Flexible Cellulose-Based Electrodes: Towards Eco-friendly All-paper Batteries

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In the present work an easy paper-making technique is used for the manufacture of low cost and low environmental impact all-paper-based Li-ion cells. The cells are composed of two paper-like electrodes, prepared using micrometric-sized graphite (anode) and $LiFePO_4$ (cathode) as active materials and truly natural microfibrillated cellulose as binder, and paper hand-sheets soaked in a standard liquid electrolyte solution as separator between them. The specific capacity obtained is even superior to that of standard PVdF-binded cell assembled with the same electrodes, and remains stable over prolonged cycling, indicating that the cellulose fibres do not affect the cycling stability. In this study, no organic solvents or synthetic polymer binders are used all along the production of the cell components which, in addition, can be easily re-dispersed in water by simple mechanical stirring as well as common paper handsheets.

1. Introduction

Li-ion batteries (LIBs) are the most employed power sources in portable electronics and are promising as storage/power systems into larger units, like renewable energy plants and hybrid-electric transportation vehicles (Goodenough et al., 2013). Although performance enhancement through new optimised materials is important for LIBS larger diffusion, fundamental goals are the development of easily up-scalable and recyclable devices, along with the reduction of production costs. Enhancement of the mechanical properties through the introduction of flexible electrodes will enable these cells to be embedded into various functional systems in a wide range of innovative products such as smart cards, displays and implantable medical devices. Moreover, in order to lower their cost and reduce their environmental impact of LIBs, an effort must be made to reduce the amount of inactive components in the cell, to substitute high cost materials, such as synthetic polymer binders/separators and organic solvents, with low-cost and environmentally friendly materials and to develop new eco-friendly processes for the manufacture of cell components.

Usually, commercial LiBs consist of a graphite-based anode, a transition metal oxide based cathode (e.g., $LiCoO_2$) and a liquid electrolyte solution consisting of alkyl carbonate mixtures (e.g., ethylene carbonate and diethyl carbonate in 1/1 w/w ratio) and containing a lithium salt dissolved (e.g., $LiPF_6$). Other cell components like current collectors, binders and packaging are generally inactive, thus highly influencing the device cost and weight, but negatively affecting the overall energy density output. The widespread diffusion and optimistic mid-term predictions, estimating a ca. 50 times increase in the demand for Li-ion batteries (Jeong et al., 2011), and the need of flexible batteries for applications such as wearable devices (Rogers et al., 2010), ink jet-printed radio-frequency identification (RFID) tags (Shao et al., 2012) and roll-up reading devices (Chung et al., 2009) bring to search innovative, abundant and, recyclable and eco-friendly materials. For these reasons, there is an on-going effort for substituting organic solvents and synthetic binders (e.g., methylpyrrolidone, poly vinylidene fluoride) with water and cellulose derivatives (cheap, recyclable, raw materials) for the formulation of both anodic (Lestriez et al, 2007; Courtel et al.,

2011) and cathodic (Porcher et al., 2011) slurries; moreover, toxic and expensive cathodic materials (i.e., $LiCoO_2$) are going to be substituted by eco-friendly and more disposable $LiFePO_4$ (Li et al., 2009).

The water-based process consists in the coating of a metal substrate (Al for the cathode and Cu for the anode) with the correspondent electrode slurry, followed by the solvent evaporation, electrodes lamination and coupling with a porous separator (Zackrisson et al. 2010). The assembly keeps on with electrolyte impregnation and cell sealing similarly to a standard assembly procedure. Recent works demonstrated that natural cellulose in the form of both fibres and microfibrils can be used as binder for the elaboration of single cell components (i.e., anode, cathode and separator) by casting or filtration (Jabbour et al., 2012a; Leijonmarck et al., 2013a) and of complete flexible cells by filtration (Jabbour et al., 2013; Leijonmarck et al., 2013b) with good results. Other quick and flexible manufacturing techniques, such as spray coating (Singh et al., 2012), printing (Hu et al., 2010) and textile impregnation (Hu et al., 2011) can be successfully implemented. All 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 capacity production technologies. Therefore, the process of choice for electrodes manufacturing remains at present the conventional coating of metal foils with slurries containing toxic and expansive materials. The implementation of a pilot line procedure for the large-scale production of lithium battery negative electrodes, made of graphite as active material and microfibrillated cellulose as binder, through the spray coating method and the use of papermaking technologies has been recently demonstrated by our research groups (Beneventi et al., 2014). Here, we demonstrate that the same process can be used for the production of paper-based cathodes, then presenting the first successful assembly of the newly elaborated self-standing electrodes into a flexible Lab-scale Li-ion cell exploiting the use of a truly natural binder and water as solvent. The system assembled in a pouch type cell shows remarkably stable cycling characteristics upon prolonged cycling at ambient temperature. In our opinion, the manufacture of low cost and eco-friendly all-paper-based Li-ion cells could result fundamental for the next generation of auxiliary power generators, to be implemented for instance into futuristic hybrid and solar cars that may use photovoltaic arrays (Giannoulli et al., 2012).

2. Materials and methods

Water was added to a bleached softwood pulp (BSP, Södra Blue) in order to bring the fibre at 0.8% consistency after intensive beating up to 87 °SR (Schopper-Riegler degree) in a 16" double disc refiner. The pulp slurry was then diluted and the machine head box was fed with a fibre concentration of 0.1 % and a constant flow of 24 $m^3 h^{-1}$ to produce a thin BSP paper which will be used as substrate for coating the active material slurry. A hardwood bleached Kraft pulp was used in order to produce microfibrillated cellulose (MFC). 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 dry pulp. Aim of this first refining stage was to obtain a slightly refined pulp with drainage and a low beating degree close to 25 °SR. An enzymatic treatment was then applied to the pre-refined pulp at 5 % consistency with a commercial cellulase, FibreCare R (Novozymes, Denmark). The pulp was incubated for 1 hour 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 of 300-400 μm and to drastically enhance the fibres fibrillation. The pre-treated pulp was finally diluted at 2% consistency and used to produce the 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^{-1}. Five steps at different pressures were successively performed into the homogenizer to produce the final MFC suspension.

The cathodic aqueous slurry composition was: 69.2 wt.% of $LiFePO_4$ (Clariant, Life Power P2), 22.8 % carbon black (CB), 5.5 % MFC, 0.3 % carboxymethyl cellulose (CMC) and 0.2 % $Al_2SO_4·18H_2O$ (alum). In a typical preparation, CMC was dissolved in the MFC slurry and then carbon black was added. $LiFePO_4$ and alum were then added and thoroughly dispersed. Alum was used in order to promote the coagulation of carbon black with graphite and MFC as well as to favour water removal during slurry dewatering (Jabbour et al., 2013) while CB is the conductivity enhancer. 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°Deg) was used to finally deposit the slurry on the BSP film. The deposition was performed following the procedure described in (Beneventi et al., 2014) for graphite-based anodes.

The electrochemical behaviour of the prepared $LiFePO_4$-based sheets as potential Li-ion battery cathode was tested at ambient temperature using ECC-Std lithium test cells purchased from EL-Cell, Germany (http://el-cell.com/products/test-cells) and assembled in an Ar-filled dry glove box (MBraun Labstar, O_2 and H_2O content < 0.1 ppm). Lithium metal was used both as counter and reference electrode. The liquid electrolyte used was a 1.0 M solution of $LiClO_4$ in a 1:1 mixture of ethylene carbonate and diethyl carbonate (EC:DEC, Solvionic, France, battery grade) soaked on a standard glass–wool (Whatman GF/A) separator. A complete Li-ion cell was also assembled in a "pouch" envelop, following the procedure previously reported (Nair et al., 2013). It was composed by the paper-$LiFePO_4$ cathode under study, a

paper-graphite anode (Beneventi et al., 2014) and two layers of specifically prepared paper handsheets separator soaked in the same liquid electrolyte described above. An Arbin Instrument Testing System model BT-2000 was used for the electrochemical evaluation. The cells were charged and discharged at several constant current regimes; all current density and specific capacity calculations were based on the LiFePO$_4$ active material mass (theoretical specific capacity of 170 mAh g^{-1}). Before cell assembly, each electrode was dried at 170 °C under high vacuum for 5 h to ensure complete water removal. 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

After the deposition of the LiFePO$_4$/CB/MFC slurry over the wet fibre mat and its subsequent compression a smooth BSP sheet coated by a homogeneously distributed LiFePO$_4$/CB/MFC layer free of visible defects was obtained. In Table 1 the main characteristics of the so obtained cathode are listed: the thickness and weight of the sample are very low due to the absence of the metal current collector sheet. Thanks to the CB addition, conductivity values are obtained well suitable for the envisaged application.

Table 1. Main properties of LiFePO$_4$/CB/MFC cathode sheets elaborated by pilot spray coating.

Basis weight (g m^{-2})	Thickness (μm)	Retention (%)	R$_{sq}$ (Ω sq^{-1})	σ (S m^{-1})	Gurley (s)
37	57	~80	1004	83	136

Analysing the SEM images shown in Fig. 1, it is possible to notice that the electrode has a relatively heterogeneous surface and a dense bulk due to the tight entanglement of the highly flexible fibres and microfibrils generated during intensive beating (see the cross-sectional image of Fig. 1a).
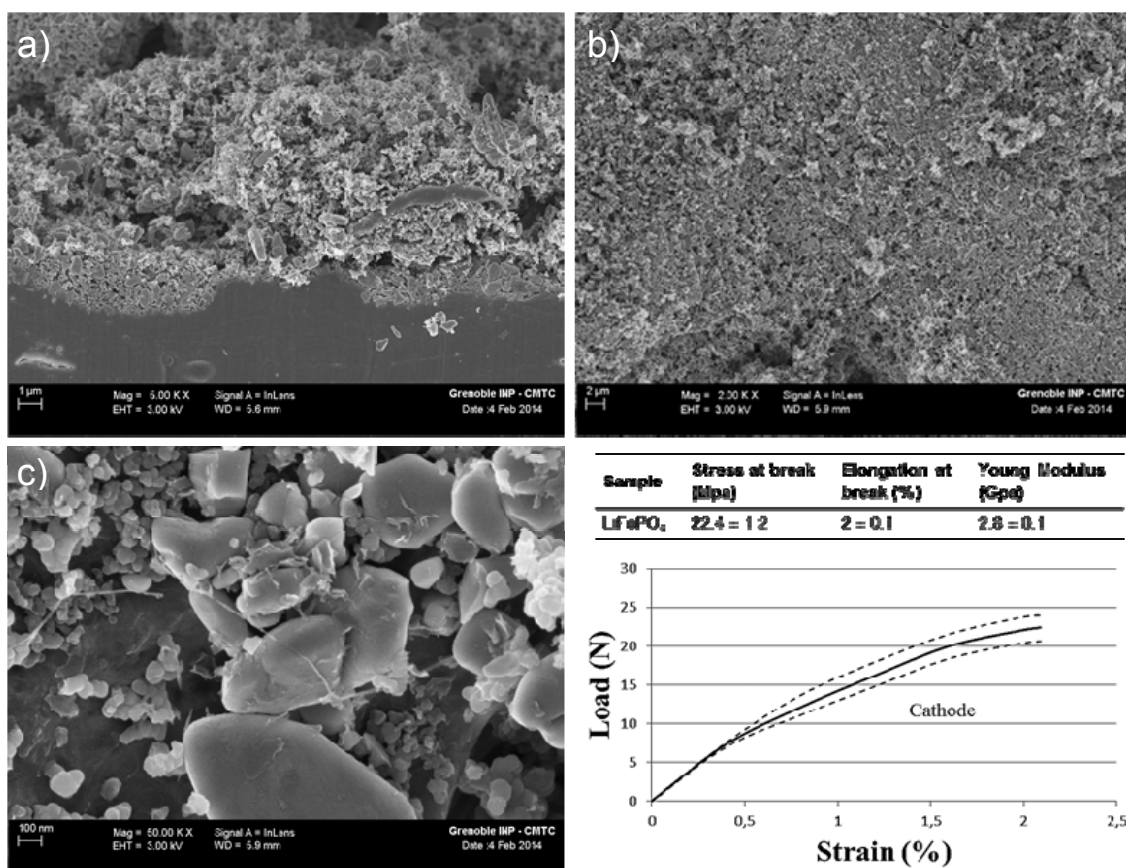

Sample	Stress at break (kPa)	Elongation at break (%)	Young Modulus (Gpa)
LiFePO$_4$	22.4 ± 1.2	2 ± 0.1	2.8 ± 0.1

Figure 1. SEM images of the spray-coated LiFePO$_4$ cathode sheet: a) cross-section, b,c) surface at different magnifications. The stress-strain curve and mechanical properties are also shown.

The image at higher magnification clearly shows that $LiFePO_4$ and CB particles are homogeneously dispersed in the whole network and that cellulose microfibrils form a finer network embedding the active material particles and consolidating the whole sheet structure.

The $LiFePO_4$/CB/MFC conductive electrode layer displayed a stress-strain curve and Young Modulus typical of paper sheets made of highly beaten softwood fibres (see Fig. 1) (Jabbour et al., 2012b). According to the recent literature (Jabbour et al., 2012a; Leijonmarck et al., 2013a), the obtained Young Modulus and stress at break are one up to two orders of magnitude higher than those of other cellulose-based Li-ion battery electrodes. These outstanding mechanical properties will account for a great mechanical resistance which is fundamental for the production of bendable cells.

In order to demonstrate the feasibility of this novel process for the production of high performing self-standing Li-ion battery electrodes, the prepared $LiFePO_4$-based sheet was assembled in a liquid electrolyte based lithium cell. Its electrochemical behaviour tested at ambient temperature and different current rates upon long-term cycling. The results are plotted in Fig. 2 which shows the specific capacity of the $LiFePO_4$/CB/MFC electrode as a function of both the cycle number and the increasing current regime (from C/10 to 5C, where 1C indicates the amount of current needed to fully charge or discharge the $LiFePO_4$ electrode in one hour). The cell delivered almost full specific capacity (i.e., 160 mAh g^{-1}) at low C/10 and the capacity retention while increasing the current regimes was overall satisfying. The cell demonstrated a stable behaviour at each of the tested currents and delivered specific capacity exceeding 140 mAh g^{-1} during cycling at reasonably high 1C rate (i.e., about 87 % of the initial capacity at C/10). In the inset, typical charge/discharge profiles are shown which were clearly well in accordance with the characteristic behaviour of the cathode material under study upon lithium insertion/de-insertion (Jabbour et al., 2013). In addition, the Coulombic efficiency (i.e., percentage ratio between the discharge and charge specific capacities) was always above 99.5% after the first cycles and remained highly stable throughout the cycles (even approaching 100 % at 1C rate), indicating good mechanical integrity of the cathode and excellent reversible cycling stability. Finally, it is important to note that the system behaviour remained correct after prolonged cycling even at very high 5C current regime, with no abnormal drift: in fact, reducing the current rate to 1C almost completely restored the specific capacity.
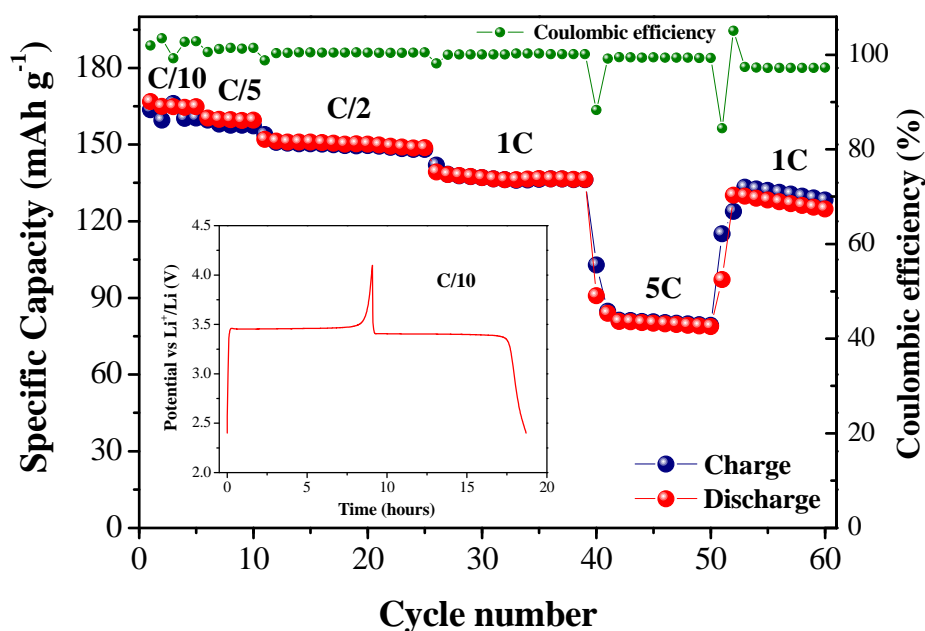

Figure 2. Ambient temperature specific capacity of the $LiFePO_4$/CB/MFC bi-layered electrode plotted as a function of the cycle number and at different discharge/charge current regimes. Inset shows the typical potential vs. time profile at C/10.

Then, it is noteworthy recalling that the specific production process adopted does not involve any organic solvents or synthetic polymer binders. Thus, as already reported (Alava et al., 2006), after prolonged cycling in lithium cells, the paper-electrodes can be easily redispersed in water by simple mechanical stirring, as well as common paper hand sheets. Upon using adequate separation techniques, such highly intriguing characteristics may lead towards the recovering of the paper battery materials and components using rapid and well-known water-based recycling processes.

Finally, a complete Li-ion test cell was fabricated by contacting the paper-based $LiFePO_4$ under study with a paper-like graphite-based anode layer (Beneventi et al., 2014), separated by two layers of specifically designed cellulose handsheets separator having a total Gurley air permeance of about 16 s (each about 100 μm thick and Gurley air permeance of about 8 s) (Jabbour et al., 2013). The assembly was housed in a coffee bag envelope (pouch cell) and, successively, sealed by hot pressing at about 100 °C. The Li-ion paper cell had an active material mass loading of about 4.5 mg cm^{-2} in $LiFePO_4$ active material and about 2.2 mg cm^{-2} in graphite active material. The selected current regimes were based on the active material mass of the $LiFePO_4$ limiting electrode using as reference value its theoretical specific capacity.

Fig. 3(a) shows a photograph of the paper-cell components before cell assembly, while Fig. 3(b) shows the cycling behaviour of the paper-cell at ambient temperature (the specific capacity was here normalised with respect to the corresponding $LiFePO_4$ capacity shown in Fig. 2). The cell operating potential was around 3.3 V vs. Li/Li^+ reflecting the electrochemical process of lithium cycling transfer from the cathode to the anode (Gerbaldi et al., 2010):

$$LiFePO_4 + 6C \quad \leftrightarrow \quad Li_xC_6 + Li_{(1-x)}FePO_4$$

It can be observed that the specific capacity of the paper-cell was near 100 % of the corresponding $LiFePO_4$. The cycling performances were found to be highly stable up to 100 cycles (in the inset some typical charge/discharge potential vs. time profiles of the Li-ion paper cell), showing the typical behaviour expected on the basis of the electrochemical insertion/deinsertion reaction with lithium ions for the electrodes used (Jabbour et al., 2013).
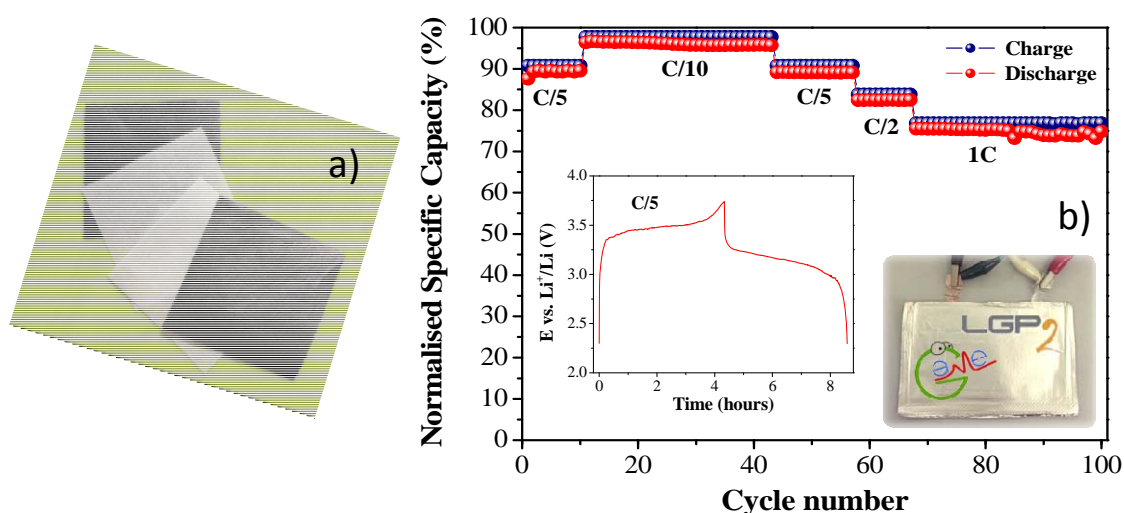

Figure 3. Ambient temperature electrochemical performances of the Li-ion paper-cell obtained by sandwiching two layers of paper separator between the two electrodes: a) paper-cell components (paper-cathode, paper-separators and paper-anode, respectively, from left to right); b) normalised specific capacity, that is percentage with respect to the $LiFePO_4$ specific capacity shown in Fig. 2 (in the inset, charge/discharge potential vs. time profiles at the 50th cycle at C/5 rate).

4. Conclusions

In this work, we demonstrated that spray coating of aqueous slurries may be successfully implemented on a pilot paper machine for the rapid and reliable large-scale production of self-standing Li-ion battery cathodes using truly natural microfibrillated cellulose as binder. The proposed water-based process is up-scalable capitalizing on papermaking technical expertise, thus allowing the production of large-surface electrodes with increased overall throughput. Furthermore, the choice of a bio-sourced binder accounts for the development of easily recyclable secondary Li-ion batteries to be integrated in active low cost flexible devices or to be variously shaped as required by emerging high-end markets.

The evaluation of the electrochemical behaviour at ambient temperature during long-term discharge/charge cycling demonstrated that it is possible to build the electrodes working properly and having characteristics similar to PVdF-bonded electrodes crafted with standard recipe. Moreover, it is demonstrated the possibility to assembly full Li-ion cells showing stable performance at each of the tested current and high Coulombic efficiency.

The obtained results enlighten the promising prospect of the specific procedures and preparation technique adopted showing that the presence of cellulose fibres does not affect the cycling ability of the

cell. Thus, the development of environmentally friendly production processes and easily recyclable devices is an open challenge for the future advancement of Li-ion batteries.

References

Alava M., Niskanen K., 2006, The physics of paper, Rep. Prog. Phys. 69,669-723.

Beneventi D., Chaussy D., Curtil D., Zolin L., Bruno E., Bongiovanni R., Destro M., Gerbaldi C., Penazzi N., Tapin-Lingua S., 2014, Pilot-scale elaboration of graphite/microfibrillated cellulose anodes for Li-ion batteries by spray deposition on a forming paper sheet, Chem. Eng. J. 243, 372-379.

Chung I.J., Kang I., 2009, Flexible display technology – Opportunity and challenge to new business applications, Molecular Crystals and Liquid Crystals 507, 1–17.

Courtel F.M., Niketic S., Duguay D., Abu-Lebdeh Y., Davidson I., 2011, Water-soluble binders for MCMB carbon anodes for lithium-ion batteries, J. Power Sources 196, 2128-2134.

Gerbaldi C., 2010, All-solid-state lithium-based polymer cells for high-temperature applications, Ionics 16, 771-786.

Giannoulli M., Yianoulis P., 2012, Study on the incorporation of photovoltaic systems as an auxiliary power source for hybrid and electric vehicles, Solar Energy 86, 441-451.

Goodenough J.B., Park K.-S., 2013, The Li-Ion Rechargeable Battery: A Perspective, J. Am. Chem. Soc. 135, 1167-1176.

Hu L., Wu H., Cui Y., 2010, Printed energy storage devices by integration of electrodes and separators into single sheets of paper, Appl. Phys. Lett. 96, 183502-183504.

Hu L., La Mantia F., Wu H., Xie X., McDonough J., Pasta M., Cui Y., 2011, Lithium-ion textile batteries with large areal mass loading, Adv. Energy Mater. 1, 1012-1017.

Jabbour L., Destro M., Gerbaldi C., Chaussy D., Penazzi N., Beneventi D., 2012a, Aqueous processing of cellulose based paper-anodes for flexible Li-ion batteries, J. Mater. Chem. 22, 3227-3233.

Jabbour L., Destro M., Gerbaldi C., Chaussy D., Penazzi N., Beneventi D., 2012b, Use of paper-making techniques for the production of Li-ion paper-batteries, Nord. Pulp Paper Res. J. 27, 472-475.

Jabbour L., Destro M., Chaussy D., Gerbaldi C., Penazzi N., Bodoardo S., Beneventi D., 2013, Flexible cellulose/LiFePO$_4$ paper-cathodes, Cellulose 20, 571-582.

Jeong G., Kim Y.-U., Kim H., Kim Y.-J., Sohn H.-J., 2011, Prospective materials and applications for Li secondary batteries, En. Env. Sci. 4, 1986-2002.

Leijonmarck S., Cornell A., Lindbergh G., Wågberg L., 2013a, Flexible nano-paper-based positive electrodes for Li-ion batteries-Preparation process and properties, Nano Energy 2, 794-800.

Leijonmarck S., Cornell A., Lindbergh G., Wagberg L., 2013b, Single-paper flexible Li-ion battery cells through a papermaking process based on nano-fibrillated cellulose, J. Mater. Chem. A1, 4671-4677.

Lestriez B., Bahri S., Sandu I., Rué L., Guyomard D., 2007, On the binding mechanism of CMC in Si negative electrodes for Li-ion batteries, Electrochem. Commun. 9, 2801-2806.

Li Z., Zhang D., Yang F., 2009, Developments of lithium-ion batteries and challenges of LiFePO$_4$ as one promising cathode material, J. Mater. Sci. 44, 2435-2443.

Nair J., Destro M., Gerbaldi C., Bongiovanni R., Penazzi N., 2013, Novel multiphase electrode/electrolyte composites for next generation of flexible polymeric Li-ion cells, J. Appl. Electrochem. 43, 137-145.

Porcher W., Lestriez B., Jouanneau S., Guyomard D., 2009, Design of aqueous processed thick LiFePO$_4$ composite electrodes for high-energy lithium battery, J. Electrochem. Soc. 156, 133-144.

Rogers J. A., Someya T., Huang Y.G., 2010, Materials and mechanics for stretchable electronic, Science 327, 1603–1607.

Shao B.T., Chen Q., Liu R., Zheng L.R., 2012, Design of fully printable and configurable chipless RFID tag on flexible substrate, Microwave Opt. Technol. Lett. 54, 226–230.

Singh N., Galande C., Miranda A., Mathkar A., Gao W., Mohana Reddy A.L., Vlad A., Ajayan P.M., 2012, Paintable battery, Scientific Reports 2, 481.

Zackrisson M., Avellan L., Ornelius J., 2010, Life cycle assessment of lithium-ion batteries for plug-in hybrid electric vehicles – Critical issues, J. Cleaner Prod. 18, 1519-1529.