

SafeCap : Ionic liquids Supercapacitor

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ABSTRACT

In order to meet the requirements for high power energy storage for spatial applications, Hutchinson is developing ionic liquids based supercapacitors. Ionic liquids are allowing higher energy density systems operating in a wider temperature range with overall improved safety as compared to traditional organic solvent-based systems.

INTRODUCTION

Supercapacitor is a product which fills the gap between batteries and capacitors in terms of power and energy density. From a general point of view, batteries, and more precisely Li-ion batteries, can store high energy densities (up to 180 Wh/kg for commercial products, 150 Wh/kg for last space qualified cells) with low power densities (up to 1kW/kg). Therefore, they are often oversized to deliver the high current peaks requirement for high power applications. Furthermore, their performances and lifetime are dramatically impacted by both low (below -30°C) and high temperatures (higher than 60°C).

Electrochemical Double Layer Capacitors, also called supercapacitors, enable to deliver very high power density (15 kW/kg) with lower stored energy than that of batteries (5 Wh/kg). Due to the very high reversibility of their chemistry, they possess a very long lifetime (sustaining more than 1,000,000 charge/discharge cycles).

IONIC LIQUIDS AS SAFER SUPERCAPACITOR ELECTROLYTES

Owing to its wide potential range, acetonitrile is the most commonly used solvent in supercapacitors; nevertheless this solvent has demonstrated a safety weakness as it is toxic, flammable and explosive at high temperature. Acetonitrile forms very toxic compounds, such as hydrogen cyanide, upon combustion. The use of acetonitrile as a solvent has thus been banned in Japan [1].

In this context, Hutchinson has developed a safer innovative supercapacitor for energy storage solutions. Contrarily to the common supercapacitor, SafeCap cells use an ionic liquid electrolyte (non-toxic, non-flammable). Furthermore, ionic liquids have extremely low vapor pressure and remain chemically stable over a very wide temperature range.

ENERGY DENSITY IN THE WIDER TEMPERATURE RANGE: AN OPTIMIZED TRADE-OFF BETWEEN CARBON POROSITY, ELECTROLYTE PROPERTIES AND CELL DESIGN

The energy density of a supercapacitor (E in Wh/kg) is determined both by the gravimetric capacitance of the active material used (C in F/g_{carbon}) and the nominal potential of the cell (U_{nom} in V), but also the total mass of the system, which can be accounted for by the design factor (Fd).

$$E = \frac{1}{2 * 4 * 3.6} CV^2 / Fd$$

Nominal potential is limited below 3 V when using organic solvents, such as acetonitrile or propylene carbonate, while ionic liquids have demonstrated cyclability above 3.2 V (figure 1).

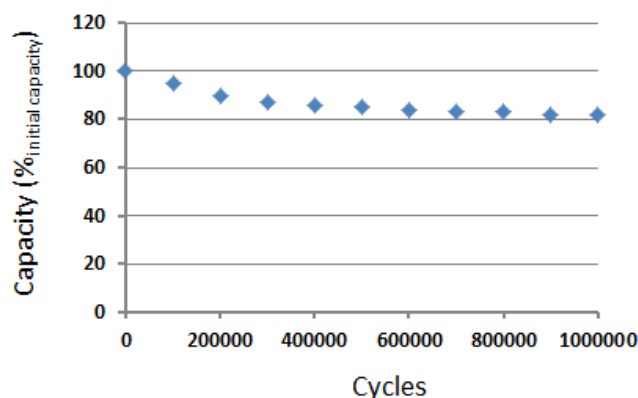


Fig 1. Variation of capacity of an ionic liquid pouch cell cycled at 3.2 V

The gravimetric capacitance of porous carbons has shown to be very similar when using organic solvent or ionic liquids. This capacitance can be enhanced by matching the porous texture of the carbon to the size of the ions composing the electrolyte [2]. Decreasing the size of the pores can also considerably decrease the design factor. Indeed, the lower the porous volume of the carbon, the lower the amount of electrolyte used, therefore the lower the design factor. Hutchinson has accumulated considerable experience in the synthesis of its own activated carbon and the ability to tailor its porous texture.

However, narrowing the diameter of the pores can also be detrimental to the wettability of the electrode by the electrolyte as well as to the mobility of the ions in the pores. In order to maximize the improvement in capacitance and maintain it at high power loads, surface treatment of the carbon is mandatory. Again this treatment depends on the electrolyte used. Hutchinson has developed different carbon surface treatments, optimized for electrolytes ranging from aqueous to ionic liquids.

The thickness of the electrodes has a considerable impact on the energy and power density of the cells. The thicker the active material coating on the electrode, the lower the relative weight of the current collector on the total system's weight (thus the higher the energy and power density at the cell level). However, a thicker coating will also lead to a higher internal resistance and thus decrease the power density of the cell. To reach high energy density, while maintaining low internal resistances, Hutchinson has optimized the coating formulation but also its adhesion to the current collector by developing primary coatings.

The electrolyte determines the temperature range on which the supercapacitor can be used. Acetonitrile-based electrolytes allow high ionic conductivity over low and medium temperatures (from -30°C to 60°C). However, above 60°C , ageing of the system is considerably accelerated, and acetonitrile boils at 82°C . Therefore, high temperature range is inaccessible to acetonitrile-based systems. Through electrolyte formulation, ionic liquids can offer conductivity at low temperatures and safe working behavior at very high temperature, above 100°C .

SPACE APPLICATIONS

Supercapacitors are interesting solutions for applications such as hybridization of batteries or very high power demanding applications. Using supercapacitors in parallel with batteries allows decreasing the amount and duration of power loads on the batteries, and extends thus the lifetime of the whole energy storage system. Furthermore, since supercapacitors possess very high specific power, the whole size of the hybrid energy storage system can also be decreased. The very high cyclability of supercapacitors is a considerable advantage for such applications in satellites with very long expected lifetime. Considering launchers, supercapacitors are promising solutions for electromechanical thrust vector actuation systems and pyrotechnics systems which are requiring very power. In that case, the high specific power of supercapacitors will allow decreasing the weight of the energy storage system while improving its reliability. Indeed, supercapacitors are able to sustain such high power without any loss in performance, and are not as sensitive to heat generation as lithium-ion batteries.

For these applications, ionic liquids supercapacitors are particularly suitable owing to their higher energy density ($> 10 \text{ Wh/kg}$), together with the intrinsic high power density of supercapacitors, which are both maintained over a large temperature range, from -40°C to 100°C . Their chemical inertness, non-flammability, complete insensitivity to heat, and non-volatility, even under very low pressure, are considerable advantages in terms of reliability and safety, all the more regarding the extreme environmental conditions encountered in space applications.

Furthermore, the requirements for both applications cited are completely different, and optimized systems can be proposed for each of them. This can only be done by adapting simultaneously each sub-component of the supercapacitor (electrolyte formulation, carbon, electrodes formulation, cell design), to reach the optimal trade-off.

REFERENCES

[1] Misao Shiba, JCR-link Co, Ltd. Jun 4, 2012

[2] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P. L. Taberna, Anomalous Increase in Carbon Capacitance at Pore Sizes Less Than 1 Nanometer, *Science*, Vol. 313, pp. 1760-1762, 2006