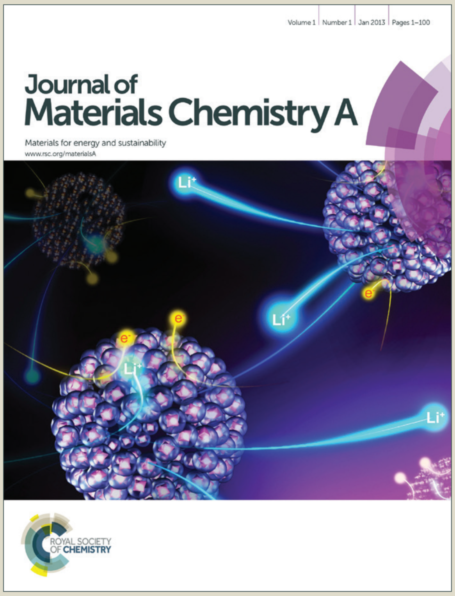
Journal of
Materials Chemistry A

Accepted Manuscript



# Aqueous processing of paper separators by filtration dewatering: towards Li-ion paper batteries

*Lorenzo Zolin,* [a,b,d,*] *Matteo Destro,*[d] *Didier Chaussy,*[a,b,c] *Nerino Penazzi,*[d] *Claudio Gerbaldi,*[d] *Davide Beneventi,*[a,b,c]

[a] Univ. Grenoble Alpes, LGP2, F-38000 Grenoble, France

[b] CNRS, LGP2, F-38000 Grenoble, France

[c] Agefpi, LGP2, F-38000 Grenoble, France

[d] Politecnico di Torino, Department of Applied Science and Technology - DISAT, CHENERGY Group, GAME Lab, Corso Duca degli Abruzzi 24, 10129 Torino, Italy.

KEYWORDS: water based process, cellulose, paper, separator, lithium battery, filtration

ABSTRACT: Despite the high number of research articles regarding the development of new high performing electrolytes for Li-ion batteries, relatively little work has been done in the investigation of green, mechanically robust and safe commercially applicable paper separators. In this work, newly elaborated paper separators made of natural cellulose fibres are prepared by filtration dewatering. Paper separators show high porosity, wettability and mechanical robustness along with remarkable ionic transport characteristics.

The novel approach is conceptually validated by constant current charge/discharge cycling in lab-scale Li-ion all-paper “pouch” cell assembled with a four-layer handsheet stacking separator in combination with graphite-based paper-anode and a $LiFePO_4$-based paper-cathode. This unravels the possibility to implement the newly elaborated paper separators in safe, green and cost effective energy storage devices especially as it is obtained by rapid, low-cost and eco-friendly water-based paper-making techniques.

## 1. INTRODUCTION

The separator [1, 2, 3] is a critical component in batteries assembled with standard liquid electrolyte. It is placed between the positive and the negative electrode to prevent direct electrical contact between them while enabling free ionic transport and isolating electronic flow. A good separator needs to be chemically and electrochemically stable towards both the electrolyte and the electrode materials and must be mechanically robust; moreover, it should have sufficient porosity to absorb enough liquid electrolyte to assure a high ionic conductivity. However, the presence of the separator adds electrical resistance and takes up part of the limited space inside the battery, which negatively affects the overall device performance.

Since the time of their first development, nearly all microporous polymer membranes used as separator in current Li-ion batteries are based on semi-crystalline polyolefin materials [4, 5]. Nevertheless, in the last years a strong interest is mounting in developing flexible, lightweight energy storage devices to meet the various power needs of consumer electronics and military devices. Recent woks on this topic [6, 7, 8, 9, 10] highlighted that paper-like energy storage devices, such as flexible Li-ion batteries using paper as both the mechanical support and the separator, can be well adapted for low-cost applications, and that natural materials such as cellulose and its derivatives can be effectively used to substitute synthetic polymers in battery manufacturing. Moreover, the microporous polymer membranes used so far in Li-ion batteries are rather expensive and not easily disposable at the end of the battery life. Therefore, the use of natural cellulosic paper sheets or cellulosic composite separators in Li-ion batteries can be of interest once some safety issues are solved [11, 12, 13]. At present, the paper battery cannot stop the reaction when a runaway occurs, differently from a polymeric membrane that melts at high temperature eventually insulating the anode and the cathode.

Selection of an appropriate separator is critical to the battery performance, including energy density, power density, cycle life and safety. For high energy and power densities, the separator is required to be thin as well as highly porous while still remaining mechanically robust and abusable.

As already demonstrated in previous works [14, 15, 16], our research groups are involved in the study and development of paper-based energy storage and conversion devices exploiting the use of natural cellulose fibres. In view of the possible preparation of lithium battery components and cells by exploiting rapid, low-cost and eco-friendly water-based paper-making techniques, in this work we produced cellulose hand-sheets and thoroughly investigated their properties and characteristics as Li-ion battery separators.

## 2. EXPERIMENTAL

### 2.1 Fibres preparation and characterization

A bleached softwood pulp (FB, Södra Blue) was beaten in order to obtain fibres having beating freeness degree ranging between 20 and 90° Schopper-Riegler (SR) in a Valley beater [17] at 2 % consistency and 5 kg load. Note that the beating freeness degree provides a qualitative information on the fibrillation/size of cellulosic fibres. In agreement with the standard ISO 5267 [18], the freeness was evaluated by drainage measurements. Handsheets having basis weight ranging between 13 and 60 g $m^{-2}$ were produced using a Rapid Köthen handsheet former (Frank). After dewatering, the wet fibre mat was pressed between two blotting paper towels and pressed twice at 120 N $m^{-1}$ using a soft roll (0.12 m diameter, 0.25 m length and 3.0 kg mass). The obtained sheet was then dried under vacuum at 90 °C for 10 min before use. The consistency of the fibre slurries was ranged between 0.5 and 2 % w/w in order to adjust the basis weight of the final paper separator.

The retention of cellulose fibres on the filtration mat was evaluated as the ratio between the weight of the dry handsheet and the weight of the dry mass of cellulose dispersed in the slurry used for samples elaboration.

The air permeability, expressed as the time needed by 100 mL of air to flow through the paper sample (6.45 $cm^2$), and the thickness of single- and bi-layered sheets were respectively measured using a standard Gurley SPS Tester and a mechanical calliper (Adamel Lhomargy, MI20). The traction tests were performed on 5×1.5 $cm^2$ samples at a strain rate of 10 mm $min^{-1}$ (Inström). Thermal properties were investigated by means of Thermo-Gravimetric Analysis (TGA) on a TGA/SDTA-851 instrument from METTLER (Switzerland), up to 600 °C under both air and $N_2$ atmosphere.

The electrolyte uptake was obtained by measuring the weight of the paper separator before and after soaking in liquid electrolyte at different time, and successively calculated using the following equation: electrolyte uptake = $(W_f - W_i) / W_i \times 100\%$, where $W_i$ and $W_f$ are the weight of the separator before and after soaking in the liquid electrolyte, respectively. A 1.0 M $LiClO_4$ solution in a 1:1 mixture of ethylene carbonate and diethyl carbonate (EC:DEC) was used as the liquid electrolyte all along this work. EC and DEC, both battery grade, were provided by Solvay Solef, the lithium perchlorate salt was provided by Solvionic.

The ionic conductivity was determined by electrochemical impedance spectroscopy (EIS) analysis at ambient temperature. For EIS measurements, EL-test cells model ECC-Std purchased from EL-Cell GmbH, Germany (see http://el-cell.com/products/test-cells/ecc-std) were assembled by contacting 2.54 $cm^2$ discs of paper separator between two stainless steel current collectors. Before testing, the paper separator was dried at 170 °C under high vacuum for 5 h. The whole procedure was carried out in an environmentally controlled dry room (10 $m^2$, R.H. < 2 % ± 1 at 20 °C) produced by SOIMAR (Caluso, Italy). The EIS response was analysed in the frequency range between 100 kHz and 100 mHz at the open circuit potential, using a PARSTAT-2273 potentiostat/galvanostat/Frequency Response Analyser (FRA) instrument equipped with a fitting program provided with the Electrochemistry Power Suite software (version 2.58, Princeton Applied Research).

### 2.2 Electrodes preparation and characterization

The cellulose fibres (FB) bonded electrodes were obtained by filtration of an aqueous suspension of fibres, fillers and active materials, as for the production of paper sheets; therefore, they will be referred to as paper-electrodes in the manuscript. In a typical procedure, aqueous suspensions, containing highly beaten cellulose fibres (90 °SR), the active material and, eventually, a conductivity enhancer (i.e., carbon black, CB) were prepared by mechanical stirring, in order to obtain the electrode forming slurries. The active materials were graphite (GP, Timcal SLP 30) for the anode and lithium iron phosphate ($LiFePO_4$, Clariant LP2) for the cathode. Carboxymethyl cellulose (CMC) was used as dispersant for CB particles and to reduce fibre flocculation during filtration, thus resulting in improved homogeneity. Moreover, aluminium sulphate hydrate - $Al_2(SO_4)_3 \cdot 14H_2O$ (Alum, Sigma Aldrich) was used to screen the anionic charges present onto the cellulose surface and to promote the coagulation of CB particles onto fibres. The composition of aqueous suspensions used for electrodes elaboration is provided in Table 1.

| Sample | Graphite–based anode | $LiFePO_4$–based cathode |
|---|---|---|
| **Active material** | 82.5 % (graphite powder) | 69 % ($LiFePO_4$) |
| **CB** | 8.5 % | 22 % |
| **FB** | 5.5 % | 5.5 % |
| **CMC** | 3.3 % | 3.3 % |
| **Alum** | 0.2 % | 0.2 % |
| **Consistency** | 20 g $L^{-1}$ | 20 g $L^{-1}$ |

**Table 1.** Aqueous suspensions composition for the electrodes.

The procedure was previously tuned by Jabbour et al. [8], and hereby optimized. The electrode forming slurries (i.e., GP/CB/FB composite paper-anode [14] and $LiFePO_4$/CB/FB paper-cathode [16]) were filtered on a Buchner funnel. The filtering cloth was made by a sheet of the same fibres used as binder, so that this resulting paper sheet remains adherent to the electrode active material mat, also acting as a pre-separator to improve the compatibility with the paper handsheet separator once assembled in the test cell. The consistency of the forming slurries and the filtering threshold of the filtration cloth were selected in order to optimize the process, mainly reducing the filtration time. Before filtration, the slurries were stirred for about 30 minutes with a mechanical stirrer at 1000 rpm. After filtration, wet-samples were sandwiched between two blotting papers, pressed by a 3 kg roll (4 passages) and, then, dried under vacuum for 10 minutes at 90 °C. After drying, samples were stored for at least 24 h under controlled conditions (23 °C and 50 % RH) before further characterization. 100 mL of the respective starting slurry with a consistency of 20 g $L^{-1}$ was used for producing each of the electrodes. The filtration procedure resulted in an anode and a cathode of 1.96 and 1.94 g, respectively, which accounts for a rather complete materials' retention upon filtration.

In order to evaluate their specific capacity, each of the electrodes was cycled against Li metal in Swagelok-type cells. Subsequently, complete Li-ion cells were assembled in a “pouch” envelop, following the procedure previously reported by Nair et al. [19] using the paper-electrodes and the paper-separator prepared. An Arbin Instrument Testing System model BT-2000 was used for the electrochemical tests. Before cell assembly, electrodes and paper separators were dried at 170 °C under high vacuum for 5 h (thus fully excluding moisture and other impurities) and, then, transferred in the dry room. In order to verify the reproducibility of the obtained results, measurements were carried out on at least three different cells assembled with electrodes randomly selected in different portions of the sheet.

## 3. RESULTS AND DISCUSSIONS

The paper sheet must have some particular characteristics that makes it suitable for the envisaged application: (*i*) it must operate as a separator in Li-ion batteries, thus avoiding electronic contact between the electrodes, and (*ii*) it must also retain particles during the electrode casting by filtration, thus avoiding the migration of conductive particles to the back side in order to avoid internal short circuiting. Furthermore, it must have a porous structure assuring a high electrolyte uptake that is necessary to provide a high ionic conductivity in the electrochemical device as well as to ensure good particle retention during filtration.

In this work, samples of variable basic weight and thickness were prepared using papermaking of fibres with different beating degree (see Table 2). Pristine samples are made of pure FB without additives.

| Sample | Beating degree (°SR) | Basic weight (g $m^{-2}$) | Thickness (µm) | Gurley (sec) | Porosity |
|---|---|---|---|---|---|
| **A1** | 35 | 15 | 34 | / | 0.73 |
| **A2** | 50 | 15 | 37 | / | 0.72 |
| **A3** | 65 | 15 | 36 | / | 0.71 |
| **A4** | 80 | 15 | 29 | / | 0.65 |
| **A5** | 90 | 15 | 24 | 4.26 | 0.54 |
| **B1** | 35 | 30 | 59 | / | 0.69 |
| **B2** | 50 | 30 | 55 | / | 0.68 |
| **B3** | 65 | 30 | 56 | / | 0.68 |
| **B4** | 80 | 30 | 53 | / | 0.62 |
| **B5** | 90 | 30 | 38 | 92.17 | 0.52 |
| **C1** | 35 | 60 | 112 | / | 0.64 |
| **C2** | 50 | 60 | 106 | / | 0.62 |
| **C3** | 65 | 60 | 106 | / | 0.62 |
| **C4** | 80 | 60 | 106 | / | 0.59 |
| **C5** | 90 | 60 | 78 | 1355 | 0.50 |

**Table 2**. Main characteristics of the natural cellulose handsheet separators under study.

A decrease in the basis weight of the paper separator led to the formation of a faint network of fibres, which could not be properly detached, from the sheet forming fabric. Moreover, if the paper was too thin (i.e., below 20 µm), pinholes could eventually form thus generating direct paths between the anode and cathode; this would eventually lead the two electrodes to come in direct contact, resulting in short-circuiting of the cell. Whereas, an increase of basic weight would lead to lower sheet calculated apparent porosity, thus resulting in air permeability and worst electrochemical performance in real battery configuration.

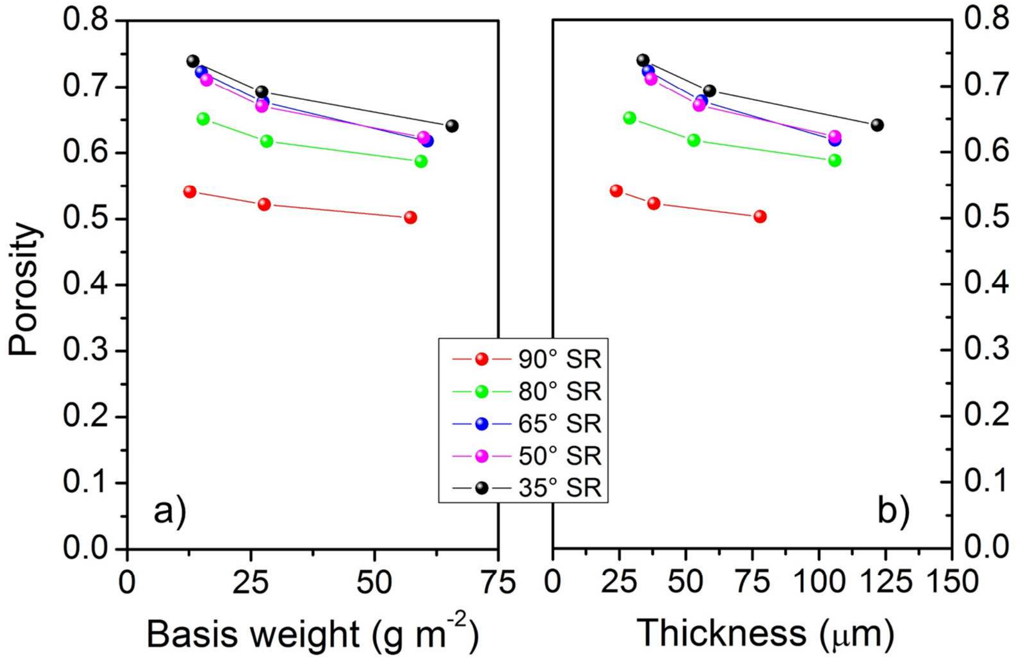


**Figure 1.** Porosity related to the basis weight (a) or the thickness (b) of the different cellulose hand-sheets with different beating degrees.

Figure 1 shows how the porosity was affected by the beating degree, the basis weight and the thickness. Porosity was inversely proportional to the beating degree, basis weight and thickness. This is due to intensive beating, which induces fibres destructuration and the production of fine cellulosic material (i.e., microfibrils and fibres debris) resulting in the formation of a densely packed fibre mat during sheet formation. Whereas, the increase of the basis weight (or the thickness) promotes the mechanical retention of cellulose fine elements in the fibre mat during the filtration process (retention ranged from 77 % for the 15 g m$^{-2}$ basis weight samples to 98 % for the 60 g m$^{-2}$ ones) and the formation of a low porosity fibre network. This results in lowering of the volume available for the electrolyte uptake and creating a structure with high tortuosity.

These hypotheses are confirmed by the electrolyte uptake test. Figure 2 and Table 3 show that handsheets with higher basis weight displayed lower electrolyte retention. As previously enlightened, this is most likely due to finest fibre retention. Electrolyte uptake significantly increased when stacking a higher number of paper handsheets. This was ascribed to the fact that the electrolyte may found more free volume to fill inside the surface roughness of stacked sheets.

| **Number of sheets** | **Basis weight (g m$^{-2}$)** | **Thickness (µm)** | **Dry weight (mg)** | **Weight after 5 min soaking (mg - %)** | **Weight after 1 h soaking (mg - %)** |
|---|---|---|---|---|---|
| **1** | 15 | 44 | 1.4 | 4.4 – 325 % | 5.1 – 377 % |
| **2** | 15 | 90 | 2.7 | 9.9 – 366 % | 10.6 – 392 % |
| **4** | 15 | 178 | 5.4 | 22.2 – 411 % | 23.1 – 425 % |
| **1** | 30 | 67 | 2.3 | 6.6 – 286 % | 7.1 – 304 % |
| **2** | 30 | 135 | 4.6 | 14.5 – 315 % | 14.8 – 321% |
| **4** | 30 | 278 | 9.3 | 31.2 – 335 % | 31.5 – 338 % |
| **1** | 60 | 127 | 5.0 | 12.4 – 248 % | 12.7 – 254 % |
| **2** | 60 | 259 | 10.2 | 27.3 – 267 % | 28.1 – 275 % |
| **4** | 60 | 515 | 20.8 | 63.1 – 302 % | 65.1 – 312 % |

**Table 3**. Electrolyte uptake values of the different cellulose handsheets beaten at 80 °SR.

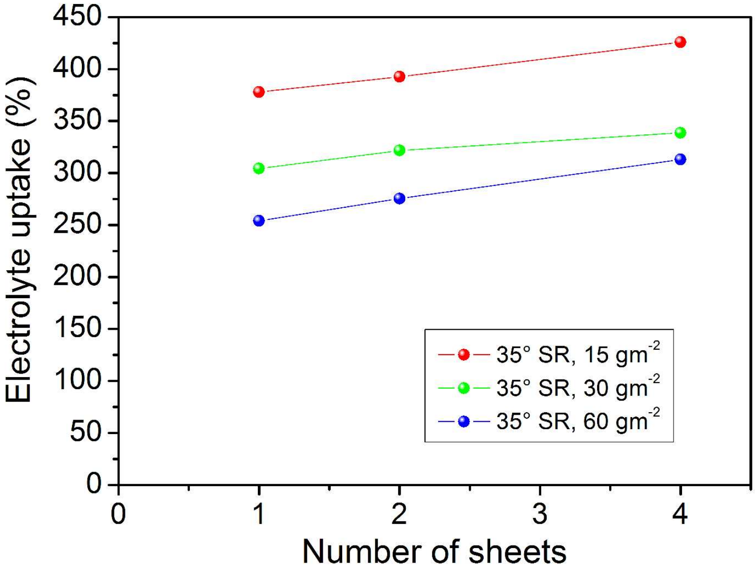


**Figure 2.** Electrolyte uptake of the different cellulose hand-sheets beaten at 35 °SR degree after 1 h of soaking time.

As shown in Figure 3 and Table 4, a decrease in the basis weight as well as in the fibre beating degree led to a drop of the handsheet mechanical properties that could cause severe breakage during cycling of the Li-ion cell.

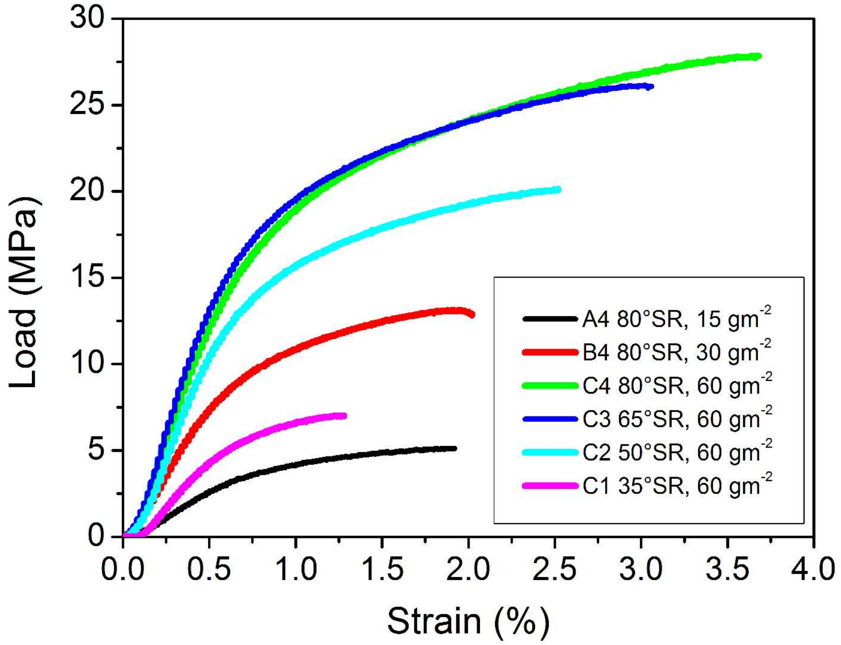


**Figure 3.** Traction tests plot for the different cellulose hand-sheets. Tests were completed 5 times for each of the samples; the results displayed are the average values.

| Sample | Load at break (MPa) | Elongation at break (%) | Young Modulus (GPa) |
|---|---|---|---|
| **C1** | 7.0 | 1.2 | 3.1 |
| **C2** | 20.1 | 2.6 | 3.6 |
| **C3** | 25.5 | 3.1 | 4.9 |
| **C4** | 27.7 | 3.7 | 5.8 |
| **B4** | 13.0 | 2.0 | 4.5 |
| **A4** | 5.0 | 1.9 | 2.2 |

**Table 4.** Summary of the results of the traction tests on the different cellulose hand-sheets. Tests were completed 5 times for each of the samples; the results displayed are the average values.

On the contrary, an increase in the basis weight led to lower sheet porosity, increased air permeability and, correspondingly, decreased ionic conductivity. Moreover, the increase in the separator weight (i.e., the mass of non-active material) induced a decrease in the specific energy density of the final Li-ion cell.

Figure 4 shows that the ionic conductivity increased with the increase in handsheet porosity, which also resulted in an increased electrolyte uptake. A value widely considered sufficient for the targeted application is about 1 mS cm$^{-1}$ [2]. Therefore, it seems that, in line with a higher electrolyte uptake, thin separators produced with lightly beaten fibres provide better performances.

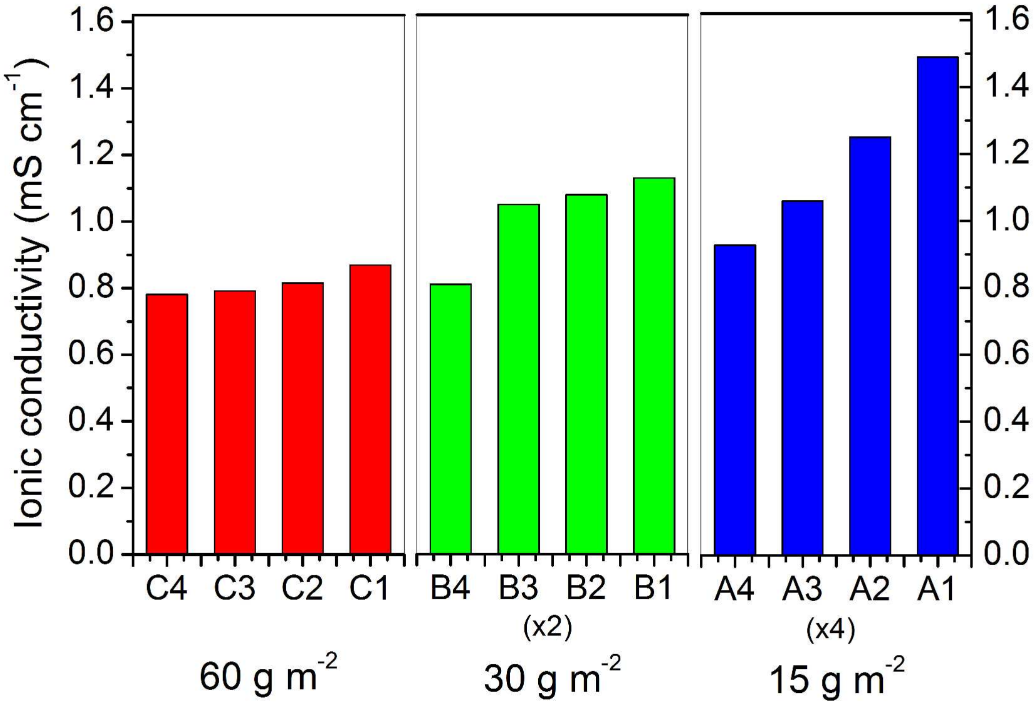


**Figure 4.** Ionic conductivity at room temperature. On the x-axis, the different samples' name is provided; it must be noted that the number of stacked handsheets was different for different basis weight (i.e., 1 for C series of samples, 2 for B series and 4 for A series), in order to obtain separators having comparable thicknesses of around 140 μm.

The MacMullin ($N_M$) number [20] was calculated in order to exclude the influence of the liquid electrolyte on the ionic conductivity.

This number is defined as $N_M = R / R_0$, where R is the resistance of the porous media saturated with the liquid electrolyte and $R_0$ is the bulk resistance of the same liquid electrolyte [21]. The ionic conductivity measured for the liquid electrolyte used in this work (i.e., 1 M $LiClO_4$ in EC:DEC) is equal to 5 mS $cm^{-1}$. The resulting averaged $N_M$ values are listed in Table 5.

| Sample | Number of sheets | Thickness (µm) | $N_M$ |
|---|---|---|---|
| **A1** | 4 | 136 | 3.33 |
| **A2** | 4 | 148 | 4.05 |
| **A3** | 4 | 144 | 4.58 |
| **A4** | 4 | 116 | 5.21 |
| **B1** | 2 | 118 | 4.58 |
| **B2** | 2 | 110 | 4.85 |
| **B3** | 2 | 112 | 4.91 |
| **B4** | 2 | 106 | 6.25 |
| **C1** | 1 | 112 | 6.02 |
| **C2** | 1 | 106 | 6.17 |
| **C3** | 1 | 106 | 6.41 |
| **C4** | 1 | 106 | 6.67 |

**Table 5.** Averaged MacMullin numbers ($N_M$) for the different paper handsheet separators prepared, evaluated at ambient temperature.

Clearly, all of the newly elaborated paper handsheet separators imbued with liquid electrolyte were able to maintain an electrolyte conductivity ranging between 15 and 30%. Noteworthy, these values are higher than the typical numbers of PE–PP based commercial Li-ion battery membrane separators (i.e., 10 % of electrolyte conductivity, $N_M$ around 10 [22-23]).

Sample A3, being representative for all the cellulose handsheets prepared, was then subjected to thermogravimetric analysis (TGA) in order to evaluate the decomposition temperature both under air and nitrogen flow (see Figure 5). For the sake of comparison, the TGA analysis of a classic trilayered polypropylene / polyethylene (PP/PE/PP) Celgard® separator is also shown.

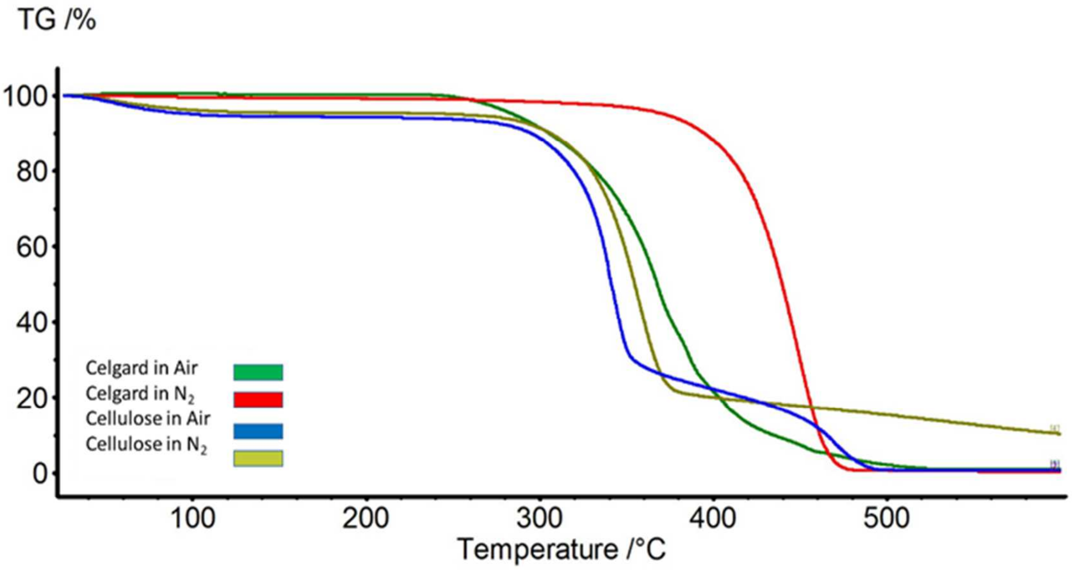


**Figure 5.** Comparison between the TGA responses both under air and in $N_2$ flux of a commercial trilayered polypropylene / polyethylene (PP/PE/PP) Celgard® polyolefin separator and a cellulose handmade separator (specifically, sample A3, representative for all of the samples prepared).

It is possible to observe that, excluding the cellulose weight loss due to elimination of adsorbed water, the handmade sheets have resistance to temperature absolutely comparable (in fact, even slightly better as for the decomposition threshold occurring about 30-50 °C later) to commercial Celgard® when both are tested under air flow. The thermogravimetric profiles reveal that the cellulose handsheet was stable up to around 300 °C, both under nitrogen as well as air flux. The first dip of about 5 wt.% before reaching 100 °C is ascribable to the loss of humidity that may absorbed during the handling of the samples for testing. This indicates that the separator easily absorbs moisture, which can react with the electrolyte and influence the cyclic stability if not properly eliminated. This is the main reason why the paper separator as well as all the paper-based components were dried at 170 °C under high vacuum for 5 h, and also carefully treated in the dry room, before cell assembly and testing. The thermal resistance of commercial Celgard® was definitely higher under $N_2$ flux (i.e., no weight loss occurring up to 400 °C); nevertheless, when one considers the thermal behaviour under air flux that is under real cell failure conditions, the cellulose handsheet separator results definitely safer than the commercial polyolefin one.

By the results above discussed, it was demonstrated that natural cellulose handsheets can be used as separators for Li-ion battery applications ensuring remarkable mechanical properties, improved thermal resistance under air flow compared to ordinary polyolefin separator; in addition, cellulose is a cheap, natural, abundant material, easily dispensable/recyclable at the end of life [24].

Moreover, in this work, we propose to filtrate the electrode materials directly on a filtering cloth in order to obtain a pre-separator and the electrodes' film in a single stage procedure. The filtering cloth was made by a sheet of the same fibres used as binder as well as to produce the handsheet separator, so that this resulting paper sheet remains adherent to the electrode active material mat. As a result, it would also act as a pre-separator to improve the compatibility with the paper handsheet separator once assembled in the test cell. Thus, several preliminary tests were carried out in order to evaluate the active material particle retention of the pre-separator filtering cloth [14].

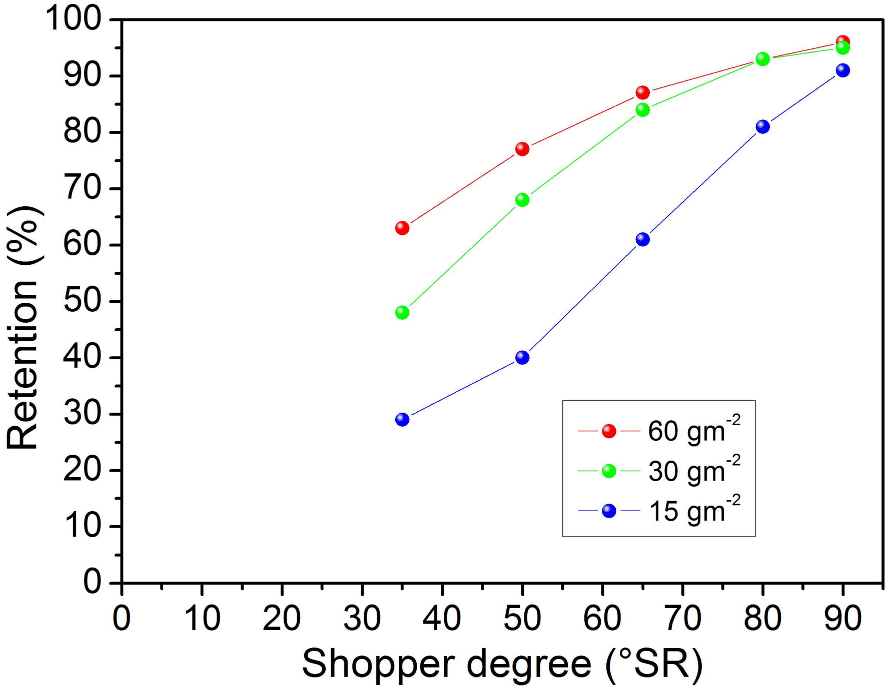


**Figure 6.** Retention tests of graphite active material particles upon filtration on cellulose handsheets.

Figure 6 shows that films with high basis weight had a better retention. Nevertheless, the beating degree appeared most likely the key parameter. In fact, more fibrillated fibres, which are obtained by intensive beating, allowed obtaining a closer structure that brings about a better retention.

Summarizing, a thick sheet produced with intensively beaten fibres displays higher retention of active material and mechanical properties. On the contrary, a thin and less beaten separator leads to high porosity, electrolyte uptake and permeability. All these characteristics lead to a lower resistance for the ions to cross the membrane while reversibly moving from an electrode to the other. Therefore, it is important to find a good compromise between all the examined characteristics in order to find the optimum separator for Li-ion batteries. In our present case, the better compromise was obtained by stacking four handsheets having basis weight of 15 g m$^{-2}$ and processed with 65 °SR fibres (namely, sample A3).

In order to confirm that such a cellulose handsheet stacking may be effectively exploited as separator, it was assembled in a full Li-ion cell using a graphite-based paper anode [14] and a $LiFePO_4$-based paper cathode [16]. This test was performed just to demonstrate the feasibility and the successful nature of the proof-of-concept, which was proposed here in order to confirm that the pure cellulose separator could properly operate in cost-effective, green Li-ion cell. The study on electrodes, their thickness modification and materials' weight balancing to get optimum performance are out of the scope of the present study.

| Sample | Basis weight (g m$^{-2}$) | Thickness (µm) | Active mater. weight (mg cm$^{-2}$) | Bulk density (g cm$^{-3}$) | Capacity (mAh cm$^{-2}$) (@ 0.85 mA) |
|---|---|---|---|---|---|
| **Graphite - based anode** | 42 | 71.5 | 2.5 | 0.59 | 0.76 |
| **Paper separator** | 15 (×4) | 36 (×4) | - | 0.54 | - |
| **$LiFePO_4$ – based cathode** | 41 | 131.6 | 1.2 | 0.31 | 0.19 |

**Table 6.** Characteristics of the different paper-cell components, the reported specific capacity values were obtained by means of half-cell test vs. Li-metal foil.

The proof-of-concept Li-ion paper-cell was assembled by sandwiching the paper separator (made of four paper hand-sheets, each about 36 µm thick) between a paper-based cathode (131.6 µm thick) and a graphite-based paper-anode (71.5 µm thick). The aspect as well as bendable characteristics of the different Li-ion paper-cell components are shown in Figure 7. The average values of basis weight, thickness, and capacity delivered of the forming electrodes are listed in

Table 6. As mentioned above, it is evident that the cathode and anode active material are unbalanced and unsuitable for a deep and thorough electrochemical analysis on the characteristics and performance of the electrodes and complete cell, which is out of the aim of this work.

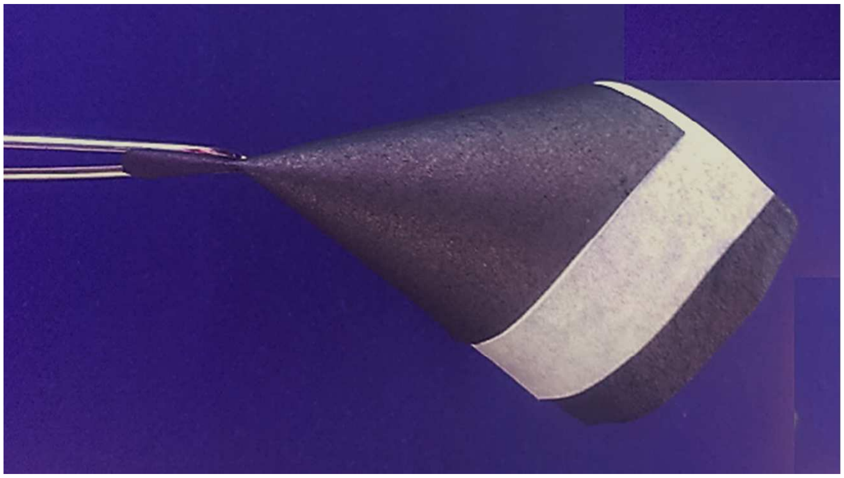


**Figure 7.** Aspect of the flexible Li-ion paper-cell components (from left to right, paper-based cathode, paper hand-sheets serving as separator and paper-based anode) used in the proof-of-concept Li-ion paper cell.

All current density and specific capacity calculations were based on the $LiFePO_4$ active material mass (theoretical specific capacity of 170 mAh $g^{-1}$). Considering the basis weight and thickness of the components, the proof-of-concept all-paper Li-ion cell had an overall basis weight of 143 g $m^{-2}$ and a whole thickness of about 350 μm. The density of the paper-cathode was noticeably lower with respect to that of the paper-anode. In fact, while the basis weight was formally the same, the cathode film produced was more than 2 times thicker than the anode. The marked difference in density between the positive and the negative paper-electrode films, together with the well-known difference in theoretical specific capacity between $LiFePO_4$ and graphite, resulted in a capacity ratio of about 4 (anode capacity/cathode capacity) for the proof-of-concept Li-ion cell. The single-electrode capacity was evaluated by testing both the electrodes in half-cell vs. Li-metal foil, at ambient temperature and with a current regime of 0.65 mA, corresponding to a C-rate of C/5 based on the cathode active material. The overall performance of the negative and positive electrodes separately tested in standard lab-scale test cells against a lithium metal counter electrode may be referred in previously published research articles [15,16].

In order to control the single-electrode potential during complete cell cycling, a lithium metal foil was added, in direct contact to the electrolyte, acting as reference electrode, thus allowing a proper monitoring on the potential profiles of each electrode separately (single-electrode potential), while cycled in Li-ion cell configuration. By this approach it was possible, for instance, to check whether the GP-based paper anode potential fell below 0.0 V vs. $Li/Li^+$, thus resulting in Li metal plating. Figure 8(a) shows the potential vs. time profiles of the single-electrodes of a Li-ion cell during charge/discharge cycling, where the blue line represents the $LiFePO_4$ cathode potential, the black line the graphitic anode one and the red line is the complete Li-ion cell potential. This cell did not undergo anodic pre-activation, thus the irreversible capacity loss during SEI layer formation was clearly evident during the initial cycle. The anodic potential remained above the Li-plating warning limit of 0.0 V vs. $Li/Li^+$, and the overall Li-ion cell potential demonstrated to be highly stable upon cycling at C/5 current regime.

Overall, from Figure 8(b) it can be observed that the specific capacity of the all-paper-cell approached 120 mAh $g^{-1}$ upon initial discharge at low C/5 current regime. The difference between this specific capacity value and the one obtained in the $LiFePO_4$/Li test cell (see ref. [16]) can be ascribed to the non-optimised balance on the electrodes' weight. The cycling performance was found to be highly stable up to 150 cycles, showing the typical behaviour expected because of the electrochemical insertion/deinsertion reaction with lithium ions for the electrodes used in the complete Li-ion system [24]. Moreover, the system demonstrated very good capacity retention while increasing the current regime, as it was able to provide more than 100 mAh $g^{-1}$ at relatively high 1C rate. This accounts for the good ionic conduction through the separator. After the initial forming cycles, the Coulombic efficiency rapidly increased to above 99% and, subsequently, remained highly stable throughout the cycles, indicating that the formed surface films remained intact and showed excellent reversible cycling after the surface reactions were completed.

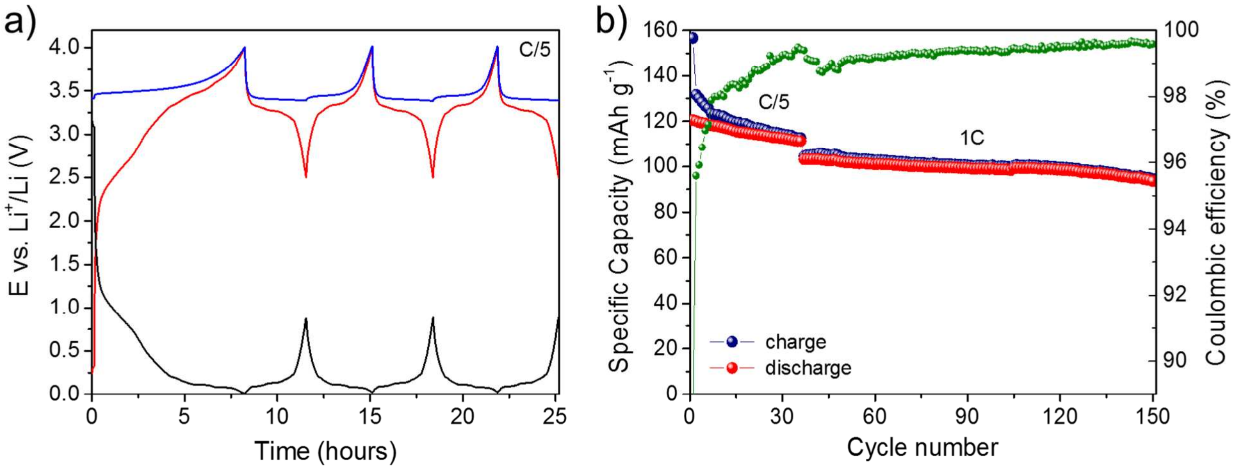


**Figure 8.** Ambient temperature galvanostatic cycling behaviour of the lab-scale all-paper Li-ion "pouch" cell. a) Complete cell profile (red line) along with both cathodic (blue line) and anodic (black line) electrode profiles extracted from the cycling test performed at C/5 current regime (the single-electrode potential was obtained using a Li-metal reference electrode); b) specific capacity vs. cycle number at C/5 and 1C current rates.

In order to effectively confirm the thermal stability of the newly elaborated paper handsheet-stacking separator, the electrochemical response in Li-ion paper cell was also evaluated in terms of constant current charge/discharge cycling at different temperatures, specifically 0, 10 and 60

°C (see Figure S1 in Supporting Information). Noteworthy, all of the test cells demonstrated the ability to be reversibly cycled at each of the selected temperatures, still retaining stable response at each of the current densities applied. This is a convincing indication of the purity and the integrity of the paper handsheet-stacking separators, thus evidencing their applicability in Li-ion secondary batteries in a wide temperature range.

Noteworthy, no organic solvents or synthetic polymer binders were used for the production of all the paper-cell components thus leading to an easy and green water-based preparation method. Moreover, cellulose fibres appear as promising candidates for the production of mechanically robust and safe separators for flexible lithium-based energy storage devices.

## 4. CONCLUSIONS

In this work, we demonstrate the effective preparation of natural cellulose handsheet separators having high porosity, wettability and mechanical strength along with remarkable ionic conductivity values. The truly water-based filtration procedure is simple, rapid and cheap; along with the ready availability of natural cellulose fibres, it allows the production of eco-friendly and sustainable materials.

A proof-of-concept lab-scale Li-ion all-paper pouch cell was assembled exploiting the use of the newly elaborated paper handsheets as separator sandwiched between a graphite-based paper anode and a $LiFePO_4$-based paper-cathode. The cell demonstrated highly stable performance upon cycling with a discharge capacity approaching 120 mAh $g^{-1}$ at an intermediate C/5 rate and a good rate capability as for the specific capacity exceeding 100 mAh $g^{-1}$ at 1C. Therefore, we confirmed the possibility to assemble eco-friendly all-paper-cells exploiting natural paper handsheet as separator as well as natural cellulose fibres as the electrode active material binder and water-based papermaking techniques for their production. With its ease of fabrication, eco compatibility and good performance, this novel approach will have a significant impact on practical applications that require high specific energy, low cost and sustainability.

## AUTHOR INFORMATION

### Corresponding Author

*(Lorenzo Zolin, lorenzo.zolin@lgp2.grenoble-inp.fr Grenoble Institute of Technology, UMR 5518 CNRS-Grenoble-INP, Domaine Universitaire, 461 rue de la Papeterie, BP 65, 38402 St. Martin d'Hères, France.

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## ACKNOWLEDGMENTS

LGP2 is part of the LabEx Tec 21 (Investissements d'Avenir – grant agreement n° ANR-11-LABX-0030) and of the Energies du Futur and PolyNat Carnot Institutes (Investissements d'Avenir – grant agreements n° ANR-11-CARN-007-01 and ANR-11-CARN-030-01).

We appreciated the help of Dr. Federico Bella (Politecnico di Torino) with the TGA analysis.

## ABBREVIATIONS

Alum, aluminum sulfate hydrate $Al_2(SO_4)_3 \cdot 14H_2O$; CB, carbon black; CMC, carboxymethyl cellulose CNT, carbon nanotube; EIS, electrochemical impedance spectroscopy; FB, cellulose fiber; GP, graphite powder; SR, Schopper – Riegler; TGA, thermogravimetric analysis.

REFERENCES

[1] S. S. Zhang, A review on the separators of liquid electrolyte Li-ion, J. Power Sources 2007, **164**, 351.

[2] H. Tanji, Secondary Batteries – Lithium Rechargeable Systems – Lithium-ion | Separators; Encyclopedia of Electrochemical Power Sources, Reference Module in Chemistry, Molecular Sciences and Chemical Engineering 2009, 356.

[3] W. Böhnstedt, A review of future directions in automotive battery separators, J Power Sources 2004, **133**, 59.

[4] D. Linden, T. B. Reddy, Handbook of Batteries, third ed., McGraw-Hill, New York, 2002, chapter 34, 34.1

[5] P. Arora and Z. Zhang, Battery separators, Chem. Rev. 2004, **104**, 4419.

[6] H. Nishide and K. Oyaizu, Toward flexible batteries, Science 2008, **319**, 737.

[7] J. Chen, Y. Liu, A. I. Minett, C. Lynam, J. Wang and G. G. Wallace, Flexible, aligned carbon nanotube/conducting polymer electrodes for a lithium-ion battery, Chem. mater. 2007, **19**, 3595.

[8] L. Jabbour, M. Destro, C. Gerbaldi, D. Chaussy, N. Penazzi and D. Beneventi, Aqueous processing of cellulose based paper-anodes for flexible Li-ion batteries, J. Mater. Chem. 2012, **22**, 3227.

[9] L. Jabbour, M. Destro, D. Chaussy, C. Gerbaldi, N. Penazzi, S. Bodoardo and D. Beneventi, Flexible cellulose/$LiFePO_4$ paper-cathodes: toward eco-friendly all-paper Li-ion batteries, Cellulose 2013, **12**, 571.

[10] S. Leijonmarck, A. Cornell, G. Lindbergh and L. Wagberg, Single-paper flexible Li-ion battery cells through a paper-making process based on nano-fibrillated cellulose, J. Mater. Chem. A 2013, **1**, 4671.

[11] X. Huang, Separator technologies for lithium-ion batteries, J. Solid State Electr. 2011, **15**, 649.

[12] F. Jiang, L. Yin, Q. Yu, C. Zhong and J. Zhang, Bacterial cellulose nanofibrous membrane as thermal stable separator for lithium-ion batteries, J. Power Sources 2015, **279**, 21.

[13] L. C. Zhang, X. Sun, Z. Hu, C. C. Yuan and C. H. Chen, Rice paper as a separator membrane in lithium-ion batteries, J. Power Sources 2012, **204**, 149.

[14] D. Beneventi, D. Chaussy, D. Curtil, L. Zolin, E. Bruno, R. Bongiovanni, M. Destro, C. Gerbaldi, N. Penazzi and S.Tapin-Lingua, Pilot-scale elaboration of graphite/microfibrillated cellulose anodes for Li-ion batteries by spray deposition on a forming paper sheet, Chem. Eng. J. 2004, **243**, 372.

[15] D. Beneventi, D. Chaussy, D. Curtil, L. Zolin, C. Gerbaldi and N. Penazzi, Highly Porous Paper Loading with Microfibrillated Cellulose by Spray Coating on Wet Substrates, Ind. Eng. Chem. Res. 2014, **53**, 10982.

[16] L. Zolin, M. Destro, D. Curtil, D. Chaussy, N. Penazzi, D. Beneventi and C. Gerbaldi, Flexible Cellulose-Based Electrodes: Towards Eco-friendly All-paper Batteries, Chemical Engineering Transactions 2014, 361.

[17] ISO 5264-2:2002, Pulps - Laboratory beating - Part 2: PFI mill method, American, National Standards Institute (ANSI), 2007.

[18] ISO 5267-2:2001, Pulps - Determination of drainability - Part 2: Canadian Standard freeness method, American National Standards Institute (ANSI), 2007.

[19] J. Nair, M. Destro, C. Gerbaldi, R. Bongiovanni and N. Penazzi, Novel multiphase electrode/electrolyte composites for next generation of flexible polymeric Li-ion cells, J. Appl. Electrochem. 2013, **43**, 137.

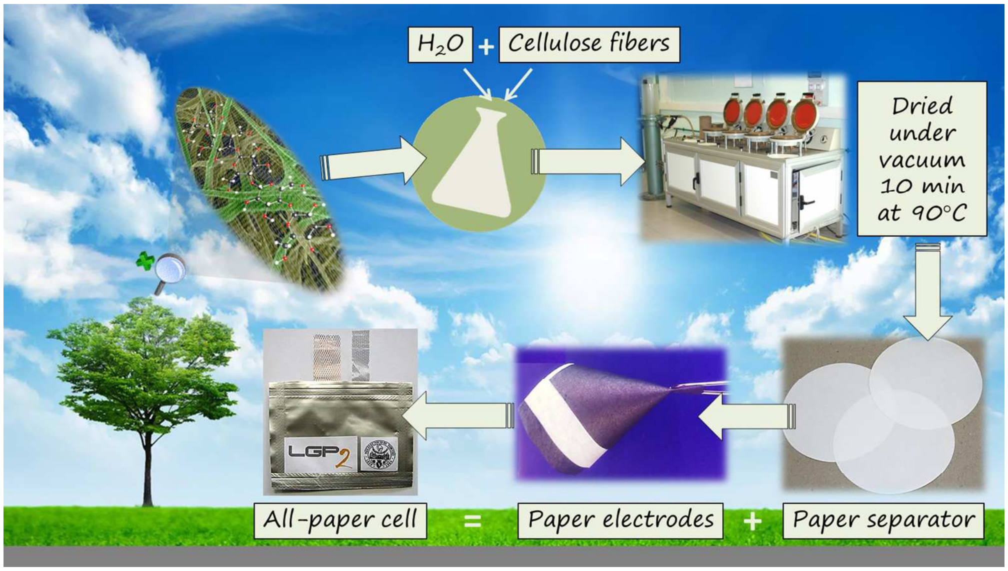
[20] L.F. Krol, D. Beneventi, F. Alloin, D. Chaussy, Microfibrillated cellulose-$SiO_2$ composite nanopapers produced by spray deposition, J. Mater. Sci. 2015, **50**, 4095.

[21] M.J. Martínez, S. Shimpalee, J.W. Van Zee, Measurement of MacMullin Numbers for PEMFC Gas-Diffusion Media, J. Electrochem. Soc. 2009, **156**, B80.

[22] J.-H. Kim, J.-H. Kim, E.-S.Choi, H.K. Yu, J.H. Kim, Q. Wu, S.-J. Chun, S.-Y.Lee, S.-Y. Lee, Colloidal silica nanoparticle assisted structural control of cellulose nanofiber paper separators for lithium-ion batteries, J. Power Source 2013, **242**, 533.

[23] S.-J. Chun, E.-S. Choi, E.-H. Lee, J.H. Kim, S.-Y. Lee, S.-Y. Lee, Eco-friendly cellulose nanofiber paper-derived separator membranes featuring tunable nanoporous network channels for lithium-ion batteries, J Mater Chem 2012, **22**, 16618.

[24] L. Jabbour, M. Destro, C. Gerbaldi, D. Chaussy, N. Penazzi and D. Beneventi, Use of paper-making techniques for the production of Li-ion paper-batteries, Nord. Pulp. Paper Res. J. 2012, **27**, 472.


$H_2O$ + Cellulose fibers
Dried under vacuum 10 min at 90°C
All-paper cell = Paper electrodes + Paper separator
LGP2