

# Novel superacid-based lithium electrolytes for lithium ion and lithium polymer rechargeable batteries

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## Abstract

The objective of this work is to synthesize new and novel superacid-based lithium salts with large anions that will easily ionize in solvent mixtures and in polymer complexes providing improved conductivity and high electrochemical stability. The preparation of lithium imide salts, their solution conductivities and electrochemical stabilities are described. The preparation of solid polymer electrolyte films and their conductivities are described. Experimental data on lithium ion cells fabricated using electrolyte solutions of two representative lithium imide salts are presented. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Superacid-based lithium salts; Lithium ion batteries

## 1. Introduction

Electrolyte materials and particularly solid polymer electrolytes with high conductivity and electrochemical stability and compatibility with the electrodes are needed for improved lithium batteries. The state-of-the-art electrolytes have poor conductivity that limits the rate capability and their poor compatibility with the electrodes particularly lithium anode leads to poor cycle life. Lithium transport properties and interfacial stability of the electrolyte in lithium cells are influenced by the structure and properties of lithium polymer electrolyte material [1]. Important factors that contribute to enhanced transport properties of the electrolytes are the local segmental mobility of the solvating group in the polymer, the amorphous phase in the electrolyte and the concentration of carrier ions [1–3]. The objective of this work is to synthesize new and novel superacid-based lithium salts with improved ionic conductivity and interfacial stability. Several new lithium imide salts with large anions have been synthesized and characterized for electrochemical stability and conductivity suitable for rechargeable lithium batteries. These batteries have the potential for special medical devices and in space applications.

## 2. Experimental

Superacid-based lithium salts are perfluoroalkylsulfonimides of lithium with large anions. They can be represented

by the general formula,  $C_nF_{2n+1}SO_3Li$ , where  $n = 4, 8$ , etc. [2–5]. Most of these superacid-based lithium salts are prepared as described elsewhere [2–6]. For example, the superacid-based salt trifluoromethyl sulfonyl perfluorobutylsulfonimide of lithium ( $CF_3SO_2NLiSO_2C_4F_9$ ) used in this study is prepared by the reaction of perfluorobutylsulfonyl fluoride with ammonia and *n*-butyl lithium followed by treating with suitable perfluoroalkylsulfonyl fluoride [2–5]. Other imide salts prepared are bis-nanofluorobutylsulfonylimide of lithium ( $C_4F_9SO_2$ )<sub>2</sub>NLi, trifluoromethyl sulfonylfluorooctane sulfonimide of lithium ( $CF_3SO_2NLiSO_2C_8F_{17}$ ), bis(fluorobutyl-sulfonyl) dilithium imide ( $C_4F_9SO_2N$ )<sub>2</sub>Li<sub>2</sub> and N(methoxyethyl) perfluorobutyl sulfonimide of lithium ( $CH_3OCH_2-CH_2-SO_2C_4F_9$ )NLi. The imide salts solubility in mixed solvent system of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (34:33:33 vol.%) is dependent on their molecular weight and structure. Trifluoromethylsulfonyl perfluorobutyl imide of lithium is highly soluble in the solvent mixture and 1 M solution of the salt has a conductivity of  $6.6 \times 10^{-3}$  S/cm at room temperature where as a 0.4 M solution of *N*-(methoxy ethyl) fluorobutyl sulfonyl imide has a conductivity of  $2.26 \times 10^{-4}$  S/cm. Both of these salts show electrochemical stability from 0 to 4.5 V versus Li.

In addition to the imide salts described above, several new salts have also been synthesized and characterized. Some of these are, trifluoroacetyl trifluoromethane sulfonimide of lithium ( $CF_3CONLiSO_2CF_3$ ), lithium diethyltrifluoromethane sulfonylphosphonamide ( $C_2H_5O$ )<sub>2</sub>PONLiSO<sub>2</sub>CF<sub>3</sub>, and lithium imide salts containing heterocyclic ring such as

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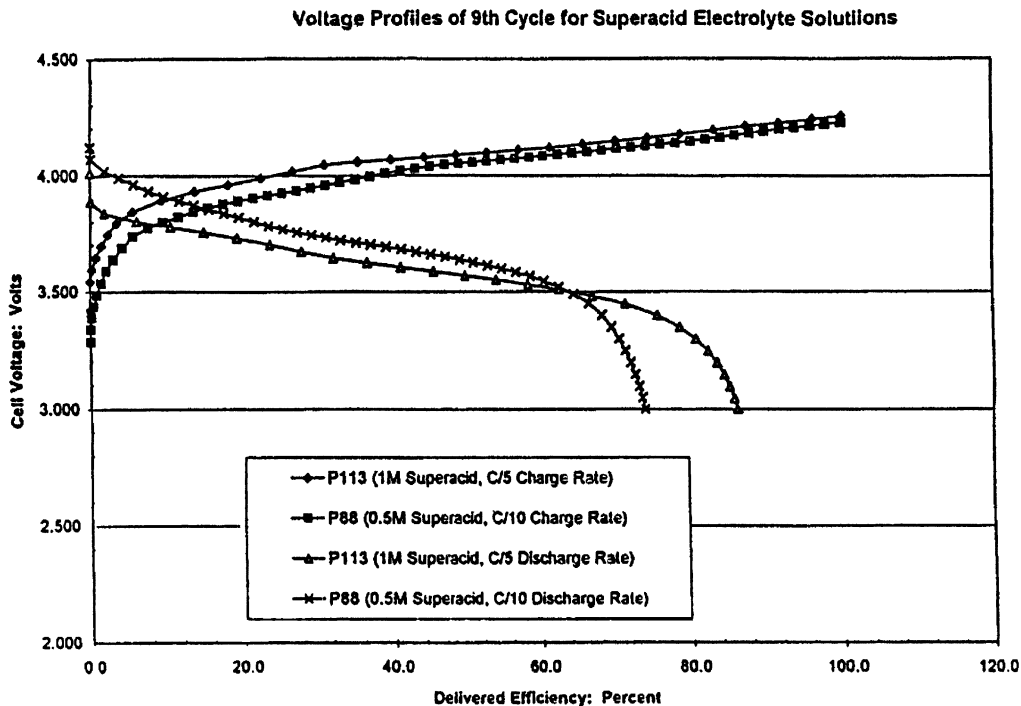


Fig. 1. Charge–discharge voltage profiles of 100 mAh Li-ion cells containing superacid-based lithium salt, trifluoromethylsulfonylperfluorobutylsulfonimide.

melamine with trifluoromethylsulfonyl groups at 1, 3 and 5 positions. Solutions of these salts have conductivities in the range of  $2 \times 10^{-4}$  to  $3.5 \times 10^{-4}$  S/cm at room temperature. Studies have been conducted with trifluoromethylsulfonyl-

perfluorobutyl sulfonimide of lithium because this salt has high solubility in mixed solvent system, it has good electrochemical stability up to 4.5 V and it is not corrosive to current collectors such as aluminum [5]. It has been used as

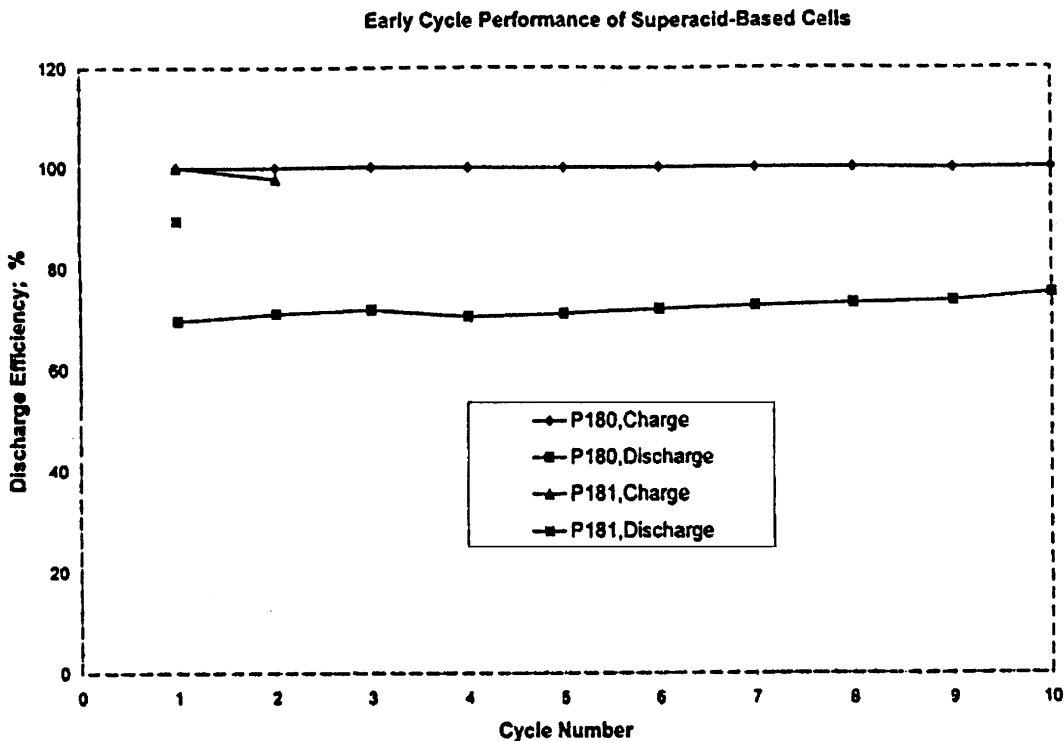


Fig. 2. Profiles of discharge efficiency versus cycle number of 100 mAh Li-ion cells containing superacid-based lithium salt trifluoromethylsulfonylperfluorobutylsulfonimide.

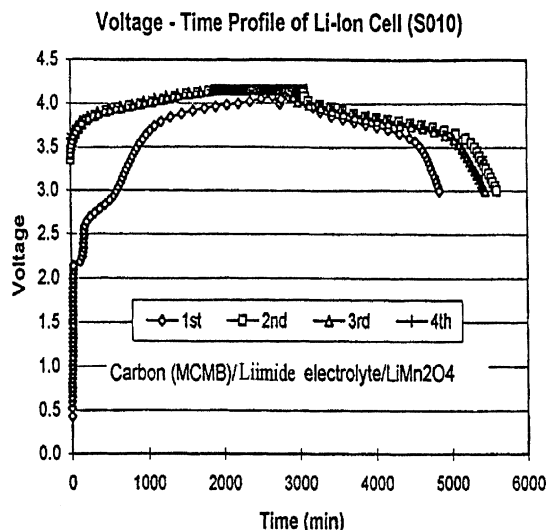


Fig. 3. Voltage–time profiles of charging and discharging of cells with manganese dioxide cathode.

the superacid-based salt in studies on prototype lithium ion cells with lithium Cobalt oxide cathode and the carbon anode made of Mesocarbon Microbeads (MCMB #1028, Osaka Gas). The charge–discharge voltage profiles of cells of nominal capacity of 100 mAh are shown (Fig. 1). The profiles of discharge efficiency versus cycle number of cells are shown (Fig. 2).

Solid polymer electrolyte (SPE) films of this imide salt were prepared with polyethylene oxide with different Li/O ratios [5]. Their conductivities were measured as a function of temperature. The effect of inert filler materials such as micron-size amorphous silicon dioxide and aluminum oxide on mechanical properties and conductivity are evaluated. The room temperature conductivities of the films are in the range  $1 \times 10^{-5}$  to  $5 \times 10^{-5}$  S/cm.

Prototype lithium ion cells of nominal capacity of 70 mAh were fabricated using solutions of *N*-(2-methoxyethyl) perfluorobutyl sulfonimide, with MCMB anode and lithium manganese dioxide cathode. Charge–discharge voltage profiles as a function of cycle number are shown (Fig. 3).

### 3. Results and discussion

The performance characteristics of laboratory prototype lithium ion cells of nominal capacity of 100 mAh made with lithium cobalt oxide cathode, and MCMB anode containing solutions of the superacid-based salt of lithium were evaluated. They show low impedance, excellent rate capability and good cyclability. Studies of charge–discharge profiles of cells at two concentrations of the salt solution (0.5 and 1.0 M) at charge–discharge rates of *C*/10 and *C*/5, respectively, show that the lower concentration solution can sustain lower charge–discharge rate (Fig. 1). However, the charge–

discharge voltages for different concentrations at different rates are quite consistent. The drop in discharge efficiency of cells after about 10 cycles is attributed partly to increased cell impedance. It is found that the purity of the superacid-based salt has a great influence on the cycling capability of lithium ion cells. Lithium ion pouch type cells using purified superacid-based salt solution with lithium cobalt oxide cathode and MCMB anode show excellent charge–discharge efficiency as a function of cycle life (Fig. 2).

Lithium ion prototype cells of nominal capacity of 70 mAh prepared using the solution of *N*-(2-methoxyethyl) perfluorobutyl sulfonimide with MCMB anode and lithium manganese dioxide cathode were prepared [5]. These cells were charged at constant current to 4.35 V at *C*/20 rate and held at that voltage until the current drops to 1/10 of the initial value. Then they were discharged at *C*/20 rate 3.2 V cut off. The voltage–time profile shows that charging and discharging voltages are quite reproducible over the entire set of cycles (Fig. 3).

### 4. Conclusions

Several new and novel superacid-based lithium salts with large anions have been synthesized and characterized. The most promising lithium salts have been used to prepare solutions in mixed solvent system and to prepare solid polymer electrolyte films. Lithium ion cells have been fabricated using Mesocarbon microbeads anodes and with lithium cobalt oxide cathode and lithium manganese dioxide cathode. These cells have been used to test for charge–discharge performance and cycle life. The cells show promising results in terms of rate capability and charge–discharge efficiency.

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### References

- [1] M. Armand, *Solid State Ionics* 69 (1994) 309.
- [2] M. Armand, European Patent 89-402744, 891004; *Chem. Abstr.* 113 (15) (1981) 131568r.
- [3] W. Qui, D.J. Burton, *J. Fluorine Chem.* 60 (1993) 90.
- [4] G. Nagasubramania, D.H. Shen, S. Surampudi, Q. Wangland, G.K. Surya Prakash, *Electrochim. Acta* 40 (13/14) (1995) 2280.
- [5] H.V. Venkatesetty, in: *Proceedings of the 15th Annual Battery Conference on Applications and Advances*, California State University, Long Beach, California, 11–14 January 2000.
- [6] F.B. Dias, L. Plomp, J.B.J. Veldhuis, *J. Power Sources* 88 (2000) 169.