HF AND H_2O REMOVAL FROM ORGANIC ELECTROLYTES

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Purpose

One of the problems faced by the lithium ion battery (LIB) industry is the contamination of the electrolyte by H_2O which generates HF, thus impacting the cycling life of the battery. Entegris developed an H_2O purifier and an HF purifier in order to keep the levels of the two contaminants low.

State of the Art

In lithium ion batteries, electrolytes are based on a mixture of carbonates (solvent), $LiPF_6$ salt (or other fluorinated salts) and different types of additives. Organic electrolytes are highly hygroscopic, and the water amount needs to be lowered in order to avoid formation of free acids, especially hydrofluoric acid (HF). Presence of HF in the electrolyte has been investigated and explained. The two causes for the formation of HF in the electrolyte are a) the hydrolysis of $LiPF_6$ (eq. 1, 2, 3) [1] and b) the decomposition of the $LiPF_6$ salt (eq. 4, 5) [1, 2]:

$$LiPF_6 + H_2O \rightarrow LiF + 2HF + POF_3 \quad (1)$$

$$POF_3 + H_2O \rightarrow POF_2(OH) + HF \quad (2)$$

$$POF_2(OH) + H_2O \rightarrow POF(OH)_2 + HF \quad (3)$$

$LiPF_6$ is unstable and its equilibrium can be shifted (especially if exposed to temperatures higher than 40°C), as follows:

$$PF_6^- \leftrightarrow F^- + PF_5 \quad (4)$$

$$PF_5 + H_2O \rightarrow 2HF + POF_3 \quad (5)$$

H_2O and HF have been identified as harmful contaminants by electrolyte and battery manufacturers for many years, and their effects on the battery performance have been widely described in the literature.[3] Presence of HF leads to a decrease in battery cycling life as is also shown in numerous articles.[4, 5] This has been attributed to the positive material's dissolution (involving gas generation and blocking of the lithium cation penetration into the active material) as well as aluminum current collector's corrosion.[4] Moreover, some work describes battery cycling life improvement when the amount of HF is below 10 ppm.[5]

Solution

The solution described here is to use a purification line composed of HF and H_2O purifiers in order to obtain an electrolyte with a contamination concentration which will be one or two orders of magnitude lower than the initial levels. As the presence of H_2O leads to the formation of HF, both of them need to be removed.

The evolution of HF concentration with time depends on the initial level of H_2O, as shown in Figure 1. A fresh electrolyte, even kept in a dry room, exhibits a linear increase of HF with time, proving that traces of moisture react with the salt and need to be removed (curve 2). Moreover, the addition of H_2O dramatically increases the formation of HF (curve 1). With the addition of an HF adsorbent, the total amount is kept low, around 4 ppm (curve 3).

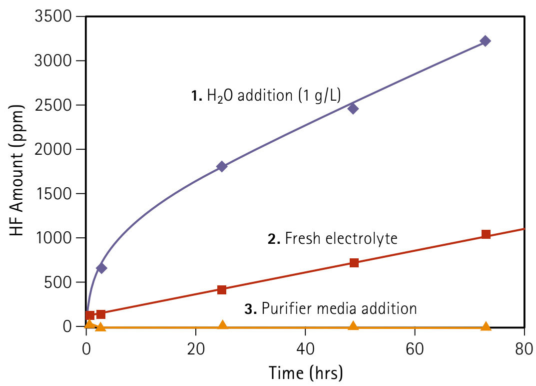

Figure 1. HF amount in the electrolyte with time under different conditions

This removal mechanism is based on chemical adsorption of HF or H_2O by the media contained in the purifier. Removal rate depends on flow rate and inlet HF/H_2O concentrations.

Testing and Results

This section reports the efficiency of an HF purifier assembled on the electrolyte testing line for different types of electrolytes. Internal data were first obtained to determine the efficiency of the HF purifier on a 1M $LiPF_6$ EC/DEC (1/1) binary electrolyte. This fresh electrolyte exhibits a very low amount of H_2O (Figure 2a). Evolution of both HF and H_2O versus electrolyte throughput was measured. Measurements show a decrease from a two-digit- to a one-digit level of the HF concentration.

The HF purifier has also been validated by an electrolyte manufacturer; the results are shown in Figure 2b. The data from A to D show that the amount of HF is reduced by 60 to 75%, depending on the HF concentration inlet. Moreover, samples E and F that were purposely contaminated exhibit a decrease in HF of between 70 and 87%. This evaluation was performed in order to determine whether contaminated electrolyte could be reprocessed instead of being discarded, hence significant savings in the manufacturing line.

As H_2O generates HF, it is also necessary to remove the H_2O. Figure 3 shows the performance of a lab-scale purification performed on a binary electrolyte. The following figure shows H_2O removal efficiency of the purifier located on the line: the purifier efficiency remains constant (around 90%) while electrolyte is flowing through it. The H_2O loading amount represents the mass of electrolyte flowing through the purifier (having a constant mass of adsorbent media).

A lithium ion battery manufacturer evaluated the influence of electrolyte purification on 4Ah prismatic cells. Battery cells were filled with fresh battery-grade electrolyte containing less than 10 ppm of H_2O and purified electrolyte. Both HF and H_2O purifiers, placed before the nozzle, were installed directly on the line at the filling stage. Then HF and H_2O concentrations were

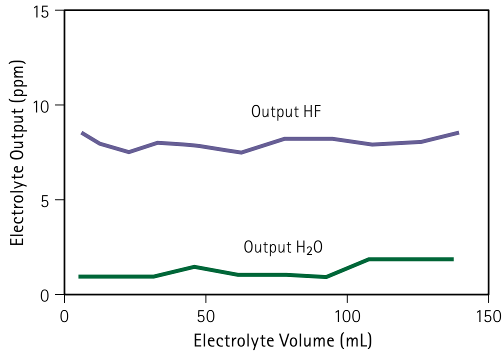

Figure 2a. HF purifier for a fixed inlet (HF and H_2O)

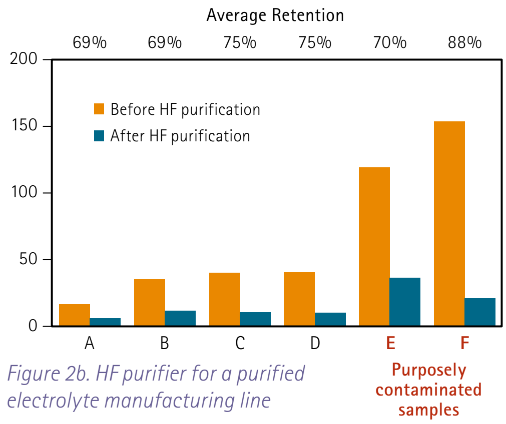

Figure 2b. HF purifier for a purified electrolyte manufacturing line

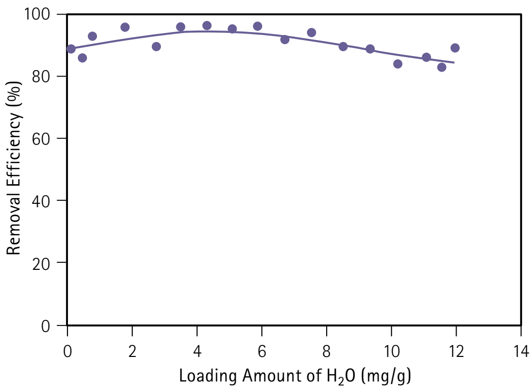

Figure 3. H_2O removal efficiency versus H_2O loading amount

measured. A cycling life improvement was observed as shown in Figure 4. At 500 cycles, the discharge normalized capacity was still above 80%, proving the great influence the removal of HF and H_2O has on delaying the aging mechanisms toward higher cycle numbers.

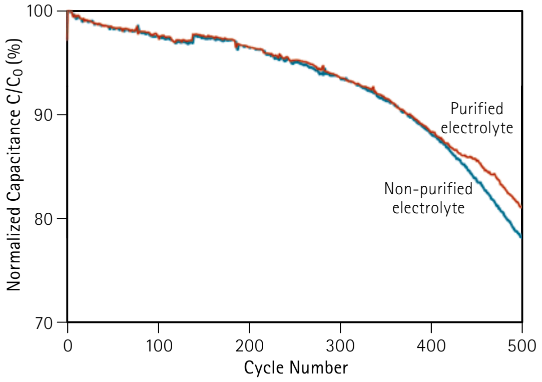

Figure 4. Normalized capacitance (%) vs. cycle number of cells using non-purified (blue curve) and purified electrolytes (red curve)

An optimal electrolyte purification setup requires both HF and H_2O purifiers. Use of filters is also recommended to decrease the particle number contained in the electrolyte (especially LiF crystals, a by-product of the reaction between H_2O and $LiPF_6$).

Summary

This application note describes the solution developed by Entegris to remove H_2O and HF contaminants from organic electrolytes. These purifiers meet the needs of the lithium ion battery industry to bring these contaminants below the 10 ppm level.

References

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