Contents lists available at ScienceDirect





Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Liquid electrolytes based on new lithium conductive imidazole salts

L. Niedzicki^{a,*}, M. Kasprzyk^a, K. Kuziak^a, G.Z. Żukowska^a, M. Marcinek^a, W. Wieczorek^a, M. Armand^b

^a Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland ^b LRCS, University de Picardie Jules Verne, UMR 6007 CNRS, 33 rue de Saint-Leu, 80039 Amiens, France

ARTICLE INFO

Article history: Received 24 May 2010 Received in revised form 15 July 2010 Accepted 29 August 2010 Available online 8 September 2010

Keywords: Lithium electrolytes Lithium salts Conductivity Transference number Interfacial stability

ABSTRACT

In the present paper new generation of imidazole-derived lithium salts (LiTDI–lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide, LiPDI–lithium 4,5-dicyano-2-(pentafluoroethyl)imidazolide and LiHDI–lithium 4,5-dicyano-2-(n-heptafluoropropyl)imidazolide) applied in a model liquid electrolyte, with propylene carbonate used as a solvent, is described. Room temperature ionic conductivities measured by Impedance Spectroscopy are as high as 10^{-2} to 10^{-3} S cm⁻¹ for the 0.1–1 mol dm⁻³ salt concentration range. Lithium cation transference numbers calculated using the Bruce–Vincent method exceed 0.4 at salt concentration equal to 1 mol dm⁻³. Interface resistance measurements showed good stability at high–0.5 mol dm⁻³ or low–0.01 mol dm⁻³ salt concentrations. Ionic associations were estimated using Fuoss–Kraus semiempirical method revealing relatively low association rates. The effect of anion structure on ionic interactions and electrochemical characteristics of the studied electrolytes is discussed.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Lithium-ion batteries that supply energy for electric engines in cars and other devices are mostly based on electrolytes using LiPF₆ (lithium hexafluorophosphate) as the salt. However, this particular salt exhibits corrosive properties. This is mostly because it is an easy subject to hydrolysis (e.g. with the presence of traces of moisture) with release of HF (hydrogen fluoride) [1–3]. Therefore, special attention is needed to assure high purity of electrolyte for its proper work. Synthesis conditions for obtaining battery-grade LiPF₆ are also quite demanding. Although these are well known facts for years, still, there is almost no other salt used in the battery industry. Salts used before initiation of the lithium batteries market in 1991 were too toxic for application (LiAsF₆), too volatile with cathodic materials (LiClO₄)—also being considered as an explosive, had unsatisfactory low ionic conductivity (LiCF₃SO₃) or formed highly resistive SEI—Solid Electrolyte Interface (LiBF₄) [4].

For the last twenty years there were only few new lithium salts introduced to the real life systems, none of them successful enough to be widely used by lithium battery manufacturers. Imide salts (e.g. LiTFSI–LiN(SO₂CF₃)₂ [5], LiBETI–LiN(SO₂C₂F₅)₂ [6]) and methide salts (e.g. LiC(SO₂CF₃)₃ [7]) appeared to be corrosive against Al current collectors [8]. Orthoborate chelate-type class salts (e.g. LiBOB–lithium bis(oxalate)borate [9]) formed too

resistive SEI and their conductivity in liquid and (or) solid solvent was too low for practical applications. LiTFAB–class salts (lithium tetrakis(haloacyloxy)borates [10]) and phosphate ones (e.g. LiFAP–LiPF₃(CF₂CF₃)₃ [11]) suffer from expensive synthesis when in mass production.

To sum it up, there is still an urgent need for a better conducting inexpensive salt to be used in lithium batteries.

To this end, new lithium salts, directly "tailored" for the lithium and lithium-ion cells application were synthesized [12]. These salts were based on stable structure of imidazole aromatic ring with covalently bonded electrophilic groups. Unlike many structures proposed by other researchers [13,14], in our approach the imidazole ring is connected to electrophilic groups via carbon, instead of nitrogen atoms. Such structure is even more electrochemically and thermally stable. Also, as the effect of superior charge dislocation in the anion, anion-cation interactions weaken, and so are the association constants. All of these increase the ionic mobility of the salt, regardless its anion size. As a result of these tailored structures syntheses, three new salts-LiTDI (lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide), LiPDI (lithium 4,5-dicyano-2-(pentafluoroethyl)imidazolide) and LiHDI (lithium 4,5-dicyano-2-(n-heptafluoropropyl)imidazolide) [12,15] have been obtained.

Lithium salts have to fulfill or surpass numbers of requirements in order to be used in lithium batteries. The most important are: solubility in a given solvent (at least up to conductivity maximum), high ionic mobility (conductivity), electrochemical stability in wide potential window (at least 0–4 V vs. Li), chemical stability against all

^{*} Corresponding author. Tel.: +48 22 234 7421; fax: +48 22 628 2741. *E-mail address*: lniedzicki@ch.pw.edu.pl (L. Niedzicki).

^{0378-7753/\$ -} see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.jpowsour.2010.08.097



Fig. 1. Structures of LiTDI (lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide), LiPDI (lithium 4,5-dicyano-2-(pentafluoroethyl)imidazolide) and LiHDI (lithium 4,5-dicyano-2-(n-heptafluoropropyl)imidazolide).

other cell elements (solvent, electrodic materials, charge collectors, etc.), thermal stability (up to 70 °C), high transference number and low association rate at high concentrations. Electrolytes obtained by dissolution of these new salts in PEO-oligomers have ionic conductivity and lithium cation transference number sufficient for the lithium-ion cells application [16].

It has been shown that new salts have thermal (up to 250 °C, proved by TGA, DTA and DSC measurements) and electrochemical (preferably up to 4.8 V vs. Li) stability. Up to 250 °C there was also no melting point, no sign of flame in air atmosphere or signs of decomposition under both argon or air atmosphere (both dry and moist) [12]. Salts are also non-hygroscopic, but also stable in wet atmosphere or even water solutions.

The present paper covers our latest research on the modern imidazole-class salts, showing how these new salts fulfill and exceed most of the requirements listed above when dissolved in propylene carbonate.

2. Experimental

2.1. Sample preparation

All three new salts, LiTDI, LiPDI and LiHDI (Fig. 1) were prepared according to the synthetic route described elsewhere [12]. Prior to the dissolution in propylene carbonate all salts were vacuumdried at 130 °C for 4 h. Propylene carbonate was used as provided (anhydrous, 99.7%, Sigma–Aldrich). All preparation steps were carried out in an argon filled drybox containing less then 3 ppm of water, with all operations taking place at 25 °C. Lithium metal foil (1.5 mm thick, 99.9% purity, Aldrich) was used for electrodes in lithium cation transference number and interfacial stability measurements. Polypropylene separators soaked with electrolyte were used for lithium metal symmetrical-cell assembly.

2.2. Electrochemical characterization

2.2.1. Electrochemical impedance spectroscopy—ionic conductivity

lonic conductivity of propylene carbonate solutions was measured for all salts in the concentration range of 4 decades (from 1 to 3.3×10^{-4} mol dm⁻³). Measurements were performed using electrochemical impedance spectroscopy (EIS) in the temperature range from 20 to 70 °C. Electrolytes were sandwiched between stainless steel blocking electrodes and placed in a cryostat–thermostat system. A Swagelok-type cylindrical cell with electrolyte film thickness of between 170 and 180 µm (measured each time with 1 µm precision). All impedance measurements were carried out on the computer-interfaced VMP3 (Biologic Claix France) multichannel potentiostat within frequency range from 500 kHz to 100 mHz with 10 mV a.c. signal.

2.2.2. Electrochemical impedance spectroscopy—Li/electrolyte interfacial stability

Interfacial stability was measured over 40 days for 0.01 mol dm⁻³ salts concentration and 80 days for 0.5 mol dm⁻³ salts concentrations. Li/electrolyte/Li symmetric cells were stored at room temperature and impedance spectra within range from 500 kHz to 100 mHz were recorded on VMP3 multichannel potentiostat. All measurements were carried out at 20 °C temperature. Spectra were analyzed with Equivalent-circuit 4.55 application developed by Bernard A. Boukamp [17,18] and each spectrum was fitted with an equivalent circuit which allowed to separate resistance contributions between different phenomena. This circuit consisted of two parts connected in series:

- 1. electrolyte resistance (R_e) ;
- 2. parallel combination of interfacial resistance (R_i) and constant phase element associated with it.

In order to verify the reproducibility of obtained results, each solution was tested on four samples.

2.2.3. Lithium transference number

Lithium cation transference numbers (t_+) were calculated using d.c. polarization method combined with a.c. impedance method introduced by Bruce and Vincent [19]. Impedance spectroscopy measurements were performed on VMP3 multichannel potentiostat with a.c. signal of 10 mV in 500 kHz to 100 mHz range. Impedance spectra were analyzed with the Equivalent-circuit 4.55 program [17,18] as described above. Polarization measurements were also executed on the VMP3 multichannel potentiostat. Polarization with 20 mV potential difference was applied on each sample until current reached steady-state (defined as a state were current difference in the last 10 min was lower than 1% relatively). All measurements took place at the temperature of 20 °C. The t_+ for every concentration of each salt was measured on three samples for higher consistency of data. Then the lithium cation transference number was calculated as:

$$t_{+} = \frac{I_{\rm s}(\Delta V - R_0 I_0)}{I_0(\Delta V - R_{\rm s} I_{\rm s})}$$

where: ΔV -d.c. voltage applied; R_0 -initial passive layer resistance; R_s -steady-state passive layer resistance; I_0 -initial current; I_s -steady-state current.

Resulting individual *t*₊ values were calculated with error always smaller than 0.02. Standard deviation of results at each concentration was always smaller than 0.06.

2.2.4. Fuoss-Kraus formalism-ionic association estimation

Ionic fractions quantitative estimation was done using Fuoss–Kraus formalism [20] adopted for polymer electrolytes by Vincent and co-workers [21]. The method consists of limiting conductance measurement, then calculation of ion pair and triplets

Download English Version:

https://daneshyari.com/en/article/1289637

Download Persian Version:

https://daneshyari.com/article/1289637

Daneshyari.com