Metadata of the chapter that will be visualized in SpringerLink

Book Title	Electric Vehicle Batterie	es: Moving from Research towards Innovation	
Series Title			
Chapter Title	GREENLION Project: Advanced Manufacturing Processes for Low Cost Greener Li-Ion Batteries		
Copyright Year	2014		
Copyright HolderName	Springer International Pr	ublishing Switzerland	
Corresponding Author	Family Name	Meatza	
	Particle	de	
	Given Name	Iratxe	
	Prefix		
	Suffix		
	Division		
	Organization	IK4-CIDETEC	
	Address	Pº Miramon 196, 20009, Donostia-San Sebastián, Spain	
	Division		
	Organization	Igor Cantero, Iratxe de Meatza, CEGASA	
	Address	Artapadura 11, 01013, Vitoria-Gasteiz, Spain	
	Email	imeatza@grupocegasa.com	
Author	Family Name	Miguel	
	Particle		
	Given Name	Oscar	
	Prefix		
	Suffix		
	Division		
	Organization	IK4-CIDETEC	
	Address	Pº Miramon 196, 20009, Donostia-San Sebastián, Spain	
	Email	omiguel@cidetec.es	
Author	Family Name	Cendoya	
	Particle		
	Given Name	Iosu	
	Prefix		
	Suffix		
	Division		
	Organization	IK4-CIDETEC	
	Address	Pº Miramon 196, 20009, Donostia-San Sebastián, Spain	
	Email		
Author	Family Name	Kim	
	Particle		
	Given Name	Guk-Tae	
	Prefix		
	Suffix		

	Division	Department of Physical Chemistry
	Organization	MEET Battery Research Centre, University of Muenster
	Address	Corrensstr. 28/30, 48149, Muenster, Germany
	Email	
Author	Family Name	Löffler
	Particle	
	Given Name	Nicholas
	Prefix	
	Suffix	
	Division	Department of Physical Chemistry
	Organization	MEET Battery Research Centre, University of Muenster
	Address	Corrensstr. 28/30, 48149, Muenster, Germany
	Email	
Author	Family Name	Laszczynski
	Particle	
	Given Name	Nina
	Prefix	
	Suffix	
	Division	Department of Physical Chemistry
	Organization	MEET Battery Research Centre, University of Muenster
	Address	Corrensstr. 28/30, 48149, Muenster, Germany
	Email	
Author	Family Name	Passerini
	Particle	
	Given Name	Stefano
	Prefix	
	Suffix	
	Division	Department of Physical Chemistry
	Organization	MEET Battery Research Centre, University of Muenster
	Address	Corrensstr. 28/30, 48149, Muenster, Germany
	Email	stefano.passerini@uni-muenster.de
Author	Family Name	Schweizer
	Particle	
	Given Name	Peter M.
	Prefix	
	Suffix	
	Division	
	Organization	Polytype Converting AG
	Address	26, route de la Glâne, 1184, 1701, Fribourg, Switzerland
	Email	Peter.Schweizer@polytype.com
Author	Family Name	Castiglione
	Particle	
	Given Name	Francesca
	Prefix	
	Suffix	

	Division	Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta"
	Organization	Politecnico di Milano
	Address	Via L. Mancinelli, 7, 20131, Milan, Italy
	Email	\square
Author	Family Name	Mele
	Particle	
	Given Name	Andrea
	Prefix	
	Suffix	
	Division	Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta"
	Organization	Politecnico di Milano
	Address	Via L. Mancinelli, 7, 20131, Milan, Italy
	Email	mele@chem.polimi.it
Author	Family Name	Appetecchi
	Particle	
	Given Name	Giovanni Battista
	Prefix	
	Suffix	
	Division	ENEA (Italian National Agency for New Technologies Energy and Sustainable Economic Development)
	Organization	Technical Unit UTRINN-IFC, Casaccia Research Center
	Address	Via Anguillarese 301, 00123, Rome, Italy
	Email	gianni.appetecchi@enea.it
Author	Family Name	Moreno
	Particle	
	Given Name	Margherita
	Prefix	
	Suffix	
	Division	ENEA (Italian National Agency for New Technologies Energy and Sustainable Economic Development)
	Organization	Technical Unit UTRINN-IFC, Casaccia Research Center
	Address	Via Anguillarese 301, 00123, Rome, Italy
	Email	
Author	Family Name	Brandon
	Particle	
	Given Name	Michael
	Prefix	
	Suffix	
	Division	Department of Chemical and Environmental Sciences, Materials and Surface Science Institute
	Organization	University of Limerick
	Address	Limerick, Ireland
	Email	
Author	Family Name	Kennedy
	Particle	

	Prefix	
	Suffix	
	Division	Department of Chemical and Environmental Sciences, Materials and Surface Science Institute
	Organization	University of Limerick
	Address	Limerick, Ireland
	Email	
Author	Family Name	Mullane
	Particle	
	Given Name	Emma
	Prefix	
	Suffix	
	Division	Department of Chemical and Environmental Sciences, Materials and Surface Science Institute
	Organization	University of Limerick
	Address	Limerick, Ireland
	Email	
Author	Family Name	Ryan
	Particle	
	Given Name	Kevin M.
	Prefix	
	Suffix	
	Division	Department of Chemical and Environmental Sciences, Materials and Surface Science Institute
	Organization	University of Limerick
	Address	Limerick, Ireland
	Email	Kevin.M.Ryan@ul.ie
Author	Family Name	Cantero
	Particle	
	Given Name	Igor
	Prefix	
	Suffix	
	Division	
	Organization	Igor Cantero, Iratxe de Meatza, CEGASA
	Address	Artapadura 11, 01013, Vitoria-Gasteiz, Spain
	Email	
Author	Family Name	Olive
	Particle	
	Given Name	Maxime
	Prefix	
	Suffix	
	Division	
	Organization	RESCOLL
	Address	8 Allée Geoffroy Saint Hilaire, CS 30021, 33615, Pessac Cedex, France
	Email	maxime.olive@rescoll.fr

Abstract	GREENLION is a Large Scale Collaborative Project within the FP7 (GC.NMP.2011-1) leading to the manufacturing of greener and cheaper Li-Ion batteries for electric vehicle applications via the use of water soluble, fluorine-free, high thermally stable binders, which would eliminate the use of VOCs and reduce the cell assembly cost. The project has 6 key objectives: (i) development of new active and inactive battery materials viable for water processes (green chemistry); (ii) development of innovative processes (coating from aqueous slurries) capable of reducing electrode production cost and avoid environmental pollution; (iii) development of new assembly procedures (including laser cutting and high temperature pre-treatment) capable of substantially reduce the time and the cost of cell fabrication; (iv) lighter battery modules with easier disassembly through eco-designed bonding techniques; (v) waste reduction, which, by making use of the water solubility of the binder, allows the extensive recovery of the active and inactive battery materials; and (vi) development of automated process and construction of fully integrated battery module for electric vehicle applications with optimized electrodes, cells, and other ancillaries. Achievements during the first 18 months of the project, especially on materials development and water-based electrode
	fabrication are reported herein.
Keywords (separated by '-')	Electric vehicles - Energy storage - Batteries - Alloys anodes - Water-based binders - Innovative processing - Battery manufacturing - Automation



4 Iratxe de Meatza, Oscar Miguel, Iosu Cendoya, Guk-Tae Kim,

- 5 Nicholas Löffler, Nina Laszczynski, Stefano Passerini,
- ⁶ Peter M. Schweizer, Francesca Castiglione, Andrea Mele,
- 7 Giovanni Battista Appetecchi, Margherita Moreno, Michael Brandon,
- 8 Tadhg Kennedy, Emma Mullane, Kevin M. Ryan, Igor Cantero
- 9 and Maxime Olive

Abstract GREENLION is a Large Scale Collaborative Project within the FP7 10 (GC.NMP.2011-1) leading to the manufacturing of greener and cheaper Li-Ion 11 batteries for electric vehicle applications via the use of water soluble, fluorine-free, 12 high thermally stable binders, which would eliminate the use of VOCs and reduce 13 the cell assembly cost. The project has 6 key objectives: (i) development of new 14 active and inactive battery materials viable for water processes (green chemistry); 15 (ii) development of innovative processes (coating from aqueous slurries) capable of 16 reducing electrode production cost and avoid environmental pollution; (iii) devel-17 opment of new assembly procedures (including laser cutting and high temperature 18 pre-treatment) capable of substantially reduce the time and the cost of cell fabri-19 cation; (iv) lighter battery modules with easier disassembly through eco-designed 20 bonding techniques; (v) waste reduction, which, by making use of the water 21

I. de Meatza (\boxtimes) · O. Miguel · I. Cendoya

IK4-CIDETEC, P° Miramon 196, 20009 Donostia-San Sebastián, Spain e-mail: imeatza@grupocegasa.com

O. Miguel e-mail: omiguel@cidetec.es

G.-T. Kim · N. Löffler · N. Laszczynski · S. Passerini Department of Physical Chemistry, MEET Battery Research Centre, University of Muenster, Corrensstr. 28/30, 48149 Muenster, Germany e-mail: stefano.passerini@uni-muenster.de

P.M. Schweizer Polytype Converting AG, 26, route de la Glâne, 1184, 1701 Fribourg, Switzerland e-mail: Peter.Schweizer@polytype.com

F. Castiglione · A. Mele

Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano, Via L. Mancinelli, 7, 20131 Milan, Italy e-mail: mele@chem.polimi.it

© Springer International Publishing Switzerland 2014 E. Briec and B. Müller (eds.), *Electric Vehicle Batteries: Moving from Research towards Innovation*, Lecture Notes in Mobility, DOI 10.1007/978-3-319-12706-4_4

I. de Meatza et al.

solubility of the binder, allows the extensive recovery of the active and inactive 22 battery materials; and (vi) development of automated process and construction of 23 fully integrated battery module for electric vehicle applications with optimized 24 electrodes, cells, and other ancillaries. Achievements during the first 18 months of 25 the project, especially on materials development and water-based electrode fabri-26 cation are reported herein. 27

Keywords Electric vehicles • Energy storage • Batteries • Alloys anodes • Water-28 based binders · Innovative processing · Battery manufacturing · Automation 29

30

1 Introduction and State of the Art 31

Society's current individual mobility behavior is creating a plethora of looming 32 problems, such as fossil carbon intensity and the concomitant consequences 33 regarding fossil resource supply or the emissions of pollutants such as nitrogen and 34 sulfur oxides (NO_x, SO_2) and particulate matter. While pollutant problems can be 35 addressed by catalytic converters and filters, expectations run high that the green-36 house gas and resource problems can be addressed by substituting internal com-37 bustion engine (ICE) cars with battery powered electric cars (BEV). Most of the 38 major car manufacturers have announced BEVs as part of their product lines in the 39 immediate future. 40

Lithium ion batteries already dominate the consumer portable electronic and 41 telecommunications market due to their higher power and energy density and they 42 are also indicated as the option for the next generation of hybrid and electric 43 vehicles (HEV, EV). The wide deployment of lithium ion batteries in the auto-44 motive industry would have tremendous consequences on the battery-market and it 45 would further strengthen the central role of these systems in the field of energy 46

M. Brandon · T. Kennedy · E. Mullane · K.M. Ryan Department of Chemical and Environmental Sciences, Materials and Surface Science Institute, University of Limerick, Limerick, Ireland e-mail: Kevin.M.Ryan@ul.ie

I. de Meatza · I. Cantero

Igor Cantero, Iratxe de Meatza, CEGASA, Artapadura 11, 01013 Vitoria-Gasteiz, Spain M. Olive

RESCOLL, 8 Allée Geoffroy Saint Hilaire, CS 30021, 33615 Pessac Cedex, France e-mail: maxime.olive@rescoll.fr

G.B. Appetecchi · M. Moreno ENEA (Italian National Agency for New Technologies Energy and Sustainable Economic Development), Technical Unit UTRINN-IFC, Casaccia Research Center, Via Anguillarese 301, 00123 Rome, Italy e-mail: gianni.appetecchi@enea.it



Fig. 1 Key levels of battery manufacturing value chain under development in GREENLION

47 storage. For that, considerable efforts are now focused on the development and 48 realization of lithium ion batteries able to fulfill the requirement necessary for the 49 application in HEV and EV. When the present lithium ion technology is considered, 50 the safety and cost of batteries appear as the main drawbacks holding the intro-51 duction of this technology into the automotive market.

In order to tackle these issues from the manufacturing perspective before the final battery pack integration, the GREENLION consortium has identified three key levels in the value chain (Fig. 1), namely battery components, especially electrode processing, individual cells and battery modules, oriented to the battery pack for EVs.

As stated previously, the automotive industry is demanding for safe and low cost lithium ion (Li-ion) batteries to bring to the market higher range and affordable BEVs to substitute the ICE vehicles that won the battle a 100 years ago, due to Ford's mass production line, low oil cost and insufficient battery technology of the time.

The current Li-ion battery manufacturing process has advanced greatly in the last 20 years thanks to the consumer portable electronic industry and those developments are also the basis for the production of large format cells demanded for automotive application. The Li-ion battery production comprises a sequence of steps that can be summarized as electrode preparation, cell fabrication and battery module assembly, as presented in Figs. 1 and 2.

68 1.1 Electrodes

The initial large scale automotive prototype lithium ion batteries use hard carbon or graphite as negative electrode materials, and nickel-substituted cobalt and/or manganese oxide (NCA, NMC), manganese spinel oxide or lithium iron phosphate as cathode active materials. Since for this first stage, the basic formulations and



I. de Meatza et al.



ECO: Eco-friendly; COST: Lower cost; WASTE: waste reduction; RECYC: easier recycling

Fig. 2 Breakdown of steps for Li-ion battery manufacturing and improvements proposed in GREENLION

9	Layout: T1 Standard Unicode	Book ID: 329226_1_En	Book ISBN: 978-3-319-12705-7
Ņ	Chapter No.: 4	Date: 19-10-2014 Time: 2:21 pm	Page: 5/16

GREENLION Project: Advanced Manufacturing Processes ...

materials from consumer batteries are being used, the costs of the electrodes still
 need to be decreased for the final use in automotive batteries.

Numerous groups have been studying and developing new electrode and elec-75 trolyte materials with suitable characteristics and improved performance for the 76 realization of greener and lower cost batteries, and promising results have already 77 been achieved [1, 2]. However, to realize batteries with such kinds of properties, not 78 only active and electrolyte materials have to be taken into account but, in general, 79 all the battery components and even the process to realize the batteries need to be 80 considered and improved. Apart from the continuous research on materials with 81 increasing energy and power density, safety, durability and cycle life (targets of at 82 least 30 % improvement for 2020), current estimations point to a 10-15 % 83 reduction cost from the active materials that can reach up to 35 % through electrode 84 process optimization [3]. 85

Several studies are now also focused on the improvement of the inactive materials as well as of the electrode production. In this context, a key role is certainly played by the binder. As a matter of fact, this component is not only responsible for the binding of the active materials and the conductive agent to the metal current collectors, but it also strongly affects the electrode processing. Consequently, the improvement of the binder must necessarily be considered as a key point for the development of new safe and greener batteries.

An interesting example of the influence of the binder is observed when the 93 preparation of electrodes based on lithium iron phosphate (LiFePO₄) is considered. 94 LiFePO₄ displays high stability of the capacity during prolonged cycling; it is 95 environment-friendly, cheap, and safe [4, 5]. Because of these characteristics, it is 96 considered as a very attractive cathodic material. So far, however, most of the 97 research and the development in composite cathodes have been focused on the use 98 of fluorinated binders and practically all commercial lithium-ion batteries are made 99 using poly(vinylidene fluoride) (PVDF) as the binder. However, this polymer is 100 costly (industrial cost in the multiton scale is around 15-18 EUR/kg); it requires the 101 use of volatile organic compounds that are often toxic (like N-methyl pyrrolidone, 102 NMP) in the processing, and it is not easily disposable at the end of the battery life. 103 The introduction of alternative binders, as well as an improved preparation pro-104 cedure, is necessary. 105

Recently, alternative binders have been introduced for the manufacture of 106 anodes for lithium-ion batteries, like styrene butadiene rubber (SBR) that can be 107 processed in water. Among them, one of the most interesting is certainly the sodium 108 salt of carboxymethyl cellulose (CMC), which is a water-soluble material. This is 109 certainly the greatest advantage of CMC because it allows processing in aqueous 110 slurries rather than in polluting, health and environment unfriendly, volatile 111 organic-compound-based slurries. The second great advantage of CMC resides in 112 its easy disposability at the end of the life of the battery. Once the electrode is 113 extracted, the active electrode material can be easily recovered by pyrolysis of the 114 binder. Last but not least is the material cost. The CMC industrial price is about 1-2 115 EUR/kg, i.e., about 1 order of magnitude lower than PVDF. 116

1.2 Cell Assembly

6

117

Chapter No.: 4

Layout: T1 Standard Unicode

Battery pricing is significantly impacted by material costs and manufacturing cost in mass production due to the multitude of operations and the precision required. The electrode thickness produced at the first step can range from 0.05 to 0.2 mm depending on the electrode type (cathode or anode), the intended application of the battery (high capacity or high power) and the cell design (cylindrical or planar).

Cylindrical cells, where components are staked and wound to be inserted into 123 cylindrical cases, and prismatic cells, with stacked electrodes and separators, are 124 currently the predominant designs. Pouch cells are prismatic cells with aluminum-125 polymer soft pack instead of metal can, so they achieve a packaging efficiency of 126 90-95 % and higher energy density. With high volume, any reasonable size can be 127 produced economically. Lithium polymer pouch cells are increasingly being con-128 sidered as alternatives to large prismatic cells for automotive applications; because 129 their form is flexible they can be packaged more efficiently, and reduced cell 130 packaging overheads result in high battery energy density. Due to large surface area 131 and aspect ratio they have good heat dissipation. However, the cells have low 132 mechanical stability and therefore more robust packaging is required. 133

134 **1.3 Module Design and Assembly**

In order to develop a battery module as a building block of a battery pack, first of all 135 it is highly convenient to have as much information as possible about the charac-136 teristics of the vehicle to be powered by the energy stored in the battery in terms of 137 weight, friction, aerodynamic coefficient, efficiency, voltage and current of the 138 power train, ... Besides, others features related to the vehicle performance must be 139 defined, as the energy storage will be sized in order to cope with these requirements, 140 such as autonomy, acceleration, maximum speed, cruise speed, etc., referred to a 141 given driving cycle. 142

According to the vehicle characteristics and requirements, and once the cell has 143 been selected, tested and modeled, all this information will be used to determine the 144 required number of cells and modules and their series/parallel connection inside-145 respectively-the module and the battery pack, so that the required voltage, current, 146 energy and power values are met. In order to define the optimum possible 147 arrangement, the resulting module will be simulated—both electrical and thermally 148 —out of the previously obtained models of the cells. Special consideration should 149 be put in the lay-out of the cells since the thermal behavior of the module will 150 strongly depend on this. 151

Most of the systems using batteries require a certain number of cells connected in series and parallel in order to achieve the desired voltages and current. Therefore, all the cells should be kept in the same state of charge (SOC) in such a way that the capacity of the resulting module or battery-pack is not reduced due to a weak cell

ß	Layout: T1 Standard Unicode	Book ID: 329226_1_En	Book ISBN: 978-3-319-12705-7
)	Chapter No.: 4	Date: 19-10-2014 Time: 2:21 pm	Page: 7/16

GREENLION Project: Advanced Manufacturing Processes ...

that reaches the cut-off voltage sooner than the rest, or to an incomplete charge 156 caused by a cell with a voltage higher than the others. Therefore, a cell balancing system that keeps the cells in the same SOC is required to improve the performance 158 of the module. 159

Besides, special care must be taken in order to ensure that no cell is over charged 160 or discharged, due to the electrochemical inequalities of the cells inherent to the 161 manufacturing process or to uneven working or balancing conditions. Otherwise, the 162 users' and cells' integrity could be compromised, as dangerous amounts of flam-163 mable gases and/or toxic chemicals can be released, and even end up in an explosion. 164

In order to have an optimal use of the module, it is highly convenient to have 165 access to the information concerning the state of charge (SOC, which is the 166 remaining charge in the cells) and state of health (SOH, which is the capacity of the 167 cells at a given time compared to that when they were new) of the cells. For all this 168 reasons, a Battery Management System (BMS) is required in any system using 169 lithium-ion cells. 170

The operation of batteries depends on an electrochemical process for both 171 charging and discharging, and it is widely known that these chemical reactions are 172 significantly dependent on temperature. Nominal battery performance is usually 173 specified for working temperatures somewhere in the +20 to +30 °C range. How-174 ever, the working temperature conditions of the cells can deviate substantially from 175 nominal values, in such a way that batteries are operated at higher or lower tem-176 peratures. As a consequence, the performance of the cells is strongly affected: in 177 general terms, discharge time (and therefore, capacity) decreases at lower temper-178 atures, and the number of charge and discharge cycles is reduced when working at 179 higher temperatures. 180

Besides, and from a safety point of view, it is extremely important to avoid a 181 thermal runaway (uncontrolled temperature increase) in the cells since dangerous 182 amounts of flammable gases and/or toxic chemicals can be released, and even end 183 up in an explosion. 184

Therefore, a Thermal Management Systems (TMS) is required to maintain the 185 cells within a safe temperature range that, besides, allows optimizing the perfor-186 mance of the module. In order to cool-down or heat-up the cells, different systems 187 can be used, being air or liquid cooling the most usual choices. 188

2 Project Description 189

2.1 Project Approach and Objectives 190

In the GREENLION project (www.greenlionproject.eu), we address the issues cited 191 previously by the industrial development of eco-designed processes at the electrode, 192 cell and battery module level. At the electrode processing stage (that will be 193 otherwise independent of the active materials chemistry), developing and making 194 use of: 195

196

197

198

200

201

- 1. aqueous slurries rather than toxic organic volatile compounds (25 % cost reduction):
- 2. non-thermoplastic polymers that allow for high temperature drying, which results in shorter and less expensive assembly procedure (10 % efficiency); and 199
 - 3. easily disposable non-fluorinated polymers (at expected 10 times less materials cost).

At the **cell assembly level**, further improvements to the existing procedures as 202 well as changes at some steps of the assembly process will be developed to increase 203 energy efficiency and shorten times (and hence lower costs) during the manufac-204 turing process, by implementing: 205

- 1. laser cutting instead of mechanical notching of the electrodes (15 % cost), 206
- 2. adjusted stack winding of components from aqueous-based electrodes and their 207 drying process before electrolyte filling and sealing, to lower dry room 208 requirements, 200
- 3. environmentally friendly bonding process for more effective and long-life cell 210 sealing, and 211
- 4. adjusted formation step time (ideally for electrodes with reduced formation 212 cycle) in cell manufacturing line (5 % time reduction). 213

Finally, developing a modular battery allows an easier handling of cells within a 214 complete battery pack. At this battery module level, GREENLION project will 215 design an autonomous unit including its own electrical and thermal management as 216 a simple and reliable building block that will allow the manufacturing and main-217 tenance of the whole battery packs easier and more inexpensively, with the lowest 218 possible environmental impact. This will be achieved by: 219

- 1. lighter battery module designs (including electronics) with the possibility of 220 implementing air cooled solutions instead of liquid cooling systems (expected 221 20 % less weight), 222
- 2. bonding process of module housing for safe operation but easy disassembling 223 for maintenance and reuse/recycling at their end-of-life, and 224
- 3. automation of module assembly process (3 s/cell vs. manual assembly). 225

These developments will be scaled-up and realized in pilot lines during the 226 project, following a continuous environmental assessment of materials and pro-227 cesses. A validation of the finally assembled battery module will be carried out lead 228 by the automotive end-user who will also provide the targets and specifications for 229 (H)EV application. 230

General project approach and objectives are summarized in Fig. 2. Progress 231 beyond current State of the Art is also indicated. 232



9	Layout: T1 Standard Unicode	Book ID: 329226_1_En	Book ISBN: 978-3-319-12705-7
l)	Chapter No.: 4	Date: 19-10-2014 Time: 2:21 pm	Page: 9/16

GREENLION Project: Advanced Manufacturing Processes ...

2.2 Project Consortium

The scientific and technological cooperation in GREENLION consortium and their 234 roles in the project are well balanced covering the complete chain from raw 235 material, scientific comprehension, technological research and end users. As an 236 essential part of the project, the industrial partners will commit to exploit all 237 commercial aspects of the new manufacturing processes. To this purpose, the 238 industrial partnership was designed to combine Li-ion cells and module manufac-239 turers (CEGASA), processing equipment manufacturers (POLYTYPE and 240 KEMET), material suppliers (SOLVAY and TIMCAL), automation of assembly 241 processes providers (MONDRAGON ASSEMBLY), recycling and waste treatment 242 services suppliers (TECNICAS REUNIDAS), and car manufacturers (SEAT and 243 VOLKSWAGEN). The research institutions (CIDETEC, ENEA, RESCOLL, AIT) 244 and universities (University of Muenster, Politecnico di Milano, University of 245 Limerick) in GREENLION consortium provide complementary skills and expertise 246 in the relevant fields of research and development that are necessary to achieve the 247 project objectives. 248

3 Outcome of the Project

3.1 Baseline for GREENLION Project and Performance Indicators

Knowledge will be generated well beyond state of the art and the limitations of
 current Li-ion battery manufacturing process. In particular, Table 1 summarizes and
 quantifies the most significant targets.

255 3.2 Expected Impact of the Project

GREENLION will provide advances to a number of scientific and engineering challenges for battery cell and module manufacturing, and their performance thereof. The successful resolution of these will lead to breakthroughs in automotive lithium ion batteries for electric vehicles and thus to the development of a sustainable mobility and quality of life.

Greening our transport system is necessary not only to avoid the influence of oil supply (\$147 per barrel peak in 2008) but also to achieve EU and international targets in emissions reductions. In the EU, 19 % of total greenhouse gas emissions and 28 % of CO₂ emissions in 2005 are linked to the transport sector. More than 90 % of the total EU transport-related emissions are due to road transport. While

9	Layout: T1 Standard Unicode	Book ID: 329226_1_En		Book ISBN: 978-3-319-12705-7
Ŋ	Chapter No.: 4	Date: 19-10-2014 Time:	2:21 pm	Page: 10/16

I. de Meatza et al.

Table 1	Summary of most re	levant GREENLION	performance indicator	s and targets
---------	--------------------	------------------	-----------------------	---------------

	Proposed innovation-performance indicators
Electrode	Development of innovative electrodes realized by water-based processes to realize electrodes characterized by: (i) high thermal stability to allow high-temperature drying (>150 °C) in order to allow assembly in less stringent dry room operating conditions and reduce post-coating treatment time); (ii) high electrochemical stability to allow the use of high voltage cathodes (at least 5 V vs. Li/Li ⁺); (iii) high capacity retention upon cycling (more than 80 % of initial capacity after 1,000 cycles)
	The final goal is to obtain anodes and cathodes for lithium-ion batteries with storage capacities as high as, respectively, 300 and 150 mAh/g (excluding the weight of the current collectors), and surface loadings of, at least, 5 mAh/cm ²
Cell	Implement laser cutting/slitting instead of mechanical notching of the electrodes achieving negligible degradation of active material in the cut area, reduction of burrs resulting in a safer cell, expected 15 % cost saving due to reduced maintenance and higher process efficiency
	Based on such innovative electrodes, GREENLION proposes to design and develop cells capable of delivering a specific energy of 200 Wh/kg, which is the actual target for automotive applications
Module	Lighter battery module designs (including electronics) by evaluating the implementation air cooled solutions instead of liquid cooling systems (20 % less weight)
	Automation of module assembly process with a handling time down to 3 s per cell) will enable cost reduction and quality in line with what achieved in the highly automated cell manufacturing

total EU emissions declined, transport emissions increased continuously between
 1990 and 2005 due to high growth in both passenger (28 %) and freight transport
 (62 %).

Current and near-term (i.e. Li-ion) battery technology development is one of the 269 key factors on the Mobility Electrification and the large scale production of these 270 automotive batteries and reducing their costs is, in fact, critical for market entry and 271 acceptance of Electric Vehicles. In order to achieve a break-even cost with internal 272 combustion engines, battery costs must be reduced from the current estimated range 273 of 675–500 € per kilowatt-hour (kWh) at high volume production (order of 100 k 274 units) down to 350-275 C/kWh by 2020. R&D to improve power (W/kg) and 275 energy density (Wh/kg) in order to increase driving autonomy, reductions in 276 recharge time and achieving life cycles that approach vehicle life spans is also 277 imperative. Increasing production rate from 10,000 to 100,000 batteries/year 278 reduces cost by $\sim 30-40 \%$ [6]. 279

GREENLION addresses further reduction costs driven not only by high volume
 manufacturing, but also from the components processing conditions. The use of water
 based binders, an order of magnitude cheaper than conventional fluorinated ones will
 drive down the cell manufacturing costs, besides being more environmentally
 friendly and eco-sustainable at the end of life of the cells. Besides the improvement in
 environmental, health and safety terms (including "working-condition-friendly"

Ð	Layout: T1 Standard Unicode	Book ID: 329226_1_En	Book ISBN: 978-3-319-12705-7
Ņ	Chapter No.: 4	Date: 19-10-2014 Time: 2:21 pm	Page: 11/16

GREENLION Project: Advanced Manufacturing Processes ...

considerations), the initial inversion and running costs of the solvent recovery system would be avoided and water is indeed cheaper than NMP. Even though in current production plants the recovered NMP is purified and offered again at 50 % of the cost of pure solvent, distilled water is also cheaper (0.20 ϵ/L) than 50 % of pure NMP 0.90 ϵ/L (~1.8 ϵ/L pure).

Expected impact in the field of new competitive processes, by means of production automation is also foreseen. Not only will the results of the project efforts enable lower cost and greener lithium battery packs production, but also equipment manufacturing and high added value processes will be developed. These new automated processes will contribute to a substantial cost reduction of lithium battery packs, and will facilitate their introduction to mass production.

Automation and new process development will improve the quality and yield of the production, while at same time reduces labor costs per kWh. This project, with the development of the specific equipments for module assembling, will enable a cycle time of 3 s for each cell. This results in a module production capacity of 880 MWh/year.

Globally, automation and equipment development in this project will enable a cost reduction of the whole battery pack of 15 %. Having in mind that only 24 % of the cost is related to the module/pack manufacturing (60 % are materials components and 16 % are transports and others), it represents a major step in the way to mass production. Market growing will also pull down the prices of the materials, and it will open the way to the mass production at competitive costs.

308 3.3 Results Achieved

GREENLION is currently at month 18 of a 4 year-long workplan. During this first stage of the project, efforts have been mainly focused on the electrode processing step, with the development and testing of active materials and binders suitable for water-based slurry formulations and electrode coating process. First selected formulations have been used for small scale GEN1 prototype pouch cell assembly while the optimized module design and assembly process is underway. These results and advances are summarized in the following sections.

316 3.3.1 Materials Development and Water-Based Electrode Processing

Among the main research topics of the GREENLION Project, are to be highlighted the development of ionic liquid-based electrolytes and the realization of electrodes, prepared through innovative, eco-friendly process routes, based on high-voltage cathode and large-capacity anode materials. There is growing up interest in replacing the organic solvents currently used in lithium batteries [7–9] with ionic liquids, ILs, since their non-flammability and negligible vapor pressure in conjunction with wide chemical, electrochemical and thermal stability, high ionic

286

287

288

289

290

(F)	Layout: T1 Standard Unicode	Book ID: 329226_1_En		Book ISBN: 978-3-319-12705-7
	Chapter No.: 4	Date: 19-10-2014	Time: 2:21 pm	Page: 12/16

conductivity and heat capacity. Our basic idea is to favorably combine different IL 324 sets in order to obtain ionic liquid mixtures with improved performance. For 325 instance, N-methyl-N-propylpyrrolidinium bis(fluorosulfonyl)imide (PYR₁₃FSI) 326 was found to exhibit moderate viscosity and low melting point, allowing fast ion 327 conduction even at low temperatures [10]. On other hand, the much cheaper N-328 methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR₁₃TFSI) 329 shows wider thermal and electrochemical stability [11]. In order to verify if these 330 characteristics could be combined, PYR13FSI-PYR13TFSI mixtures were prepared 331 and investigated in terms of NMR spectroscopy, transport properties and density 332 measurements. 333

Remarkable conduction values, e.g., approaching 10^{-3} Scm⁻¹, are achieved already at -20 °C for mole fraction ranging from $0.6 \le x \le 0.8$ whereas both the raw ionic liquid materials (PYR₁₃FSI and PYR₁₃TFSI) are solid at this temperature (see Fig. 3). This highlights the synergic effect exhibited in ionic liquid mixtures, especially for low temperature applications.

NMR heteronuclear NOE correlation experiments (HOESY) experiments have been successfully used for the assessment of the intermolecular contacts between the F atoms of the anions and the H atoms of the cations in pyrrolidinium based ionic liquids, thus providing information on the local structural organization. The experiments have shown a peculiar cation-anion organization in the three investigated blends responsible of their favorable physico-chemical characteristics.

High nominal voltage cathode materials, combined with large capacity anodes 345 are appealing issues for the realization of lithium batteries with high gravimetrical 346 and volumetric energy. In this first stage of GREENLION, cathodes based on 347 LiNixMnvCo1-x-vO2 (NMC) and anodes based on carbonaceous materials 348 (graphite, SLP) have been developed. The composite electrodes were fabricated 349 using the fluorine-free, water-soluble, natural binder carboxymethylcellulose 350 sodium salt (CMC) instead of the more expensive and less environmentally friendly 351 polyvinyliden-di-fluoride (PVdF) in N-methyl-pyrrolidone (NMP). The use of 352 CMC allows also easier recycling of the battery components. For instance, the 353 dissolution in water of the binder allows, for example, a full recovery of the metallic 354 current collectors [12, 13]. 355

Commercially available NMC cathode and Timcal SLP 30® graphite anode 356 tapes based on the aqueous CMC binders were prepared using a pre-pilot automated 357 coating line. The cycling performance tests (Fig. 4) evidenced a time-stable 358 capacity of 130 mA h g^{-1} for more than 40 cycles with coulombic efficiency higher 359 than 99.0 % for the NMC cathodes. The SLP 30® anodes showed very good 360 performance in terms of reversibility of the intercalation process. The specific 361 capacity leveled 375 mA h g⁻¹ after a few cycles. Upon 80 cycles, the SLP 30® 362 electrodes showed still high cycling stability and columbic efficiency above 99.9 %. 363 These results support for a further development of the aqueous CMC binder-based 364 electrodes. 365

In addition, alternative water-soluble binders have been studied. Impressive electrochemical performance has recently been reported for Si nanopowder [14] and nanowire [15] anodes prepared from aqueous slurries using 15 wt% alginate as

(H)	Layout: T1 Standard Unicode	Book ID: 329226_1_En	Book ISBN: 978-3-319-12705-7
	Chapter No.: 4	Date: 19-10-2014 Time: 2:21 pm	Page: 13/16

GREENLION Project: Advanced Manufacturing Processes ...

13

40°C

20°C

10°C

20°C 30°C

40°C 50°C

60°C

70°C

80°C 90°C

Fig. 3 Ionic conductivity 10^{-2} (upper panel) and density (lower panel) versus Ionic conductivity / S cm 10⁻³ PYR₁₃FSI mole ratio dependence for (x)PYR13FSI/ 0°C (1-x)PYR13TFSI binary 10⁻⁴ electrolyte mixtures at -10°C different temperatures 10⁻⁵ 10-6 10⁻⁷ -20°C -30°C 10^{-8} 0.0 0.2 0.4 0.6 0.8 1.0 1.44 1.42 1.40 Density / g cm⁻³ 1.38 1.36 1.34 1.32 1.30 1.28 0.2 0.0 0.4 0.6 0.8 1.0 PYR₁₃FSI mole fraction

³⁶⁹ binder. To date, however, no study has been undertaken using alginates as the
³⁷⁰ binder for graphitic anodes, which are almost ubiquitous in present lithium ion
³⁷¹ battery technology. It is apparent from Fig. 5 that the graphite anode with 7.5 wt%
³⁷² alginate outperforms that with 10 wt% PVDF (a common commercial level) over
³⁷³ the course of the first 65 charge/discharge cycles. This result suggests that alginate
³⁷⁴ may be a suitable candidate for aqueous manufacturing of anodes.

The CMC based formulations will be the first to be trialed in pilot line in order to develop optimized coating machinery and electrodes for cell assembly. The most efficient way of manufacturing battery electrodes is to simultaneously coat both

(I (Layout: T1 Standard Unicode	Book ID: 329226_1_En		Book ISBN: 978-3-319-12705-7
	Chapter No.: 4	Date: 19-10-2014	Time: 2:21 pm	Page: 14/16

I. de Meatza et al.





sides of the substrate and to use a flotation dryer for removing the solvent. This
 configuration requires one of the coatings to be applied in the so called kiss coating
 mode as depicted in Fig. 6 for the slot coating process.

Coating trials have been carried out on a pilot machine, allowing the adjustment of parameters to achieve an excellent uniformity of the kiss-coated layer, i.e. by suppressing cross lines generated by web flutter in the flotation dryer, and by suppressing longitudinal bands generated by web deformations upstream of the slot die.

385 3.3.2 Cell Assembly and Module Design

During the first year, GEN0 prototype cells (10–14 Ah) were assembled as baseline for the project, from electrodes prepared with commercially available water-soluble binders and graphite/LiFePO₄ (C/LFP) chemistry.

The NMC and SLP 30® electrodes (around 1 m²) prepared in a pre-pilot automated coating line were used to assemble GEN1 small pouch cells (0.5–1.5 Ah) as shown in Fig. 7, following the first large cell design (30 Ah target) proposed to fulfill the energy requirements of the end-users for an efficient automotive battery module.

(R)	Layout: T1 Standard Unicode	Book ID: 329226_1_En		Book ISBN: 978-3-319-12705-7
	Chapter No.: 4	Date: 19-10-2014	Time: 2:21 pm	Page: 15/16

GREENLION Project: Advanced Manufacturing Processes ...



Fig. 5 Comparison of the specific discharge (delithiation) capacities of anodes prepared using polyvinylidene fluoride (PVDF) or alginate binders. The only other component of the anodes was the active graphite material—TIMREX® SLP30 by TIMCAL. The first and second charge/discharge cycles were conducted at slow rates of C/40 and C/25 respectively to facilitate the formation of a stable SEI layer. Voltage limits were between 5 mV and 1.5 V versus Li/Li⁺. The electrolyte was 1 M (EC:DMC, 1:1 v/v) and the experiments were conducted at ambient room temperature



Fig. 6 Schematic view of coating the web-underside by the slot coating process operating in the kiss or tensioned-web mode



Fig. 7 From *left* to *right* CMC-based electrodes prepared in pre-pilot coating line, *GEN0* C/LFP cell, *GEN1* small pouch cell with SLP 30® and NMC electrodes and schematic *GEN2* power cell and module design

B & W IN PRINT

While laser notching trials of electrodes with both PVDF and water-based binders are underway, conventional cutting dies (mechanical notching) and manual stacking process were used for GEN0 and GEN1 cell assembly. Automated stacking-winding will be implemented for the GEN2 cell that has been adopted as the most efficient electrical and thermal design for high power performance.

The design of a lighter battery module suitable for automated assembly and easier disassembly is ongoing, coupled to the GEN2 power oriented cell design. Different aspects such as minimum mechanical fitting by the assembly process, modular assembly including liquid cooled cold plates, mechanical absorption of cell swelling and venting are under consideration.

404 **References**

- 405 1. van Schalkwijk WA, Scrosati B (2002) Advances in lithium-ion batteries. Kluwer Academic,
 406 New York
- 2. Nazri G-A, Pistoia G (2004) Lithium batteries. Kluwer Academic, New York
- Joint European Commission/EPoSS/ERTRAC Expert Workshop (2009) Batteries and storage
 systems for the fully electric vehicle, 19 June 2009
- 410
 4. Arnold G, Garche J, Hemmer R, Ströbele S, Vogler C, Wohlfahrt-Mehrens M (2003) J Power
 411
 Sources 247:119–121
 - 5. Striebel K, Shim J, Sierra A, Yang H, Song XY, Kostecki R, McCarthy M (2005) J Power Sources 146:33
- 414 6. Howell D (2010) DOE annual merit review meeting
- 7. Shin J-H, Henderson WA, Appetecchi GB, Alessandrini F, Passerini S (2005) Electrochim
 Acta 50:3859
- 417 8. Appetecchi GB, Montanino M, Balducci A, Lux SF, Winter M, Passerini S (2009) J Power
 418 Sources 192:599
- 9. Balducci A, Jeong SS, Kim GT, Passerini S, Winter M, Schmuck M, Appetecchi GB, Marcilla
 R, Mecerreyes D, Barsukov I, Khomenko V, Cantero I, De Meatza I, Holzapfel M, Tran N
 (2011) J Power Sources 196:9719
- 422 10. Appetecchi GB, Montanino M, Balducci A, Lux SF, Winter M, Passerini S (2009) J Power
 423 Sources 192:599
- 424 11. Appetecchi GB, Montanino M, Carewska M, Moreno M, Alessandrini F, Passerini S (2011)
 425 Electrochim Acta 56:1300
- 426 12. Kim GT, Jeong SS, Joost M, Rocca E, Winter M, Passerini S, Balducci A (2010) J Power
 427 Sources 195:6130
- 428 13. Lux SF, Schappacher F, Balducci A, Passerini S, Winter M (2010) J Electrochem Soc 157(3):
 429 A320
- I4. Kovalenko I, Zdyrko B, Magasinski A, Hertzberg B, Milicev Z, Burtovyy R, Luzinov I,
 Yushin G (2011) Science 334:75
- 432 15. Ge M, Rong J, Fang X, Zhou C (2012) Nano Lett 12:2318

394

395

396

397

398

412

Author Query Form

 Book ID :
 329226_1_En

 Chapter No.:
 4

<u>)</u> Springer

the language of science

Please ensure you fill out your response to the queries raised below and return this form along with your corrections

Dear Author

During the process of typesetting your chapter, the following queries have arisen. Please check your typeset proof carefully against the queries listed below and mark the necessary changes either directly on the proof/online grid or in the 'Author's response' area provided below

Query Refs.	Details Required	Author's Response
AQ1	No Queries	

Author Proof

MARKED PROOF

Please correct and return this set

Please use the proof correction marks shown below for all alterations and corrections. If you wish to return your proof by fax you should ensure that all amendments are written clearly in dark ink and are made well within the page margins.

Instruction to printer	Textual mark	Marginal mark
Leave unchanged Insert in text the matter indicated in the margin	••• under matter to remain k	
Delete	 / through single character, rule or underline or ⊢ through all characters to be deleted 	of or of
Substitute character or substitute part of one or more word(s)	/ through letter or	new character / or new characters /
Change to italics Change to capitals	 under matter to be changed under matter to be changed 	
Change to small capitals Change to bold type	$=$ under matter to be changed \sim under matter to be changed	~
Change to bold italic	$\overline{\nabla}$ under matter to be changed	
Change italic to upright type	(As above)	<i>₹</i> 4⁄
Change bold to non-bold type	(As above)	
Insert 'superior' character	/ through character or k where required	y or X under character e.g. y or X →
Insert 'inferior' character	(As above)	k over character e.g. $\frac{1}{2}$
Insert full stop	(As above)	0
Insert comma	(As above)	,
Insert single quotation marks	(As above)	Ý or ¼ and/or Ý or ¼
Insert double quotation marks	(As above)	У́ог Х́and/or У́ог Х́
Insert hyphen	(As above)	H
Start new paragraph	_ _	_ _
No new paragraph	ے	<u>(</u>
Transpose		
Close up	linking characters	\bigcirc
Insert or substitute space between characters or words	/ through character or k where required	Y
Reduce space between characters or words	between characters or words affected	\uparrow