Comparison of organic and inorganic gelation agents in ethylene carbonate based electrolytes for lithium-ion batteries

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Abstract

Two types of electrolyte which are suitable for lithium-ion batteries are investigated. In both cases the basic electrolyte is a mixture of organic solvents such as ethylene carbonate (EC) and propylene carbonate (PC) or EC and dimethyl carbonate (DMC). The lithium salts applied are $LiClO_4$, $LiPF_6$, LiTFMSI and LiTFMS. Gel-type electrolytes were prepared by adding a few wt.% of highly dispersed silica (HDS) to the liquid electrolyte. If hydrophilic HDS is used, thixotropic gels are formed. The second type of electrolytes are poly(acrylonitrile) (PAN) based. These electrolytes can be prepared as dimensionally stable films. The conductivity of the HDS gel electrolytes is very close to that of the liquid electrolyte. PAN-based electrolytes exhibit lower conductivities than the comparable liquid electrolytes. If a lithium anode is used in a rechargeable battery, PAN-based electrolytes offer significant advantages, since they are efficient to avoid internal short circuits due to lithium dendrite formation. A small test battery of the type lithium/PAN-based electrolyte/$LiCoO_2$ was deep-cycled for about 450 times without any indication of internal shorts. © 1997 Published by Elsevier Science S.A.

Keywords: Lithium-ion batteries; Ethylene carbonate; Organic solvents; Gelation agents

1. Introduction

The application of polymer electrolytes in rechargeable lithium batteries or in lithium-ion batteries is very attractive [1].

If the mechanical strength of such a polymer is sufficiently high no separator is required in a battery. Thus, the filling process in battery manufacturing can be omitted. Together with the application of film-coating techniques, this may lead to more efficient manufacturing and to a greater flexibility in the design of batteries.

Since the conductivities of polymer electrolytes are usually rather moderate ($< 10^{-4}\ \Omega^{-1}\ cm^{-1}$), we focussed on the investigation of highly plasticized polymers [2,3] and on gelled organic electrolytes [4]. The gelation agents were highly dispersed silica (HDS) types, whereas the organic plasticized polymer electrolyte was based on poly(acrylonitrile) (PAN).

2. Experimental

The starting electrolytes ethylene carbonate (EC)–propylene carbonate (PC)–$LiPF_6$ and EC–dimethyl carbonate (DMC)–LiTFMSI were carefully prepared and dried over molecular sieves (4 Å). The water content determined with the Karl–Fischer method was always below 50 ppm.

EC–PC–PAN plasticized electrolytes were prepared by mixing the electrolyte components at temperatures between 100 and 120 °C. The resulting highly viscous solution was cast into small circular discs with a thickness of 1 mm and a diameter of 15 mm.

For the gel electrolytes mainly the EC–DMC–LiTFMSI liquid electrolyte was used as a starting material. The applied HDS was Aerosil 200 from Degussa, or Cab-O-Sil H5 from Cabot. The Aerosils were dried for 3 h at 450 °C prior to use. For the gel preparation a defined volume of liquid electrolyte was filled in a glass flask and 4–6 w/o of HDS were added. The mixture was then stirred with a magnetic stirrer in the closed flask.

All operations of moisture sensitive materials were made in an argon-filled glove box or at least in a dry-room.

The PAN-based polymer electrolyte could be prepared as a free standing stable film. With such films complete batteries in a laboratory set-up were built and used for electrochemical measurements.

The conductivity of PAN-based electrolytes were measured by placing the film between two stainless-steel electrodes and using the a.c. impedance technique (Solartron Model 1250) in a frequency range between 1 Hz and 65 kHz.

For the calculation of the conductivity values of the bulk electrolyte the high frequency intercept of the Nyquist plot with the real axis was used.

The conductivity of HDS-based gels was determined by using a standard conductivity measurement cell with platinized platinum electrodes.

For charge/discharge cycling in the galvanostatic mode, a battery test equipment (Delphin/Control 300) was used. Data acquisition and evaluation was made with a standard PC.

3. Results and discussion

For the preparation of PAN-based electrolyte, EC–PC solvent mixtures were preferred. This is mainly due to the fast drying out of plasticized polymers using DMC or DEC as a plasticizer component, because these solvents have a very low boiling point. Furthermore, in a complete battery the internal pressure which rises at elevated temperatures due to solvent evaporation will be also much lower with EC–PC.

In Fig. 1 the conductivity of a PAN-based electrolyte with the following composition 38mol%EC–33mol%PC–8mol%LiTFMS–21mol%PAN shown in comparison with the conductivity of a liquid EC–PC (1:1 vol.%) LiTFMS (1 M) electrolyte.

The conductivity at 20 °C which was measured is 2×10^{-3} Ω^{-1} cm^{-1} for a 40mol%EC–34mol%PC–21mol%PAN–5mol%LiTFMS electrolyte [5].

Since the PAN–EC–PC mixture does not react with LiPF$_6$, this salt can be used as well. However, it has to be considered that the plasticized electrolytes are prepared, in general, by mixing the components at temperatures around 100 °C in the case of an EC–PC solvent mixture. At such high temperatures LiPF$_6$ tends to be unstable and may form HF traces, PF$_5$ or other detrimental decomposition products.

Therefore, we preferred to apply LiTFMS or LiAsF$_6$ which are thermally more stable in plasticized PAN electrolytes prepared according to this method. We succeeded, however, by a modified preparation technique, to prepare a PAN–LiPF$_6$ film as well.

The conductivity results of this electrolyte compared with the PAN electrolyte with LiTFMS is shown in Fig. 2.

The conductivity of the LiPF$_6$-containing PAN-based electrolyte is very close to that determined for the LiTFMS-containing PAN electrolyte over the complete temperature range.

In all cases, regardless of the type of lithium salt, stable, free standing films with a rubber-like consistency were obtained. The stability of these films is sufficient high to omit an additional separator. On the other hand, the flexibility of the film is advantageous in establishing a good contact between the electrodes and the polymer-based electrolyte.

For the preparation of a highly dispersed silica (HDS) gel, the addition of 4–6 w/o of hydrophilic Aerosil 200 or Cab-O-Sil H5 was sufficient. The relative content of liquid electrolyte in a HDS gel is higher than in a plasticized PAN electrolyte.

The conductivity of an EC–DMC–LiTFMSI–HDS gel in comparison with the basic liquid electrolyte and with a comparable EC–PC–PAN–LiTFMSI electrolyte is shown in Fig. 3.

With hydrophilic HDS, thixotropic gels are formed which have a paste-like consistency.

If one compares the conductivity values of an EC–DMC–LiTFMSI–HDS gel with the values obtained from a plasticized PAN with an EC–PC–LiTFMSI liquid electrolyte component, it turns out that the conductivity of the HDS gel is considerably higher. In fact, the conductivity of the HDS gel is very close to that of the liquid electrolyte. This is surprising since the viscosity of such gels is high compared with that of liquid electrolytes. A possible explanation is, that
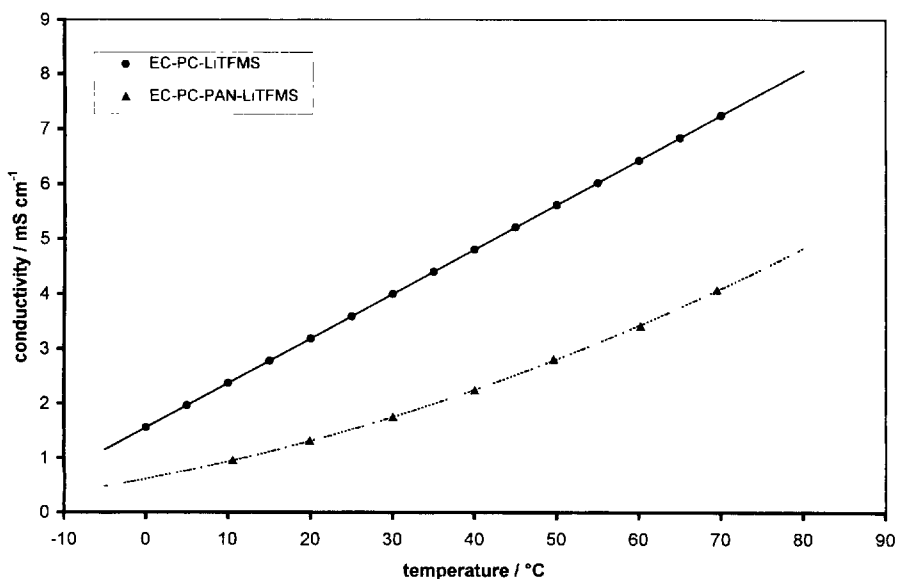

Fig. 1. Conductivity vs. temperature plots of EC–PC–LiTFMS liquid electrolyte and of PAN plasticized with EC–PC–PAN–LiTFMS electrolyte.
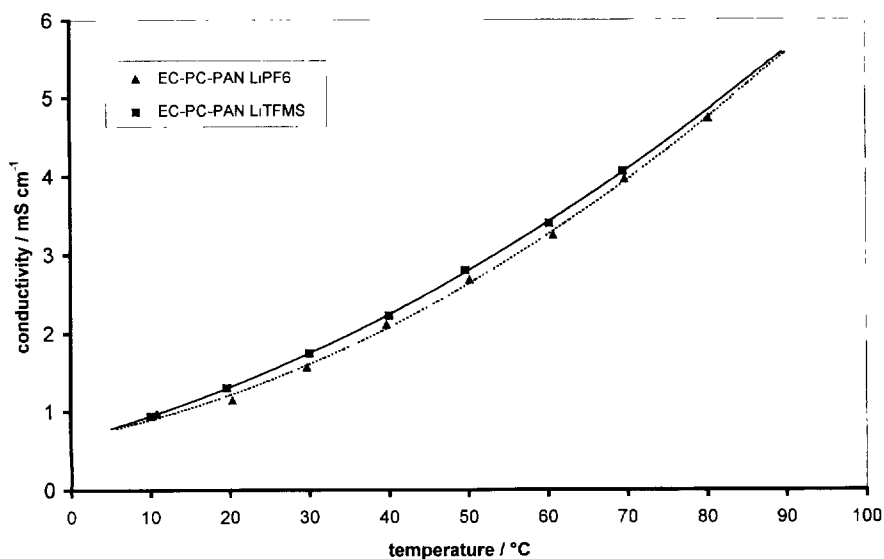
Fig. 2. Conductivity vs. temperature plots of EC–PC–PAN–LiPF$_6$ and EC–PC–PAN–LiTFMS plasticized electrolytes.
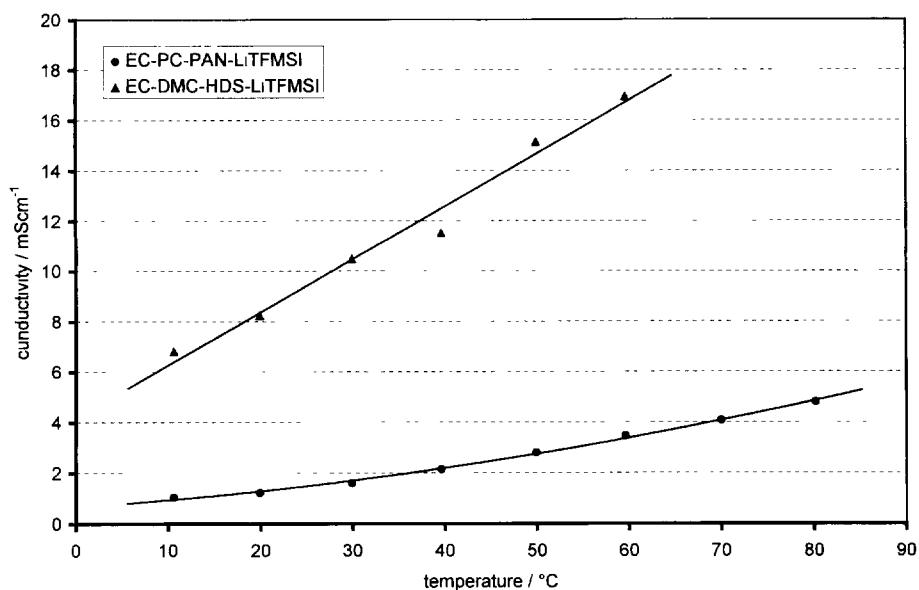

Fig. 3. Conductivity vs. temperature plots of EC–PC–PAN–LiTFMSI plasticized electrolyte and of EC–DMC–HDS–LiTFMSI gelled electrolyte.

the content of the liquid electrolyte is high (94–96%) and that the silica particles form only a relatively loose network allowing free movement of the solvated lithium ions. The result also shows that there are only very small interactions, between the silica particles and the lithium ions. This can be understood since in the HDS only a few polar groups (Si–OH groups) are present which have hydrogen bonding amongst themselves.

In the PAN-based electrolyte, the content of liquid electrolyte is still high (around 74% w/o), but much lower than in the HDS gels. In the PAN-based electrolyte, the polymer is obviously not only a loose network like in the HDS gels, but a more rigid structure formed by polymer chains. The PAN-based electrolyte is a stable 'solid' film and not a gelous paste.

Thus the different physical properties may well explain why the conductivity in the PAN-based electrolyte is lower than in the HDS gels.

Taking the above-mentioned physical properties of the PAN-based electrolytes into account, their conductivity is remarkably high.

In contrast to the PAN electrolyte in hydrophilic HDS gels, LiPF$_6$ cannot be applied as a salt to facilitate the lithium-ion transport in this electrolyte. Obviously, LiPF$_6$ reacts with the remaining Si–OH to form HF traces and other decomposition products, e.g. POF$_3$ or PF$_3$. The HF and eventually other products as well seem to react with the silicon itself under formation of, probably, SiF$_4$. Even though the exact mechanism has not been proven it is likely that not only the –OH groups react since the decomposition and the gas evolution are important.

By investigating the electrochemical stability window of HDS gels with LiTFMS salt on inert electrodes (platinum), it was found that the stability range is at least 4.1 V versus lithium [4].
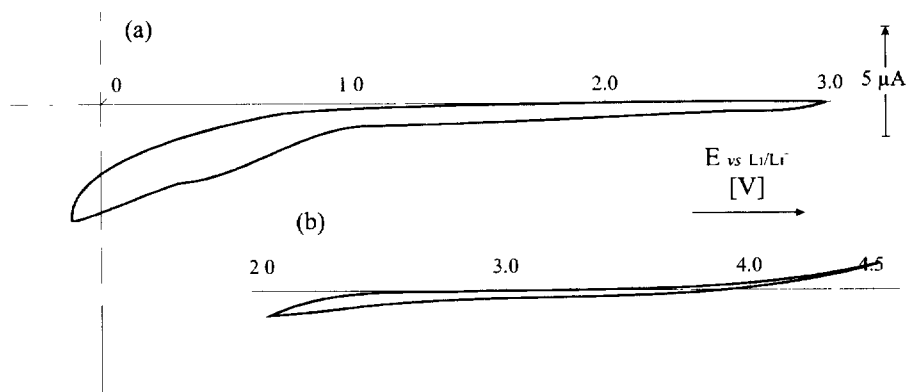
Fig. 4. Cyclic voltammogram of EC–PC–PAN–LiPF$_6$ plasticized electrolyte: (a) working electrode, stainless steel, and (b) working electrode: aluminum. Scan-rate: 50 μV/s, and reference electrode: lithium
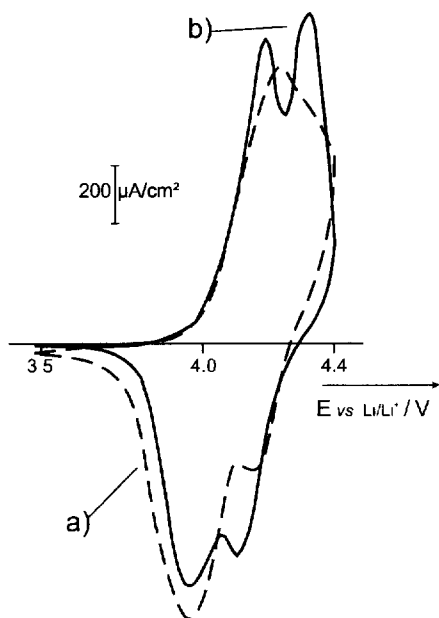

Fig. 5. Cyclic voltammograms of LiMn$_2$O$_4$ electrodes in (a) liquid EC–DMC–LiPF$_6$ electrolyte and (b) plasticized EC–PC–PAN–LiPF$_6$ electrolyte. Scan-rate: 50 μV/s, and reference electrode: lithium.

Fig. 6. Schematic drawing of a test cell (4 5 cm^2 electrode area)

Making similar measurements with the basic organic electrolyte which was used for the preparation of this gel a comparable stability range is found. Similar results are also obtained in the PAN-based electrolyte with LiTFMSI salt.

These results prove that at least not the gel former (HDS) or the polymer matrix (PAN) are limiting the stability.

The electrochemical stability window of an EC–PC–PAN–LiPF$_6$ electrolyte was measured similarly as for the HDS gel by applying cyclic voltammetry. The result is shown in Fig. 4.

The stability range in this case is well above 4 V versus lithium. This result together with the above-discussed results proves that the component limiting the electrochemical stability range is LiTMSI.

According to the limited choice in lithium salts which can be applied in HDS gels, these gels, at least if metallic lithium or graphite is used as an anode, should be used only in combination with LiCoO$_2$ (possibly also with mixed Li–Ni–Co oxides or LiNiO$_2$). Due to the larger stability range of the
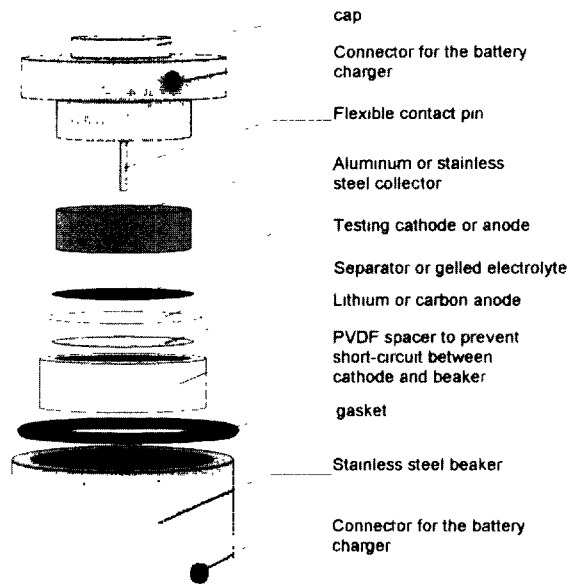
PAN-based polymer electrolyte, in this case also LiMn$_2$O$_4$ can be favourably used.

Fig. 5 shows a cyclic voltammogram of an LiMn$_2$O$_4$ electrode in liquid EC–DMC–LiPF$_6$ electrolyte and EC–PC–LiPF$_6$–PAN electrolyte.

The reversibility and power capability of the electrodes is comparable, independent whether it is a liquid electrolyte or a PAN-based gelled electrolyte.

A slight difference in the two curves is that the peaks in the voltammogram which is recorded in the PAN based electrolyte are broader than those in the liquid electrolyte. This indicates that the charge transfer through the electrode/electrolyte interface in the plasticised PAN electrolyte is hindered compared with the liquid system.

4. Small test batteries

A key problem in using lithium metal anodes in rechargeable batteries is the dendritic deposition of lithium during charging. Thus after about 200–300 deep-cycles (in the best
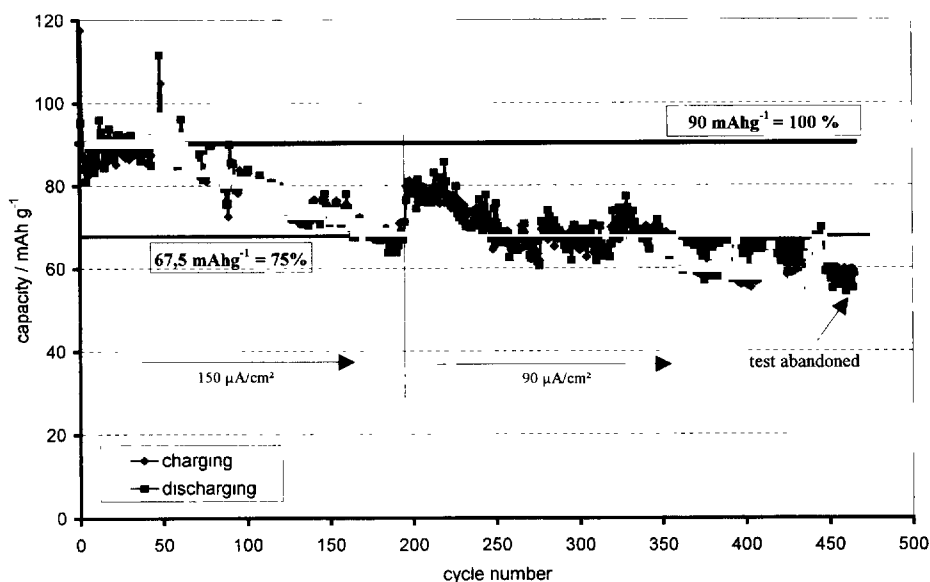
Fig. 7 Capacity vs cycle number of a lithium/EC–PC–PAN electrolyte/LiCoO₂ test battery. Current density changed after 196 cycles from 150 to 90 μA/cm².
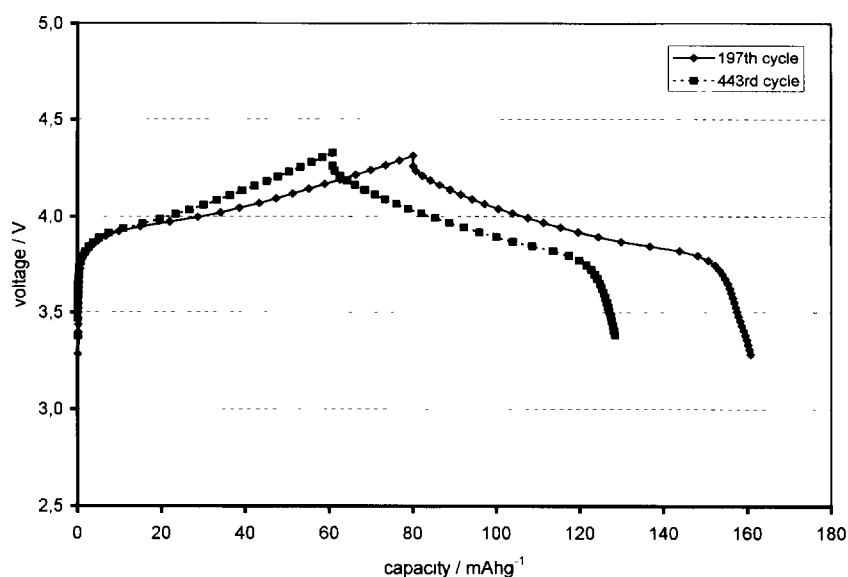

Fig. 8. Selected cycles from the test battery lithium/EC–PC–PAN electrolyte/LiCoO₂ (see Fig. 7). Cycle nos.: 197 and 443 and current density: 90 μA/cm².

case), problems may come along with such batteries due to the formation of internal shorts.

Due to the positive test results with the PAN-based electrolytes being described above, it was worthwhile to investigate the cycling behaviour of a complete lithium anode/polymer-based electrolyte/intercalation cathode battery. Since LiCoO₂ is the best characterised cathode material with a stable cycling behaviour, this was chosen for the test.

The electrolyte was EC–PC–LiAsF₆–PAN. The test battery was set up in a demountable device which is shown in Fig. 6.

The cycling behaviour of this test battery was very good and more than 450 deep-cycles were achieved. Even after the test was abandoned and the battery was disassembled and carefully examined, no indication of any internal shorts or

dendrite growth through the polymer-based electrolyte were detected.

The capacity versus cycle life of this test battery is shown in Fig. 7. After 200 cycles the current density which was originally 150 μA/cm² was reduced to 90 μA/cm².

This resulted in the recovery of capacity which is seen in the figure.

The fading of the capacity during cycling may be due to several reasons. It may be partly due to increasing surface resistance on the lithium anode, since fresh deposited lithium will react again with the liquid components in the PAN-based electrolyte or eventually with the PAN polymer itself.

Fig. 8 shows two cycles from this battery, the cycles 197 and 443. From the shape of these curves it can be seen that the internal impedance of the cell is increasing.

Another effect which may contribute to the impedance increase is the evaporation of the liquid electrolyte, since the device for the set-up of the battery was not fully hermetically closed. Even though the boiling points of EC and PC are very high, during the test period of six months some evaporation may have occurred as well as some water uptake (even in the glove box in which this experiment was made).

It can be stated that it is possible, when PAN-based electrolytes are used, to achieve much higher cycle numbers in rechargeable batteries with lithium anodes than in those with liquid electrolyte.

5. Conclusions

EC–PC–PAN-based electrolytes were prepared as free standing films. Different lithium salts as e.g. $LiAsF_6$, $LiPF_6$ and LiTFMSI were used. Using the same salt type (Li-TFMSI) a gel-type electrolyte with highly dispersed silica (HDS) exhibits a conductivity which is very close to that of the basis liquid electrolyte. An explanation for this result may be that the HDS is forming only a relatively loose network with very low interaction between the lithium ions and the network.

The conductivity of the corresponding PAN-based electrolyte is significantly lower, but still sufficient to allow its application in lithium rechargeable batteries. Even in this case where the electrolyte is a free standing film, the liquid content was 74% w/o. Since the conductivity is in the order of 10^{-3} Ω^{-1} cm^{-1}, it may be assumed that the ionic transport is mainly determined by the liquid components and that the ions have the possibility of a relatively free movement.

The conductivity of electrolytes with $LiPF_6$ or $LiAsF_6$ is higher than with LiTFMSI or LiTFMS. However, $LiPF_6$ cannot be used in HDS-based gels, since it leads to decomposition reactions of the silica, forming gaseous reaction products. Thus, for HDS-based gels other salts such as e.g. $LiClO_4$, LiTFMSI or LiTFMS have to be used. A disadvantage of LiTMSI is that it is limiting the electrochemical stability range of an electrolyte at ~ 4.1 V.

In PAN-based electrolytes, however, no significant difference in conductivity between the electrolytes containing $LiPF_6$ or LiTFMS was found. This leads to the conclusion that the conductivity mechanisms in the liquid electrolytes and in the PAN-based electrolytes are different.

Both types of electrolytes (HDS-based and PAN-based) can be used in lithium-ion-type cells as long as the stability window is not exceeded. The PAN-based electrolyte was applied in a small test battery with a lithium anode. It turned out that the electrolyte is very effective in supressing internal shorts in the battery caused by lithium dendrites.

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