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 alcohols 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 sensitive 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
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
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
### Doping with methanol and ethanol

<table>
<thead>
<tr>
<th>Doping level</th>
<th>theo. HF-content</th>
<th>mea. HF-content</th>
</tr>
</thead>
<tbody>
<tr>
<td>90ppm MeOH*</td>
<td>133ppm</td>
<td>97ppm</td>
</tr>
<tr>
<td>201ppm MeOH §</td>
<td>183ppm</td>
<td>67ppm</td>
</tr>
<tr>
<td>90ppm EtOH*</td>
<td>133ppm</td>
<td>111ppm</td>
</tr>
<tr>
<td>201ppm EtOH §</td>
<td>183ppm</td>
<td>61ppm</td>
</tr>
</tbody>
</table>

*1m LiPF$_6$ in EC:DMC (1:1 wt%):
  initial amounts of H$_2$O: 7ppm
  HF: 77ppm

§ 1m LiPF$_6$ in EC:DMC (1:1 wt%):
  initial amounts of H$_2$O: 4ppm
  HF: 58ppm
Doping with 84 ppm H₂O

1 m LiPF₆ in EC:DMC (1:1 wt%):
initial amounts of H₂O: 6 ppm*
HF: 77 ppm

*special treatment

Concentration / ppm

0 20 40 60 80 100 120 140 160 180

0,0 0,5 1,0 1,5 2,0 2,5

Time / days

MERCK
Results

- Fast reaction of protic species with LiPF$_6$
- Detected by products of the reaction with H$_2$O 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 alcohols with LiPF$_6$ are not clear so far
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
  - H2O-and HF-concentration
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
Analytical methods

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

**H₂O**
- device: Karl-Fischer-Titrator
- sample volume: 3 x 1.5ml
- time needed: 15min
- method: acid/base titration
Conclusions

- Protic impurities react with LiPF₆ 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
Packing materials

• Material requests:
  - no diffusion of $\text{H}_2\text{O}$ 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