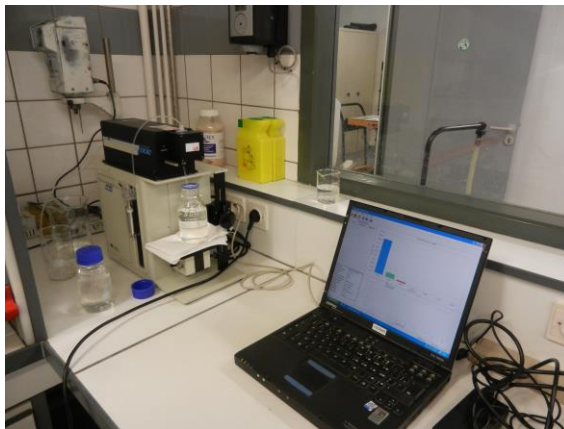


EUROPEAN LI-ION BATTERY ADVANCED MANUFACTURING FOR ELECTRIC VEHICLES



Process cleanliness control in
battery cell manufacturing

*A Way to Improve Increase Lithium-Ion Battery Quality, Production
Yield and Safety*



Process cleanliness control in battery cell manufacturing

A way to increase Lithium-Ion battery quality, yield, safety...

During the production of Li-ion batteries, numerous parameters are responsible for the contamination of the battery elements. Those contaminants are not clearly identified and their impact on the battery performance is not known. However, decreasing scrap rates, improving battery yield, safety and performance represents some key parameters to optimize production.

The goal is to detect the contamination occurring during the production of the battery and determine if there is an effect on performance. A partnership between SAFT and Entegris was developed to achieve this objective. The association between a high level battery manufacturer and an expert in contamination control solutions enables to bring more data on critical contaminants at the manufacturing stage and their impact on the battery.

In the ELIBAMA project, several performance indicators were identified through the topic of clean manufacturing:

- ✓ Reduction of the cell scrap rate,
- ✓ Reduction of particle contamination during manufacturing,
- ✓ Improvement of the ISO class of the dry room at SAFT Bordeaux.

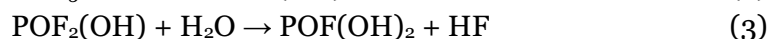
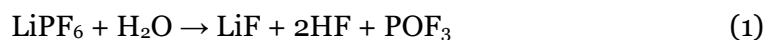
State of the art

In the battery industry, there is no open discussion in the industry about the search of contaminants due to a poor knowledge of the identification of critical contaminants during the production associated to a large variety of materials used at the cathode and a lack of standards for this industry. Manufacturing plants developed their own knowledge on process and return on experience. Effort has not yet been made to move toward contamination control solutions such as in the semi-conductor industry for example. In the semi-conductor industry, the production of micro chip is composed of several hundred process steps; each step is carefully monitored and controlled to ensure the wafer surfaces are contamination-free in order to reach a maximum yield; cost reduction drives this industry. A clean production lays on various parameters such as good housekeeping (FIFO, tidy up...), input substitution (introduction of less toxic material, renewable materials...), better process control (procedure, equipment instructions...), equipment modification (run the process at higher efficiency), technology change.

In the battery industry, all contaminants do not have to be removed because they are not all critical so a selection has to be done. Many efforts have been made by the scientific community to understand the nature and sources of battery failure; it is an indirect way to track the critical contamination that will affect the performance resulting to battery waste. Among the contaminants that are known, we can classify them in 2 large categories: ionic contamination and particulate contamination.

- ***Particulate contamination:*** this is mostly represented by the metallic particles which were well known for some time as harmful contaminants. In 1991, Sony is the first manufacturer to report metallic contamination attributed to the welding step; they observed a large amount of Ni, Cu and Fe that created battery safety issue and resulted into a massive recall and battery loss [1]. Other manufacturers also claim some contamination problem during production [2]. Metallic particles are active materials and can create self discharge or other faradaic reactions (especially at the cathode) compared to non metallic particles that are not reactive to the potential and will be less harmful. Moreover they are quite hard and are well known to generate short circuits either when enrolled between electrodes and separator or generated by the process (welding, contact of materials with stainless steel rolls). In this case, particles have to be controlled. However, the solutions implemented are not well described and depend on various parameters such as process, materials...

- ***Ionic contamination:*** the main contaminant is moisture. This factor probably remains the most studied one because it has a detrimental effect on the battery performance. H₂O is affecting the ageing of materials and is generating HF in the electrolyte. HF is a common source of contamination described in the literature for many years [3]. H₂O reacts with LiPF₆ salt in electrolyte according to the following equations which represent the hydrolysis of LiPF₆. Equations 1 to 3 are linked to the hydrolysis of LiPF₆ (eq. 1,2,3):



Several papers reported the correlation between HF generation during battery cycling with capacitance fading either at the positive or negative electrodes [4,5]. The nature of the fading depends on the nature of the materials. In the case of positive electrode, dissolution of active material by HF occurs and a more pronounced performance degradation is observed.

Contamination in the battery industry is not well known even if some efforts and attempts have been developed to limit it through numerous methods and techniques. Some examples are listed in the scheme below (**Figure 1**). The parameters in the red boxes are the most critical. The yellow box tells where the contamination could be found while the green boxes are some examples of solutions. The sources of contamination and their solutions depend on the manufacturing plants.

Moisture control represents then a large part of battery manufacturer's investments. Usually, dry rooms are well designed to decrease moisture down to a low level. For the manufacturers who do not produce into dry rooms, glove boxes are necessary for certain manufacturing steps.

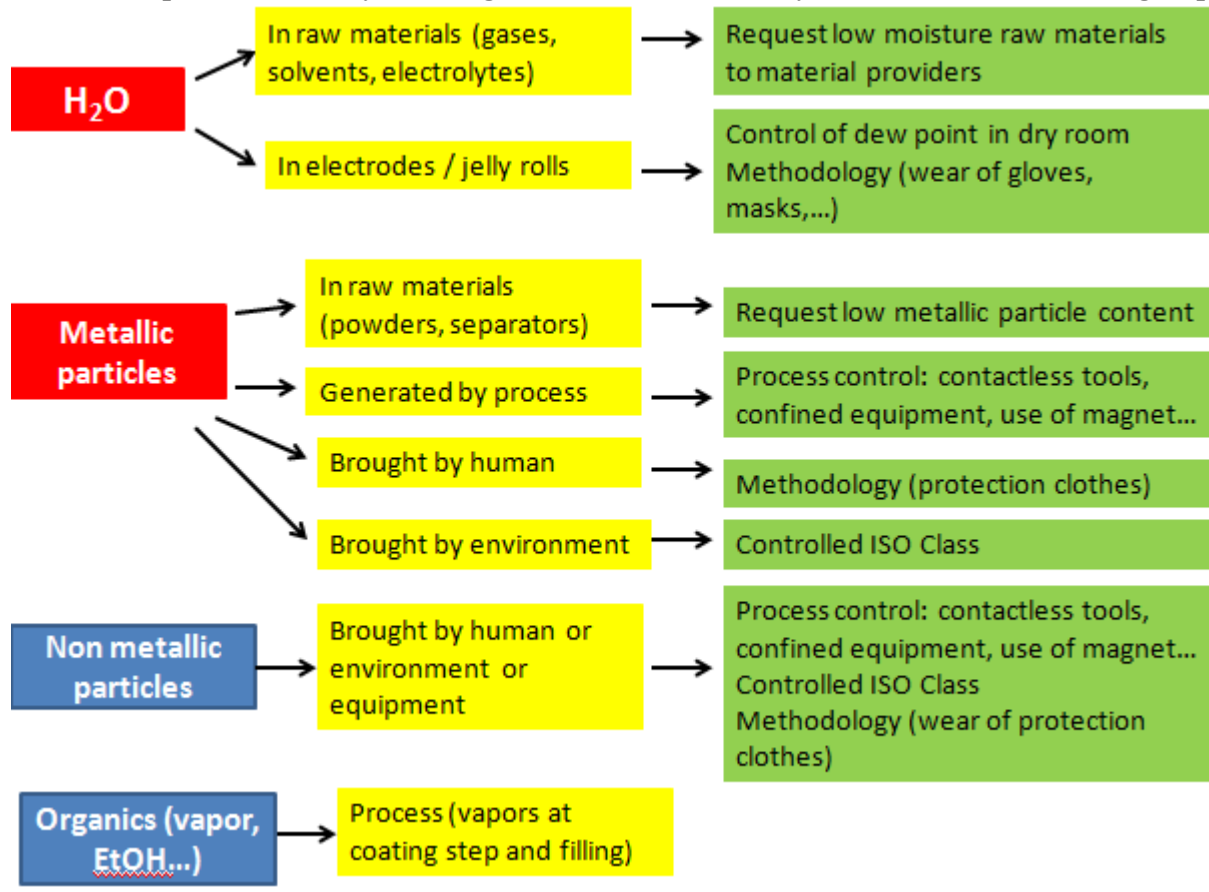


Figure 1: Scheme representing the contaminants, sources and some solutions.

However, there is no information about the contamination threshold that is acceptable and won't impact the battery. The literature reports some clues about mechanisms occurring in a button cell or small cell due to degradation of materials but do not reflect the real mechanisms in large prismatic cells for example. Contamination won't have the same effect on the battery depending on many intrinsic parameters (such as materials, processes, environment, size and structure of the battery...) so the solutions have to be adapted accordingly.

ELIBAMA Breakthrough

One task of the program is dedicated to detect and eliminate the contaminants that could contaminate the battery elements. The solutions implemented are described and the impact on the battery using electrical tests is explained.

a. Audit of manufacturing plants

To control the Process Cleanliness during cell manufacturing, SAFT and Entegris used the SAFT Quality System (reasoning and tools) which are commonly used in many industries. A general approach and a methodology have been developed between the 2 partners to detect the most critical sources of contamination, whatever the technologies and processes being used. During one year, the methodology has been tested to define if the goal was achieved; as this was proven to be successful, the methodology has been also applied to the CEA pilot line.

One of the tools used is the Ishikawa diagram represented in **Figure 2**. The parameters that could bring contamination are listed in **Figure 2** and classified in different factors (man, machine, media, method, materials, and measurement).

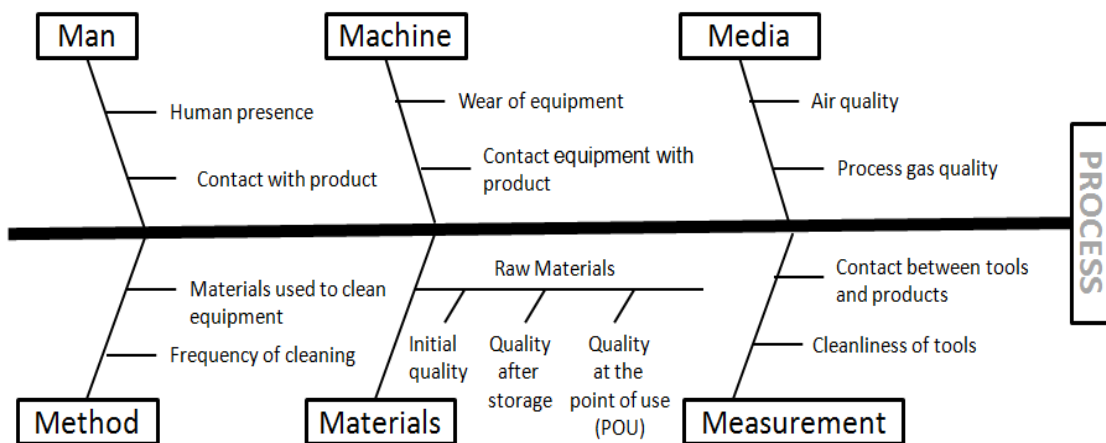


Figure 2: Ishikawa diagram: example of the potential contaminants listed by process.

The different parameters described in the Ishikawa diagram are reported into a Failure Mode and Effect Analysis document and are rated depending on the volume production, process, raw materials... **Figure 3** represents the comparison for both sites of the most potential harmful contaminants at each process step. The criteria and rating have been specified by production teams to calculate the Risk Priority Number, that represents a threshold. The parameters with a number above the RPN represent the ones that will be investigated during the audit. It is clear that the contamination has not been taken into account the same way depending on the production site. However, few similar trends can be observed such as the impact of man and measurement is negligible. The electrode fabrication steps (from mixing to drying) represent the main contribution in comparison to the cell assembly steps (from winding to filling) and this trend is more pronounced in the case of the CEA.

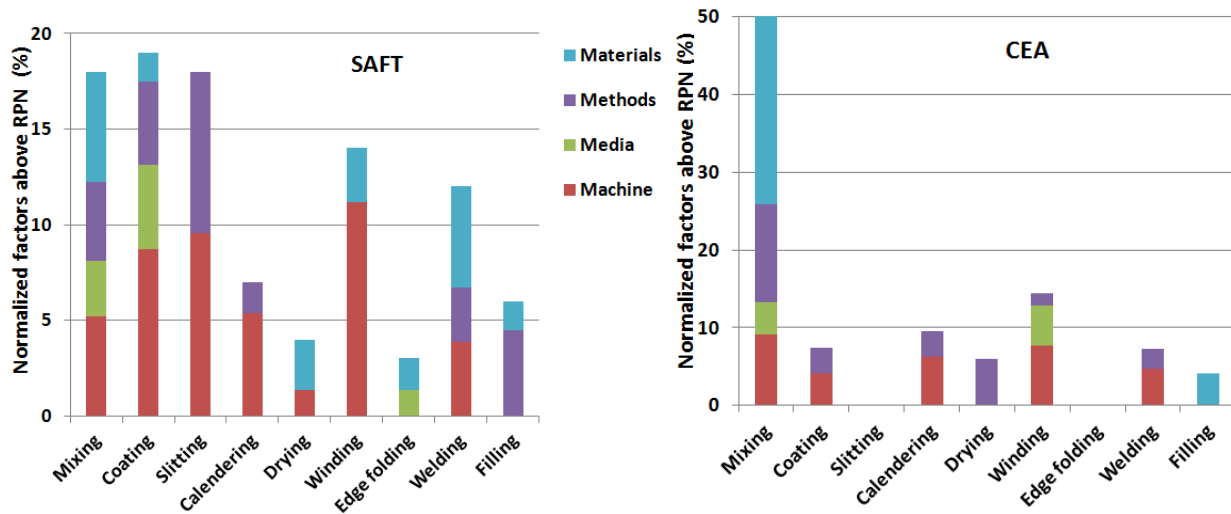


Figure 3: Comparison of the main contaminants found for each step of the manufacturing.

Sampling methodologies associated to analytical tools were used to determine whether contamination is present or overestimated. The use of analytical tools to detect the nature and source of contamination occurring during battery production is shown in **Figure 4**. By analogy with the semi-conductor industry, we classified the contamination sources into 4 categories: environment, human, process and raw materials. For each factor, appropriate analyses were used to detect and identify the nature and sources of contamination.

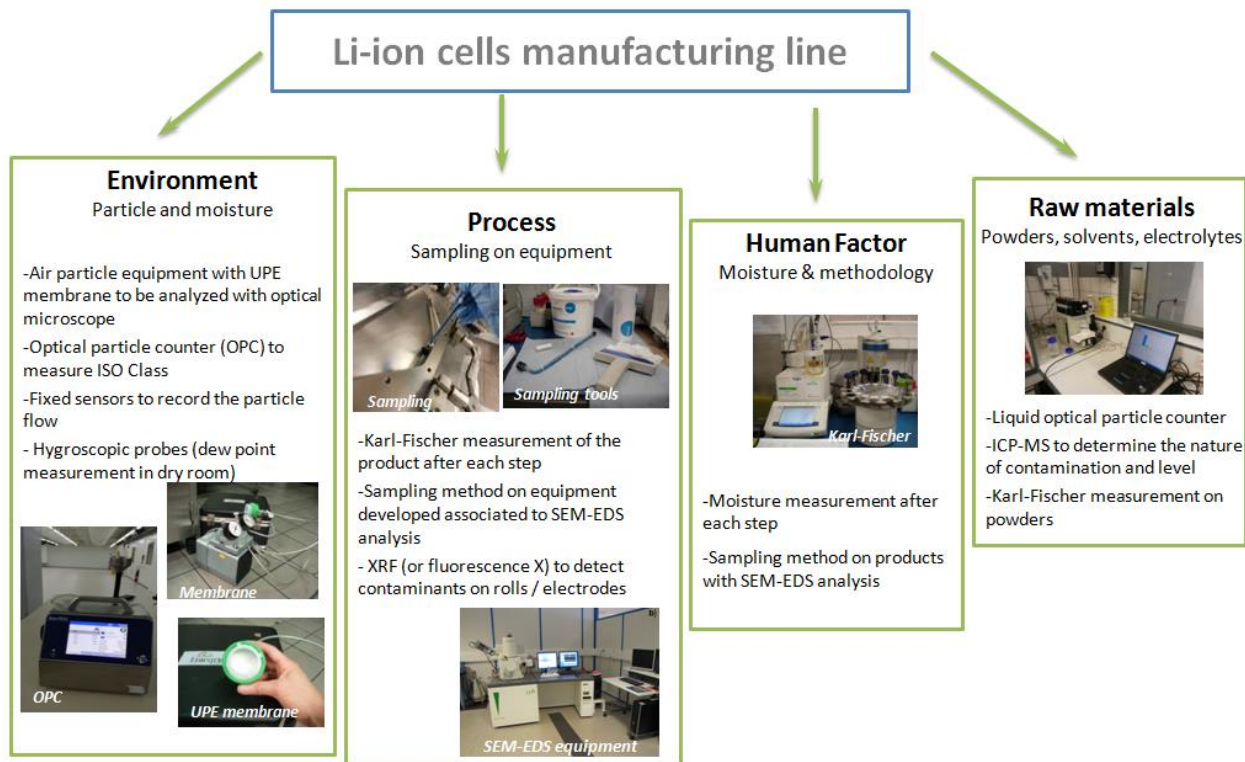


Figure 4: Analytical tools used to identify the contamination coming from the different factors at each process step.

The results of the audit from the two sites show similar trend.

- *Fabrication of the slurry*: the audit confirms the presence of contamination mostly linked to equipment wear and raw material quality issues (discussed in section b).
- *Electrode fabrication*: various contaminants, mostly metallic particles have been found especially due to the contact of the product with equipment.
- *Cell assembly*: air particle count is increased. Metallic particles are found mostly on the equipment and in the air. Processes were responsible for the presence and generation of particles.
- *Cell filling*: at this stage, the contamination is coming from the raw material (electrolyte) and is treated in the following part.

The audit concluded that all factors contribute in different way to contamination and solutions have been implemented accordingly. Even if the audit has been performed on the 2 sites, the solutions have been implemented only on SAFT site due to the volume production.

b. Filtration of raw materials

Quality of raw materials has been investigated. This section reports the results obtained on filtration of solvents and electrolytes. For both of them, volumes and flow rates are quite different so an adequate filtration had to be chosen. Regarding the solvents, a large carter housing with a membrane filter is needed for the high flow rates and volumes (**Figure 5a**). For the electrolyte, the tight space on the equipment associate to process conditions drive us to the choice of a small disposable filter (**Figure 5b**).

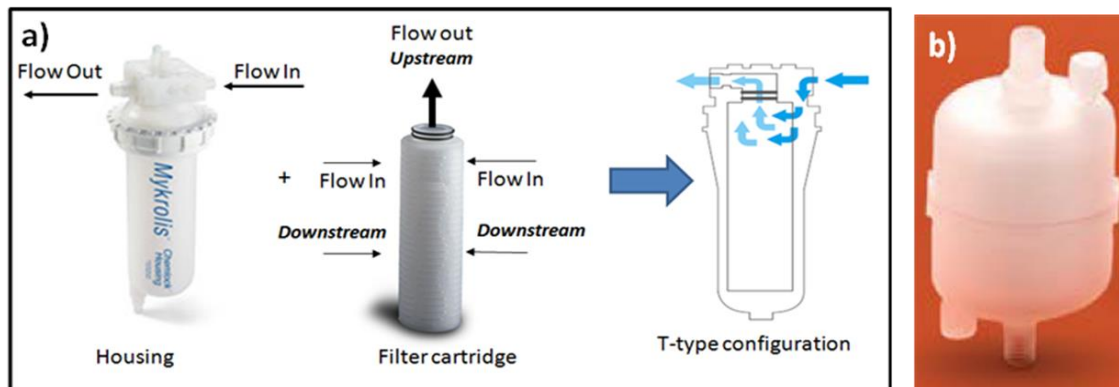


Figure 5: a) Carter housing and filter pictures; b) Disposable filter.

- *Solvent filtration at the mixing step*:

An Optical Particle Counter (OPC) has been used to measure the particle counts in the solvents in function of the particle size: NMP (solvent of positive electrode) and H₂O (solvent of negative electrode). Measurement at different location of the process has been done: initial quality from the tank, during transportation and at the point of use. **Figure 6** represents the solvent quality at the different stages in the process; large contamination is primary linked to solvent transportation where the particle count is largely increased. Filtration is implemented before the point of use to decrease the particle count. Regarding NMP, a membrane filter is implemented

on the distribution line to retain particles above 0.2 μm . For H_2O , a 0.1 μm filtration to retain both particles and ionic species is proposed: the goal is to purify H_2O and retain particles above 0.1 μm at the same time. In both case, filtration efficiency was calculated around 80-90% and 90-95% for NMP and H_2O respectively. This efficiency is not as high as 99.99% because of the contamination from the mixing vessel which is taken into account and contributes to the final contamination; the filter efficiency is then hidden by other factors.

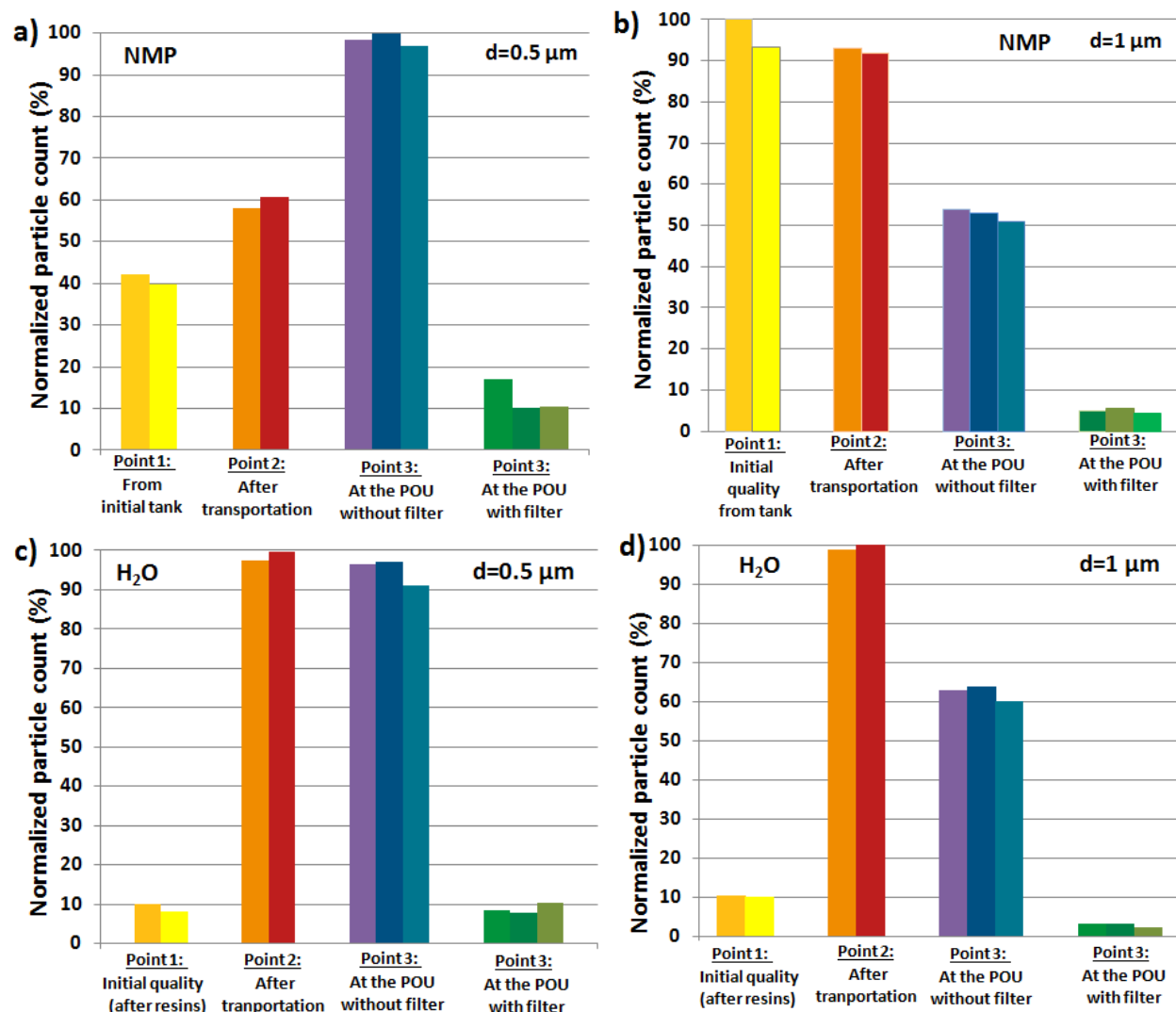


Figure 6: 0.5 μm (a,b) and 1 μm (c,d) particle count in NMP and H_2O at different locations of the process with / without filtration.

Implementation of solvent filtration positively impacts the cell quality since a decrease in the cell scrap rate was observed.

Batches of 50 cells (40 Ah) were produced using different filtration configuration and electrical tests were performed to measure the internal resistance (IR) and self-discharge (SD). **Figure 7** represents the IR and SD deviation of cells assembled with *non filtered slurries*, *NMP filtration*, *H_2O filtration* and *filtration on both solvents*. Cells manufactured with non-filtered solvents

have higher IR and SD standard deviation compared to cells produced with filtered solvents; standard deviation of those cells is normalized to 1. The better cell scrap rate (i.e. minimum standard deviation) is obtained for cells using filtered NMP. Filter post-mortem analyses have been performed to identify the nature of particles retained by the membrane; membrane is analyzed via SEM-EDX. The identification of the elements eliminated by the filter could help understanding the reason of the standard deviation decrease. Regarding the NMP filter membrane, mostly metallic particles were found while on the H₂O membrane, mineral particles were detected.

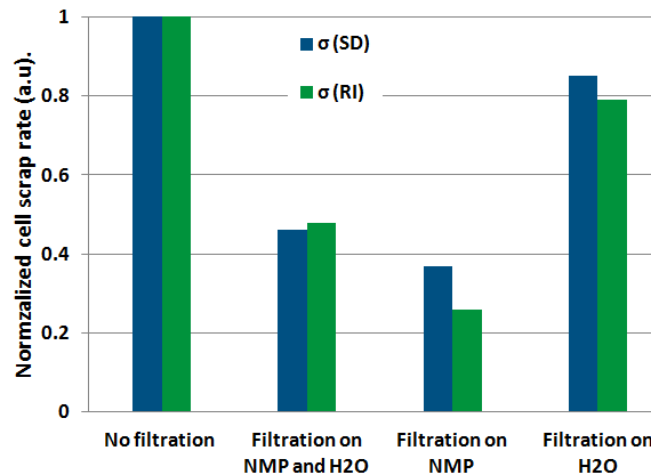


Figure 7: Self-Discharge and Internal Resistance standard deviation for cells assembled with electrodes produced with/without filtration. (+)=NMP filtration, (-)=H₂O filtration.

- *Electrolyte filtration at the filling step:*

Figure 8 represents the electrolyte filtration. For this step, a small size disposable filter was used to retain particles above 0.1 μm . The initial quality of the electrolyte is variable as seen in **Figure 8** (blue bars). The filter was placed the nearest to the point of use and the efficiency was then calculated. The electrolyte flowing through numerous pipes, containers and valves before the dispense system is getting more and more particles. Filtration enables a large decrease of particles down to a low level close to the electrolyte initial quality.

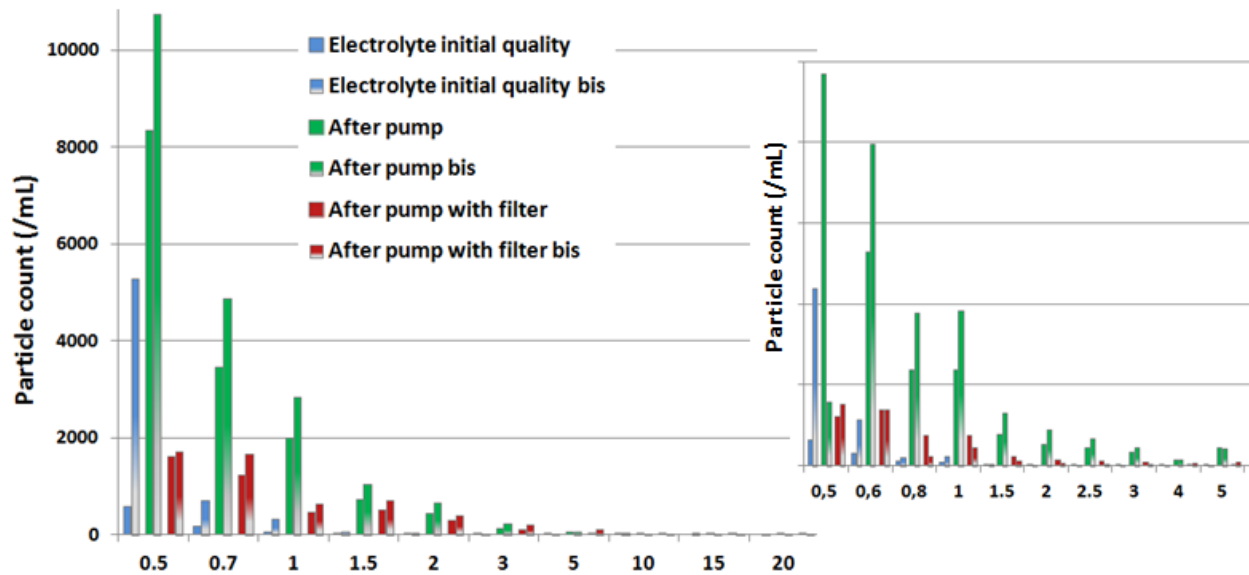


Figure 8: Results of particle count of the electrolyte with / without filtration a) and b) zoom on the particle size below 5 μm .

c. Dry room air quality control

The objective was to reach an ISO Class of 7 for particles of 0.5 and 5 μm and understand the correlation between the ISO Class variations with the various parameters of the dry room. Air quality is controlled via:

- portative Optical Particle Counter measuring the ISO class of 0.3, 0.5, 1, 10 and 25 μm particle size at six points of the dry room (3 points in the assembly area and 3 in the electrode fabrication area). The average value of the ISO class for both area is reported in **Figure 9**.
- 2 fixed probes located at the electrode fabrication and assembly area to measure the evolution of particle number with time with / without activity (**Figure 10**).

Figure 9 represents the evolution of the ISO Class during the project. The end of the audit phase (2013) concluded that main improvement has to be made on 0.5 μm particles. Two main solutions have been implemented to achieve the ISO 7:

- 1st solution: modification of the mesh size sleeve that blows the air in the dry room (red bars in **Figure 9**)
- 2nd solution: air recirculation modification by adding filters to retain particles below 0.5 μm (yellow, purple and blue bars in **Figure 9**).

The 1st solution slightly decreases the ISO class (red bars) while the air filtration has quite a large impact on the dry room air quality. The ISO class after filtration implementation has been measured with and without activity. A certified organism confirmed the ISO Class below 7 for the 0.5 and 5 μm particles at the end of the project while there was activity in the dry room.

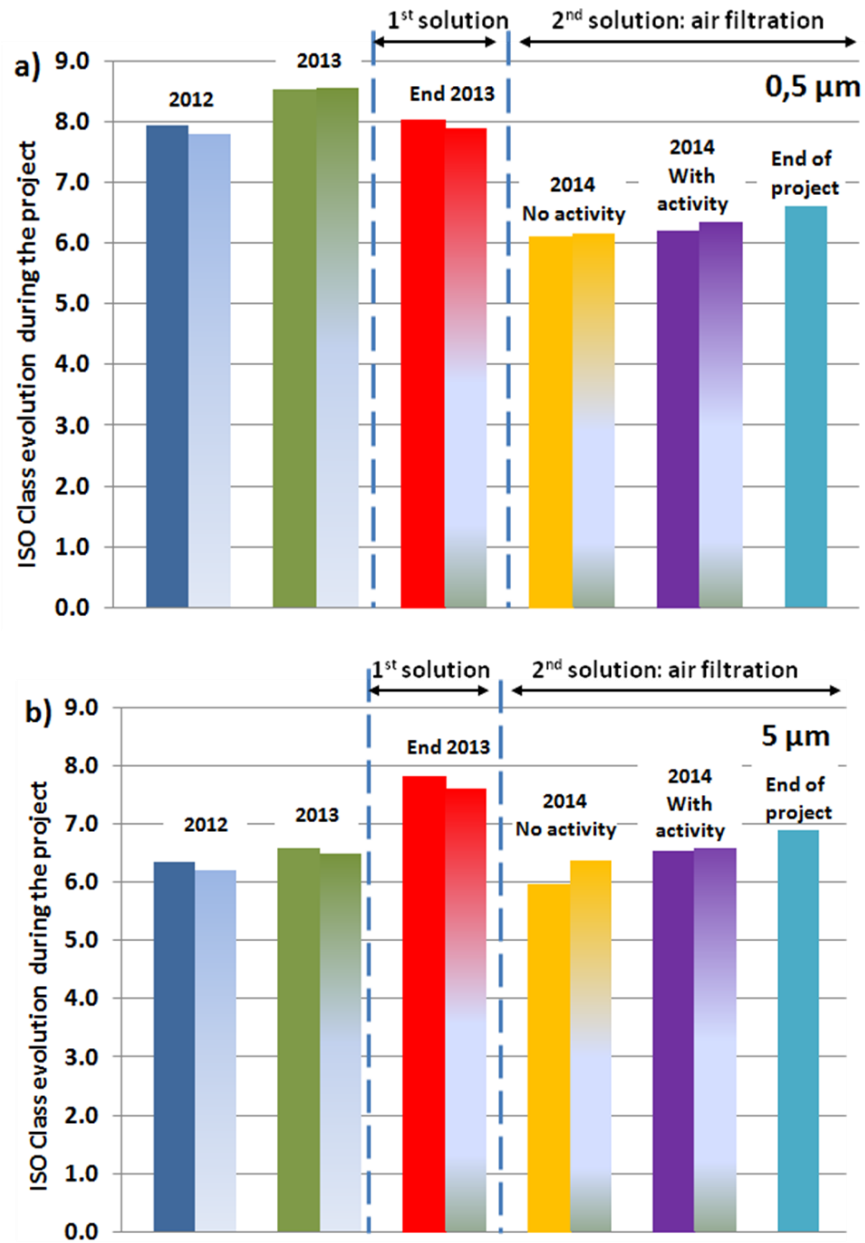


Figure 9: ISO class evolution since beginning of the project for the assembly (plain color) and electrode fabrication area (light color) and for the 0.5 µm particle a) and 5 µm particle b).

Figure 10 illustrates an example of the particle count with and without production. The impact of human factors has also been measured. It was shown that both have an impact on the particle count increase.

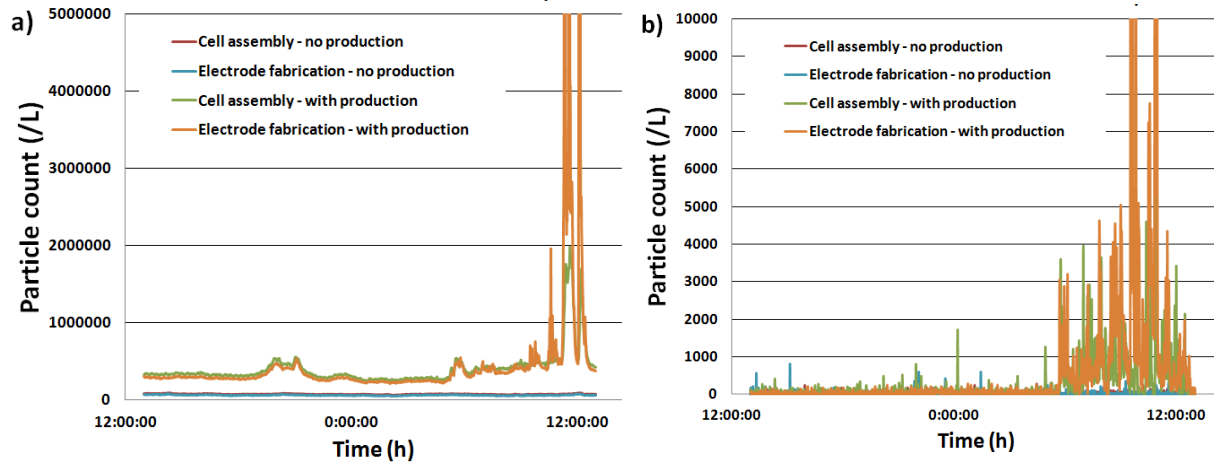


Figure 10: Impact of production on particle count variation of 0.5 a) and 5 μm b) in the electrode fabrication and cell assembly area.

d. Statistical analysis on cell performances

Figure 11 shows the implementation time line of the different clean manufacturing solutions at SAFT Bordeaux and/or Nersac. In order to check if these solutions have an impact on cell performances, statistical analysis has been performed all along the project.

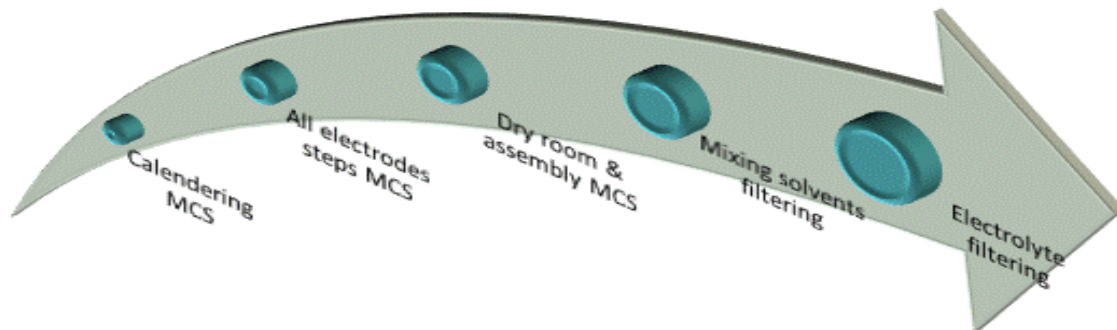


Figure 11: Implementation time line

Many cylindrical cells (more than 30000) were performed since the beginning of the project, with different nominal capacity values, ranging from 30 to 45 Ah.

Statistical analysis on cell performances (initial capacity, internal resistance, self-discharge) has shown that these solutions have no impact on capacity and self-discharge, but only on self-discharge. Indeed, as illustrated in **Figure 12** below, dry

room air quality and all electrode cleaning systems, including calendaring, have shown to have a strong impact on self-discharge values, leading to a significant decrease of number of cells with high and medium self-discharge values. Meanwhile, filtration of solvents and electrolyte are mainly acting to very low values and are significantly leading to reduced standard deviation for better focused performance and quality.

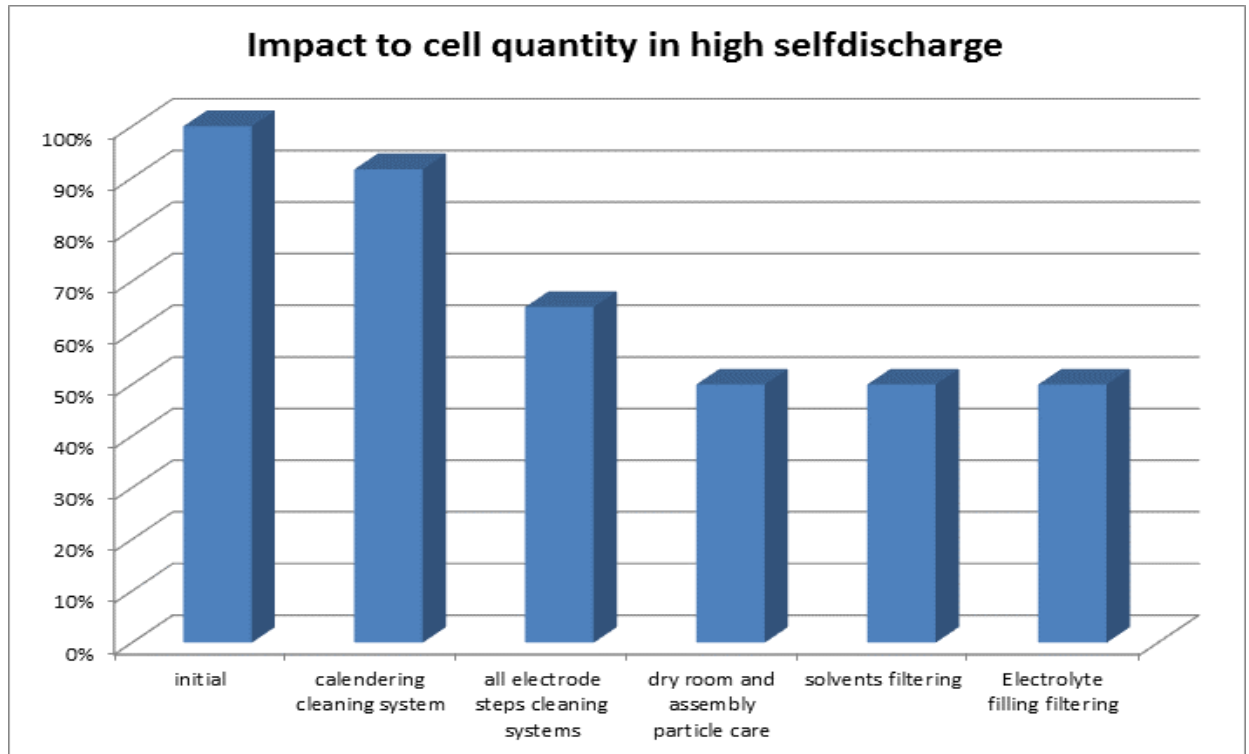


Figure 12: Impact of each Methods & Cleaning Systems step to high self-discharge.

Overall, thanks to these clean manufacturing solutions, self-discharge scrap rate has been divided by two, which was an important objective of ELIBAMA project. Therefore, most of these Methods & Cleaning Systems are now implemented at SAFT Bordeaux and Nersac production lines. Finally, in order to have more statistic data (especially for the electrolyte filtering, which was the last implemented step), measurements during several years will be necessary.

Conclusion

The methodology developed during the program between SAFT and Entegris appears to be quite accurate to determine the sources of contamination and enables to implement solutions when needed. Different solutions were implemented: work methodology, process modification and filtration solutions were among the major changes. By analogy with the semi-conductor industry, contaminants are classified in environment, material, process, human factor.

Filtration solutions of raw materials (solvents and electrolytes) were implemented and a positive impact of the filtration solutions on the cell scrap rate was measured; a cell scrap rate decrease higher than 50% was calculated with solvent filtration. This observation indicates that the particles contained in the solvents and in slurries will be responsible for some performance deviation due to different factors.

Another important objective was to decrease the ISO Class from the starting point of the project (ISO Class > 8) and decreases it to 7 for the 0.5 and 5 μm . This objective was reached at the end of the project with an ISO Class of 6.9 and 6.4 respectively for the 0.5 and 5 μm . A major modification of the dry room air entrance was performed and the

In this project, we demonstrated that contamination control is an important parameter to take into account to improve scrap rate. Contamination control solutions were then efficient to improve this key factor.

Perspectives for the future

Raw material filtration has been proven to be efficient for the battery industry. However, the filtration system needs to be adapted according to the volume of production. The solution implemented resulting in a yield improvement shows there is room for battery cost decrease.

A complex model for the return on investment can be developed by the battery manufacturer depending on the volume production, battery size, manufacturing cost...

Figure 13 is an example of solutions developed for raw materials that increase battery performance either in term of scrap rate (like in this project), battery life time (use of purifier to remove HF from the electrolyte) or in term of solvent waste decrease (NMP recycling).

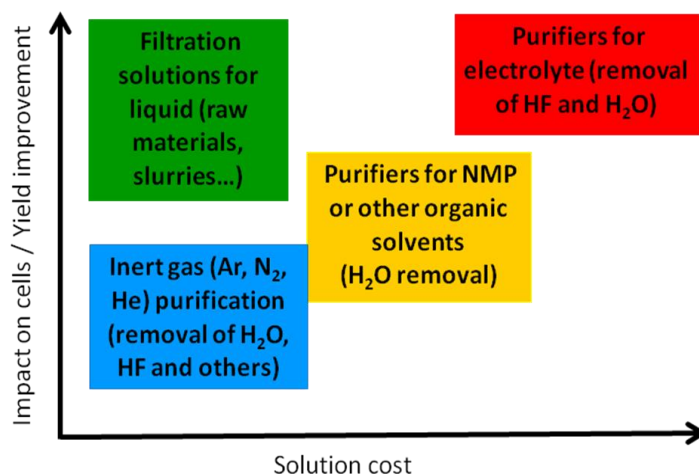


Figure 13: Contamination control solutions developed for raw materials.

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