Electrochemical Double Layer Capacitors: Challenges and Solutions

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Abstract- Some new approaches aimed at increasing the electrochemical double layer capacitor (EDLC) energy and power densities have been described and discussed. As shown, a significant increase in energy can be achieved due to so-called parallel hybridization of the electrode/electrolyte system if both positive and negative electrodes contain nanoporous carbon and lithiated metal oxides as balanced mixtures. The organic electrolyte in such hybrids is also compatible with both EDLC and battery electrode components. This type of hybridization enables to reach the specific energy of 30… 40 Wh/kg for a packaged cell. It has also been shown how the study of electrolyte in-pore mobility can help to select the best nanoporous carbons for positive and negative electrodes and thus to substantially enhance the EDLC power output and efficiency.

Keywords- Hybrid Capacitor, Electrolyte in-Pore Mobility, High Efficiency

I. INTRODUCTION

As a common design [1-3] the electrochemical double layer capacitor (EDLC), also known by names of ultracapacitor or supercapacitor, comprises two nanoporous carbon electrodes interleaved with an insulating but porous film and soaked with organic electrolyte. In most cases the electrodes of ca. 0.1 mm thick are fabricated of the same carbon material, though, in some special cases the electrode material and/or thickness can differ to best match the capacitance of positive and negative electrodes. EDLC 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 portable spot or stud welding machines, etc. For many of those applications, in particular for automotive ones, the EDLC 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 minimize the cooling requirements and the size (hence, also cost) of the entire solution involving the EDLC. Besides, an increase in the EDLC energy density could obviously expand their application areas but still remains a good challenge.

Our approach to the EDLC design aimed at a substantial increase in its power density and efficiency is based on the fact that the diffusion coefficients (or mobility) of positive or negative electrolyte ions are different in nanopores of various carbons. Besides, the electrochemical stability of electrolytes in positive or negative potential range depends on the electrode carbon material. Bearing this in mind, special pulsed gradient NMR and electrochemical techniques were developed to measure the mobility of electrolyte ions in nanopores of various carbons as well as the ranges of their electrochemical stability. This gave us a chance to select the most appropriate positive and negative electrode materials, which can typically be different [4]. As a result, the EDLC devices of superior power capability (up to 100 kW/kg) and high efficiency were developed with their performance being verified in several recognized laboratories [5-7] and also by some automobile producers.

Yet another approach was used [8, 9] to substantially increase the specific energy of EDLC devices while maintaining their high specific power and efficiency. To achieve this, both positive and negative electrodes were hybridized, namely, were fabricated of mixtures of nanoporous carbon and lithiated metal oxide powders with thoroughly matched operating potential ranges and energy/power ratio of the mixture components. Such a design, which can be called a parallel Li-ion capacitor (//LIC) or otherwise a nano-carbon-enhanced Li-ion battery, does provide the energy density of 30… 40 Wh/kg, i.e., the energy density of Pb-acid battery with the high power output, fast charge-discharge and high efficiency typical for EDLC devices.

II. PROJECTED ENERGY AND POWER LIMITS OF EDLC

The energy (in Joules) stored in the EDLC is proportional to its voltage squared and capacitance:

$$E = \frac{1}{2} C U^2 \tag{1}$$

This shows two ways to increase the energy: due to an increase in capacitance, C, and/or due to an increase in working voltage, U.

Since the capacitance value is known to be proportional to the electrode surface area, many efforts aimed at increasing the surface of carbon materials, which can potentially be used in the EDLC electrode fabrication, have been made [2]. As a

theoretical limit, a single graphene sheet is normally considered with its surface area of 2630 m^2/g on both sides of the sheet [10]. However, to evaluate the upper capacitance limit, one should take into account that only half of this value is available to take part in the electric double layer formation. This can be illustrated in Fig. 1, wherein two processes are compared: (a) double layer formation on both sides of a thick enough graphitic or amorphous carbon layer, and (b) double layer formation at a single graphene sheet.
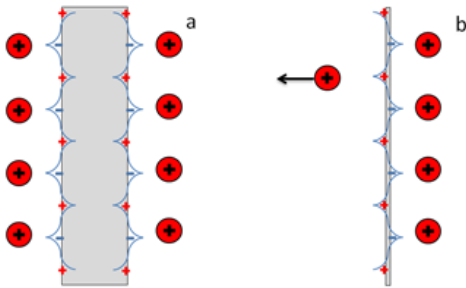

Figure 1. Schematic view of the electric double layer formation at the surface of thick carbon layer (a), or at the graphene sheet surface (b).

In (a) case there is a chance for adsorption of electrolyte ions on both sides of a carbon layer or in close vicinity from each other since a thick graphite/carbon layer can provide enough charges to form the corresponding image forces that can even eliminate the electrostatic repulsion of ions inside nanopores [11]. In (b) case a half of the total surface area can form the image charge only. Obviously, similar picture would take place at the counter electrode with electrolyte ions of the opposite (negative) sign. This model agrees in general with experimental results and conclusions made by Kötz et al. [12] who suggested the capacitance saturation might occur in case of very thin pore walls. So, the maximum used surface area in graphene case can hardly exceed 1300 m^2/g. This results in the maximum capacitance of the order of 260 F/g, if a reliable value [1,13,14] of electric double layer capacitance of ca. 20 µF/cm^2 has been chosen for evaluations.

For nanoporous (amorphous) carbons a reliable value [14] of electric double layer capacitance is about 10 µF/cm^2. Since some of those carbons can demonstrate the surface area of up to 2000 m^2/g, the capacitance can reach 200 F/g per carbon mass in one electrode provided that there is no capacitance saturation [12]. Now, it should be noted that any EDLC comprises two electrodes (negative and positive) connected in series through the electrolyte. If the two electrodes have approximately the same mass and capacitance, the system of these two double layer capacitors would have the specific capacitance (per carbon mass in both electrodes) of 65 F/g in case of graphene or 50 F/g in case of activated carbon. To be more precise, if we take into account that each electrode contains about 10% of a binder (and in some cases also a conductive additive), the maximum values become ca. 58 F/g in case of graphene or 45 F/g in case of activated carbon.

At this stage it is worth noting that gravimetric capacitance is less important for the EDLC performance than volumetric one since the electrodes typically contribute about 50% to the volume of the EDLC cell but about 20% only to its mass. So, if we take into account typical densities of ca. 0.6 g/cc for electrodes fabricated of nanoporous activated carbons and ca. 0.2 g/cc for electrodes fabricated of graphene, we can see a significant volumetric advantage of EDLC comprising activated carbon electrodes with their maximum value of ca. 27 F/cc as compared with graphene-based electrodes with their maximum value of ca. 12 F/cc.

Regarding the working voltage, 2.7V is the most typical value, though some EDLC producers demonstrate 2.85 or 3.0V today with organic electrolytes and activated carbon electrodes. In near future the value of 3.5V looks like a good challenge. If the value of 3.0V is chosen, the specific energy according to (1) and capacitance evaluations made above can reach 200 kJ/kg or 120 kJ/liter per unit mass or volume of both electrodes fabricated of nanoporous carbon. If the electrode contributions to the total EDLC mass or volume are taken into account, the maximum specific energy values, which can be anticipated for a packaged EDLC cell with the working voltage of 3.0V are 40 kJ/kg (12 Wh/kg) or 60 kJ/liter (17 Wh/liter). An increase in voltage up to 3.5V would result in higher values by a factor of 1.36, i.e., 16 Wh/kg and 23 Wh/liter can be considered as a practical limit for 3.5V EDLC energy density. So, in the next section it will be discussed how close one can approach to this limit.

As regards the EDLC power output, it is also proportional to voltage U squared and inversely proportional to the EDLC internal resistance R_{in}:

$$P = U^2/4R_{in} \qquad (2)$$

The working voltage of EDLC devices with organic electrolytes, as mentioned above, varies in a rather narrow range between 2.7V and 3.0V (with a challenging prospect to reach 3.5V), and therefore, this value even being squared can change the power by a factor of 2 at most. On the other hand, from our practice, a reduction in the EDLC internal resistance can enhance its power output by an order of magnitude or even more. Besides, low internal resistance also implies the low voltage drop ($\Delta U = I R_{in}$) when the current I starts flowing through the circuit, and high efficiency, η, which can be presented as follows:

$$\eta = \frac{E_{out}}{E_{in}} = \frac{R_{load}}{R_{load} + R_{in}} \qquad (3)$$

where E_{out} is the energy delivered to the load, E_{in} is the total energy stored in the EDLC, and R_{Load} is the load resistance.

Since all these characteristics are very important for successful and effective EDLC application, various contributions to the internal resistance should thoroughly be analyzed. The following simple equivalent circuit can describe R_{in} as the sum of a few resistors connected in series:

$$R_{in} = R_{Al} + R_{Al\text{-}C} + R_{C} + R_{el-macro} + R_{el-nano} \qquad (4)$$

In this equation R_{Al} is the resistance of current collectors and current leads, which are typically made of Al, $R_{Al\text{-}C}$ is the contact resistance between the Al collector surface and active electrode layer, R_{C} is the ohmic resistance of nanoporous

carbon electrodes, $R_{el-macro}$ is the electrolyte resistance in macro-pores (and this is approximately the same as in bulk solution), and $R_{el-nano}$ is the electrolyte resistance in nanopores of carbon electrodes. So, the practical low limit of R_{in} value might be reached if the sum of last four resistances in (4) becomes close to the R_{Al} value as the lowest in this series. It is a good challenge, no doubt, and below it will be shown how close one can approach to this goal.

III. EDLC ENERGY: HOW IT CAN BE INCREASED SIGNIFICANTLY

In Table 1 some recent achievements in high energy EDLC technology are listed. For this comparison we have selected the relatively large packaged cells of 3000F - 4500F produced by Maxwell Technologies [15], as the EDLC market leader, and by two start-ups: Skeleton Technologies and Yunasko [www.skeletontech.com & www.yunasko.com].

TABLE I.   EDLC ENERGY STORED

Company, cell type, capacitance, F	Rated voltage, V	Energy density, Wh/kg	Energy density, Wh/L
Maxwell Technologies (USA), DuraBlue, 3400 - 3550	2.85	$7.4^* – 7.7^*$	~10
Skeleton Technologies (Estonia), SPE3500 - SCA4500	2.85	9.3 – 9.6	13 – 14
Yunasko (Ukraine), YEDLC 3000 - 3600	2.7	6.3* – 7.5*	8.5 – 10

*Rated and maximum values

This Table reflects the current status of EDLC technology, and if the voltage level of 3.0V is reached (of note, all three listed companies claim that they already manufacture such cells) Skeleton Technologies would be very close to the targeted value of 12 Wh/kg and 17 Wh/L estimated above. For two other companies the energy level would be still lower by 20-30%, though it can be accounted for the commercially available carbons of relatively low cost (ca.\$20/kg) used in both technologies. The carbide derived carbon (also named as curved graphene) used in Skeleton Technology electrodes demonstrates larger specific capacitance but is obviously much more expensive.

As can be seen, the energy level being already reached or further projected for carbon-carbon EDLC devices is still low for many applications, and some new approaches should be employed to increase it significantly. As one of those approaches, the hybridization of the electrochemical system can be realized, the system thus comprising the nano-sized carbons and some battery-type materials – e.g., see [16].

Hybrid devices were first developed by ESMA and ELTON [17], the devices comprising a negative electrode manufactured from nanoporous carbon material, a positive electrode made of nickel hydroxide and an aqueous alkaline electrolyte. Thus, the technology looks like a hybrid between EDLC and alkaline (or nickel-metal-hydride) battery.

Similar hybrid devices have recently been developed by Axion Power [18] by name of lead-acid-carbon batteries, wherein a positive electrode (lead dioxide) and electrolyte have been borrowed from lead-acid technology and negative electrode (nanoporous carbon) – from EDLC technology.

Another promising methodology has recently appeared due to hybridizing the EDLC with Li-ion battery – e.g., see [16, 19]. This type of devices, usually called as LIC (Lithium-ion capacitor), comprises a negative electrode and Li-salt containing electrolyte typical for Li-ion battery technology. As the negative (intercalating) electrode graphite or lithium-titanate (LTO) can be used. The latter was first developed by Amatucci - see, e.g., a comprehensive description [20]. The next step of this technology was recently offered by Naoi et al. [21] who developed the composite anode materials comprising the nano-particles of LTO, which are dispersed on carbon nanofibers. Positive electrode in all those LIC's is fabricated from a nanostructured carbon material that forms an electric double layer on its surface as in the EDLC technology but not involving the intercalation or de-intercalation processes. One of the best known commercial LIC devices is currently produced by JM Energy [22] by the trade name of ULTIMO.

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 if compared with typical EDLC. Such a modest improvement in the EDLC 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 (EDLC 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 [9, 23] that can be called a parallel combination of Li-ion and EDLC 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 from mixtures of nanoporous carbon powders and lithiated metal oxides/phosphates to meet the chemistry requirements of both EDLC and Li-ion battery technologies. As an example, the negative electrode comprises LTO, and positive one comprises lithiated manganese oxide both being mixed with Kuraray YP50F carbon, some kind of binder and conductive additive like carbon black followed by fabricating the corresponding electrodes.

- Electrode ingredients should thoroughly be adjusted by their mass and potential range in order to best match their electrochemical characteristics thus providing smooth charge-discharge processes.

- From all the organic electrolytes known in Li-ion and EDLC technologies, acetonitrile is preferred as a solvent to provide the high conductivity and wide operating temperature range. The salt(s) dissolved in the electrolyte must obviously contain Li-ions to support the intercalation processes and optionally alkylammonium-ions typically used in EDLC technology.

Fig. 2 illustrates typical charge-discharge curves of thus fabricated //LIC cells packaged in a laminated pouch-type shell (total mass of about 80 g, capacity of 1.3 Ah).
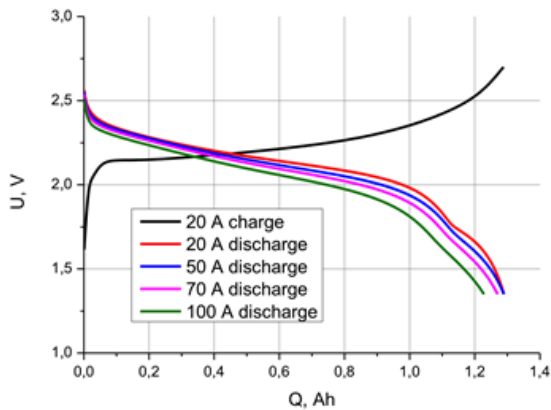

Figure 2. Charge-discharge curves of a //LIC prototype of 1.3 Ah

As can be seen, after charging the //LIC device with the current of 20 A (or ca. 15 C rate), it can be discharged with currents up to 100 A (or ca. 77 C rate) or even higher. It is worth noting that the charge-discharge curves include an obvious plateau, which is not typical for EDLC but rather for batteries at high C rates. The specific energy stored in those //LIC cells is about 35 Wh/kg, which is notably higher than for other hybrid technologies mentioned above.

Performance of //LIC prototypes is also illustrated in Fig. 3, wherein the Ragone plots for three various technologies are compared. The upper curve 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 high power EDLC devices (see in the next section) while their power output exceeds that of Li-ion batteries if the efficiency is taken into account.
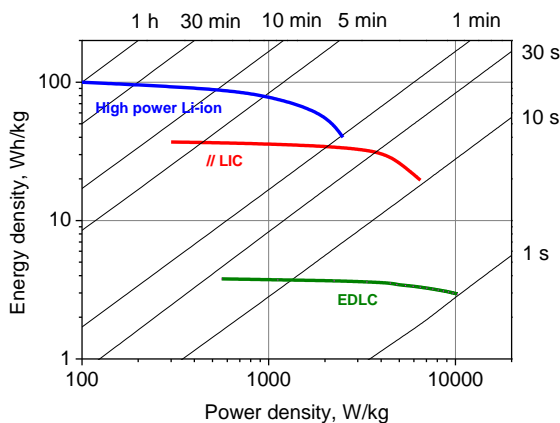

Figure 3. Ragone plots for three various technologies: high power Li-ion, //LIC, EDLC

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, Fig. 3 and some experimental data [25] on portable welding machines with the use of EDLC power supply units show that EDLC can most effectively be employed if the high power pulses of short duration (from milliseconds to 30 s) are needed. The niche between the two well-known technologies can be filled with //LIC that can most effectively be used between ca. 30 s and 10 min. It should also be noted that //LIC can fully be charged within ca. 2… 3 min, which is much faster than in battery technologies.

IV. EDLC POWER CAPABILITY AND EFFICIENCY

High power output and high efficiency, along with the long cycle life and wide operating temperature range, are the key advantages of EDLC devices that can open the door to more market niches. Since both power and efficiency values increase with a decrease in the EDLC internal resistance, R_{in} (see in (2) and (3)), all the contributions to the R_{in} value as presented in (4) should thoroughly be analyzed. Some possible ways to reduce the terms in the right part of (4) are considered below.

The R_{Al} contribution can easily be optimized 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 (4). So, let us see how the other terms can be minimized. Since electrodes in EDLC devices are normally fabricated flat, it is convenient to express the resistance values in $\Omega.cm^2$ per visible unit electrode area.

The contact resistance, R_{Al-C}, and ohmic resistance of carbon electrode, R_C, can be measured with the use of 4-wire method, if the electrode thickness and contacting foil are varied, e.g., replacing the Al foil by Pt one [26]. It was found that with plain Al foil the R_{Al-C} value can be about or even exceed 1 $\Omega.cm^2$ due to the native insulating oxide layer on the Al surface. However, this resistance can substantially be reduced as a result of local fusion of conductive particles (carbon black or graphite) into the Al current collector surface with the use of electric spark or laser beam technique [26]. Both methods result in local melting the Al collector surface and spot fusing the conductive particles onto the surface. This also results in breaking down the aluminum oxide layer and creating good electrical contact between the conductive particles and collector, the contact being reliable over the entire EDLC operation life.

Yet another and widely used method to reduce the contact resistance is a substantial increase in the contact area due to etching the Al foil surface, and there are many companies throughout the world producing such etched foils. Both local fusing the conductive particles and etching the current collector surface result in significant decrease in the R_{Al-C} value that does not typically exceed 0.01 $\Omega.cm^2$.

Now, the ohmic resistance of carbon electrode, R_C, does not typically exceed 0.05 $\Omega.cm^2$, and if it is higher with some 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, ~40 nm), the carbon black particles fill in the voids among the much larger (typically of a few micron size) nanoporous carbon grains and thus do not practically reduce the electrode volumetric capacitance.

The electrolyte resistance in the electrode and separator macro-pores, $R_{el-macro}$ can be evaluated from the electrolyte conductivity and electrode-separator thickness. Given the conductivity of the most widely used acetonitrile-based electrolytes of ~55 mS/cm and electrode thickness of ~0.1 mm, the $R_{el-macro}$ value can be estimated as ca. 0.2 $\Omega.cm^2$ or a bit more because of some tortuosity of the electrode porous system. Thus, the sum of three terms in (4), namely, $R_{Al-C} + R_C + R_{el-macro}$ is of the order of 0.3 $\Omega.cm^2$, while the value of total resistance, R_{in}, measured for the best EDLC cells available on the market is of the order of 1.0 $\Omega.cm^2$ or a bit higher. This clearly indicates that the electrolyte in-pore resistance, $R_{el-nano}$, dominates and gives the lion's share in series of resistances in (4). The electrolyte ion accumulation in the electrode nanopores was shown experimentally in a recent comprehensive study [27] with the use of in situ NMR and electrochemical quartz crystal microbalance measurements. The electrolyte ions were found to be absorbed in carbon nanopores in solvated or partly de-solvated state. As the cells are charged, the NMR signals referred to cations and anions absorbed in nanopores move to a stronger field, and the process can be accompanied by ion exchange or ion accumulation depending on the electrode potential [27]. However, in order to evaluate the electrolyte in-pore resistance, the mobility of ions in nanopores should also be measured and compared.

As is well known [28], 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 at least two major factors. Kalugin et al. [29] with the use of molecular dynamic calculations have shown that the spatial confinement in carbon nanotubes can result in slow diffusion of solvent (e.g., acetonitrile) molecules. Electrostatic and/or Wan-der-Walls 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 [30] based on pulsed field-gradient NMR spectroscopy, which is widely used for measuring the diffusion coefficients in liquids. In [4] similar measurements were carried out for 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 width and shape. So, to verify this result, yet another method was used [4], namely, cyclic voltammetry measurements with a porous rotating disc

electrode (PRDE) as a working one. Obviously, in this case the compounds capable to participate in redox transformations like, e.g. ferrocene, should be involved [4] followed by plotting the diffusion current value versus the electrode rotation rate as in [31]. 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 various nanoporous carbons with the R_{in} value for EDLC devices containing same electrode materials was found [4]. In our opinion, the low in-pore resistance can be obtained with carbons containing shallow slit-type pores to allow electrolyte ions to move in and out freely.

Thus, the nanoporous carbons providing the highest electrolyte mobility in positive and negative electrodes can be selected, and such an approach enabled to manufacture at the Yunasko Pilot plant (www.yunasko.com) the EDLC devices with extremely low internal resistance [4,6,7,32], R_{in}, resulting in RC-constant values of the order of 0.1… 0.2 s. Some of the results as obtained in comparative tests in Wayne State University [7] are presented in Figs. 4 and 5.
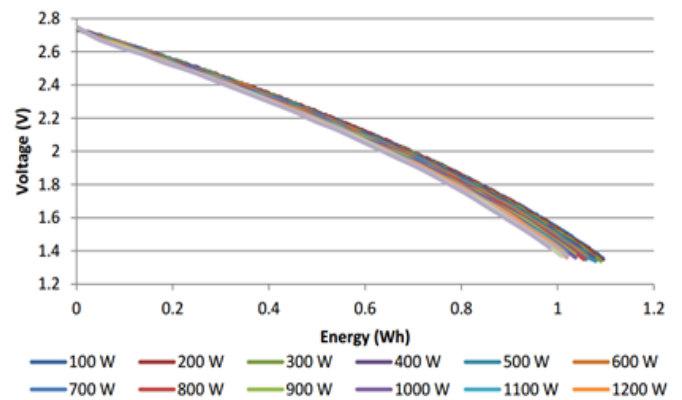

Figure 4. Constant power discharge of Yunasko 1200F/260g cell [7]
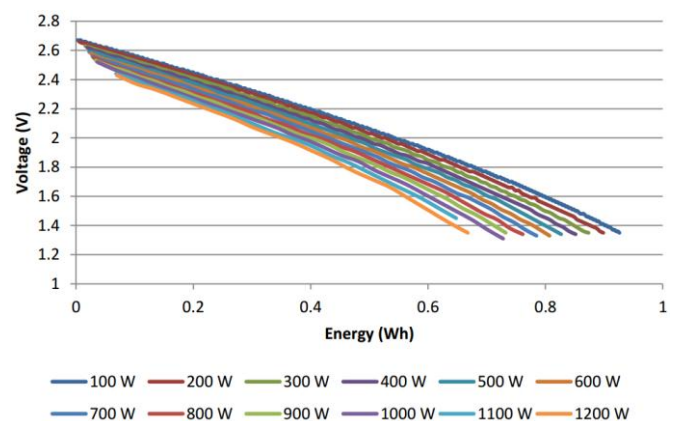

Figure 5. Constant power discharge of best-on-market 1200F/290g cell [7]

As can be seen from Fig. 4, the Yunasko EDLC cell demonstrates practically no voltage drop or energy decrease up to very high load. On the other hand, a similar best available on the market EDLC cell demonstrates an obvious voltage drop and energy decrease with an increase in load – see Fig. 5. No doubt, this substantial difference in the voltage drop and available energy results from the difference in cell resistance.

High efficiency is another advantage resulting from very low internal resistance. In our opinion, it is very important since during a quick discharge the heat generation inside the Yunasko EDLC 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 like, e.g., in stop & start systems, and lower heat generation obviously implies lower requirements to a cooling system and the 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 EDLC cells can be reduced substantially, and now in the Yunasko technology about 20% of its value comes from Al current collectors and leads. Further reduction in the R_{in} value is possible but, obviously, by a factor of approximately two only, when the Al contribution reaches about a half of the total resistance. It is also worth noting that electrochemical stability of electrolyte in positive and negative potential ranges can be different if different nano-sized carbons are used as electrodes. This enables to increase the EDLC working voltage up to 3V or even more [4, 33], and therefore, both mobility and electrochemical stability of electrolyte should be taken into account when selecting the carbons for positive or negative electrodes. However, the electrochemical studies of electrolyte stability are beyond the scope of this paper.

V. CONCLUSIONS

1. //LIC technology gives a chance to increase the EDLC energy density up to 30-40 Wh/kg while maintaining the power output typical for EDLC, namely, 3-4 kW/kg at the efficiency about 90%. The electrode components borrowed from EDLC and Li-ion technologies to fabricate hybrid //LIC electrodes should thoroughly be balanced by their energy stored and charge-discharge potential range.

2. The EDLC power output, efficiency and energy retention at high loads are determined by low internal resistance, which in its turn is mostly due to the electrolyte mobility in carbon nanopores. Because of different anion and cation in-pore mobility, different nano-sized carbons should preferably be chosen for EDLC positive and negative electrodes, respectively.

3. EDLC can most efficiently be employed if the high power pulses of short duration (from 0.1 to 30 seconds) are needed, while longer pulses (from 30 s to 10 min) can be covered by //LIC. The latter can also be fully charged within ca. 3 min.

REFERENCES

[1] B. E. Conway, Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications, Kluwer-Plenum Press, New York, 1999.

[2] F. Béguin, E. Frackowiak, Carbons for Electrochemical Energy Storage and Conversion Systems, CRC Press, 2009.

[3] P.J. Grbović, Ultra-Capacitors in Power Conversion Systems. Applications, Analysis and Design from Theory to Practice. IEEE Press, Wiley, 2014.

[4] Y. Maletin, V. Strelko, N. Stryzhakova, S. Zelinsky, A. B. Rozhenko, D. Gromadsky, V. Volkov, S. Tychina, O. Gozhenko, and D. Drobny, "Carbon based Electrochemical Double Layer Capacitors of Low Internal Resistance", Energ. Environ. Res. vol. 3 (2), pp. 156-165, November 2013. doi:10.5539/eer.v3n2p156

[5] A. Burke, Z. Liu, and H. Zhao, "Present and Future Applications of Supercapacitors in Electric and Hybrid Vehicles", [Proc. IEEE International Electric Vehicle Conference, Florence, Italy, December 2014].

[6] J. R. Miller, S. M. Butler, and S. McNeal, "Life Performance of Large Electrochemical Capacitors", [Proc. 46th Power Sources Conference, Orlando, FL, USA, pp. 380-381, February 2014]

[7] S. Ghosh, and D. Corrigan, "Directed Research Report on Performance Comparison of Commercial Supercapacitors", Detroit: Wayne State University, 2014.

[8] Y. Maletin, N. Stryzhakova, S. Zelinskyi, S. Chernukhin, D. Tretyakov, H. Mosqueda, N. Davydenko, and D. Drobnyi, "New Approach to Ultracapacitor Technology: What it Can Offer to Electrified Vehicles", J. Energy Power Engineering, vol. 9, pp. 585-591, June 2015. doi: 10.17265/1934-8975/2015.06.010

[9] Y. Maletin, N. Stryzhakova, S. Zelinsky, S. Chernukhin, and D. Tretyakov, "Hybridizing the Carbon Electrodes - a Way to Enhance the Supercapacitor Performance", [Proc. at CESEP, Poznan, Poland, Octover 2015.]

[10] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, "Electric Field Effect in Atomically Thin Carbon Films", Science, vol. 306, pp. 666-669, October 2004. doi: 10.1126/science.1102896

[11] S. Kondrat, and A. Kornyshev, "Superionic state in double-layer capacitors with nanoporous electrodes", J. Phys.: Condens. Matter, vol. 23 (2), pp. 2-10, December 2010. doi:10.1088/0953-8984/23/2/022201

[12] O. Barbieri, M. Hahn, A. Herzog, and R. Kötz, "Capacitance limits of high surface area activated carbons for double layer capacitors", Carbon, vol. 43 (6), pp.1303–1310, May 2005.doi:10.1016/j.carbon.2005.01.001

[13] H. Ji, X. Zhao, Z. Qiao, J. Jung, Y. Zhu, Y. Lu, L.L. Zhang, A.H. MacDonald, and R.S. Ruoff, "Capacitance of carbon-based electrical double-layer capacitors", Nat. Commun., vol. 5:3317 , Febrary 2014.doi: 10.1038/ncomms4317

[14] G. Gryglewicz, J. Machnikowski, E. Lorenc-Grabowska, G. Lota, and E. Franckowiak, "Effect of pore size distribution of coal-based activated carbons on double layer capacitance", Electrochimica Acta, vol. 50 (5) pp. 1197–1206, January 2005. doi: 10.1016/j.electacta.2004.07.045

[15] http://www.maxwell.com/products/ultracapacitors/durablue

[16] F. Béguin, and E. Frackowiak, Supercapacitors, Wiley-VCH, 2013.

[17] A.B. Stepanov, I.N. Varakin, V.V. Menukhov, and A.D. Klementov, "Double layer capacitor", US Pat. 6181546, publ. January 30, 2001.

[18] http://www.axionpower.com

[19] S Tasaki, N Ando, M Nagai, A Shirakami, K Matsui, and Y Hato, "Lithium ion capacitor", US Pat. 7697264, publ. April 13, 2010.

[20] G. G. Amatucci, F. Badway, A. Du Pasquier, and T. Zheng, "An Asymmetric Hybrid Nonaqueous Energy Storage Cell", J. Electrochem. Soc., vol. 148 (8), pp. A930-A939, July 2001. doi: 0013-4651/2001/148(8)/A930/10/

[21] K. Naoi, S. Ishimoto, J. Miyamoto, and W. Naoi, "Second generation 'nanohybrid supercapacitor': Evolution of capacitive energy storage devices", Energy Environ. Sci., vol. 5 (11), pp. 9363-9373, September 2012. http://dx.doi.org/10.1039/C2EE21675B

[22] http://www.jmenergy.co.jp/en/products_cell_can.html

[23] S. Chernukhin, D. Tretyakov, and Y. Maletin, "Hybrid Electrochemical Energy Storage Device", US Pat. Appl., 2014/0085773 A1, publ. March 27, 2014

[24] H. Budde-Meiwes, J. Drillkens, B. Lunz, J. Muennix, S. Rothgang, J. Kowal, and D. U. Sauer, "A review of current automotive battery technology and future prospect", [Proc: Inst. Mech. Eng. D J. Automob. Eng., 227: 761, 2013]

[25] B. Paton, D. Kaleko, and A. Slezin, "The apparatus for welding studs", UA Pat. 100828, publ. January 25, 2013.

[26] Y. Maletin, S. Podmogilny, N. Stryzhakova, A. Mironova, V. Danylin, and A. Maletin, "Electrochemical Double Layer Capacitor", US Pat. Appl., 2008/0151472 A1, publ. January 26, 2008.

[27] J. M. Griffin, A. C. Forse, W.-Y. Tsai, P.-L. Taberna, P. Simon, and C. P. Grey, "In situ NMR and electrochemical quartz crystal microbalance techniques reveal the structure of the electrical double layer in supercapacitors", Nature Materials, vol. 14, 5pp. 812–819, June 2015. doi:10.1038/nmat4318

[28] A. J. Bard, L. R. Faulkner, Electrochemical Methods. Fundamentals and Applications, 2nd ed., New York, Wiley, 2001.

[29] O. N. Kalugin, V. V. Chaban, V. V. Loskutov, and O. V. Prezhdo. "Uniform Diffusion of Acetonitrile inside Carbon Nanotubes Favors Supercapacitor Performance", Nano Letters, vol. 8 (8) pp. 2126-2130, July 2008. doi:10.1021/nl072976g

[30] Y. Cohen, L. Avram, and L. Frish, "Diffusion NMR spectroscopy in supramolecular and combinatorial chemistry: an old parameter—new insights", Angew.Chem.Int.Ed., vol. 44 (4), pp. 520-554, January 2005. doi:10.1002/anie.200300637

[31] R. T. Bonnecaze, N. Mano, B. Nam, and A. Heller, "On the behavior of the porous rotating disk electrode", J. Electrochem. Soc., vol.154 (2), pp. F44-F47, December 2007. doi: 10.1149/1.2403082

[32] Y. Maletin, N. Stryzhakova, S. Zelinskyi, D. Gromadskyi, and S. Tychyna, "Method for selecting nanoporous carbon material for polarizable electrode, method of manufacturing such polarizable electrodes and method of manufacturing electrochemical double layer capacitor". Pat. US 9524830, publ. December 20, 2016.

[33] Y. Maletin, N. Stryzhakova, S. Zelinsky, S. Chernukhin, D. Tretyakov, and S. Tychina, "How Electrochemical Science Can Improve the EDLC Performance", [Proc. AABC Europe, Strasbourg, Jun. 2013, http://www.advancedautobat.com/e-proceedings/aabc-europe-2013/le/]

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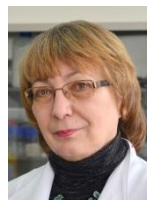
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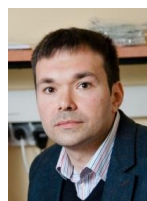
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