

TECHNOLOGY FACT SHEET

IMPROVING LOW TEMPERATURE OPERABILITY OF LITHIUM-ION BATTERIES

(Zhang, Xu, Jow)

Introduction

This invention represents a promising new electrolyte salt for the lithium-ion (Li-ion) family of secondary (rechargeable) batteries. Researchers at the Sensors and Electron Devices Directorate (SEDD) of the U.S. Army Research Laboratory (ARL), Adelphi, Maryland designed, synthesized and tested lithium trifluorochloroborate (LiBF_3Cl) as a variant for commonly-used lithium tetrafluoroborate (LiBF_4). Tests demonstrate that the substitution of a chloride for one of the fluorine to form LiBF_3Cl salt created a more conductive, better performing electrolyte at lower operating temperatures. Researchers also found that the LiBF_3Cl electrolyte is superior to LiBF_4 in forming a solid-electrolyte interphase (SEI) on anode and protecting cathode components, resulting in increased charge efficiency and prolonged battery cycle life.

Concept

Rechargeable Li-ion batteries require the use of electrolyte salts to function properly. These salts must meet a variety of critical requirements, such as electrochemical stability with the anode and cathode; passivating cathode current collector materials and forming a stable SEI at the anode; thermal stability at high temperatures; and forming a conductive electrolyte capable of operating at low temperatures.



The novel ARL electrolyte salt would promote more reliable operation in cold weather conditions (source: cars.com)

Among many commercially available lithium salts, only lithium hexafluorophosphate (LiPF_6) is found to satisfy these requirements. Yet, improving low temperature performance (*i.e.*, below minus 20 °C) of LiPF_6 has proved elusive – until now.

LiBF_4 is known to be superior to LiPF_6 in providing better low temperature performance of Li-ion batteries. This is because batteries with LiBF_4 salt have lower charge-transfer resistance, which has been identified as the major influence on low temperature operability. Compared with LiPF_6 , however, LiBF_4 has two main drawbacks: inferior ability in forming an SEI at the graphite electrode, which robs charge capacity and rate capability; and (2) low solubility at lower temperatures, which impedes limits operability (below -20 °C). Fortunately, SEDD researchers have created a solution that overcomes these obstacles.

Invention Overview

- ❖ Expand operation temperature range down to -40°C
- ❖ Method is simple to practice and adaptable for mass production
- ❖ Multiple applications including consumer electronics and electric vehicles
- ❖ TRL 5 – Fully functioning laboratory scale prototypes using novel salt
- ❖ Laboratory test data available; results published, “ LiBF_3Cl as an alternative salt for the electrolyte of Li-ion batteries,” *Journal of Power Sources* 180 (2008) 586–590
- ❖ U.S. Patent 7,833,660 B1

Doing Business with ARL

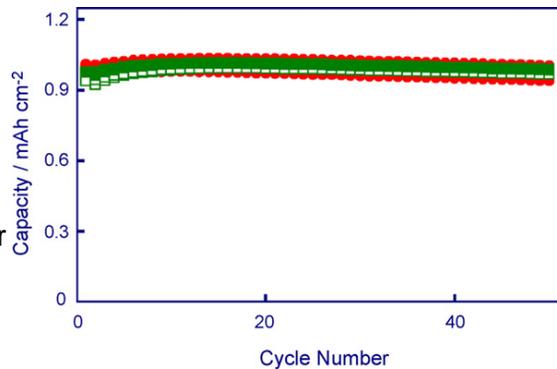
- ❖ ARL-SEDD is a leader in partnering with domestic firms
- ❖ Successfully developed and implemented innovative tools to ease the technology transfer process
- ❖ Tools includes Patent License Agreements (PLAs); Cooperative Research and Development Agreements (CRADAs); Test Services Agreement (TSA); and others
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Features/Capabilities/Intellectual Property

SEDD researchers demonstrated that reduction in the stereo-symmetry of the BF_4^- anion could alleviate the drawbacks of LiBF_4 . They synthesized a series of test salts partially substituting fluoride with chlorine (Cl). Tests demonstrated that their new salt, LiBF_3Cl , was much superior in forming SEI and stabilizing SEI at the graphite anode. It also showed higher solubility in organic solvents at low temperatures and provided Li-ion batteries with improved low temperature performance and rate capability.

Encouraged by these results, SEDD researchers created the electrolyte salt, LiBF_3Cl , and evaluated it as an alternative to LiBF_4 for use in Li-ion batteries. They found that LiBF_3Cl , like its established cousin LiBF_4 , has excellent ability in passivating aluminum cathode current collector material at high potentials. However, unlike LiBF_4 , LiBF_3Cl is more efficient in forming SEI. More importantly, LiBF_3Cl , due to its asymmetric anode structure, has higher solubility than LiBF_4 and is superior in producing an electrolyte that performs well in temperatures down to -40°C .



The chart illustrates results from five identical test cells using an LiBF_3Cl -based electrolyte. The cells maintained excellent capacity retention during prolonged cycling (source: ARL-SEDD)

Other features/capabilities/intellectual property offered by this invention include the following:

- Salt synthesis process is uncomplicated
- Adaptable to existing electrolyte manufacturing lines
- Scalable for use in large and small format batteries
- IP includes novel salt synthesis, electrolyte composition, and an assembled electrochemical device featuring the novel salt composition.

Potential Markets/Applications

Expanded capabilities in Li-ion cells open up new opportunities for use in hybrid electric vehicles and other Li-ion applications:

- Transportation – US auto manufacturers are producing and continuing to develop transportation systems featuring Li-ion technology; the ARL innovation would expand Li-ion cell applicability in vehicles that operate colder regions
- Electric Grid Services – Battery-driven contingency provisions used by utilities to keep a portion of their capacity on reserve for emergencies would be improved with lower-temp capability in many regions

Key Advantages & Benefits

- ❖ Reduce initial cycle capacity loss for SEI formation, improves battery cycle life
- ❖ Use materials of construction common to the industry
- ❖ Cost of manufacturing LiBF_3Cl anticipated to be lower than LiBF_4
- ❖ Synthesis process can be used to create ammonium-based analogues for use in supercapacitors.
- ❖ Inventor team available to work with commercialization partner

Contact Information

This technology was developed by ARL-SEDD. It is now available for licensing and CRADA opportunities.

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