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Up-scaling of Micro fibrillated Cellulose Based Positive Electrodes for Lithium Ion Batteries by Roll-To-Roll Printing Process

Oussama El Baradai, Davide Beneventi, Fannie Alloin, Yann Bultel, Mikael Party, Didier Chaussy
Univ. Grenoble Alpes, LGP2, F-38000 Grenoble, France CNRS, LGP2, F-38000 Grenoble, France
Agefpi
Univ. Grenoble Alpes, LEPMI, F-38000 Grenoble, France CNRS, LEPMI, F-38000 Grenoble, France

Abstract: - Organic free electrodes for lithium ion batteries containing cellulose derivatives components as binding and disperser respectively, lithium iron phosphate as active material and carbon black as conductive agent were manufactured by means of a large scale technique as well as screen printing process onto a cellulosic based separator. Firstly a water based ink, was formulated and rheological properties were analyzed in order to investigate the role of each component in the ink. Electrical conductivity was tuned by adjusting the content of carbon black to insure electrical percolation. The electrode exhibits a capacity of 143 mAh/g at C/10, close to the nominal capacity of the lithium iron phosphate (150 mAh/g). At higher current rates a good retention capacity was observed with 107 mAh/g at C. Finally industrial scale printed electrodes were manufactured by means of an industrial printing machine onto a cellulose based separator. The electrodes exhibit a promising capacity of 129 mAh/g at C/10 and an electrical conductivity of 21 S/m. The industrial scale approach proposed here could be a viable route to the manufacturing of large scale and eco-sustainable electrodes.

KEYWORDS: - **Lithium ion batteries-cellulose-printing-lithium iron phosphate-industrial scale.**

I. INTRODUCTION

The continuous search for more efficient, convenient, pollution free and safe energy sources involved an increasing number of researchers in academy and industry. Electrochemical systems, such as batteries and super capacitors, could efficiently store and deliver energy on demand by playing a crucial role in this domain[1].The most commercialized battery technology are lithium ion batteries (LIBs) thanks to their high energy density (≈ 180 $Whkg^{-1}$), long term stability and average voltage (3.8V)[2]. However, energy density is not the only key factor for LIBs technology. The necessity to develop batteries that can bend, twist, stretch and compress repeatedly, while maintaining their full capability, has led to numerous efforts in developing technologically challengingly to fill the requirements of new emerging markets as well as flexible electronic.[3–6].Alternatively to the conventional coating technique, printed processes have been recognized as an appropriate method of deposition, responding to the demand of low cost and flexibility dictated by the market of flexible LIBs [7]. Contrary to the coating method, printing processes allow to print patterns with a huge possibility in terms of battery shapes with minimal extra cost production. Another requirement dictated by the market is the eco-sustainability. Compared to the classical organic based system, the aqueous processing presents several advantages, mainly in term of safety and environmental impact[8].Many articles in literature report extensive study concerning aqueous processing of cathode systems[9–13]. In this sense the introduction of water processable and bio-sourced polymers such as cellulose and its derivatives is a potentially viable route to the development of green and economical LIBs [14].Nowadays the use of cellulose derivatives as binders was reported for the fabrication of free standing flexible electrodes. Micro fibrillated cellulose (MFC) graphite composites for LIBs, having excellent flexibility and good cycle performances, are described in literature. Leijonmarck et al. reported a single flexible lithium ion battery cell, where nano-fibrillated cellulose acts as binder and separator. The battery exhibited good mechanical properties with reversible capacity of 146 $mAhg^{-1}$ at C/10[15]. In the printing process domain, the requirement of eco-sustainability leads to the development of water based inks process able by printing processes. In fact a water based ink offers different advantages, such as reduced volatility and lower reactivity [16,17].Nevertheless the transition to aqueous process encountered some difficulties related to the ink formulation, viscosity control and film processing, which must be overcome for successful developing in LIBs. Moreover the rheology of the ink has to be adjusted to match specific printing process[18]. The properties of printed films strongly depend on the viscosity and the composition of the ink. The electrode performances can be affected by the mixing sequence during ink formulation. Kim et al.[19]showed how the formulation protocol modified the electrode performances in terms of charge and discharge capacities. Lee et al [20]reported how the mixing process influences the performances of $LiCoO_2$ based electrodes. In fact, at fixed solid loading, the mixing process changes dramatically the rheological properties and then the homogeneous distribution of the carbon particles inside the composite electrode. As a result electrode polarization is reduced and cyclability and rate capability are improved. Another important aspect is the implementation of a large scale approach in

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order to be competitive with the existent techniques. At present, several studies were focused on the reduction of the cost in terms of materials[21,22] or manufacturing techniques[23]. However, further investigations are necessary to be transferred at an industrial scale concept. By considering all these technological key points, we formulated, in this work, a new water based ink containing lithium iron phosphate ($LiFePO_4$) particles and MFCsbio-sourcedbinder for the development of eco-sustainable positive electrodes for LIBs. Rheological properties of the inks were tuned to be process able by a large area and low cost manufacturing technique as screen printing process. Moreover preliminary tests were performed in an industrial printing machine with the aim to implement a large scale process production of Li-ion battery electrodes.

II. EXPERIMENTAL SECTION

A. Materials

Lithium iron phosphate covered with a carbon layer (LFP/C) particles battery grade purchased by Prayon®, with a diameter of 0.1 µm and a nominal specific capacity of 150 mAh/gwere used as active material for the fabrication of positive electrode. Carbon black (CB) was provided by Rubber Team®. Carboxymethylcellulose (CMC) with an average molecular weight of 90,000 g mol^{-1} and degree of substitution (DS) of 0.7 was purchased from Aldrich. Micro fibrillated cellulose (MFC) nanoparticles derived from bleached Domsjö pulp were purchased from "Institute Technologique Forêt Cellulose Bois-construction Ameublement" FCBA. The high grammage (HG) cellulosic based substrate was provided by Papyrus®. The low grammage cellulosic based paper (LG) was purchased by SWM®.The liquid electrolyte (battery grade) composed by 1 M Lithium hexafluorophosphate ($LiPF_6$) in a 1:1:3 volume mixture of ethylene carbonate (EC), propylene carbonate (PC) and dimethylcarbonate (DMC) was provided by Purolyte®. A lithium foil was used as counter electrode. Celgard®2500 was used as further separator to insure electrical isolation. The physical characteristics of the high grammage (HG) and low grammage (LG) substrates are listed in table 1.

Table 1. Physical characteristics of the high grammage (H.G.) and low grammage (L.G.) cellulosic based substrates

		H.G.	L.G.
Thickness	µm	142	78
Grammage	g/m^2	120	23
Porosity	%	47	80
Air permeability	cm^3/cm^2min^{-1}	417	4100

B. Rheological characterization

Rheological properties of inks were measured using a plate-plate rheometer Anton Paar. Measurements were performed at 25 °C at a fixed gap of 1 mm. The samples were equilibrated 1 minute in order to remove any previous shear history. Steady state flow measurements were made from 1 s^{-1} to 10^3 s^{-1} to determine the ink viscosity. For the dynamic viscoelastic measurements, the linear viscoelastic range was determined with a stress sweep ranging from 1 Pa to 10^4Pa at a fixed frequency of 2 Hz. A frequency sweep was performed by applying a constant shear stress of 1 Pa over a frequency range from 0.1 to 100 rad/s.

C. Ink formulation

D. Ink for screen printed laboratory process

An ink containing 40wt% of dry solid content composed of 70 wt% LFP, 27wt% CB, 2wt% MFC and1 wt% CMC was formulated. The mixing sequence used to prepare inks was based on the following protocol. Firstly CMC was added in distillated water. The obtained dispersion was mixed using a mechanical stirrer RW 14 from DEK®for 5 minutes. Secondly, obtained mixture was gently mixed at 100 rpm and MFC binder was progressively added. Another mixing step at 500 rpm was necessary to insure good dispersion of prepared suspension. CB particles were added progressively to the CMC – MFC mixture and mixed at 500 rpm for 5 minutes. Finally LFP powder was added to the suspension and the system was stirred for 10 minutes at 500 rpm.In order to have a well-dispersed stable ink, the ink was homogenized by means of three roll mills 50i equipment from EXACT and dispersed at 3000 rpm for 5 minutes by using high speed disperser mixer from DISPERMAT®.

1. Ink for large-scale roll to roll manufacturing process

The roll to roll manufacturing machine required a formulation tailored for this process. An ink was formulated with 21 wt% of dry solid content composed of 75 wt% LFP, 19 wt% CB, 5 wt% MFC and 1 wt% CMC. The mixing sequence is analogue to the protocol described previously for laboratory screen printed electrodes.

E. Printing laboratory tests

Screen printing laboratory tests were performed with a DEK® Horizon 03i screen printing press. A polyamide nylon screen mesh (208 threads per inch, 40 % open area, 70 µm thread diameter and 110 µm emulsion thickness) was used to achieve printing tests. A polymer squeegee forming an angle of 60 ° with the screen and having 70 – 75 shore hardness was used. The printing speed was fixed at 110 mm/s and the printing force at 50 N. Off contact between the substrate and the mesh was fixed at 1 mm. An area (4 cm x 25 cm) was printed onto the cellulosic based substrate and dried by heating at 105 °C for 10 minutesat ambient temperatures for 24 hours.

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F. Roll to roll printing machine tests

The large-scale electrodes were manufactured by using an EM 280 hybrid printing system provided by Gallus® with a maximum printed width fixed at 282 mm. One rotary screen printer unit was used for the tests with an open area of 53 % and a thread diameter of 250 µm;the printing pressure was fixed at 0.25 MPa. Water based ink was dried with hot air at 90 °C in order to remove water content from the electrode.

G. Physical and electrical characterization

Electrode thickness was measured using a mechanical gauge (Adamel Lhomargy®) according to the ISO 534. A quanta 200 FEI ESEM (environmental scanning microscope) was used to perform surface micrographs. Cross section and part of surface images were realized by means of a Zeiss ultra 55 FESEM. The conductivity of the electrodes was measured using a four probes ohmmeter (Jandel, Universal Probe®). Roughness measurements of the electrodes were carried out with an ALICONA® Infinite Focus optic microscope.

H. Electrochemical characterization

Disks of 0.8 cm of diameter were punched out of the printed electrode and dried at 105 °C under vacuum over one night to insure the total removal of water. The electrochemical behavior of the electrodes was tested in Teflon made two electrode cells. A lithium foil was used as counter electrode. The Galvan static cycling tests were performed at ambient temperature using an Arbin® Instrument model S/N 170795. The cells were assembled in argon-filled Jacomex®, glove box with an oxygen and water content less than 10ppm.Ionic conductivity measurements were performed in Teflon made two electrodes cell, assembled in glove box. Blocking electrodes were made by 1 cm diameter stainless steel. Ionic conductivity measurements were performed by means of impedance spectroscopy over the frequency range 100 kHz – 10 mHz with ± 10 mV amplitude using a Biologic® analyzer equipped with an EC-LAB interface.

III. RESULTS AND DISCUSSION

A. Formulation and rheological properties

1. Flow state measurements

Figure 1 shows the evolution of apparent viscosity as function of shear rate at different carbon black contents. A dependence of the apparent viscosity *vs* shear rate, typical of non-Newtonian liquid, was observed. A thinning behavior was reported with a decrease of apparent viscosity when shear rates increases, as observed by Barrie et al. [24]for carbon black dispersions. When carbon black content increases, a thickening effect was observed thanks to the ability of CB particles to form a network structure. The threshold viscosity value at 1 s^{-1}suggests the formation of a structure during the rest state. As pointed out by the dashed line bordered region in the graph, at lower shear rates, ($\dot{\gamma} < 3\,s^{-1}$), rheological curves exhibit a different behavior, associated to the carbon black content. As explained by Amari et al. carbon black particles form a network structure at lower shear rate [25].Actually a pseudo-newtonian behavior was observed for inks containing 17 and 27 wt% CB. Measured viscosity values at low shear rates, were conformed with screen printing process viscosity requirements ranging between 10 and 150 Pa*s[18] .

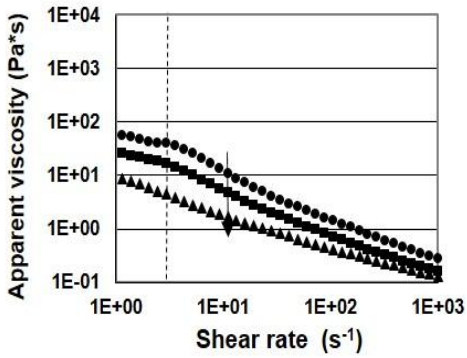

Fig 1. Viscosity as a function of shear rate for inks at 7 wt% (▲), 17wt% (■) and 27wt% (●) of carbon black content.

CB content is the parameter affecting strongly the electrical conductivity of the electrode[26]. In order to examine the effect of CB content on electrical conductivity, inks were deposed onto a cellulosic substrate and electrical conductivity was measured. Up to 17 wt% of CB, the inks present an appreciable electronic conductivity that enhances with increasing CB content. Rheological properties in table 2 confirm the thickening role played by CB in the formulation. An increment of apparent viscosity and shear stress was measured when CB content increased.

Table 2. Rheological characteristics (viscosity and shear stress) and electrical conductivity of the formulated inks as function of CB content

Ink M_s(LFP_CB_CMC_MFC)	Viscosity at $\dot{\gamma}$ = 1 s^{-1}	Shear stress at $\dot{\gamma}$ = 1 s^{-1}	Conduct.*
wt%	Pa·s	Pa	S/m
40(90_7_2_1)	9	10	Not measurable
40(80_17_2_1)	25	29	17±3
40(70_27_2_1)	56	64	35±2

*Conductivity

Despite 27 wt% of CB is notably higher than the percolation threshold in the electrode, this formulation was selected as it presents the highest electronic conductivity. Figure 2 depicts the evolution of apparent viscosity as function of shear rate. The first step consists in measuring apparent viscosity from 1 s^{-1} to 10^3 s^{-1}. A shear thinning behavior was measured. As explained by

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Lee et al. this behavior can be associated to the breakdown of agglomerates composed by cellulose and conductive components[27]. The applied shear forces induce a progressive decrease of the apparent viscosity; CMC and MFC play a role of surface modifier by affecting friction forces between particles. The same experiment was performed by varying the shear rate from 10^3 s^{-1} to 1 s^{-1}. Analogous behavior has been observed with a continuous increase of apparent viscosity when shear rate decreases.

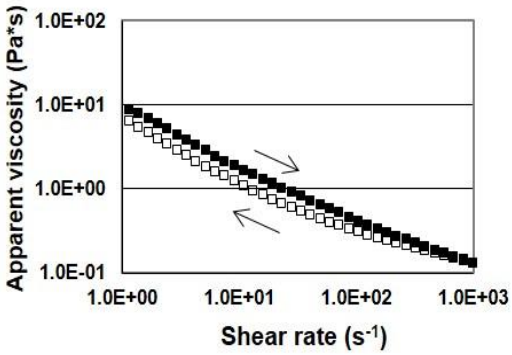

Fig 2. Apparent viscosity as function of increasing (□) and decreasing (■) shear rate of ink containing 27 wt % of CB.

2. *Oscillatory measurements*

Viscoleastic properties of the ink were investigated by oscillatory measurements. Storage and loss moduli were investigated within LVR in a frequency range from 1 to 10 Hz. As showed in figure 3 weak frequency dependence was observed for both parameters within frequency range. This is an evidence of a structured paste where the solid like behavior is predominant. This fact indicates that ink particles are connected between them in a network structure[28].

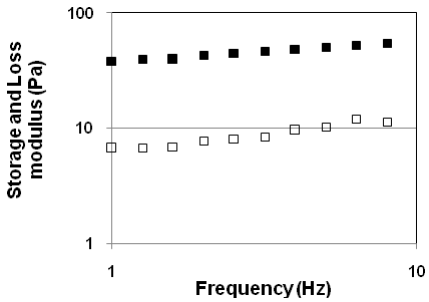

Fig 3. Storage (■) /loss modulus (□) as function of frequency of ink containing 27 wt % of CB.

3. *Influence of printing process on rheological properties*

A study of the coating thickness respect with the number of squeegee passages was realized. As showed in figure4, a linear dependence was observed until four passages. This linear dependence was previously observed in literature for screen printed solar cells [29].Up to the fourth passage the coating thickness is constant, in accordance with the fact that the theoretical volume defined as the volume between the threads of the mask and the thickness of the emulsion[30], the maximum coating thicknesses attained after 4 passages of the squeegee.

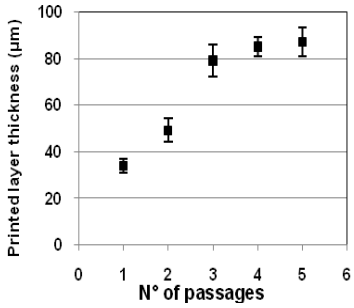

Fig 4. Printed layer thickness as function of squeegee passages.

To explain the linear dependence between coating thickness and squeegee passages, an analysis of the rheological behavior of the paste during printing process was performed. Simple shear experiments are not sufficient to completely characterize the ink. Viscoelastic measurements are more accurate to describe the viscous and elastic behaviors[31]. Neidert et al.[32] Simulated the rheological behavior of a paste prior, during and after screen printed process. The maximum shear rate of about 10^3 s^{-1} occurs when the paste is forced to pass through the screen. For our purpose we performed oscillatory measurements to simulate the ink behavior during the passage through the screen (I) and during the transfer from the screen to the substrate (II). Figure 5shows the loss angle (δ) as function of the shear stress. A δ close to 0° indicates solid like behavior whereas a δ close to 90° indicates a liquid like behavior. When ink is transferred from the screen to the substrate, the elastic behavior is predominant respect with the viscous behavior and better printability can be achieved[33]. This fact is reflected by a small loss angle δ at low shear stress. The same behavior was reported by Somalu et al. [34] for screen printing ink for fuel cell applications.

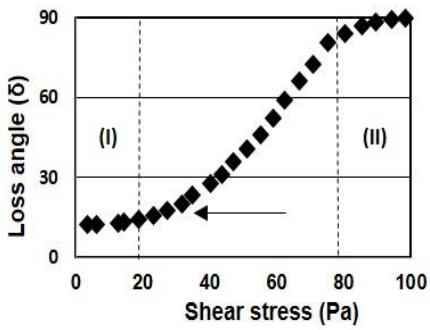

Fig 5. Loss angle as function of shear stress during printing process: (I) represents the passage of the ink through the screen while (II) represents the transfer of the ink from the screen to the substrate.

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B. Physical characterization of the electrodes

Figure6.a shows the electrode after printed process and highlights the flexibility thanks to the nature of the substrate. SEM image shows the cross section of the printed electrode (Figure 6.b). Two layers are clearly distinguished: the top layer represents the printed $LiFePO_4$ based film with a thickness of about 30 µm whereas on the bottom the cellulosic based separator is presented. The surface homogeneity of the electrode is illustrated in figure 6.c. Conventional screen printing defects such as cracking or peel off defects are not visible. At higher magnification (figure 6.d) the good dispersion of MFC (marked by 1.) and $LiFePO_4$ particles (marked by 2.) can be observed. As showed in the figure MFCs create a network structure between $LiFePO_4$ particles. This network increases the mechanical properties as described by Jabbour et al.[35].

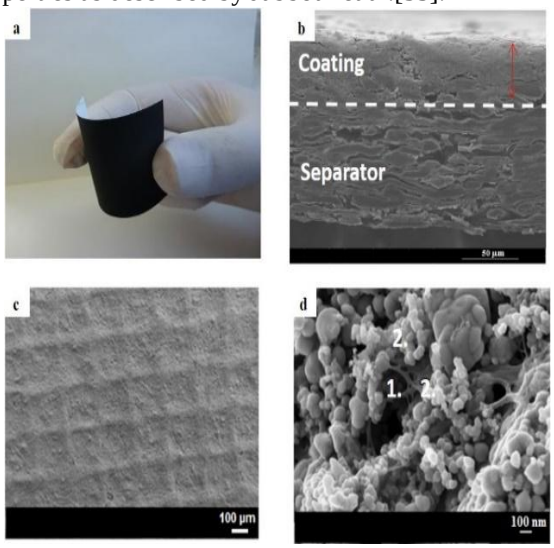

Fig 6. (a) Image illustrating the flexibility of the electrode. (b) Cross section image taken by SEM of the electrode at 100 X showing the interface between the substrate and the positive electrode. (c) Surface images taken by SEM at 50X displaying the homogeneity of the surface. (d) FESEM image taken at 50 keV showing a network structure between MFC and $LiFePO_4$ particles.

Table 3 resumes the physical properties of the printed electrodes. An electrode thickness value of 34 ±3 µm was measured. This value is in good agreement with results reported by Geyer et al.[36] for screen printed lithiated oxides, thickness of about 28 µm.Moreover, the dispersion protocol and the CB content insure high electrical conductivity value of 35±2 S/m. The measured coating weight of 31 g/m^2 is in agreement with values reported in literature for positive and negative electrodes manufactured by printing and casting technique [37,38]. The printed layer exhibits a porosity value of 68 %, comparable with screen printed electrodes having70wt % of active material powder in the formulated electrode as reported in literature [39].

Table 3. Physical characterizations of the electrode in terms of coating thickness, electronic conductivity, coating weight and porosity.

Ms(LFP_NC_CMC_MFC) / 40(70_27_2_1)		
Coating thickness	µm	34±3
Electrical conductivity	S/m	35±2
Coating weight of the layer	g/m^2	31±3
Porosity of the electrode	%	68±4

C. Electrochemical characterization of the electrodes

The cyclic voltammogram at a scan rate of 0.1 mVs^{-1} of screen printed electrodes was performed. As expected for $LiFePO_4$ based electrodes[40], an oxidation and reduction peaks at 3.6 V and 3.2 V respectively corresponding to delithiation and lithiation processes were observed. In figure7, the Galvan static cycling test is shown, at a constant C-rate of C/10, during the initial cycles. A continuous increase of the discharge and charge capacities was measured ranging from 129 mAh/g for the first discharge to 143 mAh/g, close to the nominal capacity of the $LiFePO_4$ used in this work (150 mAh/g).Furthermore a stabilization of the capacity was measured since the fifth cycle. The progressive increment of capacity is likely due to the better wet ability of electrode by the electrolyte during cycling, the same behavior was reported by Hani et al. [41].

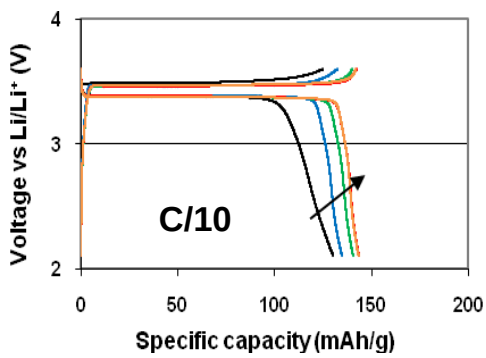

Fig 7. Discharge and charge profiles at C/10 during 5 cycles. A progressive increase of the capacity was observed until the fifth cycle.

In figure 8.a the capacities obtained at C/10 and C/5 are close, a neat decrease of the performances was observed up to C/2. The specific capacity drops from 136 mAh/g to 108 mAh/g and 106 mAh/g at C/2 and C respectively. The decrease in the specific capacity observed when increasing C-rate can be ascribed to the weak connexion between $LiFePO_4$ particles and the electronic conductive pathway due to the high porosity of the electrode i.e.

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68%[42]. A calendering process may improve the performances if performed at low calendering pressure. In fact conventional pressure load of 1 -2 ton/cm^2 used for the manufacturing of LIBs may damage the cellulosic based separator and might induce local short circuits.

Coulombic efficiency attains99.7 % after 3 cycles and remains stable for all current rates imposed, reaching 99.9 % in accordance with the electrochemical stability of $LiFePO_4$.A good capacity retention was observed with a constant capacity of 120 mAh/g during 150 cycles at C/5(figure 8.b).

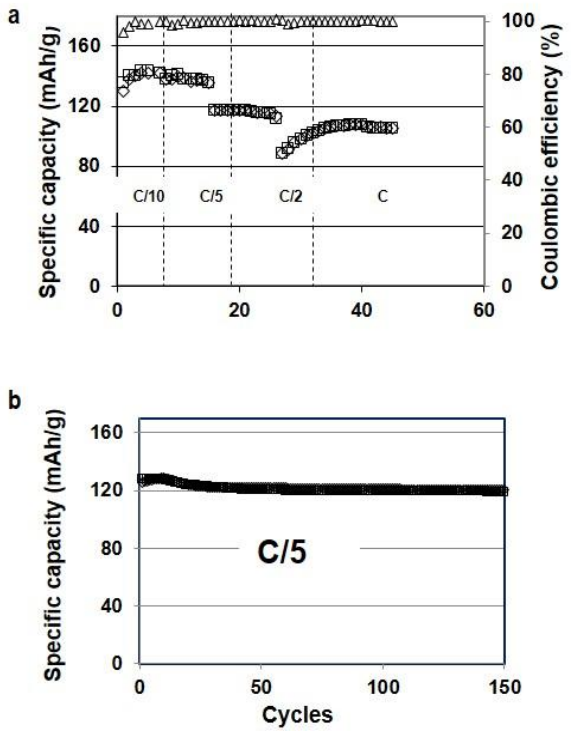

Fig 8.a Specific Charge (□)/Discharge (■) capacity and coulombic efficiency (Δ) as function of cycles. b) Charge (□) /discharge (■) specific capacity as function of cycles at C/5.

D. Scale up to an industrial process

As claimed in the introduction part, one of the objectives of this work is the production of a large scale manufactured electrodes for LIBs, in a continuous roll to roll machine. Figure9outlines the process carried out. Printing units are arranged in a row. The cellulosic based substrate (1) is diverted between the printed units (2)in order to accommodate hot hair dryers (3) with the corresponding drying length as well as well tensioning and guidance elements (4). A rewinding unit (5) collects the printed electrodes at the end of the process. As the pulsed air dryer used in this test are not enough efficient compared to Infra Red dryer for the manufacturing of printed LIBs. For this reason the speed of the machine was reduced at 5 m/min in order to maximize the evaporation time of water content inside the electrodes.

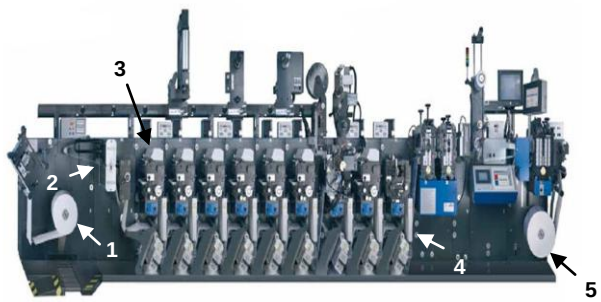

Fig 9. Roll to roll hybrid printing machine: unwinder (1), corona surface treatment (2), rotary screen printing unit (3), hot air drier (4), winding unit (5).

After printing process physical and electrochemical tests were performed to characterize large-scale manufactured electrodes. Formulation of the electrode was tailored to the new parameter of the printing machine as reported previously in the experimental section. The manufacturing process is showed during (figure10.a) and after printing step (figure10.b).

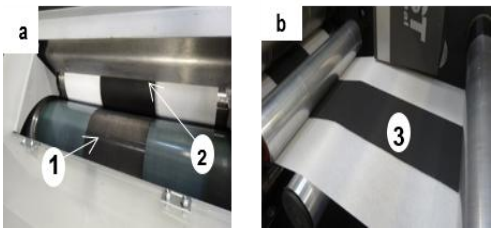

Fig 10. (a) A photograph of rotary screen printing (1) during printed process onto cellulosic based substrate (2). (b) Final large-scale printed pattern (3).

Table 4 provides the measured physical properties of the printed electrodes. Because of the new formulation required for the industrial printing machine and different printing parameters, the results are not directly comparable with the values obtained in the laboratory scale. As expected, the reduction of the dry content leads to a decrease of the thickness of the coating layer and a decrease of the coating weight as reported in literature by Krebs et al.[30]. However no variation was observed on the porosity of the electrode compared with electrodes manufactured in the laboratory and an appreciable electrical conductivity was measured for the electrodesof21 S/m.

Ms(LFP_NC_CMC_MFC) / 21(75_19_1_5)		
N° Coating layers		1
Thickness of the printed layer	µm	14±2
Coating weight of the layer	g/m^2	15±3
Electrical conductivity	S/m	21±7
Porosity	%	68±3

Table 4. Physical properties of large scale printed electrodes.

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Galvanostatic cycles at C/10 and C/5 were performed in order to examine the electrochemical performances of the electrode at low C-rates as showed in figure 11. High performances are obtained at C/10 and C/5 with 130 mAh/g and 123 mAh/g respectively. Furthermore, a high coulombic efficiency is obtained immediately with a value higher than 99% at the second cycle which remains stable.

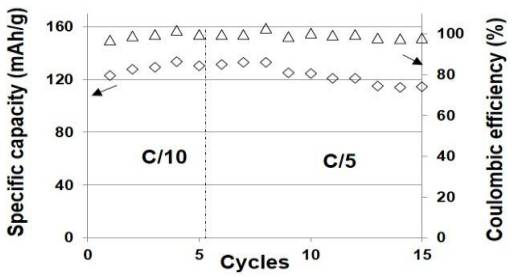

Fig 11. Specific discharge (◊) capacity and coulombic efficiency (Δ) as function of cycles for large-scale printed electrodes.

IV. CONCLUSION

The proposed work demonstrated how bio-sourced components as micro fibrillated cellulose coupled with water based solvent could be a viable route to the manufacturing of eco-sustainable positive electrodes for LIBs. As demonstrated tailored rheological properties allow the implementation of an easy up scalable manufacturing process such as screen printing technique by allowing the production of flexible electrodes printed on flexible cellulose based substrates. Physical and electrochemical results are promising for further developments. Indeed, to validate our manufacturing strategy, we performed a new procedure based on roll to roll printing technique. Preliminary results proved that screen printed electrodes can be successfully implemented on industrial scale machine for the rapid and reliable large scale production of screen printed and eco-sustainable positive electrodes.

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REFERENCES

[1] B. Scrosati, J. Garche, "Lithium batteries: Status, prospects and future", J. Power Sources. 195 (2010) 2419–2430.

[2] M. Armand, J.-M. Tarascon, "Building better batteries", Nature. 451 (2008) 652–657.

[3] N. Li, G. Zhou, F. Li, L. Wen, H.-M. Cheng, "A Self-Standing and Flexible Electrode of $Li_4Ti_5O_{12}$ Nanosheets with a N-Doped Carbon Coating for High Rate Lithium Ion Batteries", Adv. Funct. Mater. 23 (2013) 5429–5435.

[4] X. Xue, P. Deng, B. He, Y. Nie, L. Xing, Y. Zhang, et al., "Flexible Self-Charging Power Cell for One-Step Energy Conversion and Storage", Adv. Energy Mater.4 (2014).

[5] G. Nyström, A. Razaq, M. Strømme, L. Nyholm, A. Mihranyan, "Ultrafast All-Polymer Paper-Based Batteries", Nano Lett. 9 (2009) 3635–3639.

[6] H. Nishide, K. Oyaizu, "MATERIALS SCIENCE: Toward Flexible Batteries", Science. 319 (2008) 737–738.

[7] S.-H. Kim, K.-H. Choi, S.-J. Cho, S. Choi, S. Park, S.-Y. Lee, "Printable Solid-State Lithium-Ion Batteries: A New Route toward Shape-Conformable", Power Sources with Aesthetic Versatility for Flexible Electronics, Nano Lett. 15 (2015) 5168–5177.

[8] W. Porcher, P. Moreau, B. Lestriez, S. Jouanneau, F. Le Cras, D. Guyomard, "Stability of $LiFePO_4$ in water and consequence on the Li battery behaviour", Ionics. 14 (2008) 583–587.

[9] R. Dominko, M. Gaberšček, J. Drofenik, M. Bele, S. Pejovnik, "A Novel Coating Technology for Preparation of Cathodes in Li-Ion Batteries", Electrochem. Solid-State Lett. 4 (2001) A187.

[10] A. Guerfi, M. Kaneko, M. Petitclerc, M. Mori, K. Zaghib, "LiFePO4 water-soluble binder electrode for Li-ion batteries", J. Power Sources. 163 (2007) 1047–1052.

[11] W. Porcher, P. Moreau, B. Lestriez, S. Jouanneau, D. Guyomard, "Is $LiFePO_4$ Stable in Water?", Electrochem. Solid-State Lett. 11 (2008) A4.

[12] W. Porcher, B. Lestriez, S. Jouanneau, D. Guyomard, "Optimizing the surfactant for the aqueous processing of $LiFePO_4$ composite electrodes", J. Power Sources. 195 (2010) 2835–2843.

[13] S.S. Zhang, K. Xu, T.R. Jow, "Evaluation on a water-based binder for the graphite anode of Li-ion batteries", J. Power Sources. 138 (2004) 226–231.

[14] L. Jabbour, R. Bongiovanni, D. Chaussy, C. Gerbaldi, D. Beneventi, "Cellulose-based Li-ion batteries: a review, Cellulose". 20 (2013) 1523–1545.

[15] L. Jabbour, C. Gerbaldi, D. Chaussy, E. Zeno, S. Bodoardo, D. Beneventi, "Microfibrillated cellulose–graphite nanocomposites for highly flexible paper-like Li-ion battery electrodes", J. Mater. Chem. 20 (2010) 7344.

[16] K.S. Howe, E.R. Clark, J. Bowen, K. Kendall, "A novel water-based cathode ink formulation", Int. J. Hydrog. Energy. 38 (2013) 1731–1736.

[17] C.-C. Li, J.-T. Lee, X.-W. Peng, "Improvements of Dispersion Homogeneity and Cell Performance of Aqueous-Processed $LiCoO_2$ Cathodes by Using Dispersant of PAA–NH_4", J. Electrochem. Soc. 153 (2006) A809.

[18] H. Kipphan, "Handbook of print media: technologies and production methods", Springer, Berlin, 2001.

[19] W. Zhang, X. He, W. Pu, J. Li, C. Wan, "Effect of slurry preparation and dispersion on electrochemical

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ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 5, Issue 5, November 2015

performances of $LiFePO_4$ composite electrode", Ionics. 17 (2011) 473–477.

[20] G.-W. Lee, J.H. Ryu, W. Han, K.H. Ahn, S.M. Oh, "Effect of slurry preparation process on electrochemical performances of $LiCoO_2$ composite electrode", J. Power Sources. 195 (2010) 6049–6054.

[21] W. Li, Y.-X. Yin, S. Xin, W.-G. Song, Y.-G. Guo, "Low-cost and large-scale synthesis of alkaline earth metal germanate nanowires as a new class of lithium ion battery anode material", Energy Environ. Sci. 5 (2012) 8007.

[22] Y. Du, Z. Yin, X. Rui, Z. Zeng, X.-J. Wu, J. Liu, et al., "A facile, relative green, and inexpensive synthetic approach toward large-scale production of SnS_2 nanoplates for high-performance lithium-ion batteries", Nanoscale. 5 (2013) 1456.

[23] K.-Y. Kang, Y.-G. Lee, D.O. Shin, J.-C. Kim, K.M. Kim, "Performance improvements of pouch-type flexible thin-film lithium-ion batteries by modifying sequential screen-printing process", Electrochemical Acta. 138 (2014) 294–301.

[24] C.. Barrie, P.. Griffiths, R. Abbott, I. Grillo, E. Kudryashov, C. Smyth, "Rheology of aqueous carbon black dispersions", J. Colloid Interface Sci. 272 (2004) 210–217.

[25] T. Amari, K. Uesugi, H. Suzuki, "Viscoelastic properties of carbon black suspension as a flocculated percolation system", Prog. Org. Coat. 31 (1997) 171–178.

[26] T. Amari, "Flow properties and electrical conductivity of carbon black–linseed oil suspension", J. Rheol. 34 (1990) 207.

[27] J.-H. Lee, J.-S. Kim, Y.C. Kim, D.S. Zang, U. Paik, "Dispersion properties of aqueous-based LiFePO4 pastes and their electrochemical performance for lithium batteries", Ultramicroscopy. 108 (2008) 1256–1259.

[28] G.-W. Lee, J.H. Ryu, W. Han, K.H. Ahn, S.M. Oh, "Effect of slurry preparation process on electrochemical performances of $LiCoO_2$ composite electrode", J. Power Sources. 195 (2010) 6049–6054.

[29] S. Ito, P. Chen, P. Comte, M.K. Nazeeruddin, P. Liska, P. Péchy, et al., "Fabrication of screen-printing pastes from TiO2 powders for dye-sensitised solar cells", Prog. Photovolt. Res. Appl. 15 (2007) 603–612.

[30] F.C. Krebs, "Fabrication and processing of polymer solar cells: A review of printing and coating techniques", Sol. Energy Mater. Sol. Cells. 93 (2009) 394–412.

[31] M.R. Parikh, W.F. Quilty Jr, K.M. Gardiner, "SPC and setup analysis for screen printed thick films", Compon. Hybrids Manuf. Technol. IEEE Trans. On. 14 (1991) 493–498.

[32] M. Neidert, W. Zhang, D. Zhang, A. Kipka, "Screen-printing simulation study on solar cell front side AG paste", Photovolt. Spec. Conf. 2008 PVSC08 33rd IEEE, IEEE, 2008: pp. 1–4.

[33] J. Hoornstra, A.W. Weeber, H.H. de Moor, W.C. Sinke, "The importance of paste rheology in improving fine line, thick film screen printing of front side metallization", Netherlands Energy Research Foundation ECN, 1997.

[34] M.R. Somalu, N.P. Brandon, "Rheological Studies of Nickel/Scandia-Stabilized-Zirconia Screen Printing Inks for Solid Oxide Fuel Cell Anode Fabrication", J. Am. Ceram. Soc. 95 (2012) 1220–1228.

[35] J.-H. Lee, S. Lee, U. Paik, Y.-M. Choi, "Aqueous processing of natural graphite particulates for lithium-ion battery anodes and their electrochemical performance", J. Power Sources. 147 (2005) 249–255.

[36] F.M. LOPE-C2009, ed., LOPE-C International Conference and Exhibition for the Organic and Printed Electronics Industry, June 23 - 25, 2009.

[37] P.P. Prosini, R. Mancini, L. Petrucci, V. Contini, P. Villano, "$Li_4Ti_5O_{12}$ as anode in all-solid-state, plastic, lithium-ion batteries for low-power applications", Solid State Ion. 144 (2001) 185–192.

[38] A.S. Prakash, P. Manikandan, K. Ramesha, M. Sathiya, J.-M. Tarascon, A.K. Shukla, "Solution-Combustion Synthesized Nanocrystalline $Li_4Ti_5O_{12}$ As High-Rate Performance Li-Ion Battery Anode", Chem. Mater. 22 (2010) 2857–2863.

[39] D. Rotureau, J.-P. Viricelle, C. Pijolat, N. Caillol, M. Pijolat, "Development of a planar SOFC device using screen-printing technology", J. Eur. Ceram. Soc. 25 (2005) 2633–2636.

[40] D.Y.W. Yu, C. Fietzek, W. Weydanz, K. Donoue, T. Inoue, H. Kurokawa, et al., "Study of $LiFePO_4$ by Cyclic Voltammetry", J. Electrochem. Soc. 154 (2007) A253.

[41] K. Hanai, T. Maruyama, N. Imanishi, A. Hirano, Y. Takeda, O. Yamamoto,"Enhancement of electrochemical performance of lithium dry polymer battery with $LiFePO_4$/carbon composite cathode", J. Power Sources. 178 (2008) 789–794.

[42] W. Lu, A. Jansen, D. Dees, G. Henriksen, "Olivine electrode engineering impact on the electrochemical performance of lithium-ion batteries", J. Mater. Res. 25 (2010) 1656–1660.

AUTHOR'S PROFILE

Oussama El Baradai received his Ph.D. degree in '*Materials, energy and Process Engineering*' from the National Polytechnic Institute of Grenoble in 2014. He obtained the M.Sc. degree in materials from the faculty "Università degli Studi di Torino", Turin, Italy in 2011. He is co-author of two articles, 2 oral communications, 1 written communication and 1 patent in the domain of printed electrodes for lithium ion batteries. He is currently postdoc researcher at the electronic and microelectronic center of Switzerland in the domain of printed storage devices.

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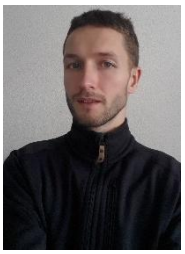
Davide Beneventi, took a degree in Materials Engineering in 1997 at the Politecnico of Turin, followed by a Master degree in Paper Science and Technology in 1998 and a Ph.D. in Chemical Engineering at the Institute National Polytechnique de Grenoble in 2002. In 1999-2004 he worked as research engineer at the Centre Technique du Papier and since 2005 he is research scientist at the National Center for Scientific Research. His studies are mainly focused on the development of new cellulose-based functional materials and on the use of froth flotation for the purification of recovered cellulose fibres.

Fannie Alloin is senior researcher (CNRS) in the LEPMI (Laboratory of electrochemistry and physico-chemistry of material and interface). She received her Ph.D Degree from the University of Grenoble, France, in 1993. She graduated from Ing. School of InstitutNationale Polytechnic of Grenoble. Her research has ranged over energy conversion, especially for lithium electrolytes (liquid electrolyte, ionic liquid, polymer electrolyte) and electrochemistry of the interface for lithium battery, lithium/sulfur and super capacitor applications. She has published 92 papers in international journals, co-authors of 20 patents. She has been main supervisor for 15 PhD students.

Professor Yann Bultel, electrochemical engineer, graduated from Grenoble Institute of Technology in 1997. He worked for Grenoble Institute of Technology since 1998 in the Laboratory of Electrochemistry and Physicochemistry of Materials and Interfaces (LEPMI). Now he has published more than 80 papers. He was also the chairperson of the 4th edition of the Fundamentals and Development of Fuel Cells conference in 2011, held in Grenoble with foreign participants about 250 from 10 different countries. He was also organizer Symposium "Physical Modeling and Simulation of Electrochemical Processes" in the 61st Annual ISE Meeting, Nice (2010) and the 63rd Annual ISE Meeting, Prague (2012). In recent years, he focused on battery and fuel cell modeling, namely, the investigation of cell ageing and diagnosis.

Professor Didier Chaussy is graduated from the French Engineering Institute of Grenoble INP in 1988 and received his Ph.D. in '*Materials and Process Engineering*' from the National Polytechnic Institute of Grenoble in 1992. He was the head of the Print Research Department at Grenoble INP Pagora until 2015. He is currently director of the Laboratory of Pulp and Paper Science and Graphic art (LGP2 UMR 5518 CNRS). He published 75 papers reviewed in international journals and participated to 34 oral communications in international conferences. He was sue director of 19 Ph.D. Thesis and he is co-author of 4 patents. His main research topics are the surface functionalization for printed electronic devoted to energy (fuel cell, Battery and solar cells) and the process engineering in calendering, thermal molding and printing processes.



Mikael Party is currently assistant engineer at the Print Research Department at Grenoble INP Pagora. He is also responsible of the technical support for the teaching session.