Effect of ultrasonic treatment of activated carbon on capacitive and pseudocapacitive energy storage in electrochemical supercapacitors

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Properties

ABSTRACT

Purpose: Use of ultrasonic radiation for improving the properties of activated carbon was the aim of this paper. Increase of density of states at Fermi level was the main factor, responsible for working characteristics of electrochemical supercapacitors.

Design/methodology/approach: Working parameters of supercapacitors on the base of activated carbon have been studied by means of precisional porometry, small angle X-ray scattering, cyclic voltamerometry, electrochemical impedance spectroscopy and computer simulation methods.

Findings: The possibility to effect the interface between activated carbon and electrolyte by means of ultrasonic treatment in cavitation and noncavitation regimes is proved. It is shown that ultrasonic treatment in noncavitation regimes causes the significant increase of density of states at Fermi level that results in better farad-volt dependences.

Research limitations/implications: This research is a complete and accomplished work.

Practical implications: Modification of electric double layer by meanans in ultrasonic treatment, proposed in this work, could be regarded as effective way to obtaine the advanced electrode materials in devices of energy generation and storage.

Originality/value: This work is important for physics, material science and chemistry because it is related with new possibilities to change the mobility of charge carries in electric double layer by means of ultrasonic irradiation.

Keywords: Ultrasonic treatment; Pseudocapacitance, Electric double layer, Nyquist plots, Hybrid supercapacitor

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1. Introduction

Supercapacitors, in which a high reversible electrochemical charge-discharge processes occur, have in few times larger the specific power and in few hundreds times the number of cycles than the chemical accumulators although their specific energy is less. Supercapacitors, depending on mechanism of storage processes, can be divided into two groups. First of them consists of so named an electrical double layer capacitors (EDLC), whose capacitance appears in electric double layer (EDL) that is formed at the boundary between the huge surface area (1000 - 3000 m^2/g) of blocking electrode with an electrolyte. According to [1] the maximum differential EDLC capacitance is not higher than 25 - 30 $\mu F/cm^2$.

To second group belongs the special kind of electrochemical supercapacitors, whose capacitance exists owing to Faraday redox-processes of definite nature [1]. Up to now no reasoned justifications concerning to neglecting the some components of capacitance for known kinds of activated carbon. Moreover, it is most probably that due to just Faraday pseudocapacitance there is inconsistency of experimentally determined values of specific capacitances (see for instance [2, 3]) with theoretically estimated value, which even out of BDM (Bockris, Devanathan and Müller) model [4] for electric double layer can not exceed the value $\sim 140 \div 150$ F/g. It is due to fact that at limited development of surface the differential capacitance of known kinds of carbon and electrolyte systems on account the increase the Thomas-Fermi screening length in electrode material no exceeds 15 - 17 $\mu F/cm^2$ [5], and electrochemical accessibility of surface equals ~ 30 % [6].

Obtained specific values of pseudocapacitance per unit electrode area are higher by one order then corresponding values the EDLC typical electrostatic capacitances. According to [7] it is suggested to increase an energy density up to value 88.5 Wh/kg for supercapacitors on the carbon-based materials with ability to ion electrochemical intercalation. On the reason that the total energy resource prevails $E = E_c \times N$ (E_c – mean energy of one "charge-discharge" cycle, N - their number) of electrochemical capacitors comparing to the chemical accumulators, at present time an intense studies, aimed on the decrease both electrostatic and pseudocapacitive contributions are carried out. Interesting are works related with searching of new kinds of carbon aerogels and nanotubes [8-10]. It should be noted that tremendous efforts are aimed on the substitution of very expensive ruthenium and iridium oxides, maintaining the specific redox-capacitances up to 900 F/g, by other cheaper materials [11, 12]. Success of this way is not as impressive as was expected, but the some promising results nevertheless were obtained. In particularly in [13] it is shown the possibility to use the abilities of anions Cl^-, Br^- to specific absorption in order to increase the specific capacitive characteristics of carbon electrode. Early in [14] we have established the reverse charge of activated carbon to 2000 F/g which was based on intercalation process of anions I^- at electrode potential values not higher than at electrode potentials, no attaining the potential of iodine extraction in free state and potential of I_3^- formation. Our studying of interrelation between porous structure, electronic properties of nanoporous carbon and capacitance of carbon-electrolyte interface shown, that the contribution of pseudocapacitive charge storage into electric double layer depends more on Fermi level position in carbon materials and depends less on an ion thermodynamic parameters in electrolyte solution [14]. Theoretical analysis of processes, which occur at interface between nanoporous carbon and electrolyte was carried out in this work and enabled us to hallmark for intercalative nature appearance as formation of discontinuous series of valence stable intercalate phases. Many problems, existing at developing a new supercapacitors are related with more general questions, depending on nanoscale processes in material science [15, 16].

The measured data on farad-volt dependences for different electolytes (KOH, KBr, CsBr, KI) show their sharp asymmetry in cathode and anode regions because of the formation of great pseudocapacitance up to 2000 F/g in anode region (KI); they also show a very small capacitive charge accumulation (no more than 5.4 F/g) in anode region (KOH). In the former case, this asymmetry is, mainly, related with shunting of Helmholtz's layer capacitance by great faradaic capacitance (pseudocapacitance); in the latter case, this is related with sharp expansion of spatial charge region in a solid. The formation of great capacitance (225 F/g) for the Cs^+ ion in negative region and supergreat pseudocapacitance (2000 F/g) for the I^- ion is caused by the ability of these ions to intercalate the nanopores of activated carbon ($d \lesssim 4.4$ Å) that requires a minimal value of chemical potential and hydration energy of the ion in a solution. The influence of electronic structure on the charge accumulation in EDL is discussed in this work. Some results related with this problem we have been obtained early in [17].

At the same time from measurements of farad-volt plots in various electrolyte solutions (KOH, KBr, CsBr, KI) follows that an essential anisotropy exists both in cathode and anode region [14]. It is shown that shunting of Helmholtz layer capacitance by one of volume charge region in solid is the reason of low specific capacitance at negative polarisation of activated carbon.

Therefore today problems, which restrict the effectiveness of capacitive and pseudocapacitive energy storage in supercapacitors are:

- limiting influence of depleted capacitance of volume charge region C_{SC} of activated carbon at negative electrode polarization in alkaline electrolyte. It is clear that unblocking of Helmholtz capacitance is promoted by increasing of C_{SC}, which in turn is proportional to density of states of delocalized charge carries at Fermi level $D(E_F)$ in accordance with well known relation [18]:

$$C_{SC} = e_0 \sqrt{\varepsilon_{SC} \varepsilon_0 D(E_F)} \tag{1}$$

- absence of effective and suitable controlling methods to control the energy topology of electron states (i.e. the controlled variability of Fermi level position) for any chosen activated carbon in order to increase the specific pseudocapacitance, especially at large current load in case of positive polarization.

Generally, using the high conductive forms of carbon (for instance the nanotubes) can help to avoid these problems. Unfortunately today high cost and problem on maintaining of hydrophility do not permit to apply this method. On that reason searching of new technology solutions in this field was the main aim of this work.

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2. Experimental

Activated carbons of various origin, obtained by means of activated carbonization of birch wood (BW), cherry fruit stones (CFS) and styrenebenzene copolymer (SBC) were chosen as materials under investigation. Their porous structure has been determined by means both of precision porometry method and small angle X-ray scattering [19] with using of ASAP 2000 M equipment and DRON-3 X-ray diffractometer. Ultrasonic treatment has been carried out in glass pyrex ampoule, in which the activated carbon, dispersed in aqueous medium was placed. Ampoule was fixed in center of piezoceramic sphere of 70 mm diameter. Ultrasonic irradiation has been performed at frequency 22 kHz. One of the main parameters of ultrasonic treatment was irradiation duration which in our experiments was chosen to be- 5-14 hours for noncavitation regime and 5-15 minutes only for cavitation one.

Electrochemical measurements have been carried out according to two- and three- electrode setups with clorine-silver reference electrode. Materials under investigation with binder (5 % of polyvinilidenefluoride) have been forced on nickel or steel set of 0.5 cm^2 area. Aqueous solutions 7.6 m KOH, 4 m KI and 2 m ZnI_2 were chosen as electrolytes. Electrode potentials E have been recounted in reference to standard hydrogen reference electrode. Extraction potentials E and chemical potentials of ions μ_s have been calculated according to well known relations [20]:

$$E = E_0 + \frac{RT}{nF} \ln\left(\frac{a_{oxid}}{a_{red}}\right) \quad (2)$$

$$\mu_s = \mu_s^{stand} + RT \ln(a_s) \quad (3)$$

where a_{oxid}, a_{red}, a_s – activities of ions in solution. Energy levels have been determined in eV according to absolute energy scale.

Impedance spectra (in frequency region 5×10^{-3} - 10^5 Hz and 5 mV of amplitude) in potentiostatic conditions, cyclic voltammograms and galvanostatic charge-discharge cycles were recorded with use of measuring equipment "Autolab" ("Eco Chemie", Holland), attached with software FRA - 2 and GPES. Obtained impedance data have been simulated to accordance with electric equivalent circuits in medium of program pack ZView 2.3 (Scribner Associates). Capacitance values for plotting a farad-volt dependences have been determined from virtual value of hodograph impedance at frequency 5×10^{-3} Hz with accuracy 2 - 8% (Kramers–Kronig test was within 10^{-6} - 10^{-5} interval) according to well known formula: $C = (j2\pi f Z'')^{-1}$.

3. Results and discussion

The size distribution functions for materials under investigation reveal the optimal [21] for capacitive charge storage pore diameter d distribution function with maximum in vicinity $d = 2$ nm and similar behavior within micro- and mesoporoes region (Fig. 1).

However a total areas of all porous surfaces, in which the formation of compact screened electric double layer is problematic ($d \lesssim 4.4$ Å), are notably different (Table 1).
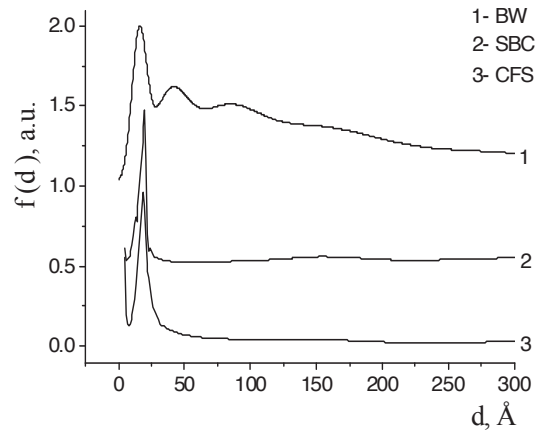

Fig. 1. Pore distribution functions versus diameter

Table 1.
Porometric characteristics of investigated carbons

Material	Specific surface area, m^2/g		
	$d \lesssim 4.4$ Å	$4.4 < d < 19$ Å	$d > 19$ Å
SBC	576	332	120
CFS	448	498	181
BW	134	264	69

Studies of ultrasonic treatment influence on specific capacitance reveal the dependence of the parameter under consideration both from irradiation condition and kind of activated carbon. It is noteworthy that cavitation regimes that were investigated here (for which the duration was not longer than 15 min.) on the reason of no admission of activated carbon dispersing by cavitation streams) change less remarkably the value of specific capacitance not only to its increase (for BW) but to decrease too (for SBC). The difference between those materials is first of all in their electron structure, characterized by different positions of Fermi level, which determines the value of electrochemical potential $\tilde{\mu}$, measured by means of experimental method [22]. These values are found to be $\tilde{\mu}$ = - 0.42 V, (BW) and - $\tilde{\mu}$ = - 4.08 V (SBC).

But as it was revealed, the cavitation regimes decrease the frequency dependence of capacitance within frequency range 1-50 Hz (Fig. 2).

It means that such the materials maintain higher power at current loads corresponding to that frequency range. Moreover they are promising for development of carbon supercapacitors for circuits with alternating current.

In order to understand the physical nature of observed phenomena let us consider the impedance spectroscopy data. First of all it should be noted that Nyquist plots for all regimes of cavitation modification have the typical shape (Fig. 3), which indicates the state of distribution ("deformability") of capacitance. This fact as well as necessary to take into account the capacitance of the volume charge region (VCR) at construction the adequate impedance model need to use de Levie model [23], modified by daisy chains of parallel $R_{SC}C_{SC}$ – link of chain, as it is shown in insert to Fig. 3.
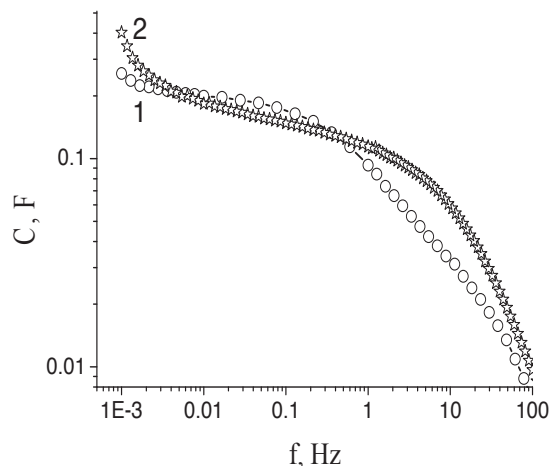

Fig. 2. Capacitance dependence versus frequency at negative polarization for BW before (1) and upon ultrasonic treatment in cavitation regimes (2)
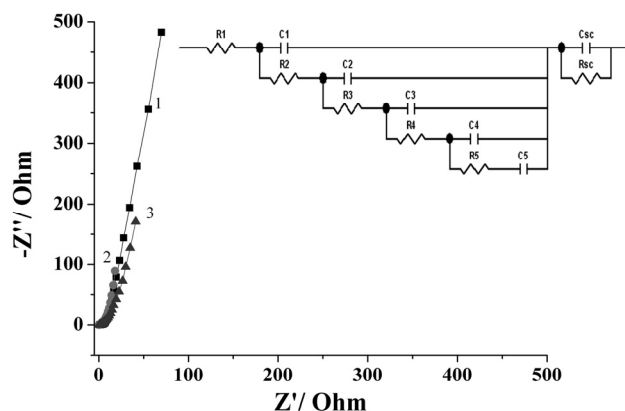

Fig. 3. Nyquist plot behaviour for initial carbon (1) and upon cavitation ultrasonic irradiation in 50 ml H_2O during 5 min (2) and 20 min (3). Insert - equivalent electric circuit

Here R_{SC} and C_{SC} – resistivity and capacitance of VCR respectively. It was shown by computer parametric identification that there is a correlation between parameters of electric double layer and values of specific capacitance at galvanostatic discharge [17].

Above all it can be seen that ultrasonic irradiation promotes decrease of C_{SC} -value (unmonotone with increasing both t and

C), that in compliance with (1) is the evidence of decrease of density of states at Fermi level. The direct confirmation of that was obtained in our studies by means of electron emission X-ray spectroscopy. Hence, the spectrum of valence band for initial activated carbon has a two- shoulder shape with significant decrease of intensity at attaining of bonding energy to Fermi level. The intensity at Fermi level, which is proportional to the electron density, equals $I(E_F)$=13630 a.u. After ultrasonic irradiation the shape of valence band shows no significant changes, but the visible intensity decrease at Fermi level to $I(E_F)$=9300 a.u. is observed.

At the same time it is shown that ultrasonic irradiation leads also to R_{SC} decrease with non-monotone behavior, which is not adequate to non-monotone behavior of C_{SC} that no correlates with decrease of $D(E_F)$. Thus, C_{SC} and R_{SC} decrease have not their adequate representation in decrease of measured specific discharge capacitance C in "charge-discharge" galvanostatic cycles [17]. This allows asserting that as decisive factor for C– value should be chosen the time constant $R_{SC}C_{SC}$ -link (inset to Fig. 3), which in fact represents:

a) the shunting of C_{SC} by resistance of VCR, i.e. in this case R_{SC} reveals the fact that effective unblocking of Helmholtz capacitance is observed when the time of plate charging C_{SC} is higher than the period of its oscillations;

b) the symmetrisation of voltage-current characteristic for regions of cathode and anode polarisation. Thus, the values of measured capacitance correlate in nontrivial way with parameters of EDL.

The data, obtained for materials under investigation allowed us to state that in hierarchy aspect for the equal values of active surface areas the most effective unblocking of Helmholtz capacitance can be reached when the resistance of VCR is low (inset to Fig. 3).

Table 2.
Distribution of chemical elements before– and after ultrasonic treatment of carbon material

Element	weight %		atomic %	
	initial	after ultrasonic treatment	initial	after ultrasonic treatment
C	91.5	95.0	94.3	96.3
O	6.5	4.7	5.0	3.6
Mg	0.2	-	0.1	-
K	1.2	-	0.4	-
Ca	0.6	0.3	0.2	0.1
Total	100.00	100.00	100.00	100.00

Concerning to physical nature of observed changes that it includes at least two aspects:

a) we deal with untypical for carbon-graphite materials, but well known for semiconductors [24] phenomenon of admixture redistribution, stimulated by ultrasonic radiation that results in modification of impurity energetic topology,

b) the strong dependence of mobility and may be philinity on fractal structure.

The direct confirmation of the first of them follows from the data of both quantitative and qualitative analysis of carbon materials before and after ultrasonic treatment in different regimes by means of scanning electron microscope JEOL. Data on distribution of chemical elements, which materials under investigation consist of, are listed in table 2.

In other words by means of ultrasonic irradiation it is possible to control the surface electron states, created by impurities as well as intrinsic defects.

The aspect of physical nature of observed changes means that dominating contribution to R_{SC} value makes no the concentration of delocalized electrons, but the mobility, which should be related to kind of fractal structure. Comparison of C_H and S is a good evidence of this [17].

The question arises whether the mechanism of effect in noncavitation regime on storage properties of activated carbon is adequate. In order to answer this question the attention should be paid on the first fact that C values represent evidently the notable pseudocapacitive contribution at negative polarization of nature origin carbon materials. Secondly, the increase of maximum capacitance in 7.6 m KOH solution in both cathode and anode region and change of the farad-volt curve behaviour after ultrasonic noncavitation treatment show that already no interval, where the capacitance decreases with increasing of anode polarization potential (Fig. 4) (which is the characteristic of initial material - curve 1) and its increasing from minimum value 155 F/g at 0.1 V to 166 F/g at 0.3 V (curve 2).

Minimum in C-E dependence at 0.1 V corresponds to zero charge as it is commonly observed for neutral and acid electrolyte. Limitation of further charging is related with attaining of discharge potential OH⁻ ion which forms the Helmholtz layer within that range of potential values.
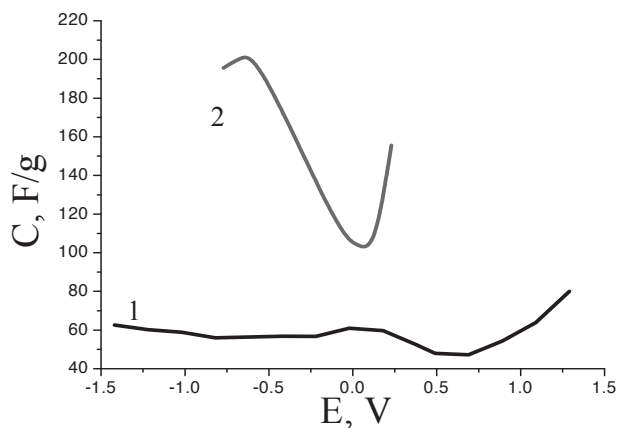
Using the relation (1) for experimentally obtained values of differential capacitance at zero charge value of potential φ_{zc} and value of $C_H = 20$ μF/cm², $\varepsilon = 3.3$ [25], the differential capacitance $C_{SC} = 44$ μF/cm² and density of states at Fermi level $D(E_F) = 4.1 \times 10^{22}$ cm⁻³×eV⁻¹ have been calculated. The last value is by 200 times larger than $D(E_F)$ for initial activated carbon that contrary to cavitation treatment just maintain in that case the unblocking of Helmholtz layer capacitance C_H.

Special attention is being paid to results on anode polarization of investigated carbons in ZnI₂ solution (Fig. 5). Obtained colossal value of C indicates preferred and decisive contribution of the pseudocapacitance. From literature data follows the ability of I⁻ to specific absorption on the surface of platinum and mercury as well as property of positive carbons to absorb the anions from solutions [13, 26]. For our case, taking into account the large number of nonelectrolytic poroes (table 1), the intercalative nature of pseudocapacitance, which was proved by us both in theoretical and experimental way, should be expected to be pronounced.
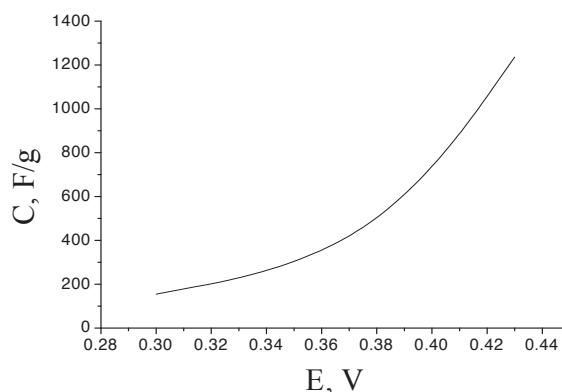

Fig. 5. Farad-volt dependence for ACM in 4 m KI within positive potential region

Besides, in -Z'' - Z' plots for ACM electrodes in 2 m KI solution at mean frequencies, as it should be expected, the faraday loop can be selected.
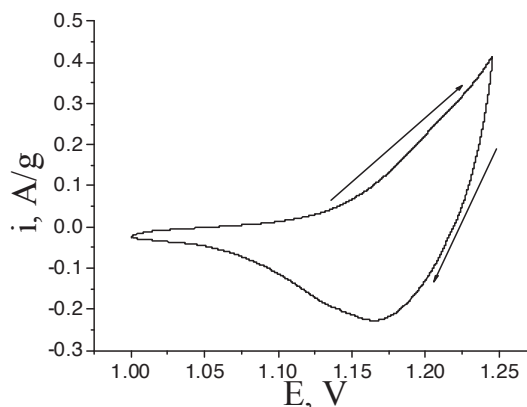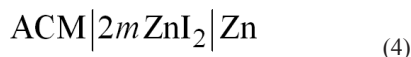

Fig. 6. Cyclic voltage-current plot, recorded with scanning rate $v_p = 2 \times 10^{-4}$ V/s of ACM electrode in 2 m ZnI₂

Fig. 4. Farad-volt dependences in 7.6 m KOH for initial activated carbon (1) and after noncavition ultrasonic treatment (2)

The reversibility of processes for ACM electrode in $2\,m\,ZnI_2$ aqeous solutions (Fig. 6) is illustrated in cyclic voltage-current plots, recorded according to three-electrode circuit at tenth cycle.

The possibility of practical application of large reversible I-intercallative pseudocapacitance of ACM porous structure has been investigated in $2\,m\,ZnI_2$ solution with zinc-metallic antielectrode and reference electrode. Thermodynamic parameters of I^- ion in that electrolyte are in fact the same as for $4\,m\,KI$ solution. The next electrochemical system was used at measuring:

$$ACM \big| 2m\,ZnI_2 \big| Zn \tag{4}$$

which had the voltage of opened circuit $E_{oc} = 1.10$ V. The minimum in cyclic volt-amperogram, recorded to three-electrode circuit (Fig. 6) corresponds to the maximum cathode (discharge) current. The discharge capacitance, calculated for those conditions in $2\,m\,ZnI_2$ solution was found to be 1150 F/g.

For electrode charging with the two-electrode setup, the anode polarisation in potentiostatic conditions at 1.245 V was applied. Galvanostatic discharge with current $I = 0.5$ A/g runs at mean discharge current 1.14 V and provide discharge capacitance 1100 F/g (43 mAh/g). Specific energy equals $W = 49$ Wh/kg.

4. Conclusions

1. Noncavitation regime in ultrasonic treatment of activated carbon results in more than by two orders increase of density of states at Fermi level that is decisive factor in colossal increasing of specific capacitance, mainly due to the unblocking of Helmholtz capacitance by volume charge region capacitance in carbon.

2. The main factor, which is responsible for the improving of working characteristics in cavitation regime of ultrasonic irradiation is the remarkable reduction of the time constant of $R_{SC}C_{SC}$ – chain generally and R_{SC} – in particular. The changes of double electric layer parameters are directly related with the fractal dimension, which in turn increases the percolation mobility of charge carries at given parameters of ultrasonic radiation.

3. The effect of cavitation at ultrasonic irradiation on the pseudocapacitive energy storage leads to decrease of the capacitance frequency dependence and increase of faraday loop.

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