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# Pilot-scale elaboration of graphite/microfibrillated cellulose anodes for Li-ion batteries by spray deposition on a forming paper sheet

D. Beneventi [a,*], D. Chaussy [a], D. Curtil [a], L. Zolin [b], E. Bruno [a,b], R. Bongiovanni [b], M. Destro [b], C. Gerbaldi [b], N. Penazzi [b], Sandra Tapin-Lingua [c]

[a] Grenoble Institute of Technology, UMR 5518 CNRS-Grenoble-INP, Domaine Universitaire, 461 rue de la Papeterie, BP 65, 38402 St. Martin d'Hères, France
[b] Politecnico di Torino, Department of Applied Science and Technology – DISAT, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[c] FCBA – Pôle Nouveaux Matériaux, Domaine Universitaire, CS 90251, 38044 Grenoble Cedex 9, France

## HIGHLIGHTS

- Processing of Li ion cell electrodes on a pilot paper machine by spray coating.
- Use of microfibrillated cellulose in the formulation of the electrode slurry.
- Electrodes displayed excellent mechanical properties and good cycling performances.
- Pilot scale validation of new/high throughput technology for electrodes processing.

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## ABSTRACT

A new spray coating water-based process is here proposed for the rapid and reliable large-scale production of self-standing Li-ion battery electrodes using truly natural microfibrillated cellulose as binder. The graphite/carbon black microfibrillated cellulose slurry was spray coated on a wet paper substrate which, subsequently pressed and dried on a conventional pilot paper machine, led to the formation of a bilayered electrode with excellent mechanical properties, cycling performances vs Li metal comparable to those of anodes with standard composition, (i.e. Young Modulus of 2.5 GPa and specific capacity of 350 mAh $g^{-1}$ at 0.1 C) but a Coulombic efficiency (ca. 98% in the first 50 cycles) which needs to be improved to maintain good cycling performances in Li-ion systems.

This work demonstrated that well-established industrial papermaking techniques and materials can be adapted to the elaboration of well-functioning electrodes thus paving the way for the transfer the Li-ion battery industrial area of high-throughput paper production technologies.

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## 1. Introduction

Owing to an ever increasing demand for lightweight and reliable energy sources, over the last decade Li-ion batteries arose as the energy storage system of choice for both mobile electronic devices and stationary/powertrain applications [1–4]. This widespread diffusion and optimistic mid-term predictions, estimating a ca. 50 times increase in the demand for Li-ion batteries [4–6], led to reconsider materials and processes for Li-ion cells production in order to shift towards manufacturing processes with low environmental impact and batteries with higher recyclability.

Within this context, organic solvents and synthetic polymers (i.e., methylpyrrolidone and poly vinyldiene fluoride) have been progressively substituted with water and cellulose derivatives for the formulation of both anodic [7–10] and cathodic [11–13] slurries and unsustainable $LiCoO_2$ with $LiFePO_4$ [14]. The shift towards a water-based process has been carried out without substantial changes in the cell manufacturing process which, leaving aside electrolyte impregnation and cell sealing, consists in the coating of a metal substrate (Al for the cathode and Cu for the anode) with the corresponding electrode slurry, solvent evaporation and electrodes lamination and coupling with a porous separator [15,16].

In fairly recent works, natural cellulose in the form of both wood fibres and microfibrillated cellulose has been effectively used as binder for the elaboration of both single cell components (i.e., anode, cathode and separator) by casting [17] or filtration [18,19] and of complete flexible cells by filtration [20,21]. These works, showing that self-standing cell components and complete cells can be elaborated using filtration methods, demonstrate that conventional well-established papermaking technologies with high mass production capacity [22] could be adapted to battery

* Corresponding author. Tel.: +33 4 76 82 69 54; fax: +33 4 76 82 69 33.
*E-mail address:* davide.beneventi@pagora.grenoble-inp.fr (D. Beneventi).

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manufacturing. Other quick and flexible manufacturing techniques, such as spray coating [23], printing [24] and textile impregnation [25,26] have been successfully used with conventional solvent-based formulations for the elaboration of electrodes and complete cells. Despite their high potential, the proposed processes are still at the laboratory scale and none of them can couple the use of water based electrode formulations and biosourced binders with flexible and high production capacity technologies. Thereafter, the conventional coating of metal foils with organic slurries remains the process of reference for electrodes manufacturing.

In this respect, the aim of this work is to demonstrate that newly developed electrode formulations based on the use of microfibrillated cellulose as binder, spray coating and papermaking technologies can be effectively implemented on a pilot line for the large-scale production of Li-ion battery electrodes.

## 2. Materials and methods

### 2.1. Formulation of paper substrate and anode slurry

#### 2.1.1. Paper substrate

A bleached softwood pulp (BSP, Södra Blue) was intensively beaten up to a Schopper-Riegler freeness degree (which provides qualitative information on pulp components fibrillation/size) of 90°SR in a Valley beater at 2% consistency and 5 kg load and hand sheets with basis weight ranging between 13 and 60 g $m^{-2}$ were elaborated using a Rapid Köthen hand sheet former (Frank). The wet fibre mat was then sandwiched between two absorbent papers 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.

In order to evaluate the retention ability of graphite particles by the BSP wet fibre mat, bi-layered sheets were prepared on the hand sheet former by the sequential filtration of the beaten BSP and a 1.8% consistency graphite (Timcal SLP 30) aqueous slurry, followed by sheet drying under vacuum after compression at 120 N $m^{-1}$. The volume of beaten BSP and graphite slurries were adjusted in order to pour into the hand sheet former 0.5–2 g of BSP and 1.8 g of graphite.

Retention of cellulose fibres and graphite in single- and bi-layered sheets was evaluated as the ratio between the weight of dry samples and the weight of dry solid material (i.e., BSP and/or graphite) used for samples elaboration.

The air permeability, expressed as the time needed by 100 mL of air to flow through the paper sample, and the thickness of single- and bi-layered sheets were measured using a standard Gurley SPS Tester and a mechanical caliper (Adamel Lhomargy, MI20), respectively. The sheet resistance ($R_s$) of both single- and bi-layered sheets was determined using a four-probe technique (Jandel universal probe) and film conductivity ($\sigma$) was calculated as $\sigma = 1/(R_s \times d)$, where $d$ is the thickness of the conducting film.

#### 2.1.2. Anode slurry formulation

Microfibrillated cellulose (MFC) was produced with a hardwood bleached Kraft pulp. The cellulose pulp was disintegrated in water at 5% consistency for 15 min. Subsequently, a pre-refining stage was carried out using a 12″ single-disc pilot refiner system on 5 kg of oven dried pulp. The objective of this first refining stage was to obtain a slightly refined pulp with a drainage index close to 25°SR.

An enzymatic treatment was then applied on the pre-refined pulp at 5% consistency with a commercial cellulase, FibreCare R (Novozymes, Denmark), at a concentration of about 1 mL/kg. The pulp was incubated for 1 h at 50 °C.

A second refining stage was performed on the enzymatically pre-treated pulp at 5% consistency. The objectives of this stronger refining were to cut the fibres to obtain a fibre length between 300 and 400 μm and to drastically enhance the fibres fibrillation. This second refining stage was performed in the same 12″ disk refiner as used for the pre-refining step.

The pre-treated pulp was finally diluted at 2% consistency and used to produce MFC.

The equipment used for the production of microfibrillated cellulose is a homogenizer Ariete NS3075 (GEA NiroSoavi, Italy) working at a maximum flow about 1000 L/h. Five passes, i.e. 1 at 1000 bars and 4 at 1450 bars, were successively performed into the homogenizer to produce the final MFC suspension.

Aqueous slurries composed by 82.6% graphite (abbreviated as GP, Timcal, SLP 30), 8.3% carbon black (abbreviated as CB, Timcal, super C 45 Li), 5.8% MFC, 2.9% carboxymethyl cellulose (abbreviated as CMC, 90,000 g/mol, DS 0.6, Aldrich) and 0.4% $Al_2SO_4$ 18 $H_2O$ (alum), having a dry solid content ranging between 25% and 15% were prepared by dissolving CMC in the MFC slurry and the subsequent addition of carbon black. After CB dispersion by intensive stirring, GP was added and dispersed. Alum was finally added in order to promote the coagulation of carbon black with graphite and MFC and to favour water removal during slurry dewatering [20].

A commercial airless spray system (Wagner, Project Pro 119) operated at a nominal pressure of 200 bars and equipped with an elliptical section nozzle (0.76 × 0.38 mm, spray jet nominal angle 40°) was then used to test the spraying ability of the anode slurry on both BSP hand sheets and other substrates (i.e., smooth polyester films and copy paper). Each substrate was fixed to a PVC base and spray-coated manually keeping the nozzle at 40 cm from the substrate and moving it back and forth 3–4 times. The effective mass flow rate of the spray system, as obtained by weighing the mass of slurry sprayed during 10 s and averaged on 5 measurements, was 0.9 ± 0.1 kg $min^{-1}$.

### 2.2. Spray coating and pilot line set-up

Pilot runs for the production of anodes by spray deposition were performed on a pilot paper machine which, as shown in Fig. 1a, is equipped with 80 cm width Fourdrinier sheet formation section (wet-end), two dewatering presses each one applying a linear force of 30 kN $m^{-1}$ and a drying section.

In order to produce the paper substrate, the softwood pulp was beaten at 87°SR in a 16″ double disc refiner and stored in a retention tank at 0.8% consistency. A flow of 3 $m^3$ $h^{-1}$ of the 0.8% pulp slurry was diluted with 21 $m^3$ $h^{-1}$ of water and the machine head box was feed with a constant flow of 24 $m^3$ $h^{-1}$ with a fibre concentration of 0.1%. The basis weight of the paper sheet was adjusted by modifying the speed of the paper machine which ranged between 5 and 25 m $min^{-1}$.

As schematized in Fig. 1a, the spray head was placed 40 cm above the Fourdrinier wet-end, ca. 5 cm after the dry line, when cellulose fibres start to form a consolidated network. Preliminary viscosity measurements performed on GP/CB slurries containing 10% MFC or 10% CMC as binder and a dry solid content of 25%, showed that (Fig. 1b) the use of MFC instead CMC induced a pronounced shear thinning behaviour and a general increase in the slurry viscosity. This trend was associated to the typical structuration of MFC into a high viscosity hydrogel [27,28]. In order to match with the operating conditions of the spray system used in this study and to prevent nozzle clogging and flow fluctuations, the GP/CB/MFC slurry was therefore diluted to 15%. According to the experimental conditions used for both BSP sheet processing and the GP/CB/MFC layer deposition, the calculated mass ratio between the GP/CB/MFC layer and the BSP paper sheet had a constant

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