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## Towards Environmentally Friendly High-Energy Cathodes for Sustainable Lithium-Ion Batteries

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### Abstract

The EU-funded collaborative MARS-EV Project (FP7, grant agreement 609201) has been targeting *inter alia* the realization of aqueous electrode processing technologies for high-energy lithium-ion positive electrodes with a particular focus on achieving the high recycling requirements established by the European Commission in its Battery Directive 2006/66 EG, stipulating a minimum recycling rate of 50%. Indeed, the aqueous electrode fabrication does not only allow for avoiding the use of environmentally hazardous, toxic, and expensive organic solvents as well as the need for super-dry conditions up to the cell assembly, but moreover a facilitated recycling process due to the water-soluble binding agents. Additionally, of great importance with regard to the latter is the careful selection of the cathode chemistry – not least with respect to economic aspects.

Herein, we summarize the results and progresses obtained within MARS-EV, highlighting their importance for the realization of environmentally friendly lithium-ion batteries for a sustainably electrified transportation.

*Keywords:* aqueous electrode processing; binder; recycling; lithium-ion cathode; battery

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## 1. Introduction

Due to their paramount energy and power density as well as excellent energy storage efficiency lithium-ion batteries are the power source of choice for the electrification of the modern transportation sector (Bresser et al., 2014; Notter et al., 2010; Scrosati and Garche, 2010). The, as a consequence, continuously increasing demand for lithium-ion cells, however, results also in a simultaneously increasing need to consider the overall environmental impact of these batteries – including the selection of largely available materials, environmentally friendly fabrication processes, and sustainable recycling procedures (Larcher and Tarascon, 2015).

In this regard, the EU-funded collaborative MARS-EV Project (FP7, grant agreement 609201) has been targeting to overcome the ageing phenomena in lithium-ion battery cells with a particular focus on the development of environmentally friendly high-energy cathodes and anodes, obtained by scaled-up synthesis methods, and the implementation of safe electrolyte systems. The subsequent industrial prototype cell assembly and testing in combination with a thorough modelling study allowed for an enhanced understanding of the ageing of these cells at the electrode and system level. This comprehensive development of sustainable lithium-ion cells, providing a capacity of several Ah, was eventually complemented by a complete life cycle assessment of the herein developed technology. The overall concept of the MARS-EV project is illustrated in *Figure 1*. As shown therein, MARS-EV has brought together scientific and industrial partners with highly complementary competences and expertise, covering the whole value chain from material suppliers to lithium-ion cell manufacturers, allowing for a direct transfer of the obtained results in order to strengthen the European battery fabrication capacities.

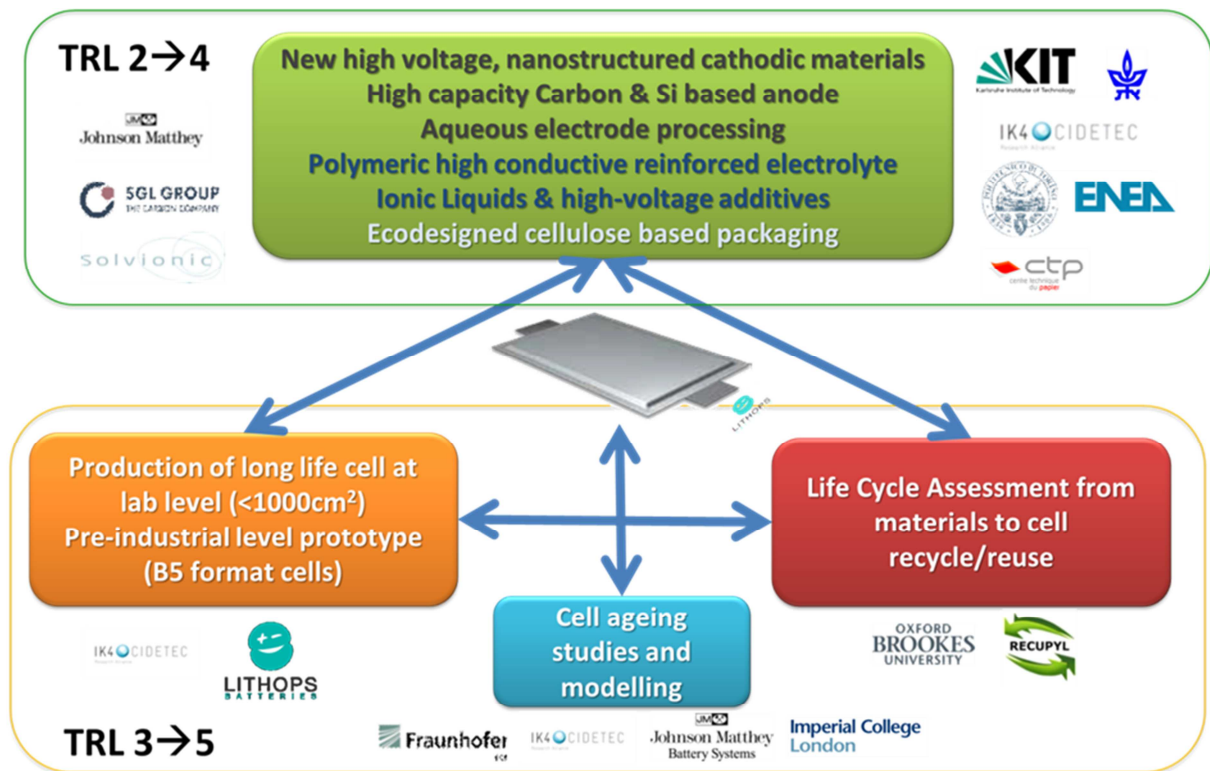


Fig. 1 Overall concept of the MARS-EV project, including the technology readiness level (TRL) of the main tasks and the involved partners

In this project framework, one great goal has been the realization of aqueous electrode processing technologies for the selected high-energy lithium-ion cathodes by replacing the presently used poly(vinylidene difluoride) (PVdF) binder, which requires the utilization of environmentally hazardous, toxic, and expensive organic solvents like *N*-methyl-2-pyrrolidone (NMP) and super-dry cell assembly conditions (Bresser et al., 2014; Nishi, 2001). In addition, the use of water-soluble binding agents allows for a facilitated recycling process, being of great importance with respect to the high recycling requirements established by the European Commission in its Battery Directive 2006/66 EG, stipulating a minimum recycling rate of 50%.

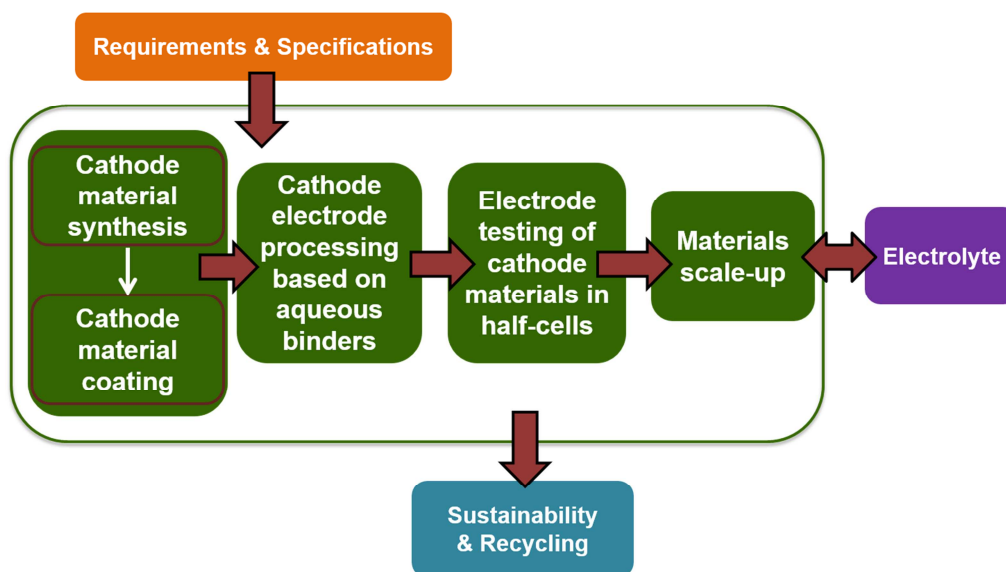


Fig. 2 Experimental rationale for the identification, selection, as well as the further investigation and optimization of the herein studied cathode materials with the eventual link to the corresponding tailoring of the electrolyte composition and recycling aspects

Herein, we present a summary of the obtained results and progresses, starting from the careful selection of suitable cathode material candidates and continuing with the development of complementary strategies to enable the aqueous processing of these water-sensitive compounds before eventually reporting on the progress in recycling (see also the overall experimental rationale schematically illustrated in *Figure 2*), exemplarily studied for water-processed  $\text{LiFePO}_4$  (LFP) electrodes, serving as a model due to its well established implementation in commercial lithium-ion cells.

## 2. Development and Selection of Suitable Cathode Material Candidates

In a first step, the development of suitable cathode materials was conducted, targeting (i) the implementation of sustainable large-scale synthesis routes and (ii) an energy density of  $900 \text{ Wh kg}^{-1}$  on the positive active material level, considering a theoretical lithium metal anode. In an attempt to realize the first (i), the two partners ENEA (Rome, Italy) and POLITO (Politecnico di Torino, Italy) focused on the ionothermal synthesis of LFP by using ionic liquids as synthesis media, which can be recovered afterwards and thus continuously reutilized (Recham et al., 2009). They successfully obtained a phase-pure, nanostructured active material, rendering this method generally suitable for a wide range of other cathode material candidates. For the achievement of the second target (ii), POLITO successfully synthesized fluorinated LFP ( $\text{Li}_2\text{FePO}_4\text{F}$ ), by conducting a solid-state synthesis of  $\text{NaLiFePO}_4\text{F}$  followed by the electrochemical exchange substitution of Na by Li (Khasanova et al., 2012). Cathodes based on this active material, indeed, revealed an increased de-/lithiation potential compared to LFP as a result of the introduction of the fluorine anion, but the overall energy density remained below the envisioned  $900 \text{ Wh kg}^{-1}$ , not least due to the limited utilization of the two lithium ions. Similarly, the evaluation of lithium manganese silicate as high-energy cathode revealed high specific capacities of almost  $220 \text{ mAh g}^{-1}$ . The relatively large voltage hysteresis for the charge and discharge process, however, currently limits its applicability in commercial cells prior to a thorough investigation of its origin and the achievement of strategies to overcome this issue.

Thus, the further work focused on nanostructured Li-rich NMC ( $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08}]\text{O}_2$ ; *Figure 3*), synthesized by a co-precipitation method and providing specific capacities of about  $220$  and  $190 \text{ mAh g}^{-1}$ , when dis-/charged at C rates of  $0.2\text{C}$  and  $1\text{C}$ , respectively (Birrozzi et al., 2016; Laszczynski et al., 2015; Li et al., 2011). Indeed, benefitting of the development of new electrolyte compositions, carried out within the scope of the MARS-EV project, lab-scale lithium-ion full-cells, comprising these cathodes and graphite anodes revealed a capacity retention of  $85\%$  after  $485$  cycles and a remarkable specific energy of  $370 \text{ Wh kg}^{-1}$  based on the mass of the cathode and anode active materials (Birrozzi et al., 2016).

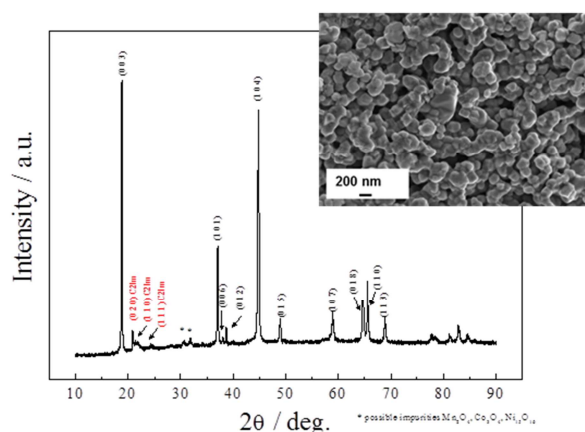


Fig. 3 X-ray diffractogram and SEM (scanning electron microscopy) micrograph (inset) of Li-rich NMC

### 3. Complementary Strategies to Enable Aqueous Cathode Processing

Motivated by the outstanding cycling stability and specific energy of the above mentioned Li-rich/graphite lithium-ion full-cells, the next goal was the achievement of Li-rich cathodes prepared by using water-soluble polymers as binding agents. The great challenge in this regard, however, is the pronounced water-sensitivity of lithium transition metal oxides, resulting in substantial lithium leaching, LiOH formation and, as a consequence, active material degradation and corrosion of the aluminium current collector (Loeffler et al., 2014). In an attempt to overcome this issue, two complementary strategies were pursued: one targeting the stabilization of the particle surface by applying a protective  $\text{VO}_x$  coating (Laszczyński et al., 2015); the other one striving for a further enhanced long-term cycling performance by employing alternative water-soluble binding agents and additive-modified electrode preparation processes. As the results of the latter one are about to be published, we may herein just briefly summarize at this point that this approach, indeed, lead to increased specific capacities and improved capacity retentions while simultaneously preventing the aluminium corrosion. The study will be presented in detail at the conference. Nonetheless, the prevention of the current collector corrosion was also successfully achieved by the first approach, i.e., the application of a vanadium oxide coating (Laszczyński et al., 2015). Moreover, the specific capacity was increased by ca.  $30 \text{ mAh g}^{-1}$  (i.e., from about  $230$  to ca.  $260 \text{ mAh g}^{-1}$  at C/10), further confirming the advantageous impact of the surface-stabilizing coating layer.

Beside this remarkable progress, however, an alternative high-energy cathode material was selected for the subsequent synthesis up-scaling by means of flame spray pyrolysis (conducted at Johnson Matthey, JM, UK) due the given time constraints within the frame of the MARS-EV project:  $\text{LiCoPO}_4$  (LCP). As a result of the high de-/lithiation potential at about  $4.8 \text{ V vs. Li/Li}^+$ , LCP provides a theoretical specific energy of ca.  $850 \text{ Wh kg}^{-1}$ , i.e., a value very close to the targeted  $900 \text{ Wh kg}^{-1}$ . The progress made on the aqueous electrode processing achieved for Li-rich NMC enabled us to successfully fabricate also LCP-based electrodes using water as the binder solvent and electrode composite dispersant. Two important aspects for achieving homogeneously coated and mechanically stable electrodes revealed to be the initial homogenization of the spherical secondary particle size, for instance, by sieving the as-synthesized powder as well as the application of modified (pre-)mixing strategies. Generally, the utilization of sodium carboxymethyl cellulose (CMC) as (main) binding agent lead to the best results in terms of both the mechanical properties of the thus obtained electrodes and their electrochemical performance with respect to cycling stability and achievable specific capacities. Nevertheless, the even more severe challenge when dealing with such high-voltage cathodes, commonly cycled up to about  $5.0 \text{ V vs. Li/Li}^+$  concerns the anodic stability of the electrolyte (Laszczyński et al., 2016; Xu, 2004). Following the results obtained for  $\text{VO}_x$ -coated Li-rich NMC, also LCP was coated with such a vanadium oxide surface layer (Laszczyński et al., 2016). Better performance with regard to reversible capacity and capacity retention upon cycling, however, were obtained when applying a carbonaceous coating instead, revealing an initial reversible capacity of  $120 \text{ mAh g}^{-1}$  and still  $70 \text{ mAh g}^{-1}$  after 112 cycles (compared to ca.  $20 \text{ mAh g}^{-1}$  for the non-coated LCP-based electrodes). Accordingly, the large-scale synthesis has been modified to provide *in situ* carbon-coated spherical LCP secondary particles, consisting of fine primary nanoparticles as shown in Figure 4 (patent application GB1609016.9).

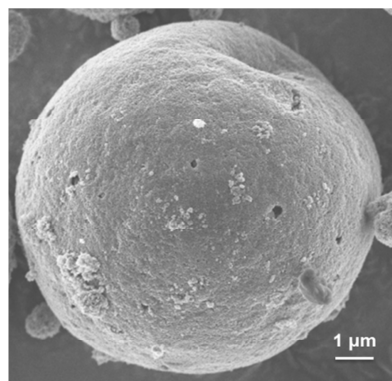


Fig. 4 SEM micrograph of a secondary carbon-coated LCP particle, obtained by means of flame spray pyrolysis

Further improvement of the cycling stability of electrodes based on this newly developed synthesis was eventually realized by optimizing the electrolyte composition (*Figure 5*) introducing low percentages of Additive #1 (blue) and Additive #2 (green) compared to those electrodes cycled in a standard electrolyte composition (orange). Interestingly, the introduction of Additive #2 revealed a dramatically improved cycling stability, while the use of Additive #1 led to a substantially enhanced coulombic efficiency. Similarly to the work on the aqueous electrode processing of Li-rich NMC, we may at this point refer to the presentation to be given for all further details (including the nature of the two additives and a full-cell study employing graphite anodes), as the corresponding publication is presently in progress.

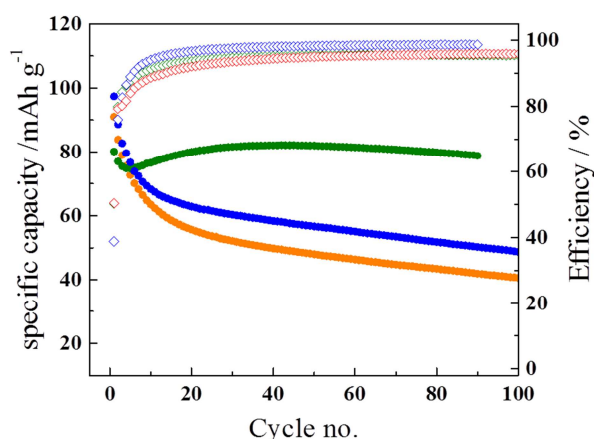


Fig. 5 Galvanostatic cycling of carbon-coated LCP-based electrodes, employing CMC as binder; the reference cell (orange) comprised a standard organic electrolyte (1M LiPF<sub>6</sub> in EC:DMC, 1:1; UBE), the other two cells, shown in blue and green, comprised a small percentage of Additive #1 and Additive #2, respectively; all cells were cycled at C/10 based on the theoretical specific capacity of LCP (167 mAh g<sup>-1</sup>) and had an average active material mass loading of about 5 mg cm<sup>-2</sup>

#### 4. Progress in Recycling of Aqueous Lithium-Ion Cathodes

As mentioned in the Introduction, the rather new Battery Directive 2006/66 EG, written and released by the European Commission, targets a very high overall recycling rate of at least 50% for lithium-ion battery cells that have reached their end of life (commonly around 80% of the initial reversible capacity). In fact, recycling of the comprised elements and compounds becomes even more important when considering the limited availability of some of these elements like lithium (Tarascon, 2010) or, even more, cobalt (Lindsay and Kerr, 2011) and the ratio of energy required for the lithium-ion cell fabrication compared to the energy stored in such batteries over the entire lifetime (Barnhart and Benson, 2013). Addressing this issue, the MARS-EV partners and in particular RECUPYL (Domène, France) studied the maximum achievable recycling rate, striving for values far exceeding the legally required 50%. As such a comprehensive investigation is very material-intensive – not least with

respect to the eventually envisioned up-scaling to enable the recycling of tons of used lithium-ion batteries – this work was conducted on LFP-based electrodes, serving as a model compound for other common lithium-ion cathodes, specifically the herein developed carbon-coated LCP.

In a first step, the cells and later on the cathode tapes were mechanically shredded and crushed to obtain a homogenous powder out of which the transition metal can be leached. The subsequent chemical treatment (pH adjustment and oxidation) finally revealed the corresponding oxide. The simultaneously extracted lithium carbonate was proven to have a purity of 99.8%, with Na, K, and Ca impurities in the ppm range, thus, very well fitting the general market requirements and being equal to or exceeding the purity of other commercially distributed lithium carbonate samples. *Table 1* summarizes the rate of extraction and the overall achieved recycling rate at the end of the MARS-EV project for all the comprised elements and components. It may be noted that the remarkable recycling rate of 76.61% corresponds to the successfully recovery of 776 kg of materials out of 1,000 kg of batteries.

In fact, this great recycling rate particularly benefits of the utilization of water-soluble binders, as the overall recycling process is largely water-based. Nonetheless, the whole recycling process requires several safety measures like an initial discharging of the battery cells, the application of a very dry atmosphere and a controlled temperature as well as the implementation of appropriate ventilation and exhaust gas systems in order to prevent any accidental heat increase, potentially leading to a thermal runaway of the cell and eventually to an ignition of the flammable cell components or even an explosion of the cell as well as the release of highly toxic and corrosive compounds like HF or fluoroalcohols (Hammami et al., 2003; Kalhoff et al., 2015), both providing a substantial risk to human health and the environment.

Table 1. Relative content, rate of extraction and overall recycling rate for all elements and components comprised in a lithium-ion cell based on LFP cathodes.

<i>Element / Component</i>	<i>LFP-C</i>	<i>Rate of extraction</i>	<i>Recycling rate at the end of the project in 2017</i>
Fe	11.00%	90%	9.90%
P	6.11%	98%	5.99%
Binder	2.50%	0%	0%
Li	2.83%	90%	2.55%
Al+Cu	30.90%	90%	27.81%
Solvents	13.00%	0%	0%
Separator	2.00%	90%	1.80%
Carbon	18.00%	90%	16.20%
O (oxides)	12.61%	98%	12.36%
TOTAL			76.61%

## 5. Conclusions

Within the MARS-EV project, we have successfully developed new aqueous electrode preparation strategies for high-energy lithium-ion cathodes, specifically Li-rich NMC and LCP, including active material coatings (e.g., vanadium oxide and carbon), alternative water-soluble binders, and electrode slurry additives. In combination with the introduction of novel electrolyte additives, the resulting cathodes revealed enhanced reversible capacities and improved cycling stability compared to the neat electrolyte systems. Moreover, the large-scale synthesis of well-defined secondary particles composed of nano-sized high-voltage carbon-coated LCP was realized, providing a promising pathway for future high-energy lithium-ion batteries with respect to the identification of suitable electrolyte additives, jointly ensuring a stabilized electrode/electrolyte interface and thus addressing the greatest challenge for this active material class – the oxidative electrolyte decomposition at such high potentials. Finally, the recycling process for water-based lithium-ion cathodes, exemplarily performed for LFP as state-of-the-art active material, has been optimized, achieving a remarkable overall recycling rate of 76.61% of the total elements and components of industrially fabricated lithium-ion cells.



## Experimental

All experimental information is given in the herein cited scientific publications, i.e., the paper on the investigation of new electrolyte additives for Li-rich NMC (Birrozzi et al., 2016), the one on VO<sub>x</sub>-coated Li-rich NMC (Laszczynski et al., 2015), and the paper on VO<sub>x</sub>- and carbon-coated LCP (Laszczynski et al., 2016). The experimental details regarding the comparative study on different water-soluble binding agents for Li-rich NMC, the up-scaling of the carbon-coated LCP synthesis, and the development of new electrolyte additives for high-voltage LCP cathodes are included in the upcoming manuscripts, dealing with these topics. Generally, however, the experimental methods follow those reported in the earlier mentioned papers, while the exact electrode and electrolyte compositions cannot be disclosed at present.

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