Journal of Power Sources 251 (2014) 451–458

Contents lists available at ScienceDirect

Journal of Power Sources

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

All fluorine-free lithium battery electrolytes

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HIGHLIGHTS

- $LiB(CN)_4$ and LiDCTA are applied in all fluorine-free PEGDME/PAN electrolytes.
- $Li/LiFePO_4$ cells with fluorine-free electrolytes cycle 15 times with CE $\leq$98%.
- Alternative solvents are needed to increase the electrolyte anodic stability.

ARTICLE INFO

Article history:
Received 8 September 2013
Received in revised form
24 October 2013
Accepted 9 November 2013
Available online 28 November 2013

Dedications: In memoriam of Prof. Per Jacobsson.

Keywords:
Fluorine-free
Lithium salt
Polymer
Electrolyte
Battery

ABSTRACT

Fluorine-free lithium battery electrolytes have been prepared from lithium salts with nitrile based anions, $LiB(CN)_4$ or LiDCTA, dissolved in PEGDME or PC. After soaked into electrospun PAN membranes the resulting electrolytes were tested for physical and electrochemical properties and compared with reference PAN electrolytes containing $LiPF_6$ or LiTFSI. The fluorine-free electrolytes were successfully cycled in $Li/LiFePO_4$ cells at room temperature with up to 98% Coulombic efficiency. Small and qualitatively different effects were observed with the addition of Al_2O_3 particles to the PAN membranes, which could be of importance for long-term performance. However, for fluorine-free electrolytes to be truly competitive, the relatively low anodic stability and elevated temperature performance must first of all be improved by a change of solvent – or addition of co-solvents. Further work in this direction is encouraged by the strong influence of the solvent (PC or PEGDME) on the properties of the LiDCTA electrolytes demonstrated in this work.

1. Introduction

There is an on-going paradigm shift in energy generation with new demands on energy storage solutions, such as batteries. In particular in the automotive industry, batteries are increasingly implemented to support electric propulsion to different degrees. In effect, new targets are set for battery safety, cost, and performance [1].

Li-ion batteries are facing safety challenges, being plagued by the reactivity of the highly volatile organic solvents and the use of the meta-stable $LiPF_6$, acting as an initiator of electrolyte decomposition [2–6]. This results in a sensitivity to high temperature operation, where degradation occurs faster, and a risk of releasing toxic [7] and bioaccumulating [8] decomposition products. Degradation is mitigated, but not stopped, only by including a cocktail of electrolyte additives [9], which adds to the complexity and already high cost of the electrolyte [10]. Thus, there are several strong incentives to develop and evaluate alternative electrolytes beyond the state of the art, both in terms of salts and solvents. Furthermore, the advent of the Li–S and Li–air battery concepts relies on the development of new, stable electrolyte materials that can tackle the specific challenges of these technologies, such as controlling polysulphide dissolution (Li–S) [11] or resist electrolyte attack by oxygen radicals ($Li–O_2$) [12].

Fluorine-free electrolytes represent a promising route to improve Li-battery electrolytes in general, since electrolyte safety, stability, as well as cost are associated negatively with the use of a fluorine salt. However, it represents a challenge to find a suitable combination of salt and solvent that can fulfill the requirements of electrolyte stability and electrode compatibility [13]. Yoon et al.

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http://dx.doi.org/10.1016/j.jpowsour.2013.11.042

recently used the nitrile based dicyanamide (DCA^-) anion as a cost effective, low viscous, and low volatile component of ionic liquid (IL) electrolytes for Li-battery applications [14]. In addition to demonstrating 200 cycles at 80 °C in Li/$LiFePO_4$ cells with good capacity retention, tests also showed the electrolyte to be tolerant towards low levels of moisture, which in a conventional electrolyte with $LiPF_6$ would initiate electrolyte decomposition [2]. This is a most welcome result that may ease the very strict constraints of low ppm water and benefit large-scale production and overall electrolyte cost. However, compared to molecular solvents ILs are expensive, and furthermore DCA^- has a low oxidation stability (<4 V), which limits the choice of cathode.

Amongst nitrile anion alternatives, $B(CN)_4^-$ and several other hypothetical anions have been predicted to be more tolerant towards oxidation than DCA^- [15]. Although $LiB(CN)_4$ has a low solubility in ILs, we have previously demonstrated this salt to be successfully implemented in polyethylene glycol dimethyl ether (PEGDME) electrolytes [16]. For these solvents, $LiPF_6$ and similar salts were early on avoided, because of the risk of chain scission initiated by the corresponding Lewis acids (PF_5) [17]. Another nitrile salt of potential use in lithium battery electrolytes is lithium 4,5-dicyano-1,2,3-triazolate (LiDCTA) [18,19]. It was first implemented in solid poly(ethylene oxide) (PEO) electrolytes, where it showed high Li^+ transference numbers and a strong plasticizing effect [18], and has since been investigated as a component of ILs [20] and served as model for the design of new lithium salts [21–23]. However, investigations of its use in alternative electrolytes have been far from exhausted and it may be a suitable candidate salt for PEGDME based electrolytes. PEGDME has recently been advocated as the solvent of choice for safe 2 V Li-ion batteries, for use with a TiO_2 anode and $LiCoO_2$ cathode, and also the low molecular weight PEGDMEs, commonly referred to as glymes, are receiving considerable attention across different battery technology platforms [24–28] – also in conceptually new high concentration lithium salt electrolytes [29].

Here we investigate electrolytes based on $LiB(CN)_4$ in PEGDME and LiDCTA in PEGDME or propylene carbonate (PC), which are absorbed into highly porous polyacrylonitrile (PAN) membranes (Fig. 1). We compare the physical and electrochemical properties of these electrolytes with $LiPF_6$:PC and LiTFSI:PEGDME electrolytes in PAN membranes, and address critical properties, such as the stability towards a Li anode and the anodic stability at several surfaces, including the compatibility with an Al current collector. Furthermore, by impregnating the PAN membranes with ceramic particles like Al_2O_3, we briefly investigate composite electrolytes as a possible route to enhance the performance by changing the electrolyte/electrode interface.

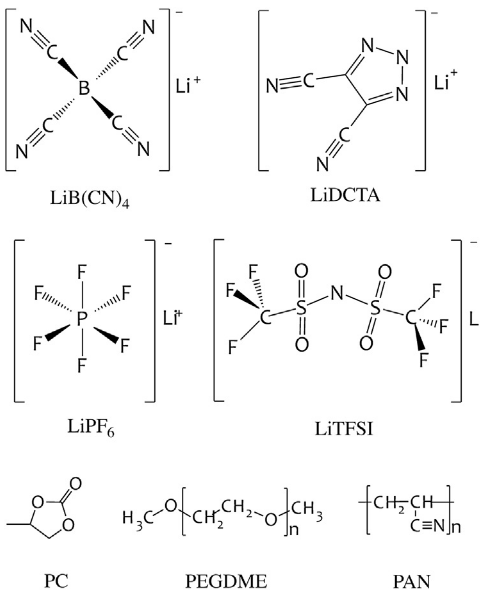

Fig. 1. Lithium salts, solvents (PC, PEGDME) and membrane (PAN) used to prepare the electrolytes in this work.

2. Experimental

The $LiB(CN)_4$ salt was prepared by ion exchange from the corresponding *N*-butyl-*N*-methylpyrrolidinium IL ($C_4mpyrB(CN)_4$, Merck High Purity) according to the procedure reported in Ref. [30]. The LiDCTA salt was synthesized in a two steps procedure. First, the acid form of 4,5-dicarbonitrile-1,2,3-triazole (HDCTA) was synthesized as follow: 62.37 g of diaminomaleonitrile (98%, Aldrich) was dissolved in 500 mL of diethyl ether placed in an ice bath. After 30 min, *tert*-butyl nitrile (90%, Aldrich) was added. After stirring for 8 h, the solution was stored at 4 °C for another 48 h. The resulting solution (containing dark solid particles) was centrifuged and the liquid phase was evaporated at 50 °C resulting in crude HDCTA (55.2 g) in the form of a brownish/reddish powder with white crystals. The HDCTA was sublimated repetitively until pure white crystals were obtained. Next, LiDCTA was obtained by reacting HDCTA with a 10% excess of Li_2CO_3 in anhydrous acetonitrile. The solution was filtered to remove solids and the acetonitrile was evaporated to give LiDCTA in the form of a white powder. The LiDCTA as obtained was dried at 80 °C under vacuum for 48 h. Commercial reference salts, $LiPF_6$ and LiTFSI, were obtained from Aldrich (99%). All salts were dried at 80 °C for three days prior to the electrolyte preparation, except $LiPF_6$ which was used as-received.

Polyethylene glycol dimethyl ether (PEGDME, $\langle M_w \rangle = 500$, Aldrich) and PC (Aldrich, anhydrous) were used as-received to prepare 1 M electrolytes. The water level of the $LiPF_6$:PC and LiDCTA:PC electrolytes were determined to 30 and 50 ppm, respectively, by Karl Fischer titration (Metrohm KF Coulometer). The water content of the PEGDME electrolytes was ~700 ppm, as measured for 1 M LiTFSI:PEGDME. The higher water content relative the PC electrolytes were accepted since the nitrile and LiTFSI salts are stable in the presence of water.

Electrospun microporous polyacrylonitrile (PAN, $M_w = 150{,}000$, Polysciences) membranes were prepared at room temperature as reported in Ref. [31]. A 12 wt.% solution of PAN in dimethylformamide was electrospun using an electric voltage of 20 kV. A ~100 μm thin film was collected on an aluminum foil and vacuum dried at 60 °C for 12 h, before punched into circular membranes (diameter 16 mm). In addition, PAN:Al_2O_3 membranes were prepared by adding 6% Al_2O_3 (nanopowder, Aldrich) to the slurry used for electrospinning. The final electrolytes were obtained by immersing the membranes in the 1 M electrolytes for ~1 min. The PAN membrane dry weights were 5–10 mg and when soaked 80–170 mg. All materials were handled in an Ar-filled glove box with a moisture level <10 ppm.

The positive electrode was prepared by mixing the $LiFePO_4$ active material with carbon black (Super-P) and a poly(vinylidene fluoride) (PVdF) binder in a 80:10:10 weight ratio. The carbon coated (5 wt.%) $LiFePO_4$ was synthesized via a mechanical activation process reported before [32]. The components were mixed in a high-energy mill at room temperature for 30 min, using *N*-methylpyrrolidone (NMP) as a supporting solvent, to produce a homogeneous slurry cast on aluminum foil and dried under vacuum at 80 °C for 12 h to give a ~20 μm thick film. The film was cut into circular discs with a diameter of 1 cm and a mass ~2.0 mg, for subsequent use as cathodes.

Ionic conductivity measurements were performed by dielectric spectroscopy in the frequency range 100 mHz–10 MHz using a