**Publishable Summary**

The Energy Caps project funded by the FP7-Marie Curie-IAPP EU program succeeded to build a sustainable and safe hybrid supercapacitor with high specific energy and maintained high specific power and long cycle life device by gathering experts from both academia and industry. All these challenges were achieved thanks to the consortium represented by five partners, including one large company (Solvay), two SMEs (Yunasko and Recupyl), and two Universities (Poznan University of Technology and Kyiv National University of Technologies and Design), located in four different countries. The partners have mutually seconded personnel to exchange their complementary knowledge. At the early stage of the project, the research program focused on the development of the individual cell components such as, new electrodes, a high-performance polymer separator and an optimized electrolyte mixture with special attention to lowest environmental impact and low cost. Subsequently, these components were combined, first in a lab cell and later in a larger prototype. The recyclability of the device components was assessed throughout the project, and towards the end, the environmental impact of manufacturing and recycling process was successfully evaluated.

The efforts on the electrode development are highly critical since the process of electrode development drastically impacts the performance of the final device. Best performing activated carbon or graphite was selected after several material screenings in lab cells. In further attempts to find an eco-friendly solvent for electrode fabrication process, instead of commonly used N-Methyl-2-pyrrolidone (NMP), water based binders were introduced in the electrode slurry to reduce the production cost and environmental impact of lithium-ion capacitors. Despite the challenging electrode preparation step, Solvay aqueous PVDF dispersions were successfully implemented as alternative binders. In order to boost the specific capacitance and power density of hybrid supercapacitor, Li-based positive electrode materials were blended with activated-carbon electrodes so as to manufacture hybrid type positive electrodes. The best performing cathode was obtained by combining the mixture of lithium iron phosphate (LFP) with activated carbon (AC). For the negative electrode side, carbon-based materials such as graphite, hard carbon or lithium titanium oxide (LTO) were used. Electrodes with high homogeneity, reproducibility, free of defects with perfect adhesion to the current collector were accomplished.

Comparing to commercial separators, lab produced PVDF separator has very high porosity due to the fine adjustment of the solvent, non-solvent, polymer ratio and phase separation process of the dope solution. Selection of those components established a compromise of high ionic conductivity, pore size, and mechanical strength. The integration of woven type glass fiber support brought the advantage of high mechanical and thermal stability, almost no size and volume change at high temperatures. PVDF particularly can bring the advantage of a good adhesion between the separator and the electrode. Glass fiber reinforced PVDF separator shows very high wettability in carbonate-based electrolytes. Comparative electrochemical tests revealed better performance, especially at higher current loads for both symmetric and hybrid designs demonstrating the crucial effect of the separator on high-power systems.

The selection of the electrolyte components is exceptionally critical for ensuring the device performance and particularly the safety. The design of the electrolyte was made depending on the hybrid capacitor type. As for the LIC design using graphitic anode, a mixture of linear (DMC) and cyclic carbonates (EC or 1FEC) as co-solvent together with lithium hexafluorophosphate ($LiPF_6$, 1M) or bis (trifluoromethyl sulfonyl (LiTFSI, 1.2M) as electrolyte salt was chosen. From a technical point of view, the high ionic conductivity is directly associated to the specific power of the device. Therefore, acetonitrile (AN) was chosen as the preferred solvent for the advanced LIC design which employs LTO as an anode, due to its low viscosity, wide electrochemical window and high dielectric constant. Nevertheless, AN's low stability against reduction is a critical problem that hinders its use with graphite anode and thus for graphite-based LIC design. The electrolyte additive has a major impact on the life time of the LIC device as the gas formation is directly related to electrolyte decomposition which may lead to serious safety issues. The cycle life improvement was due to the formation of a more stable ~~and flexible~~ SEI layer and a better protection of graphite from further electrolyte decomposition. Different fluorinated compounds were tested as electrolyte additive and fluoroethylene carbonate (F1EC) was determined as the best performing additive (1-5 wt. %). The improvement of capacity performance was observed in an electrolyte containing 2% of F1EC, especially noticeable beneficial impact reported when LIC was charged at high-current densities. Furthermore, molecular modeling was performed in order to support experimental work and to further understand the interaction between electrode materials and electrolyte. The choice of the LiTFSI salt in combination with F1EC as an electrolyte co-solvent (20-33 wt. %) or with acetonitrile electrolyte solvent was demonstrated as the key to high temperature continuous operation (~ 65°C). The temperature limit was then only dictated by AN's boiling point.

Following to the selection of the cell components and cell configuration, the different types of hybrid capacitors were designed and tested in lab cells. In particular, classical LICs were assembled with activated carbon at positive electrode, graphitic carbon at the negative electrode side. This so-called serial LIC system was tested in a coin cell system. The other alternative configurations of the hybrid system were built by employing LFP-Activated Carbon (cathode)/Graphite (anode) and LFP- Activated Carbon (cathode)/LTO (anode) systems which are also called parallel LIC configurations.

Good cycling stabilities of lab-designed cells were also demonstrated with more than 90% of stable initial capacitance after ~10000 cycles at a current density of 20C (Charge time: ~3 min) and a Coulombic efficiency close to 100%. The efforts performed at lab cell manufacturing were taken to the next prototyping level by YUNASKO. Two different prototypes were constructed; activated carbon and $LiFePO_4$ (LFP+AC) hybrid positive electrode combined with two different negative electrodes which are $Li_4Ti_5O_{12}$ (LTO, Prototype-1) or Hard Carbon (HC, Prototype-2). Acetonitrile based electrolyte was used for Prototype-1, an electrolyte based on ethylene carbonate and dimethyl carbonate mixture was used in Prototype-2. Specific energy values of 60 Wh/kg for LTO/LFP+AC and 86 Wh/kg for HC/LFP+AC prototypes have been achieved; the former was identified as the prototype with highest power capability which can reach up to ~4kW/kg (at ~80% of efficiency). No performance degradation has been observed during the electrochemical tests. Based on previous lab cell trial, it is estimated that the prototype values could still be improved and raised to 86 Wh/kg and 100 Wh/kg, respectively. The reason of these discrepancies is that many iterations have been achieved at the lab cell level in order to optimize the cell design while only one has been achieved at the prototyping step which involves much more resources. All the values are calculated based on the active material excluding the packaging of the cell.

For the recycling of hybrid LIC systems, an environmentally benign incineration free approach was used since organic compounds are an important source of $CO_2$ emissions, and fluorine compounds are very sensitive to thermal processes and may lead to HF or $F_2$ evolution. The green recycling approach also known as “cold fraction” was applied. This approach includes the polymer separation through a dedicated physical treatment to separate the metallic, the non-metallic and the powder fractions. The outcomes of the Energy Caps project will have an important impact in different applications areas such as renewable energy storage and green transport and will therefore contribute to tackle several societal challenges identified in the Europe 2020 strategy. At the end of the project designed LICs offer several unequaled sets of properties (energy, power, safety and lifetime) outperforming currently existing technologies. The high efficiency of these devises enables an “unlimited” number of quick and repeated cycles at high energy and high power with a minimum of heat generation, which cannot be achieved by any other system. This asset is particularly appealing for hybrid vehicles. In comparison with lithium batteries, the lower heat production allows the use of simpler, cheaper and more reliable cooling systems. In comparison with existing supercapacitor, the acceleration can be maintained up to 10 times longer, because of the higher-energy density. This is partially valuable for sport and race hybrid vehicles. Hybrid trucks and buses with frequent start/stop are also interesting application where LIC will offer competitive assets. The unpredictable character of renewable energies, such as wind and solar energies locks the growth of these energies or imposes the use of fossil-fuel generators of electricity, which are now able to start within about 10 seconds to a minute. There is then a need for a powerful energy storage system to hold the electric grid operational during this very short gap. The LICs are the most competitive tools to fill this gap between the electricity shortage and the effective start of the generators.

A particular attention was devoted to the recyclability of the developed supercapacitor. Within the project, it has been developed a process achieving the Recycling Efficiency of 50% imposed by EU Directive 06-66 and with low carbon print. The project will finally contribute to promote the European Scientific Excellence in the area of supercapacitors for energy efficiency and transport applications, and will offer the basis for long-lasting collaborations, which will benefit the knowledge-based economy in Europe. The consortium partners were actively involved in international conferences, workshops and seminars with the purpose of promoting the results of the project and engaging with relevant stakeholders from the academic and industrial sectors. Additionally, the project has developed a testing methodology manual for the testing of hybrid supercapacitor cells and stacks that can be downloaded from the project website.

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