Electrolytes – Quality at Point of Use

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Abstract:

Lithium Ion 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 to market for Lithium secondary batteries. Based on the growing interest for commercial use of batteries also the materials have to be reviewed in order to meet large scale production needs.
The requirements especially for electrolytes for lithium batteries are extremely high. The solvents and the lithium salts should be of highest purity. So the supply of these chemicals including packaging, transportation and storage but also the handling in production are critical items in this field.
Protic impurities are very critical for LiPF6 based electrolytes. The influence of water is tremendous. But also the other protic impurities like alcoholes are playing an important role for the electrolyte quality. The reaction of these species with LiPF6 leads to formation of HF which further reacts with cathode materials (spinel) and anode. To understand the role of the protic impurities more clearly the electrolyte was doped with such compounds and was analyzed for protic impurities and HF. These results which directly show the relation between impurities and quality will be presented and discussed.
In addition several investigations on different packaging materials as well as methods to analyze and handle the sensititive material will be addressed.

These questions which are only partly discussed in literature so far and never been investigated systematically cover some of the key parameters for understanding of the battery chemicals. This investigation and understanding however is of major importance for scientist and engineers in the field of Lithium ion and Lithium polymer batteries.

Electrolyte Impurities

- **Some impurities are always present in high purity solvent and salt**
- **Several ways how impurities and by products are formed in electrolytes:**
  - reaction of impurities with the salt, e.g. $LiPF_6$
  - reaction of solvent s with the electrodes
  - decomposition of the solvents over time
  - reaction of impurities with the electrodes
  - others

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Main impurities

Specials

- water
- hydrofluoric acid
- anions, e.g. Cl^-
- cations, e.g. Na^+

Analytical methods

- Karl-Fischer titration
- Neutralization titration
- Gas chromatography
- Raman spectroscopy
- NMR spectroscopy
- Ion-Chromatography
- Atom absorption spectroscopy

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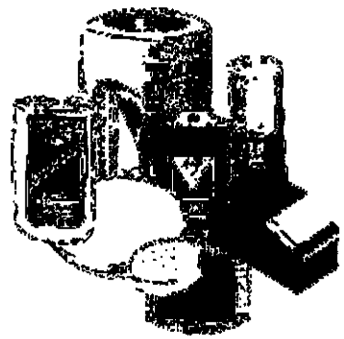

Protic impurities: experimental procedure

- A known amount of the protic impurity was solved in the electrolyte
- The concentration of the protic impurity and HF were measured as a function of time
- Formed impurities were detected by gas chromatography or other methods

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Doping with methanol and ethanol

Doping level	theo. HF-content	mea. HF-content
90ppm MeOH*	133ppm	97ppm
201ppm MeOH §	183ppm	67ppm
90ppm EtOH*	133ppm	111ppm
201ppm EtOH §	183ppm	61ppm

*1m $LiPF_6$ in EC:DMC (1:1 wt%):
initial amounts of H_20: 7ppm
HF: 77ppm

§ 1m $LiPF_6$ in EC:DMC (1:1 wt%):
initial amounts of H_20: 4ppm
HF: 58ppm

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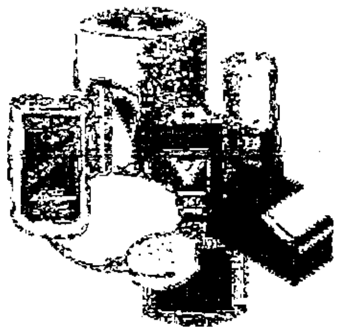
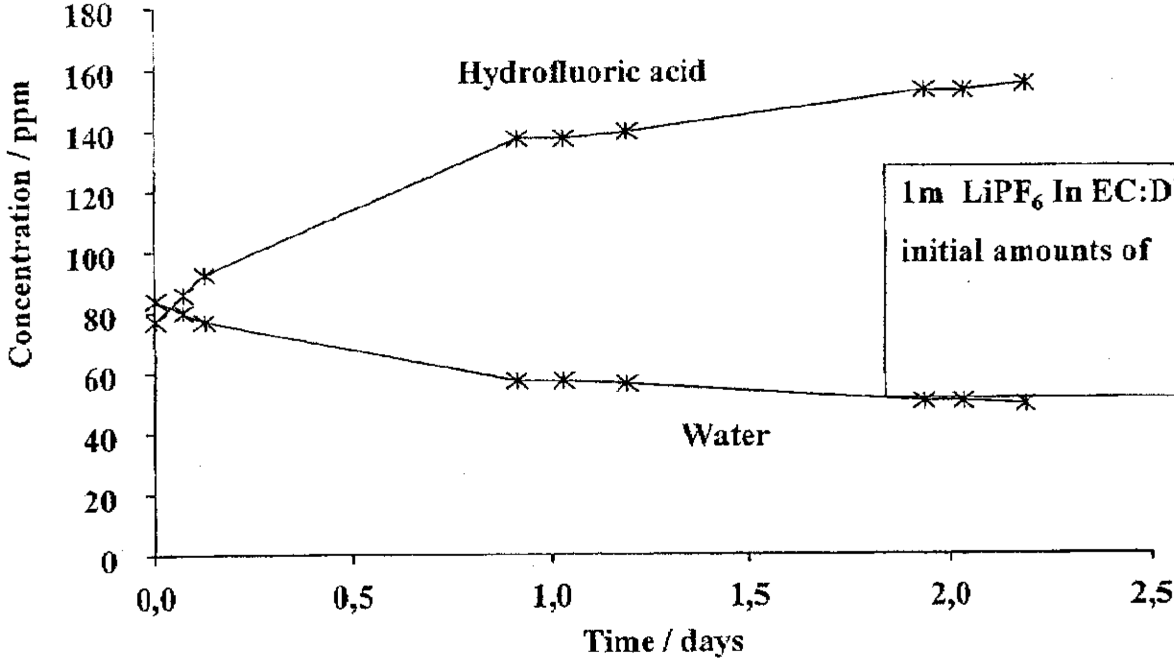


Doping with 84 ppm H_2O



1m $LiPF_6$ In EC:DMC (1:1 wt%):
initial amounts of H_2O: 6 ppm*
HF: 77 ppm

*special treatment

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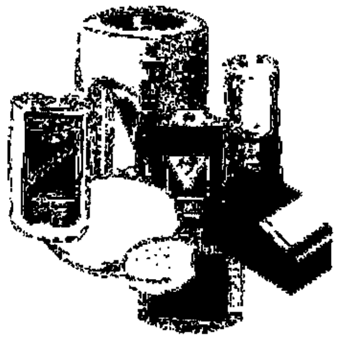

Results

- Fast reaction of protic species with $LiPF_6$
- Detected by products of the reaction with H_2O so far:
  - **POF_3**
  - further not identified species
- Methanol and ethanol react at low concentrations markedly with $LiPF_6$
- At higher concentrations the reaction rate decreases
- The reaction mechanisms of alcoholes with LiPF6 are not clear so far

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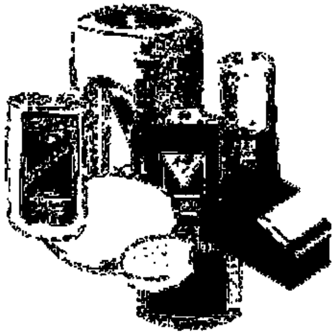

Experimental Tests

- **Procedure**
  - Pretreatment of the container
  - Filling with electrolyte
  - Storage under different conditions:
    - temperature
    - relative humidity
    - time
- **Check of the bottle and the electrolyte in certain periods:**
    - tightness
    - corrosion
    - H20-and HF-concentration

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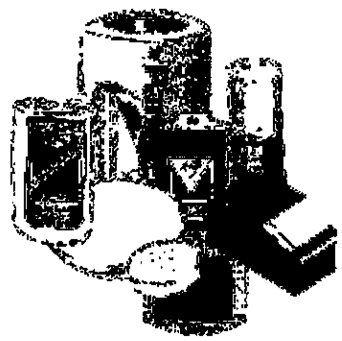

Important Parameters

Conductivity

- device: Knick conductometer, climatic chamber
- sample volume: 10ml
- time needed: 1h/temperature

Viscosity

- device: Ubbelode viscosimeter, thermostatic bath, measurement device
- sample volume: 5 - 10ml
- time needed: 1.5h

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Analytical methods

HF

- device: Analytical balance; tight glasses with septum sytings
- sample volume: 3 x 2ml
- time needed: 20 - 25min
- method :acid/base titration

H_2O

- device: Karl-Fischer-Titrator
- sample volume: 3 x 1.5ml
- time needed: 15min
- method:acid/base titration

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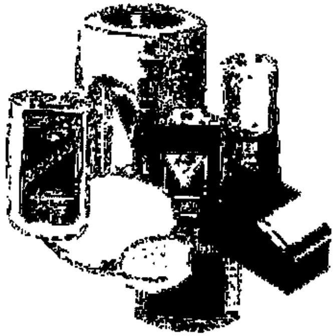

Conclusions

- **Protic impurities react with $LiPF_6$ forming HF**
  - Minimization the water content
  - Careful process analysis during electrolyte production
- **Container materials**
  - stainless steel
  - aluminum
- **Supply System Selectimate**
  - point of use guarantee with electrolyte

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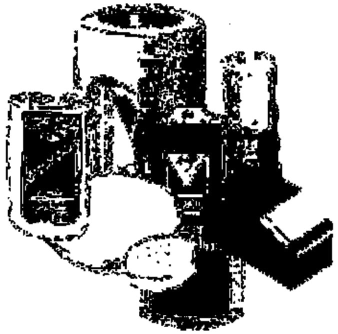

Packing materials

- **Material requests:**
  - no diffusion of H_2O from the atmosphere and from the packing material into the electrolyte
  - no diffusion of solvents through the materials
  - no chemical reactions with the electrolyte
  - the seal must be absolutely tight
- **Selection of possible materials**
- **Experimental tests**
- **Safety tests**

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