Impact of innovative ILHYPOS supercapacitors on a fuel cell vehicle

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Abstract

Electrochemical capacitors (SC) are receiving increasing attention as possible enabling technologies in applications where high power is required for short times, such as in hybrid vehicles (HEV) and uninterruptible power systems (UPS). Moreover, there are some applications using fuel cells (FC) as power generators, whose energy efficiency is greatly reduced whenever FC power variations are significant. In 2005 the European Commission (EC) funded the ILHYPOS project, mainly aimed at the research and development of innovative SCs with highly improved specific performances (specific energy and power), and based on environmentally acceptable materials, such as ionic liquids, a novel electrolyte class of materials, with a working voltage in excess of 5 V. The improvements of SC performances were pursued also studying new electrode materials and/or cell designs: specific energy in excess of 40 Wh/kg, based only on active material weights have been estimated, in configurations with electronic conducting polymers or activated carbons in asymmetric configurations. As part of the Project ILHYPOS, the possible impact of the studied SCs has been evaluated by means of simulations in defined applications, such as those in fuel cell vehicles (FCV) and UPS, powered by fuel cells. The simulations for vehicle applications have been performed by using conventional standardized and real duty cycles. The sizing of the ILHYPOS SCs has been carried out with developed mathematical models and applied to a FC hybrid electric van, a test prototype developed by an Italian small enterprise. This paper first highlights the most recent achievements of the ILHYPOS Project and, then, presents the impacts of the developed SCs with respect to commercial SCs and a drivetrain with and without SCs.

Keywords: HEV, supercapacitors, materials, simulation

1 Introduction

Electrochemical capacitors, also called supercapacitors or ultracapacitors (SC), are attracting wide attention in electrically-driven vehicles (battery-powered = EVs, hybrid electric = HEVs, fuel cell electric vehicles = FCEVs), as high power storage devices aimed at improving overall vehicle efficiency, with more regenerative braking energy recovery, lower size and/ or at extending life of storage battery, and increasing performance capability when combined with low power density generation systems such as fuel cells. Multiple functions in advanced vehicles are

now envisaged and investigated for SCs, significantly impacting overall drive-train configurations, complexity and complete vehicle cost and performances.

Commercially available SCs, currently based on organic electrolytes (normally named electrochemical double layer capacitors = EDLCs), are electrochemical devices with very promising technical characteristics in terms of specific power and energy, but they need further improvements to fully meet the technical, economical and environmental (due to the use of unsafe or environmentally unacceptable chemicals) requirements of some of the envisaged functions in future EVs, HEVs and FCEVs.

A European project, named ILHYPOS (**I**onic **L**iquid-based **HY**brid **PO**wer **S**upercapacitors) project, was partially funded by the European Commission (EC) and started at the end of 2005 with the involvement of eight European participating organizations from three European countries: ENEA, University of Bologna, Arcotronics Technologies and Micro-vett (Italy), Université Paul Sabatier and Conservatoire National des Arts and Metiers (France) and Evonik-Degussa and Leclanché Lithium (Germany). The project had the scope to overcome some of the current commercial SC limitations by developing a green, safe, and high energy (>15 Wh/kg) and power (>7 kW/kg) Hybrid SC with advanced ionic liquids (ILs) for application in electric vehicles and in delocalized energy production plants using fuel cells. More details about the ILHYPOS Project general description are in [1].

As a consequence, the project aimed at developing new materials, new SC designs, coupling high surface area carbons and/or electronically conducting polymers as electrodes with a novel electrolyte using ionic liquids, and new preparation processes (as soft-packaged laminated SCs).

The most intriguing results so far achieved regard the improved ionic conductivity (initially restricted at temperatures over 80 °C and during the project extended at room temperature and also below 0 °C) of the green (environmentally acceptable) electrolyte component (mixture of ionic liquids), extremely stable well beyond 5 V; an electronically conducting polymer (ECP) used as positive electrode, with still limited stability with IL-based electrolytes; optimized activated carbons for hybrid (with carbon negative electrode and ECP positive one) and asymmetric

(carbon for positive and negative electrode with different active material loading) SC cell configurations; and component preparation and cell assembly processes using lamination and wound stack technology in addition to soft-pack lamination technology.

In parallel to the basic and applied research work on materials, cell design and fabrication and assembly processes, the impacts of ILHYPOS novel SCs have been estimated for a FCV, already developed, by using a simulation model (2, 3). The scope of such simulations was to clearly identify the technical requirements of the SCs under development and their advantages in comparison with commercial SCs and the present vehicle without any SC.

The paper highlights chief achievements of the ILHYPOS Project on materials research, cell design and assembly and first prototypes production and testing, and gives details about the simulation results, emphasizing the positive impact of the SCs under development on the reference vehicle performance. Finally, the definition of numerical design SC indicators will be discussed to establish general rules (figure of merits) to choose SC in various applications.

2 Chief achievements on materials and cell prototype

The main project targets were scientifically and technologically challenging, because required substantial research and development on novel materials and preparation processes of components, complete cells and modules. Significant improvements were achieved on ILs and derived electrolytes to assure a good ionic conductivity at temperatures well below 80 °C, which was the standard at the beginning of the project; on electrode materials, particularly in the positive one, and compositions, to overcome the standard value of 80-90 F/g of conventional activated carbon to up to 150 F/g with novel materials and to guarantee compatibility with ILs for long life stability; on cell design the initial hybrid configuration (activated carbon at the negative electrode and electronic conducting polymers = ECP at the positive) was integrated with new designs based mainly on optimised carbons in symmetric (preliminary formulation) and asymmetric (different loading of the negative and positive electrode) configurations; and finally, the preparation processes for materials, electrodes and ILs (and related electrolytes) were scaled up to produce in a repeatable and, possibly, economical

way sufficient amounts for optimising the processes and producing prototype cells and modules in a pilot production line.

2.1 Materials results

Various families of high purity ILs have been synthesised with a simplified process and scaled up to kg production. The electrochemical stability window exceeds 5 V in a large temperature range between -20 °C and 90 °C, while the ionic conductivity has satisfactorily met the project target at 60 °C ($\geq 5\times10^{-3}$ Scm^{-1}) but even at low temperatures ($\leq$ -20 °C) with values higher than $\geq 10^{-3}$ Scm^{-1}. Fig. 1 presents the ionic conductivity of various ILs developed in the project, compared with the targets.
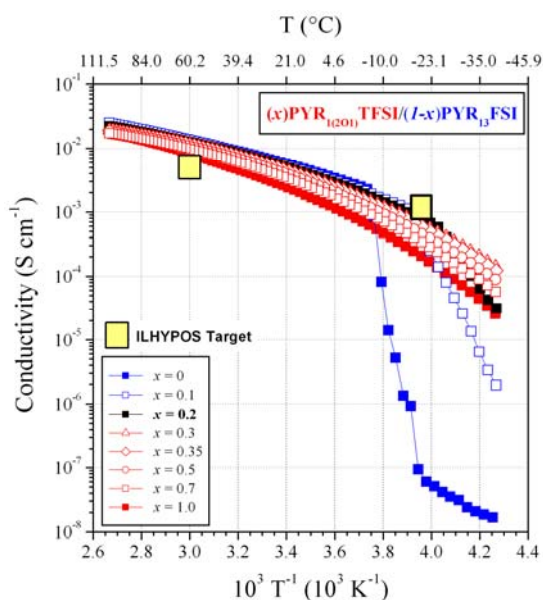

Figure 1: Ionic conductivity of ILHYPOS IL mixtures.

Various electrode materials have been investigated and selected. A high stability activated carbon has been at the end identified with a specific capacitance of about 90 F/g. Fig. 2 clearly shows the specific capacitance and the stability of the carbon during cycling, as a result of the stability of the internal resistance (ESR) during cycling.
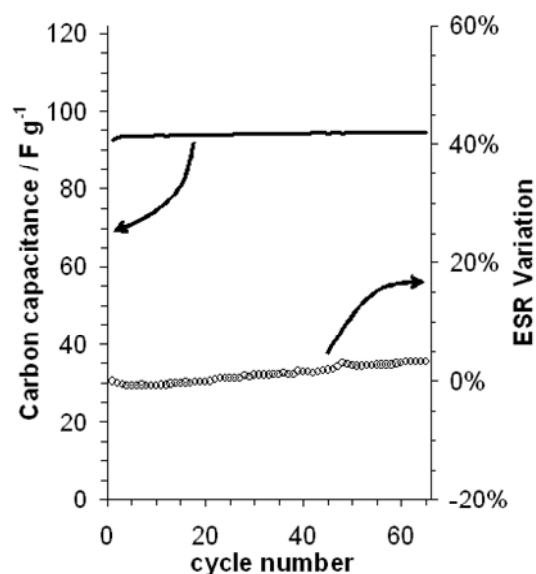

Figure 2: High stability activated carbon.

Electronic conducting polymers (ECP, such as pMeT = polymethyl thiophene), directly electropolymerised on current collectors in ILs to form positive electrodes after further treatments, easily reached a specific capacitance of 200 and over F/g, beyond the project targets, but subsequent durability testing in lab cells showed a significant capacitance fade (about 50%) after 5,000 cycles. Consequently, further research was required for improving stability and alternative solutions were even investigated.

2.2 Cell design and process development

Three different configurations of prototype cells were designed to verify some optimisation and assembly process aspects:

1. A symmetric carbon/IL electrolyte/carbon design was initially used to analyse the preparation and the assembly processes.
2. A hybrid configuration carbon/IL electrolyte/ECP was then chosen, according to the project objective, to verify basic performances and potential improvements in stability due to the optimisation of the assembly process.
3. An asymmetric carbon/IL electrolyte/ carbon was, selected as a novel alternative, not initially scheduled, to fully meet project targets, thanks to the selection of high stability activated carbons.

Fig. 3 shows the symmetric cells tested for basic performance evaluation and life cycling. A

simplified testing procedure was applied with similar charge and discharge conditions, limiting the working voltage at 3.4 V. The average capacitance was about 400 F in about 90 g.

Figure 3: Carbon/IL/carbon symmetric ILHYPOS prototype cells.

The delivered specific energy E_{max} was in average 27 Wh/kg, based on the following equation:

$$E_{max} = \frac{3}{8} \cdot C_{SC} \cdot \frac{V^2}{M_{composites}} \qquad (1)$$

where C_{SC} is the capacitance in Farad, V is the working voltage in Volt and $M_{composites}$ is the mass in kg of the active materials of the electrodes. Also the specific power P_{max} was calculated, according to the following definition, to give an average of 3.7 kW/kg:

$$P_{max} = \frac{V^2}{4 \cdot R \cdot M_{composites}} \qquad (2)$$

where R is the internal resistance.

A prototype symmetric cell has been also cycled exceeding 22,000 complete charge/discharge cycles, with a significant deterioration probably due to the working voltage and the high temperature.

Based on the above results and on the optimisation analyses, two final cell designs were defined and selected: the hybrid (HYSC) and the asymmetric (AEDLC) one. For the hybrid configuration, a specific energy of about 50 Wh/kg (based on active materials weight) is foreseen, while for the asymmetric configuration a value of more than 40 Wh/kg is calculated: these values greatly depend on the working temperature and voltage that may vary from 3.7 to 4.2 V.

An example of expected values at module level are reported in Fig. 4 at 60 °C (the temperature

target in the project) and compared with the DOE Power Assisted HEV target for SCs.
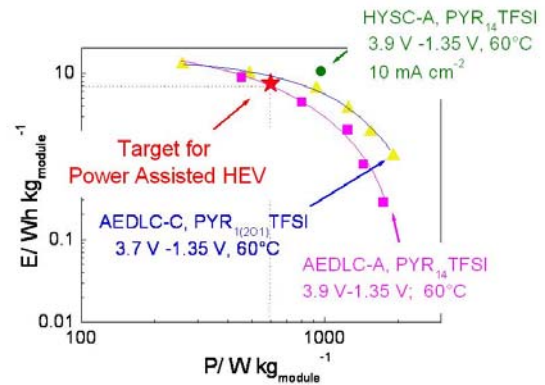

Figure 4: ILHYPOS SCs designed performances at 60 °C compared with DOE SC Power Assist target.

Cell components for the last two configurations have been prepared by means of coating processes in hundreds of meters and made available, together with various litres of ILs for the subsequent cell and module assembly. The assembly line, based on the Wound Stack technology and depicted in Fig. 5, is now assembling prototype cells.
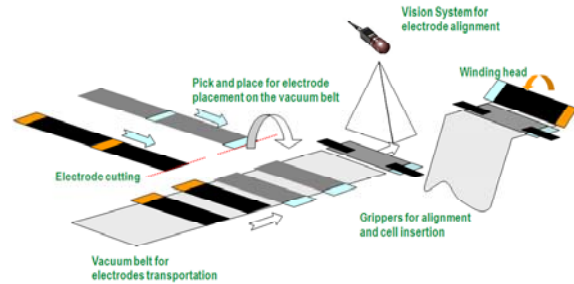

Figure 5: Assembly line lay-out.

Modules of different overall capacitance (up to 2.1 kF), voltage (up to 92.5 V) and power (up to 5.2 kW) have been designed and are under assembly.

3 SC impact analysis

The definition of the application requirements for the developed SCs according to determined duty cycles and the possible role and impact of SCs in FCVs have been investigated by means of mathematical models, applied to a reference van, named NEO (**N**o **E**mission **O**utfit). The reference vehicle for the simulations is a series-hybrid electric prototype, developed by Micro-vett, of the 'range extender' type, with a storage battery able to supply the traction power, while a FC system recharges the battery and extends the vehicle range, well beyond that available with the battery alone. The FC system power is lower than that

required for moving the vehicle, with 30-kW continuous power and a 60-kW peak power (for 2 minutes). The rated powertrain voltage (V_{link}) is 280 V, corresponding to the voltage of the 64Ah Zebra ($Na-NiCl_2$) battery system. The simulation work has been concentrated on simulating a modified vehicle configuration with the addition of the SC systems in order to reduce maximum current and peak power and extend cycle life of the battery system.

3.1 Sizing the SC pack for the NEO

The initial analysis was aimed at dimensioning the SC pack in the modified reference vehicle. To do so some simplification assumptions were necessary, to define some typical operating conditions:

- The FC is kept off.
- The SC pack is the only component assisting the battery during acceleration and regenerative braking.
- In addition, the SC sizing considers the worst cases: maximum acceleration and deceleration.

The original NEO configuration has an electric generator, composed by the FC system in parallel with a Zebra battery. The introduction of the SC system also modifies the actual NEO working strategy.

In the actual configuration the NEO power traction is fed by the FC (giving electrical current) through a DC/DC converter, while the battery system gives the remaining current and fixes the link voltage. In the modified version, the FC and the SC supply the current, while the battery maintains the same functions as in the previous version. The DC/DC used with the SC also allows a wide range of working voltage increasing the maximum energy and power supplied by the SC. In this way, the decoupling of the SC (instead of a simple parallel configuration with the battery without converter) avoids the need of over sizing the SC to meet the energy requirements of the application.

A block diagram of drive-train was redesigned and used to define the functions of the energy management systems and the various main components: such as, the back-up battery, the braking resistance, auxiliary loads and the power flow control device. Each of these components plays some roles and functions in the drive-train. The energy management system allows for the control and management of the distribution of load power between the FC, the SC and the battery. It is a micro controller with a measuring system, which acquires a set of parameters on-line, elaborates them and drives the converters. It can be also used to calculate the state of health of the various components and give indications for maintenance. The use of this device and the related algorithm are functional in optimising the SC behaviour and their sizing. The choice of the converters topology and the link voltage imply further operating conditions and limitations for the SC voltage. More details about the topology effect are presented in [2].

In the simulation, the "*gradient method*" has been applied to the NEO lay-out: this method limits the temporal variation of the current of the FC. The maximum value and gradient of the FC depend on the temperature variation, while the battery parameters are constant. In addition, for the initial simulation, the worst case of no FC current contribution is considered, taking into account the specific NEO configuration of a "range extender" type, in which the battery normally operates alone to power the vehicle.

Various operating conditions have been analysed for defining the simulation algorithm. A set of algorithm conditions have been selected:

1. A reference state-of-charge (SOC) of the SC is defined as well as a charging law.
2. The power required by the vehicle loads is added or subtracted to the power supplied/required by the SC in order to reach the reference SOC.
3. The maximum power from or to the battery is defined according to the constraints on gradient and maximum current.
4. The balance power is supplied by the SC.

With these conditions, it is possible to manage the fast power transients, during which the battery is not able to recharge the SC, and the slow transients (almost constant power), during which the SC may be recharged. This allows to automatically change the status of the SC from discharging to charging at the end of transients.

A critical point is the selection of the reference SOC and the charging law of the SC, in order to be able to recharge or discharge the SC in most cases without overcharging the battery. The choice of the reference SOC depends on the general sizing of the systems. For such a reason, it is advisable to define a maximum and a minimum SOC, in function of the voltage. The ideal situation would be that the SC can supply energy and power between the reference SOC and the minimum during

acceleration and between the reference and the maximum SOC during braking to recover all the braking energy.

The first step is the definition of the NEO maximum power requirement, corresponding to the acceleration from idle to top speed and the deceleration from the top speed to zero. Fig. 6 shows the power requirement of the NEO, when it works at maximum torque.
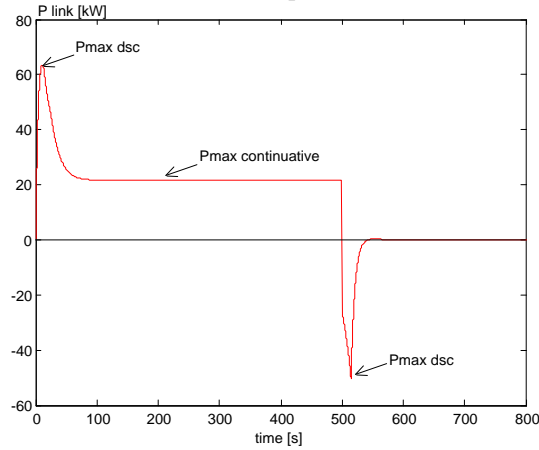
Figure 6: NEO power requirement.

The calculation methodology may consider 2 alternative possibilities:

1. The first one considers only the acceleration with an optimal control system of the SC maximizing the energy recovered during braking.
2. The second one imposes that the SC is always able to meet both acceleration and deceleration/braking power needs.

As a second step, the battery current variations must be defined and the limits (min and max), taking into account that they do not depend on temperature or on the battery SOC (as in the case of Zebra battery). Four values were initially defined.

With input data as shortly summarized above, a simulation model, presented in detail in [3], purposely developed for the NEO configuration. The preliminary simulations for the sizing of the NEO SC system used some simplifying assumptions: no battery current gradients; no SC management. Table 1 summarises the simulation results with the dimensioning of the SC for different capacitances with the SC voltage varying from 83 V to 250 V.

Table 1: SC sizing for NEO from simulations.

C (F)	Regenerative braking	P_{max}(kW)	Energy (kJ)
24	No	33	633
36	Yes	33	994
29	No	41	780
44	Yes	41	1193

3.2 Impact of ILHYPOS SC for the NEO

The results of the above simulations were initially used with the target performances (specific energy $\geq$ 15 Wh/kg and specific power $\geq$ 7 kW/kg) of ILHYPOS SC and declared values of commercial SCs. From this assumption, the energy in Wh is calculated along with the SC weight (without ancillaries: control device, case, thermal management and so on) and summarised in Table 2.

Table 2: ILHYPOS SC sizing.

C (F)	P_{max} (kW)	EC (Wh)	SC weight (kg)
24	33	176	11.8
36	33	276	18.4
29	41	217	14.5
44	41	331	22

The SC system may be assembled using unit cell connected in a series-parallel configuration, as illustrated in Fig. 7.
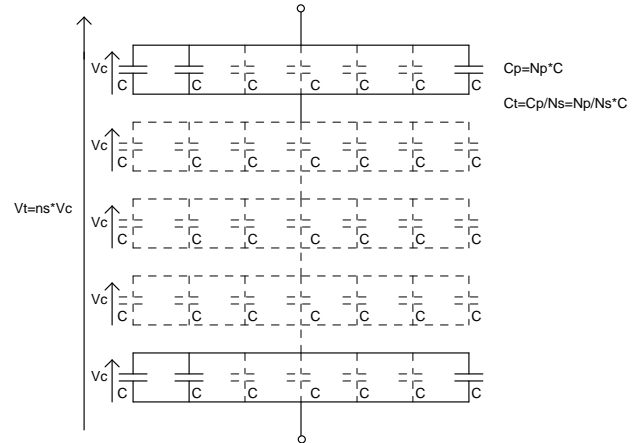
Figure 7: Possible ILHYPOS SC assembly for NEO.

The maximum voltage per single elementary SC unit is limited, for the moment for safety reasons, to 3.2V, but the ILHYPOS SCs may work safely up to 3.7-3.9 V. The number of elementary serial branches is 78 to reach the maximum design voltage of 250V.

For each branch, it is possible to calculate the total capacitance of, respectively, 1872, 2808, 2262, 3432 F for the values in Table 2. By using a reference unit capacitance of 500 F, it has achieved, respectively, 4, 6, 5 and 7 parallel branches. The comparison with commercial SCs from Maxwell and Ness is also interesting, by supposing the same energy content and a maximum working voltage for the ILHYPOS SC of 3.5 V. Table 3 summarises the results of such a comparison.

Table 3: SC dimensioning comparison.

Model	C (F)	V_{max} (V)	N_{cell}	SC weight (kg)
Maxwell	3000	2.7	93	256
Ness	5085	2.7	93	248
Ilhypos	3000	3.5	72	95

3.3 Simulation verifications with various duty cycles

The results of simulations have been then verified using different duty cycles: ECE15, HYZEM and a real working cycle, recorded by Micro-vett during an experimental campaign. The simulations confirmed the possibility of the modified NEO with ILHYPOS SCs to substantially follow the various duty cycles with interesting estimated hydrogen saving, as shown in Table 4.

Table 4: Hydrogen saving of NEO with ILHYPOS SCs.

Duty Cycle	H_2 saving (%)
Urban Ece 15	32.3
Real Micro-vett	4.0
Hyzem	13.6
Hyzem_70	19.6

3.4 General sizing index

As a result of the simulation work, a general rule has been extrapolated by defining a numerical approximation index (Fdr = Relative Dimensioning Factor) aimed at quantifying the potential advantages in using SCs based on ILs in comparison with the conventional ones. In particular, Table 3 compares various SCs with the same total capacitance C_t but different working voltages with a significant reduction in the total number of elementary units.

By considering the ratio of components for two cases (for example, ILHYPOS and Maxwell), it is achieved:

$$Fdr = \frac{n_{p\,ilhy}}{n_{p\,max\,w}} \frac{n_{s\,ilhy}}{n_{s\,max\,w}} = \frac{4*72}{5*93} = 0.62 \quad (3)$$

where n_p and n_s refer to the number of units in parallel and series, respectively.

From the ratio Fdr, it is then possible to calculate other ratios for other parameters, (such as: weight, volume) and therefore compare alternative solutions.

The approximate value of the ratio Fdr is calculated starting an SC pack of a total capacitance C_t, by connecting in series/parallel some SCs of capacitance C_p:

$$C_t = C_p \frac{n_p}{n_s} \quad (4)$$

The calculated value of Fdr is normally approximated because the numbers n_p and n_s are always integer.

The number n_p can be obtained by:

$$\frac{C_t}{C_p} n_s = n_p \quad (5)$$

and by multiplying Equ. (5) with n_s it is achieved:

$$\frac{C_t}{C_p} n_s n_s = n_p n_s \quad (6)$$

But the value of n_s is easily got by the approximate ratio of the maximum voltage of the SC pack with the maximum voltage of each unit:

$$n_s = \frac{V_t}{V_{max\,c}} \quad (7)$$

If the SC pack is composed of SC with the same capacitance but different working voltage, it is obtained:

$$\frac{\frac{C_t}{C_p} n_{s1}^2}{\frac{C_t}{C_p} n_{s2}^2} = \frac{n_{p1} n_{s1}}{n_{p2} n_{s2}} = Fdr \quad (8)$$

Or even:

$$Fdr = \left(\frac{V_{max\,p2}}{V_{max\,p1}}\right)^2 = \frac{n_{p1} n_{s1}}{n_{p2} n_{s2}} \quad (9)$$

It is evident from Equ. (9) the advantage to use SCs with higher working voltages. In case of SC packs with different capacitance, the Fdr would be:

$$Fdr = \frac{C_{p2}}{C_{p1}} \left(\frac{V_{max\,p2}}{V_{max\,p1}}\right)^2 = \frac{n_{p1} n_{s1}}{n_{p2} n_{s2}} \quad (10)$$

As a conclusion, the ratio *Fdr* is an indicative index (neglecting voltage drops and approximation in using integer numbers for series and parallel branches) for comparing SCs of different technologies, as demonstrated in Table 5.

Table 5: *Fdr* values for different SC comparisons.

SC types	Real	Approximated
Maxwell/Ness	1.66	1.69
Maxwell/Ilhy	1.61	1.68
Ness/Ilhy	0.97	0.99

4   Conclusions

The European project ILHYPOS has been progressing on new SC technology mostly based on ILs with some interesting results:

- High performances SC have been designed and partially tested in a variety of configurations (symmetric, asymmetric and hybrid) with specific characteristics higher than the present ones.
- Novel materials and cell design using "green" components have been developed:
- Preparation and production processes as well as assembly pilot line have been developed and validated.
- Various prototype cells have been produced and tested and many other are other production together with some modules with different characteristics.
- Finally, the potential impact and advantages of these novel SCs have been analysed with simulations on a reference vehicle, currently powered with battery and FC.
- An indicative evaluation index has been also developed as a rough design tool for comparing different SC technologies.
- Some research and analysis work is still required for economically analysing the potential costs of these new systems and the possibility of a full scale production.

Acknowledgments

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