Methods for the fast detection of water and degradation changes in lithium based electrolytes

Antonín Šimek
Department of Electrical and Electronic Technology
Faculty of Electrical Engineering and Communication
Brno University of Technology
Brno, Czech Republic
Antonin.Simek1@vut.cz

Ondřej Čech
Department of Electrical and Electronic Technology
Faculty of Electrical Engineering and Communication
Brno University of Technology
Brno, Czech republic
cechondrej@vut.cz

Abstract—This paper deals with lithium-ion batteries, specifically the electrolytes used. The degradation mechanisms of lithium-ion batteries are addressed, with a focus on electrolyte degradation. A considerable part is then devoted to the degradation of lithium hexafluorophosphate, especially after exposure to water or moisture. The decomposition of the lithium salt is linked to the evolution of hydrofluoric acid, whose influence on the electrolyte parameters and methods of fast detection is the subject of the experimental section.

Keywords—lithium-ion batteries, electrolytes, degradation mechanisms, safety, water contamination, fast detection

I. INTRODUCTION

Over the past three decades, lithium-ion batteries have made a significant contribution to the energy storage systems. Lithium-ion batteries have become the preferred power source in consumer electronics and are continuously entering new market segments. At the same time this technology is rapidly growing in the field of electric vehicles and stationary energy storages. This is mainly due to their superior characteristics in terms of relatively high energy and power density (both volumetric and gravimetric), high energy efficiency, possibility of fast charging, adjustable battery size and sufficient safety features compared to other types of batteries. [1]

In general, lithium-ion batteries consist of a positive and negative electrode, an electrolyte, a separator and a casing. This system works on the intercalation principle, with the negative electrode most often made of graphite, and the positive electrode made of transition metal oxides such as Lithium Cobalt Oxide (LiCoO₂, or LCO), Lithium Nickel Manganese Cobalt Oxides (LiNi₀.₅Mn₀.₅CoO₂, or NMC), Lithium Iron Phosphate (LiFePO₄, or LFP), and others [2]. These electrodes are separated by a porous separator that prevents electrical contact between the two electrodes, but at the same time allows lithium ions to pass between the positive and negative electrode. The conductive pathway for the lithium ions is then formed by the electrolyte, which is generally a lithium salt dissolved in a suitable solvent or a mixture of solvents [2]. The composition of electrolytes for lithium-ion batteries is the main focus of this paper.

The limiting factors of a battery are its internal components. The electrodes, in particular the positive electrode, is the limiting factor in terms of overall battery capacity, energy density and cyclability. In contrast, the electrolyte determines the maximum current density, time stability and safety. This is due to the fact that the electrolyte is in close interaction with all other components such as the positive and negative electrodes as well as the separator. [3]

The interface between each electrode and the electrolyte determines the requirements for chemical stability, thereby greatly limiting the range of usable materials. The chemical compatibility of the electrodes with the electrolyte is ensured by the formation of passivation layers, referred to as Solid Electrolyte Interface (SEI for short). The formation and physical properties of these protective layers depend on the nature of the electrodes. Thus, more and more attention is being paid to the study of the electrolyte composition to ensure the stability and durability of the entire battery system. [3]

II. LITHIUM-ION BATTERY DEGRADATION

Increased demands for lithium-ion batteries not only in automotive applications, such as early mentioned increased energy density, fast charging capabilities and improved safety, are accompanied by phenomena that negatively affect battery performance [1]. This so called degradation mechanisms (or aging) of lithium-ion batteries are shown on Fig 1 bellow. This figure shows the basic structural components of a lithium-ion battery and their associated degradation mechanisms. The primary degradation mechanisms are marked in green, the secondary mechanisms are marked in red [4].

Fig. 1. Illustration of degradation mechanisms on basic lithium-ion battery components. [4]

As can be seen in Figure 1, the primary degradation mechanisms include particle cracking at the positive and negative electrodes, SEI formation and growth (at both positive and negative electrodes), structural changes of the positive...
Electrolytes for Lithium-Ion Batteries

Electrolytes for lithium-based batteries in general can be divided into five different groups:

- non-aqueous electrolytes made out of a lithium salt dissolved in an suitable organic solvent or mixture of solvents;
- aqueous solutions consisting of a lithium salt solubilized in water;
- ionic liquids from organic lithium salts;
- polymer electrolytes (both gel and solid polymers) and
- hybrid electrolytes. [3]

In this paper the attention will be mainly paid to non-aqueous electrolytes since most of the electrolyte used in commercial lithium-ion batteries are non-aqueous solutions [3]. Focus will be paid to basic requirements for these electrolytes, as well as the most commonly used materials for non-aqueous electrolytes. A considerable part will also be devoted to the already mentioned degradation of electrolytes, especially in connection with the evolution of hydrofluoric acid after exposure to the moisture.

A. Electrolyte Requirements

The electrolyte is therefore an internal part of the battery which must be sufficiently stable with respect to the cathode and anode material and should not undergo chemical changes during battery operation. The ideal electrolyte should therefore meet the following criteria [3]:

- It should be a good ionic conductor as well as an electrical insulator. A good ionic conductivity is necessary because of the easy transport of Li\(^+\) ions between the anode and cathode during charging/discharging, and the insulation resistance is necessary to prevent self-discharge and short circuit.
- It should have a wide potential window meeting the range of working potentials of the anode and cathode material to avoid electrolyte decomposition at higher potentials.
- It should be thermally stable over a wide range of temperatures so that it does not approach the boiling point or freezing point during operation.
- It must have low environmental toxicity and generally meet the conditions limiting environmental contamination.
- It should be made from sustainable materials. In other words, the electrolyte should not be made from low abundant elements, and the production process should have as least impact to the environment as possible. At the same time, the costs of preparing the raw materials and the total cost of electrolyte should be as low as possible. [3]

In addition to the requirements mentioned above, the electrolyte plays a very important role in initial cycling. During the first cycles, SEI is formed on the negative electrode and CEI (Cathode Electrolyte Interface) on the positive electrode [5]. This electrode-electrolyte interphases consists of salt/solvent-based inorganic and organic parts is electrically insulated while the ionic conductivity remains [1].

B. Electrolyte Composition

Lithium-ion batteries electrolytes are most often composed of a solution of Lithium Hexafluorphosphate (or LiPF\(_6\)) in mixture of carbon based solvents (or carbonates) [5].

These carbonates most commonly include Ethylene Carbonate (EC), Dimethyl Carbonate (DMC) and Diethyl Carbonate (DEC) [7]. Other carbonates and often used solvents are listed in Table 1. Mentioned solvents are used because of their acceptable stability for use in 4 V cathode systems and their stability to the lithiated graphite used for the negative electrode. Their other advantageous properties include high polarity, relatively good operating temperature range, sufficiently low toxicity and acceptable safety. [6]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Formula</th>
<th>(\rho) [g/cm(^3)]</th>
<th>(\eta) [mPa.s]</th>
<th>(\eta_{\infty}) [mPa.s]</th>
<th>(\eta_{gel}) [mPa.s]</th>
<th>BP [°C]</th>
<th>FP [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Carbonate (EC)</td>
<td>C(_2)H(_2)O(_3)</td>
<td>0.95</td>
<td>1.9</td>
<td>1.32</td>
<td>238</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>Propylene Carbonate (PC)</td>
<td>C(_3)H(_4)O(_3)</td>
<td>0.65</td>
<td>2.5</td>
<td>1.20</td>
<td>242</td>
<td>138</td>
<td></td>
</tr>
<tr>
<td>Dimethyl Carbonate (DMC)</td>
<td>C(_2)H(_4)O(_3)</td>
<td>3.1</td>
<td>0.59</td>
<td>1.06</td>
<td>90</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Ethyl-Methyl Carbonate (EMC)</td>
<td>C(_2)H(_6)O(_4)</td>
<td>3.0</td>
<td>0.65</td>
<td>1.01</td>
<td>108</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Diethyl Carbonate (DEC)</td>
<td>C(_2)H(_6)O(_4)</td>
<td>2.8</td>
<td>0.75</td>
<td>0.97</td>
<td>127</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

Table I: Basic Properties of Carbonate Solvents [6]
Table 1 above lists the most commonly used carbonates and their basic properties. Among the properties listed are the chemical formula, relative permittivity ($\varepsilon_r$), viscosity ($\eta$), density ($\rho$), boiling point (BP) and flash point (FP). All properties listed are for 25 °C except for ethylene carbonate, for which the properties are listed for 40 °C [3].

According to [6], the use of LiPF$_6$ salt is to some extent a compromise, as other commercially available lithium salts have too many disadvantages. For example, LiAsF$_6$ is poisonous; LiClO$_4$ is explosive; LiBF$_6$ exhibits significant problems at the negative electrode as it tends to react between the BF$_4^-$ anion and the negative electrode surface; LiSO$_2$CF$_3$ exhibits too low ionic conductivity; and LiN(SO$_2$CF$_3$)$_2$ exhibits problems at the positive electrode as there is insufficient passivation, resulting in corrosion of the aluminium current collector. [6]

C. Advanced Electrolyte Composition to Increase Battery Performance and Safety

In recent years, there has been a great effort to increase the overall power that a battery cell can deliver. One way to achieve this increase in performance is through the use of new solvents, lithium salts and other additives that can affect performance of the system [6]. Another much-discussed problem with lithium-ion batteries is their safety, especially fire safety. In some respects, these concerns are preventing further use of this type of technology [9]. However, according to [9], most of the fire risks are due to the unstable and highly flammable electrolytes composed of LiPF$_6$ and carbonate solvents.

1) Solvents Perspective

According to [6], new solvents include organic sulphur compounds such as Propylene Sulphite (C$_3$H$_6$OS), fluorine-substituted compounds and organo-phosphorous compounds. It is further argued in [8] that by using non-flammable phosphate compounds such as Dimethyl Methyl Phosphonate (DMMP), Triethyl Phosphate (TEP) and Trimethyl Phosphate (TMP) instead of conventional carbonate solvents, some degree of safety was achieved, but with an impact on performance. In fact, the poor reducing stability of these solvents leads to the decomposition of the solvents on the graphite electrode, resulting in a reduction in the system performance.

2) Lithium Salts Perspective

It has also been found that safety problems arise due to a thermally unstable salt, which is most commonly LiPF$_6$. Under unsuitable conditions, the heat and by-products generated by the decomposition of LiPF$_6$ accelerate a number of exothermic reactions. These reactions include the decomposition of the SEI layer, which leads to further reactions between the electrode and the electrolyte. During these reactions, oxygen evolution and heat release occur, which can lead to battery fires. Therefore, replacing the LiPF$_6$ salt with a more stable salt appears to be a solution to this problem. This was achieved by using Lithium bis(fluorosulfonyl)imide (or LiFSI for short) and Lithium bis(trifluoromethanesulfonyl)imide (or LiTFSI for short). [7]

The problem with these salts, however, is the lack of formation of passivation layers on the aluminium current collector, which leads to its corrosion at potentials higher than 3.8 V. However, it was found that corrosion of the current collector occurs only with weak LiTFSI solutions. In fact, when a higher concentration of this salt was used, the collector was passivated by a layer of Aluminum Fluoride (AlF$_3$), which suppresses surface corrosion. Moreover, by increasing the concentration of LiTFSI, the proportion of flammable solvents is reduced, which increases the safety of the batteries. [7]

IV. ELECTROLYTE DEGRADATION AND DECOMPOSITION

The aforementioned LiPF$_6$ dissolved in carbonate solvents shows a good compromise between operating temperature, ionic conductivity, SEI formation and potential window. However, the lack of redox stability leads to degradation mechanisms that manifest themselves in electrolyte decomposition. Electrolyte aging can be divided into:

- contribution to interphase formation;
- solvent decomposition and
- salt decomposition. [1]

A. LiPF$_6$ Decomposition

Although the most commonly used lithium salt, LiPF$_6$, is relatively stable in a dry inert atmosphere up to 107 °C, this salt suffers from degradation when exposed to traces of water, moisture, or even alcohols [8].

In [8] it is shown that the degradation starts with the decomposition of LiPF$_6$ according to equation (1). According to this equation, LiPF$_6$ decomposes to form Lithium Fluoride (LiF) and Phosphorous Pentfluoride (PF$_5$).

$$\text{LiPF}_6 \rightarrow \text{LiF} + \text{PF}_5$$
(1)

PF$_5$ can further react with water (H$_2$O) or moisture to release Hydrofluoric Acid (HF) and Phosphoryl Fluoride (POF$_3$). This process can be described by equation (2):

$$\text{PF}_5 + \text{H}_2\text{O} \rightarrow \text{POF}_3 + 2\text{HF}$$
(2)

The reaction described by equation (1) is almost negligible at room temperature. However, in an electrolyte environment, the interaction between PF$_5$ and solvent molecules (EC and DEC) can shift the equilibrium of the reaction to the right, resulting in increased HF formation. Decomposition is not only catalysed by elevated temperature or the presence of moisture, but is also activated by the release of protons(H$^+$) during LiF formation either in the SEI at the negative electrode or in the CEI at the positive electrode. [8]

$$\text{Li}^+ + \text{HF} \leftrightarrow \text{LiF(s)} + \text{H}^+$$
(3)

The precipitation of LiF(s) described by equation (3) and therefore the lithium ion removal from the solvated system has no direct effect on the formation of HF. Released protons may further react with LiPF$_6$ molecules to form additional HF which is described by the equation (4) and (5). [8]

$$\text{H}^+ + \text{PF}_6 \leftrightarrow \text{H}^–\text{F}^–\text{PF}_5$$
(4)
$$\text{H}^–\text{F}^–\text{PF}_5 \rightarrow \text{HF} + \text{PF}_3$$
(5)

The HF produced by the reactions described above dramatically affects battery life and performance [8]. Thus, the moisture content during the battery manufacturing process is one of the most important factors affecting the quality of both
the electrolyte and the entire battery system. Indeed, even trace amounts of water can lead to significant deviations from normal behaviour. Figure 2 shows some of the undesirable chemical and electrochemical reactions, the most important being the degradation of the cathode, anode and electrolyte itself. [9]

![Diagram showing the effect of water on the electrodes and electrolyte degradation](image)

Fig. 2. Diagram showing the effect of water on the electrodes and electrolyte degradation [10]

V. EXPERIMENTAL

In the experimental part the potential window and stability of the electrolyte 1M LiPF₆ in EC:DMC 1:2 (i.e. 1 mol·l⁻¹ of LiPF₆ dissolved in mixture of solvents composed from EC and DMC in 1:2 ratio) was tested. Furthermore, detection of the presence of water and degraded electrolyte was performed using fast electrochemical screening methods. For the potential window measurements, electrochemical test cells (ECC) from El-Cell were used. Their assembly and general handling of the electrolyte was carried out in a Jacomex glove box under the argon inert atmosphere (both H₂O and O₂ concentration below 1 ppm). Electrochemical measurements were then performed on a BioLogic VMP3 multi-channel potentiostat.

Potential window and stability measurements were performed using four different test cell configurations. Each configuration is used to test stability against specific battery components:

- **Steel-Steel configuration** (empty test cell with Whatman glass separator) to measure the stability of the electrolyte against the applied potential and when in contact with the separator and metal parts of the battery.

- **Li-Steel configuration** (lithium metal on one side, empty measuring cell on the other, Whatman glass separator in between) for measuring the stability of the electrolyte in the presence of lithium metal and Li⁺ ions.

- **Li-Cu configuration** (lithium metal on one side, copper disk on the other, Whatman glass separator in between) for measuring the stability of the electrolyte against the copper current collector.

- **Li-Al configuration** (lithium metal on one side, aluminium disc on the other, Whatman glass separator in between) for measuring the stability of the electrolyte against the aluminium current collector.

As part of the electrochemical measurements, the open circuit voltage (OCV for short) was first measured for one hour. Subsequently, a set of voltammetric measurements were performed in which the current response to the applied potential was measured. As part of these measurements, linear sweep voltammetry (LSV for short) and twenty cycles of cyclic voltammetry (CV for short). The scan rate of these methods was chosen to be 5 mV.s⁻¹. Potential range was chosen from 0.05 to 5.5 V for the Steel-Steel and Li-Steel configurations, 0.05 to 2.5 V for the Li-Cu configuration and 2.5 to 5.5 V for the Li-Al configuration. These potential ranges were chosen based on consultation with the supervisor, taking into account the stability of the materials used.

VI. RESULTS AND DISCUSSION

This section will discuss the measured results on the above mentioned test cell configurations. All measurements were carried out with a three-electrode configuration. Since there were many test configurations and a lot of obtained data, only a comparison between pure and H₂O contaminated electrolyte will be presented here.

A. Difference in obtained CV curves between pure and contaminated electrolyte

Figure 3 shows the CV curves obtained from measurements on the Li-Al configuration. The orange colour corresponds to the pure electrolyte, the blue colour corresponds to the electrolyte contaminated with 250 ppm H₂O. The red arrows then indicate what happened to the measured curves with increasing number of cycles. This colour coding is used for all the following results.

![CV curves of pure and contaminated electrolyte with 250 ppm H₂O on Li-Al configuration](image)

Fig. 3. CV curves of pure and contaminated electrolyte with 250 ppm H₂O on Li-Al configuration

From Figure 3 can be shown, that intense peak at a potential of approximately 4.2 V was present in the contaminated electrolyte. Furthermore, small micro-short circuits can be observed around potential of 3.2 V, which are most likely due to damage to the separator caused by etching of fibre glass separator.

Figure 4 shows the CV curves measured on the Li-Cu conjugation. Intense peaks at a potential of approximately 1.9 V can be observed in these curves which probably correspond to the electrolysis of H₂O. At lower potentials it is then possible to observe small spikes, which are probably due to damage to the separator caused by HF. Similarly to Figure 4, in Figure 5, where the curves for the Li-Steel configuration are plotted, it is possible to observe the appearance of peaks at a potential of approximately 1.5 to 2.0 V, which should also correspond to the electrolysis of H₂O.
Figure 6 shows the results obtained from OCV measurements on a Li-Cu configuration using a water-contaminated electrolyte.

Figure 6 is based on two reference measurements on pure electrolyte, which are plotted in blue and orange. For both measurements, the OCV was around 1.85 V. Approximately 1.5 hours from water contamination, an OCV ranging from 2.0 to 2.25 V was measured, which is plotted in grey. After 54 hours, an OCV of around 3.0 V was measured, on which there are also small spikes caused by the breakdown of the separator. This measurement is plotted in red. After 96 hours from water contamination, the measured OCV was around 3.0 V, but with the difference that there are significant voltage drops caused by micro-short circuits through the HF-etched separator. These results show that the degradation of the electrolyte by the presence of water causes an increase in the open circuit voltage and also increases the HF concentration.

VII. CONCLUSION

The electrolytes for commercial lithium-ion batteries most often consist of LiPF$_6$ dissolved in carbonate solvents (such as EC or DMC). LiPF$_6$ has been found to be very sensitive to the presence of water and moisture, as it decomposes to form hydrofluoric acid when contaminated. This is why any contact with water and moisture during the battery manufacturing process must be avoided to ensure long-term reliability and service life. Usually the presence of water is detected by Karl-Fisher titration, which is a relatively complex and time-consuming method. During our research, rapid electrochemical screening methods were used, which can also detect the presence of water and degraded electrolyte.

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