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Influence of New Aprotic Electrolytes on Negative Electrode Materials for Lithium-ion Batteries

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This paper briefly describes experiments which investigate mutual compatibility of aprotic solvents and negative electrode materials. The work follows the current trend of enhancing fire safety by using new kinds of aprotic solvents. Solvents and their mixtures used in this work have a higher flash point than solvents commonly used in lithium-ion batteries, e.g. sulfolane. The influence of electrolytes on the proper operation of negative electrode materials was considered. In these experiments, graphite and lithium titanate oxide, $Li_4Ti_5O_{12}$ were used as a negative electrode materials. Various combinations of aprotic solvents and negative electrode materials were tested. The main objective of these experiments was to find an aprotic electrolyte with a higher fire safety that can properly operate in a system containing standard negative electrode materials, used in lithium-ion batteries. Also the stability of the SEI layer has been investigated in different electrolytes.

Keywords: Graphite, Lithium-titanate, LTO, Sulfolane, Aprotic solvents, Safety

1. INTRODUCTION

Lithium-ion batteries are without doubt one of the most promising electrochemical energy sources. Nowadays, the quick development of lithium-ion batteries (hereinafter LiBs) brings about new types of LiBs with better capacity characteristics, higher specific voltage, high cyclability, material stability and other parameters. The introduction of LiBs in electronic applications like small portable devices is well-known together with evolution of electric cars increased interest to use the LiBs for electric propulsion. With using of LiBs in electric vehicles, as well as in high power applications, the issue of safety is coming to the forefront. In terms of safety, aprotic electrolyte is the most difficult part of the LiB system with poor thermal resistance. In case of thermal stress the electrolyte may decompose. The product of electrolyte decomposition can obtain the nature of the gas or solid state and thus worsen battery characteristics, which may lead to evolution of gases. The evolution of hydrogen and other gases may result in a dangerous mixture in the case of contact with oxygen, especially in an enclosed space. For high power application, it is necessary to find an aprotic electrolyte that can remain stable in a wide range of temperatures while maintaining good electric conductivity [1–5]. Another requirement for aprotic electrolyte is the electrochemical compatibility with the electrode material in the range of working potential window.

The most widespread negative electrode material for LiBs is graphite. Graphite is a stable and reliable active material, its operation is based on intercalation reaction of lithium ions among graphene sheets. Negative electrodes made from graphite have discharge potential plateau around 0.25 V vs. Li/Li^+ and theoretical capacity 372 mAh/g. In LiB’s cells the Solid Electrolyte Interface (SEI) layer will be formed on the surface of graphite anode during the first charge cycle. This interface is conductive for Li^+ ions but not for electrons, which protecting the graphite from co-intercalation of electrolyte solvent molecules, at the same time consuming Li-ions in the formation of SEI leading to an irreversible capacity loss. The properties of the SEI layer significantly influence LiB characteristics such as self-discharge rate, current loading, lifetime and cyclability. This layer is necessary for proper operation of the LiB. The composition, constitution and structure of the SEI layer depends on the electrolytes and aprotic solvents used in the battery [6–8].

Recently, the most widely used negative electrode materials are lithium titanate oxides, $Li_4Ti_5O_{12}$ (LTO). In comparison with graphite, LTO displays a different spinel structure, good reversibility and stability. The LTO anode material has a higher discharge potential plateau - approx. 1.55 V vs. Li/Li^+, the theoretical capacity of LTO is 175 mAh/g. The spinel LTO shows an excellent structural stability of nearly zero-strain during lithium ion insertion/extraction, leading to high rate capability and reversibility during charge-discharge cycling. Moreover, $Li_4Ti_5O_{12}$ is cheap and non-toxic, and it is easier to produce than other alloy-based anodes. As it does not act as a low – potential Li^+ ion source during the charge-discharge process, $Li_4Ti_5O_{12}$ needs to be coupled with a 4 V cathode such as $LiCoO_2$ or $LiMn_2O_4$ to provide a battery cell with an operating voltage of approximately 2.5 V. It is known that lithium reacts with $Li_4Ti_5O_{12}$ according to the kinetic reaction:

$$Li_4Ti_5O_{12} + 3(Li^+) + 3e^- \rightarrow Li_7Ti_5O_{12} \quad (1)$$

where lithium insertion into the $Li_7Ti_5O_{12}$ spinal displaces tetrahedrally coordinated lithium ions into octahedral sites, resulting in the formation of a rock salt-type $Li_7Ti_5O_{12}$ crystals [9–12]. The high redox potential of LTO reduces electric power that can be supplied to load, this drawback can be tackled by using high voltage positive materials, e.g. $LiNi_{0.5}Mn_{1.5}O_4$. These high voltage materials give a nominal voltage around 4.9 V vs. Li/Li^+ in comparison with standard cathode materials which provide voltage around 3.7 V vs. Li/Li^+. On the other hand, the high working potential makes it possible to use different kinds of electrolyte solvents without the danger of their decomposition at a low electrode potential. The high working electrode potential also inhibits the growth of lithium dendrites, which may cause a short circuit in the cell [13,14].

An electrolyte is one of the key parts of the lithium ion batteries. The main task of electrolyte is to conduct ions between electrodes. Electrolyte is important regarding the battery capacity, cyclic and safety properties [15]. The demands on electrolytes are high from the physical as well as economical point of view. The electrolyte and electrode materials are the most expensive parts of the battery. Commercial batteries are using lithium salt, mostly $LiPF_6$ dissolved in an organic solvent. The required properties are achieved by combination of different solvents, one with high relative permittivity and high dynamic viscosity e.g. ethylene carbonate and second with low dynamic viscosity and relative permittivity usually an organic solvent on linear ester base such as dimethyl carbonate or ethyl methyl carbonate (EMC). These blends exhibit an extraordinary balance between properties such as a good ionic conductivity and passivation of aluminium current collector [16]. This philosophy was respected in our experiments. Most of the materials used in lithium ion batteries are flammable and can be considered as safety risk. Overcharging, overheating or mechanical damaging can cause ignition or explosion of electrolytes [17]. This is the reason for searching of new less flammable or non-flammable materials. A solvent chosen to increase the fire safety in batteries in this study was sulfolane (SL). The sulfolane is an aprotic solvent obtaining sulphur which is known for its high dielectric constant 46.4, high flashpoint 166 °C and bowling point 280 °C. Sulfolane also has a high cryoscopic constant 65.5 $K \cdot kg \cdot mol^{-1}$ and a high oxidation potential > 5.3 V [15,17]. Another benefits are stability at high temperatures as well as a high current rate-capability. In comparison with batteries which using common carbon solvents [15], SL based electrolytes provide significantly higher conductivity than EC/DMC under lower temperatures [16]. The second solvent in our experiments was a solvent known from the electrotechnology practice such as propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC). The main reason for the use of a second solvent was to lower the dynamic viscosity. Both electrodes, anode and cathode, are unstable against the electrolyte and it comes to degradation. For this reason, a SEI layer is formed on the electrode – electrolyte interface to protect electrode material against further reaction. It was found that sulphur rich compounds (such as sulfolane) are better conductors of Li^+ ions [17].

The salt chosen for measurement was $LiPF_{6.}$ There were several reasons – to achieve a higher conductivity than with a cheaper salt $LiClO_4$ and to minimize the decrease of sulfolane oxidation potential. The highest oxidation potential can be found in the pristine solvent. When $LiPF_6$ is added, its oxidation potential can be slightly decreased [18]. It was observed that the sulfolane stability is highly dependent on the anion type (PF_6^-, ClO_4^-, BF_4^-) and it slightly decreases with the presence of the PF_6^- anion in the system SL/$LiPF_6$, the major degradation factor is the SL–SL–e cluster decomposition [18]. When studying the materials and their properties, we considered their use in a high voltage batteries.

In this paper we report a comprehensive series of measurements using two types of electrodes (graphite and LTO) in combination with five different electrolytes (EC/DMC, SL, SL/PC, SL/DMF and SL/EC). Furthermore, we investigated the novel properties of the electrolytes mixtures which are influencing the SEI layer formation on graphite and LTO electrodes.

2. EXPERIMENTS

2.1. Electrode fabrication

LTO powder (Sigma-Aldrich) with particle size < 100 nm was used as an active electrode material. Because of its poor electric conductivity the LTO material was coated with amorphous (microcrystalline) carbon layer (carbon black). This additive ensures good electric conductivity among the LTO particles and the copper current collector. As a binder was used polyvinylidene fluoride (PVDF) thermoplastic powder. The weight ratios of electrode components were set to 80 wt% of active electrode material, 10 wt% of conductive additive and 10 wt% of PVDF binder. In the first stage of electrode manufacturing process, the PVDF was dissolved in N-Methyl-2-pyrrolidone (NMP) solution. In the next step the carbon black additive was added; this slurry was homogenized for 5 hours with magnetic stirrer. Next, LTO active material was added and the slurry prepared in this way was homogenized for 24 hours. The slurry was coated on a copper foil after homogenization. Cu foil thickness was 35 μm and the thickness of slurry that has been deposited onto the copper foil was controlled by a coating bar. In our experiment, a slurry film with thickness of 200 μm was chosen. After the coating stage, the electrode was dried for 24 hours at 50 °C. The last stage was cutting off individual electrodes and their pressing; the calculated optimal pressing force was 2 tons.cm^{-2}. A 18 mm diameter disks were cut out from the coated foil. The electrolytes were prepared in a glove box (Jacomex) under an inert atmosphere of argon. The solvents for electrolytes preparation were distilled and dried with the use of a molecular sieve to minimize the water content. The $LiPF_6$ salt (Sigma Aldrich) was also dried in argon atmosphere in a dry climatic cell at 80 °C for 24 hours. The electrolytes were always prepared in the 1 mol·l^{-1} concentration in blends of two solvents, sulfolane and a second solvent in the 1:1 volume ratio.

2.2. Measurement method

As an investigation method for half-cell system characterization was chosen the galvanostatic cycling with potential limitation (GCPL) technique on potentiostat BioLogic. This technique allows applying a constant current to the electrochemical cell while its potential is monitored and kept between two potential limits. Electrochemical studies were performed in El-Cell® type cells.

Each time a potential limit is reached, the current is reversed and this procedure is repeated, according to the chosen number of cycles. The time under constant current for each step of charge/discharge is used to determine the quantity of electrical charge capacity (C) per mass of active electrode material under test. The current density was determined as a function of the cycling rate noted as C/n. In experiments, current density relating to one-fifth of nominal material capacity i.e. 0.2 C was used. The GCPL potential range for LTO and graphite material was chosen based on the common working potential level. In the case of LTO it was the range from 1 V to 2.5 V vs. Li/Li$^+$ and for graphite from 0 V to 2.5 V vs. Li/Li$^+$. The galvanostatic charge-discharge cycling was performed at room temperature at 0.2 C-rate.

3. RESULTS AND DISCUSSION

Alkyl carbonates such as ethylene carbonate (EC), diethyl carbonate (DEC), methyl ethyl carbonate (EMC) and dimethyl carbonate (DMC) are among the most important solvents for electrolytes of lithium-ion batteries because they are aprotic, polar and non-volatile [19]. Sulfolane (SL) is a common solvent known for high dielectric constant, boiling point, flash point, electrochemical stability and solubility. Concerning the previously published results on EMC/SL electrolyte with LiODFB [20], SL/DMS and SL/DES with LiBOB [21,22] or SL/DEC with LiBOB [23] we decided to study the series of EC/DMC, SL/PC, SL/EC, SL/DMF and SL electrolytes in combination with $LiPF_6$ and different salts to realize advanced complementation.

Fig. 1 and Fig. 2 shows the charge–discharge voltage profiles (first two cycles) of EC/DMC-graphite and EC/DMC-LTO cells at 0.2 C rate between 0 and 2.5V and 1 and 2,5V. The reversible specific capacity of natural graphite working with the EC/DMC, $LiClO_4$ electrolyte typically ranges from 300 to 370 mAh g^{-1} [24] what is in agreement with our results. A charge–discharge curve plateau of EC/DMC-LTO sample over a wide voltage range was observed at approximately 1.6 V (vs. Li/Li^+). The small voltage difference between the charge–discharge plateaus indicates its good kinetics (Fig. 2). The initial sharp decrease in charge capacity over the first cycle can be attributed to the formation of the SEI layer. In figures where the first two charge-discharge cycles are shown; the first charging and discharging is represented by the dashed line and the second charge-discharge cycle is represented by solid line.

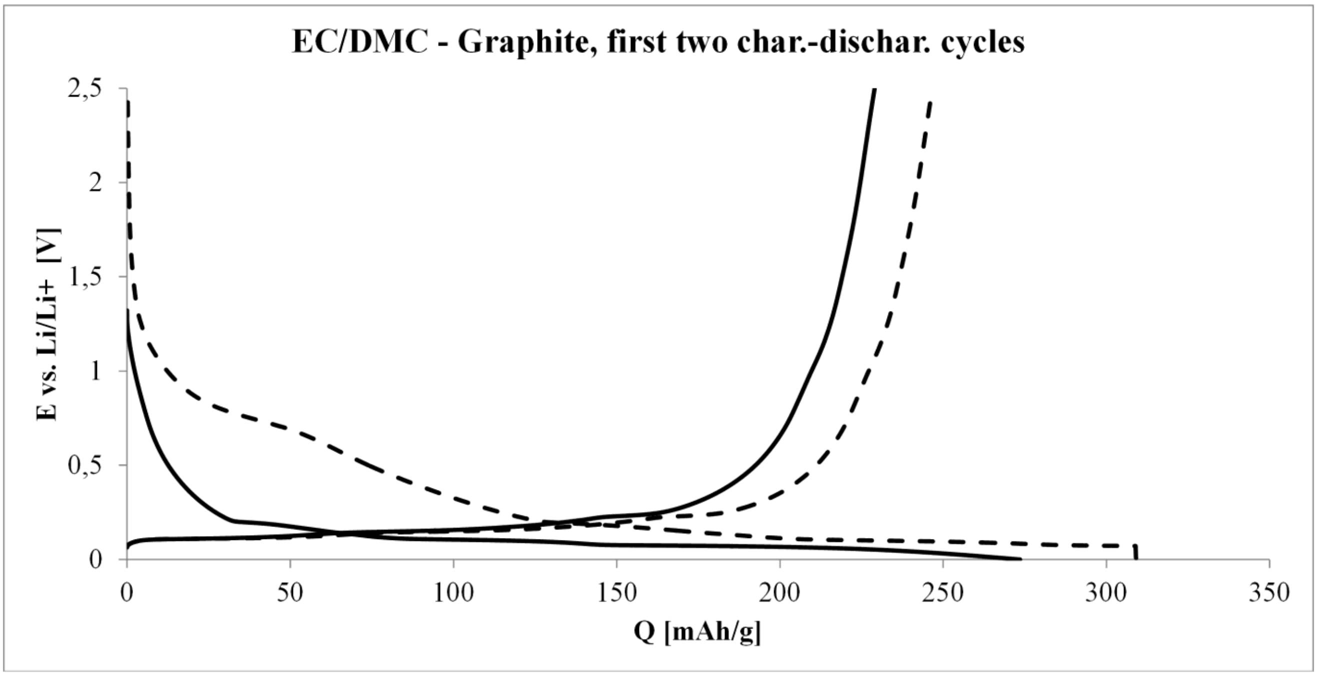

Figure 1. Voltage profiles on the first and second cycle (····1^{st} and — 2^{nd}) of graphite with EC-DMC electrolyte, which were recorded at 0.2C rate between 0 and 2.5V.

Figure 2 and Figure 4 show an additional capacity which may be caused by carbon conductive additives in LTO material. When LTO and sulfolane are combined, the conductive carbon additives are decomposed, thus the LTO particles lose contact with the collector, as can be observed in Figure 5. The experiment with sulfolane and graphite (Figure 3) proves the inclination of sulfolane to do decomposition of carbon conductive additives. Fig. 3 give the initial and second charge/discharge curves for SL and graphite electrode, it displayed a discharge capacity of 4 mAh/g. Low capacity is attributed to the destroyed interphase contact caused by SL solvent. This behaviour of conductive additive decomposition is now observed also in case of EC/DMC electrolyte. On the other hand, the common used mixture of EC/DMC works properly with both electrode materials as depicted in Figure 1, Figure 2 and Figure 5.

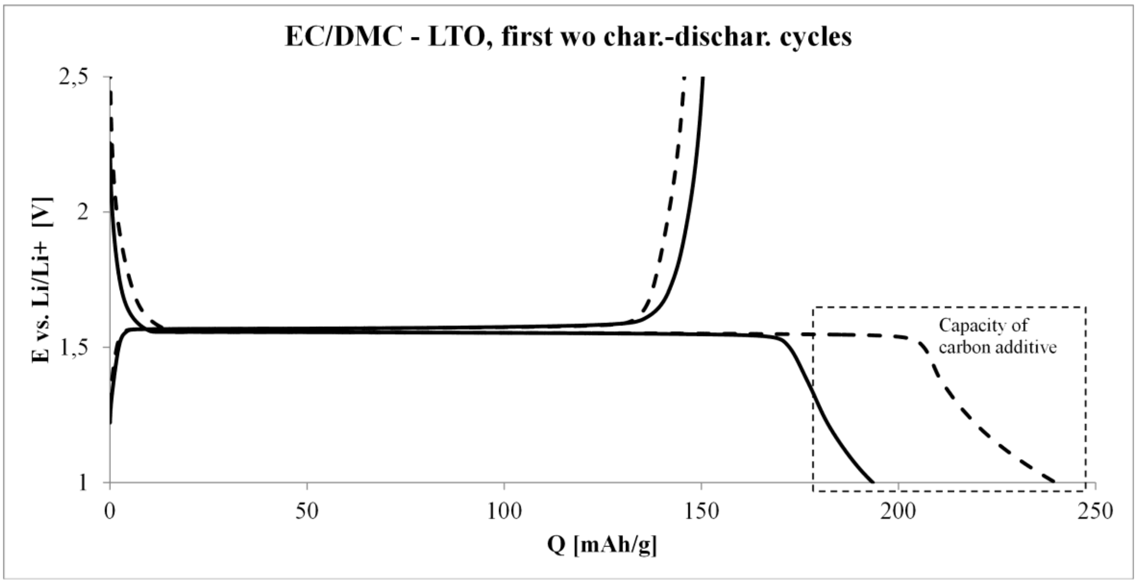

Figure 2. The galvanostatic charge-discharge cycles (····1st and ─ 2nd) of EC/DMC-LTO sample.

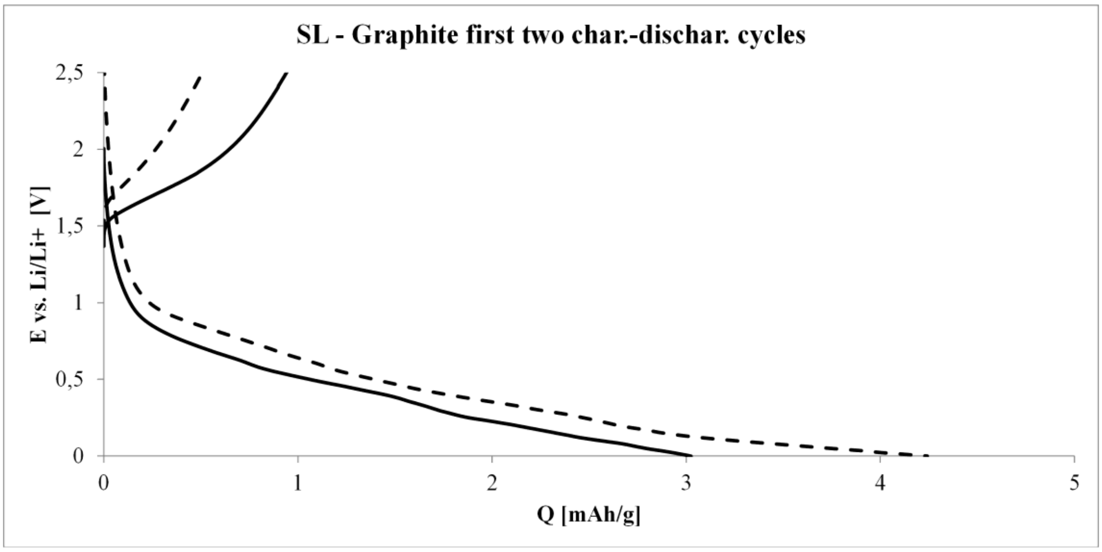

Figure 3. The galvanostatic charge-discharge cycles (····1st and ─ 2nd) of SL-graphite sample at 0.2 C-rate.

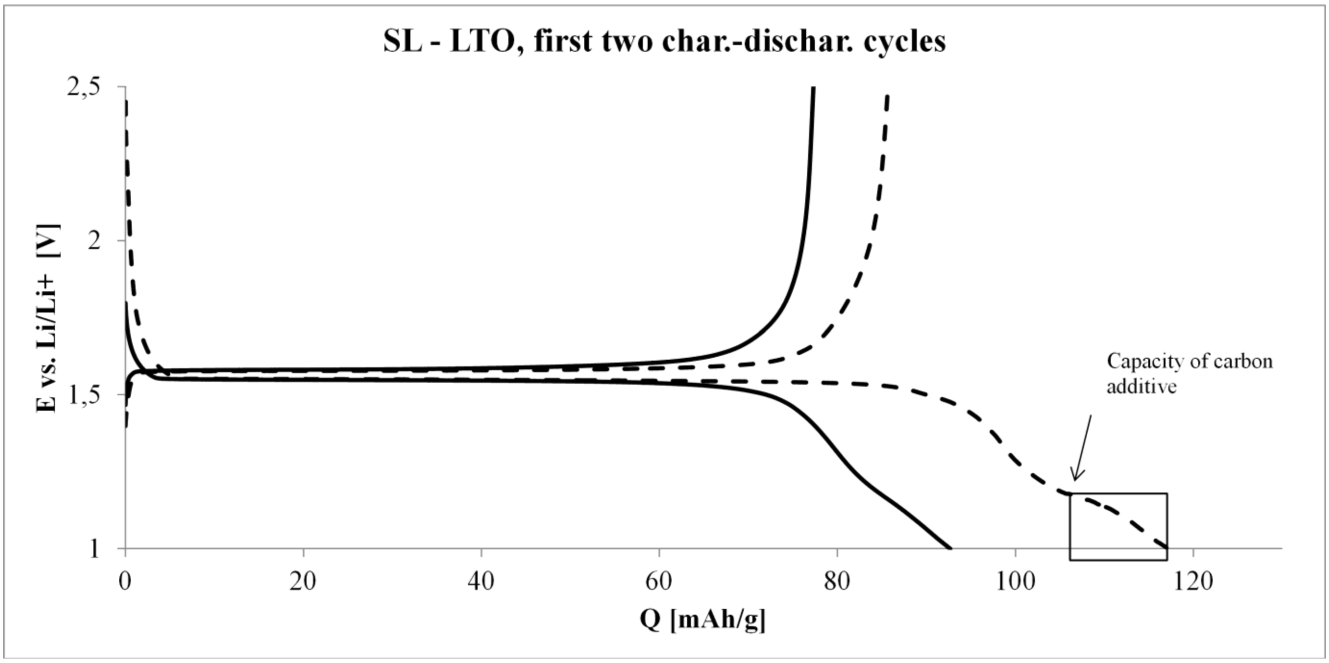

Figure 4. The galvanostatic charge-discharge cycles (····1st and — 2nd) of SL-LTO sample with marked capacity of carbon additive.

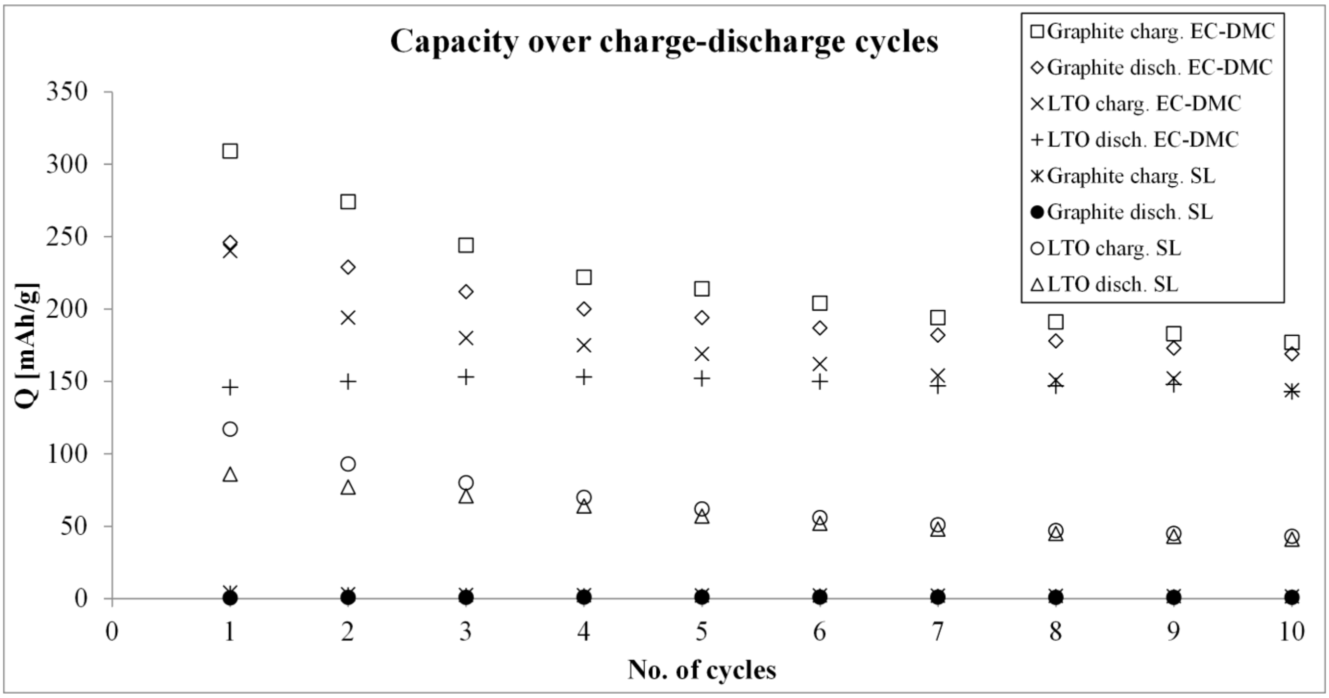

Figure 5. Charge and discharge capacity vs. cycle numbers at 0.2 C-rate for graphite and LTO sample with different electrolytes.

As can be seen from Figure 5 the graphite and SL combination provides almost zero capacity; in the comparison with other samples it reaches a maximum 5 mA.h/g discharge capacity performance. Figure 6 and Figure 7 below show the charge-discharge characteristics of graphite with the mixture of

SL and N,N-dimethylformamide (DMF). The higher charge capacity in the first cycle of graphite can be caused by formation of the SEI layer that is made from the decomposition products of electrolyte solvents. This mixture proves interesting stability with graphite as it is presented in Figure 10. The SL-PC solvents mixture exhibited a high range of graphite destruction appearing as an extremely high capacity in the first charging cycle of over 2000 mAh/g and the stable capacity is stabilized 80 mAh/g approximately (Figure 8 and Figure 9). Sulfolane is the main and key reason during the formation process of an excellent SEI layer, which is dense, thin, uniform and stable [25]. This statement was also confirmed by our measurements.

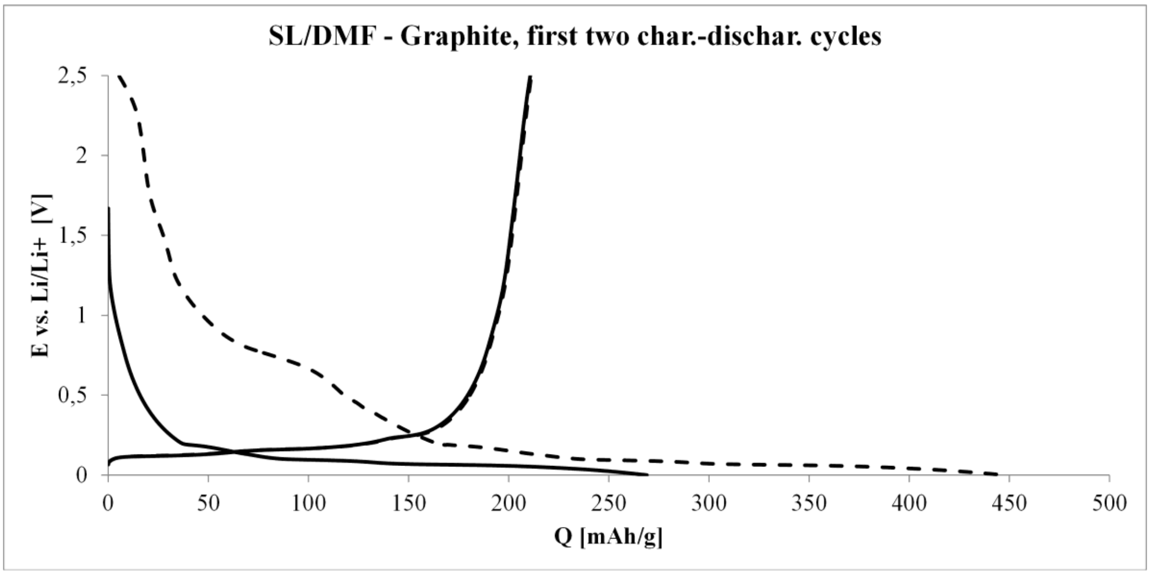

Figure 6. The galvanostatic charge-discharge cycles (····1st and — 2nd) of SL/DMF-graphite sample at 0.2 C-rate.

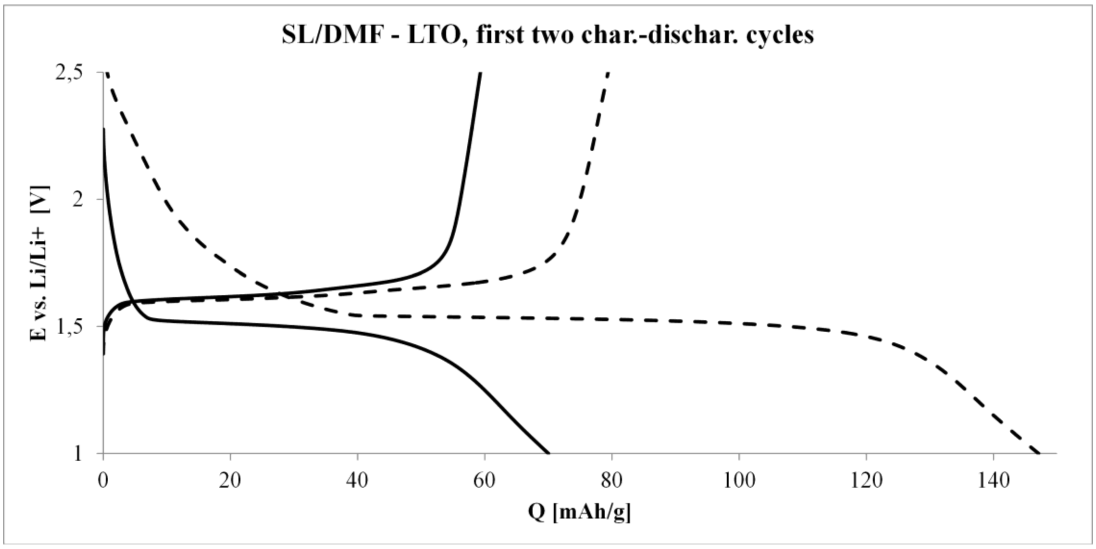

Figure 7. The galvanostatic charge-discharge cycles (····1st and — 2nd) of SL/DMF-LTO sample at 0.2 C-rate.

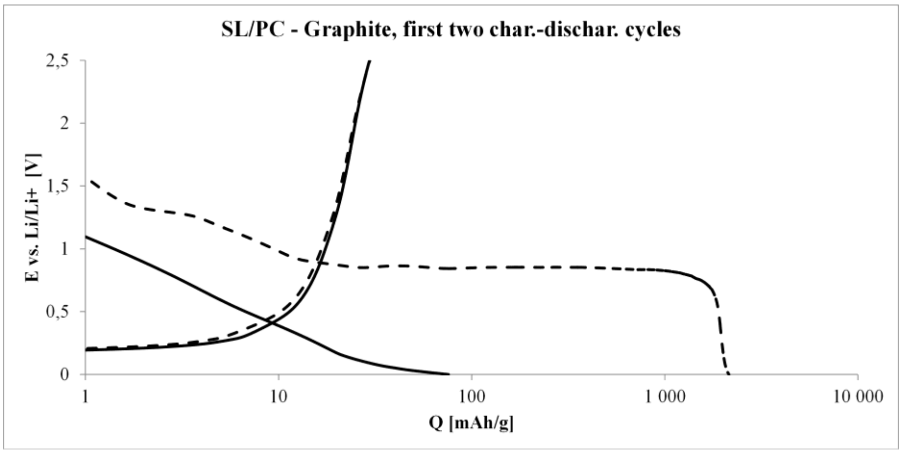

Figure 8. The galvanostatic charge-discharge cycles (····1st and — 2nd) of SL/PC-graphite sample at 0.2 C-rate.

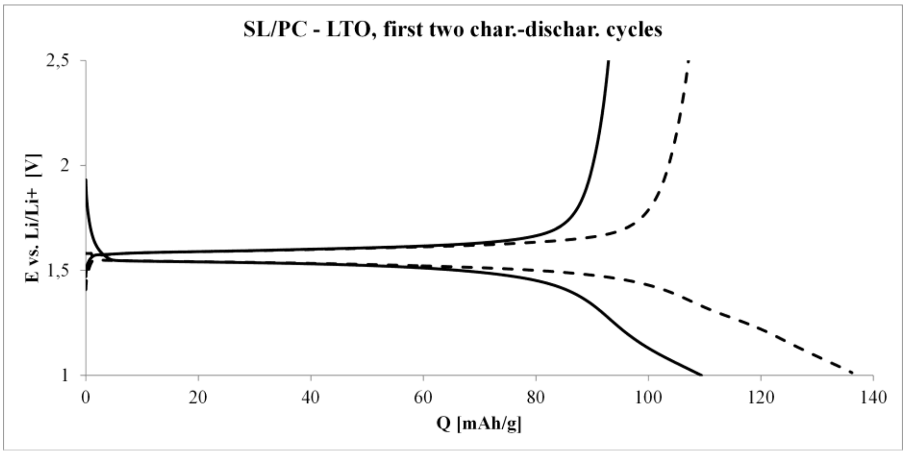

Figure 9. The galvanostatic charge-discharge cycles (····1st and — 2nd) of SL/PC-LTO sample at 0.2 C-rate.

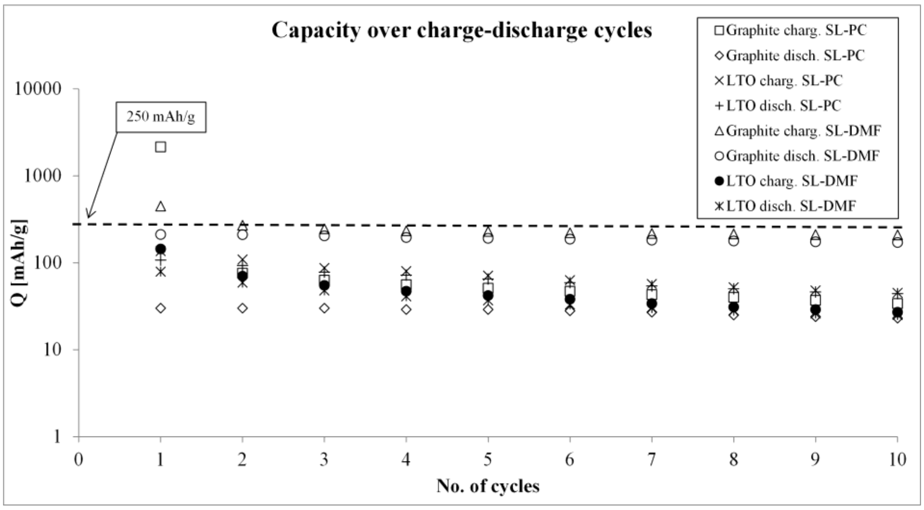

Figure 10. Charge and discharge capacity vs. cycle numbers at 0.2 C-rate for graphite and LTO samples with different electrolytes.

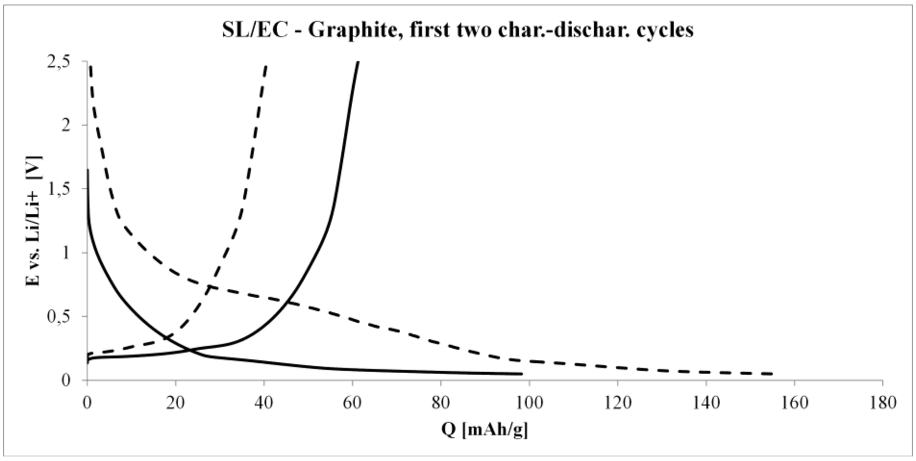

Figure 11. The galvanostatic charge-discharge cycles (····1st and — 2nd) of SL/EC-graphite sample at 0.2 C-rate.

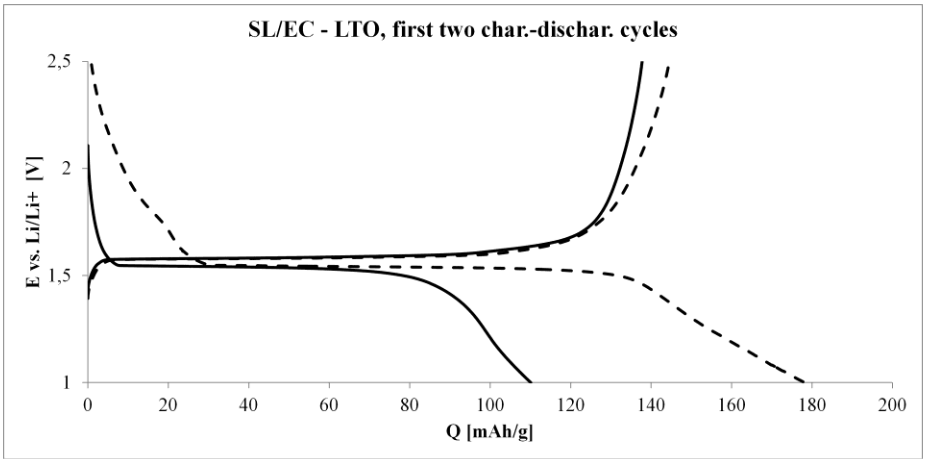

Figure 12. The galvanostatic charge-discharge cycles (····1st and — 2nd) of SL/EC-LTO sample at 0.2 C-rate.

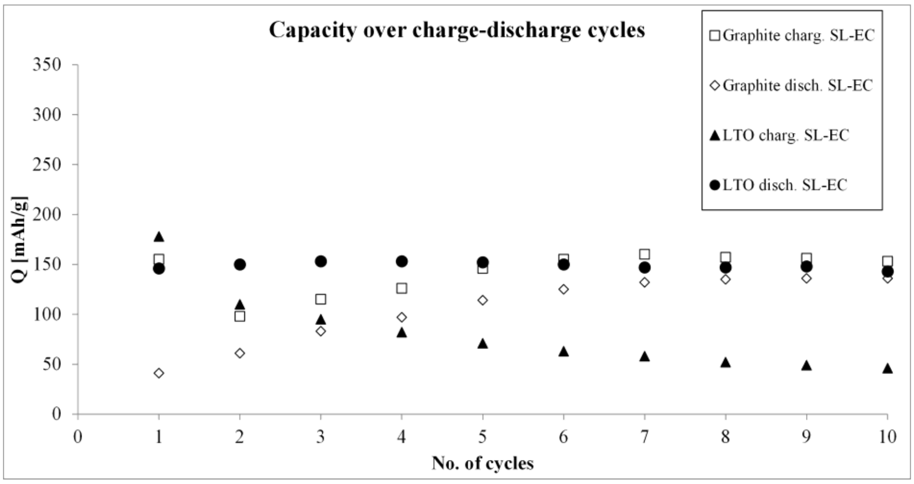

Figure 13. Charge and discharge capacity vs. cycle numbers at 0.2 C-rate for graphite and LTO samples with SL/EC electrolyte.

The mixture of SL-EC showed an unexpected behavior in both cases (graphite, LTO). The graphite electrode shows a high irreversible capacity in the first cycle along with reduced charged capacity in the second one. In the other cycles the charging and discharging capacity is getting higher up to stable 150 mAh/g capacity with small irreversible losses. The LTO material with SL-EC presented showed an extraordinary behavior. Overall, the SL-based cell has better large current discharge capability than EC/DMC-based cell [25]. We suppose it was due to the synergetic collaboration between the two solvents. Especially high relative permittivity enhances salt dissolving into ions and sulfolane is the main reason to obtain an excellent and stable SEI layer.

4. CONCLUSIONS

The series of electrolytes with $LiPF_6$ and graphite or LTO electrode were examined in this study. Concerning the previously published results we decided to study the series of EC/DMC, SL/PC, SL/EC, SL/DMF and SL electrolytes in combination with $LiPF_6$ and different electrodes to realize advanced complementation. Experiments illustrate development of an SEI layer in various electrolyte environments which are influencing the properties and characteristics of the SEI layer. Sulfolane acts as a decomposition reagent for carbon materials. The results show strong influence of SEI composition on electrode capacity performance, the SEI layer primarily depending on aprotic solvents used in electrolyte with working potential window of the cell.

The solvents mixture SL/PC, brought unexpectedly very good results despite well-known negative influence of PC on anode. The good results were probably caused by sulfolane which helps to stabilize the negative electrode surface. Another solvents mixture with good performance was SL/DMF. This system is created by two solvents with high relative permittivity each. The biggest benefit of DMF is its low dynamic viscosity which contributes to high ion mobility and high specific conductivity. The capacity of the graphite electrode after 10 cycles in SL/DMF electrolyte established at the level of ca. 200 mAh g^{-1}. Based on obtained results, single SL itself does not work properly with graphite and carbon materials. Used with the other solvents, DMF for example, may SL contribute to electrolyte higher fire safety along with preservation of good charge-discharge characteristics and battery rate-performance. Sulfolane is the main reason during the formation process of an excellent SEI layer, what was confirmed by the best results obtained for carbon electrode in combination with SL and DMF electrolyte. Obtained results allow the application of different electrolyte combinations also in large-scale, commercial chemical power sources.

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References

1. R. Yazami, *Synthetic Metals*, 20(3) (1987) 383-386

2. L. Zhao, I. Watanabe, T. Doi, S. Okada, J. Yamaki, *Journal of Power Sources*, 161(2) (2006), 1275-1280.
3. M. B. Dines, *Materials Research Bulletin*, 10 (4) (1975) 287-291
4. R. Yazami, *Synthetic Metals*, 7(3) (1983) 169-176
5. Ch. Ch. Hung, *Carbon*, 33(3) (1995) 315-322
6. B.V. Ratnakumar, M.C. Smart, S. Surampudi, *Journal of Power Sources*, 97–98 (2001) 137-139
7. K. Sang-Pil, C.T. Adri, D. Van, B.S. Vivek, *Journal of Power Sources*, 196(20) (2011) 8590-8597
8. M.C. Smart, B.V. Ratnakumar, S. Surampudi, Y. Wang, X. Zhang, S.G. Greenbaum, A. Hightower, C.C. Ahn, B. Fultz, *Journal of The Electrochemical Society*, 146(11) (1999) 3963-3969
9. S. R. Sivakkumar, A.G. Pandolfo, *Electrochimica Acta*, 65 (2012) 280-287
10. M. Holzapfel, A. Martinent, F. Alloin, B. Le Gorrec, R. Yazami, C. Montella, *Journal of Electroanalytical Chemistry*, 546 (2003) 41-50
11. S. Huang, F. Fan, J. Li, S. Zhang, T. Zhu, *Acta Materialia*, 61(12) (2013) 4354-4364.
12. S. Malmgren, K. Ciosek, R. Lindblad, S. Plogmaker, J. Kühn, H. Rensmo, K. Edström, M. Hahlin, *Electrochimica Acta*, Volume 105 (2013) 83-91
13. H.Y. Wang, F.M. Wang, *Journal of Power Sources*, 233 (2013) 1-5
14. J. Światowska, V. Lair, C. Pereira-Nabais, G. Cote, P. Marcus, A. Chagnes, *Applied Surface Science*, 257(21) (2011) 9110-9119
15. S. Li, Y. Zhao, X. Shi, B. Li, X. XU, W. Zhao, X. Cui, *Electrochimica Acta*, 65 (2012) 221-227
16. S. Li, B. Li, X. Xu, X. Shi, Y.Zhao, L. Mao, X. Cui, *Journal of Power Sources*, 209 (2012) 295-300
17. A. Lewandowski, B. Kurc, I. Stepniak, A. Swiderska-Mocek, X. Xu, W. Zhao, X. Cui, *Electrochimica Acta*, 56(17) (2011) 5972-5978.
18. L. Xing, W. Tu, J. Vatamanu, Q. Liu, W. Huang, Y. Wang, H. Zhou, R. Zeng a W. Li, *Electrochimica Acta*,133 (2014) 117-122
19. C.R. Yang, Y.Y. Wang, C.C. Wan, *J. Power Sources*, 72 (1998), pp. 66–71
20. S. Li, X. Xu, X. Shi, B. Li, Y. Zhao, H. Zhang, Y. Li, W. Zhao, X. Cui, L. Mao, *Journal of Power Sources*, 217 (2012) 503-508
21. S. Li, B. Li, X. Xu, X. Shi, Y. Zhao, L. Mao, X. Cui, *Journal of Power Sources*, 209 (2012) 295–300
22. L.P. Mao, B.C. Li, X.L. Cui, Y.Y. Zhao, X.L. Xu, X.M. Shi, S.Y. Li, F.Q. Li, *Electrochimica Acta*, 79 (2012) 197-201
23. S.Y. Li, Y.Y. Zhao, X.M. Shi, B.C. Li, X.L. Xu, X.L. Cui, *Electrochimica Acta*, 65 (2012) 221–227
24. Z. Ogumi, M. Inaba, Advances in Lithium-ion Batteries, edited by W.A. van Schalkwijk, B. Scrosati, Kluwer (2002) (Chapter 2)
25. S.Y. Li, W. Zhao, X.L. Cui, Y.Y. Zhao, B.C. Li, H.M. Zhang, Y.L. Li, G.X. Li, X.S. Ye, Y.C. Luo, *Electrochimica Acta*, 91(2013) 282-292