

New Approaches to Increase Ultracapacitor Energy, Power and Efficiency

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Abstract- New approaches aimed at increasing the ultracapacitor (UC) energy and power densities are described and discussed. An increase in energy has been achieved due to so-called parallel hybridization of the electrode/electrolyte system, wherein both positive and negative electrodes contain nanoporous carbon and Li-intercalated metal oxides as balanced mixtures. The organic electrolyte is also compatible with both UC and battery electrode components. This technology enables to reach the specific energy of about 35 Wh/kg for a packaged cell that can be charged within 2-3 minutes. Yet another approach based on studying the electrolyte in-pore mobility in positive and negative electrodes enables to substantially increase the UC power output and efficiency.

Keywords- hybrid ultracapacitor, energy density, in-pore mobility, efficiency

I. INTRODUCTION

Ultracapacitor (UC) is one of the names used for an electrochemical capacitor that can store large energy density, as compared with other types of capacitors, resulting from charge separation in the electrical double layer at the electrode electrolyte interface [1-3]. Large electrostatic capacitance and, hence, energy is due to the choice of nanostructured carbon materials (nanoporous activated carbon, carbon nanotubes, graphene, etc.) that are typically used in UC electrodes, the materials having a huge surface area of the order of 1000... 2000 m²/g.

UC devices have an obvious advantage in high power applications, in particular, if very fast and repeatable charge/discharge events are critical like, e.g., in regenerative braking or stop & start systems in hybrid cars, in pitch-controlled wind turbines, in portable spot or stud welding machines, etc. For many of those applications the UC internal resistance should further be reduced from the currently available level in order to maximize their efficiency and power output, and thus to give a chance to reduce the size (hence, also cost) of the entire solution. Besides, an increase in the energy density from currently available level of 5-7 Wh/kg for pure UC or 10-14 Wh/kg for hybrid devices could obviously expand their application areas but still remains a good challenge.

Our approach aimed at a substantial increase in the UC power density and efficiency is based on the fact that the

electrolyte mobility in nanopores of various carbons can differ significantly. Besides, the electrochemical stability of electrolytes in positive or negative potential range depends on the carbon used to fabricate the corresponding electrode. Bearing this in mind, special techniques were developed to select the most appropriate positive and negative electrode materials, which can typically be different [4]. As a result, the UC devices of superior power capability (up to 100 kW/kg) and high efficiency were developed with their performance being verified in several recognized laboratories [5, 6, 7] and also by some automobile producers.

Yet another approach was used [8, 9] to substantially increase the specific energy of UC devices while maintaining their high power output, efficiency and quick charge. To achieve such a challenging goal, both positive and negative electrodes were hybridized, namely, comprised mixtures of nanoporous carbon and lithiated metal oxide powders with thoroughly matched operating potential ranges and energy/power ratio of the mixture components. This design, which can be called a parallel Li-ion capacitor (//LIC) or otherwise a nanocarbon-enhanced Li-ion battery, does provide the energy density of 30-40 Wh/kg with high power output and charging time within 2-3 min.

II. UC POWER DENSITY AND EFFICIENCY

High power output and high efficiency, along with the long cycle life, safe operation and wide operating temperature range, are the key advantages of UC devices today that open the doors to more and more market niches. Since both power and efficiency values increase with decreasing the UC internal resistance, R_{in} , all the contributions to the R_{in} value should thoroughly be analyzed and minimized. A simple equivalent circuit to describe the contributions can be presented by Eq. (1) and illustrated at a UC schematic cross section in Fig. 1.

$$R_{in} = R_1 + R_2 + R_3 + R_4 + R_5, \quad (1)$$

where R_1 is the ohmic resistance of current collectors and current leads, R_2 is the contact resistance at the "current collector – active electrode layer" interface, R_3 is the ohmic resistance of the active electrode layer, R_4 is the electrolyte resistance in nanopores of the active electrode layer, and R_5 is

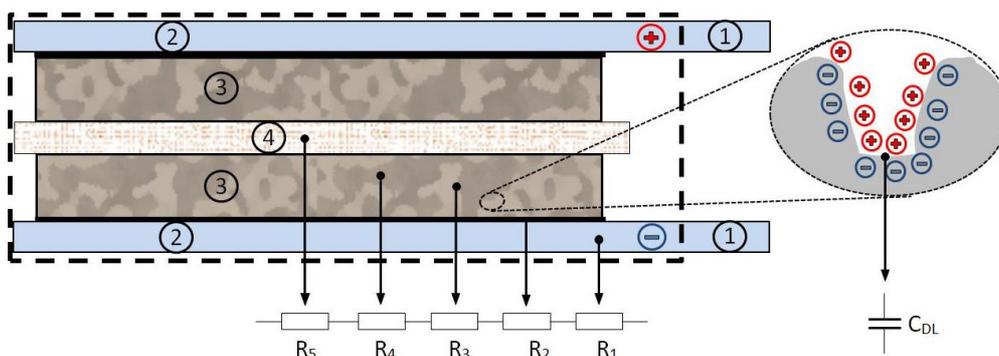


Fig. 1. Schematic cross section of a UC cell: 1 – current leads; 2 – current collectors; 3 – active electrode layers; 4 – porous insulating film (separator). In the enlarged zone on the right, the formation of a double electric layer with a capacitance C_{DL} in a separate slit-like nanopore is illustrated. The zones related with resistances $R_1 \dots R_5$, as in Eq. 1 are also indicated.

the electrolyte resistance in macropores of the active electrode layer and separator. The contributions of these components to the total R_{in} value are obviously unequal, so consider them one by one.

The R_1 value can easily be minimized by varying the length and cross section of aluminum current collectors and leads/terminals, and this resistance is, no doubt, the lowest and in many cases negligible term in the right part of Eq. 1. The contact resistance, R_2 , and ohmic resistance of the active electrode layer, R_3 , can be measured with the use of 4-wire method according to the procedure [10], and it was found that R_3 value does not typically contribute more that 5% to the total R_{in} value and, if it is higher for some types of nanoporous carbons, it can easily be reduced to this level by adding the carbon black to the electrode composition. It is also worth noting, that if the nano-sized spherical carbon black is used (e.g., SuperP-Li, Timcal, grain size of about 40 nm), the carbon black particles fill in the voids among the much larger nanoporous carbon grains (typically of a few micron size) and thus do not practically reduce the electrode volumetric capacitance. On the other hand, it has been found [10] that with plain Al foil as a current collector, the contact resistance, R_2 , can contribute significantly to UC internal resistance due to the native insulating oxide layer on the Al surface. In order to reduce the contact resistance, the area of contact between the current collector and active electrode layer can substantially be increased by etching the Al foil surface, and there are many companies throughout the world producing such etched foils. Yet another method to reduce the R_2 value was offered in [10, 11], the method providing the local fusion of conductive graphite particles into the plain Al foil surface with the use of electric spark treatment. Both methods - local fusion of conductive particles and etching the current collector surface - result in significant decrease in the R_2 value that does not typically exceed 1-2% of the total R_{in} value.

The electrolyte conductivity in the electrode and separator macro-pores is practically the same as in bulk solution, and therefore, the electrolyte resistance R_5 value can be evaluated

from the known electrolyte conductivity and electrode/separator thickness. Our estimations show that R_5 value can contribute approximately 20% to the total R_{in} value. Thus, the sum of four terms in Eq. 1, namely, $R_1 + R_2 + R_3 + R_5$ contributes about 30% only to the UC internal resistance, while the electrolyte resistance in electrode nanopores, R_4 , obviously, dominates and gives approximately 70%. Therefore, one of key objectives of our study was to measure the electrolyte in-pore mobility in various carbons in order to select the most appropriate materials for positive and negative UC electrodes.

As is well known [12], the ion mobility and, correspondingly, the electrolyte conductivity are proportional to the diffusion coefficients of ions. A significant reduction in electrolyte diffusion coefficients inside carbon nanopores can be accounted for by at least two major factors. Kalugin et al. [13] with the use of molecular dynamic calculations have shown that the spatial confinement in carbon nanotubes can result in slow diffusion of solvent molecules. Electrostatic and/or Van-der-Waals interactions between the electrolyte species and conductive pore walls can be yet another factor, though these interactions can hardly be evaluated quantitatively because of complexity of the system. On the other hand, two experimental methods have recently been developed [4] that enable to estimate and compare the electrolyte in-pore mobility in various nanoporous carbons in order to best match the nanoporous electrode and organic electrolyte.

The first method is actually a version of the well known technique based on pulsed field-gradient NMR spectroscopy [14], which is widely used for measuring the diffusion coefficients in liquids. In [4] similar measurements were carried out using the nanoporous carbon powders impregnated with typical EDLC electrolytes. Of course, the diffusion coefficients thus obtained reflect some averaged (effective) values due to rather wide distribution of pore size. So, to verify this result, yet another method was used [4], namely, cyclic voltammetry measurements if a porous rotating disc electrode (PRDE) was used as a working electrode. Obviously, in this case the compounds capable to participate in redox

transformations should be involved [4] followed by plotting the diffusion current value versus the electrode rotation rate as in [15]. Both methods give similar results, and indeed, they demonstrate a significant slowdown of electrolyte diffusion in carbon nanopores. Besides, a good correlation of effective diffusion coefficients for cations and anions of organic electrolytes impregnating different nanoporous carbons with the R_m value for UC devices containing the corresponding electrode materials was observed [4]. Further this approach was used to select the most appropriate electrode materials for UC with extremely low internal resistance and RC constant value of the order of 0.1 - 0.2 s [16], as was also confirmed by comparative tests in JME [6] and Wayne State University [7]. Some of the test results [7] are listed in Table 1. Here it is worth noting that yet another advantage that results from very low internal resistance and can also be seen in Table 1 is the high efficiency of Yunasko UC cells. In our opinion, it is very important since during a quick discharge the heat generation inside the Yunasko UC cell is about 1-2% of the stored energy only and three-four times less than for best competing cells. This can be of particular importance if a number of repeatable charge-discharge events are needed, and, obviously, lower heat generation implies lower requirements to a cooling system and improved safety.

Thus, provided that carbon materials for positive and negative electrodes are chosen in accordance with the electrolyte mobility in their nanoporous structure, the internal resistance of UC cells can be reduced substantially, and even further reduction in the R_m value is possible, in our opinion, by a factor of approximately two.

TABLE I

INTERNAL RESISTANCE AND EFFICIENCY AT CONSTANT POWER (CP) DISCHARGE WITHIN 10 OR 5 SECONDS FOR TWO 1200F UC CELLS [7]

UC cell 1200F	Internal resistance, mΩ	Efficiency @ CP 10 s discharge, %	Efficiency @ CP 5 s discharge, %
Best-on-market	0.40	96.7	93.9
Yunasko	0.09	99.2	98.3

III. UC ENERGY DENSITY: HOW IT CAN BE INCREASED SIGNIFICANTLY

As is known, the energy density of about 7 Wh/kg as reached today [17] or further projected for carbon-carbon UC devices is still low for many applications, and some new approaches should be pursued to increase it significantly. As one of those approaches, the hybridization of the electrochemical system can be implemented, the system thus comprising the nano-structured carbons and some battery-type materials – see, e.g., in [2].

The first hybrid devices were invented by ESMA, Russia in mid-1990s [18], the devices comprising a positive electrode (nickel oxide) from alkaline battery technology and negative electrode (nanoporous carbon) from UC technology. Similar hybridization but “UC and lead-acid battery” has been realized by Axion Power in Canada [19]. A more recent and promising technology is aimed at hybridizing UC and Li-ion battery [20], and a number of various modifications is known today by the general name of LIC (Li-ion capacitor) – e.g., see [21, 22]. One of the best commercial LIC devices is currently produced by JM Energy by the trade name of ULTIMO [23].

All types of hybridization mentioned above provide an increase in specific energy up to 10-15 Wh/kg, and in many cases at the expense of much lower power density and efficiency as compared with typical UC. Such a modest improvement in the UC performance can be accounted for the following reason. All these hybrid technologies combine a high-energy electrode (that of battery type) with a low-energy one (that of UC type) connected in series, and in such a serial combination the low-energy electrode obviously limits the total energy. To avoid this limitation, a different design has recently been developed [8, 9] that can be called a parallel combination of Li-ion and UC electrode components. This technology is denoted as //LIC below and can be presented in more detail as follows:

- Electrodes, both positive and negative, are fabricated with the use of mixtures of nanoporous carbon powder and lithiated metal oxides/phosphates as active ingredients to meet the chemistry requirements of both UC and Li-ion battery technologies. As an example, the negative electrode comprises lithium titanate (LTO), while the positive one comprises lithiated manganese oxide (LMO) and lithium iron phosphate (LFP), both electrodes also containing Kuraray YP50F carbon powder.
- These active electrode ingredients should thoroughly be adjusted by their mass and potential range in order to best match their electrochemical characteristics and provide smooth charge-discharge processes.
- Beside the active electrode ingredients, some kind of binder and conductive particles, e.g., polyvinylidene fluoride (PVdF) and carbon black should be added followed by fabricating the corresponding electrodes.
- From all the organic electrolytes known in Li-ion and UC technologies, acetonitrile is preferred as a solvent to provide the high conductivity and wide operating temperature range. The salts in the electrolyte typically contain both Li^+ and R_4N^+ ions known in both technologies.

Fig. 2-1 illustrates typical charge-discharge curves of thus fabricated //LIC cells packaged in a laminated pouch-type shell (total mass of 85 g). For comparison purposes the same figure also illustrates the charge-discharge curves for a UC cell of the same mass of 85 g (see Fig. 2-2). Both curves were obtained

under the same 20A constant current (CC) conditions. As can be seen from Fig. 2-1, the //LIC charge-discharge curves include an obvious plateau, which is not typical for UC devices, and the curve looks like that for batteries at high C-rates. The specific energy stored in those //LIC cells is about 35 Wh/kg, which is notably higher than that for UC cells or for currently known hybrid technologies mentioned above. It is also worth noting that after charging the //LIC device with the current of 20 A (or ca. 15C-rate), it can be discharged with currents up to 100 A (or ca. 77C-rate) or even higher still demonstrating a smooth slope on a discharge curve. So, as an alternative, this hybrid technology can be called as a “nanoporous carbon enhanced Li-ion battery”.

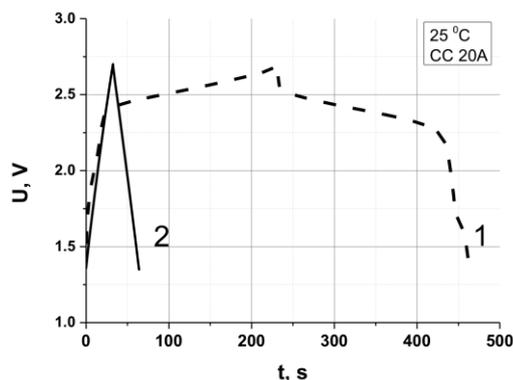


Fig. 2. Charge-discharge curves of a //LIC cell (1) and a UC cell (2) under 20A constant current (CC) conditions at 25 °C; both cells have the same mass of 85 g.

Performance of //LIC prototypes is also illustrated in Fig. 3, wherein the Ragone plots for three different technologies are compared. The upper curve (3) for high power Li-ion batteries illustrates the values presented in a recent comprehensive review [24] and averaged by us. As can be seen from Fig. 3, //LIC devices give a chance to substantially increase the energy density as compared with UC while their power output exceeds that of Li-ion batteries significantly if the efficiency is taken into account.

In Fig. 3 the discharge time for these three different technologies is also shown to demonstrate that high power Li-ion batteries are effective if the discharge time is about 10 min or more. On the other hand, UC devices can most efficiently be employed if the high power pulses of short duration (from fractions of a second to ca. 20 s) are needed. The niche between the two well-known technologies can be filled with //LIC that can most effectively be used between ca. 20 s and 10 min. It is worth noting that //LIC can fully be charged within ca. 3 min, which is much faster than in battery technologies. The cycle life of //LIC devices is also intermediate between Li-ion battery and UC and reaches 30K deep charge-discharge cycles.

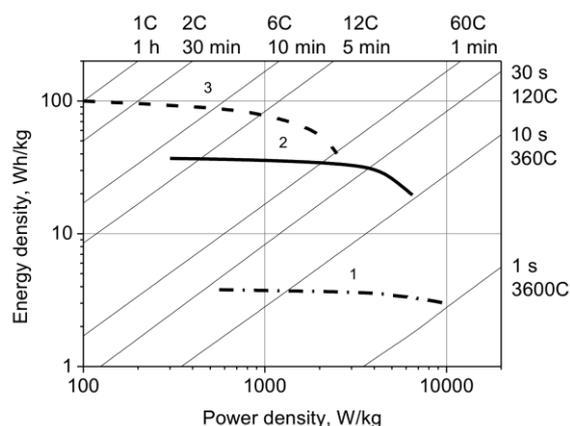


Fig. 3. Ragone plots for high power UC (1), //LIC hybrid device (2), and high power Li-ion battery (3).

IV. CONCLUSIONS

1. The ultracapacitor (UC) power output and efficiency are due to its low internal resistance, which in its turn is mostly determined by the electrolyte mobility in carbon electrode nanopores. Since the in-pore mobility of anions and cations can differ significantly, different nano-structured carbons should preferably be chosen for UC positive and negative electrodes.
2. A proprietary technology with both positive and negative electrodes being hybridized (//LIC) gives a chance to increase the UC energy density up to 30-40 Wh/kg while maintaining the power output typical for UC, namely, 3-4 kW/kg at the efficiency above 80%. The electrode components borrowed from UC and Li-ion technologies to fabricate hybrid //LIC electrodes should thoroughly be balanced by their energy stored and charge-discharge potential range.
3. UC devices can most efficiently be employed if the high power pulses of short duration (from fractions of a second to ca. 20 seconds) are needed, while longer pulses (from 20 s to 10 min) can be covered by //LIC devices. The latter can also be fully charged within ca. 3 minutes and can withstand about 30K deep charge-discharge cycles.

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