

# Properties and potential application of silica-gelled electrolytes for lithium-ion batteries

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## Abstract

The properties of gelled electrolytes based on liquid organic electrolytes are investigated. The gelation agents are highly dispersed silica (HDS) which are added in a quantity of a few wt %. Drying conditions for the HDS are described as well as the analytical values for the residual water. Two basically different types of HDS are investigated: (i) hydrophilic and (ii) hydrophobic material. Whereas the hydrophilic HDS contains SiOH groups on the surface of the silica particles, in the hydrophobic HDS, these SiOH are normally methylated. With hydrophilic HDS, thixotropic gels can be prepared. Conductivity data for EC-DMC/LiTFMSI gels are comparable with the values obtained for the liquid electrolyte. The electrochemical stability window for such a gel electrolyte is at least between 0–4.1 V versus lithium. Metallic lithium and the intercalation cathodes ( $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ) can be reversibly cycled in this electrolyte. No specific detrimental effects due to the addition of HDS were observed. © 1997 Elsevier Science S.A.

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## 1. Introduction

Rechargeable lithium batteries, due to their favourable properties, e.g. high energy density (gravimetric and volumetric) and high voltage attracted a lot of attention since more than 20 years. Whereas in the beginning of the research only liquid electrolytes based on organic solvents were taken into account, in the meantime a lot of work was focussed on the development of polymeric electrolytes [1–6]. In the last decade, most efforts were targeted to research in 'pure' lithium-ion conducting polymer electrolytes [1,2]. During the last few years, however, due to the insufficient conductivity of these polymer electrolytes, the investigation of plasticized and/or gelled polymer electrolytes became popular, e.g. PAN- or PMMA-based materials [3–6]. In contrast to numerous investigations in the above-mentioned electrolyte types, the use of inorganic gelation agents, e.g. highly dispersed silica (HDS) was studied only for organic electrolytes which are suitable for lithium primary batteries [7].

However, suitable electrolytes for the new generation of lithium-ion batteries are different, since other solvents have to be used and the required stability window for the electrolyte is much larger. Therefore, this work deals with investigations

on HDS-based gelled organic electrolytes and on highly plasticized polymer electrolytes which can be applied in lithium-ion batteries.

## 2. Experimental

Different types of highly dispersed silica materials were used. From Degussa, the hydrophilic type A 200 and the hydrophobic types R812 were investigated. From Cabot the types CAB-O-Sil M5 and CAB-O-Sil H5 were used.

Various drying procedures were tested, e.g. 200 °C for 72 h; 225 °C for 72 h in vacuum, 450 °C for 3 h. The dried samples were taken from the 450 °C hot oven and transferred to tight glass flasks in a dry room. FT-IR spectra were recorded by using the diffusive reflection infrared technique (DRIFT).

Aside from the recording of IR spectra of the HDS, the water content was determined by the Karl-Fischer titration.

High purity organic solvents were used without further distillation (Merck). The liquid organic electrolytes contained less than 30 ppm water (determined by the Karl-Fischer titration).

For the preparation of gels, about 4 w/o of HDS were added to the premixed organic electrolyte and the mixture was stirred intensively with a magnetic stirrer.

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Cyclic voltammograms were recorded with a sweep generator (VSG 72, Bank) and a potentiostat (MP81, Bank).

Conductivities were determined with a conductivity meter at a frequency of 1000 Hz. A standard measurement cell with platinized platinum electrodes was used. The samples were equilibrated in a thermostate bath at each temperature for at least 1 h prior to the measurement.

### 3. Results and discussion

Plasticized or gelled electrolytes contain large quantities of liquid electrolyte (in polymer gels up to  $\sim 75$  w/o). By using inorganic gelation agents, especially of the HDS type, the liquid content is even higher, e.g. up to 96%. As a consequence the liquid electrolyte components are determining to a large extent the electrochemical properties of such electrolytes, such as stability versus electrode materials.

Therefore before preparing gels, the properties of liquid electrolytes suitable for an application in lithium-ion batteries were determined. Electrolyte mixtures chosen were ethylene carbonate (EC)–propylene carbonate (PC), but mainly EC–dimethyl carbonate (DMC) with various lithium salts:  $\text{LiPF}_6$ ,

$\text{LiTFMSI}$  (lithium (bis) trifluoromethanesulfonimide), and  $\text{LiTFMS}$  (lithium trifluoromethanesulfonate).

The results show that in the same solvent mixture EC–DMC (50–50%) with the same salt concentration the conductivity is increasing in the following order  $\text{LiTFMS} < \text{LiTFMSI} < \text{LiPF}_6$ . The conductivity curves are shown in Fig. 1.

After these liquid electrolytes were characterized, gels were prepared by adding a few w/o of HDS to the electrolytes. Table 1 gives a list of the HDS types investigated and some of their properties.

Generally, one should differentiate hydrophobic and hydrophilic HDS types. Hydrophilic HDS can be regarded as the standard type. The hydrophilic behaviour is caused by Si–OH groups on the surface which tend to form hydrogen bridged bonding with water molecules. In the hydrophobic types the surface–OH groups are reacted with dichloromethyl silane and are methylated [8].

The –OH groups and absorbed water can be very easily detected in IR spectra (Fig. 2). The very strong and sharp IR absorption at  $3750\text{ cm}^{-1}$  is due to an –O–H stretching vibration, whereas bridged –O–H groups show absorptions between  $3000\text{--}3800\text{ cm}^{-1}$ . In this range also physically

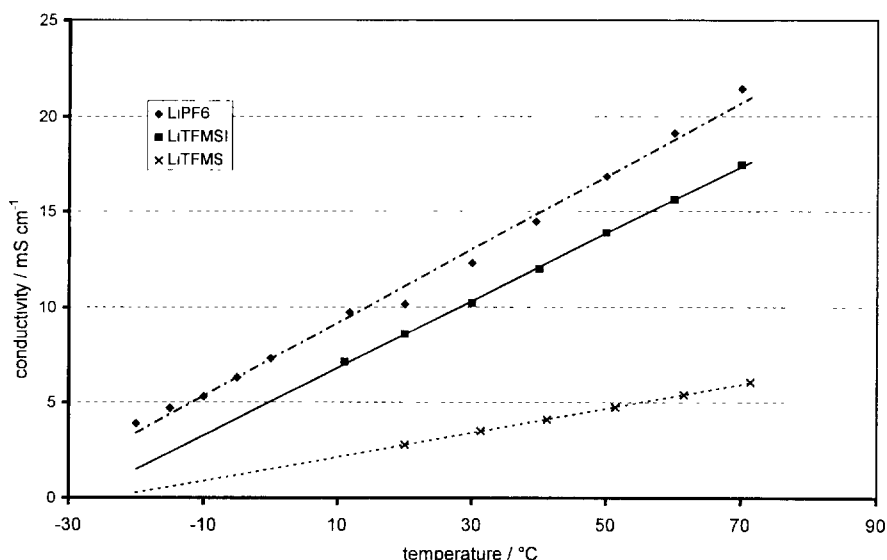


Fig. 1. Conductivity vs. temperature plots of EC–DMC electrolytes with 1 M  $\text{LiPF}_6$ , or 1 M  $\text{LiTFMSI}$  or 1 M  $\text{LiTFMS}$ .

Table 1

Overview on some properties of HDS-materials

HDS type	Specific surface area <sup>a</sup> (m <sup>2</sup> /g)	Properties		Water content (ppm) <sup>b</sup>	
		Hydrophobic	Hydrophilic	Undried	Dried
Aerosil 200	200	0	+	15500	~ 600
Aerosil R 812	260	+	0	2000	~ 300
Aerosil R 805	150	+	0	2400	1000
Cab-O-Sil M5	200	0	+	~ 6300	590
Cab-O-Sil H5	300	0	+	~ 11000	1200

<sup>a</sup> Mean value.

<sup>b</sup> Determined with KF method.

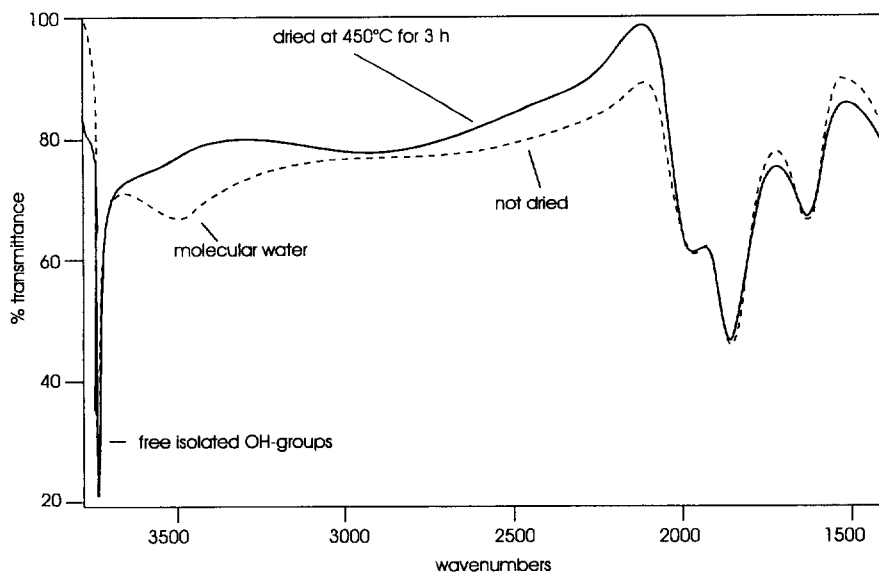


Fig. 2. IR spectra of dried and not dried highly dispersed silica, showing OH groups and absorbed water.

absorbed water shows a very broad, unspecific IR absorption [8].

First, gels were prepared by simply using HDS samples as received, but in the continuation of the experiments dried samples were used (see Table 1). From the values in Table 1 it is quite obvious that hydrophobic HDS is much easier to dry than hydrophilic. This is in full agreement with the expectations since, in contrast to the hydrophilic samples in the hydrophobic material, the water is not bonded through hydrogen bridges.

For the preparation of gels a content of 4–6 w/o of HDS is sufficient. A significant difference between the application of hydrophobic and hydrophilic HDS is that the resulting gels are non-thixotropic (hydrophobic HDS) or thixotropic (hydrophilic HDS). This difference is due to the effect that

in a gel based on hydrophilic HDS hydrogen bonds are formed between the –OH groups of different silica particles thus forming chains and networks between those particles. In addition to that an interaction between the organic solvents and the –OH groups via weak hydrogen bonding is also possible. During stirring the network is destroyed and thus the sample becomes a viscous liquid. After stopping the stirring the hydrogen bonds and the network formation is re-established.

This effect cannot be observed with hydrophobic material since no hydrogen bonds are formed. In this case the gel is more pasteous and less stable than with the hydrophilic HDS.

The conductivities of a liquid EC–DMC/LiTFMSI electrolyte and of a gelled electrolyte using 4 w/o of hydrophilic HDS and the same liquid electrolyte are shown in Fig. 3. As

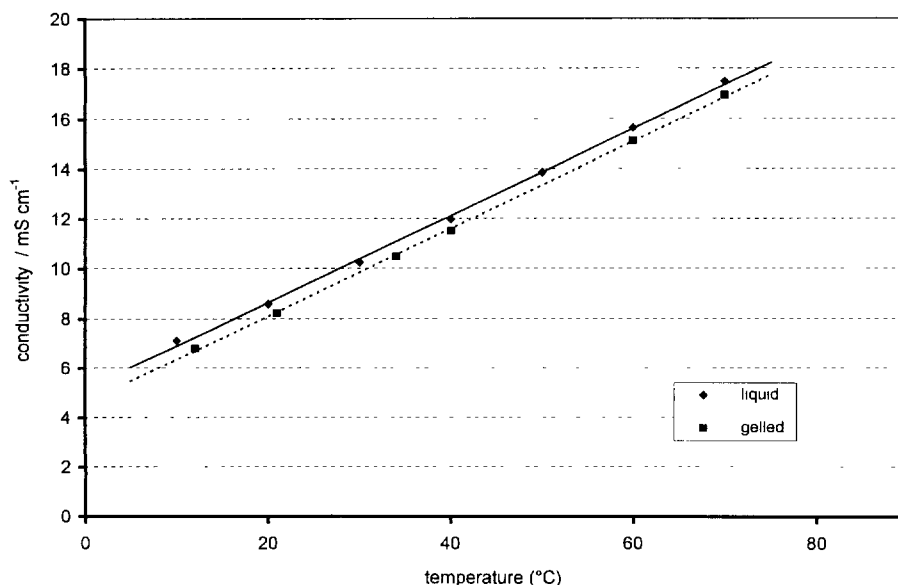


Fig. 3. Conductivity vs. temperature plots of EC–DMC/1 M LiTFMSI electrolytes (liquid and gelled by addition of 4 w/o hydrophilic HDS).

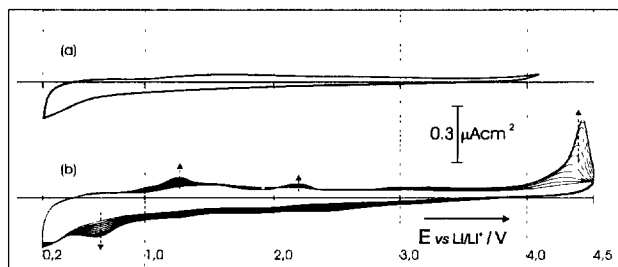


Fig. 4. Cyclic voltammogram of EC-DMC/LiTFMSI-HDS gelled electrolyte, working electrode platinum; scan-rate: 10 mV/s (a) Voltage reversal at 4.1 V vs. Li, and (b) voltage reversal at 4.5 V vs. Li

the figure shows, the difference in conductivity between the two electrolytes gelled and not gelled is only marginal. This looks surprising on the first sight since the viscosity of such a gel is very high. On the other hand, however, the gel contains about 95% of liquid electrolyte. Obviously, the ions can move relatively free within the network formed by the silica particles.

The electrochemical stability window of the described gelled electrolyte (EC-DMC/LiTFMSI 4 w/o HDS) was determined by using cyclic voltammetry (Fig. 4). From the upper curve in the figure it can be seen that the stability window from lithium potential is to +4.1 V on platinum electrodes (in the cathodic potential range the voltage scan was reversed before lithium deposition occurred, to avoid contamination of the platinum measuring electrode with alloyed lithium). If the limit of +4.1 V is exceeded an anodic current starts due to a decomposition reaction. The reaction products create additional current peaks in the following cycles of the voltammogram.

The same peaks due to decomposition products are observed in the liquid electrolyte if the same potential range is scanned. In contrast to the liquid electrolyte, the decomposition products in the gelled electrolyte are removed much slower from the electrode surface. This causes an increase in the oxidation peaks with each scan.

Since the behaviour of the electrolyte in contact with the active electrodes may be different from that on platinum electrodes, cyclic voltammograms were also recorded on active cathodes.

Fig. 5 shows the results for  $\text{LiMn}_2\text{O}_4$  in an EC-PC/LiTFMSI-HDS gel. Due to the limited stability window of the electrolyte, the upper potential was around 4.1 V, which means that the capacity of  $\text{LiMn}_2\text{O}_4$  cannot be fully used.

During the first three cycles a slight shifting of the anodic current peak to higher potentials is observed, obviously due to an increasing IR drop in the cell. However, after the third cycle the voltammogram becomes fairly stable and shows a nice reversible behaviour.

#### 4. Conclusions

Investigations with gelled electrolytes, based on the addition of a few w/o of highly dispersed silica to a liquid organic

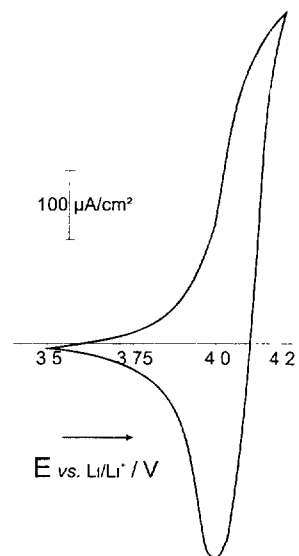


Fig. 5. Cyclic voltammogram of an  $\text{LiMn}_2\text{O}_4$  electrode (on aluminum substrate) in EC-DMC/LiTFMSI-HDS gelled electrolyte, scan-rate: 10 mV/s

electrolyte show that such electrolytes may be used in lithium-ion batteries. An interesting result is that the conductivity of such inorganic gelled electrolytes is nearly the same as that of the basis liquid electrolytes. This seems to be due to the fact that the HDS is forming only a very loose network which does not disturb the ionic transport.

The electrochemical stability window was determined by means of cyclic voltammetry. Due to the fact that  $\text{LiPF}_6$  cannot be used as a salt in the presence of hydrophilic HDS, because of the decomposition reactions [9] LiTFMSI was used. This limits the electrochemical stability range to about +4.1 V versus lithium. The limited stability, however, is not due to the solvents or the HDS, but to the salt.

HDS can be dried, so that no physically adsorbed water is present anymore. The remaining -OH groups do not seem to create a problem regarding the stability of the electrolyte or electrodes, since the lithium metal as well as the cathode materials  $\text{LiCoO}_2$  or  $\text{LiMn}_2\text{O}_4$  can be cycled reversibly in such HDS gels. In fact, the number of -OH groups in the electrolyte is relatively small. Based on the data of one HDS manufacturer [10], the calculated concentration is ~300 ppm. This might seem high compared with a water content of the electrolyte of 30 ppm, however, in contrast to water, the -OH is bonded to the silica particles and cannot diffuse easily to the electrode surface. It is thus plausible to assume only a reaction between the -OH which are directly at the electrode/electrolyte interface and the electrodes.

In conclusion, it can be stated that HDS-based gels can be applied in lithium-ion batteries as long as a voltage range of about -4.1 V is not exceeded. If more stable lithium salts are available, this voltage range can be extended.

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