



# Development of new pyrazole-based lithium salts for battery applications – Do established basic design concepts really work?

Mariano Grünebaum<sup>a,\*,1</sup>, Annika Buchheit<sup>b,2</sup>, Daniel Krause<sup>a,3</sup>,  
Martin Manuel Hiller<sup>c,4</sup>, Christina Schmidt<sup>b,5</sup>, Martin Winter<sup>a,d,6</sup>,  
Hans-Dieter Wiemhöfer<sup>b,7</sup>

<sup>a</sup> Helmholtz-Institute Münster, IEK-12, Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149, Münster, Germany

<sup>b</sup> Institute for Inorganic and Analytical Chemistry, University of Münster, Corrensstr. 28/30, 48149, Münster, Germany

<sup>c</sup> Robert Bosch GmbH, Zentrum für Forschung und Voraentwicklung, Robert-Bosch-Campus 1, 71272, Renningen, Germany

<sup>d</sup> MEET Battery Research Center, University of Münster, Corrensstr. 46, 48149, Münster, Germany

## ARTICLE INFO

### Article history:

Received 16 April 2018

Received in revised form

25 July 2018

Accepted 13 August 2018

Available online 17 August 2018

### Keywords:

Electrolyte salt anion

Electrochemistry

Heterocycles

Lithium ion battery

Basic concepts

## ABSTRACT

This work is focused on applying structural concepts and basic chemical principles to model two *N*-heterocyclic lithium salts, based on trifluoromethyl substituted pyrazolide anions. An easily upscalable preparation method without difficult purification steps was also developed. In a comparative study, the physicochemical properties of the two new lithium salts were investigated, particularly the effect of an additional BF<sub>3</sub>-group at the nitrogen atom. In comparison to non-substituted lithium pyrazolide, the BF<sub>3</sub>-addition led to a strong improvement of thermal and electrochemical stability, ionic conductivity, as well as better C-rate and cycling performance. Furthermore, the anodic stability of Al current collectors was investigated and compared to commercial lithium salts, namely LiPF<sub>6</sub> and lithium bis((trifluoromethyl)sulfonyl)imide (LiTFSI). Possible mechanisms that lead to the presented improvements are discussed.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

Lithium ion batteries are featured by high power and energy densities, high efficiency, longevity and environmental friendliness and thus have found wide application in the area of consumer electronics and electromobility [1,2]. A crucial point for next generation lithium metal batteries and dual-ion cells for stationary

energy storage will be the development of highly conducting and electrochemically stable lithium salts without anodic dissolution of Al current collectors [3–8].

Commercially and commonly used lithium salts still exhibit drawbacks. One of the first investigated salts is LiClO<sub>4</sub>, which can violently react in organic solvents or gel-polymer electrolytes and eventually can lead to explosion at elevated temperatures. Additionally, it should not be used at potentials >4.5 V vs. Li/Li<sup>+</sup>, as it degrades to ClO<sub>2</sub>, HCl and O<sub>2</sub>, which is an explosive mixture [9–13]. The by far most often commercially used salt is LiPF<sub>6</sub>, which decomposes in the presence of moisture and reacts with electrolytes at elevated temperatures resulting in the formation of POF<sub>3</sub>, PF<sub>5</sub>, LiF, HF and other decomposition products [14–16]. Another class are perfluoroalkyl sulfonyl-acid based lithium salts like LiTFSI, lithium bis((perfluoroethyl)sulfonyl)imide (LiBETI) and LiC(SO<sub>2</sub>CF<sub>3</sub>)<sub>3</sub> (LiTriTFSM), which show high electrochemical stability and solubility in the common organic solvents used in lithium ion cells [17–19]. However, all these salts are unable to form passivation layers on Al current collectors and thus lead to Al degradation by anodic dissolution [20,21]. Furthermore, they are still too expensive for commercial applications. In summary, lithium salts with

\* Corresponding author.

E-mail addresses: [m.gruenebaum@fz-juelich.de](mailto:m.gruenebaum@fz-juelich.de) (M. Grünebaum), [annika.buchheit@uni-muenster.de](mailto:annika.buchheit@uni-muenster.de) (A. Buchheit), [dan.krause@fz-juelich.de](mailto:dan.krause@fz-juelich.de) (D. Krause), [martin.manuel.hiller@gmail.com](mailto:martin.manuel.hiller@gmail.com) (M.M. Hiller), [schmidt.christina@uni-muenster.de](mailto:schmidt.christina@uni-muenster.de) (C. Schmidt), [m.winter@fz-juelich.de](mailto:m.winter@fz-juelich.de), [mwint\\_01@uni-muenster.de](mailto:mwint_01@uni-muenster.de) (M. Winter), [hdw@uni-muenster.de](mailto:hdw@uni-muenster.de) (H.-D. Wiemhöfer).

<sup>1</sup> [http://www.fz-juelich.de/jiek/jiek-12/EN/Home/home\\_node.html](http://www.fz-juelich.de/jiek/jiek-12/EN/Home/home_node.html)

<sup>2</sup> <http://www.uni-muenster.de/Chemie.ac/wiemho/index.html>

<sup>3</sup> [http://www.fz-juelich.de/jiek/jiek-12/EN/Home/home\\_node.html](http://www.fz-juelich.de/jiek/jiek-12/EN/Home/home_node.html)

<sup>4</sup> [www.bosch-renningen.de](http://www.bosch-renningen.de)

<sup>5</sup> <http://www.uni-muenster.de/Chemie.ac/wiemho/index.html>

<sup>6</sup> [http://www.fz-juelich.de/jiek/jiek-12/EN/Home/home\\_node.html](http://www.fz-juelich.de/jiek/jiek-12/EN/Home/home_node.html), <http://www.uni-muenster.de/MEET>

<sup>7</sup> <http://www.uni-muenster.de/Chemie.ac/wiemho/index.html>

enhanced electrochemical properties at affordable costs are still on demand.

## 2. Theory and concepts

In this context, well-known structural concepts and basic chemical principles are used to design new anions for lithium salts [22–29].

### 2.1. Hard and soft acids and bases (HSAB)

To improve ionic conductivity and solubility of the anions, the principles of the HSAB theory were used. To understand the effects of hard/hard and hard/soft interaction, Stenger et al. showed at the example of simple lithium halides, that LiF (hard/hard cation-anion interaction) has a solubility of 0.0024 g LiF in 100 g of methanol, whereas the solubility increases from LiF to LiI (hard/soft interaction) which shows a solubility of 298 g in 100 g methanol [30]. Due to the fact that  $\text{Li}^+$  ions are hard, the anion must be soft to ensure a high solubility and thus high conductivity. Introducing charge distributing and oxidation stable heteroaromatic rings as substituents into an anion can be considered as an application of this concept. In our case, an - according to the HSAB theory - soft pyrazole-based hetero-aromatic structure was investigated (Fig. 1).

### 2.2. Negative inductive effect ( $-I$ effect)

In addition to the application of HSAB-principles, the introduction of electronegative substituents or strong electron withdrawing groups like fluorine or perfluorinated alkyl chains (Fig. 1) is of great interest for the design of new salts [31]. An induced  $-I$  effect on the heteroaromatic structure distributes the density of the negative charge over the molecule and therefore should increase the anodic and thermal stability as well as lower the overall basicity of the anions (Fig. 1). A comparison with two lithium salts, which were prepared and investigated by Barthel et al. (Fig. 2), shows the effect of introducing fluorine to the structure. The anodic stability increased by +0.5 V [32]. We decided to apply trifluoromethyl groups at the 3- and 5-position of the pyrazole ring to enforce an even stronger  $-I$  effect on the ring. Pyrazole-based salts with an additional substitution at the 4-position were not investigated because from a synthetic point of view they are difficult to access. 3,5-Disubstituted pyrazoles are easily accessible from the corresponding  $\beta$ -diketones [33].

### 2.3. Modification group and sterically demanding effects

The most important concept is to apply an additional

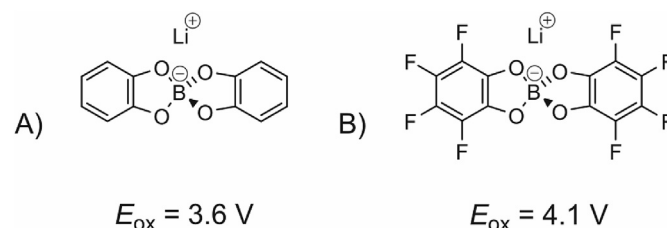


Fig. 2. Anodic stability vs.  $\text{Li}/\text{Li}^+$  of A) non-fluorinated B) fluorinated lithium bis-[1,2-benzodiolato(2-)-O,O']borate.

modification at the nitrogen atoms of the pyrazole-based ring to alter the electronic of the pyrazole ring, as well as to apply an additional small sterical demanding effect at the nitrogen atoms (Fig. 1). Therefore, two salts with and without a modifying group are compared in this work. This modification should affect the physicochemical properties in two ways: First, the group should hinder the coordination of lithium ions direct to the nitrogen atoms and therefore reduce the nucleophilicity of the pyrazole ring, see Fig. 3. Second, an additional small sterically shielding effect of the modification group could prevent direct interaction of the two nitrogen atoms of the aromatic ring with the electrode surface, which should lead to increased electrochemical stability. Additionally, the electron withdrawing effect of the  $\text{BF}_3$ -group should lead to an increased anodic stability (see 2.2).

For a comparison of non-modified (1) and modified (2) pyrazolides (Fig. 4), we decided to use a single  $\text{BF}_3$ -group to achieve a simple electron withdrawn and sterical shielding. It can conveniently be applied by adding  $\text{BF}_3$ -etherate to the prepared lithium pyrazolide (1), whereas the lithium pyrazolide itself is accessible via lithiation of 3,5-bis(trifluoromethyl)pyrazole with *n*-butyllithium in diethyl ether at  $-78^\circ\text{C}$ . A detailed preparation protocol of lithium salt 1 & 2 can be found in the experimental section.

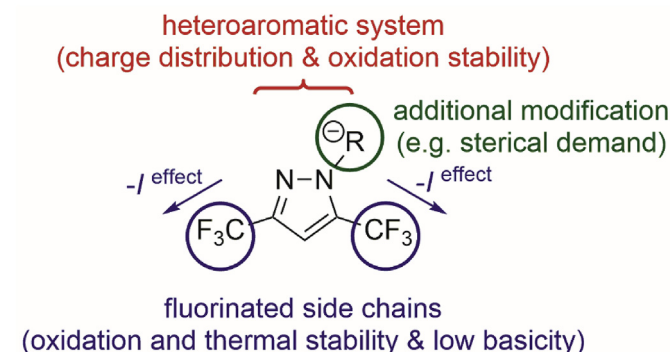


Fig. 1. Structural design of soft pyrazolide anions.

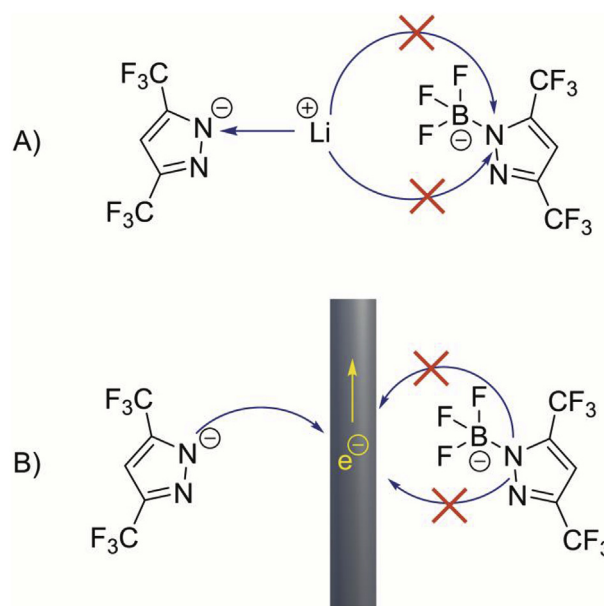


Fig. 3. A) Reduction of nucleophilicity by a sterically demanding  $\text{BF}_3$ -group and B) anticipated sterical shielding and electron withdrawing effect preventing early oxidation on electrode surfaces.

Download English Version:

<https://daneshyari.com/en/article/11000506>

Download Persian Version:

<https://daneshyari.com/article/11000506>

[Daneshyari.com](https://daneshyari.com)