Li salt rich separator for Li-ion batteries

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Abstract

In order to reduce the duration of the electrolyte filling step, a new concept of separator embedding itself Li salt thanks to a Li salt rich film coated on. The objective of study was to quantify the impact (benefits and drawbacks) of a Li salt containing PVdF based film deposited by coating onto a conventional polyolefin based separator. A protocol for elaborating the salt based polymeric solution to be coated onto a commercial polyolefin separator was developed at CEA/LITEN. Separators were coated with solutions at a defined coating thickness. The samples were characterized in terms of salt loading, morphology of the layers, adhesion of the film on the separator, ionic conductivity and ability to be soaked by the electrolyte. Some cycling tests were undertaken in full coin cells Cgr / LiFePO4 and soft pouch cells with samples of coated separators in order to evaluate the impact of the manufacturing conditions on the electrical performances. The impact of the storage conditions of the coated separator was also studied

Keywords: coated separator, Li-ion batteries, soft pouch cells, salt loading, SEM

I - Introduction

Solvay proposes a new concept of separator embedding itself Li salt thanks to a Li salt rich film coated on (Patent Solvay).
The objective of the present study was to quantify the impact (benefits and drawbacks) of a Li salt containing PVdF based film deposited by coating onto a conventional polyolefin based separator. The thin coated layer is composed of Solef® PVdF containing LiTFSI salt in appropriate amount. The separator selected for the study was the Celgard® 2320.

After having developed the method for manufacturing such a coated separator, electrical evaluations were conducted in representative intermediate capacity-level Li-ion cells, trials with pilot coating machines were also performed to demonstrate the feasibility of coating a separator at industrial level and the impact of the storage were also studied.

II- Development of the formulation of the ink

The aim was to design an ink composed of PVdF dissolved in solvent and containing LiTFSI salt with appropriate rheological characteristics, especially in terms of viscosity, to be coated on a polyolefin separator.

A protocol for elaborating the LiTFSI based polymeric solution to be coated onto a commercial polyolefin separator was developed at CEA/LITEN. The investigations lead on its preparation and some various characterizations as the dilution of the materials and the viscosity.

The lab coatings conditions of the solution onto the separator to reach the loading target were investigated: in anhydrous air (typically in a dry room at dew point -40°C).

As mentioned previously, Celgard® 2320 separators were coated with solutions at a defined coating thickness and dried in temperature.

III- Characterization of the LiTFSI coated separator

The different samples were so characterized in terms of shrinkage, salt loading, morphology of the layers, adhesion of the LiTFSI film on the separator, ionic conductivity and ability to be soaked by the electrolyte.

- *Skrinkage of separator*

To evaluate the shrinkage of the neat separator, several samples with the same dimensions (43mm x 43mm) were prepared and stored in an oven at 80°C. Their length and width were so measured at different time.

- *Salt loading*

The objective of the study was so to determine the coating thickness required to reach a target loading. Coating trials were done at different wet thickness.

- *Morphology of the coated separator*

Samples of separators coated with solutions were prepared for observations by Scanning Electronic Microscopy (SEM). They were cryo-fractured and gold metallized prior to the observations.(Figure 1 and 2).

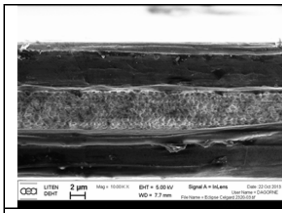

Figure 1: Separator Celgard®

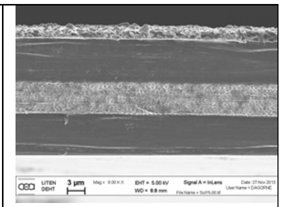

Figure 2: Separator Celgard® with thin coated layer.

- Wettability of the coated separator by the electrolyte

In order to evaluate the wettability of the coated separator by the electrolyte, measurements of contact angle were carried out in dry room. The measurements were performed by deposition of a drop of electrolyte on the coated separator. (Figure 3 and 4).

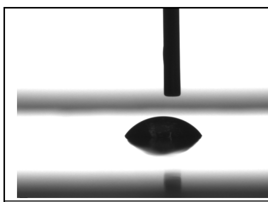

Figure 3: Contact angle measurement on separator Celgard® 2320

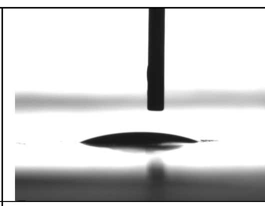

Figure 4: Contact angle measurement on Separator Celgard® 2320 with thin coated layer

- *Adhesion of the coated film on Celgard 2320 separator*

To estimate the adhesion of the film on the separator, peeling tests were performed on the coated separators in dry room.

- Ionic conductivity of the separator

In order to evaluate the ionic conductivity of the coated separator, coin cells constituted of two stainless steel disks separated by a pellet of coated separator (thickness Ep) and soaked with electrolyte were assembled.
The measurement of their resistance (R) by Electrochemical Impedance Spectrometry (EIS) thanks to Bio-Logic VMP multipotentiostat allows determining the ionic conductivity of the coated

separator.

The values of the ionic conductivity calculated from the resistance measured on the coated separators and their thickness are close to $0.3 mS.cm^{-1}$, comparable with the ionic conductivity measured on the neat separator (i.e. ~$0.4 mS.cm^{-1}$).

- *Evaluation of LiTFSI salt dissolution into the electrolyte by atomic absorption spectroscopy*

Celgard® 2320 separator was coated and dried. Samples of the coated separators (10cm x 10cm) were then immersed into 5 mL of neat carbonate during 2 weeks. The concentrations of LiTFSI were analyzed by Atomic Absorption in order to determine accurately the Li content (see Figure 5).

Figure 5 : Perkin Elmer AAnalyst 400 Atomic Absorption Spectrometry

III – Coating trials on large length

The objective of the coating trials on the industrial coating machines was:
- To demonstrate the feasibility of coating a LiTFSI rich polymeric film on large length of separator;
- Then to manufacture enough amount of coated separator for the assembly of some 53437 pouch cells in order to validate the coated separator on large wound prismatic configuration.

Two coating technologies were tested:
- One based on the reverse roll principle (Figure 6 : INGECAL equipment)
- The second on the use of slot die (Figure 7 :COATEMA equipment)

Figure 6: Reverse roll coating machine

Figure 7: Slot die coating machine

The tests revealed promising, demonstrating the feasibility of the separator coating at industrial level.

IV- Electrochemical characterization

Some cycling tests were undertaken in full coin cells Cgr / $LiFePO_4$ with samples of (coated) separators in order to evaluate the impact of the manufacturing conditions on the electrical performances. Thus the effect of the drying temperature on the neat separator and the effect of the composition of LiTFSI based polymeric solution used for the coated films was investigated through some discharge/charge cycles.

To reach the battery format dedicated to the consumer electronics market, CEA also tested in cycling the coated Celgard® 2320 separator in CEA standard wound prismatic cells, i.e. in soft pouch (500mAh – Figure 9).

Figure 8: Coin cell

Figure 9: CEA soft pouch cells (500mAh)

V-Impact of the storage conditions of coated separator on the performances in cycling

The impact of the storage conditions was also studied. Bands of Celgard®2320 separator were coated by LiTFSI rich. A half of the samples was stored in normal conditions during 1 week without any particular precautions when the second part was stored in dry conditions (dry room, dew point of -20°C).

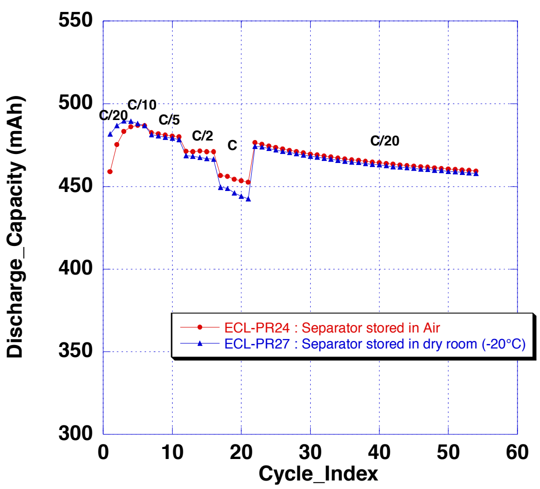

Figure 9: Electrical performances in cycling of Cgr/$LiFePO_4$ based 53437 pouch cells with different storage conditions of Celgard® 2320 separator.

It seems that the storage of such coated separators in air without any specific conditions (during one week) does not induce any consequences on the electrical performances.

VI – Conclusion and perspectives

In a preliminary study, a protocol for elaborating the LiTFSI based polymeric solution to be coated onto a commercial Celgard®2320 polyolefin separator was developed.

To coat a commercial polyolefin separator with a LiTFSI rich PVdF based film seems to improve clearly its wettability towards the electrolyte, without modifying its performances in cycling.

some coating trials were performed on pilot equipment using two technologies: one based on the reverse roll principle (INGECAL equipment) and the second on the use of slot die technique (COATEMA equipment). The tests revealed promising, demonstrating the feasibility of the separator coating at industrial level.

Moreover, it seems that the storage of such coated separators in air without any specific conditions (during one week) does not induce any consequences on the electrical performances.

However it would be interesting to evaluate the electrical behavior of bigger cells with coated separator.

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