ELECTRODES CALENDERING

How to have the best calender process for best calendar life?
ELECTRODES CALENDERING

How to have the best calender process for best calendar life?

State of the art of calendering

Generally speaking, calendering seems to be a mastered technology. For now several centuries, man has been trying to press between two rolls all kinds of materials as varied as they are numerous. Each time he has met technical problems to put machines (tools) and materials in adequacy.

Relation of calendering to Battery did not escape this rule and even more so as the problem is doubled where positive and negative electrodes (cathode - anode) are concerned. In spite of a calender simple aspect (two rollers facing each other !), the calendering process is complex and so are the steering parameters, especially with heterogeneous, multiple and diversified materials…

Thus, for the main components that are rollers, it is necessary to take into account diameters, hardness, surface finish, geometry, precision, nature, temperature, etc… along with the calendering force to apply and the choice of the calendering mode to operate. Transposed to battery use, these parameters must be studied according to the material requirements. Electrode calendering has two main purposes: porosity reduction and thickness mastering, while keeping in mind precisions linked to these two factors.

For the time being, there remains to stabilize processes according to chemistry evolutions of active materials (and binders).

ELIBAMA breakthrough

Up to now, SAFT and many other Li-ion battery manufacturers produce electrodes at a standard porosity, which is supposed to be optimal. With the aim of storing more and more energy in Li-ion batteries, one way of work is to reduce these porosities, in order to comply with ELIBAMA objectives: reducing the global cell production costs and increasing the energy density (in Wh/L), given that more electrodes could be stored in the same cell. This was the objective of this Task in the frame of ELIBAMA.
Apparatus developed and used in ELIBAMA

SAFT and INGECAL decided to use pre-heating chambers before calendering the electrodes (*Figure 1*). This system was placed just above the electrode on the production line. This system is supposed to make the electrodes more malleable for a stronger calendering. Thus, electrodes will be heated longer and not only at the compression point between the cylinders. The temperature can be controlled by the operator and can reach up to 180°C.

*Figure 1. Pre-heating chambers*

Up to now, SAFT has used measurement device which has an important margin of error relatively to the accuracy needed. With the aim of getting more accurate results, a new system has been experimented in ELIBAMA project. The sensor is mechanically able to move all along the electrode, which is an interesting asset to control if the thickness is more or less identical anywhere at the surface of the electrode.

**Achieved porosities and electrode properties**

Let’s say that the standard porosity corresponds to 100%. In this study and using pre-heating chambers, it has been shown experimentally that calendering at porosity lower than 78% for the positive and 65% for the negative causes damage on the electrodes. Actually, such a pressure leads to many tears which cause downtime on the production line.

Therefore, three porosities have been targeted for each electrode:

- For the positive one: 100% (standard), 89% (intermediate) and 78% (minimal)
- For the negative one: 100% (standard), 82.5% (intermediate) and 65% (minimal)

The electrodes previously calendered have been analyzed in laboratory. The aim was to confirm the porosity targeted for the calendering step and also to determine the median pore size for each porosity vs. 100% calendered (normalized to 100%). From the *Figure 2*, two observations can be noticed:
The pores sizes are considerably reduced for the electrodes at the lowest porosity in comparison with the standard porosities (close to 4 times smaller for the negative one and 5 times for the positive one).

The pre-heating system affects neither the pores sizes nor the global porosity.

Such pore sizes lead to many difficulties when the cells will be filled, given that the path for the electrolyte will be considerably reduced. Filling parameters were therefore adapted in order to fill the cells completely.

<table>
<thead>
<tr>
<th>Negative electrode</th>
<th>Median pore size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td></td>
</tr>
<tr>
<td>Non calendered</td>
<td>232%</td>
</tr>
<tr>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>82.5%</td>
<td>53%</td>
</tr>
<tr>
<td>65%</td>
<td>30%</td>
</tr>
<tr>
<td>65% without pre-heating chambers</td>
<td>26%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Positive electrode</th>
<th>Median pore size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td></td>
</tr>
<tr>
<td>Non calendered</td>
<td>220%</td>
</tr>
<tr>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>89%</td>
<td>93%</td>
</tr>
<tr>
<td>78%</td>
<td>20%</td>
</tr>
<tr>
<td>78% without pre-heating chambers</td>
<td>20%</td>
</tr>
</tbody>
</table>

**Figure 2. Determination of median pore size for both positive and negative electrodes**

The adhesion for the standard porosity has been normalized at 100%. As described in **Figure 3**, two different behaviors are observed. As far as the negative electrode is concerned, the reduction of porosity does not lead to an adhesion increase. On the contrary, the adhesion of the positive electrode goes up when the porosity goes down. The positive effect of the calendaring step is therefore highlighted in this study.
Figure 3. Measurements of adhesion for both positive and negative electrodes

Conclusions

Electrode porosities have been successfully decreased to -22% for the positive one and -35% for the negative one. The use of new systems seems promising. From this initial work, two mains observations have been done.

First, the presence of the pre-heating chambers seems to exhibit a good effect on the electrodes, at least mechanically. Indeed, some marks have been noticed on the negative electrode. By the way, it is interesting to see that the pores are much smaller at low porosity.

Secondly, the adhesion is definitely improved at low porosity as far as the positive electrode is concerned. This observation is also promising because it could make possible the reduction of binder percentage in the positive formulation, and thus increase the active material percentage.

Electrical performances are still on-going but initial capacity gain of +10% is already obtained. Cycling/calendar life is still under assessment.
Perspectives for the future

The calender market in the battery sector has not yet reached a level that will allow manufacturers to significantly increase their research work.

Achievement of this technology will compulsorily request further research in such fields as metallurgy, machining processes, thermal models.

In parallel to a necessary evolution of calenders to reach a productivity level coherent with the need, battery production modes should also be a research axis not to be neglected.

Contacts and references

**SAFT: Julien Bréger**
Julien.Breger@saftbatteries.com

**INGECAL: Didier Perroncel**
didier.perroncel@ingecal.fr

*The ELIBAMA project is granted by the European Commission under the “Nanosciences, nanotechnologies, materials & new production technologies” (NMP) Theme of the 7th Framework Programme for Research and Technological Development.*