

Carbon Based Electrochemical Double Layer Capacitors of Low Internal Resistance

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Abstract

Based on nanoporous carbon electrodes electrochemical double layer capacitors (EDLC), otherwise known as supercapacitors or ultracapacitors, are currently widely used in various energy storage technologies, wherein the EDLC low internal resistance and long cycle life are at an advantage. It is still a good challenge to further reduce the internal resistance of EDLC since this can result in higher power density and higher efficiency of these promising power supply units. In this work it has been found that the EDLC internal resistance depends strongly on the electrolyte diffusion in the carbon electrode nanopores, and two techniques to measure the in-pore diffusion coefficients, namely, those based on spin-echo NMR or cyclic voltammetry with the use of porous rotating disc electrode are described. Cyclic voltammetry, impedance spectroscopy and transmission electron microscopy have also been used to select the best EDLC components. As a result, EDLC devices of very low internal resistance and high power density have been developed.

Keywords: double layer capacitor, in-pore electrolyte diffusion, low resistance

1. Introduction

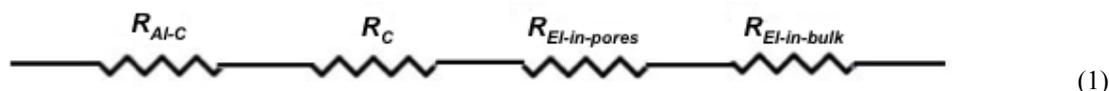
1.1 Why It Is of Interest

There is an obvious increasing interest in electrochemical double layer capacitor (EDLC) technology and application all over the world, in particular, in renewable energy and hybrid vehicle applications. However, the EDLC market growth is still rather modest. In our opinion, the main reason for a certain skepticism from automakers side is, on the one hand, a fast progress in Li-ion technology over the past two decades, while, on the other hand, a rather slow progress in EDLC technology. As pure “physical” devices, which do not involve any chemical or electrochemical transformations, any charge or mass transfer through the electrode-electrolyte interface, EDLC’s must demonstrate much faster charge/discharge operations and longer cycle life than any “chemical” batteries (Conway, 1999). Given this, EDLC devices can provide the key to a number of efficient power solutions that are mainly related with various backup systems to compensate short-term voltage surges or drops or with load leveling the batteries in various combined power sources. Low internal resistance can be one of key advantages of EDLC over all other types of energy storage devices since the round trip efficiency and power capability of the devices are inversely proportional to their internal resistance. Besides, low internal resistance predetermines the effectiveness of EDLC application in combined power supply units, wherein an EDLC device is connected with a battery either in parallel or in series. Additionally, high efficiency implies low heat generation and, hence, improved safety. This, accompanied by EDLC long life cycle and wide operation temperature range, can help them to clear their way to the market. To realize it, EDLC devices must clearly demonstrate much higher power capability than Li-ion or any other type of batteries, but this is not always the case. What are the reasons?

1.2 What Are the Hurdles to Overcome

The most substantial contributors to the EDLC internal resistance are (see a simplified equivalent circuit in

sketch (1) below): contact resistance between Al current collector and active carbon electrode (R_{Al-C}); ohmic resistance of active carbon electrode layer (R_C); electrolyte resistance in the electrode nanopores ($R_{El-in-pores}$); and electrolyte resistance in the bulk solution including electrode and separator macropores ($R_{El-in-bulk}$).



High contact resistance, R_{Al-C} , can result from the native oxide film on the aluminum surface and its effect on EDLC performance is thoroughly discussed in our previous work (Maletin et al., 2008) and also in Section 4 below.

Ohmic resistance of the active electrode layer, R_C , can substantially be reduced by adding a small amount (2–5% wt.) of conductive additives such as carbon black or graphite. On the other hand, it has been found (Maletin et al., 2008; Maletin et al., 2012) that the electrolyte conductivity, though being high enough in the bulk solution, can significantly be reduced in the electrode nanopores, and this can result in the lion's share of an unexpectedly high internal resistance of EDLC devices. Experimental study of this phenomenon is the main subject of the present paper.

1.3 Our Approach to Solve the Problem

According to well-known equations (Bard & Faulkner, 2001, p.137) the electrolyte conductivity is proportional to mobility or to diffusion coefficients of the corresponding ions. On the other hand, there is no potential gradient in narrow pores (if the pore width is close to the Debye length, or to 1–2 nm in concentrated electrolytes, which are normally used in EDLC technology), and therefore, diffusion is the only driving force for charge-discharge processes in nanoporous EDLC electrodes (Maletin et al., 2006). Bearing that in mind, in the present study two known independent experimental techniques based on NMR or electrochemical measurements have been modified and used to measure the diffusion coefficients of the electrolyte inside the carbon nanopores.

Since cost is another important issue that hinders the EDLC way to the market, in the present study we are mostly focused on the low cost nanoporous carbons based on natural carbonaceous materials, e.g., coconut shell. In some cases the surface of initial carbons was doped with N-heteroatoms as was offered by Strelko, Stryzhakova, Gozhenko, and Maletin (2009).

2. Method

2.1 Design of EDLC Prototypes and Their Performance Measurements

Two-electrode capacitor prototypes were used for performance measurements of various nanoporous carbons and EDLC design solutions. The electrodes were typically prepared by mixing the nanoporous carbon powder with PTFE suspension in water (the latter was used as a binder) until a homogeneous mixture was obtained. No conductive additives were normally added since the carbons selected in this work provided fairly low ohmic resistance, R_C . The mixture was rolled to form sheets of 40–100 micron thick followed by cutting off the separate carbon electrodes. The active carbon electrodes thus obtained had their geometric surface area of 15 cm² each and contained 93% of carbon and 7% of PTFE binder. They were then applied onto electric-spark treated aluminum foil (Maletin et al., 2008) used as a current collector of 15 or 20 micron thick and dried at 220 °C under vacuum for 6 hours. A couple of electrodes were then interleaved with a porous insulating sheet (separator) and placed into laminated aluminum shell. The prototypes thus fabricated were filled with 1.3 M Et₃MeN (TEMA) BF₄ in acetonitrile and sealed. All the assembly operations were carried out in a dry box. Larger EDLC devices comprising a number of positive and negative electrodes connected in parallel and forming a stack with the capacitance between 400 and 1500 F were assembled at Yunasko Pilot Plant according to the same technology.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out with the help of Voltalab-80 PGZ-402 unit. Galvanostatic charge-discharge cycling with the help of Arbin BT-2000 testing unit was also used to measure the capacitance and internal resistance of large EDLC prototypes. The CV measurements were mostly carried out within the voltage range of 0–3 V with the scan rate of 10 mV.s⁻¹. In some cases the voltage range was extended to 3.5 V. Also in some cases three-electrode CV measurements were used to study the behavior of various EDLC components in either positive or negative voltage range. The current loads between 0.1 and 1.0 A.F⁻¹ were used for galvanostatic charge-discharge cycling of the prototypes of different size/capacitance with the sampling rate of 10 ms. All the measurements were carried out at 25 °C except special life cycle tests that were carried out at 60 °C.

The internal resistance (R_{in}) and capacitance (C) values were calculated from galvanostatic cycling results in accordance with the FreedomCAR Ultracapacitor Test Manual (2004).

2.2 Study of Nanoporous Carbon Structure and Surface Chemistry

The following nanoporous carbon powders have been chosen for this study:

- A. ZL-302 (Huzhou Sensheng Activated Carbon Co., Ltd);
- B. ZL-302-N (ZL-302 carbon powder thermally treated with melamine and containing 15 atomic % of nitrogen on its surface);
- C. NY1151 (Kuraray Chemical Co.,Ltd);
- D. YP80F (Kuraray Chemical Co.,Ltd);
- E. YP50F (Kuraray Chemical Co.,Ltd);
- F. HDLC 20B STUW (Haycarb PLC);
- G. NC2-1E (EnerG2 Technologies Inc.);
- H. P2-15 (EnerG2 Technologies Inc.);
- I. Y-Carbon (Y-Carbon Inc.).

The porous structure of carbon materials has been studied with the help of transmission electron microscopy (TEM) with the use of Jeol JEM-2100F, and also from nitrogen adsorption/desorption isotherms at 77 K using a Nova 2200e Surface Area & Pore Size Analyser (Quantachrome Instruments).

The concentration of nitrogen heteroatoms on carbon surface has been measured with the help of XPS with the use of KRATOS-800XPS, energy resolution of 1.2 eV, $K\alpha$ (Al), $h\nu=1486.6$ eV, spectral data being treated with the help of XPSpeak 4.0.

2.3 Diffusion Coefficient Measurements

For NMR diffusion measurements the carbon powders listed above were impregnated with ethyl trimethyl ammonium tetrafluoroborate ($\text{EtMe}_3\text{NBF}_4$) dissolved in either acetonitrile (CH_3CN) or acetonitrile- d_3 (CD_3CN) followed by placing each powder into a 5 mm standard NMR tube. All ^1H NMR diffusion measurements have been carried out using a Bruker AVANCE 400 spectrometer equipped with the wide-bore magnet. A 5 mm “diff60” diffusion probe head (Bruker) with gradient coils in Z direction was used to generate magnetic field gradient. All experiments were performed at 25 °C. The 90° pulse lengths (14.5–18.5 μs) were determined for every sample using the standard routine. The T_1 relaxation times were measured by standard inversion-recovery. The T_2 relaxation times were determined with the Carr-Purcell-Meiboom-Gill (CPMG) standard sequence. The PGSTE “Pulse Gradient Stimulated Echo” method (DifSte Bruker standard pulse sequence) described by Tanner (1970) and by Cohen, Avram, & Frish (2005) was used for the diffusion measurements. The “diff” automated routine was employed to prepare all the parameters for the diffusion experiments. The square field gradient pulses (δ) and delay between two first radiofrequency pulses (τ) were chosen short enough (0.4 ms and 1.1 ms, respectively) in order to measure the diffusion coefficients for samples with very short (< 2 ms) T_2 relaxation times. 32 intensity points were acquired and number of transitions was between 8 and 64, depending on the signal intensity and resulting signal-to-noise ratio. The data were processed in the standard way using the T_1/T_2 routine and approximating the resulting curve on two different values of diffusion coefficients. The resulting values of self-diffusion coefficients were averaged over three measurements.

The ^{19}F NMR diffusion measurements have been carried out with the use of AVANCE-III-400 spectrometer following the same procedure as described above for ^1H self-diffusion experiments.

As an alternative independent method for diffusion coefficient measurements, a version of the well-known rotating disc electrode (RDE) method (Bard & Faulkner, 2001, p.335) has also been used. The disc electrode (BASi RDE-1) was made of a graphite rod of 3 mm in diameter and covered with a nanoporous carbon layer of 40 micron thick. Rotation rates of 500, 750, 1000, 1250 and 1500 rpm were chosen for measurements. As a reversible redox-pair for RDE measurements, the ferrocene molecule/ferrocenium cation (Fc/Fc^+) pair has been chosen since the Fc^+ cation is similar by its size and insignificant solvation effect to tetraalkylammonium cations used in EDLC technology. For RDE diffusion current measurements an Fc sample of 4 mmol. dm^{-3} was dissolved in 1.3 M $\text{Et}_3\text{MeNBF}_4$ solution in acetonitrile. The potential scan rate in CV measurements was 0.5 $\text{mV}\cdot\text{s}^{-1}$. The $\text{Ag}/\text{AgCl}/\text{KCl}$ (1 M) reference electrode was connected with the working electrolyte through a salt bridge.

3. Results

3.1 Study of the Carbon Pore Structure

Most of the carbon materials listed in Section 2.2 have been selected so that they have their pore size in the range

between 1 and 10 nm with a large portion concentrated between 1 and 3 nm. Some examples can be seen in Figure 1 wherein the pore size distribution for three promising carbons is illustrated.

One more criterion for preliminary carbon material selection in this work is the presence of mostly shallow slit-shaped pores or just shear cracks of graphene layers in the carbon matrix – see, e.g., in Figure 2, which presents the TEM image for HDLC 20B STUW (F) carbon powder.

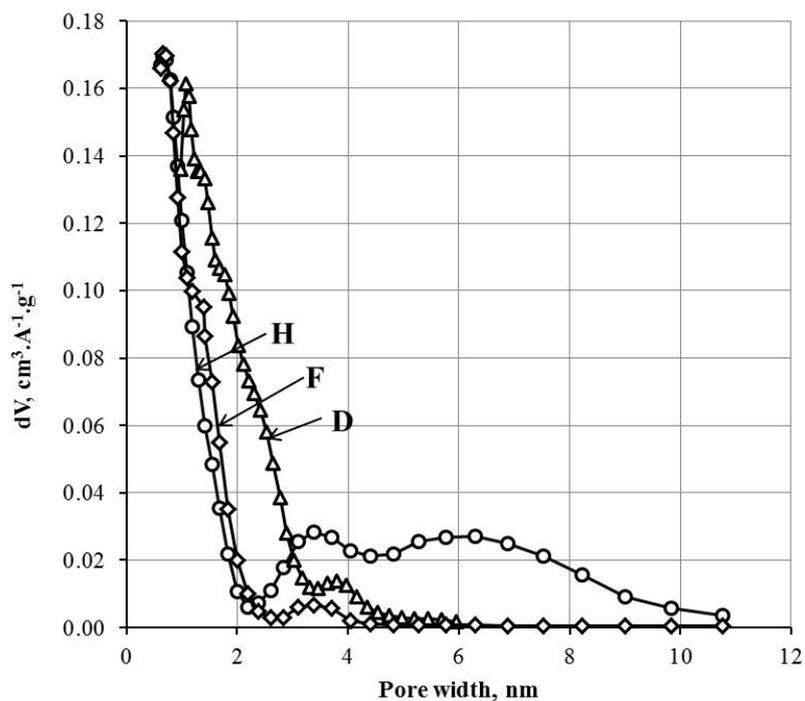


Figure 1. Pore size distribution obtained from nitrogen adsorption/desorption isotherms with the use of DFT calculations for some of the tested carbon powders (as listed in Section 2.2)

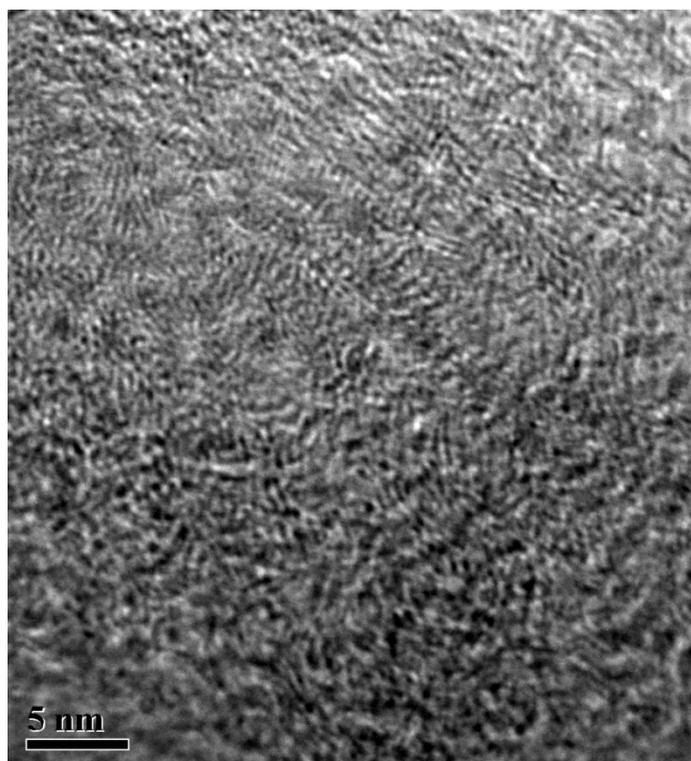


Figure 2. TEM image of F (HDLC 20B STUW) carbon powder

3.2 Electrochemical Measurements

Further, the carbon materials listed in Section 2.2 were studied with the use of CV method. A special reference electrode was developed to be used in organic electrolytes, the electrode potential being stable over practically unlimited time and giving a chance to register CV and charge-discharge curves in both positive and negative ranges from the equilibrium potential of carbon material. For the sake of generality, we use the Li/Li^+ potential as “zero point” in our scale of potentials.

A typical example of CV measurements with the use of three-electrode cell is illustrated in Figure 3-a, wherein a good behaviour of carbon materials selected for positive or negative electrode can be seen in a wide potential range. It should also be noted that a carbon material selected for the positive electrode may be different from that selected for the negative electrode to keep the electrode potential within the certain range when assembling the EDLC. As a result, a CV curve of an EDLC prototype assembled with the use of thus selected electrodes is presented in Figure 3-b.

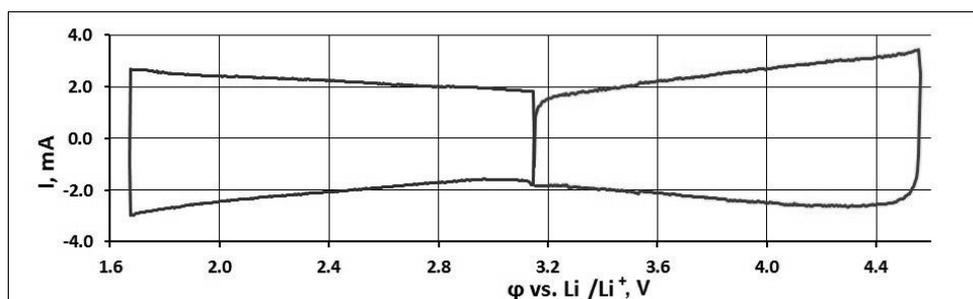


Figure 3-a. Cyclic voltammery curves in positive (right) and negative (left) ranges from the equilibrium potential of nanoporous carbon as a working electrode in a three-electrode cell (room temperature; electrolyte: 1.3 M TEMA BF_4 in acetonitrile; scan rate: 10 mV s^{-1})

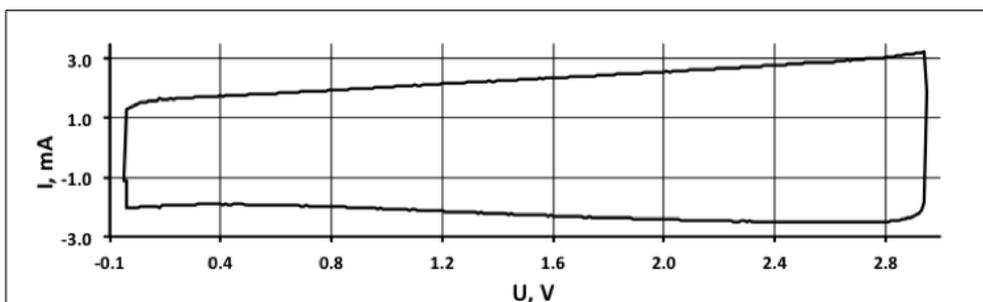


Figure 3-b. Cyclic voltammery curve of an EDLC prototype with positive and negative electrodes as in Figure 3-a, each electrode area being of 15 cm^2 (room temperature; electrolyte: 1.3 M TEMA BF_4 in acetonitrile; scan rate: 10 mV s^{-1})

Figure 4 illustrates the EIS results (Nyquist plots) for three different designs of EDLC devices. Curve 1 illustrates the case of poor electrical contact between the aluminium current collector and active electrode layer resulting in high contact resistance. Curve 2 reflects the design with low contact resistance though with the electrochemical system (i.e. nanoporous carbon electrodes and organic electrolyte) non-optimized properly. The optimization can be achieved due to CV measurements like those presented in Figure 3 above and also due to diffusion coefficient measurements described below. The Nyquist plot for the optimized design is presented by Curve 3 in Figure 4.

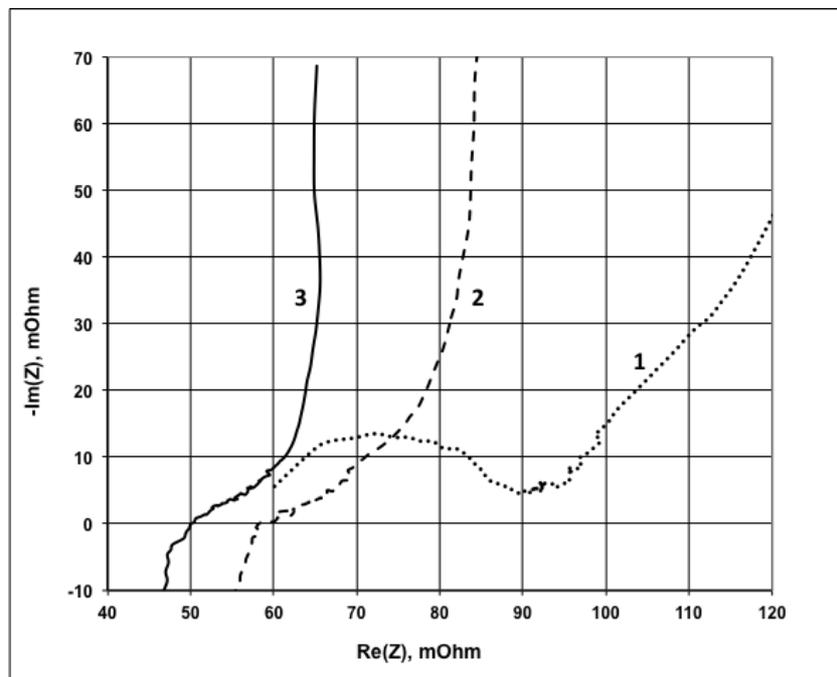


Figure 4. Nyquist plots for EDLC prototypes: 1 - with poor contact between the current collector and active carbon layer (high contact resistance); 2 - with improved contact resistance but non-optimized electrochemical system; 3 - with fully optimized design

3.3 In-Pore Diffusion Coefficient Measurements

After impregnating carbon powders with electrolyte, the electrolyte translational self-diffusion coefficients have been calculated from the attenuation of the NMR signals due to the application of the gradient pulses of the constant lengths but various strengths using Equation (2) (Price, 1997):

$$I = I_0 \exp \left[-D_0 \gamma^2 \delta^2 g^2 \left(\Delta - \frac{\delta}{3} \right) \right] \quad (2)$$

where I and I_0 are the NMR signal intensities in the presence and in the absence of the gradient respectively, γ is the gyromagnetic ratio of the nucleus under observation, δ and g are the duration and the strength of the applied gradient pulse, respectively, D_0 is the self-diffusion coefficient, and Δ is the time interval between the two successive gradient pulses.

It has been found that the theoretical curve practically coincides with experimental values if the attenuation of NMR signals is expressed as a sum of two Equations (2) with different D_0 values, a quickly diffusing one ($\sim 10^{-9} \text{ m}^2 \text{ s}^{-1}$) and slowly diffusing one ($\sim 10^{-10} \text{ m}^2 \text{ s}^{-1}$). This can reflect the fast diffusion in bulk solution or in macropores and slow diffusion in nanopores.

The resulting values of thus found effective diffusion coefficients have been averaged over three measurements and are plotted in Figures 5 and 6 (for BF_4^- anions and EtMe_3N^+ cations, respectively) for various nanoporous carbons vs. the internal resistance of EDLC prototypes comprising the same carbons in electrodes. As can be seen from these figures, there is a fairly good correlation between diffusion coefficients of electrolyte ions in carbon nanopores and the internal resistance of the corresponding EDLC prototypes. However, it should be noted that some carbons cannot be used for NMR measurements because of the very short correlation time of electrolytes in their pores resulting in unreliable diffusion coefficient evaluations. Therefore, we have also developed another method to measure the diffusion coefficients of electrolyte ions in carbon nanopores, namely, a version of the well-known RDE method-see Section 2.3 for details. The behaviour of porous rotating disc electrode (PRDE) has recently been studied by Bonnacaze, Mano, Nam, and Heller (2007). To evaluate the diffusion coefficients from PRDE measurements we have used the Levich equation:

$$i = \pm 0.62 n C_0 F D^{2/3} \nu^{-1/6} \omega^{1/2} \quad (3)$$

where i is the limiting diffusion current value, n is the number of electrons in the electrode semi-reaction, C_0 is the concentration of the reacting species, F is the Faraday constant, D is the diffusion coefficient, ν is the kinematic viscosity, and ω is the rotation rate.

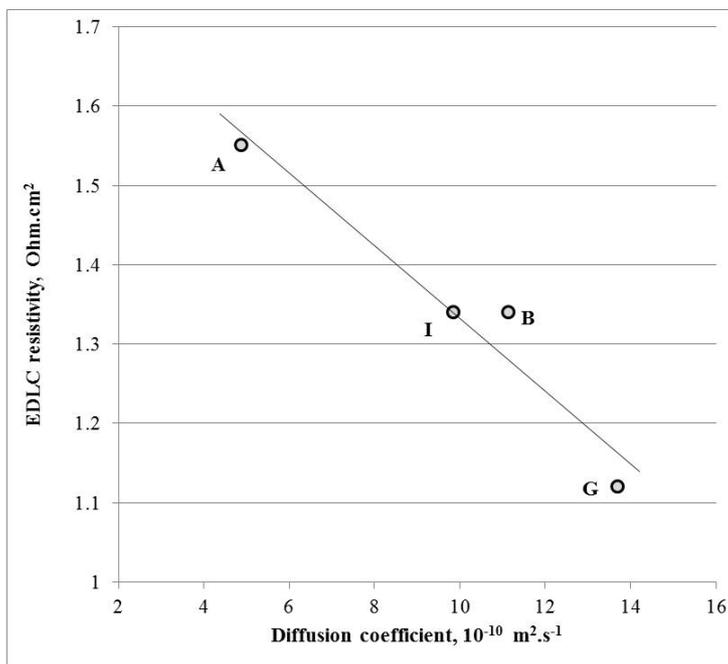


Figure 5. Internal resistance of EDLC prototypes comprising electrodes of different nanoporous carbons, as listed in Section 2.2, vs. the diffusion coefficients of BF_4^- anions in those carbons (^{19}F NMR measurements)

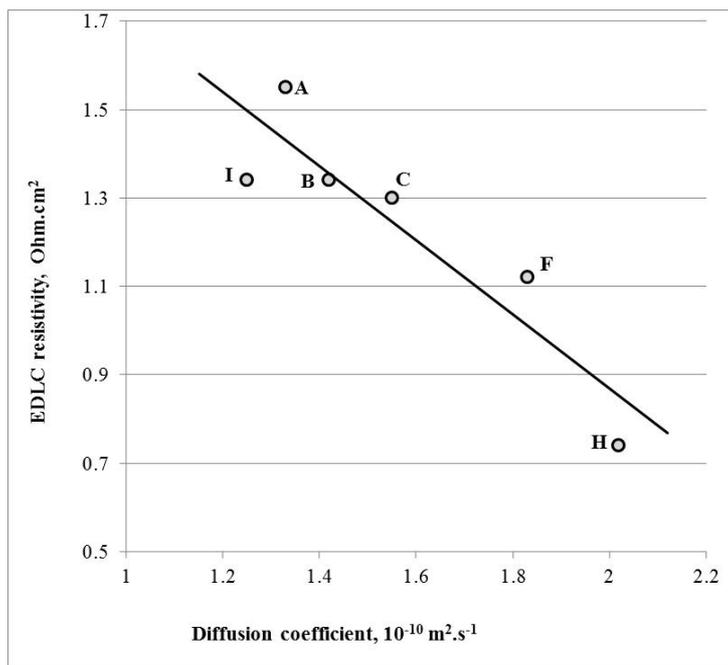


Figure 6. Internal resistance of EDLC prototypes comprising electrodes of different nanoporous carbons, as listed in Section 2.2, vs. the diffusion coefficients of EtMe_3N^+ cations in those carbons (^1H NMR measurements)

The results of PRDE measurements of the electrolyte diffusion in various nanoporous carbons, which are listed in Section 2.2, are plotted in Figure 7 vs. the internal resistance of EDLC prototypes comprising the same

carbons in electrodes.

Both NMR and PRDE methods, as illustrated in Figures 5–7, have been employed to select the low resistance electrodes for EDLC manufacture, and the results for large EDLC prototypes are briefly listed in Table 1 below.

Table 1. Performance of Yunasko EDLC devices (rated voltage 2.7 V)

Capacitance, F	Internal resistance, mOhm	Time constant (RC), s	Spec. energy ($CU^2/2$), W.h kg^{-1}	Spec. power (@95% eff.), kW kg^{-1}	Max. spec. power, kW kg^{-1}
480 ^a	0.20	0.10	4.9	10.2	91
1200 ^{a,b}	0.10	0.12	5.3	8.9	79
1500 ^b	0.09	0.14	6.1	9.1	81

^{a)} Also tested at the Institute of Transportation Studies, Davis, CA; ^{b)} Also tested at JME Inc., Cleveland, OH.

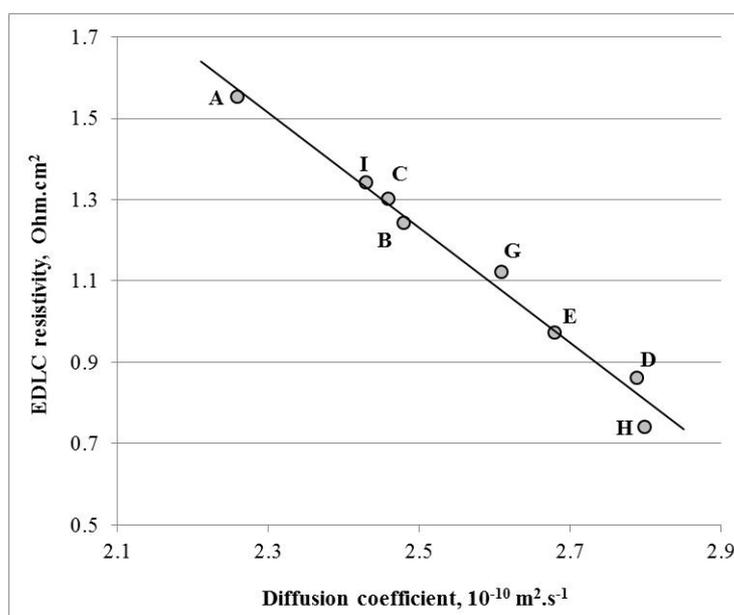


Figure 7. Correlation between EDLC internal resistance and diffusion coefficients of ferrocenium-cation in pores of various carbons listed in Section 2.2 and used in electrodes (PRDE measurements)

The cells listed in Table 1 were also tested for their life cycle according to IEC 62391 endurance test procedure, and after holding the cells for at least 2000 hours at 60 °C and 2.7 V they demonstrated the capacitance retention within 70% and an increase in internal resistance not exceeding 100%.

4. Discussion

Though being beyond the scope of this paper, some methods to reduce the R_{Al-C} contact resistance (see sketch (1)) have recently been disclosed by Maletin et al. (2008). The electrical contact between the active electrode layer and aluminum current collector can be significantly improved due to conductive carbon particles to be locally and individually fused into the current collector surface. New versions of those methods, in particular, the electric spark treatment with the use of graphite electrode are effectively employed in our current technology resulting in a very low contact resistance value, normally not exceeding 10 mOhm $\cdot cm^2$.

As regards the choice of nanoporous carbon materials to be used in EDLC electrodes, the materials having shallow slit-shaped pores with their width between 1 and 3 nm (see examples in Figures 1 and 2) look preferable for EDLC electrode application. From our experience the carbons comprising larger mesopores have significantly lower surface area while those with pores predominantly below 1 nm demonstrate too high resistance to be effectively used in EDLC devices.

CV measurements with the use of a three-electrode cell and EIS measurements give a chance to optimize the electrochemical system design in order to improve the EDLC performance. Similar CV and dilatometric studies for different carbon materials and electrolytes were carried out by Hahn, Barbieri, Gallay, & Kötzt (2006), and as have now been shown in our work the optimized EDLC prototypes demonstrate a fairly good rectangular shape of CV curves with no visible faradaic processes within a voltage range as wide as 2.9 V and also the lowest resistance and close to ideal vertical line in Nyquist plots at low frequencies— see Figures 3 and 4.

As was found in our NMR measurements, the T_1 and T_2 relaxation times of various nuclei of the electrolyte species (^1H , ^{11}B , ^{19}F) change significantly when the electrolyte enters the carbon pores, and this can reflect a strong interaction of electrolyte species with the carbon matrix – see also a similar conclusion made by Price (1997). This phenomenon and some other NMR results will be discussed in more detail in our forthcoming publications, while here we would like to focus on the diffusion coefficient values since they illustrate the electrolyte dynamics in carbon nanopores. Of course, the D_0 values measured for the fluid phase in nanopores are not the true self-diffusion coefficients, but rather the effective molecular diffusivities D_{eff} (Price, 1997). Nevertheless, as can be seen from Figures 5–7, there is a remarkable correlation between the internal resistance of EDLC device and ion diffusion in pores of the corresponding carbon electrode material. Absolute values of diffusion coefficients of EtMe_3N^+ and Fc^+ cations, though being measured by different methods, are close (cf. Figures 6 and 7), and the difference can be accounted for slightly different size of these cations. It is also worth noting that the diffusion coefficient of Fc^+ cations, when being measured with the use of a flat graphite electrode, is $1.01 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$, which significantly exceeds the values in carbon nanopores presented in Figure 7.

It should also be noted that the positive and negative electrodes are typically different to best match the different mobility of anions and cations in their pores. Besides, it has been found that the diffusion coefficients of electrolytes can be increased and, correspondingly, the pore resistance can be reduced due to doping the carbon surface with nitrogen atoms (Strelko et al., 2009). This effect can be accounted for reducing the interaction between the carbon matrix and electrolyte ions.

The test results listed in Table 1 and also verified by independent experts clearly show a very low internal resistance of EDLC devices based on optimized electrochemical systems with their RC-constant values being between 0.1 and 0.2 s and maximum power density reaching 80–90 kW/kg. These RC-constant values are lower by a factor of 2–3, and correspondingly, power capabilities of EDLC devices presented in Table 1 are by far higher than those of the best competing devices (Miller, Butler, Ryan, & McNeal, 2013).

Very low internal resistance of EDLC devices thus fabricated makes it possible to avoid significant heating during the operation, even under high load conditions. As an example, a module of 16 V comprising 6 single cells of 1200 F each connected in series has the internal resistance below 1 mOhm and after continuous charge/discharge cycling with the current value of 200 A running over 8 hours demonstrates an increase in temperature of about 10–12 °C only.

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