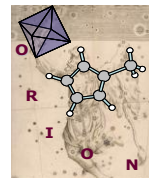


Executive Summary

ORION project, “Ordered Inorganic-Organic Hybrids using Ionic Liquids for Emerging Applications” has been a large scale collaborative RTD project funded by the European Commission under the NMP 2008-2.4-1 Inorganic-Organic Hybrid Materials. ORION has put together a multidisciplinary consortium of leading European Universities [Ecole Polytechnique Fédérale de Lausanne (EPFL), Universität Münster, Universitat de Valencia, Université de Mons-Hainaut and Universitat Jaume I], Research Institutes [IK4-Cidetec, Institute for Physical and Chemical Processes (IPCF-CNR), Laboratoire de Chimie des Polymères Organiques from CNRS, Laboratoire d'Innovation pour les Technologies des Energies Nouvelles (LITEN-CEA), Interuniversitair Micro-Electronica Centrum the National (IMEC) and J. Heyrovsky Institute of Physical Chemistry] and Industries [Johnson&Matthey, Fiat, Cegasa, Solvionic, Solaronix], with the overall goal of advancing the fabrication of inorganic-organic hybrid materials for application in batteries, solar cells and light emitting devices. Briefly, during the first year of the project, the main focus was on the definition of the materials requirements for the final applications and the synthesis of reference materials. During the M12-M30 period, an excellent cooperation (e.g. > 2-3 collaborations/partner) between the different partners was reached. The intra and inter-workpackage collaborations have been crucially exploited for the synthesis, characterization and modelling of innovative hybrid materials as well as their evaluation in different devices such as batteries and solar cells. As an example, the collaborative work and discussions were crucial for selecting the materials for the project demonstrators. The latter were the main focus during the last period (i.e. M30-M48) of the project. However, the generation of cutting-edge knowledge at the laboratory scale was especially active during whole project. A flash view of some significant technical results of the project can be found in the online version of the ORION's newsletter (<http://orionproject.wordpress.com/>). It is noted that 11 patent applications have been submitted to National and/or European Patent Offices. The list of the scientific publications – 71 in top-class peer-review journals such as Nature Photonics, NanoLetters, Angewandte Chemie-International Edition and Advanced Materials- is available in the project website (<http://www.cidetec.es/ORION>). Furthermore, two videos of the ORION demonstrators have been recently uploaded to youtube (<http://www.youtube.com/watch?v=fcBLO-Hjgo4>). They are also accessible in the Materials Blog of the Industrial Technologies Portal of the European Commission (http://ec.europa.eu/research/industrial_technologies/materials-blog_en.html), where the potential impact of the ORION project is highlighted.

Additionally to the technical aspects, special attention to training and dissemination activities has been paid. Concretely, two Summer Schools were organized in Italy and Spain in 2011 and 2013, respectively. Also important, the ORION consortium defined the “Plan for Using and Disseminating the Foreground”, which will be considered for the ulterior exploitation actions. Potential economic impact on the involved industrial partners –new products have introduced in some of their catalogs- and the society in general is detected.



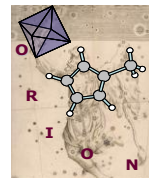
Project context and main objectives

The field of hybrid inorganic-organic materials has bloomed at the interface of many conventional disciplines and is producing an amazing variety of materials ranging from molecular to supramolecular structures, xerogels, mesoporous inorganic oxides, sol-gel hybrids and metal-organic frameworks. The properties of these materials not only depend on the chemical nature of the inorganic and organic material, but also synergistic combination of their properties to create new functionalities. Historically, inorganic-organic materials have found applications in a number of fields such as optics, protective and decorative coatings and catalysis. However, recent progresses on their design and multifunctionality are extending their applications to other fields such as electronics, energy, sensors, biology, gas purification and storage and information technologies.

Besides the different starting compounds of inorganic-organic hybrids such as organosilicates, metal alkoxides, inorganic nanoparticles, polysilsesquioxanes, dendrimers or block copolymers, ionic liquids are emerging as components of choice because of their ability to induce order and functionality into inorganic-organic hybrid materials. In this sense, ORION aimed at taking advantage of the properties of ionic liquids to guide the growth of inorganic nanomaterials and functionalize their surfaces in order to obtain a novel family of hybrid materials for emerging applications. As an example, intrinsic functionalities of the ionic liquids such as high ionic conductivity and electroactivity can be mentioned. ORION also dealt with the morphological, electrochemical and electro-optical characterization of these new inorganic-organic hybrid materials. Special emphasis was focused on their potential application in energy conversion and storage devices such as excitonic solar cells and Li-ion batteries. The synthesis and characterization was combined with high level modelling of the novel hybrid materials.

The main concept of the ORION project is the development of a new family of functional inorganic-organic hybrids materials for emerging energy devices such as solar cells, batteries and light emitting diodes. The hybrids will be composed of inorganic nanomaterials such as TiO_2 , ZnO and $\text{Li}_x\text{Ti}_y\text{O}_z$ and new functional ionic liquids as the organic components. Among the different kinds of hybrid material developed, two different complementary generations of inorganic/ionic liquid hybrids can be highlighted. First, "ORION generation 1" inorganic-organic hybrids were successfully synthesized and evaluated in lithium ion batteries. On the other hand, "ORION generation 2" inorganic-organic hybrids were successfully developed and integrated in emerging solar cells technologies such as Dye-sensitized (DSC) and organic (OPV) ones. In this case, the hybrid materials contain an additional building block named light sensitizer (dye, semiconducting polymer or quantum dot).

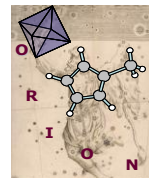
ORION put together a multidisciplinary consortium of leading European universities, research institutes and industries with the overall goal of developing new knowledge on the fabrication of inorganic-organic hybrid materials using ionic liquids. Maximum research efforts within ORION were addressed to achieve inorganic-organic hybrids with designed functionalities and to evaluate their potential in energy conversion, storage and saving applications. The final goal was optimize the best possible materials and processing methods for increasing the performance of Li-ion batteries, excitonic solar cells and light emitting devices. The work in ORION was associated with the search of new sustainable materials for two of the alternative and complementary solutions to the energy shortage and high-oil price coming era.



The scientific and technological cooperation in ORION consortium and their roles in the project were well balanced covering the complete chain from raw material, scientific comprehension, technological research and end users with broad application range. As an essential part of the project, the industrial partners played a crucial role to guide the research investments according to the market needs and/or opportunities. They were also especially involved in the up-scaling developments. To this purpose, the industrial partnership was designed to combine innovative materials suppliers such as Johnson&Matthey (inorganic nanoparticles), SOLVIONIC (ionic liquids), NANOCO (quantum dots) with leading companies in device applications such as CEGASA (batteries), SOLARONIX (dye sensitized solar cells) and FIAT(CRF) (integration of devices in automotive sector). The consortium is formed by 17 partners from 8 countries including 6 Research Institutions, 5 Universities, and 6 Industries (including 3 SMEs). The research institutions in ORION consortium provided complementary skills and expertises in the relevant fields of research and development that were key to achieve the project objectives.

Among the main ORION scientific and technical objectives, the next ones can be highlighted:

- o Design and processing of inorganic-organic hybrid materials for energy applications.
- o Synthesis of new functional ionic liquids and polymeric ionic liquid block copolymers including particular chemical functional groups enabling them to act as functional templates in the synthesis of inorganic-organic hybrids.
- o Development of ordered hybrid materials composed of an inorganic component and ionic liquid for battery applications. (Generation 1)
- o Synthesis of light sensitizers (organic dyes, quantum dots and semiconducting polymers) with adequate functionality to be added to the inorganic-organic hybrids.
- o Development of complex ordered hybrid materials composed of an inorganic component, ionic liquid component and a third component named light sensitizer (organic dye, semiconducting polymer or quantum dot) for innovative solar cells. (Generation 2)
- o Complete characterization of innovative hybrid materials: morphological characterization, electrochemical and charge carrier transport studies including ionic, electrical and hole conductivities, and functional performance (half-cell devices).
- o Theoretical modelling of new inorganic-organic materials and prediction of their properties and performance in devices.
- o Processing of inorganic-organic hybrids by different methods including ink-jet printing and screen printing.
- o Development and optimization of innovative inorganic-organic electrode materials for lithium ion batteries with enhanced performance (e.g. 50% improvement of the power density and cyclability).
- o Development and optimization of innovative inorganic-organic hybrid for emerging solar cells with high efficiencies (>10%) and high durability (10000 h) (30% improvement).
- o Evaluation of the organic/inorganic hybrid materials in light emitting devices as complementary final application.
- o Fabrication of Li-ion batteries prototypes based on materials developed in the project.
- o Fabrication of excitonic solar cell prototypes based on the materials developed in the project.



o Development of demonstrators based on energetically autonomous devices for automotive applications, combining the batteries and solar cells prototypes developed in the project.

Main Scientific and Technical results/foregrounds

The main scientific and technical results are briefly described below. Although most of the described progresses resulted from the contributions from several workpackages, the workpackage structure is here followed in order to facilitate the evaluation of the project.

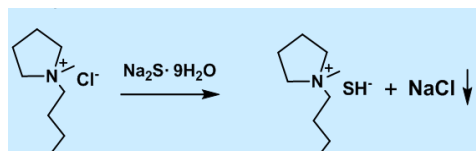
WP1- Selection and synthesis of Reference materials

The main objectives of this workpackage were a) to define the material requirements for final applications (**Task 1.1**) and b) synthesise ionic liquids (**Task 1.2**), inorganic materials (**Task 1.3**) and sensitizers (**Task 1.4**) for Batteries and Solar Cells applications.

Under **Task 1.1**, CRF proposed two automotive applications – an autodimming rear view mirror and a courtesy light- to be used as ORION demonstrators. Batteries and the solar cells developed within ORION project were proposed to be integrated in the two automotive devices in order to make them energetically autonomous. The material requirement definition was carried in collaboration with **CEGASA**, **CEA-LITEN** and **SOLARONIX**. This task was crucial in order to guide the ORION research activities. As an example, not only the range of the consumption (in the range of 80-300 mAh, depending on the demonstrator), but also the space and shape features for the integration of batteries and photovoltaic modules were crucial in order to select the best hybrid materials (WP2) and devices (WP5) to be scaled up for the demonstrators in WP6. Further details regarding the demonstrators can be found in the WP6 section.



Under **Task 1.2**, a wide range of ionic liquids and polymeric ionic liquids block co-polymers have been synthesised. As an example, **CIDETEC** developed a simple synthesis route to obtain a new family of ionic liquids containing sulfide anions.^{1,2}

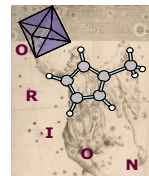


LCPO-CNRS developed a novel synthetic route to prepare new poly(ionic liquid)s (PILs) and PIL-based block copolymers (PIL BCPs). A lot of work was carried out to develop a synthetic route for the preparation of ionic liquids block co-polymers.^{3,4} Although the chemistry was proved to be very challenging, the

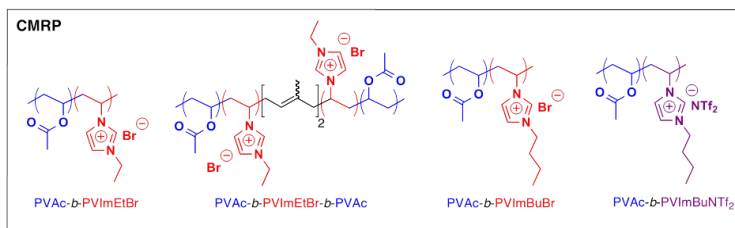
¹ Patent application: PCT/EP/2011/058143

² V. Jovanovski, V. González-Pedro, S. Giménez, E. Azaceta, G. Cabañero, H-J. Grande, R. Tena-Zaera, I. Mora-Seró, J. Bisquert, *J. Am. Chem.Soc.* 2011, 133, 20156–20159.

³ C. Detrembleur, A. Debuigne, M. Hurtgen, C. Jérôme, J. Pinaud, M. Fèvre, P. Coupillaud, J. Vignolle, D. Taton *Macromolecules* 2011, 44, 6397.

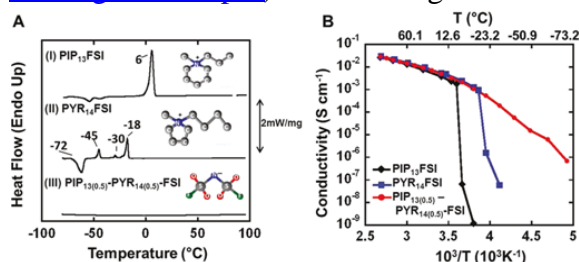


obtained materials open wide avenues to be used as building blocks for hybrid materials in WP2. In addition to the BCP structures, and as a potential contingency solution, PIL samples based on poly(1-vinyl-3-isopropyl imidazolium bromide) and poly(1-vinyl-3-butyl imidazolium bromide) were synthesized by free-radical (non-controlled) polymerization of corresponding monomers. Subsequent substitution of hydroxide (OH⁻) counter-anions for bromide ones afforded stable methanolic solutions of PIL with OH⁻ counter-anions. As an example, such polymeric ionic liquids (PILs) have been tested by CIDETEC as precursors for the growth of ZnO/IL hybrid nanoparticles in WP2. Similarly, IPCF-CNR, used poly(1-vinyl-3-butyl imidazolium) featuring PF₆⁻ as counter anions as polymeric stabilizer for the growth of narrow bandgap nano-crystal composites.



MUENSTER has been performing fundamental studies on the synthesis of ionic liquids and formulation of ionic liquid based electrolytes for Li battery application. The latter included the use of ionic liquids provided by SOLVIONIC. The ionic liquids were either used as additives for advanced electrolytes or as precursor for polymeric ionic liquid polymer preparation to be used as binder for Li-ion batteries. NMR studies, based on relaxation times, showed that the cation of pyrrolidinium-based ILs aggregates in a micelle-like way, which is all the more marked that the pyrrolidinium cation is substituted by a long alkyl chain.^{5,6,7} Further insights were gained from the collaborative piece of work between MUENSTER and UMH (WP4).

It is worth to note the large family of ionic liquid and derivative metal salts (e.g. zinc bis(trifluoromethanesulfonyl)imide, Zn(TFSI)₂) developed by SOLVIONIC and their availability during whole project for the ORION partners. Thanks to the excellent results of using them as precursors (WP2) and efficient dissemination activities by the different ORION partners, an appealing market window appeared for the above mentioned metal salts. As a consequence, SOLVIONIC scaled up the some of the winner candidates and new products were launched in their catalogue. They can be found on the website (<http://en.solvionic.com/files/solvionic/catalogues/catalogue-2013/Metallic-Salts-Catalogue-2013.pdf>). Concerning the ionic liquids, a wide range of ionic liquids were selected and provided to partners in charge of characterization of electrode materials developed in the project (WP3 and WP5). Thanks to feedback from testing, several generations of ionic liquids were synthesized and one was selected for the final demonstrators (WP6). The selected product is actually a eutectic mixture, which can lead to a dramatic extension of the temperature range of electrochemical energy storage systems.



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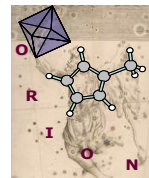
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⁴ P. Coupillaud, M. Fèvre, A.-L. Wirotius, K. Aissou, G. Fleury A. Debuigne, C. Detrembleur, D. Mecerreyes, J. Vignolle D. Taton submitted to *Macromolecular Rapid Commun.* 2013.

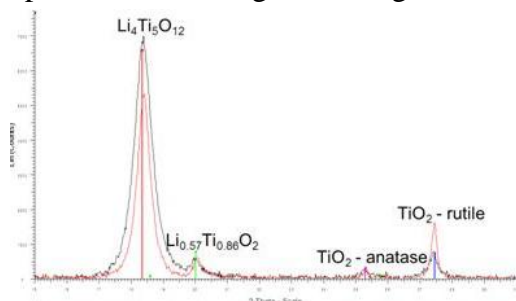
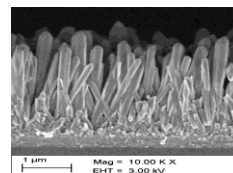
⁵ M. Kunze, S. Jeong, E. Paillard, M. Winter, S. Passerini, *J. Phys. Chem. C*, (2010) 114 (28), 12364–12369

⁶ M. Kunze, S. Jeong, E. Paillard, M. Schönhoff, M. Winter, S. Passerini, *Adv. Energy Mater.* (2011) 1 (2), 274-281

⁷ F. Castiglione, E. Ragg, A. Mele, G.B.Appetecchi, M. Montanino, S. Passerini, *J. Phys.Chem.Lett.*, (2011) 2(3), 153-157

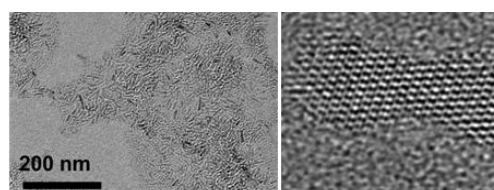


Task 1.3 was devoted to develop inorganic nanoparticles and nanowires for batteries and solar cells applications. CIDETEC developed an electrochemical-based route to obtain –at industrial competitive growth rate- arrays of zinc oxide nanowires with tailored morphology and properties. Furthermore, ZnO colloidal nanoparticles and derivative inks⁸ were synthesized with well suited properties to process flexible light emitting sources, as demonstrated by UVEG in WP3.

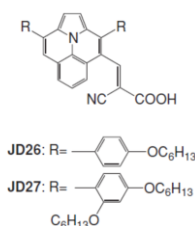


Johnson Matthey developed various materials for batteries application using flame spray pyrolysis. Olivine type materials as well as spinels materials were synthesised for the use in the cathode. Lithium titanate, titania, cobalt oxide, and are just few examples of the type of materials synthesised for the use in anode.^{9,10,11}

On the other hand, **ICPF-CNR** developed an advanced synthesis route to obtain anatase TiO₂ nanorods. Briefly, the nanorods, capped with oleic acid, were synthesised by a low temperature colloidal route based on thermal decomposition of the precursors in presence of coordinating agents. As MÜNSTER demonstrated good performance TiO₂-nanorods and derivative hybrid materials (WP2) as Li-insertion material (WP3),^{12,13} the synthesis set-up was adapted to obtain larger nanorod amounts need for their evaluation in devices (WP5). This was also needed for the evaluation of these TiO₂ NRs as anode building blocks in Dye-sensitized Solar Cells by SOLARONIX (WP5), showing interesting performance and pointing therefore out their multifunctional properties.



Light sensitizers such as quantum dots, semiconducting polymers and dyes were developed under **Task 1.4**. **ICPF-CNR** synthesised and characterised QDs as light sensitizers in solar devices. Lead sulfide nanocubes (PbS NCs)¹⁴ and lead sulphide/cadmium sulfide nanocrystals¹⁵ can be highlighted as two examples of success in photovoltaic and electroluminescent devices, respectively. The evaluation of QDs in devices was carried out in collaboration with EPFL, CIDETEC, and UJI (WP5).



EPFL developed a range of dyes to be used as light sensitizer for Dye-sensitized Solar Cells (DSCs). Among the different families, it is worth to highlight the Squaraines^{16,17} –with ability to harvest the Near

⁸ M. Sessolo, H.J. Bolink, H. Brine, H. Prima-García, R. Tena-Zaera, J. Mater. Chem., 2012, 22, 4916–4920

⁹ D. Bresser, E. Paillard, M. Copley, P. Bishop, M. Winter, S. Passerini, Journal of Power Sources 219 (2012) 217-222

¹⁰ Patent application: GB1112248.8

¹¹ Patent application: GB1306814.3

¹² D. Bresser, E. Paillard, E. Binetti, S. Krueger, M. Striccoli, M. Winter, S. Passerini, J. Power Sources, 206 (2012) 301–309

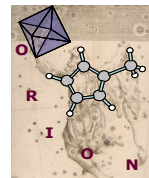
¹³ Patent application: PCT/EP/2011/059148

¹⁴ A. Loiudice, A. Rizzo, G. Grancini, M. Biasiucci, M. R. Belviso, M. Corricelli, M. L. Curri, M. Striccoli, A. Agostiano, P. D. Cozzoli, A. Petrozza, G. Lanzani, G. Gigli, Energy Environ. Sci., 2013, 6, 1565

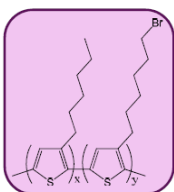
¹⁵ R. S. Sánchez, E. Binetti, G. Garcia-Belmonte, M. Striccoli, I. Mora-Seró, submitted to Nature Photonics

¹⁶ Y. Shi, R.B.M. Hill, J-H Yum, A. Dualeh, S. Barlow, M. Grätzel, S.R. Marder, Md.K. Nazeeruddin, Angewandte Chemie-International Edition, 50 (29) 6619-6621 (2011).

¹⁷ A. Dualeh, J.H. Delcamp, M.K. Nazeeruddin, M. Grätzel, Applied Physics Letters 100(17) 173512 (2012)



InfraRed radiation- and Ullazines¹⁸ due to their promising performance in solid-state DSC (WP5). EPFL developed also cutting-edge approaches to synthesize and integrate synergistically in DSCs zinc(II) porphyrins, reaching power conversion efficiency as high as 13 %¹⁹, which is defining the state of the art of the technology.



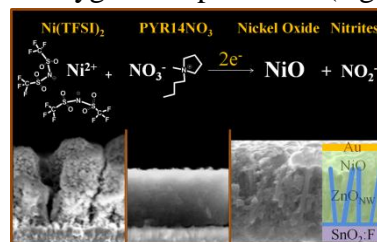
IMEC exploited its large background in the polymer synthesis to develop advanced synthetic approaches to obtain a large family of low bandgap polymers and copolymers,^{20,21,22} which open wide possibilities for the ionic functionalization in order to obtain hybrid materials containing light sensitizer building blocks (WP2).

All in all, an advanced version of materials from different families - including ionic liquids, inorganic nanowires and nanoparticles, molecular dyes and polymers- was successfully synthesized in WP1. These materials will be used as building blocks for the synthesis of hybrid materials in WP2 and as reference materials in devices (WP5). It is worth to note the novelty of these reference materials. Indeed, some of them by themselves allowed to progress beyond the art of the devices investigated in WP5.

WP2- Synthesis of Inorganic-Organic Hybrid Materials

The main objectives of this workpackage were to synthesize a) inorganic-organic materials composed of inorganic oxides and ionic liquids (**Task 2.1**) and b) complex inorganic-organic architectures including an additional building block, namely quantum dots, semiconducting polymer or molecular dye (**Task 2.2**).

Under **Task 2.1**, CIDETEC, in collaboration with SOLVIONIC, has developed an innovative electrochemical route to obtain metal oxide/ionic liquid hybrid thin films. The approach is based on the electrochemical reduction of an oxygenated precursor (e.g. O_2 ²³ or NO_3^- ²⁴) in aprotic ionic liquids containing metal cations (e.g. metal salts developed by SOLVIONIC in WP1). By this way, hybrid films constituted by the metal oxide (e.g. ZnO,²⁴ NiO,²⁵ CuO_x , CoO_x , MgO) and ionic liquid moieties have been obtained, demonstrating the generality of the deposition approach. These materials have been physico-chemically characterized in WP3 and evaluated in energy devices in WP5. As an example, in WP5, Dye-sensitized Solar Cells based on ZnO/PYR₁₄TFSI hybrid anodes show better performance than those based on ZnO pure anodes.²⁶ Additionally to be an effective way to obtain hybrid films



¹⁸ A. Dualeh, R. Humphry-Baker, JH. Delcamp, MK. Nazeeruddin, M. Gratzel, *Advanced Energy Materials*, 3 (2013) 496-504.

¹⁹ MK. Nazeeruddin et al. manuscript in preparation

²⁰ D. Bevk, L. Marin, L. Lutsen, D. Vanderzandeab, W. Maes, *RSC Advances*, 3 (2013) 11418-11431.

²¹ L. Marin, H. Penxten, S. V. Mierloo, R. Carleer, L. Lutsen, D. Vanderzande, W. Maes, *Journal of Polymer Science Part A-Polymer Chemistry*, 51 (2013) 4912-4922.

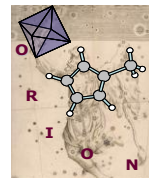
²² W. Vanormelingena, P. Verstappena, V. Maesa, D. Bevka, L. Lutsena, D. Vanderzandea, W. Maes, *Synlett*, 24 (2013) 2389-2392.

²³ E. Azaceta, R. Marcilla, D. Mecerreyes, M. Ungureanu, A. Dev, T. Voss, S. Fantini, H-J. Grande, G. Cabanero, R. Tena-Zaera, *Phys. Chem. Chem. Phys.*, 2011, 13, 13433-13440.

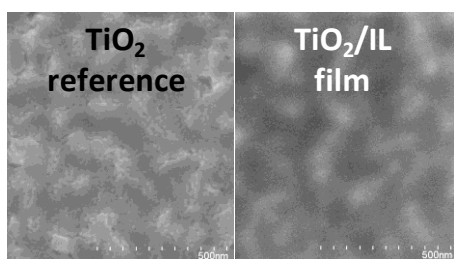
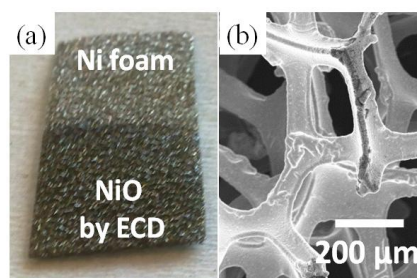
²⁴ E. Azaceta, N. T. T. Ngo, D. F. Pickup, C. Rogero, J. E. Ortega, O. Miguel, H.-J. Grande and R. Tena-Zaera, *Electrochim. Acta* 2013, 96, 261.

²⁵ E. Azaceta, S. Chavhan, P. Rossi, M. Paderi, S. Fantini, M. Ungureanu, O. Miguel, H-J. Grande, R. Tena-Zaera, *Electrochimica Acta* 71 (2012) 39-43

²⁶ E. Azaceta, J. Idigoras, J. Echeberria, A. Zukal, L. Kavan, O. Miguel, H-J. Grande, J.A. Anta and R. Tena-Zaera, *J. Mater. Chem. A*, 2013, 1, 10173.



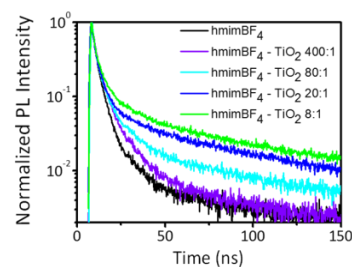
(i.e. metal oxide with additional functionalities), the deposition technique exhibits the value added of allowing the deposition of metal oxide films without the formation of metal hydroxides as intermediate and/or final reaction compounds. This is possible thanks to the aprotic character of the used ionic liquids (e.g. 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)) and is crucial for the single-step deposition of oxides of metals such as Ni, for which the $\text{Ni}(\text{OH})_2$ phase is stable until relatively high temperatures (i.e. 350°C). It is worth to note that for the metal oxides such as ZnO , which deposition is compatible with protic reaction media (e.g. water), the developed route also provided value added because films with innovative properties have been obtained. As the ionic liquid moieties can be removed by relatively soft post-deposition treatments, the developed electrodeposition technique served to obtain not only hybrid films with additional functionalities (as deposited material), but also pure metal oxide films (i.e. after a soft annealing) with innovative properties. As a further evidence of the versatility of the deposition technique, CIDETEC successfully deposited a conformal thin film of NiO on Ni foam substrates, obtaining Ni/ NiO core-shell foams with attractive performance as cathode in Li-ion batteries as demonstrated by CEGASA in WP5.



JHIPC proposed an innovative deposition technique –based on the ionic liquids and/or polymeric ionic liquids developed by SOLVIONIC, CIDETEC and LCPO in WP1- to obtain TiO_2 -ionic liquid hybrid films.²⁷ Interestingly, the morphology and properties of the films can be tailored as a function of the nature of the ionic liquid. As an example, methyl-3-

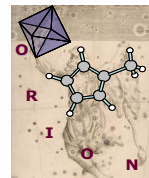
octylimidazolium chloride and butyl-methylimidazolium acetate, turned out to be promising materials for creating quality mesoporous films with good crystallinity. Polycrystalline dense layers (in contrast to the reference TiO_2 films, no cracks) were prepared by butyl-methylimidazolium acetate, butyl-methylimidazolium trifluoroacetate or poly(hexafluorobutyl) methacrylate. In general, the quality of the hybrid film has been found mainly related to the surface chemistry and dispersion properties more than to the electronegativity of halogens in the ionic liquid template. It is worth to note that the dense films show very good mechanical and acid resistance. Indeed, they have been evaluated by SOLARONIX as a compact blocking layer in DSCs (WP5). Moreover, the dense films has also a beneficial effect for morphology of the TiO_2 electro-spun anatase nanofiber-based anodes that results in an enhancement of the solar efficiency of dye sensitized solar cells, as demonstrated by EPFL in WP5.²⁸ Furthermore, JHIPC developed an ionic liquid-assisted hydrothermal synthesis route that allow to obtain hybrid nanopowders constituted of anatase and $\text{TiO}_2(\text{B})$ phases.

CNR-IPCF investigated the preparation of metal oxide/ionic liquid hybrid materials by combining pre-



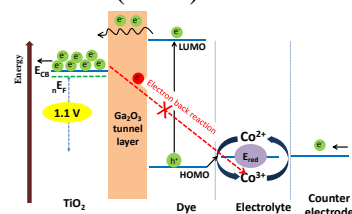
²⁷ Prochazka J., Kavan L., Zukalova M., Janda P., Jirkovsky J., Vlckova-Zivcova Z., Poruba A., Bedu M., Dobbelin M., Tena-Zaera R.: *J. Mater. Res.*, 28, 385–393 (2013).

²⁸ Krysova H., Zukal A., Trckova-Barakova J., Chandiran A. K. Nazeeruddin M. K., Graetzel M., Kavan L. *Chimia*, 67, 149–154 (2013).



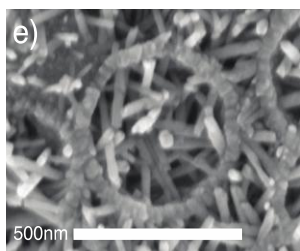
synthesized inorganic oxide nanoparticles (WP1) and imidazolium-based ionic liquids (WP1, SOLVIONIC). In particular, the preparative protocols were optimized for obtaining hybrids based on imidazolium ILs and TiO₂ nanorods synthesized in WP1 by CNR-IPCF and SOLVIONIC, respectively. The physical characterization of the hybrid material (e.g. time resolved photoluminescence) demonstrated the presence of charge-transfer phenomena from photoexcited TiO₂ nanorods to imidazolium rings of ionic liquids.²⁹ The cutting-edge knowledge gained into the interaction of nanocrystals and ionic liquids³⁰ may be of considerable interest for the hybrid materials community and was critically considered for the design of batteries and solar cells (WP5).

EPFL developed different families of innovative hybrid materials to be evaluated as advanced anodes in Dye-sensitized Solar Cells (DSC) in WP5. It is worth to highlight the TiO₂/Ga₂O₃ hybrid films,³¹ in which the Ga₂O₃ sub-nanometer shell play as a tunneling layer that blocks efficiently the electron back reaction and, therefore, the recombination losses in DSCs (WP5).^{32, 33}

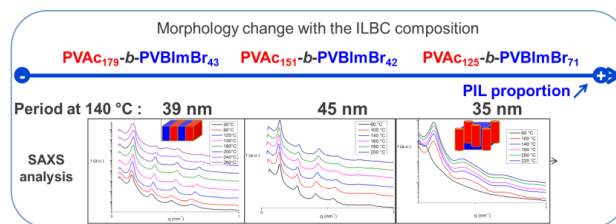


Alternative hybrid materials to block the recombination were also developed. As an example, the influence of the interface modification of TiO₂ surface, by coadsorbents, on the photovoltaic performances of the high efficiency dye sensitized solar cells was investigated. The effect of different functional group of the coadsorbents namely, carboxylic (4-guanidino butyric acid, chenodeoxycholic acid), phosphinic (dineohexyl phosphinic acid) and phosphonic (dodecyl phosphonic acid) acids, were explored. The presence of the

coadsorbents on the TiO₂ surface was studied using ATR-FTIR spectroscopy. The role of these coadsorbents on the band edge shift versus the recombination resistance was clarified in detail. Furthermore, hybrid materials based on a continuous TiO₂ shell deposited on an insulating scaffold (e.g. SiO₂³⁴) or complex architectures such as ZnO inverse opals filled with ZnO nanowires³⁵ –obtained in collaboration with **CIDETEC**–.



aaa **LCPO-CNRS** was able to elaborate a library of functional poly(ionic liquid)s (PILs) and PIL-based block copolymers (PIL BCPs) as reference materials. The main task of LCPO-CNRS in WP2 was to evaluate the potential of PIL BCPs to generate ordered self-assembled



²⁹ E. Binetti, A. Panniello, L. Triggiani, R. Tommasi, A. Agostiano, M. L. Curri, M. Striccoli, *J. Phys. Chem. B* 2012, 116, 3512–3518

³⁰ E. Binetti, A. Panniello, R. Tommasi, A. Agostiano, S. Fantini, M.L. Curri, M. Striccoli, *J. Phys. Chem. C* 2013, 117, 12923–12929.

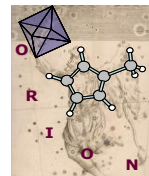
³¹ Patent application: PCT/IB2011/055550.

³² Chandiran, A. K.; Tetreault, N.; Humphry-Baker, R.; Kessler, F.; Baranoff, E.; Yi, C.; Nazeeruddin, M. K.; Grätzel, M. *Nano Lett.* 2012, 12, 3941–3947.

³³ Chandiran, A. K.; Nazeeruddin, M. K.; Grätzel, M. *Adv. Funct. Mater.* 2013, DOI: 10.1002/adfm.201302352

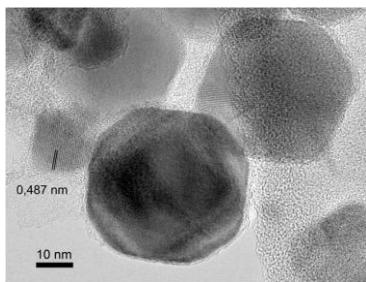
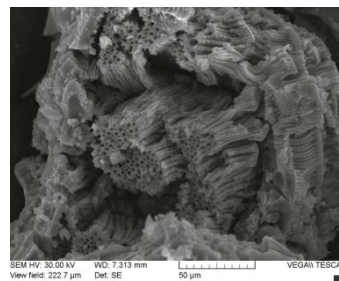
³⁴ Chandiran, A. K.; Comte, P.; Humphry-Baker, R.; Kessler, F.; Yi, C.; Nazeeruddin, M. K.; Grätzel, M. *Adv. Funct. Mater.* 2013, 23, 2775–2781.

³⁵ Labouchiere, P.; Chandiran, A.K.; Moehl, T.; Harms, H.; Chavhan, S.; Tena-Zaera, R.; Nazeeruddin, M.K.; Grätzel, M.; Tetreault, N. submitted.



mesostructures at the solid state. It was thus established, by combined techniques including DSC, TGA, temperature-dependent synchrotron SAXS, and TEM, that highly ordered lamellar or hexagonally packed cylindrical morphologies could be achieved by self-assembly in bulk of poly(vinyl acetate)-*b*-poly(*N*-vinyl-3-butylimidazolium), PVAc-*b*-PVBuIm PIL BCP carrying a bromine counter-anion. Of particular interest, observation of relatively long-range order with interdomain spacings in the range of 30-40 nm, which is ~ 20-30% higher than values generally reported with more “conventional” BCPs, suggests that these PIL BCPs self-assemble in a strong micro-phase separation regime. This also indicates that PIL chains exhibit a high degree of chain stretching. In addition, simple anion exchange, from bromide (Br⁻) to bis(trifluorosulfonyl)imide (Tf₂N⁻), allowed changing the volume fraction of PIL BCPs, thus enabling to vary domain sizes.⁴ Finally, PVAc blocks could be also subjected to hydrolysis, forming hydrophilic poly(vinyl alcohol), witnessing the versatility of this novel PIL BCP platform.

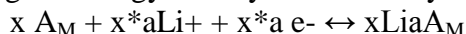
SOLARONIX developed titania tubular microchannel arrays, which are specially appealing to be used as anode in DSCs based on ionic liquid electrolytes. When using ionic liquid electrolytes, viscosity may be one of the main issue that limits charge transport and consequently device efficiency. Titania electrode porosity is a key parameter to be optimized to allow better electrolyte penetration. Well-aligned hierarchical titania tubular macrochannel arrays with high surface area were synthesized via a facile one-step ammonia hydrothermal synthesis process without using sacrificial structure-directing templates. The interconnected macro-mesoporous samples possess a high surface area of around 140 m²g⁻¹ measured by BET technique. These titania particles were formulated as a screen printable ink and the resulting titania electrodes demonstrated a higher dye loading, thanks to the enhanced specific area. Furthermore, the tubular macro channels provide better electrolyte penetration, a desirable feature when using viscous or ionic liquid based electrolytes. Dye-sensitized solar cells based on titania tubular microchannel arrays were tested in WP5 and showed an improved power conversion efficiency in comparison with classical titania nanoparticles.



On the other hand, **MUENSTER** synthesized hybrid conversion/alloying oxides, which incorporate a transition metal ($T_M = \text{Co, Fe, Cu} \dots$) and an alloying material ($A_M = \text{Sn, Zn, Si}$), to allow for a conversion reaction thanks to the presence of T_M .

$$A_M x T_M y O_z + 2z \text{Li}^+ + 2ze^- \leftrightarrow y T_{M\text{nano}} + z \text{Li}_2\text{O} + x A_M$$

In addition thanks to A_M , after the first reduction to the metal form, it can be further alloyed, leading to more capacity which in addition occurs at lower potential, increasing the energy density of the battery:

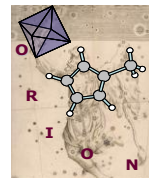


Finally, $(x a + z) \text{Li}^+$ can be stored into the material. ZnFe_2O_4 was proposed as a first example of this class of materials, reaching very appealing electrochemical behavior as it will be discussed in WP3.^{36,37,38} Based on the same idea Muenster developed a

³⁶ Patent application: DE-10-2012-101-457.4 (PCT/EP2013/053541)

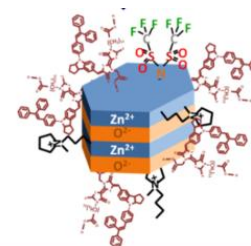
³⁷ F. Mueller, D. Bresser, E. Paillard, M. Winter, S. Passerini, *J. Power Sources* 236 (2013) 87

³⁸ D. Bresser, E. Paillard, R. Kloepsch, S. Krueger, M. Fiedler, R. Schmitz, D. Baither, M. Winter, S. Passerini, *Adv. Energy Mater.* 3 (4) (2012) 513



synthetic route for obtaining ZnO particles and ZnO nanoparticles doped with transition metals (Fe or Co and possibly Cu).^{39,40}

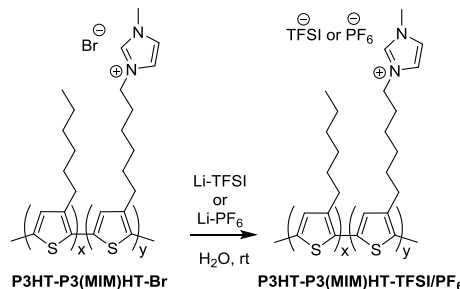
Under **Task 2.2**, a further development of the ionic liquid-based deposition protocol, developed under task 2.1, allowed to **CIDETEC** to reach the successful synthesis of an unambiguous example of 2nd generation ORION hybrid materials, which are constituted by metal oxides, ionic liquid and molecular dyes. As it will be shown in WP5, the presence of ionic liquid moieties was crucial to enhance the photovoltage in the final DSCs thanks to the upward displacement of the conduction band of the ZnO.²⁶



ZnO-PYR14TFSI-D358

CNR-IPCF investigated other family of 2nd generation ORION hybrid materials based on the dispersion of semiconductor quantum dots (QDs) in imidazolium-based ionic liquids¹ (also functionalized) and in polymeric ionic liquids. For this purpose (CdSe)ZnS, CdSe and PbS nanocrystals were synthesized by colloidal chemistry routes, with good control on size, shape, size distribution and crystalline phase. Imidazolium-based ILs and polymeric imidazolium ILs were provided by SOLVIONIC and CNRS-LCPO ORION partners, respectively. In order to improve nanoparticle and QD affinity and dispersion in IL or PIL host medium, nanocrystals surface was processed by capping exchange procedures performed using polar ligands that enable NC dispersion in polar solvents, mainly dimethylsulphoxide (DMSO).⁴¹ (NH₄)₂S was used to process CdSe QDs and to obtain DMSO dispersion of both imidazolium TFSI based ILs and imidazolium based PILs, also properly functionalized with functional groups showing high affinity with NC surface, and provided by Solvionic and CNRS-LCPO, respectively.⁴²

Another family, named ionic solar light absorber co-polymers, of 2nd generation ORION hybrid materials was investigated by **IMEC**. Concretely, the P3HT-P3BHT precursor copolymers –obtained in WP1- were converted to ionic copolymers by treatment with *N*-methylimidazole. It is known that imidazolium-type ionic liquids with bromine counter ions are hygroscopic and only fairly soluble in most common (low to medium polarity) organic solvents. For that reason IMEC have exchanged the bromine counter ions for some of the ionic polymers to bis(trifluoromethanesulfonyl)imide (TFSI) and/or hexafluorophosphate (PF₆⁻) counter ions, which are known to be more hydrophobic.



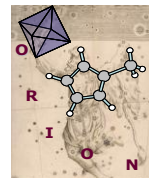
The anion exchange procedures were found very straightforward. The relevance of the counter ions for OPV applications has already been demonstrated previously. Upon exchanging the bromine counter ions of the P3(MIM)HT-Br homopolymer for TFSI, the material became more soluble in solvents suitable for bi-layer processing, resulting in neat films as prepared by meniscus coating from 2,2,3,3-tetrafluoro-1-propanol

³⁹ D. Bresser et al., DE-10-2012-107-199.3 (PCT/EP2013/066354)

⁴⁰ D. Bresser, F. Mueller, M. Fiedler, S. Krueger, R. Kloepsch, D. Baither, M. Winter, E. Paillard, S. Passerini, submitted to *Energ. Env. Sci.*

⁴¹ A. Panniello, E. Binetti, C. Ingrosso, M.L. Curri, A. Agostiano, R. Tommasi, M. Striccoli, *J Nanopart Res* (2013) 15:1567

⁴² A. Panniello, C. Ingrosso, P. Coupillaud, M. Tamborra, E. Binetti, M.L. Curri, A. Agostiano, D. Taton, M. Striccoli, *Materials* 7 (2014) 591-610

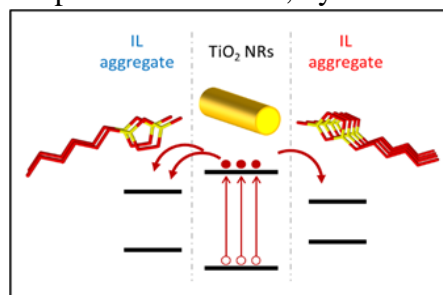


(TFP). The counter ions are also of particular relevance when one desires to take additional advantage of ionic movement to assist in the charge separation process. To broaden the structural variation, some other ionic (co)polythiophene derivatives were also synthesized in an analogous way to allow fine tuning of the polymer polarity and the solution behavior. As it will be shown in WP5, these ionic co-polymers served to enhance the performance of Bulk HeteroJunction (BHJ) solar cells.⁴³

WP3- Characterization and Processing of ordered inorganic-organic hybrid materials

The main objective of this workpackage was to characterize the materials obtained in the other workpackages, studying their physico-chemical and structural (**Task 3.1**), electrochemical (**Task 3.2**) and electro-optical (**Task 3.3**) properties. Additionally, in **Task 3.4** (Processing methods of inorganic-organic hybrids), special attention was also paid to the formulation of inks to be used for the application of large-scale coating solutions in order to pave the way to the fabrication of demonstrators in WP6.

Under **Task 3.1**, CNR-IPCF characterized the different inorganic/ionic liquid hybrid materials developed in WP2 such as TiO₂ NRs/IL (first generation) and CdSe(ZnS) QDs dispersed in ILs (second generation). As a first step, the optical properties of the imidazolium ILs were deeply investigated by spectroscopic measurements, by both time integrated and time resolved techniques, to provide a better understanding of their physical and chemical behaviour. The obtained results contributed to get insight the effect of alkyl chain and anion type on the emission characteristics, and, hence, on the presence of associated structures of imidazolium cations responsible of the emission properties of ILs.⁴⁴ Furthermore, in collaboration with SOLVIONIC, a systematic investigation of the optical and morphological properties of such first generation inorganic/IL hybrids (e.g. TiO NRs/imidazolium ILs) was carried out to study the interaction among the two components they are made of. Time integrated and time resolved spectroscopic measurements demonstrate charge transfer from colloidal TiO₂ NRs to imidazolium ILs occurring in solution.⁴⁵ Such investigation is of large scientific and technological interest in the implementation of TiO₂ NR /ILs hybrid materials in innovative energy devices (WP5). The optical properties of the second generation ORION hybrid materials were also deeply studied by spectroscopic investigations, while the hybrid morphological features were investigated by AFM characterization. The latter, performed on hybrid materials deposited on silicon, confirmed the organization of the ionic liquids and hybrids in super-structures.⁴⁶

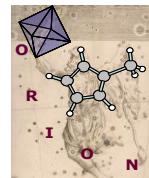


⁴³ J. Kesters, T. Ghos, H. Penxten, J. Drijkoningen, T. Vangerven, D. M. Lyons, B. Verreet, T. Aernouts, L. Lutsen, D. Vanderzande, J. Manca, W. Maes, *Advanced Energy Materials*, 3 (2013) 1180-1185.

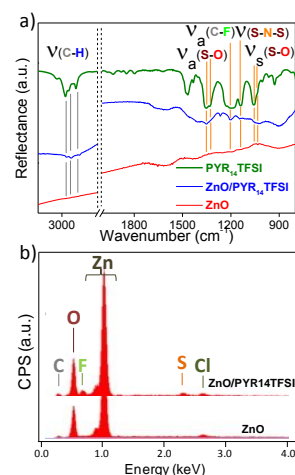
⁴⁴ E. Binetti, A. Panniello, L. Triggiani, R. Tommasi, A. Agostiano, M. L. Curri, M. Striccoli, *J. Phys. Chem. B*, 116 (2012) 3512–3518

⁴⁵ E. Binetti, A. Panniello, R. Tommasi, A. Agostiano, S. Fantini, M.L. Curri, M. Striccoli, *J. Phys. Chem. C*, 117 (2013)12923–12929

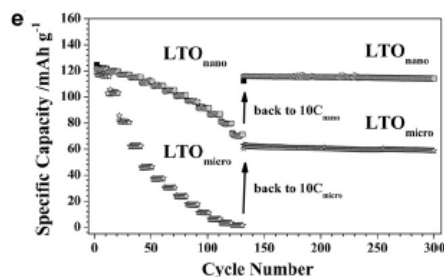
⁴⁶ A. Panniello, E. Binetti, C. Ingrosso, M.L. Curri, A. Agostiano, R. Tommasi, M. Striccoli, *J. Nanopart. Res.* 15 (2013) 1567



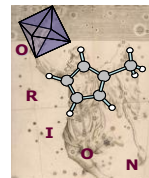
CIDETEC developed a particular characterization protocol based on the combination and correlative analysis of different techniques such as Field Emission Scanning Electron Microscopy (FESEM), X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), X-Ray Photoemission (XPS) and optical spectroscopy. By this way, CIDETEC partner was able to characterize successfully the first (i.e. inorganic/ionic liquid)²³ and second²⁶ (i.e. inorganic/ionic liquid/light sensitizer) generation of “ORION hybrid materials” obtained in WP2. It is worth to note that thermal annealing treatments were also included in the characterization protocol in order to remove the ionic liquid moieties and have access to the inorganic moiety data in order to facilitate the comparison to the reference materials.



Under **Task 3.2, MUESTER** carried out an advanced electrochemical characterization of materials provided by different partners in order to guide their application in Li-ion batteries. A large number of prospective active materials for battery electrode were characterized and tested. In order to obtain the best performing electrodes, some materials were first processed into nanocomposites including carbon and the respective processes as well as their use in battery were patented.^{36,39} Later on, some composite were also prepared either from commercial nanoparticles or from particles synthesized in Muenster. As a result, electrodes with capacity well above ORION⁷ target for anode (900 mAh g⁻¹) were obtained by the introduction of hybrid conversion/alloying materials. In addition to the active materials for Li-ion battery, a polymer from IMEC was tested as conductive agent for Li-metal polymer battery with little success and a new polymeric ionic liquid nano latex binder was introduced and tested in battery electrodes with good performance.⁴⁷ Below is a summarizing list, classified as a function of the provider partner, of the materials electrochemically characterized by Muenster. J.M.: TiO₂, LTO (3), SiO₂, Co₃O₄, Li₄Ti₅O₁₂ (3), LiMnPO₄, ZnO, LiFePO₄ (3), LiMn_{0.5}Ni_{0.5}O₂, LiNi_{0.33}Mn_{0.33}Co_{0.33}O, LiMn₂O₄, LTO (+Co₃O₄) (2), LTO (+SnO₂) (2), CoFe₂O₄, ZnFe₂O₄ (+Sn), ZnFe₂O₄ (+Fe), SOLVIONIC (5 samples): IL monomers (4), crosslinker + IL electrolyte, CNR-ICPF (3 samples): TiO₂-NRs (several batches), TiO₂-NRs + SWCNT, Fe₂O₃ nanocrystals, CNRS-LCPO: Two ionic liquid crosslinkers, MUESTER: CoO-C, ZnFe₂O₄-C, Zn_{0.9}Fe_{0.1}O, Zn_{0.9}Co_{0.1}O, Sn-C. Among these materials, it is worth to highlight some due to their relevance in the project. LiFePO₄, synthesized by JM in WP1, was used as starting material to prepare hybrid derivatives (i.e. carbon coated). The latter exhibited promising electrochemical performances (e.g. capacity > 150 mAh/g) and were selected for preparing prototypes by CEA (WP6). It is worth to mention that LiFePO₄ was the first material to be processed in a carbon containing composite and started the trend followed by MUESTER within ORION: the application of the concept of either carbon coating or carbon containing composite preparation. LiMn₂O₄ gave promising electrochemical behavior (capacity > 110 mAh/g, i.e. close to the theoretical value: 148 mAh/g). As a consequence, LiMn₂O₄ and hybrids



⁴⁷ J. v. Zamory, M. Bedu, S. Fantini, S. Passerini, E. Paillard, *J. Power Sources* 240 (2013) 745



were initially selected for prototyping. However, as explained in WP6, problems in the processing of large scale electrodes were found. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) was used as a first unambiguous example to show that very high rate performance can be achieved when the size of the particle is low enough.⁴⁸ LTO-based hybrids were also selected for the final prototypes.

Oleic acid stabilized TiO_2 anatase nanorods, from CNR-ICPF (WP1), were used to prepare TiO_2 -C hybrid nanocomposite. As a result, in a first study, extra carbon was obtained from the oleic acid carbonization and excellent performances were obtained, both in terms of capacity as the highest values ever reported for TiO_2 anatase were obtained. Even more interestingly, good rate performance and excellent cycling stability was obtained.^{13,49} It is noted that PVdF was used as a binder. Furthermore, MUENSTER extended the hybrid nanocomposite synthesis and characterization to TiO_2 nanorods capped with polyacrylonitrile block copolymers.^{50,51} MUENSTER characterized Co_3O_4 nanoparticles (from JM, WP1) showing high capacities (i.e. above 1300 mAh g^{-1}), but unfortunately subject to severe capacity fading, which is rather common for nanometric conversion materials. As a solution, MUENSTER developed a process to prepare a

hybrid carbon composite from these particles. During the composite preparation, the particles are reduced to CoO and partially to Co . As a result, the capacity decrease to the 800 mAh g^{-1} range (still twice that of graphite) and the cycling stability was strongly improved.⁵²

On the other hand, MUENSTER characterized electrochemically the new family of hybrid materials synthesized by itself in WP2 (i.e. conversion/alloying oxides, which incorporate a transition metal ($T_M = \text{Co}, \text{Fe}, \text{Cu} \dots$) and an alloying material ($A_M = \text{Sn}, \text{Zn}, \text{Si}$)). Overall, very large capacities in the 1000 mAh g^{-1} range were obtained ZnFe_2O_4 -C, together with ultra high rate performance and cycling stability.³⁸ Other materials of the family such as $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O}$, which benefits from being processed into a carbon nanocomposite, and $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ that performs rather steadily without the need of carbon coating were also characterized. These two materials had never been reported as active materials for Li-ion batteries and offer large capacities of c.a. 800 - 1000 mAh g^{-1} as well as improved energy densities as compared with ZnFe_2O_4 due to a lower operating voltage.⁵³

⁴⁸ D. Bresser, E. Paillard, M. Copley, P. Bishop, M. Winter, S. Passerini, *J. Power Sources* 219 (2012) 217

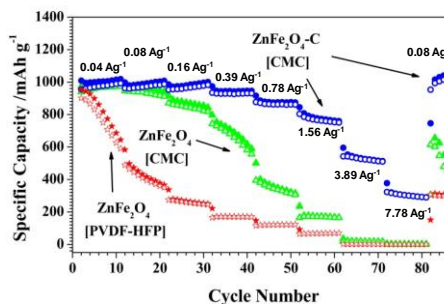
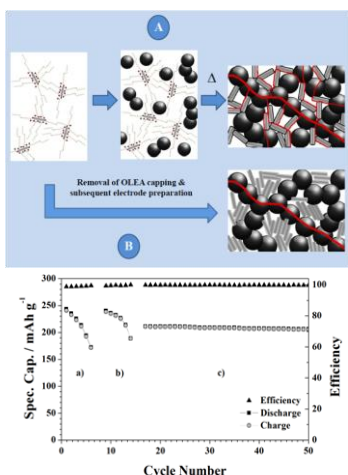
⁴⁹ D. Bresser, E. Paillard, E. Binetti, S. Krueger, M. Striccoli, M. Winter, S. Passerini, *J. Power Sources* 206 (2012) 301

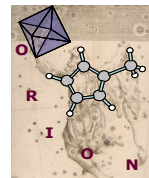
⁵⁰ B. Oschmann D. Bresser, M. Nawaz Tahir, K. Fischer, W. Tremel, S. Passerini, R. Zentel, , *Macromol. Rapid Commun* (2013) DOI: 10.1002/marc.201300531

⁵¹ D. Bresser, B. Oschmann, M. N. Tahir, W. Tremel, R. Zentel, S. Passerini, *Journal of Power Sources*, 2013, DOI: 10.1016/j.jpowsour.2013.10.013

⁵² Patent application: DE-10-2011-057-015.2

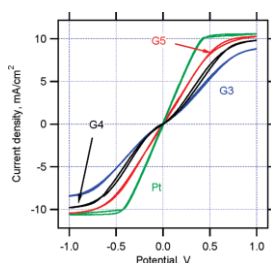
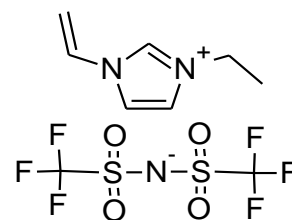
⁵³ D. Bresser, F. Mueller, M. Fiedler, S. Krueger, R. Kloepsch, D. Baither, M. Winter, E. Paillard, S. Passerini, *Chem. Mater.* 25 (2013) 4977–4985





CEA characterized several materials prepared by Flame Spray Pyrolysis (JM, WP1) which is an innovative technique to synthesize inorganic compounds with high surface area. 5 materials (LiMn_2O_4 , $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$, $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, LiMnPO_4 and LiFePO_4) have been selected as active materials for positive electrodes and 7 (SiO_2 , TiO_2 , Co_3O_4 , CoFe_2O_4 , SnO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$) for negative electrodes. Based on discussions with CEGASA and MUENSTER, various formulations in organic or aqueous media have been developed in order to prepare electrodes by coating at the laboratory scale. Indeed, the particular properties of these compounds (especially, their very high surface area) required to change the parameters of formulations i.e. the nature and the ratio of binder, solvent or conductive agents in order to obtain usable slurries. This research leads CEA to develop new binder which has been patented.⁵⁴

Concerning materials for positive electrode, CEA develops an efficient post-treatment of LiFePO_4 (carbon coating) in order to prepare a composite material which presents high and stable electrochemical performances and has consequently been selected as active materials for positive electrodes. Specific equipment has been designed in order to scale-up this process and 300g of carbon coated LiFePO_4 has been produced for WP5. For negative electrodes, as received $\text{Li}_4\text{Ti}_5\text{O}_{12}$ shows good electrochemical performances but severe problems has been encountered for the formulation of the slurries at pilot scale. Consequently CEA decided to treat these powders at high temperature in order to increase the particle size and prepare 200g of post-treated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for WP5. In collaboration with SOLVIONIC, CEA also synthesized some innovative ionic binders by polymerization of ionic liquids based monomers and incorporate them in the formulation of LiFePO_4 based electrodes. The electrochemical performances of these electrodes should still be optimized but it was the first example of application of PIL (Polymerizable Ionic Liquids) as binders for electrodes.



JHIPC characterized electrochemically the hybrid nanopowders based on a mixtures of anatase and $\text{TiO}_2(\text{B})$ phases, obtained in WP2, in order to correlate the preparation parameters and additives with the electrochemical behavior and content of $\text{TiO}_2(\text{B})$. The polarity of organic solvent and ionic liquids was found critical to control the yield of $\text{TiO}_2(\text{B})$.⁵⁵ On the other hand, JHIPC performed advanced electrochemical characterization of innovative hybrid optically transparent cathodes, containing graphene nanoplatelets. In comparison to the reference system (i.e. FTO/Pt), it is worth to note that the latter exhibit significantly higher electrochemical activity in the ionic liquid-based electrolytes. Graphene nanoplatelets have large number of active edge sites for I_3^-/I^- electrocatalysis. Consistent with the impedance data on symmetrical dummy cells, the graphene cathodes exhibit better performance in ionic liquid based dye-sensitized solar cells (WP5).^{56,57,58} The potential of grapheme as non-calcined conductive additive in LiFePO_4 -based hybrid materials for batteries was also demonstrated.

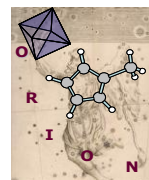
⁵⁴ CEA patent application, in preparation

⁵⁵ Mansfeldova V., Laskova B., Krysova H., Zukalova M. and Kavan L. *Catalysis Today*, under review

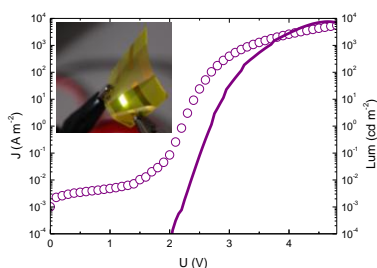
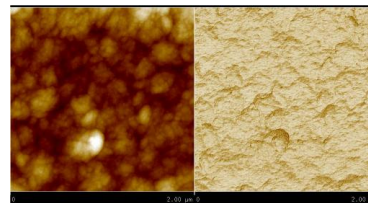
⁵⁶ Kavan L., Yum H.J. and Grätzel M. *ACS Nano*, 5, 165–172 (2011).

⁵⁷ Kavan L., Yum J.H. and Grätzel M., *Electrochim. Acta*, in press, DOI: 10.1016/j.electacta.2013.08.112

⁵⁸ Ahmad S., Guillen E., Kavan L., Grätzel M. and Nazeeruddin M. K. *Energy Environ. Sci.*, DOI: 10.1039/C3EE41888J



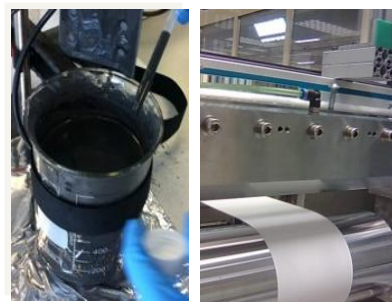
Under **Task 3.3**, **CRF** carried out the electro-optical characterization of metal oxide/IL hybrid films obtained by CIDETEC (WP2). Firstly, Atomic Force Microscopy (AFM) was used to characterize the roughness of the films. Then, surface potential or current measurements were performed in contact mode. I-V characteristic curves were collected applying a spatial offset to center the tip over a single surface point. In good agreement with results from the electrical characterization techniques (e.g. four-point probe), conductive-AFM analysis showed the semiconducting behavior of the hybrid films.²⁵



UVEG evaluated hybrid organic-inorganic materials for charge injection layers in hybrid organic-inorganic light-emitting diodes (HyLEDs). Among them, can be highlighted the ZnO nanoparticles, synthesized by CIDETEC in WP1, that can be processed at low temperatures (i.e. 25 – 150 °C) into an electron injecting electrode for HyLEDs. Thanks to their excellent optoelectronic properties and room temperature

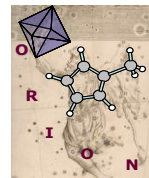
processing, flexible HyLEDs with high luminance and good efficiencies were fabricated.⁵⁹ Furthermore, the reduction of the injection barrier for electrons in ZnO/IL hybrid films was successfully demonstrated, allowing the obtaining of high electroluminescence efficiency at low operating voltages.

Under **Task 3.4**, **CEGASA** focused its efforts on developing performance-competitive slurry formulations and coating conditions to finally produce electrodes for pouch cell assembly and demonstrators in WP6. Taking into account results from the task 3.2, the main efforts were focused on the scale-up of anodic coatings using Li₄Ti₅O₁₂ (LTO) and cathodes with LiMn₂O₄(LMO). The special conditions of having nanosized and high surface area active materials has required the testing and adaptation of suitable stirrers to prepare homogeneous mixtures (active material/carbon/binder) while avoiding agglomeration. The process optimization allowed to obtain low loading of nano-LTO (<4 mg/cm²) water-based electrode coatings and finally scaled-up anode manufacturing from nanoparticle active materials using PVDF as binder (NMP solvent). High loadings (from 5 to 8.5 mg/cm²), expected for cell fabrication but difficult to achieve for high surface area nanomaterials, were successfully reached.



SOLARONIX developed improved screen printable TiO₂ inks by using an organic binder. The addition of 18 nm in diameter anatase TiO₂ nanoparticles and TiO₂ nanorods provided by CNR-IPCF (WP1) in the paste formulations was also investigated. The improvements in titania inks helped enhancing significantly the DSC performances (WP5). Another breakthrough in the field of DSSC would be to be able to screen print the electrolyte instead of injecting a solution into a pre sealed device. SOLARONIX developed a formulation based on the addition of silica nanoparticles (2-

⁵⁹ M. Sessolo, H.J. Bolink, H. Brine, H. Prima-Garcia, R. Tena-Zaera, *J. Mat. Chem.*, 22, 4916-4920 (2012).

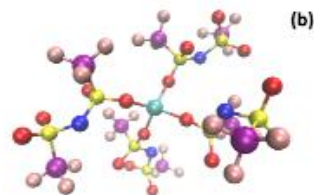


3 % wt.) to the ionic liquid electrolyte. The new formulation resulted in a screen printable paste with optimum viscosity. Very interestingly, in WP5, no changes in the power conversion efficiency were detected in DSCs fabricated with vs. the reference devices. A more elegant way based on the gelification of the electrolyte using ionic liquid monomers and crosslinkers (WP2) was also investigated to reach printable DSC electrolytes. Ionic liquid monomers were supplied by SOLVIONIC and crosslinker by CNRS LCPO. Innovative gel electrolyte formulations were developed by SOLARONIX. However, the resulting electrolyte still needs to be optimized.

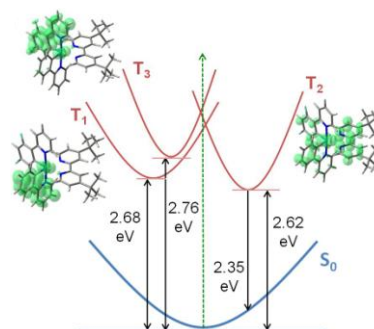
WP4- Modelling and Simulation

The main objective of this workpackage was to predict and/or provide further understanding into the microscopic morphology of the hybrid systems (**Task 4.1**), the molecular-structure and electronic properties of organic/inorganic interfaces (**Task 4.2**) and electronic transport in devices, including phenomena occurring at the material interfaces (**Task 4.3**).

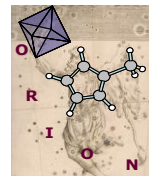
Under **Task 4.1**, UMONS developed new Molecular Dynamics (MD) simulations to study the supramolecular structure and transport properties of ionic liquids containing lithium salts. Special focus was paid on two reference systems: (i) $\text{PYR}_{14}\text{TFSI}$ containing a 0.10 mol fraction of LiTFSI , and (ii) $\text{PYR}_{14}\text{FSI}$ containing a 0.10 mol fraction of LiFSI . The modelling studies were carried out in close collaboration with MUNSTER, who provide experimental data on the shear viscosity and diffusion constants. The molecular-scale structure has been examined, based on a Radial Distribution Function (RDF) analysis. The results clearly showed that the Li^+ is bonded to four (T)FSI anions in the first coordination shell, with the PYR_{14}^+ cations located in the second shell. The study pointed out that Li^+ cations are coordinated by four oxygen atoms. Thus, one can conclude that Li^+ is coordinated by four oxygen atoms belonging to four different (T)FSI molecules. The mechanisms for Li^+ ion transport were also investigated. There are two limiting mechanisms for the Li^+ cation transport: on one hand, Li^+ cations can diffuse with their coordination shells as lithium complexes (vehicular mechanism). A fast exchange of anions was concluded, suggesting that there is a significant contribution to the Li^+ transport from the structure-diffusion mechanism. As the temperature increases, the self-diffusion coefficients also increase but the residence time decreases in a proportion such that Li^+ transport is clearly consistent with the structure-diffusion mechanism.⁶⁰



UVEG focused on the quantum chemical calculations of light-emitting molecules. It can be highlighted results on molecules based on isocyanide and tris-heteroleptic complexes. As an example of molecules with isocyanide ligands, nNew bis-cyclometalated, cationic Ir(III) complexes $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{CN-tert-C}_4\text{H}_9)_2](\text{CF}_3\text{SO}_3)$ were investigated with 2-phenylpyridines ($\text{C}^{\wedge}\text{N}$) and strong-field, non-chromophoric neutral tert-butyl isocyanides. To tune the photophysical properties of the complexes, the

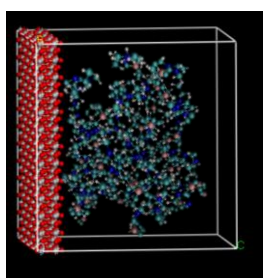
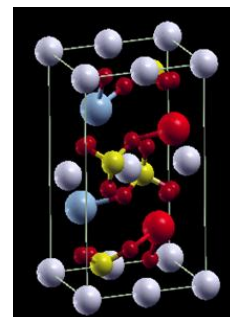


⁶⁰ C. J. F. Solano, S. Jeremias, E. Paillard, D. Beljonne, R. Lazzaroni; ; *J. Chem. Phys.*, 139 (2013) 034502

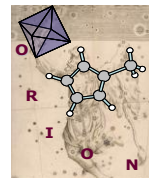


cyclometalating 2-phenylpyridine ligands were modified with electron-withdrawing (4-F and 5-CF₃), electron-donating (4-OCH₃), and bulky (4-*tert*-butyl and 5-CF₃) substituents. The resulting cationic Ir(III) isocyanide complexes emit phosphorescence at higher energies. Concerning the tris-heteroleptic complexes, in a new process, EPFL has developed the synthesis of a very efficient, pure green-light emitting Ir-iTMC containing two different C^N ligands, 2-phenylpyridine (ppy) and 2-(2,4-difluorophenyl)pyridine (diFppy), and one N^N ligand, 4,4'-di-*tert*-butyl-2,2'-bipyridine) (dtb-bpy), thereafter referred as “complex 2”. To gain insight into the electronic and optical properties of “complex 2”, UVEG performed DFT calculations on the [Ir(ppy)(diFppy)(dtb-bpy)]⁺ cation in acetonitrile solution. To investigate the nature of the emitting excited state, the low-lying triplet states of “complex 2” were calculated using the time-dependent DFT (TD-DFT) approach. The lowest triplet states of “complex 2” (T₁, T₂, and T₃) are calculated 2.68, 2.62, and 2.76 eV above S₀ (adiabatic energy differences), respectively, and T₂ is the most stable triplet (Figure 4.4c). The unpaired-electron spin-density distribution computed for the optimized geometry of T₂ confirms the mixed ³MLCT/³LLCT character of this state, and illustrates the higher contribution of the ppy ligand, compared with the diFppy ligand, to the electron transfer that takes place in this state to the diimine ligand. The calculations therefore predict that emission in “complex 2” occurs from the T₂ ³MLCT/³LLCT triplet that implies an electron transfer from the Ir–ppy environment to the diimine ligand. The CT nature of the emitting triplet is in agreement with the broad and unstructured aspect of the experimental emission band.

CRF simulated the properties of LiFePO₄, LiMnPO₄ and mixed systems (LiMn_{1-x}Fe_xPO₄) as electrodes materials for Li-ion batteries. The simulations were performed using Density Functional Theory (DFT) implemented in Quantum Espresso codes. Vanderbilt’s ultra-soft pseudo-potentials were employed to reduce the calculation weight. Preliminary calculations allowed to select the GGA functional and ferromagnetic configuration for the following simulations. In general, the obtained variation trend for the cell volume and bandgaps was in good agreement with the experimental data. However, according to the GGA+U model, the lithium extraction potential for partially lithiated structures is independent from the lithium content and higher than the extraction potential from the fully lithiated structure. For this reason, the calculations predict that the delithiation process occurs with the separation of two phases: the completely de-lithiated one and the initial structure containing the full lithium content. This means that GGA+U is not able to describe the multi-redox system discriminating between Mn³⁺/Mn²⁺ and the Fe³⁺/Fe²⁺ redox couples. This can be related to the non-correct description of the localization of d-orbitals within this model.



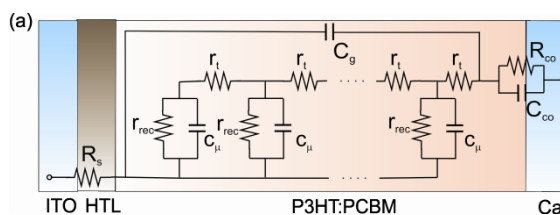
Under **Task 4.2**, UMONS performed pioneering studies on the interaction between the ionic liquids (IL) and metal oxide surfaces. As an example, a periodic simulation box containing ethyl-methyl imidazolium tetrafluoroborate (EMIMBF₄) (i.e. the reference ionic liquid) was put in contact with a frozen TiO₂ surface (anatase (001) or rutile (110)). The force field was adjusted to account for the interaction between the ionic liquid and the oxide surface, based on the results of DFT calculations



on simple model systems. The formation of a dense layer of ionic liquid anions adsorbed on the oxide surface was concluded. Electrostatic interactions lead to the formation of a cation layer on top of the anion layer. The width of that layer is somewhat broader, due to the larger size and conformational flexibility of studied cations. The alternating layering extends for two more periods, up to about 20 Å from the surface. Further away, the density of the anions and cations become equal and the IL layer is homogeneous, as expected for a liquid.

Under **Task 4.3**, UJI developed modeling and simulation tools, mainly based on the electrical impedance spectroscopy, for gaining a deeper understanding of the mechanisms limiting the performance of hybrid and organic solar cells and nanomaterials-based Li-ion batteries. As an example, intense work on the development of impedance models of quantum-dot based photovoltaic devices (QDSC) was carried out, demonstrating that ionic liquid containing S^{2-}/S_n^{2-} redox couples –developed by CIDETEC in WP1- appear to be highly attractive not only for enhancing the robustness and performance of innovative solar cell architectures, such as QDSC, but also to surpass the limitations of old concepts and therefore revive their strong potentials.² The studies were also extended to co-sensitized (combined QD and commercial dye absorption) solar cells.⁶¹ It is worth to note that impedance spectroscopy models were able to capture the kinetics of back reaction. The key factor reducing the efficiency of this kind of solar cells was then identified. On the other hand, UJI modelled the electrical response of organic solar cells, which is by far much more challenging. The use of both highly and poorly efficient cathodes in combination with impedance

spectroscopy allowed for a clear-cut separation of the physical mechanisms occurring within the active layer bulk from those taking place at the organic blend-contact interface. The impedance analysis demonstrated that charge carriers (electrons) move by diffusion within extended quasi-neutral regions, so that the cell operation is governed by the kinetic competition between charge transport towards the outer contacts and loss by recombination. This modelling achievement allows identifying mechanisms (transport and carrier recombination) limiting the cell performance.^{62,63} Additionally, in the field of nanomaterials for Li-ion batteries, UJI developed a new equivalent circuit that directly models the conversion reaction process was set up by fitting the Nyquist plots from IS analysis. The conversion reaction sub-circuit reproduces the hysteresis in the discharge/charge voltage profile, indicating that the hysteretic behaviour has a thermodynamic origin rather than being limited by Li^+ transport.⁶⁴ The validity of the model was checked in innovative $ZnFe_2O_4$ -based anodes developed by MUNSTER in WP3. Therefore, UJI contributed significantly to solve the lack of convincing electrical

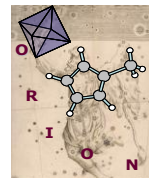


⁶¹ V. González-Pedro, Q. Shen, V. Jovanovski, S. Giménez, R. Tena-Zaera, T. Toyoda, I. Mora-Seró, *Electrochimica Acta* Volume 100 (2013) 35–43

⁶² T. Ripollés-Sanchis, A. Guerrero, J. Bisquert, G. Garcia-Belmonte, *Journal of Physical Chemistry C*, 116 (2012) 16925–16933.

⁶³ A. Guerrero, T. Ripollés-Sanchis, P. P. Boix, G. Garcia-Belmonte, *Organic Electronics*, 13 (2012) 2326–2332

⁶⁴ C. Xu, Y. Zeng, X. Rui, J. Zhu, H. Tan, A. Guerrero, J. Toribio, J. Bisquert, G. Garcia-Belmonte, Q. Yan, *J. Phys. Chem C*. 117 (2013) 17462–17469



models specifically focused to analyze the behaviour of conversion-reaction electrodes.⁶⁵

WP5- Testing and Evaluation in Energy Devices

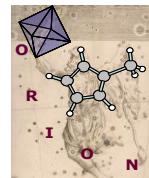
The main objectives of this workpackage were: a) evaluate the performance of novel inorganic-organic hybrid materials in lithium batteries (**Task 5.1**), innovative solar cells (**Task 5.2**) and light emitting devices (**Task 5.3**). The optimization of the selected devices, in order to pave the way to the demonstrators (WP6), was also considered crucial.

Following the interesting results obtained in WP3, under **Task 5.1**, **MUNSTER** carried out tests of different materials in full battery devices. As an example, on the basis of results obtained in WP3 for LTO,⁴⁸ improved results were obtained by combining optimized material from Johnson Matthey (WP1) and CMC as an environmentally friendly binder. In particular the electrolyte reactivity was significantly decreased, allowing to cycle steadily at 230 mAh g⁻¹.⁶⁶ LTO was then selected for prototyping, while J.M. is filing a patent on the nanoparticle preparation process (and Muenster thus waiting for publication). The material was also tested versus three different ionic liquid based electrolytes and with conventional electrolyte at 40°C, which revealed rather high reactivity, probably due to the large surface area of the powder and possibly its surface chemistry. The LiMn₂O₄-C hybrid composites can be noted as another example. Although very high rate performance was reported for LiMn₂O₄ within WP3, strong difficulties to cast high mass loading electrodes and rather high electrolyte reactivity were found in WP5. Thus, MUENSTER attempted to obtain hybrid nanocomposites including carbon, especially as CEGASA showed that the particles were so small that it was impossible to obtain stable slurry dispersion. The composite synthesis was found very challenging, given the low thermal stability of the material. Finally, higher mass loading was reached, but with an increase of the parasitic reaction, probably due to insufficient carbonization temperature. The evaluation tests of Sn-C hybrid composites, in Li-ion and Na-ion batteries, can be also highlighted. Taking into account the excellent results obtained from carbon nanocomposites for insertion (TiO₂-NRs), conversion (CoO-C) and hybrid conversion/alloying (ZnFe₂O₄ and Zn_{0.9}TM_{0.1}) materials, MUNSTER extended the approach for alloying materials to produced micrometric carbon secondary particles including metallic Sn nanoparticles, making use of the carbon to reduce SnO_x to metallic Sn and to protect Sn from rapid oxidation under air while confining the particles and buffering the volume changes. The resulting material was then tested both as an anode for Li-ion batteries and to host Na, for Na ion batteries, which led to state of the art performance.⁶⁷ Also important, concerning the separators, MUENSTER tested 6 different separators in terms of Gurley and McMullin numbers, in combination with three different IL-based electrolytes (both from Solvionic and self-prepared in Muenster). As a result, interesting alternatives to the glass fiber separators, which are too thick for prototypes -especially given the need of rolling the ensemble (separator + electrodes) at CEA-, were transferred to the WP6.

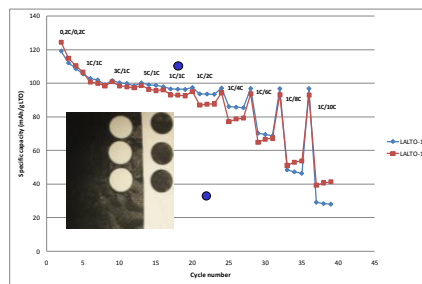
⁶⁵ G. García-Belmonte et al. manuscript in preparation

⁶⁶ D. Bresser et al. manuscript in preparation

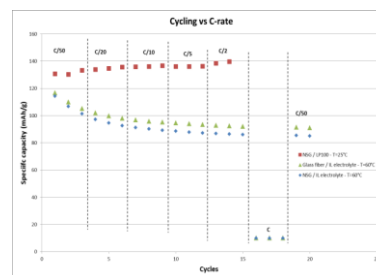
⁶⁷ D. Bresser, F. Müller, D. Buchholz, S. Krueger, M. Winter, E. Paillard, S. Passerini, *Electrochim. Acta*, In Press, DOI: [10.1016/j.electacta.2013.09.007](https://doi.org/10.1016/j.electacta.2013.09.007)



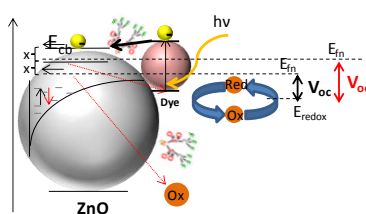
CEGASA focused here its main efforts on the electrochemical characterization in coin cells of the scaled-up electrode formulations developed in WP3, in order to be validated for use in the prototype cells in WP6. During the first half of the project, the selection of suitable materials carried out in WP3 focused the development work on anodic coatings using nanoparticles of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and cathodes with LiMn_2O_4 (LMO) from Johnson Matthey. All slurries prepared for LMO showed high instability and very poor adhesion and no coatings were obtained for testing. Therefore, CEGASA centered its efforts in the formulation and processing scale-up of nano-LTO electrodes. Following the optimization of slurry stability and coating process, technical electrodes with nano-LTO active material and PVDF as binder were fabricated. The final electrode prepared for the cell prototype assembly in WP6 achieved the target performance of $1\text{mAh}/\text{cm}^2$ at 1C ($110\text{mAh}/\text{g}$). This has demonstrated the viability of scaled-up electrode fabrication using high specific area nanomaterials, which processing was found very difficult. Additionally, CEGASA tested a novel hybrid high capacity anode material (Ni/NiO/IL) developed by CIDETEC in WP2 through electrodeposition from ionic liquid-based electrolytes. Stable high specific capacity ($1000\text{mAh}/\text{g}$) over 100 cycles was reached.⁶⁸



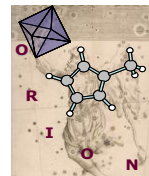
CEA investigate the processing of several electrodes at pilot scale using materials selected in WP3. Several organic based inks using carbon coated LiFePO_4 have been developed and prepared at pilot scale. These slurries have been coated on CEA's pilot line in order to produce several electrodes with various mass loading. Similar work was carried out using $\text{Li}_4\text{Ti}_5\text{O}_{12}$, but using aqueous formulations. The resulting electrodes were tested in full lithium coin cells, but also used to assemble the final prototypes (WP6). It is worth to note that CEA and CEGASA exchanged electrodes in order to test them in various configurations. As a result, CEGASA decided to integrate CEA's positive electrodes in their prototypes. CEA invested also significant efforts to find a separator compatible with the ionic liquid-based electrolytes. By this way, full lithium batteries using electrodes, new separators and ionic liquids were assembled and electrochemically tested. The results confirmed that various chosen components could be used in final prototypes for WP6.



Under **Task 5.2**, **CIDETEC** evaluated the hybrid materials -developed in WP2 and characterized in WP3- in different kinds of solar cells such as Dye-sensitized Solar Cells (DSC) and Semiconductor-sensitized Solar Cells (SSC). It is worth to highlight the enhanced performance of DSCs based on $\text{ZnO}/\text{IL}/\text{dye}$ (i.e. 2nd ORION hybrid generation material) photoanodes in comparison to those built from the reference ZnO/dye photoanodes. An improvement of $\sim 80\%$ in the power conversion efficiency was

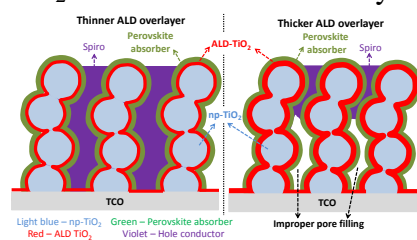


⁶⁸Azaceta et al. Manuscript in preparation



reached mainly thanks to the increase, up to ~ 180 mV, of the photovoltage. Furthermore, the device characterization by impedance spectroscopy pointed out the upward displacement of the ZnO conduction band in hybrid anodes as the main origin of the improvement.²⁶ This result demonstrates the great potential of metal oxide/IL hybrid materials in excitonic solar cells and opens wide avenues for improvement in these emerging photovoltaic technologies. Additionally, CIDETEC also demonstrated that metal oxide/IL hybrid materials may be used to enhance the versatility in the fabrication of SSCs. In this context, it is also interested to highlight that the innovative electrodeposition route developed in WP2 to obtain thin films of metal oxides and/or metal oxides/ionic liquid hybrid materials made possible to fabricate all-oxide SSCs, which are highly appealing in terms of robustness, by using low temperature deposition technology. On the other hand, CIDETEC, EPFL and UVEG partners defined a collaborative strategy to investigate the emerging perovskite solar cells. By this way, CIDETEC focused on planar heterojunction architecture solar cells based on charge carrier selective inorganic contacts. The resulting piece of work was novel in comparison to the previous approaches and highly complementary to the research by EPFL (i.e. nanostructured perovskite solar cells) and UVEG (i.e. perovskite solar cell with organic charge carrier selective contacts). Concretely, CIDETEC partner investigated the use of CuSCN as an inorganic hole conductor, reaching power conversion efficiency of ~ 6.4 %. This inorganic nature of the hole transporting material may have significant beneficial effects in terms of device robustness and lifetime.

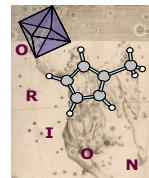
In tandem to the work done by CIDETEC on the perovskite solar cells, **EPFL** investigated the inorganic-organic lead iodide $\text{CH}_3\text{NH}_3\text{PbI}_3$ based perovskite solar cells. As an example, EPFL developed innovative device architectures based on the use of ALD deposited TiO_2 overlayers onto the mesoporous TiO_2 scaffold. As the overlayers were demonstrated to be conformal and pinhole-free, the need for the frequently used blocking underlayer was avoided.⁶⁹ Furthermore, EPFL has carried out an accurate study of lead-iodide perovskite sensitized solid-state solar cells using impedance spectroscopy. An additional charge transport pathway via the perovskite film on top of the blocking layer and the TiO_2 was observed. The behavior and appearance of the new impedance spectroscopy features were found to be inherent to the nature of the perovskite material and is affected by its morphology, stoichiometry and crystallinity.⁷⁰ It is noted that EPFL was one of the main players in the emergence of the perovskite solar cells as a very appealing cost- and performance-competitive photovoltaics technology. Although the youngness of the perovskite solar cells, EPFL reached power conversion efficiencies in the range from 12 to 15 % by using different materials and devices architectures, which is an indication about the large versatility and potential of this emerging photovoltaics technology. In the field of DSCs, EPFL applied cutting-edge strategies based on materials developed in WP1 and WP2 that allowed progress beyond of the estate of the art of the technology. Concerning the molecular dyes, EPFL evaluated the photovoltaic performance of several types of sensitizers from WP1. As an example, squaraine sensitizers were synthesised and displayed promising potential as near-infrared light (IR) absorbers for liquid and solid-state devices.^{71,72} In a similar attempt to increase the



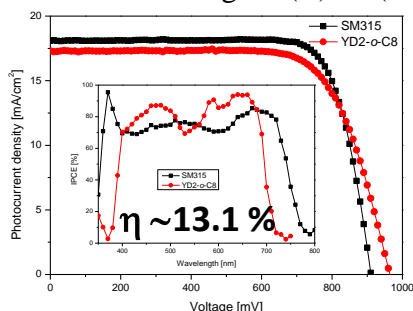
⁶⁹ Yella, A. et al. 2013 Manuscript in prepaton.

⁷⁰ Dualeh, A., Moehl, T., T treault, N., Teuscher, J., Gao, P., Nazeeruddin, M.K., Gr tzel, M. *NanoLetters* 8 (2013) 362–373

⁷¹ Shi, Y., et al. (2011). *Angewandte Chemie*, 123(29), 6749–6751. doi:10.1002/ange.201101362



near-IR absorption, Zn(II) porphyrins synthesized in WP1, showed panchromatic absorption, with near-IR spectral response, leading to power conversion efficiencies of over 13% using Co(II)/Co(III) redox electrolyte.⁷³ The photovoltaic performance of a new class of ullazine dyes (WP1) was also characterized. The differences in their properties and behavior in ssDSCs was correlated to their individual molecular components.⁷⁴ As most of the new dyes were evaluated in solid state DSCs, EPFL also conducted in-depth characterization of these devices, investigating the temperature dependence of the transport properties of the hole transporting material.⁷⁵



Following the activities developed in WP2 about the synthesis of advanced photoanodes, EPFL evaluated here the advantages and disadvantages of the approaches there proposed (e.g. surface adsorption of organic coadsorbents or atomic layer deposition (ALD) of insulating oxides³⁵) to passivate and/or modify the nanostructured metal oxide (e.g. mesoporous TiO₂, hierarchical ZnO) surface for application as photoanodes in DSCs. Photovoltaic as well as transient photocurrent and photovoltage decay studies revealed trends in the charge transfer dynamics that were used to optimize device performance. A new procedure for the low-temperature processing route of TiO₂ for photoanodes was developed. As did in the perovskite solar cells, crystalline TiO₂ deposited by ALD on an insulating scaffold was systematically studied in terms of charge transport and performance.⁷⁶ A critical thickness of the TiO₂ overlayer of 6 nm was found to be sufficient to form a continuous percolation pathway.⁷⁷ EPFL also evaluated the novel 3D structures, consisting of inverse opals with ZnO nanowires for photoanodes in DSCs, developed in collaboration with CIDETEC in WP2. Cutting-edge knowledge on their integration in DSCs was generated.³¹

SOLARONIX evaluated the potential of ionic liquid based electrolytes in DSCs in terms of efficiency and stability. Several formulations based on ionic liquid supplied by partner SOLVIONIC were evaluated in real devices using the classical ionic liquid test architecture. On the basis of the first results and according to WP2, WP3 development several optimizations were realized in order to increase device efficiency. Thousands of laboratory-scale DSCs were made during the project. Starting from around 2% at the

Task 5.2. Ordered inorganic-organic hybrids in innovative solar cells

J	V _{oc}	FF	Eff.
7.69	0.595	0.65	2.97 %

Fine tune the TiO₂ layering and add the TiCl₄ treatment

J	V _{oc}	FF	Eff.
10.01	0.690	0.71	4.91 %

Dye: D5

J	V _{oc}	FF	Eff.
11.84	0.660	0.66	5.10 %

EtOH / t-BuOH optimization + N719

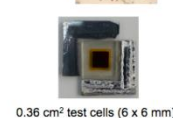
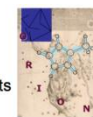
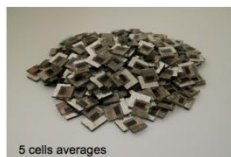
J	V _{oc}	FF	Eff.
11.89	0.667	0.70	5.55 %

Sulfolane optimization + N719

J	V _{oc}	FF	Eff.
14.83	0.668	0.68	6.7 %

Solaronix HT/SP + Titania micro channels 7 μm Mosalyte TDE-250 (S) and N719 Ru Dye

J	V _{oc}	FF	Eff.
16.80	0.698	0.67	7.53 %



Project M36

State of the art at end of ORION

⁷² Dualeh, A., et al. (2012). *Applied Physics Letters*, 100(17), 173512. doi:10.1063/1.4707374

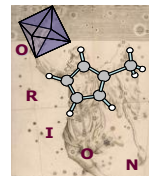
⁷³ Mathews, S. et al. Manuscript in preparation

⁷⁴ Dualeh, A., et al. (2013). *Advanced Energy Materials*, 3(4), 496–504. doi:10.1002/aenm.201200701

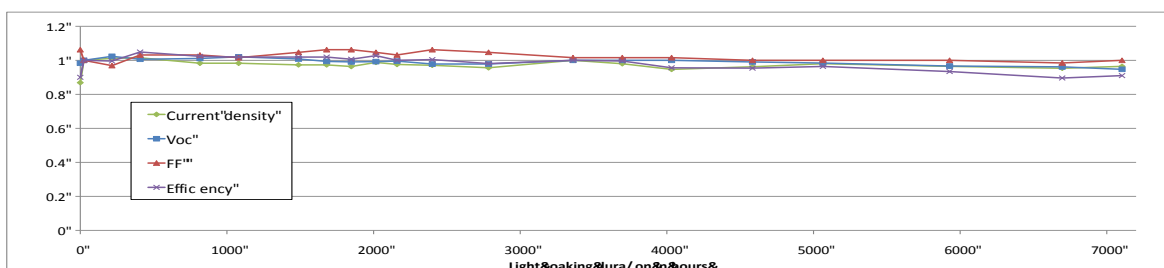
⁷⁵ Dualeh, A., et al. (2013). *ACS Nano*, 7(3), 2292–2301. doi: 10.1021/nn4005473

⁷⁶ Chandiran, A. K., et al. *ACS Applied Materials & Interfaces*, 5(8), 3487–3493. doi:10.1021/am400866s

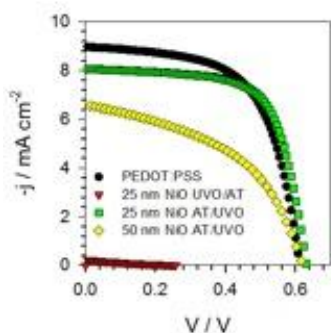
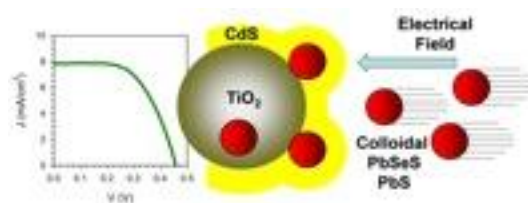
⁷⁷ Chandiran, A. K., et al. (2013). *Advanced Functional Materials*, 23(21), 2775–2781.



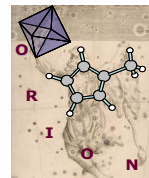
beginning, due to a good feedback between partners and work packages, the progression was constant during the project. Finally, summing up all the improvements developed during ORION (WP2: new titania nanoparticles, WP3: processing methods) and using the optimized formulation coded Mosalyte TDE-250(S), the efficiency reached the impressive value of 7.53% in the last month of the project. Accurate stability tests were also carried out. DSCs made with N-719 dye, Mosalyte TDE-250 or Mosalyte TDE-250(S) (with sulfolane additive) electrolytes, were placed under constant illumination, one sun AM 1.5G, at 65 °C. All cells exhibited extremely good stability (with around 5% loss in 2900h in the case of sulfolane electrolyte and with less than 20% loss in 7000h in the case of Mosalyte TDE-250. Furthermore no physical changes could be observed during the light soaking accelerated aging or the thermal cycles (-40°C till +80°C) resistance tests which is crucial for the aesthetic aspect of the product. It is worth to mention that these stability tests results are impressive and equivalent to several years of outdoor use under our latitudes. It is highlighted that the present results already led to a new addition to SOLARONIX catalog. Since January 2013, Mosalyte TDE-250 can be bought online (<http://shop.solaronix.com/electrolytes/non-volatile-electrolytes/mosalyte-tde250.html>) and the ORION funding is acknowledged in the website. In few months the sulfolane modified version Mosalyte TDE-250(S) will be introduced as well.



UJI focused on the evaluation of materials from WWP1 and WP2 in two different types of solar cells named quantum dot solar cells (QDSC) and organic solar cells. In the QDSC field, UJI demonstrated the great potential of the ionic liquid family containing the sulfide/polysulfide redox couple developed by CIDETEC in WP1. First of all, CdSe QDSCs with significantly improved stability in comparison to the reference devices (i.e. based on aqueous electrolytes) were successfully fabricated.² The same family of electrolytes was crucially used to fabricate



co-sensitized QD/dye solar cells. Co-sensitized devices showed enhanced photocurrent by extending the light absorption range. Additionally, a clear increase of photoinjection as a consequence of a decrease of the internal recombination (electron-hole recombination in the QD before electron injection) by fast trapping/transfer of holes in the presence of dye was demonstrated.⁶¹ Also nanostructured TiO₂ photoanodes with colloidal QDs of PbSeS (synthesized by NANOCO in WP1) and PbS with different sizes were evaluated. UJI showed the electrophoretic deposition method can be used



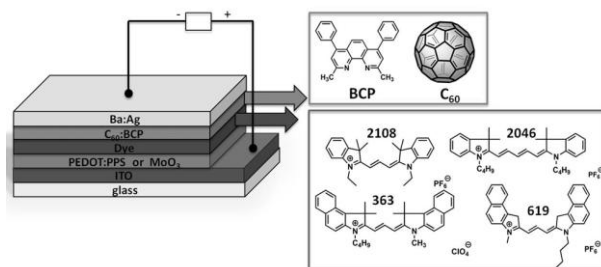
advantageously for fast sensitization of the photoanode with these QDs. Better results for the smallest QDs are obtained, with efficiencies of 2.1%.⁷⁸ On the other hand, in the field of organic solar cells, UJI evaluated the integration of NiO and NiO/IL hybrid films electrodeposited by CIDETEC (WP2) in bulk heterojunction solar cells. A superior electrical performance than PEDOT:PSS was demonstrated for those NiO and derivative films when used as anode interlayers. The impedance analysis allows quantifying the carrier selectivity degree of the NiO-modified cathode.⁷⁹

By integrating organic and hybrid materials developed in WP1 and WP2, IMEC and UVEG –in close collaboration- proposed a solution-processed planar heterojunction OPV system using an ionic poly(3-alkylthiophene) (e.g. P3(mim)HT-TFSI) as the donor material and PC61BM or PC71BM as the acceptor. Due to the ionic nature of the polythiophene it is completely insoluble in chlorobenzene, used to deposit the fullerene acceptor layer. This, together with the high film qualities obtained by meniscus coating, allowed for the preparation of neat bi-layer devices. The best performing devices with active layers of 40 nm using PC71BM as the acceptor exhibited power conversion efficiencies in excess of 1.5% (1.9% for the best device), which are high enough to provide the proof of concept for this innovative ionic polymers and device architecture.⁸⁰

On the other hand, IMEC implemented a specific type of electron transport material, i.e. a conjugated polyelectrolyte (CPE) based on an amphiphilic polythiophene with appended ionic liquid-like polar groups, to boost the internal cell parameters of devices based on PCDTBT:PC₇₁BM and PCPDT-DTTzTz:PC₇₁BM photoactive layers. IMEC showed that the device performance of polymer solar cells can be remarkably improved by incorporation of a thin electron transport layer based on an imidazolium-substituted ionic polythiophene (20% increase in PCE up to an average value of 6.2% for PCDTBT:PC₇₁BM).⁴³ Additionally, the molecular weight of the hydrophilic polymer was identified as an important factor determining the overall performance (In the table, P1 and P3 have the lowest and largest molecular weight).

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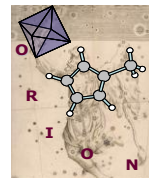
UVEG evaluated hybrid organic-inorganic materials in photovoltaic devices. The main emphasis was on ion containing semiconducting materials. Additionally to the work done in collaboration with IMEC, UVEG evaluated ionic cyanine dyes in double layer planar-heterojunction



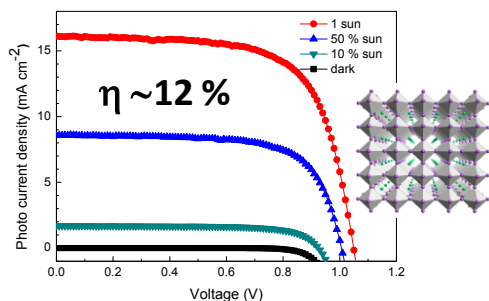
⁷⁸ N.P. Benekohal, V. González-Pedro, P.P. Boix, S. Chavhan, R. Tena-Zaera, G. P. Demopoulos, I. Mora-Seró, *J. Phys. Chem. C*, 116 (2012) 16391–16397.

⁷⁹ T. Ripolles-Sanchis, A. Guerrero, E. Azaceta, R. Tena-Zaera, G. Garcia-Belmonte, *Solar Energy Materials and Solar Cells*, 117 (2013) 564–5681.

⁸⁰ T. Ghoos, O. Malinkiewicz, B. Conings, L. Lutsen, D. J. Vanderzande, H. J. Bolink, W. Maes, *RSC Adv.* **2013**, in press.



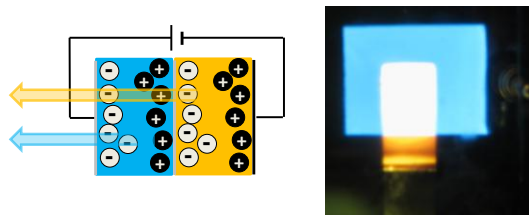
solar cells. Average power conversion efficiencies were reached. This finding demonstrates that ionic absorbers are interesting materials for use in solar cells as they allow the preparation of solution processed double layer devices.⁸¹ On the other hand, in the field of the perovskite solar cells, UVEG deposited successfully homogeneous thin films of $\text{CH}_3\text{NH}_3\text{PbI}_3$ by co-evaporation. The latter appears to be an appealing



alternative to wet-chemistry methods, for which obtaining homogeneous layers of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is not evident. In collaboration with EPFL, UVEG developed a complementary approach to those developed by CIDETEC and based on the use of organic materials as electron and hole selective contacts. All in all, power conversion efficiencies of 12 % were reached,⁸² providing larger versatility in the material choice and opening wide avenues of progress in

the perovskite solar cell technology.

Under **task 5.3**, UVEG achieved a breakthrough in the operation of Light Emitting Electrochemical Cells (LECs) by combining an ionic iridium complex with high photoluminescence quantum yield with an ionic liquid, and a pulsed current driving scheme. Using these conditions, sub-second turn-on time was achieved in combination with a lifetime in excess of 4000 hours at a luminance level of 650 cd/m^2 . Another highlight was the preparation of a white light-emitting tandem LEC using solution processing of the light-emitting layers.⁸³ It is worth to remind that the latter is very difficult for OLEDs due to the use of air-unstable doped injection layers adjacent to the middle electrode.



WP6- Demonstration Prototypes

The first objective of this workpackage was to demonstrate the viability of using the ORION hybrid materials in different industrial prototypes: a) Li-ion batteries (**Task 6.1**), innovative solar cells (**Task 6.2**). The second and ultimate objective was to combine the battery and solar cell prototypes in demonstrator for automotive applications.

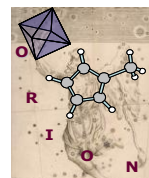
Under **Task 6.1**, CEA assembled two series of prototypes in various configurations in order to test together and validate the performances of all components developed in the previous WPs. Indeed the used electrodes have been produced by CEA and CEGASA

⁸¹ O. Malinkiewicz, T. Grancha, A. Molina-Ontoria, A. Soriano, H. Brine, H. J. Bolink, *Adv. Ener. Mater.* 2013, 3, 472-477.

57. Electrodeposited NiO anode interlayers: Enhancement of the charge carrier selectivity in organic solar cells, T.Ripolles-Sanchis, A. Guerrero, E. Azaceta, R. Tena-Zaera, G. Garcia-Belmonte, *Solar Energy Materials and Solar Cells*, 117 (2013) 564–5681.

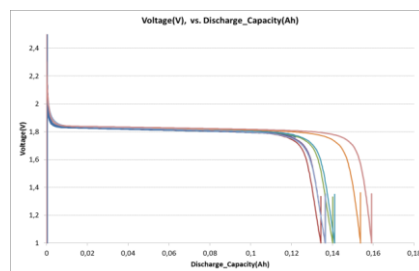
⁸² O. Malinkiewicz, Y. Aswani, Y. H. Lee, M. Minguez Espallargas, M. Graetzel, M. K. Nazeeruddin and H. J. Bolink, *Nature photonics*. DOI 10.1038/nphoton.2013.341

⁸³ T. Akatsuka, C. Roldan-Cramona, E. Orti, H. J. Bolink, *Adv. Mater.* 2013, DOI 10.1002/adma.201303552



during WP5 and they contain active materials selected and prepared by JM, MUENSTER and CEA in WP1 and WP3. The specific separator has been identified by CEA during WP5 and the electrolytes have been provided by SOLVIONIC and characterized by CEA and MUENSTER in

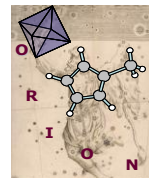
WP3. Firstly 4 prototypes, 2 with conventional electrolytes and 2 with ionic liquids based ones have been assembled and characterized. Some problems have been encountered during the process and lead to thicker cells than expected. Nevertheless these prototypes have been electrochemically tested and sent to CRF for preliminary trials in the ORION demonstrators. Then a series of 7 final cells have been assembled using all components developed in previous WPs, especially ionic liquids based electrolytes. These lithium batteries were fully characterized and presented expected performances which fulfil requirements defined at the beginning of the project. All batteries were sent to CRF and integrated in courtesy light. To our knowledge, this is the first example of the development of prototypes using ionic liquids based electrolytes at the prototype scale.



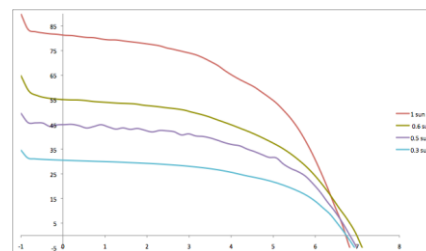
CEGASA proposed different pouch cell geometries adapted to the demonstrator requirements and available space to integrate cells using a 3D software. An agreement to distribute the prototype cell development was achieved, by which CEGASA focused on adapting and assembling the cells for the demonstrator based on an electrochromic rearview mirror. Cutting dies and cell assembly tools were prepared for the specific electrode size required for these ORION Demo cells. **CEGASA** (nano-LTO) and **CEA** (C-LFP) demonstrated the feasibility of processing ORION materials with the electrode fabrication, assembly and delivery of cells matching requirements of the demonstrators. For mirror demonstrator, although 2 prototype cells assembled with Ionic Liquid electrolyte were not able to charge and discharge, finally 4 cells with conventional electrolyte were fabricated and characterized prior to delivery to CRF for the successful integration in the rearview mirror.



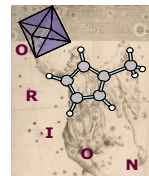
Cell	LO_1	LO_2	LO_3	LO_4
0.1C/ mAh	178	155	151	162
0.2C/ mAh	134	90	126	128
Weight/ g	15.14	15.16	15.31	15.07
R _{int} / mOhm	290	283	204	273
OCV _{discharged} / V	1.813	1.839	1.721	1.766



Under **Task 6.2**, SOLARONIX developed "W-type" modules to build up a prototype that consists in serially interconnected dye sensitized solar cells. Summing up all the improvements and enhancements developed earlier in ORION, a state of the art W-module (10 x 10 cm, 65 cm² active area) based on ionic liquid electrolyte and N-719 dye reached a nice power conversion efficiency (PCE) of 4.22 under one sun (AM1.5G). This device was measured at various sun intensities to evaluate the performance in situation matching real outdoors conditions. Under one third of sun the PCE was as high as 5.02 %. This high efficiency is the highest achieved so far on ionic liquid electrolyte based module. This figure is impressive especially considering the effective active area of 65.1 cm², the semi transparency of the module and the fact that the titania layer was only around 8 microns thick. It should be compared to the classical efficiency before ORION that was around 2% only. Further work consisted in developing thin glass based modules to be integrated in the final ORION demonstrators for automotive application. The idea was to apply the process previously developed for high efficiency modules to hundred microns thick flexible glass. A new design to fit the CRF specifications was created and consisted in an interconnected module of seven individual cells on a 7 x 10 cm substrate. Several steps of our classical process were successfully optimized for this thin glass like: a) FTO deposition, b) two glass lamination, c) hole drilling and d) titania printability and adhesion, Unfortunately making modules using 0.1 mm glass is a real challenge. Due to the high fragility of this thin glass, some modules were produced but none of the final desired size to fit CRF requirements. A good compromise to the thick 2 mm and the fragile 0.1 mm glasses is using 1 mm glass. The process was then applied on 1 mm glass that led to the production of the first thin glass ionic liquid based modules at SOLARONIX. To maximize efficiency an organic dye, D35, with a high molar extinction coefficient was used, giving a nice orange color to the modules. Twelve modules were sent to partner CRF and finally ten of them were integrated in a car windshield to power the ORION demonstrators. It is worth also to highlight that progresses made during ORION in the field of ionic liquid electrolyte (WP5) and titania



layer optimizations (WP2) pave the way to the first large scale building integrated photovoltaic (BIPV) application not to be a dream anymore and to become reality. The Swiss Tech Convention Center, located on EPFL's campus in Lausanne, has been designed to integrate the first semi transparent colored façade in the world. This facade is made using 1400 large area (35X50 cm) ionic liquid DSC modules that were built thanks to the cutting-edge knowledge acquired in the frame of the ORION project. A real scale prototype, integrating the last ORION improvements, was setup in the Swiss Jura Mountain, during summer 2012. Finally, SOLARONIX produced the required modules that are now being mounted on the facade, covering an area of 200 m² in total. Developments made in WP6, already led to new additions to SOLARONIX catalog. Since January 2013, SERIO 1010W11 (<http://shop.solaronix.com/dye-solar-cells/serio/serio-1010w11.html>), SERIO 3030W11 (<http://shop.solaronix.com/dye-solar-cells/serio/serio-3030w11.html>) and SERIO 3030W31 (<http://shop.solaronix.com/dye-solar-cells/serio/serio-3030w31.html>), which are



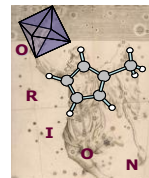
interconnected ionic liquid based dye sensitized solar cells, can be bought online and the ORION funding is acknowledged. In few months even larger versions of these modules will be introduced as well.

Under **Task 6.3**, CRF integrated successfully solar cells and the batteries prototypes, in two automotive demonstrators. The final device must be fully autonomous and independent from the main car battery; the solar cells harvest the energy that is stored in the batteries. Two demonstrators were assembled: a) courtesy light: standard courtesy-light installed on the B segment of FIAT cars and b) electrochromic mirror: auto-dimming rearview mirror of Lancia Delta. In each case a special printed circuit board (PCB) was designed by CRF in order to fit in the plastic housing together with the batteries: the electronic circuit has to manage the power harvested from the solar cells, charge the batteries in the proper way (set by CEA and CEGASA) and supply the actuator (LEDs or mirror).



The two PCBs were completely tested with a dummy load before integration in the final prototype. As soon as CRF has received the final battery prototypes from CEA and CEGASA, all the components were integrated in the plastic housing of the devices. Then, the demonstrators were tested both in indoor and outdoor conditions, together with the solar cells fabricated by Solaronix and integrated in the Lancia Delta windshield. Lifetime, charging, efficiency and capabilities were assessed: the demonstrators are fully working even in challenging conditions (e. g. current peak in mirror transitions). A complete recharge can be got in less than one day at medium sun irradiation. The main drawback is the low batteries capacity at room temperature and high current, which results in a limit to the device lifetime.

All in all, many positive results have been obtained in WP6 due to the collaboration between all project partners. Two fully working demonstrators were assembled using materials, batteries, PV cells, PCBs developed in ORION project by partners. Devices based on ORION materials, were able to withstand the challenging requirements of a real automotive application. Ten DSSC solar cells were integrated in the windshield of Lancia Delta and they were able to charge-up the batteries in less than one day, in outdoor conditions. Despite Solaronix attempts to get flexible cells, this integration is still at early stage because the cells are still too thick and rigid to be conformable to the curved shape of the windshield, anyway different solution can be explored in the future (injection molding, lamination, direct printing,...). Even the electronic circuits can be further optimized to improve efficiency and reduce size. Both batteries prototypes from CEA and CEGASA fulfilled the requirements in terms voltage and current and they fitted in the original plastic housing. In particular the mirror application was very challenging for the high current needed during dark transitions: a relevant swelling was noticed in this case, but it could be eliminated by proper preliminary cycling and degassing. The main drawback is the limited capacity of batteries at high current and low temperature, which leads to a short lifetime. Further research on the IL electrolyte is still needed to solve this problem. Finally two videos (i.e. [Light demonstrator](#) and

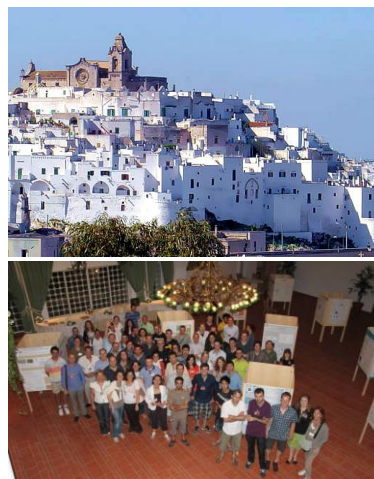


[Mirror demonstrator](#)) were recorded that show clearly the demonstrators working and the outcomes of the project. It is noted that the demonstrator videos are announced at the Materials Blog of the Research & Innovation for Industrial Technologies portal of the European Commission (http://ec.europa.eu/research/industrial_technologies/materials-blog_en.html).

WP7- Training and dissemination

The main objectives of this workpackage were: a) training of young researchers (**Task 7.1**) and b) dissemination and exploitation of the project results (**Task 7.2**).

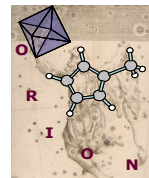
Under **Task 7.1**, CNR-IPCF, in collaboration with CIDETEC, successfully organized the Summer School entitled “*Nanostructured Hybrid Materials for Energy Conversion and Storage*” in Rosamarina di Ostuni (Br), Italy from 5 to 10 June 2011. The Summer School was intended for PhD students, post-docs and young researchers interested in nanostructured hybrid materials or related subjects. The lecturers were selected as experts in different topics of the School and all have been strongly involved in the organization of the Summer School. In total 23 lecturers coming from 10 different countries (8 European) were selected. Many of them (14) were partners of the Orion consortium and few lecturers came from Italian Research Institutions (. In addition 3 external lecturers with a well known expertise were also invited to participate at the Summer School. Proceeding books gathering the abstracts of the participants and the presentation slides of the lecturers were printed in order to facilitate the student's learning and the participation of the young researchers.. The total number of participants was 61 and 36 posters were presented. In order to publicize the Summer School, a devoted website was properly designed and issued from CNR-IPCF. The website is available at the address: <http://orion.ba.ipcf.cnr.it/>



UJI organized the Summer School entitled “*Nanostructured Hybrid Materials for Energy Devices: From experiment to modelling*” in Granada, Spain, 9 to 12 June 2013.



The Summer School was also intended for PhD students, post-docs and young researchers interested in nanostructured hybrid materials, and particularly to the connection between measuring and characterization methods and numerical simulation and device modeling. The participants were invited to present an abstract and a poster of their work in the field of hybrid nanostructured materials in a poster session. In order to disseminate knowledge regarding the event, a devoted web site (<http://orionsummerschool13.org/index.php/>) was designed and flyers and posters were properly prepared and sent to several European Scientific Institutions in order to publicize the School. In total, 17 lecturers coming from 10 different countries (8 European), 13 of them were representing partners of the

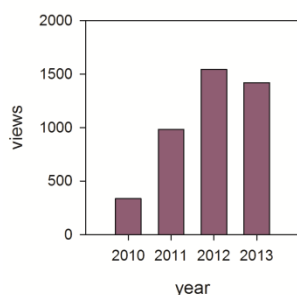


Orion Project, were selected. In addition 4 external lecturers with a well re-known expertise, at the cutting edge of research in the topics, were also invited to participate at the Summer School. The abstracts of the participants and the presentation slides of the lecturers were accessible in the School web site in order to facilitate the student's learning and the participation of the young researchers.

Under **Task 7.2, CIDETEC and UJI** carried out different dissemination and exploitation activities. Among them, it should be specially highlighted the preparation of the ORION project Newsletter, project website.

The ORION website included information for the general public and private consortium documents. The latter was especially relevant as document repository for the consortium partners. It is accessible at:

<http://www.cidetec.es/ORION/index.html>

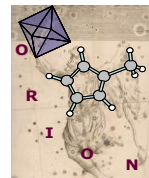


The ORION newsletter has been prepared and updated regularly informing the public on technology improvements related to ORION materials and processing. A total of 33 posts by ORION partners can be viewed. During the project period (until October 2013) a total of 4282 views have been registered what it gives an idea about the high impact on the external public. The Newsletter can be reached at: <http://orionproject.wordpress.com/>

On the other hand, the ORION project brochure was prepared at the beginning of the project describing the project objectives, participants and technologies. This was very useful to disseminate the ORION project in different events such as scientific/technology and industrial seminars, workshops, conferences and exhibitions. It is also highlighted that CIDETEC, as the project coordinator, disseminated the ORION activities and results in different events. It is here highlighted the participation in some events organized by the European Commission such the different editions (i.e. from 2010 to 2013) of EuroNanoForum as well as the EU-China Science and Technology week in the Shanghai Expo in June 2010.

Additionally to the role played by CIDETEC and UJI, it is worth to note the high investment of the whole consortium in the dissemination and exploitation activities. As a proof of the efficient results in dissemination, more than 70 papers have been published in peer-reviewed international journals. High impact journals such as Nature Photonics, Advanced Materials, ACS Nano, NanoLetters can be highlighted among them. A Plan for Using and Disseminating the Foreground was also define to pave the way for future exploitation plans. The high number of patent application (i.e. > 10) is clear evidence of the pre-exploitation actions carried out in the ORION project, but also of its industrial impact. The introduction of new products -developed in the project- in the catalogues of SOLVIONIC and SOLARONIX should be highlighted as an example of the very fruitful exploitation activities in the ORION project.

WP8- Project management

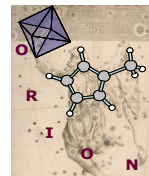


The main objectives of this work package were: a) to make sure that the activities in each of the different work packages (tasks, deliverables and milestones) are carried out in line with the agreed budget and timing; b) to coordinate the communication among the project's partners; c) to manage the communication with the European Commission and the respect to the reporting and financial management as detailed in the contract between the EU and ORION consortium.

In general, the project management was efficient and well appreciated by the partners at the end of the project. Briefly, **CIDETEC** provided administrative support for financial management and reporting, submitting all deliverables and reports to the European Commission in time. Furthermore, CIDETEC paid special attention to promote and facilitate the interaction and collaboration between the different partners. It is worth to note that the high collaborative spirit (e.g. more than 2-3 collaborations/partner) and fluent exchange of information was crucially exploited to reach the ambitious project goals, going from the synthesis of a new family of materials to the prototypes included in the project demonstrators.

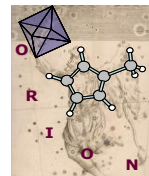
Impact

As described in the previous section and shown by the large number of scientific publications published in top class peer-review journals (see the Annex I: "scientific publication list"), the achievements reached in the ORION project in the field of inorganic/organic materials -including synthesis, characterization and modelling- allowed to progress beyond of the state in different emerging solar cells, Li-ion batteries and light emitting devices. Therefore, significant contributions to the energy conversion, storage and saving are provided. Potential impact in the global energy future, which is considered as one of the most important challenges that mankind will have to face in the 21st century, can be thus anticipated. In this context, it is worth to mention that the ORION project served as starting point to create a high-level multidisciplinary and multisector consortium with cutting-edge expertise in the field of batteries and solar cells. As shown by the ORION demonstrators -autonomous devices for automotive applications based on the ORION solar cell and battery prototypes-, the combination of both technologies is crucial to take profit of the ambient energy and develop energetically autonomous devices. The latter may have a high impact in the automotive sector because the main technological target for European OEMs (Original Equipment Manufacturers) in the next 7 years is to respect the EU regulations about CO₂ emission for 2020. The target of 95 g/km is very challenging for traditional vehicles and expensive penalties are applied for exceeding those limits. The concept of energy harvesting appears to be very appealing to contribute to the fuel saving. Moreover EU can apply some discounts on emissions if special technologies are integrated in the vehicle, e.g. solar cells. The immediate benefit is to save energy by the alternative powering to the 80-100 sensors, 50-80 processors, 80-100 actuators present in a top-segment car. Even if the energy consumed by a single device can be negligible compared to the power released by the engine it has to be considered that the solar cells are harvesting energy during all day, even when the car is just parked. The second benefit is to save weight and simplify assembling: just consider that in a medium car there are about 1-2 km of cables, which means a weight of 80-100kg. Weight reduction means fuel saving and simpler assembling leads to cost saving. For every 10% of reduction in vehicle mass an increase in fuel economy of 6-7% may be achieved. Out of the automotive sector, the ORION results may have significant impact in the field of energy harvesting in general. Indeed, the combination of solar cells and batteries may also be critical for the electricity grid applications, which demand to fill certain cost for



the grid electricity (i.e. €/kWh) instead of classically used photovoltaic energy conversion cost (i.e. €/Wp). The strong collaborative spirit and the scientific and technological skills shown by the consortium could be crucially exploited for further progresses towards a sustainable global energy future solution. Although out of the main scope of the project, the training activities such as PhD Theses and Summer Schools is also noted as guided investment for the next generation of a European scientist community well specialized in the material science and energy applications. Furthermore, the ORION activities were disseminated under general public (i.e. not limited to the scientific community) by several ways such as the project website (<http://www.cidetec.es/ORION/index.html>) and the online version of the project newsletter (<http://orionproject.wordpress.com/>). The total number of views (i.e. 4282) by the end of the project gives an idea about the significant impact on the external public. More general, two videos of the ORION demonstrators have been recently uploaded to youtube (<http://www.youtube.com/watch?v=fcBLO-Hjgo4> and <http://www.youtube.com/watch?v=kKEMxVmtOYI>). They are also accessible in the Materials Blog of the Industrial Technologies Portal of the European Commission (http://ec.europa.eu/research/industrial_technologies/materials-blog_en.html), where the potential impact of the ORION project is highlighted.

As a clear indication of the technological interest of the ORION results, 11 patent applications have been submitted to the National and/or European Patent Offices. Other patent applications are now under preparation. As can be seen in the list, six of them have been already published (see annex II: “patent list”). Although patents are often among the first steps in the exploitation plan of scientific/technological findings, it is worth to note that this was not the only exploitation way in the ORION project. Two clear examples are the direct introduction (i.e. no previous patent application) of some new products –developed in the ORION framework- in the catalog of Solvionic and Solaronix partners. Briefly, Solvionic started the commercialization of (trifluoromethanesulfonyl)imide (TFSI)-based metal salts at the end of 2010 (<http://en.solvionic.com/files/solvionic/catalogues/catalogue-2013/Metallic-Salts-Catalogue-2013.pdf>). These salts were developed at the beginning of the ORION project (WP1). The input from partners using them in the synthesis of the inorganic/organic materials (WP2, e.g. Cidetec and JHIPC) as well as in batteries (WP5, e.g. Muenster and CEA) was crucially exploited to improve the initial products and develop new ones from the same family. Furthermore, the dissemination activities such as scientific publications and talks in international conferences by the involved ORION partners were found as a very efficient supporting way to the SOLVIONIC commercialization strategy. As an indicator of the rapid international evolution, in 2011 only 11 % of the Solvionic TFSI-based salts were sold out of the EU. However, in 2012 the ratio increased until 40%. In case of Solaronix, the introduction of the new products (e.g. <http://shop.solaronix.com/electrolytes/non-volatile-electrolytes/mosalyste-tde250.html> and <http://shop.solaronix.com/dye-solar-cells/serio/serio-3030w31.html>) in the catalog was occurred recently and there is not clear statistics data yet. However, it is note that the cutting-edge knowledge acquired by Solaronix in the ORION project was crucial for the successful development of building integrated Dye-sensitized Solar Cells (DSCs) prototypes as that setup in the Swiss Jura mountain, during summer 2012. Indeed, Solaronix produced the DSC modules to cover the facade (200 m²) of the Swiss Tech Convention Center, located on EPFL’s campus in Lausanne. All in all, the economic impact of the ORION project in two SMEs is demonstrated. However, ORION has also some impact in the business of large companies such as Johnson&Matthey, Cegasa and FIAT. In the case of Johnson&Matthey, which is



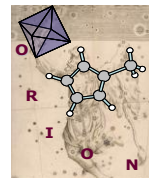
international speciality chemicals company, the ORION project helped to J&M to develop Intellectual Property in batteries (3 patent applications were submitted and are now under evaluation). The ORION project also allowed Johnson&Matthey to enter novel technologies such as Li-ion batteries. Battery Technologies is part of a new division called “New businesses” which was created in April 2013. Battery Technologies comprises Johnson&Matthey’s R&D programmes in advanced battery materials and Johnson&Matthey Battery Systems (formerly Axion), which specialises in the design, development and manufacture of integrated battery systems (<http://www.jmbatterysystems.com/home>). Meanwhile, the battery prototype developed by Cegasa contributed other alternative in the battery chemistry to the Cegasa’s strategy of offering a versatile battery technology to be adapted as a function of the needs of the end-user. Among the latter, it could be found FIAT. In the ORION project, its research center (CRF) developed successfully two different autonomous automotive application demonstrators by using solar cells and battery prototypes built by Solaronix and Cegasa partners. Both companies, together with Solvionic and Johnson Matthey as chemicals providers, are considered in the exploitation plan defined by Fiat for the automotive sector.

All in all, the impact of the socio-economic impact of the ORION project has been briefly described. The technological and potential economic impact of the project on the involved industrial partners has been individually analyzed. The close collaboration with academic and other industrial partners was crucial to reach the above described achievements.

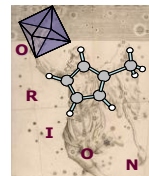
The scientific publication and published patent lists can be found below.

Annex I: Scientific Publication list

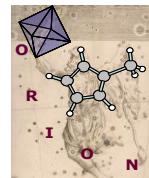
- Hybrid organic-inorganic light emitting diodes: effect of the metal oxide**, H.J. Bolink, H. Brine, E. Coronado, M. Sessolo, *Journal of Materials Chemistry*, 20(20) 4047-4049 (2010). **UVEG**
- Phosphorescent Hybrid Organic-Inorganic Light-Emitting Diodes**, H.J. Bolink, H. Brine, E. Coronado, M. Sessolo, *Advanced Materials*, 22(19) 2196-2201 (2010). **UVEG**
- Melting Behavior of Pyrrolidinium-Based Ionic Liquids and Their Binary Mixtures**, M. Kunze, S. Jeong, E. Paillard, M. Winter, S. Passerini, *Journal of Physical Chemistry C*, 114(28), 12364-12369 (2010). **MUENSTER**
- Efficient Platinum-Free Counter Electrodes for Dye-Sensitized Solar Cell Applications**, S. Ahmad, J-H Yum, H-J. Butt, Md.K. Nazeeruddin, M. Grätzel, *ChemPhysChem*, 11 (13) 2814-2819 (2010). **EPFL**
- Ionic Assisted Charge Injection in Hybrid Organic-Inorganic Light-Emitting Diodes**, H.J. Bolink, H. Brine, E. Coronado, M. Sessolo, *ACS Applied Materials & Interfaces*, 2(10), 2694-2698 (2010). **UVEG**
- Ionic Space-Charge Effects in Solid State Organic Photovoltaics**, M. Lenas, H.J. Bolink, *ACS Applied Materials & Interfaces*, 2(12), 3664-3668 (2010). **UVEG**
- Optically Transparent Cathode for Dye-Sensitized Solar Cells Based on Graphene Nanoplatelets**, L. Kavan, J-H. Yum, M. Grätzel, *ACS Nano*, 5(1), 165-172 (2011). **JHIPC and EPFL**
- Panchromatic ruthenium sensitizer based on electron-rich heteroarylvinylene pi-conjugated quaterpyridine for dye-sensitized solar cells**, A. Abbotto, F. Sauvage, C. Barolo, F. De Angelis, S. Fantacci, M. Graetzel, N. Manfredi, C. Marinzi, Md.K. Nazeeruddin, *Dalton Transactions*, 40 (1), 234-242 (2011). **EPFL**
- A High-Efficiency Panchromatic Squaraine Sensitizer for Dye-Sensitized Solar Cells**, Y. Shi, R.B.M. Hill, J-H Yum, A. Dualeh, S. Barlow, M. Grätzel, S.R. Marder, Md.K. Nazeeruddin, *Angewandte Chemie-International Edition*, 50 (29) 6619-6621 (2011). **EPFL**
- Electrochemical reduction of O(2) in 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ionic liquid containing Zn(2+) cations: deposition of**



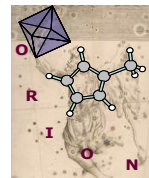
- non-polar oriented ZnO nanocrystalline films**, E. Azaceta, R. Marcilla, D. Mecerreyes, M. Ungureanu, A. Dev, T. Voss, S. Fantini, H-J. Grande, G. Cabañero, R. Tena-Zaera, *Physical Chemistry Chemical Physics*, 13, 13433-13440 (2011). **CIDETEC and SOLVIONIC**
11. **Design and Development of Functionalized Cyclometalated Ruthenium Chromophores for Light-Harvesting Applications**, K.C.D. Robson, B.D. Koivisto, A. Yella, B. Sporinova, M.K. Nazeeruddin, T. Baumgartner, M. Grätzel, C.P. Berlinguette, *Inorganic Chemistry* 50, 5494–5508 (2011). **EPFL**
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 16. **Synthesis of 1-Vinyl-3-ethylimidazolium-Based Ionic Liquid (Co)polymers by Cobalt-Mediated Radical Polymerization**, C.Detrembleur, A. Debuigne, M. Hurtgen, C. Jerome, J.Pinaud, M. Fevre, P. Coupillaud, J. Vignolle, D. Taton, *Macromolecules*, **44(16)**, 6397-6404 (2011). **LCPO-CNRS**
 17. **Bis-Donor–Bis-Acceptor Tribranched Organic Sensitizers for Dye-Sensitized Solar Cells**, A. Abbotto, V. Leandri, N. Manfredi, F. De Angelis, M. Pastore, J-H. Yum, Md. K. Nazeeruddin, M. Grätzel, *European Journal of Organic Chemistry*, 31, 6195-6205 (2011). **EPFL**
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 19. **Nanomaterials based on carbon and Ti(IV) oxides: some aspects of their electrochemistry**, L. Kavan, *International Journal of Nanotechnology*, 9, 652-679 (2012). **JHIPC**
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 24. **Spectroscopic Study on Imidazolium-Based Ionic Liquids: Effect of Alkyl Chain Length and Anion**, E. Binetti, A. Panniello, L. Triggiani, R. Tommasi, A. Agostiano, M.L. Curri, M. Striccoli, *The Journal of Physical Chemistry B*, 116(11), 3512–3518 (2012). **CNR-IPCF**
 25. **Subnanometer Ga₂O₃ Tunnelling Layer by Atomic Layer Deposition to Achieve 1.1 V Open-Circuit Potential in Dye-Sensitized Solar Cells**, AK. Chandiran, N. Tetreault, R. Humphry-Baker, F. Kessler, E. Baranoff, CY.Yi, MK. Nazeeruddin, M. Gratzel, *Nano Letters*, 12(8) 3941-3947 (2012). **EPFL**
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29. **Diffusion-Recombination Determines Collected Current and Voltage in Polymer:Fullerene Solar Cells**, T. Ripolles-Sanchis, A. Guerrero, J. Bisquert, G. Garcia-Belmonte, *Journal of Physical Chemistry C* 116(32) 16925-16933 (2012). **UJI**
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41. **Ionic liquid modified zinc oxide injection layer for inverted organic light-emitting diodes**, H. Brine, J.F. Sánchez-Royo, H.J. Bolink, *Organic Electronics* (2013),14, 164-168.
42. **One-step wet chemical deposition of NiO from the electrochemical reduction of nitrates in ionic liquid based electrolytes**, E. Azaceta, T.T. Ngo, D. Pickup, C. Rogero, J.E. Ortega, O. Miguel, H-J. Grande, R. Tena-Zaera, *Electrochimica Acta* 96 (2013), 261-267. **CIDETEC**
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44. **Flexible all-inorganic nanocrystal solar cell by room-temperature processing**, A. Loiudice, A. Rizzo, G. Grancini, M. Biasiucci, M.R. Belviso, M. Corricelli, M.L. Curri, M. Striccoli, A. Agostiano, P.D. Cozzoli, A. Petrozza, G. Lanzani, G. Gigli. *Energy & Environmental Science* DOI: 10.1039/c0xx00000x. **CNR-IPCF**
45. **Solid-State Dye-Sensitized Solar Cells Using a Novel Class of Ullazine Dyes as Sensitizers**, A. Dualeh, R. Humphry-Baker, JH. Delcamp, MK. Nazeeruddin, M. Grätzel, *Advanced Energy Materials*, 3 (2013) 496-504. **EPFL**
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Annex II: Published patent list

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Additionally, there are 5 patent applications (3 by **JOHNSON&MATTHEY**, 1 by **CEA** and 1 by **MUENSTER**) submitted to the National or European Patent offices and a couple of them under preparation.