



# Challenge in manufacturing electrolyte solutions for lithium and lithium ion batteries quality control and minimizing contamination level

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## Abstract

The quality of electrolytes for lithium batteries are a major topic in science and battery industries. The solvents and lithium salts should be of highest purity. Therefore, during preparation and handling of electrolyte solutions, the contamination level has to be minimized and the quality during packaging, storage and transportation has to be guaranteed. Especially, protic impurities are found to be very critical for  $\text{LiPF}_6$ -based electrolytes. The influence of water is reported to be tremendous. But also other protic impurities like alcohols are considered to play an important role in the electrolyte quality. The reaction of the protic impurities with  $\text{LiPF}_6$  leads to the formation of HF which further reacts with cathode active materials (e.g., spinel) and the passivating films of the cathode and anode. For a better understanding of the protic impurities and their role in the electrolyte quality a systematic investigation of different impurities was carried out. Electrolytes were doped with different protic compounds. Then the electrolyte was analyzed for protic impurities and HF in dependence of time. First results showing the relation between protic impurities and HF are presented and discussed. In addition, different packaging materials for the electrolyte solutions were investigated. Storage tests were carried out at different temperatures and in different atmospheres. Results on contamination levels, influence of packaging, high temperature storage and handling are addressed. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Electrolyte solution; Batteries; Minimizing

## 1. Introduction

Lithium secondary batteries commercially available since the early nineties in Japan are going to be more and more important for portable electronic devices and even EV applications. Today, several companies around the world are working hard to join the market for lithium secondary batteries. Based on the growing interest for commercial use of batteries also the materials for those have to be reviewed in order to meet large-scale production needs.

Liquid organic electrolytes are mostly used in commercial lithium secondary batteries of today. The chemistry and electrochemistry of these electrolytes and the interrelation of electrolytes and other materials inside the battery were addressed by many publications throughout the last years. The electrolytes under discussion for the use in secondary lithium ion batteries are mixtures of aprotic organic solvents and conductive salts. The solvents mainly used today are cyclic and aliphatic carbonates like EC, PC,

DMC, DEC, EMC and MPC. Salts providing the lithium ion conductivity are the inorganic compounds  $\text{LiPF}_6$ ,  $\text{LiBF}_4$  and  $\text{LiAsF}_6$  and organic compounds like lithium imide or methide or even other lithium salts with high dissociation constant. Beside these main components of electrolyte, most of the battery producers are adding some special additives providing advantages in either production or application.

Regarding the special needs for the electrolyte solution providing the functionality in lithium ion batteries, the whole battery system has to be addressed. Electrolytes, being the contact material between cathode, anode and separator, have major influence on the battery performance. Especially, the working temperature range, the cycling stability, the high rate capability and the safety of the whole system is strongly influenced by the electrolyte. However, the investigation of mixture composition and influence of different components on the battery performance is beyond the schedule of this paper and addressed elsewhere [1,2] but the influence of impurities in liquid electrolytes how to analyze and to avoid those in the scientific area as well as in large scale production will be major topics.

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Protic impurities in the ppm range are very difficult to measure and control but are known to have major influence in the high voltage lithium ion battery system [3]. It is reported that even trace amounts of water can have either positive [3] or negative [4] influence on the cycling and storage stability of the battery. Focusing on the  $\text{LiPF}_6$ -based electrolytes which are most important in commercial secondary lithium systems the negative influence of water is tremendous [5]. Directly related to the water is the content of HF in the  $\text{LiPF}_6$ -based systems which has to be controlled carefully. But also other protic impurities like alcohols are playing an important role in the electrolyte quality.

Procedures to analyze and to avoid protic impurities are discussed in this paper. This is not only related to the production but also very important during handling, packaging, storage and shipping. Therefore, also the investigations of container materials have to be addressed to guarantee point of use quality.

## 2. Experimental

Propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethyl carbonate (EMC) (Merck Battery Grade) and  $\text{LiPF}_6$  (Stella) were used as received. All the solvents initially contain less than 20 ppm water. All electrolyte preparation and handling was carried out in an argon-filled glove box.

The water content was analyzed by Karl–Fischer titration and the HF content by neutralization titration with NaOH. The type of impurities in the solvents were identified and determined by GC, GC-MS and GC-HS. The assay of the solvents and the impurities were determined by GC.

To determine the decomposition of the solvents, a storage stability test was performed, i.e., the solvents were stored at elevated temperatures for several days.

For the investigation of the influence of protic impurities on  $\text{LiPF}_6$ -based electrolytes, a known amount of impurity was added to the electrolyte. The electrolyte was stored for several days and was analyzed in certain intervals.

For the packing materials tests, the bottles were dried ( $70^\circ\text{C}$ , vacuum), filled with electrolyte and then were stored under definite conditions (temperature, humidity,

Table 1  
Decomposition products of different solvents after storage at  $70^\circ\text{C}$  and several days

Solvent	Detected decomposition product
PC	Propylene glycol
EC	Ethylene glycol
DMC	Methanol
DEC	Ethanol
EMC	DMC, DEC, methanol, ethanol

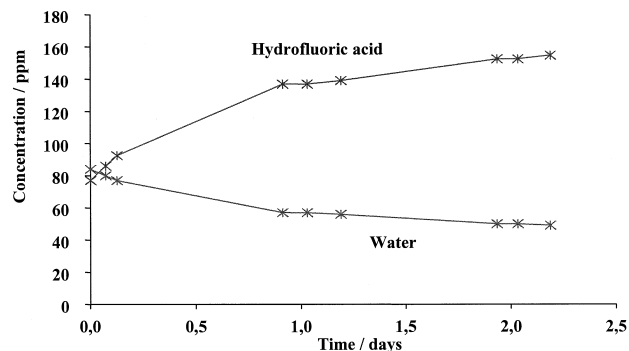


Fig. 1. HF and water content in water doped electrolyte in dependence of time. (Electrolyte: 1 m  $\text{LiPF}_6$  in EC:DMC (50:50 wt.%) doped with 84 ppm  $\text{H}_2\text{O}$ ; initial amount of HF is 77 ppm; the water content is analyzed in certain intervals, the HF content is calculated from the water content).

time). In certain time intervals, the electrolyte was analyzed for  $\text{H}_2\text{O}$  and HF. In order to check whether there is diffusion of solvents through the material or diffusion of water from the atmosphere through the material into the electrolyte, the weight of the electrolyte filled bottle was recorded as a function of time. The following materials were tested: polypropylene (PP), perfluoro alkoxyalkane (PFA), polyethylene (PE), aluminum and stainless steel.

## 3. Results and discussion

### 3.1. Solvents: decomposition reactions

Due to the high purity of the solvents, the level of decomposition products or impurities found is very low. In Table 1, the detected impurities are listed.

Mainly all impurities are formed through the reaction with water, e.g.,



Typically, these decomposition reactions happen in the presence of catalytic materials. The origin of these catalysts might be related to solvent itself.

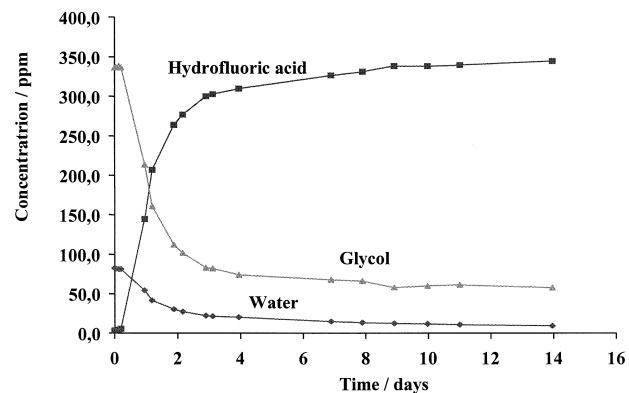


Fig. 2. HF, glycol and water content in water and glycol doped electrolyte in dependence with time. (Electrolyte: 1 m  $\text{LiPF}_6$  in EC:DMC (50:50 wt.%) doped with 84 ppm  $\text{H}_2\text{O}$  and 334 ppm glycol; initial amount of HF is 77 ppm; the  $\text{H}_2\text{O}$ -, glycol- and HF-content is analyzed in certain time intervals).

Table 2

Theoretical and measured HF contents of ethanol and methanol doped electrolytes

Impurity	Measured HF content (ppm)	Theoretical HF content (ppm)
90 ppm ethanol <sup>a</sup>	111	133
201 ppm ethanol <sup>b</sup>	61	183
90 ppm methanol <sup>a</sup>	97	133
201 ppm methanol <sup>b</sup>	67	183

<sup>a</sup>1 m LiPF<sub>6</sub> in EC:DMC (1:1), initial amount of H<sub>2</sub>O 7 ppm, HF: 58 ppm.

<sup>b</sup>1 m LiPF<sub>6</sub> in EC:DMC (1:1), initial amount of H<sub>2</sub>O 4 ppm, HF: 77 ppm.

### 3.2. Electrolytes: protic impurities

As mentioned in the Section 1, water and other protic impurities react with LiPF<sub>6</sub> forming HF and H<sub>x</sub>PO<sub>y</sub>F<sub>z</sub> species, but the detailed reaction mechanisms are unclear and still under discussion.

The measurement of water as function of time reveals that the H<sub>2</sub>O content decreases significantly (Fig. 1). For a first approximation, it is reasonable to assume that the decreasing H<sub>2</sub>O content in the electrolyte is directly related to the reaction with LiPF<sub>6</sub>. Furthermore, it is not known which acids beside HF are formed and it is hardly possible to identify the other species at present. One normally performs an acid–base titration which resulted in the total amount of acids present. So for simplicity, it is assumed that the formed acid is HF. With that assumption, one can calculate the amount of HF in the electrolyte from the measured amount of water. The curve of the HF content in Fig. 1 is calculated and not measured. A marked decrease of the water content occurs very rapidly, within the first 2 days. That process is much faster at elevated temperatures. At 40°C, it is less than 1 day. That is a clear indication that the kinetics of the reaction of water with LiPF<sub>6</sub> is fast.

The electrolytes were intensively analyzed by GC methods. With the GC-MS method, POF<sub>3</sub> and other unknown species were detected. That result indicates that the first decomposition step of LiPF<sub>6</sub> with water, i.e., LiPF<sub>6</sub> + H<sub>2</sub>O ⇒ 2HF + POF<sub>3</sub> + LiF seems to be correct. Further experiments and analytical work is in progress to get more detailed information about this decomposition.

Table 3

Storage at 40°C and 70% relative humidity

Bottle type	After 4 weeks	After 8 weeks	After 12 weeks
Aluminum	H <sub>2</sub> O: 10 ppm, HF: 50 ppm	H <sub>2</sub> O: 5 ppm, HF: 61 ppm	H <sub>2</sub> O: 6 ppm, HF: 64 ppm
PE			H <sub>2</sub> O: 12 ppm, HF: 630 ppm
Stainless steel	H <sub>2</sub> O: 6 ppm, HF: 50 ppm	H <sub>2</sub> O: 9 ppm, HF: 63 ppm	H <sub>2</sub> O: 13 ppm, HF: 59 ppm
Reference			H <sub>2</sub> O: 4 ppm, HF: 45 ppm

Electrolyte: EC:PC:DMC (1:1:3) 1 m LiPF<sub>6</sub>; the reference is a stainless steel bottle stored in a glove box.

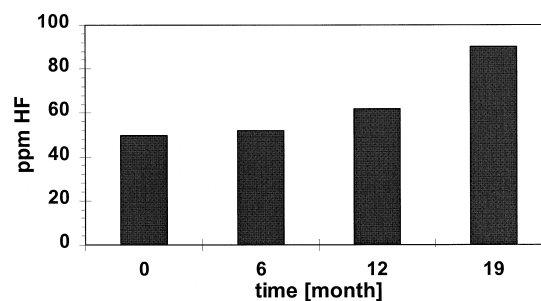


Fig. 3. HF value during storage of electrolyte in an aluminum container (aluminum bottle filled with electrolyte (1 m LiPF<sub>6</sub> in EC:PC:DMC 1:1:3), room temperature and normal atmosphere).

To check the assumption that the decrease of water is directly related to the increase of the HF content, calculated and measured HF values were compared. Within the error limit of the detection method, this assumption can be approved.

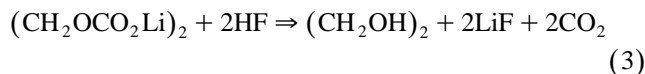
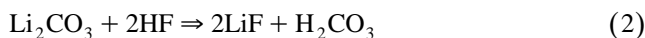
In order to check whether other protic species reacts in a similar way, the electrolyte was doped with different alcohols. In this series of experiments, we measure the HF (free acid) and assume that there is a complete reaction of the LiPF<sub>6</sub> with the protic impurities. With that assumption, one can calculate the theoretical amount of the formed HF and can compare it with the measured values.

In the case of glycol, the reaction proceeds very fast within 1 day. Comparing the theoretical value (149 ppm HF) to the measured one (145 ppm HF), a reasonable fit within the error limits can be found. In Fig. 2, an electrolyte is doped with both water and glycol. Again, it is seen that the reaction proceeds fast, within 2 days.

Similar results are obtained if either methanol or ethanol is the protic species. The kinetics of the reaction is more rapid for ethanol than for methanol. In the case of methanol, the reaction is close to be stoichiometric in the case of ethanol, however, this cannot be found. However, the stoichiometric reaction occurs only in the case of low impurity level. An increase of the methanol or ethanol amount in the electrolyte leads to a decrease of the HF level (Table 2). Further experiments are necessary to understand these phenomena.

The resulting HF (and other acidic species) is known to attack the cathode materials, especially the lithium manganese spinel, and the solid electrolyte interfaces (SEI) of the electrodes. In some cases, reaction products are gaseous

and therefore increase the pressure in the battery. Aurbach et al. [6] derived the following reactions of HF with the solid electrolyte interface



That leads to a rapid capacity loss and poor cycle life of the battery.

### 3.3. Packaging material

The packaging is the next critical step after the preparation. In a further series of experiments, different packaging materials were tested. Some of the critical requirements for the packaging materials can be summarized as follows. The material must be inert to the electrolyte, i.e., no reaction of the electrolyte with the packaging material or release of  $\text{H}_2\text{O}$  from the material into the electrolyte. The material has to be absolutely tight, i.e., there is no diffusion of solvents in one direction and no diffusion of water in the opposite direction through the packaging material.

If the weight loss is recorded as a function of time, it is obvious that polypropylene and polyethylene exhibit a significant weight loss indicating diffusion of solvents through the material. Only perfluoro alkoxyalkane shows no significant weight loss during storage. Aluminum and stainless steel are tight no diffusion of solvents was detected.

In another series of experiments, the HF content as function of storage time was measured. The storage conditions were  $40^\circ\text{C}$  and 70% rel. Humidity. In Table 3, the results are shown.

It is obvious that there is a remarkable diffusion of water from the atmosphere through polyethylene. That is also valid for polypropylene and to a less extend for perfluoro alkoxyalkane. For aluminum and stainless steel, the water and HF content remains constant within the error limits. Corrosion was not detected for all the tested materials. In another test, an aluminum bottle filled with electrolyte are stored under normal conditions and every 6 or 7

months, the electrolyte is analyzed (Fig. 3). The HF concentration remains the same within the error limits for one year.

The material tests revealed that PE, PP and PFA are not appropriate for handling and transporting the electrolytes. Only aluminum and stainless steel meet all the requirements so far and can be used as container materials. For sealing the bottles, PTFE or PE coated with PTFE is well reliable.

## 4. Conclusion

Water and other protic impurities react with the  $\text{LiPF}_6$  forming HF and other acidic species. These acids may react with the solid electrolyte interface and the cathode active materials especially lithium manganese spinel which results in a bad performance of the battery. Therefore, the content of water and protic species in the ready to use electrolyte should be as low as possible. The reaction time of different protic impurities to form acidic species is different and has to be regarded to get proper analytical results.

The tests of the different packaging materials revealed that aluminum and stainless steel are favorable for  $\text{LiPF}_6$  based electrolytes.

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