

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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## 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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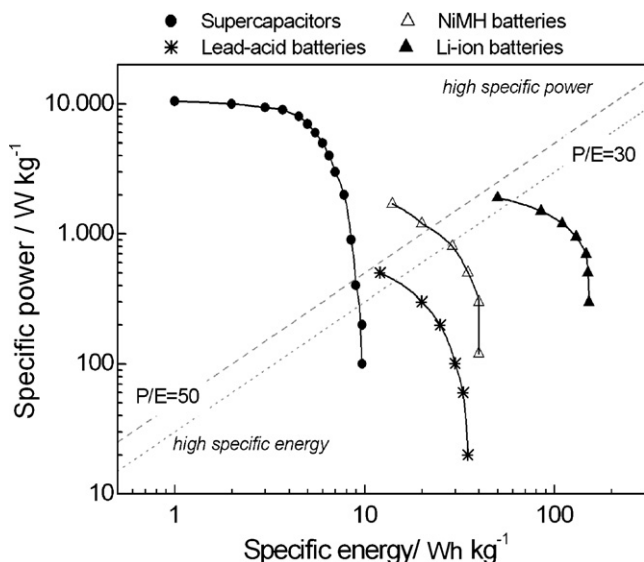


Fig. 1. Ragone plot of electrochemical systems for HEVs.

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

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