Polyethylene glycol dimethyl ether (PEGDME)-based electrolyte for lithium metal battery

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Abstract

We propose in this work a polyethylene glycol dimethyl ether (MW 500) dissolving lithium trifluoromethanesulfonate (LiCF_3SO_3) salt as suitable electrolyte media for a safe and efficient use of the lithium metal anode in battery. Voltammetry and galvanostatic tests reveal significant enhancement of the electrolyte characteristics, in terms of cycling life and chemical stability, by the addition of lithium nitrate (LiNO_3) to the solution. Furthermore, PFG NMR measurements suggest the applicability of the electrolyte in battery in terms of ionic conductivity, lithium transference number, ionic-association degree and self-diffusion coefficient. Accordingly, the electrolyte is employed in a lithium battery using lithium iron phosphate as the selected cathode. The battery delivers a stable capacity of 150 mAh g^{-1} and flat working voltage of 3.5V, thus leading to a

theoretical energy density of 520 Wh kg^{-1} . This battery is considered a suitable energy storage system for advanced applications requiring both high safety and high energy density.

Introduction

Lithium-based energy storage systems, studied since 1970s as primary battery and following within the rechargeable configuration, played crucial role in the recent development of the portable electronic technology [1]. In its most common design, a lithium battery employs a carbonate-based liquid electrolyte, a metal-oxide cathode in combination with a highly electropositive lithium metal anode, thus allowing a correspondingly high energy density [2]. However, the large scale deployment and acceptance of this powerful system has been hindered by safety issues associated with dendrite formation during cell charge, leading to internal short circuit, heat generation and flammability or, in rare cases, explosion [3]. This relevant inconvenient has been mitigated by the introduction of the lithium-ion battery, i.e., a system in which the lithium metal is replaced by a graphite intercalation anode [4]. However, this battery revealed a lower energy density with respect to lithium metal-based one, due to the higher working potential of graphite (0.2V instead of 0V vs. Li/Li^+) and to the lower specific capacity (372 mAh g^{-1} instead of 3800 mAh g^{-1} , respectively). Recently, increased energy at the cathode side has been achieved by developing efficient lithium-sulfur [5-7] and the lithium-air [8-10] batteries. Indeed, the improvement of sulfur and oxygen-based electrodes, characterized by capacity largely exceeding the value associated with the common cathodes triggered renewed interest on the lithium metal anode [11,12]. Literature works demonstrated that the use of polymer electrolyte, such as PEO (polyethylene oxide), can allow a safe use of the lithium metal anode, however only at temperature exceeding 70°C [6, 13-15]. The addition of ceramics to the polymer electrolyte revealed increased performances in terms of conductivity and lithium transference number at the lower temperatures, however further improvements are still required in order to allow proper operation of these electrolytes at room temperature [14,16]. A valid alternative to solid PEO polymer, advantageously showing suitable

room temperature conductivity and comparable safety content, is represented by highly viscose end-capped ethers, based on $(-\text{OCH}_2\text{CH}_2-)_n$ groups of short chain configuration, such as polyethylene glycol dimethyl ether (PEG-DME) [17-19]. Despite their promise in terms of suitable characteristics for application in lithium ion battery [20-21], these ethers still suffer from issues related to the stability of lithium metal-electrolyte interphase, leading to resistance increase and cell polarization [22]. Several film-forming additives have been proposed to improve the anode interphase in organic electrolytes, such as vinylene carbonate (VC) [23] and fluoroethylene carbonate (FEC) [24]. However, these additives revealed suitable properties mainly in carbonate-based solvents. Among the various additives, lithium nitrate (LiNO_3) evidenced the most favorable effect in ether-based electrolyte, and, in particular, in cells using lithium metal anode [25-27]. The reductive decomposition of the LiNO_3 at about 1.5V vs. Li/Li^+ may lead, in fact, to the formation of products migrating and precipitating at the lithium surface, thus protecting it from further side reactions [27].

In this paper we report a polyethylene glycol dimethyl ether (PEG, 500 MW) in a lithium metal cell using lithium iron phosphate (LiFePO_4) cathode. The electrolyte dissolves a lithium trifluoromethanesulfonate (LiCF_3SO_3) salt as lithium-ion conducting source, and an additional lithium nitrate (LiNO_3) salt acting as film forming agent at the lithium metal surface, thus allowing efficient behavior and low polarization of the lithium cell. Pulsed-field gradient (PFG) NMR and electrochemical measurements demonstrated the full compatibility of the electrolyte for the proposed application in terms of conductivity, lithium transport as well as stability against lithium metal.

Experimental section

Electrolyte and cathode preparation

Polyethylene glycol dimethyl ether (Sigma Aldrich, average MW 500, following indicated by the acronym PEG500DME) was dried under molecular sieves (5Å) for several days until the water content was under 10 ppm as determined by Karl Fischer titration instrument (Metrohm). Lithium-trifluoromethanesulfonate (LiCF_3SO_3 , Sigma Aldrich) and lithium nitrate (LiNO_3 , Sigma Aldrich) were dried at 100°C under vacuum for 24 hours. The electrolyte solution was prepared by dissolving 1 mol of LiCF_3SO_3 in 1 kg of PEG500DME. A second solution of the same composition as the previous, with 0.4 mol of LiNO_3 added was also prepared. The cathode film was prepared by doctor blade casting of a homogeneous slurry formed by dispersing LiFePO_4 [21], super P carbon conductor (Timcal) and polyvinylidenedifluoride (PVDF, Solvay) binder in 80:10:10 mass ratio in N-methylpyrrolidone (NMP, Aldrich). The cathode film was cast onto aluminum foil with wet thickness of 300 μm , dried under air at 70°C, disk-punched and finally dried under vacuum at 100°C for 3 hours to remove solvent and moisture traces.

Materials characterization

Self-diffusion coefficient (D) was measured with a Bruker 400 Avance III NMR spectrometer and using a PFG double-stimulated echo sequence in order to suppress convection effects [28]. The measurements were performed within temperature ranging from 20°C to 70°C, collecting the signal each 10 °C. Gradient pulses with duration = 4-5 ms and strength $g = 0\text{-}45$ G/cm, and diffusion delay of $\Delta = 500\text{-}800$ ms were used. The electrolyte conductivity (δ) was calculated by using the diffusion coefficient of the anion and the cation along with the Nernst-Einstein equation (1):

$$\delta = \frac{F^2[C]}{RT} (D_{\text{Li}} + D_{\text{CF}_3\text{SO}_3}) \quad (1)$$

where F is the Faraday constant (96485 Coulomb), [C] is the solution concentration (mol cm^{-3}), R is the ideal-gas constant ($8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the selected temperature value, D_{Li} and $D_{\text{CF}_3\text{SO}_3}$ are the self-diffusion coefficients of the Li^+ cation and CF_3SO_3^- anion, respectively, measured by

NMR. The ionic conductivity was also directly determined within temperature ranging from 20°C to 90°C by electrochemical impedance spectroscopy (EIS) in symmetric stainless steel/electrolyte/stainless steel 2032 coin cell. The cell was equipped with a Teflon separator in order to fix the cell thickness, and the impedance spectroscopy was performed in a 100 mHz - 100 kHz frequency range with a signal amplitude of 10 mV using Biological VMP3 instrument.

The ion association degree (α) was determined by using equation (2):

$$\alpha = \left(1 - \frac{\delta_{EIS}}{\delta_{NMR}}\right) \quad (2)$$

where δ_{EIS} and δ_{NMR} are the conductivity measured by EIS and calculated by equation (1), respectively.

The cation transference number (t^+), corresponding to the fraction of current carried out by the lithium ions, was calculated by using equation (3):

$$t^+ = \frac{D_{Li}}{D_{Li} + D_{CF_3SO_3}} \quad (3)$$

Cyclic voltammetry was carried out by using a three-electrodes cell with lithium metal counter and reference electrodes and a Super P coated on copper working electrode. The measurement was performed with a 10 mV s⁻¹ scan rate, within 0.01V and 3V potential window using a Biological VMP3 instrument. Swagelok, T-type lithium cells using lithium iron phosphate (LiFePO₄) cathode and PEG500DME-based electrolyte soaked in a Whatman® glass fiber separator, were galvanostatically characterized at C/5 rate (1C = 170 mA g⁻¹) using a MACCOR Series 4000 Battery Test System (Maccor Inc.).

Results and discussion

The suitability of the PEG500DME-LiCF₃SO₃ electrolyte in terms of ion mobility for application in battery has been verified both by PFG NMR and by electrochemical method. Figure 1(a) reports the self-diffusion coefficient (D) of ⁷Li, ¹⁹F and ¹H within the electrolyte, as obtained by NMR measurement (the ¹H NMR results will not be discussed further here, but they are mostly reflective of solution viscosity). The figure evidences that lithium, i.e. the smallest particle in the solution, is characterized by the lowest values of diffusion coefficient due to a high solvation degree in view of its high charge density. Furthermore, the figure reveals the expected increase of the diffusion coefficient of the various species by increasing the temperature. The diffusion coefficient of the cation (D_{Li}) and of the anion ($D_{\text{CF}_3\text{SO}_3}$) at the various temperatures, represented by D_{Li} (LiCF₃SO₃) and D_{F} (LiCF₃SO₃) in Figure 1a, respectively, are used to determine the electrolyte ionic conductivity following the Nernst-Einstein formula, see equation (1) in the experimental section. Figure 1b reports the comparison between the conductivity values determined by NMR and directly measured by electrochemical impedance spectroscopy (EIS). The figure reveals a conductivity at 30°C of nearly 10⁻³ S cm⁻¹, i.e., a satisfactory value suitable for battery application. However, the plots reveal a discrepancy between the value directly measured by EIS and that determined by employing the diffusion coefficient, i.e., the latter higher in respect to the former. Indeed, PFG NMR reveals the movement of all the species within the electrolyte solution, including single ions, neutral ionic pairs, couples and multiple associated ions. On the other hand, impedance spectroscopy records only the movement ascribed to the single charge carriers. This is a well-known and widely reported phenomena in both liquid and PEO-based solid electrolytes [29,30]. Accordingly, the ratio between the two values may be employed to determine the ionic association degree (α) using equation (2) reported in the experimental section. Figure 1(c), reporting the trend of α , reveals an increase of the ionic association by increasing the temperature as most likely ascribed to possible recombination of the various ions into couples pairs or higher multiplet. This effect is in part due to the decreasing dielectric constant and hence decreasing solvating power of the polyether host at elevated temperature [31]. Li-transference number has been determined by

NMR at the various temperatures and reported in Figure 1(d), in order to evaluate the charge fraction carried by lithium ions. The figure shows a stable value of about 0.45 in the whole temperature range that is considered a suitably high value allowing the use of the electrolyte in lithium ion batteries.

Figure 1

In order to verify the suitability of the electrolyte for lithium battery application, a Li/PEG500DME-1M LiCF₃SO₃/LiFePO₄ cell was assembled and cycled. Figure 2, reporting the voltage profile (a) and corresponding cycling behavior (b), reveals an initial cycle characterized by a typical profile centered at about 3.5V, a low charge-discharge polarization, a high efficiency and a specific capacity of about 150 mAh g⁻¹, i.e., of about 90% of the theoretical value. However, the following cycles evidence a remarkable polarization increase (Fig.2a) leading to efficiency decrease, noise, capacity fading and final cell failure (Fig.2b). These issues are attributed to an unstable solid electrolyte interphase (SEI) film at the lithium surface, or to a very poor stability of the latter.

Figure 2

It has been reported that the addition of lithium nitrate (LiNiO₃) to the electrolyte as film-forming agent may represent a suitable solution to increase the lithium cell performance [25-27]. Indeed, LiNiO₃ may decompose at about 1.5V to form a stable SEI layer protecting the lithium surface and preventing cell degradation. Accordingly, PEG500DME-LiCF₃SO₃ solution has been augmented by the addition of LiNO₃ salt and characterized by voltammetry in order to detect its decomposition potential. Figure 3 reports the cyclic voltammetry of the bare PEG500DME-based electrolyte (dark gray line) and the corresponding solution containing LiNO₃ (light green line) in a lithium cell using a carbon working electrode. The potential profiles show a huge peak around 0.5V mainly due to the reductive degradation of the PEG500DME for the bare electrolyte, and the expected additional peak at around 1.5V for the LiNO₃ containing one that is expected to form the

above mentioned protective layer [25-27]. Following the first scan, both the curves show vanishing signals, thus indicating consolidation and consequent stabilization of the formed SEI film upon the repeated cycles that is a crucial requirement for electrolyte suitability in lithium battery.

Figure 3

The voltammetry test suggests a discharge voltage lower than 1.5V in order to allow LiNO_3 decomposition with production of a passivation film preventing cell deterioration. Accordingly, we assembled a Li/PEG500DME, 1M LiCF_3SO_3 , 0.4M $\text{LiNO}_3/\text{LiFePO}_4$ cell and performed a first discharge lowering the voltage down to 1V in order to allow the LiNO_3 decomposition, while the following cycles were performed within a typical voltage range, i.e. 2.5V to 4V. Figure 4, reporting the voltage profiles (a) and the cycling behavior (b) of the lithium cell, shows a greatly enhanced behavior in terms of low polarization and cycling stability. During the first cycle the cell reveals the expected decomposition starting at about 1.5V and a following charge characterized by a specific capacity of about 170 mAh g^{-1} , comprised of irreversible reactions such as minor electrolyte oxidation and structural reorganization of the LiFePO_4 electrode [21]. During the following cycles, the cell reveals a working voltage of about 3.5V, very limited polarization and a specific capacity of about 150 mAh g^{-1} that is 90% of the theoretical value (Fig. 4a). Furthermore, the cell shows an efficiency approaching 100% and a very stable cycling trend (Fig. 4b), thus confirming the effective role of the film formed by LiNO_3 in protecting the cell from side reactions and allowing optimized cycling.

Figure 4

Conclusion

The results here reported demonstrated the suitability of a polyethylene glycol dimethyl ether (PEGDME)-based electrolyte for application in an efficient lithium battery. NMR and electrochemical tests revealed that the electrolyte has a conductivity of the order of $10^{-3} \text{ S cm}^{-1}$ and

a lithium transference number of 0.45, i.e. proper values for optimized cell performances. The addition of a lithium nitrate salt (LiNO_3) allowed the formation of a stable SEI film protecting the lithium metal and avoiding further electrolyte decomposition. Indeed, the lithium battery employing the modified electrolyte has shown high performances in terms of delivered capacity, efficiency and stability. The cell delivered a capacity of 150 mAh g^{-1} at a working voltage of 3.5 V, thus leading to a theoretical energy density of 525 Wh kg^{-1} . We believe that the data here reported may allow a safe use of lithium metal in efficient, high energy lithium batteries.

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References

- [1] B. Scrosati, J. Garche, *J. Power Sources* 195 (2010) 2419-2430
- [2] J. M. Tarascon, M. Armand, *Nature* 414 (2001) 359-367
- [3] Q. Wang, P. Ping, X. Zhao, G. Chu, J. Sun and C. Chen, *J. Power Sources* 2012, 208, 210–224
- [4] M. Lazzari and B. Scrosati, *J. electrochemical Society* 1980, 127, 773-774
- [5] M. Agostini and J. Hassoun, *Scientific Reports* 2015, 5, 7591
- [6] J. Kim, D. J. Lee, H. G. Jung, Y. K. Sun, J. Hassoun and B. Scrosati, *Advanced Functional Materials*, 2013, 23, 1076-1080
- [7] L. Suo, Y. S. Hu, H. Li, M. Armand and L. Chen, *Nature communications*, 2013, 4, 1481.
- [8] H.G. Jung, J. Hassoun, J.B. Park, Y.K. Sun and B. Scrosati, *Nature Chemistry*, 2012, 4, 579-585

- [9] B. M. Gallant, D. G. Kwabi, R. R. Mitchell, J. Zhou, C. V. Thompson and Y. Shao-Horn, *Energy & Environmental Science*, 2013, 6 , 2518-2528.
- [10] C. Laoire, S. Mukerjee, E. J. Plichta, M. A. Hendrickson and K. M. Abraham, *J. Electrochemical Society*, 2011, 158, A302-A308.
- [11] G. Zheng, S. W. Lee, Z. Liang, H. W. Lee, K. Yan, H. Yao and Y. Cui, *Nature nanotechnology*, 2014, 9, 618-623.
- [12] W. Xu, J. Wang, F. Ding, X. Chen, E. Nasybulin, Y. Zhang and J.G. Zhang, *RSC advances* 2014 , 7, 513-537
- [13] S. Rajendran, T. Mahalingam and R. Kannan, *Solid State Ionics* 2000, 130, 143–148
- [14] F. Croce, G. B. Appetecchi, L. Persi and B. Scrosati, *Nature* 1998, 394, 456-458
- [15] M. Balaish, E. Peled, D. Golodnitsky and Y. Ein-Eli, *Angewandte Chemie International Edition*, 2015, 54, 436-440.
- [16] F. Croce, R. Curini, A. Martinelli, L. Persi, F. Ronci and B. Scrosati, *J. Phys. Chem.* 1999, 103, 10632-10638
- [17] G. A. Elia, R. Bernhard and J. Hassoun, *RSC Advances*, 2015, 5, 21360-21365.
- [18] D. Marmorstein, T.H. Yu, K.A. Striebel, F.R. McLarnon, J. Hou and E.J. Cairns, *J. Power Sources* 2000, 89, 219–226
- [19] D. Devaux, R. Bouchet, D. Glé and R. Denoyel, *Solid State Ionics*, 2012, 227, 119-127.
- [20] R. Bernhard, A. Latini, S. Panero, B. Scrosati and J. Hassoun, *J. Power Sources*, 2013, 226, 329-333.
- [21] D. J Lee, J. Hassoun, S. Panero, Y. K. Sun and B. Scrosati, *Electrochemistry Communications*, 2012, 14, 43-46.
- [22] S. S. Zhang, *J. Power Sources*, 2013, 231, 153-162.

- [23] D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt and U. Heider, *Electrochimica Acta*, 2002, 47, 1423-1439.
- [24] R. Elazari, G. Salitra, G. Gershtinsky, A. Garsuch, A. Panchenko and D. Aurbach J. *Electrochemical Society*, 2012, 159, A1440-A1445.
- [25] C. Barchasz, J. C. Leprêtre, S. Patoux and F. Alloin, *J. Electrochemical Society*, 2013, 160, A430-A436.
- [26] S. Xiong, K. Xie, Y. Diao, and X. Hong, *Electrochimica Acta*, 2012, 83, 78-86.
- [27] A. Rosenman, R. Elazari, G. Salitra, E. Markevich, D. Aurbach, and A. Garsuch, *J. Electrochemical Society*, 2015, 162, A470-A473.
- [28] A. Jerschow and N. Müller, *J. Magnetic Resonance* 1997, 125, 372–375
- [29] X. Bogle, R. Vazquez, S. G. Greenbaum, A. V. W. Cresce and K. Xu, *The Journal of Physical Chemistry Letters*, 2013, 4, 1664-1668.
- [30] S. Abbrent and S. G. Greenbaum, *Current Opinion in Colloid and Interface Science*, 2013, 18, 228–244.
- [31] M.C. Wintersgill, J.J. Fontanella, M.K. Smith, Y.S. Pak, C.G. Andeen, and S.G. Greenbaum, *Journal of the Electrochemical Society*, 1988, 34, 135-235.

Figures caption

Figure 1. a) Self-diffusion coefficient (D) of ^7Li , ^{19}F and ^1H within the PEG500DME-LiCF₃SO₃ electrolyte determined by PFG NMR. b) Comparison between the conductivity values determined using self-diffusion coefficients (equation 1) and directly measured by electrochemical impedance spectroscopy (EIS). c) Ionic association degree (α) trend determined at various temperatures using self-diffusion coefficients (equation 2). d) Lithium transference number (t^+) trend determined at various temperatures (using equation 3). Temperature range 20°C-90°C. For equations (1), (2) and (3) see experimental section.

Figure 2. a) Voltage profiles and b) cycling behavior of the Li/PEG500DME, 1M LiCF₃SO₃/LiFePO₄ lithium cell cycled at a C/5 rate (1C = 170 mAh g⁻¹) within 2.5V and 4V voltage range. Room temperature (25°C)

Figure 3. Cyclic voltammetry trends of the bare PEG500DME, 1M LiCF₃SO₃ electrolyte (Dark gray line) and the corresponding solution added by 0.4M LiNO₃ (light green line) in a lithium cell using a carbon working electrode. Scan rate 0.1 mV s⁻¹, potential limits 0.01V-2V. Room temperature (25°C)

Figure 4. a) Voltage profiles and b) cycling behavior of the Li/PEG500DME, 1M LiCF₃SO₃, 0.4M LiNO₃/LiFePO₄ lithium cell cycled at a C/5 rate (1C = 170 mAh g⁻¹). First cycle performed within 1V and 4V and following cycles within 2.5V and 4V voltage range. Room temperature (25°C)

(a)

(b)

(c)

(d)

Figure 1

(a)

(b)

Figure 2

Figure 3

(a)

(b)

Figure 4

Graphical Abstract