



## Benzimidazole-derived anion for lithium-conducting electrolytes



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### H I G H L I G H T S

- New salt for lithium conducting electrolytes, the LiTDBI, is presented.
- Salt has been synthesized, characterized spectroscopically and electrochemically.
- Salt is stable up to 270 °C and up to 4.7 V vs Li.
- Electrolytes have conductivity  $>1 \text{ mS cm}^{-1}$  and very high  $\text{Li}^+$  transference number, 0.75.
- Salt has been tested in half-cell with graphite, showing good capacity retention.

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### A B S T R A C T

In this work we announce new lithium salt of 5,6-dicyano-2-(trifluoromethyl)benzimidazolide (LiTDBI) designed for application in lithium conductive electrolytes. It was synthesized and completely characterized by NMR techniques. Studies show salt's thermal stability up to 270 °C and electrochemical stability in liquid solvents up to +4.7 V vs. metallic lithium anode. Basic characterization of electrolytes made with this salt show conductivity over  $1 \text{ mS cm}^{-1}$  and unusually high transference number at high concentrations (0.74 in EC:DMC 1:2 ratio mixture) along with low onset of conductivity peak. As a final proof of concept, cycling in half-cell was performed and electrolyte based on LiTDBI showed perfect capacity retention. Such properties show remarkable progress in creating efficient lithium-conducting electrolytes with use of weakly-coordinating anions.

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### 1. Introduction

Although present in the market for a long time already, lithium-ion cell is still the energy storage technology of the fastest advancement nowadays. The momentum of that advancement is development of better and better electrode materials, which increases energy density of cells.

Electrolyte and processes that are consequence of its contents are the main factors limiting applications of newly developed electrodes. Despite that, new anions for electrolytes in lithium-ion cells are rarely covered by scientific research. Most of the works is focusing on investigation of well-known salts, when their disadvantages are many.  $\text{LiPF}_6$  – the most widely used salt in Li-ion batteries – is known to be subject to hydrolysis, forming caustic HF and toxic  $\text{POF}_3$  [1] as well as to have poor thermal stability [2,3].

Other salts, notably:  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiCF}_2\text{SO}_3$  (LiTf),  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  (LiTFSI),  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$  (LiBETI),  $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$  (LiFAP),  $\text{LiB}(\text{C}_2\text{O}_4)_2$  (LiBOB),  $\text{LiBF}_2(\text{C}_2\text{O}_4)$  (LiDFOB),  $\text{LiBF}_4$ , even mixtures of those [4] and other borates, including oxyethylene derivatives [5], were tried as lithium-ion cell components. Unfortunately, all failed to enter the wide application for various reasons, including, but not limited to: low conductivity (LiTf) [6], explosiveness ( $\text{LiClO}_4$ ) [7], corrosiveness towards other cell components (LiTFSI, LiBETI) [8], forming too thick/blocking SEI (solid electrolyte interface) ( $\text{LiBF}_4$ ) [9], obstructive toxicity ( $\text{LiAsF}_6$ ) and too high manufacturing cost (LiFAP) [10,11]. Many salts have been synthesized and tested, but never got to commercial availability.

In the recent past, our group have proposed new anions for lithium salts for electrolytes' applications [12]. TDI, PDI and HDI (4,5-dicyano-2-(perfluoroalkyl)imidazoles) were designed for unification of charge distribution by symmetry and possibility of numerous tautomeric forms occurrence. These designed structures benefitted also from lack of bulky anions disadvantages, such as

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higher viscosity of their solutions. They also displayed smaller affinity to form agglomerates, which influence ionic conductivity of electrolyte [13]. TDI anion design is beneficial in lithium-ion cell applications, as proven by independent groups [14,15]. High lithium cation conductivity (product of conductivity and lithium cation transference number) [16] and high thermal and electrochemical stability (up to 260 °C and 4.7 V vs Li, respectively) are especially worth mentioning [12].

Few years ago, new modeling studies were published that were focusing on speculation over new proposals on anions for lithium-ion cells electrolytes. As far as simulations can predict, imidazole and benzimidazole derivatives should be of the special interest for such purpose [17]. Weakly coordinating anions need to comprise electron-withdrawing groups, as well as possess stable skeleton. Such skeleton have to distribute anion's charge uniformly. As a result, lithium cation should have possibly low dissociation energy. Benzimidazole and imidazole derivatives fulfill all of these requirements. Imidazole derivatives path has been already pursued by us. They were synthesized and investigated as electrolytes. This previous research of our own leading to the LiTDI success confirmed that such direction of investigation into weakly coordinating anions has a great potential. Likewise, recent work of independent group has shown applicability of weakly coordinating anions concept in Li-ion batteries with LiTDI as the best example [18,19]. As a conclusion to a few of these modeling works [17,20], benzimidazoles are of the special interest and deserve more attention. Thus, in this paper we follow this modeling suggestion, presenting properties of the first anion of this family, 5,6-dicyano-2-(trifluoromethyl)benzimidazole.

New TDBI anion presented in this paper is the conceptual continuation of the idea which brought TDI to life. Benzimidazole skeleton with electron-withdrawing groups provide even more mesomeric forms stabilizing the anion. Better uniformity of the charge distribution takes place in such moiety. On the other hand, size of the anion is not big enough to influence viscosity to a large extent and as such, does not substantially diminish electrolyte's conductivity. Theoretical studies by Scheers et al. [17] have shown that such structure should manifest low ion pair dissociation energy – almost identical to quite successful LiTDI. In this paper we describe synthesis of the lithium salt of TDBI anion. Furthermore, salt's physicochemical and electrolytes' basic electrochemical characterization is provided. To show the proof of concept, we employed model battery-like solvent, like propylene carbonate (PC), and a typical battery solvent mixture, namely ethylene carbonate and dimethyl carbonate (EC:DMC) in a 1:2 ratio. We also test the salt for its thermal and electrochemical stability as well as cycle the salt in a half-cell.

## 2. Experimental

### 2.1. Experimental techniques

Nuclear magnetic resonance (NMR) spectra were recorded on Varian Gemini 500. Samples for NMR experiments were dissolved in deuterated dimethyl sulfoxide (DMSO- $d_6$ , 99.96 atom % D, Aldrich).  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are reported relative to DMSO- $d_6$ .

Thermogravimetric Analysis (TGA) was carried out under argon atmosphere on TA Instruments Q50 thermogravimetric analyzer. Heating rate was equal to 10 K  $\text{min}^{-1}$ .

All samples for measurements were assembled in the argon-filled drybox with moisture level below 1 ppm. Prior to the assembly, the salt was vacuum-dried for 48 h at 120 °C. Solvents (propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC)) were anhydrous and used as provided by

Sigma–Aldrich (water content <20 ppm for PC and DMC, <50 ppm for EC).

Linear sweep voltammetry (LSV), cyclic voltammetry (CV), transference number, ionic conductivity and half-cell cycling measurements were carried out on VMP3 multichannel potentiostat (Bio-Logic Science Instruments) with frequency response analyzer option. All electrochemical experiments except for the conductivity measurements were performed at ambient temperature.

In case of LSV and CV measurements were carried out in three-electrode Li|electrolyte|Pt system (with lithium metal as reference electrode). LSV scan rate was 10  $\text{mV s}^{-1}$ . CV scan rate was 5  $\text{mV s}^{-1}$ .

For ionic conductivity measurements electrochemical impedance spectroscopy (EIS) was employed and samples were thermostated for at least one hour at each temperature in Haake D50 cryostat in the –20 to +50 °C temperature range with the 10 °C interval and a precision of 0.05 °C.

Lithium cation transference number was determined using standard Bruce–Vincent–Evans method [21] using the following equation:  $T_+ = (I_s (\Delta V - I_0 R_0)) / (I_0 (\Delta V - I_s R_s))$ , where  $\Delta V$  is the polarization voltage equal to 20 mV;  $I_0$  and  $I_s$  are the initial and the steady-state current during said polarization, respectively;  $R_0$  and  $R_s$  are resistances of the solid electrolyte interface (SEI) immediately before and after the polarization, respectively. The Li|electrolyte|Li cells were used for transference number experiments. Electrochemical impedance spectroscopy (EIS) used to obtain  $R_0$  and  $R_s$  has been performed with 5 mV amplitude over the 500 kHz–100 mHz frequency range with 10 points per decade. At least three samples were measured for each electrolyte composition for more consistent data. Detailed description of this method can be found in other papers [22].

Charge-discharge half-cell cycling used the Li|electrolyte|graphite cell. Standard commercial single-coated graphite electrode from MTI-XTL was used in that experiment. Custom-made coin cell-type was used in which electrodes and separator of disk shape are sandwiched in the polypropylene tube between stainless steel punches. Cycling voltage was set in the 0.1–2.6 V range. Current was chosen in such a way that both discharge and charge processes would take 5 h (C/5 rate). Half-cell contained 0.7 mol  $\text{kg}^{-1}$  LiTDBI in EC:DMC (1:2 weight ratio) electrolyte composition. Additional measurement with the same conditions and the same cell arrangement was made for investigation of rate capability of an electrolyte.

### 2.2. Synthesis of lithium 5,6-dicyano-2-(trifluoromethyl)benzimidazole

Synthesis scheme is presented in Fig. 1.

25 g (0.22 mol) of trifluoroacetic acid (>99%, Sigma–Aldrich) precooled with water-ice mixture was mixed with 2 g (0.0127 mol) of 1,2-diamino-4,5-dicyanobenzene (>97%, Chemical-Block) under the argon atmosphere and kept under reflux for 8 h (reaction progress controlled by TLC). Upon vacuum evaporation to dry mass, the dark residue was recrystallized from acetonitrile. 2.2 g of 5,6-dicyano-2-(trifluoromethyl)benzimidazole were obtained (74% yield).  $T_m$  297–299 °C – lit [23] (different synthesis route).

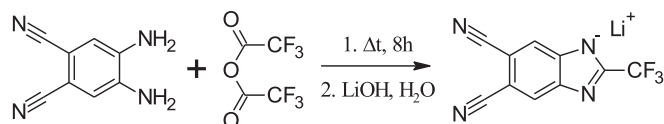


Fig. 1. Synthesis scheme for the lithium 5,6-dicyano-2-(trifluoromethyl)benzimidazole (LiTDBI) salt described in the text.

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