

Short communication

# Strategies for high-performance supercapacitors for HEV

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## Abstract

Our paper highlights the role of supercapacitors in hybrid electric vehicles (HEVs), the current response to the worldwide demand for a clean and low fuel-consuming transport. The main strategies for increasing the specific energy of supercapacitors, which are electrochemical energy storage/conversion systems of high-specific power, are discussed, with the focus on electrode material, electrolyte and electrode/electrolyte interface properties. Particular emphasis is given to the use of ionic liquids (IL), which are attracting much attention as green and solvent-free electrolytes, and to the development of high-voltage, IL-based hybrid supercapacitor with high surface area carbon negative electrode and poly(3-methylthiophene) positive. Based on the results of laboratory cells featuring *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide and 1-ethyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide ILs, the specific energies of hybrid supercapacitor modules are evaluated and compared to those expected for double-layer carbon supercapacitors displaying the same ILs.

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**Keywords:** Supercapacitor; Hybrid electric vehicle; Ionic liquid; Carbon; Poly(3-methylthiophene)

## 1. Introduction

The oil crisis and the reduced availability of fossil fuels require the development of a sustainable energy economy based on new, high-efficiency, energy-conversion technologies. Furthermore, the demand for clean energy and low-polluting transport is rapidly expanding worldwide and calls for a road transport alternative to the conventional one based on internal combustion engine (ICE) vehicles. ICE transport, indeed, is responsible for 30% of oil consumption and its intrinsic low energy-conversion efficiency strongly contributes to pollution by greenhouse gas emissions. This is where high efficiency electrochemical energy conversion/storage systems come in. While zero emission vehicles powered by advanced lithium batteries are under development for urban areas and low-emission vehicles powered by hydrogen-fed polymer membrane fuel cells represent a long-term solution even for long-range transport, hybrid electric vehicles (HEV) are a reality [1–3]. In these vehicles the synergic combination of ICE with batteries and supercapacitors controlled by power-management units

provides high fuel utilization with undoubtable benefits for fuel economy and, hence, for polluting emissions. Different combinations are pursued depending on the level of power-train hybridization, which ranges from micro- to full-HEVs. While in micro- and mild-HEVs, the electrochemical systems are mainly used for start/stop and regenerative braking, as well as for electric accessories, and do not substantially assist propulsion, in medium-HEVs they are also called upon to assist traction and in full-HEVs they provide electric-only propulsion, too [1–4]. Such different operational modes require electrochemical systems characterized by different energy (E) and power (P) content, P/E ratio (in W/Wh) and cycle-life, and the Ragone plot in Fig. 1 shows the features of lead–acid, NiMH and lithium–ion batteries and of supercapacitors on the market and under consideration for HEVs. Batteries that are high-specific energy systems are candidates for high-medium energy applications with  $P/E < 50$ , and the most advanced lithium–ion batteries are the only ones usable in full-HEV for electric-only traction. Supercapacitors are high-specific power and long cycle-life systems with  $P/E > 30$  up to more than 100, and due to their capability to store/deliver charge in a few seconds or more, outperform advanced batteries in applications having high peak to average power demand and are presently considered as the systems of choice for smoothing the strong

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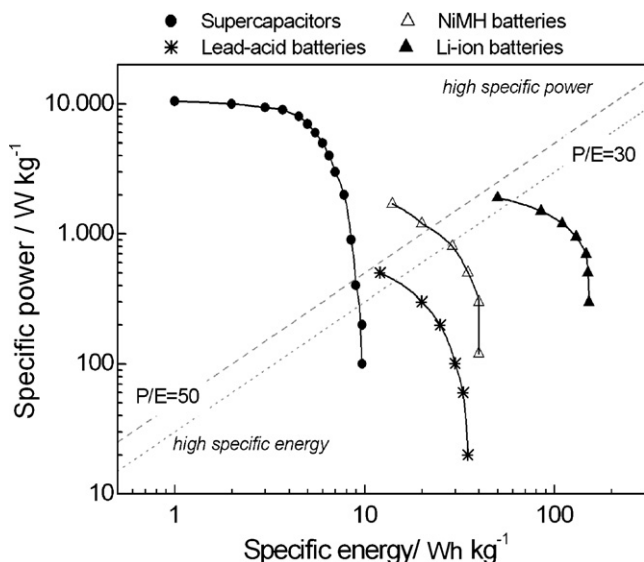


Fig. 1. Ragone plot of electrochemical systems for HEVs.

and short-time power solicitations required in transport. Thus, batteries and supercapacitors do not compete but are complementary in the development of HEVs for the high-specific energy of the former and high-specific power of the latter, notwithstanding the supercapacitors' significantly longer cycle-life more than two order of magnitude even in shallow discharge regimes. Research into these electrochemical systems for HEV applications is mainly devoted to implementing the specific energy of supercapacitors and the specific power of batteries.

## 2. Supercapacitor research and development

Last generation supercapacitors on the market for HEVs are symmetric double-layer carbon systems (EDLC) featuring activated carbon electrodes and organic electrolyte solutions based on acetonitrile (ACN) or propylene carbonate (PC), which provide cell voltage as high as 2.5–2.7 V (Maxwell Technologies, EPCOS, NessCap, Panasonic). Asymmetric (hybrid) supercapacitors based on carbon and NiOOH electrodes and aqueous electrolyte are also available (ESMA), although this configuration ensures significantly high capacitance it is characterized by a low cell voltage (<1.3 V) that is detrimental to its power performance [1–6]. In order to further increase the specific energy and power of supercapacitors and to meet cost and safety targets as well as cycle-life requirements at envisioned operating temperatures (up to 70–80 °C), much R&D effort is being devoted to new electrolyte and electrode materials and to new cell configurations [5–9].

One priority concerns electrolytes, and the research has been focusing on those displaying high ionic conductivity and a wide electrochemical stability window to achieve supercapacitors featuring low equivalent series resistance (ESR) and high cell voltage ( $V_{\max}$ ) for high-specific power  $P = (1/4)V_{\max}^2/(w_{\text{sc}} \text{ ESR})$ , where  $w_{\text{sc}}$  is the supercapacitor weight. High  $V_{\max}$  is also of primary importance for high-specific energy ( $E$ ), which is given by  $E = (3/8)C_{\text{sc}} V_{\max}^2/w_{\text{sc}}$  when it is

delivered between  $V_{\max}$  and  $1/2 V_{\max}$  and where  $C_{\text{sc}}$  is the supercapacitor capacitance resulting from each electrode capacitance ( $C_+$ ,  $C_-$ ) as per  $C_{\text{sc}}^{-1} = C_+^{-1} + C_-^{-1}$ . According to the Helmholtz model, the electrode double-layer capacitance for EDLC is  $C_{\text{dl}} = k^0 \varepsilon A/l$ , where  $k^0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$ ,  $A$  is the electrode surface area,  $l$  the double-layer thickness and  $\varepsilon$  the dielectric constant of the medium in the IHP (Inner Helmholtz plane), which is the solvent in conventional electrolyte solutions [10]. For high-specific capacitance of the EDLC ( $C_{\text{sc}}/w_{\text{sc}}$ ), and thus for high-specific energy, electrode materials and electrolytes have to be developed with attention to the electrode/electrolyte interface. In EDLCs high surface area carbons are used (activated carbons, aerogel carbons), and it is generally recognised that, for a high electrolyte-accessible surface area, carbons must also have a pore size distribution centered at values which at least match the size of the ions involved in the double-layer (>1–2 nm) and a suitable surface chemistry to improve electrode wettability with the electrolyte solutions. Indeed, while certain chemical activations carried out to increase the carbon surface area make the surface hydrophilic and thus may improve electrode performance in aqueous solutions, they may be detrimental to PC-based electrolytes, so that different treatments that make the carbon surface hydrophobic are required [6,11].

Much attention has recently been devoted to the use in supercapacitors of ionic liquids (ILs) as solvent-free “green” electrolytes for their intrinsically higher safety than ACN-based ones. Indeed, the ILs feature very low vapour pressure, high chemical, thermal and electrochemical stability, and good conductivity particularly above room temperature (RT), i.e. in conditions where conventional organic electrolytes suffer from the reduction of the electrochemical stability window [12–16]. Unlike ACN- or PC-electrolytes with alkylammonium salts, ILs should provide significantly longer cycle life at high cell voltage >3 V and above RT. Achieving high double-layer capacitance in IL, which has no solvent, also depends on the chemical nature of the IL ions. Our previous studies suggested that in IL the double-layer is constituted by a monolayer of ions up against the carbon surface and, thus, the double-layer capacitance of carbon electrodes is strongly determined by ion polarizability. This affects the dielectric constant in the double-layer as well as double-layer thickness, which in turn also depends on the preferred orientation of the ion under the applied electric field [17]. The surface features of the positive and negative carbon electrodes should thus be differently tailored in view of the different properties of the negative and positive IL counterions involved in the double-layer, hence giving rise to an asymmetric EDLC configuration.

By “asymmetric” are termed different supercapacitor configurations. While it is generally used for hybrid supercapacitors featuring positive and negative electrode materials of different nature that can also be charged/discharged via different electrostatic and faradaic modes, it may be also used for supercapacitors featuring the same material for the positive and negative electrode but with different loading. This latter strategy can be pursued, particularly in the case of IL-based EDLC, to take advantage of the whole electrochemical stability window of the electrolyte, which is typically centered far

from the potential of the discharged electrode material. The concept of a hybrid supercapacitor with aqueous or organic electrolytes, in which the two electrode materials are charged-discharged under different modes, has proved to be powerful when coupling electrodes based on activated carbons (AC) and on pseudocapacitive materials such as electronically conducting polymers (ECPs) and inorganic oxides, and lithium inorganic oxides and ECPs [5,18–23]. Indeed, this strategy enables separate electrode design in view of the required operating conditions. In the EU SCOPE Project, “Supercapacitors of Power and Energy”, hybrid supercapacitor modules (>1.5 kF) were developed with PC-Et<sub>4</sub>NBF<sub>4</sub> electrolyte and AC and poly(3-methylthiophene) (pMeT) as negative and positive electrode materials, respectively. At room temperature the modules delivered 3.5 Wh kg<sup>-1</sup> maximum specific energy between 3.0 and 1.5 V and could reach 9 Wh kg<sup>-1</sup> by design optimization for component weight distribution [21]. The same electrode materials were then used to develop AC/IL/pMeT hybrid supercapacitors operating above RT with IL electrolytes: the one with *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR<sub>14</sub>TFSI) featured cell voltage >3.4 V and cycle-life over more than 16,000 cycles at 60 °C [14].

Our work is thus focused on the optimization of carbon and polymer electrode materials for IL-based supercapacitors operating above RT, within the ongoing EU ILHYPOS Project, “Ionic liquid-based hybrid power supercapacitors”. This project’s scope is to develop a *green*, safe, and high energy and power hybrid supercapacitor based on ILs as electrolytes for application as peak power smoothing device in fuel cell-powered electric vehicles; the results should also be relevant to HEVs. The long-term goal is a 2 kF module featuring a maximum voltage at 60 °C higher than 3.5 V, maximum specific energy and power higher than 15 and 7 kW kg<sup>-1</sup>, respectively, achieved with an ESR < 5 mΩ. Such performances are particularly challenging when compared to the *E* and *P* values of commercial EDLCs with ACN and PC-based electrolytes, which at RT feature 5 Wh kg<sup>-1</sup> and 6 kW kg<sup>-1</sup> and 3 Wh kg<sup>-1</sup> and 1 kW kg<sup>-1</sup>, respectively, values that decrease above 40 °C with some safety concerns for the former [5]. The ILHYPOS supercapacitor cycle-life target is at least 100,000 cycles with 20% maximum loss of capacitance. This is achievable only by hydrophobic ILs, which are available at a high degree of purity, such as those with the bis(trifluoromethanesulfonyl)imide anion (TFSI). In order to reach these goals, much effort is being directed to the optimization of IL electrolytes and electrode materials of a hybrid supercapacitor with pMeT positive and carbon negative electrodes.

### 3. Strategies for high-performance electrode materials in ILs

The strategies we adopted for the development of high-performance electrodes in ILs, and particularly in the hydrophobic PYR<sub>14</sub>TFSI and 1-ethyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI), are primarily being devoted to enhance their capacitive response. For the

conducting polymer, we have found that different polymerization conditions affect the pseudocapacitive behaviour of pMeT in the IL [16,24]. Indeed, electropolymerization in the same IL used for the capacitance tests yields pMeT electrodes with the highest performance. In effect, when the polymer is galvanostatically prepared on current collector in PYR<sub>14</sub>TFSI or EMITFSI, it reaches 200–230 F g<sup>-1</sup> in the same ILs at 60 °C, values almost double than those displayed in the same electrolyte by the polymer prepared in ACN-Et<sub>4</sub>NBF<sub>4</sub>. This can be explained by considering the effect of the polymerization bath on pMeT morphology, which consists of interconnected polymer chains that are thinner when prepared in IL and thus provide easy electrolyte access to the polymer p-doping sites. Also note that pMeT exhibits ca. 15% lower specific capacitance in PYR<sub>14</sub>TFSI than in EMITFSI at the same doping level [16].

The direct galvanostatic polymerization of pMeT on current collector in IL followed by undoping via inversion of current polarity is a versatile technique that can be scaled for the preparation of large area electrodes by transferring industrial technologies already developed for electrochemical coatings. Furthermore, we have demonstrated that the addition of the acid trifluoromethanesulfonimide provides a clean electrosynthesis procedure in which the IL is not wasted by counterelectrode reaction nor consumed to balance the pMeT p-doping charge, with advantage in terms of costs [24]. In order to meet the requirements of electrode preparation by casting or lamination on current collector, we are developing preparations of pMeT powders in EMITFSI and PYR<sub>14</sub>TFSI ILs by both electrochemical and chemical methods. In these cases the crucial point is that the pMeT is obtained in the oxidized state (doping level up to 30–20%) with the TFSI<sup>-</sup> as p-doping anion, which, because of its high molecular weight, severely affects the specific capacitance response of the p-doped polymer.

Our work on the carbon electrodes focuses on the development of carbons of high-specific surface area that can be easily accessed by the IL electrolyte, with attention to porosity and surface chemistry. Indeed, the carbons should display a high pore volume and a pore size wider than the IL counterions involved in the double-layer charging process. They should also have a tailored surface chemistry in that it affects the electronic properties of the carbon itself and its surface polarizability as well as carbon wettability by IL ions. Hence, we are pursuing two routes: (i) surface modification of commercial activated carbon and (ii) investigation of mesoporous cryo- and xero-gel carbons whose pore size and pore-wall thickness can be controlled by chemical synthesis conditions. The highest specific capacitance values for negatively charged electrodes in IL at 60 °C, i.e. 100–110 F g<sup>-1</sup> in EMITFSI, were obtained with activated carbons treated at 1050 °C (ACT) under inert atmosphere in order to remove IL-repelling moieties, thus providing a higher accessible surface area for the double-layer charging process. We have demonstrated that while such treatment does not modify the porous texture of the carbon (which displayed ca 800 m<sup>2</sup> g<sup>-1</sup> mesoporous specific surface area), it removes electron-withdrawing groups such as C=O and results in a higher delocalization of the electron in the carbon, with a positive effect both on specific capacitance and electronic resistance. In the case of cryo/xerogel

carbons, the highest specific capacitance obtained in IL has been  $60 \text{ F g}^{-1}$  in EMITFSI, being limited by the value of a mesoporous surface area of ca.  $300 \text{ m}^2 \text{ g}^{-1}$  [16,17]. Given that we observed that in the case of xero/cryogel carbons the specific capacitance increases with the carbon mesoporous specific surface, work is in progress to develop cryo/xerogel carbons with higher mesoporosity than that obtained to date.

A very interesting result in our study is that, despite carbon morphology and surface chemistry optimization, what mainly influences the carbon capacitance response is IL structure and chemistry. Indeed, each investigated negatively charged carbon displayed significantly higher specific capacitance in EMITFSI than in  $\text{PYR}_{14}\text{TFSI}$ , and this cannot be explained by a different accessible electrode surface area for the two ILs because the carbons featured pore-size distributions centered at values wider than 2 nm and the size of both IL cations was smaller than 1 nm. We attributed the cause of the different capacitance in the two ILs to the different polarizability and structure of the  $\text{EMI}^+$  and  $\text{PYR}_{14}^+$  counterions, which result in a different dielectric constant and thickness of the double-layer. Thus, the intimate contact of the carbon with the IL counterion makes the counterion and carbon surface polarizability crucial for the double-layer charging process [17].

On the basis of the experimental-specific capacitance values of the pMeT ( $C_{\text{pMeT}}$ ) and ACT ( $C_{\text{ACT}}$ ) electrodes and of the potential ranges allowing high coulombic efficiencies for their charge–discharge processes in  $\text{PYR}_{14}\text{TFSI}$  and EMITFSI ILs and, hence, a long cycle-life supercapacitor, it is possible to define the feasible characteristics for a 2 kF module operating at  $60^\circ\text{C}$  with IL electrolyte. In a ACT/ $\text{PYR}_{14}\text{TFSI}$ /pMeT hybrid supercapacitor it is possible to reach  $C_{\text{ACT}}$  and  $C_{\text{pMeT}}$  values of  $90 \text{ F g}^{-1}$  and  $200 \text{ F g}^{-1}$ , respectively, and negative ( $\Delta V_-$ ) and positive ( $\Delta V_+$ ) electrode potential excursions of 2.4 V and 1.0 V (limited by polymer stability) for the ACT and pMeT electrodes providing a  $V_{\text{max}} > 3.7 \text{ V}$ . This cell voltage can be reached only if electrode mass loading is properly balanced: the positive to negative electrode mass ratio obtained by the equation  $R_{+/-} = \Delta V_- C_{\text{ACT}} / (\Delta V_+ C_{\text{pMeT}})$  should be 1.3. Correspondingly, supercapacitor capacitance becomes  $26 \text{ F g}^{-1}$  of total composite materials (80% pMeT and 95% ACT in the positive and negative composite) and, on the basis of an optimized weight distribution of supercapacitor components with the challenging electrode mass of 38%, the weight for a 2 kF module is 200 g. Thus, the supercapacitor, including case, would deliver a maximum specific energy of  $15 \text{ Wh kg}^{-1}$  between 3.8 and 1.9 V at  $60^\circ\text{C}$ . Interestingly, although EMITFSI has a less extended electrochemical stability window for the negative electrode than  $\text{PYR}_{14}\text{TFSI}$ 's and ensures cell voltages of 3.3 V at maximum, it permits to reach almost the same specific energy value as  $\text{PYR}_{14}\text{TFSI}$ 's because it provides higher specific capacitance than the latter. The different conductivities of the two ILs ( $6.5$  and  $25 \text{ mS cm}^{-1}$  at  $60^\circ\text{C}$  for  $\text{PYR}_{14}\text{TFSI}$  and EMITFSI, respectively) also have to be taken into account for the specific power requisites.

Even with IL-based EDLCs it should be possible to reach energy performance higher than  $10 \text{ Wh kg}^{-1}$  (including case). In fact, with properly balanced ( $R_{+/-} = 1.5$ ) ACT carbon pos-

itive and negative electrode materials (featuring  $90 \text{ F g}^{-1}$ ) and with  $\text{PYR}_{14}\text{TFSI}$  electrolyte, cell voltages as high as 3.9 V may be reached, and thus  $12 \text{ Wh kg}^{-1}$  is feasible. Indeed, while in carbon/pMeT hybrid supercapacitor the maximum cell voltage is limited by the stability of the polymer, in EDLC it is limited only by IL stability and slightly higher cell voltages are possible. However, the charging resistance of pMeT electrodes is significantly lower than that of the carbons and this is in favor of the hybrid configuration for the power requisites of the supercapacitor.

#### 4. Summary

Supercapacitors of high-specific power play an important role in HEVs and research is being devoted to increasing their specific energy. One of the strategies being pursued is the use of IL electrolytes for high cell voltage  $> 3 \text{ V}$  and, provided that electrode materials are properly designed for high-specific capacitance in the IL, such strategy results in a significant enhancement of the supercapacitor-specific energy. Carbon/ $\text{PYR}_{14}\text{TFSI}$ /pMeT hybrid modules delivering at  $60^\circ\text{C}$   $15 \text{ Wh kg}^{-1}$  between  $V_{\text{max}} > 3.5 \text{ V}$  and  $1/2 V_{\text{max}}$  should be a feasible goal.

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