of approximately 1.0 M lithium hexfluorophosphate ($LiPF_6$) dissolved in organic carbonate solvents. The most commonly used solvent system is the mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) in 3:7 ratio [9–11]. A variety of ester compounds such as methyl propionate (melting point −87.5° C) and methyl butyrate (melting point −85.8° C) have also been widely studied as potential co-solvents for low temperature applications because of their low freezing points [12,13]. The other commonly studied solvents are dimethyl carbonate (DMC), diethyl carbonate (DEC) and propylene carbonate (PC). These carbonate solvents have different chemical structures, physical and electrochemical properties [14]. Therefore, it can be assumed that by varying their ratio in a mixture, cell performance can be altered. EC is cyclic carbonate having a very high melting point (36° C). Therefore, it cannot be used alone in the cell (i.e. solid at room temperature). However, some amount of EC is needed in the solvent system as a solid electrolyte interphase (SEI) former. PC has very low melting point (−48.8° C), but its viscosity is comparably high. Also, PC intercalates into graphite and exfoliates it [15]. The PC molecules are reduced at potential about 1.0 V (Li/Li^+) giving $ROCO_2Li$ and reversible intercalation of Li^+ in graphite is not possible [16,17]. DMC is less viscous but has higher melting point (4.6° C). EMC has a low melting point (−53° C) and DEC has the lowest melting point (−74° C) among all the carbonates. The dielectric constant values of these solvents also vary widely; liquid EC (89.6 esu) and PC (65 esu) have very high values. The linear carbonates have low dielectric constants values (approximately 3 esu) [14]. When these solvents are mixed, their physical properties change dramatically [18]. Therefore, investigation of various combinations of solvents in the electrolyte have been performed systematically in this study.

It has been believed for a long time that EC is the required component in an electrolyte to successfully operate LIBs. EC is reduced (at 1.5 V Li/Li^+) on the graphite anode surface during the first lithiation cycle to produce a thin solid film called the solid electrolyte interphase layer (SEI) [19,20]. The SEI passivates the electrode and prevents the further reduction of the electrolyte in subsequent cycles thereby increasing the cycle life of the battery. The SEI should be thin, robust and should have low ionic resistivity, but high Ohmic resistivity [21]. This ensures not only the longevity of the battery life but also improves the charge transfer kinetics during charging and discharging process. Fast kinetics are desired for low temperature operations as well as electric vehicle operations. Recently, Xia et al. demonstrated that EC can be replaced completely by 2% of sacrificial additives (such as vinylene carbonate) [22]. The SEI derived from the additive only showed better high temperature stability compared to SEI from EC containing solvents. Vinylene carbonate (VC) has been widely studied as an SEI former and is the single most important additive so far [23–25]. However, the combination of VC with other additives such as LiBOB has shown a synergistic effect on cell performance and mitigating gas generation [11,26]. Other additives such as lithium difluoro(oxalato) borate, prop-1-ene-1,3-sultone, tris(trimethylsilyl) phosphite, methylene methanedisulfonate etc. have also been investigated as potential SEI formers [27,28]. The SEI forming additives get reduced on the anode surface before the main solvents (EC/EMC) get reduced. Therefore, SEI formed from additives is different in quality from an SEI formed from solvent components such as EC and other carbonates. The major components of SEI are believed to be the salts of lithium such as LiF, $Li_xPO_yF_z$, $(CH_2CO\ C\ O_2Li)_2$, Li_2CO_3, various alkoxides and oxides of lithium. Vinylene carbonate (VC) produces polymer and LiBOB produces borate species on anode surface [13,24]. Recently, it has been demonstrated that majority of the SEI is made up of $(CH_2CO\ C\ O_2Li)_2$ and LiF when EC is the SEI former [29]. However, SEI is a very complicated mixtures of solids and its composition changes as the additives are changed.

In this work 1.0 M $LiPF_6$ solution was used in various combinations of EC, PC, DMC, EMC and DEC. The goal of the study was to optimize the cell performance for both low and high temperature using the conventional electrolyte system. Vinylene carbonate and lithium bisoxalato borate were used as additives in 1% and 0.5% weight ratio, respectively in all the electrolytes. NMC (111) and graphite were used as cathode and anode active materials, respectively.

2. Experimental details

2.1. Design-of-experiment

The Design-of-Experiment (DOE) is a statistical method that allows for multiple factors to vary simultaneously. In a traditional experiment however, when studying the effects of different factors on an outcome, only one of those factors is allowed to vary while others are kept constant. The advantage of DOE over the traditional method is that not only the impact of each single factor, but also the influences of the interactions among the multiple factors on the outcome are investigated. In our experiment, the levels of the factors were selected based on the statistical algorism, so entire possible combinations of all the factors are taken into consideration. The run order sequence and the experiments was randomized so there was no possibility of any bias. After screening the multiple factors and levels, the major trends of the interaction of the factors can be determined. DOE is frequently used to determine the effect of each factor in a multiple variant environment and a promising direction for further experimentation. In fundamental scientific research, DOE can be used to survey at a large number of factors superficially rather than a small number thoroughly, so that the“big picture” is not missed. It is worth emphasizing that DOE does not reveal the underlying intrinsic scientific causes for the trends, but it can pinpoint the significant factors, on which the mechanistic research should be focused [30–32]. The factors are normally selected based on their significance of the effects on the response and the responses are the interested performance matrix to the experiment. In our study, five commercially available solvents (EC, PC, EMC, DMC and DEC) were chosen as factors (variables) with two additives as constants.

2.2. Chemicals

Lithium hexafluorophosphate ($LiPF_6$, 99.99%), battery grade lithium bisoxalatoborate (LiBOB), and vinylene carbonate (VC, 99.5%, acid < 200 ppm, H_2O < 100 ppm) were purchased from Sigma Aldrich and used without further purification. EC, PC, DMC, EMC and DEC solvents were purchased from BASF Corporation, Ohio and used without further treatments. In the NMC 111 cathode laminate, the loading of the active material was 6.80 mg/cm^2 and the reversible capacity was 0.93 mA h/cm^2; in the graphite anode laminate, the loading was 3.25 mg/cm^2. The Celgard 2325 polymer was used as separator.

2.3. Electrolyte preparation

The electrolyte compositions were selected from a comprehensive high throughput electrolyte development for commercial Li-ion cell production. All the electrolyte preparations were done in an Argon filled glove box (H_2O < 0.5 ppm, O_2 < 1 ppm). A mixture of 10.0 g of solvent combination (EC, PC, EMC, DMC, DEC) at various ratios were prepared. A total of 20 combinations were investigated based on the surface response statistical model. The selection was done with the help of MiniTab, an experiment design software. The EC concentration was allowed to vary between 20 and 30% by weight. PC was used between 5 and 30% by weight. The rest of the solvent mass was filled with linear carbonates (DMC, EMC and DEC) by imposing certain limits in the DOE.