



## Research Paper

## Liquid electrolytes containing new tailored salts for sodium-ion batteries



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## ABSTRACT

Sodium 4,5-dicyano-2-(pentafluoroethyl)imidazolate (NaPDI) and 4,5-dicyano-2-(trifluoromethyl)imidazolate (NaTDI) were tested in order to find the optimal solvent mixture composition for possible application in sodium battery electrolytes. The chemical structure of the above imidazolate salts is based on the stable imidazolium ring architecture substituted with electrophilic groups via carbon atoms. It has been shown here that electrolytes with these new salts exhibit high conductivity at room temperature and excellent electrochemical stability up to 4.5 V vs. sodium metal. Moreover, both salts are not corrosive to Al foil. The high performance of the new electrolytes in sodium battery technology was also confirmed by compatibility tests carried out with  $\text{Na}_x\text{CoO}_2$  cathode materials.

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## 1. Introduction

The progress of twenty-first century civilization will increase demand for portable and stationary energy storage devices. Currently, rechargeable battery technology is based on Li-ion technology [1]. Considering the continuous progress in the development of electrical vehicles and/or different portable devices, one must remember that the lithium sources might not be able to fulfill total market demands [2]. Keeping in mind this problem, researchers are trying to look for alternative for lithium. Perfect candidate to substitute lithium seems to be sodium, as its standard potential  $\text{Na}/\text{Na}^+$  (−2.71 V) is only slightly higher than the potential of  $\text{Li}/\text{Li}^+$  (−3.05 V). Additionally sodium belongs to “the great six” of the most abundant elements in Earth’s crust, which makes it much more cheaper than lithium [3].

First sodium battery, Na(Hg)-C cell was constructed already in 1870 [1], however it was not applied commercially due to low energy density. This limitation impeded the progress in research on sodium batteries for more than 100 years. After this long stagnation period, the next generations of Na-batteries, which appeared in 1960 (Na-S) [4] and 1980 (Na-NiCl<sub>2</sub>) [5], showed also low energy density. The breakthrough came in 2000 with development of high-temperature: Na-NaSICON-S [6] system, which exhibited much higher energy density. However, due to the

high operating temperature range, these batteries are not suitable for use in the devices conventionally working at standard conditions. Nowadays the real challenge in sodium battery technology is to shift their working temperature range from 270–350 °C to room temperature. This can be realized through the severe modification of an electrolyte. It has been shown recently that the structure of an anion in sodium salt plays the most important role, therefore the key to the success would be designing new salts with modified architecture of an anion. Especially the salts with weakly-coordinating oxygen-free anions, which would improve transport properties of sodium-conducting electrolyte are promising.

Nowadays most of electrolytes used in sodium batteries are sodium analogues of lithium ones. Since  $\text{LiPF}_6$  [7–9], that has been introduced in 1990s for lithium-ion batteries, no other salts entered into commercial rechargeable battery cells. In spite of the fact, that many other anions such as:  $\text{ClO}_4^-$  [10],  $\text{AsF}_6^-$  [11],  $\text{BF}_4^-$  [12] or  $\text{CF}_3\text{SO}_3^-$  [13] have been studied since then, only a very few new promising anions for lithium salts have been introduced. Among them lithium bis(trifluoromethane sulfone)imide ( $\text{LiTFSI}$ ) [14], lithium bis(fluorosulfonyl)imide ( $\text{LiFSI}$ ) [15] and lithium bis(perfluoroethylsulfonyl)imide ( $\text{LiBETI}$ ) [16], were considered as the most promising for widespread applications. Unfortunately, none of them is able to form a passivation layer on Al current collectors [17].  $\text{LiTFSI}$  and  $\text{LiBETI}$  are also too expensive for commercial application. After more than 20 years of studies on lithium-ion batteries there is still a lack of good candidates able to replace  $\text{LiPF}_6$ , which is definitely not ideal. The most important drawback

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of the  $\text{LiPF}_6$  use in the electrolyte system is the formation of corrosive hydrogen fluoride (HF) most probably through the slow hydrolysis with trace moisture, which gradually destroys the internal part of the cell [18]. The same problems may appear with sodium analogues.

Promising concept of new anions is based on the application of “Hückel anions” [19]. One of the most common examples of this type of anions are 4,5-dicyano-1,2,3-triazolate (DCTA) [20] and 4,5-dicyano-2-(trifluoromethyl)imidazolate (TDI) [21–23]. This particular structure is covalently bonded and shows very stable  $6\pi e^-$  (or  $10\pi$  electron if CN bonds are involved in calculations) configuration. Salts containing this type of anion were found to exhibit high ( $\sim 300^\circ\text{C}$ ) [21] thermal stability and can be produced from commercially available precursors.

Sodium analogues of 4,5-dicyano-2-(trifluoromethyl)imidazolate (TDI) and 4,5-dicyano-2-(pentafluoroethyl)imidazolate (PDI) in propylene carbonate (PC) have been already presented [24]. However, electrolytes based on pure PC meet severe problems with hard carbon negative electrode, such as capacity fading and low Coulombic efficiency [25]. This problem is related to difficulty in forming a stable SEI layer [26]. In the present publication we attempt to solve the problem of the formation of stable SEI layer by optimization of the composition of electrolytes based on two salts NaTDI and NaPDI dissolved in carbonate mixtures. Moreover, due to possible application of Al as material for anodes or cathodes, the corrosion tests of this material in the presence of selected electrolytes were also performed.

This paper is a continuation of our extensive studies on the novel salts based on the Hückel anions primarily studied as lithium electrolytes components [21]. It appeared the possibility of synthesis a sodium analogues of this salt is quite easy and opens an interesting path of practical broader application in sodium technology [24].

In this particular manuscript we present a practically useful series of data presenting optimization of the conductivity of liquid electrolytes containing novel/unconventional salts for sodium battery application. Electrolytes are combined for the very first time with cathode materials and some initial compatibility tests are shown. The compatibility with the negative electrode have been presented recently [27].

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Electrolytes

In an argon-filled glove box ( $\text{H}_2\text{O}$  and  $\text{O}_2 < 14$  ppm), the electrolytes were prepared by dissolving the requisite amount of sodium 4,5-dicyano-2-(pentafluoroethyl)imidazolate (NaPDI) or 4,5-dicyano-2-(trifluoromethyl)imidazolate (NaTDI) in: PC, EC:PC (1:1, w/w), EC:DME (1:1, w/w), EC:DME (1:2, w/w), EC/DMC (1:1, w/w), EC/DMC (1:1, w/w), EC/PC/DMC (1:1:1, w/w) in a glass flask. The synthesis route of all salts were in details described elsewhere [24].

#### 2.1.2. Electrode materials

Layered sodium cobalt oxide:  $\text{Na}_x\text{CoO}_2$  was used as cathode material in sodium cell assembly. We chose this material due to good theoretical capacity –  $110 \text{ mAhg}^{-1}$  [28]. The polycrystalline material of nominal stoichiometry:  $\text{Na}_{0.7}\text{CoO}_2$  was prepared by solid state reaction technique, using high purity sodium peroxide and  $\text{Co}_3\text{O}_4$  as starting materials. Solid reagents were mixed together in a stoichiometric ratio, pressed into pellets, and sintered in oxygen over 15 h at  $750^\circ\text{C}$ . After the first annealing the material was powdered under argon, pressed again into pellets and annealed for another 10 h in oxygen at  $800^\circ\text{C}$ . Phase purity of

the as prepared material was tested with D8 ADVANCE x-ray diffractometer with DAVINCI design, using  $\text{Cu K}\alpha$  radiation ( $1.5406 \text{ \AA}$ ) in the  $2\theta$  scale between  $10$  and  $70^\circ$ . Chemical composition of the as prepared material was determined with EDAX micro-xray fluorescence analyzer (data not shown here).

Synthesized  $\text{Na}_{0.7}\text{CoO}_2$  was coated on an aluminum foil after mixing it with acetylene black (AB) and polyvinylidene fluoride (PVDF) in the ratio  $\text{Na}_{0.7}\text{CoO}_2\text{:AB:PVDF} = 75\text{:}15\text{:}10$  in *N*-methyl-2-pyrrolidinone (NMP). Coated foil was dried in a vacuum oven at  $80^\circ\text{C}$  for 12 h. Electrodes were punched out of the coated aluminum foil in order to make 11 mm coin cells.

### 2.2. Impedance spectroscopy (EIS)

The ionic conductivity was determined with use of Electrochemical Impedance Multichannel Spectrometer VMP3 controlled by ECLab V10.02 software. The samples of electrolytes were placed into a swagelok-type cells in argon filled glove box ( $\text{O}_2$  and  $\text{H}_2\text{O} < 14$  ppm). The measurements were carried out at temperatures from  $-10$  to  $+60^\circ\text{C}$ . Prior to measurements the samples were equilibrated in HAAKE DC 50 calorimeter for 45 min at each test temperature. Measurements of impedance spectra were recorded at frequencies ranging from 10 MHz to 0.1 Hz, collecting 10 pts per each decade. Conductivities of the measured electrolytes were calculated on the basis of resistance estimated from the impedance spectra analyzed with Boukamp's Equivalent Circuit ver. 4.55 software.

### 2.3. Viscosity measurement

Viscosity tests were performed with a Physica MCR301Anton Paar Rheometer equipped with a CP40 cone plate geometry, with  $41 \mu\text{m}$  gap and precise Peltier temperature controller. For the measurement the suitable volume of the electrolyte was placed in the measuring cell and thermostated with precision of  $0.01^\circ\text{C}$  at  $20^\circ\text{C}$  before the measurement. The viscosities were estimated on the basis of flow curves recorded in controlled shear rate mode at shear rates ranging from  $0.01$  to  $1000 \text{ s}^{-1}$ .

### 2.4. FTIR

The samples of electrolytes with salt concentration above  $0.8 \text{ mol kg}^{-1}$  were sandwiched between NaCl plates in the form of thin films. Samples with lower salt concentration were placed in a cuvette with a  $0.015 \text{ mm}$  spacer. All operations were performed in argon filled glove box ( $\text{O}_2$  and  $\text{H}_2\text{O} < 14$  ppm). Infrared absorption spectra were recorded on a Perkin-Elmer System 2000 FTIR spectrometer with a wavenumber resolution of  $1 \text{ cm}^{-1}$ . All experiments were performed at room temperature.

### 2.5. Cyclic Voltammetry (CV)

Samples were packed in argon filled glove box ( $\text{O}_2$  and  $\text{H}_2\text{O} < 14$  ppm). Glassy fiber separators were immersed in the electrolyte solution  $0.75 \text{ mol kg}^{-1}$  NaTDI or NaPDI in EC:DMC (1:1 weight ratio). All electrochemical test were performed in three electrode cell: reference electrode (sodium metal), current collector (tantalum wire), working electrode (Al electrode). Scans were collected by VMP3 controlled by ECLab V10.02 software with a scan rate  $0.05 \text{ mV s}^{-1}$ .

### 2.6. Corrosion studies

Samples were packed in argon filled glove box ( $\text{O}_2$  and  $\text{H}_2\text{O} < 14$  ppm). Glassy fiber separators were immersed in the electrolyte solution with  $0.75 \text{ mol kg}^{-1}$  NaTDI or NaPDI in EC:DMC (1:1 weight

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